Detection of Organic Components of Gunshot Residue on Carbon SEM Stubs by Raman Spectroscopy

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Abstract

Current methods of gunshot residue (GSR) analysis concentrate on identification of the inorganic components of ammunition primer. Single particles with morphology indicative of formation in a high heat environment and containing the elements lead, barium, and antimony are considered characteristic of GSR. Scanning electron microscopy with energy dispersive x-ray spectrometry (SEM-EDS) is the widely accepted method to determine both elemental composition and morphology. Although this is a very effective method, the probative value of inorganic GSR analysis is limited. Not only are there limitations on the sample containing three component particles, but current and future formulations of "green" lead-free ammunition will lead to an increasing probability of false negatives.

The organic component of the GSR has not been utilized during analysis thus far. Chromatography with mass spectroscopy has been proposed as a way to identify the components of these organic compounds, but at the expense of the sample. There would be no way to identify if inorganic components are present after this examination. With recent advancements in Raman spectroscopy technology, new techniques are able to be developed.

This study introduces early research into the ability to detect and characterize organic residues deposited on the standard 12.7 mm SEM stubs, while still allowing for subsequent traditional SEM-EDS analysis.

Previously published results of the viability of organic GSR analysis by Raman spectroscopy were reproduced by firing several types of ammunition at short range into cloth targets and confirming the presence of particles of partially combusted propellant. The spectra of the unfired propellant were compared to the partially burnt propellant picked off of the fabric and were compared and seen to be consistent. To expand the scope of the initial analysis, 12.7 mm SEM stubs with adhesive carbon tabs were mounted three inches on either side of the cloth target. Spectra consistent with results from unburnt propellant were able to be obtained by targeting individual particles on the surface of the carbon tab. Positive results show that it is possible to identify organic GSR components even in the presence of broad, dominant carbon D band at 1350 cm^{-1} and G band at 1582 cm^{-1}. By using this noncontact and nondestructive approach, the GSR stub is available to be used for subsequent analysis on the SEM-EDS.

The next phase in the research involved a more realistic collection scenario. After each test firing, the shooter's hands were sampled with individual GSR stubs in accordance with normal collection of inorganic GSR. Initial manual scans detected a small number of particles consistent with organic components of the propellant of the discharged ammunition. Although the initial number of particles detected was small, the findings are considered an important proof of concept that organic portions of GSR can be detected on samples using existing collection protocols.

Future areas to be researched are the optimization of instrument parameters to be able to accurately detect organic GSR particles, correctly characterize and classify particles by propellant type, and implement the use of software mapping features to set up an automated run similar to the inorganic GSR analysis by SEM.

This study indicates that it is possible to detect organic components of GSR on a standard 12.7 mm SEM stub with adhesive carbon tab using already existing collection techniques. Since organic GSR shows far more variation both by manufacturer and even by individual types of ammunition by the same manufacturer, it may be possible to identify differing types of propellants, greatly increasing the probative power of GSR analysis.

Introduction

The analysis of gunshot residue (GSR) has been used for many years in incidents involving the discharge of firearms. The primary probative value of current GSR methods is to determine whether a person was within the proximity of a firearm discharge when they claim not to have been. (6) When a cartridge or round is fired, the primer and propellant will form combustion products that are released in a cloud that surrounds the firearm. (6) GSR is composed of unburnt and partially burnt propellant, ammunition primer, smoke, grease, lubricants, and metals from the cartridge and the weapon itself. (2) The gas that carries the GSR escapes from the firearm mainly from the muzzle, but also from the cylinder gaps (revolvers), ejection ports, and other vents in the firearm. Because of this, the residue may be deposited on the skin, hair, and clothing of the shooter or anything around them. The rapidly expanding cloud has been shown to deposit particles up to 10-12 feet away from the firearm in any direction, and up to 50 feet away in the muzzle direction. (4)

Since the late 1970s, the principal way to analyze for GSR has been to identify the inorganic components of the primer (barium, antimony, and lead) along with the morphology of the individual particles. (9) Scanning electron microscopy with energy dispersive x-ray spectrometry (SEM-EDS) has been acknowledged as the most definitive and widely used method for the analysis of inorganic GSR (1,6). SEM-EDS allows for the non-destructive identification

of GSR particles based on their characteristic morphology and elemental composition. An SEM produces an image by scanning a sample with a beam of focused electrons. GSR analysis by SEM-EDS relies upon the use of a backscatter electron (BSE) detector. Backscattered electrons originate in the electron beam of the SEM and are elastically scattered from the sample. Heavier elements are scattered more strongly than light elements, therefore an image from a heavy element will be brighter on the display. This enables particles to be "sieved" by their Z number. Contrast thresholds are determined to establish a baseline for analysis. When a particle is detected that meets the criteria, the EDS system automatically runs a brief analysis and stores the results. At the conclusion of the automated run, the analyst relocates and analyzes particles of interest to confirm both morphology and elemental composition. A particle containing all three inorganic components and having the correct spherical morphology is deemed "characteristic of GSR." (9) There are two other types of possible conclusions, "consistent with GSR" or "commonly associated with GSR." Consistent particles contain two of the three inorganic components, also with the correct spherical morphology. Particles that are commonly associated with GSR are comprised of only one of the three possible components and are only to be used as purely supportive particles. (5) A combination of characteristic and consistent particles within a population is considered to be unequivocal identification of the particles as GSR. (6)

The inorganic components of GSR do provide valuable circumstantial evidence, although even if the suspect fully acknowledges that they discharged a firearm, there is no way to prove that they discharged the gun in question. The suspect may have also been near the firearm when it was fired, leading to the GSR landing on their face, hands, or clothing. Another way a person could potentially have GSR on their person is from the transfer particulate from another person

or object. To paraphrase Locard's exchange principle, "every contact leaves a trace" and that does not exclude GSR.

To increase the probative value of these samples, there has been an increase of research into the organic components of GSR. It is known that propellant manufacturers use a number of formulations involving varying components. Detection and correct characterization of these components could lead to more accurate determination of the origin of the GSR. Since SEM-EDS detects by element and not bonds between elements, different instrumentation is required. This instrument however, must be backwards compatible with the implementation of the currently used 12.7 mm SEM stubs with adhesive carbon tape to enable both inorganic and organic analysis from the same sample. This approach is not without challenges. For example, samples must be electrically conductive so that the particles do not become charged while being scanned by the electron beam. Scanning faults and other image artifacts arise when this is the case. To overcome this, the SEM stubs are coated with carbon before being placed in the SEM for analysis. (1) The carbon coating will interfere greatly with the proposed Raman analysis. To overcome this limitation and characterize the organic compounds on the SEM stub, analysis must be performed before the sample is carbon coated for the SEM-EDS analysis protocol.

Previous research has shown that chromatography coupled with mass spectrometry is very useful in identifying organic components. (2,8) These methods are unfortunately destructive to the sample and subsequent testing cannot be performed. Raman spectroscopy, a non-contact technique, is able to identify organic components and produce a characteristic spectrum of each. A laser interacts with the molecular vibrations of individual compounds which results in the energy of the laser photons being shifted up or down. This Raman shift is detected and measured, then transformed into the characteristic spectrum. This nondestructive technique

allows for further testing by other analytical techniques. Recent improvements to Raman

spectroscopy include improved detectors for increased sensitivity and software mapping

functions which are able to scan a sample and identify materials over a large surface area. These

abilities help overcome the challenges mentioned previously.

   The first goal of this study was to reproduce prior research by López-López *et al*. where

they showed that spectra could be gained from partially burnt GSR. (3) Secondly, a signal from

the organic GSR must be detected on SEM stubs that were prepared in an environment where it

was certain that GSR would deposit on the stubs. Third, SEM stubs were collected from the test

shooter's hands in a more realistic scenario in an attempt to find and detect organic GSR.

Materials and Methods

<u>Samples</u>

   The types of ammunition used are outlined in Table 01.

Table 01. Ammunition analyzed using Raman spectroscopy before and after firing.

Number	Headstamp Codes	Caliber	Type	Manufacturer	Country
01	SPEER 40 S&W	0.40 inch	Lawman	Speer® Ammo	USA
02	R-P 38 SPL	0.38 inch	Special	Remington Arms Co.	USA
03	WIN 25 AUTO	0.25 inch	Auto	Winchester Ammunition	USA
04	A	0.22 inch	Sniper Subsonic	Aguila Ammunition	USA
05	SUPER X	0.22 inch	Extra Power	Winchester Ammunition	USA
06	V	0.22 inch	n/a	Baikal	Russia
07	G.F.L. 38 SPECIAL	0.38 inch	S+W Special	Giulio Fiocchi s.p.a.	Italy

Two cartridges from the same boxes of ammunition were used. One cartridge of each pair was

opened safely to collect the unburnt propellant. The other cartridge of each pair was fired into

white cotton cloth targets of approximately 28 cm x 20 cm size. GSR stubs were mounted approximately three inches from the center of each cloth target. These stubs were kept capped until just before the shot was fired and capped immediately following the shot. After each shot, the shooter's hands were sampled in accordance with normal field sampling protocols. (6) The shooter was instructed to wash their hands before each shot to minimize the amount of any other residues on their hands. Shots were fired from approximately 30 cm away using appropriate caliber firearms without previous cleaning.

Sample Preparation

Approximately 10 mg of unburnt propellant from the cartridge of each type of ammunition was dissolved into 500 µL of methyl ethyl ketone. The samples were then placed in an ultrasonic bath for 30 minutes at room temperature. A 50 µL aliquot was then spotted onto microscope slides containing wells and allowed to evaporate underneath a heat lamp. The unburnt propellant was also dissolved into amyl acetate using the same method, however the particles were not able to dissolve completely and the methyl ethyl ketone produced superior spectra.

Target cloths were examined under an Olympus SZX16 stereomicroscope (Shinjuku, Tokyo) and 5-10 GSR particles were manually collected using metal tweezers previously cleaned with methyl ethyl ketone and isopropanol. These particles were manually placed on a microscope slide. A variation to the original work was introduced at this point. Initially, methyl ethyl ketone was used to dissolve the particles; however experiments showed amyl acetate to be more effective at dissolving the partially burnt particles and produced superior spectra. These samples were then left to evaporate and the spectrum was recorded once complete evaporation of the solvent was achieved.

<u>SEM Stub Analysis</u>

The SEM stub was uncapped and immediately placed within the instrument. A manual scan was performed on each of the stubs to find possible organic residues. Any particles of interest were then analyzed and the spectra saved.

<u>Instrumentation</u>

A Thermo Scientific DXR Raman microscope (Waltham, MA) controlled by the Thermo Fisher Scientific Omnic for Dispersive Raman 9.2.98 in conjunction with the Omnic Atlas 9.2.91 mapping software. Measurements were taken using a 532 nm laser, with the power set at 10.0 mW and a pinhole size of 25 µm. The objective used was 50x magnification, with 0.75 numerical aperture (50x/0.75 n.a.). Twenty (20) 2-second exposures were used for both unfired and fired propellant samples.

Results

The López-López *et al*. research (3) was able to be replicated. The authors were able to gain spectra from two propellants with different stabilizers, showing the small differences between the two.

The results of this study showed that out of the seven propellants tested, all showed very similar spectra, as can be seen in Figure 01. It will be necessary to create Raman libraries of each ammunition type to be used to compare against unknowns on each sample.
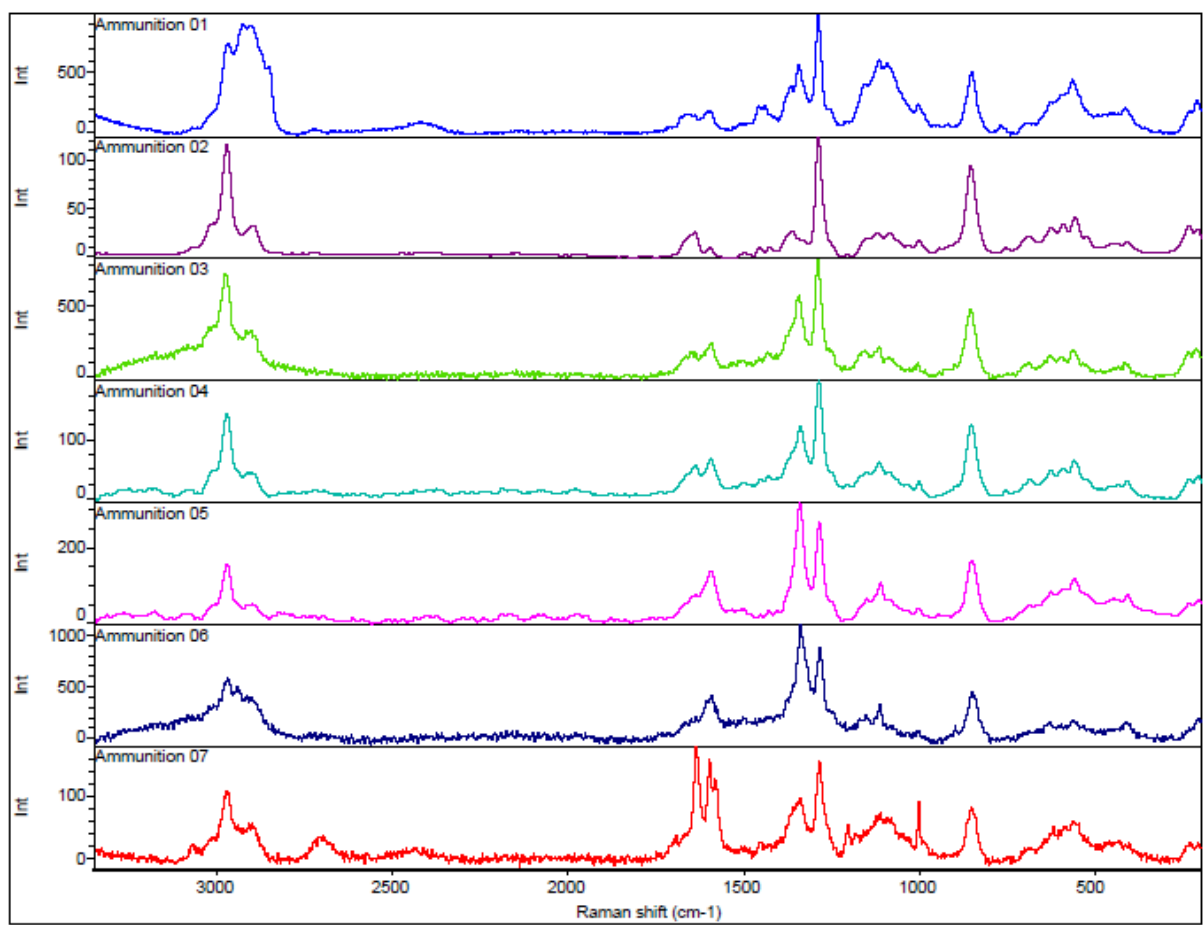
Figure 01. Raman spectra of each of the seven unfired ammunitions.

The mapping function within the Omnic Atlus software was used to analyze the dissolved partially burnt GSR particles to check for any differences in the residue remaining on the slide. A step size of 1 µm (x-y directions) was found to be the most effective step size while mapping due to the non-homogenous residue left on the slides. A 50x/0.75 n.a. objective lens was used to obtain an estimated spot size of 1.1 µm, allowing a small amount of overlap between each spot tested. The 25 µm pinhole allowed for the most accurate spectrum to be collected for each tested spot. No significant differences were found over the area of the residue from either the dissolved unburnt propellant or the partially burnt propellant. Preliminary scans of a small portion on one of the SEM stubs showed that there is a possibility of being able to map the full stub with good results. The parameters of the instrument may have to be changed to prevent the laser from

burning some of the more reactive compounds. Although the stronger laser produced a better signal from the propellant residue, it is too strong for many of the other particles found on the stubs.

By comparing the spectra of the unburnt to the partially burnt particles picked from the target cloth, it can be seen that the spectra of each have not changed. This allows for the reasonable assumption that the organic residue on the SEM stubs will likewise have undergone few changes. When manually scanning the SEM stubs, many particles stood out as potential organic gunshot residue particles. Many of these were organic compounds but they did not have spectra consistent with those of known ammunition.

A manual scan was performed on each of the carbon stubs collected, and a map of particles of interest was created using the Omnic Atlus software. Most of the particles tested were pieces of the target cloth that had been ejected from the center of the target where the bullet pierced the fabric. The two board-mounted SEM stubs from ammunition 01 contained one particle each that showed spectra consistent with the previously recorded spectrum from the unburnt propellant. These particles were clearly composed of organic residues and provided clear spectra as can be seen in Figure 02.
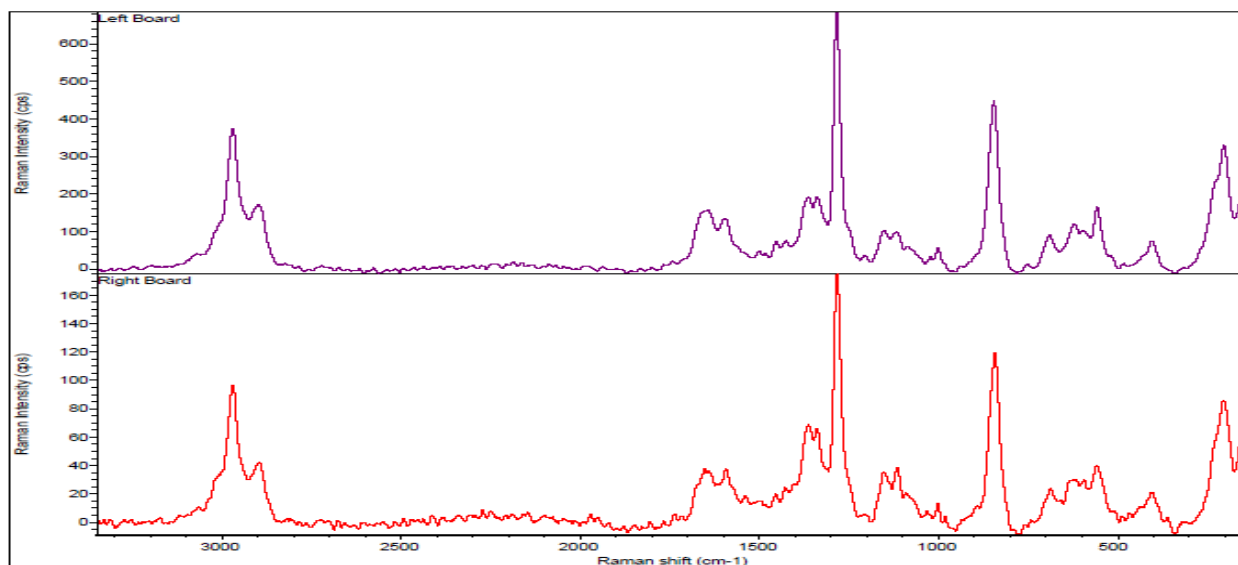
Figure 02. Raman spectra of the particles from the firing of ammunition 01 on both sides of the board compared to the unfired ammunition 01 spectrum.

Board mounted stubs (both sides) from ammunitions 07 and 08 contained pieces of intact partially burnt propellant, with ammunition 08's still in the original shape as the extracted propellant. The spectra obtained were consistent with those of the known propellants. This portion of the experiment was designed to have an artificially high probability of obtaining particles of burnt and partially burnt propellant. These larger particles are less likely to be found when the muzzle is further away due to their size and mass. Thus far, these particles are the most promising when looking for the signature spectrum.

The GSR stubs from the board used when firing ammunition 05's shooting were the only other stubs to have a trace of the organic residue spectra. The 1282 cm^{-1} band has been detected and is one of the strongest band in the ammunition spectrum. This band can be observed in spectra taken from all ammunition types used in this study; however it is not present in background spectra taken from blank carbon tabs. The background spectra contains the broad carbon D- and G-bands at 1350 cm^{-1} and 1582 cm^{-1} which will be present in the spectra gained,

but not indicative of the organic residues being targeted. In these cases, it can be seen in Figure 03, that this portion of the spectrum was overwhelmed by the broad carbon D-band at 1350 cm^{-1}. (7)
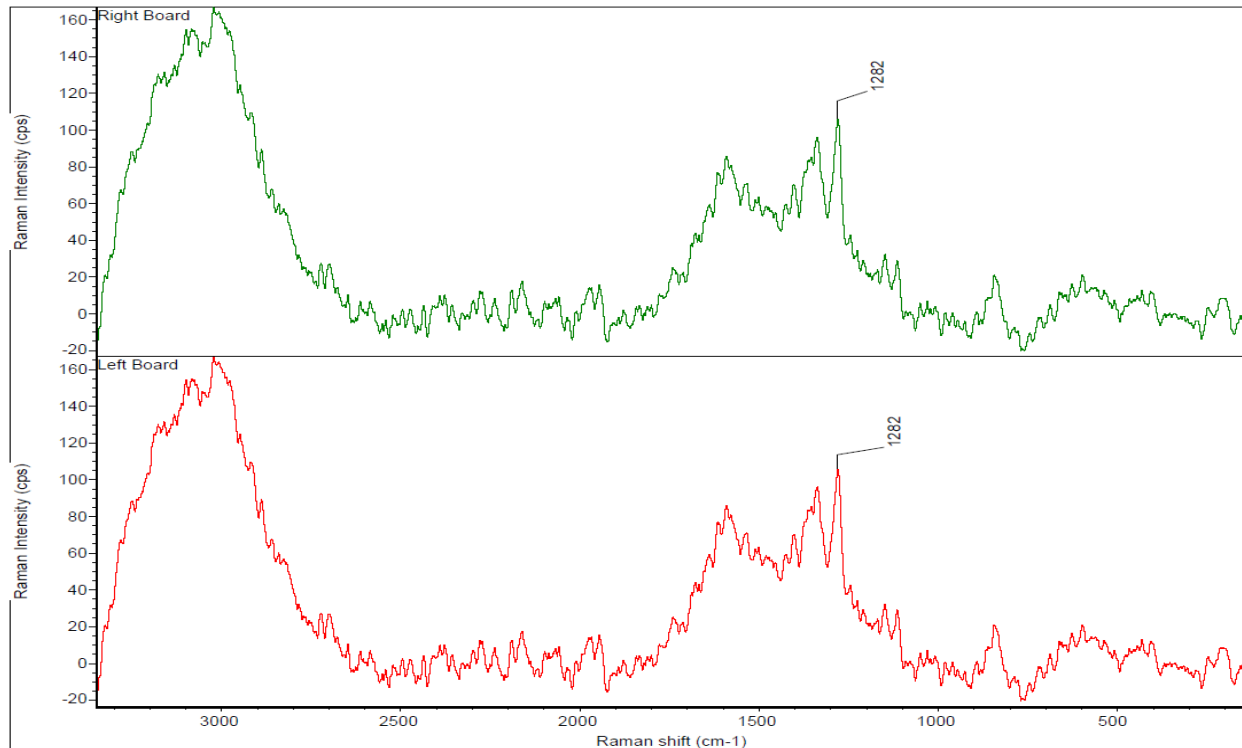

Figure 03. Raman spectroscopy of ammunition 05, from the carbon tabs on both sides of the boards.

Single particles were found on both the stub from the right side and from the left side of the board.

The targeted organic residues for the rest of the types of ammunition were not found on any of the stubs mounted on the backboards during their firings. This may be due to the broad carbon D- and G- bands drowning out any other signal. Many particles were seen that could have contained the organic residue; however their spectra only showed the carbon bands. Further studies are planned to investigate and assess the viability of detection of organic GSR by altering collection parameters for these particles.

On the carbon stubs collected from the hands of the shooter, two of the fourteen collected samples showed particulate consistent with components of the targeted propellant spectra seen in Figure 01. A singular piece of partially burnt propellant was collected off of the left hand of the shooter from ammunition 06. While there were many potential particles on each of the collected stubs from the hands, none showed the characteristic spectrum of the targeted propellant. Settings on the Raman microscope were adjusted to a 5 second exposure time, 10 times, at 2 mW to be able to obtain a spectrum (Figure 04) that adequately displayed the characteristic 1282 cm^{-1} and 853 cm^{-1} bands which are consistent with the major bands found the unfired ammunition.
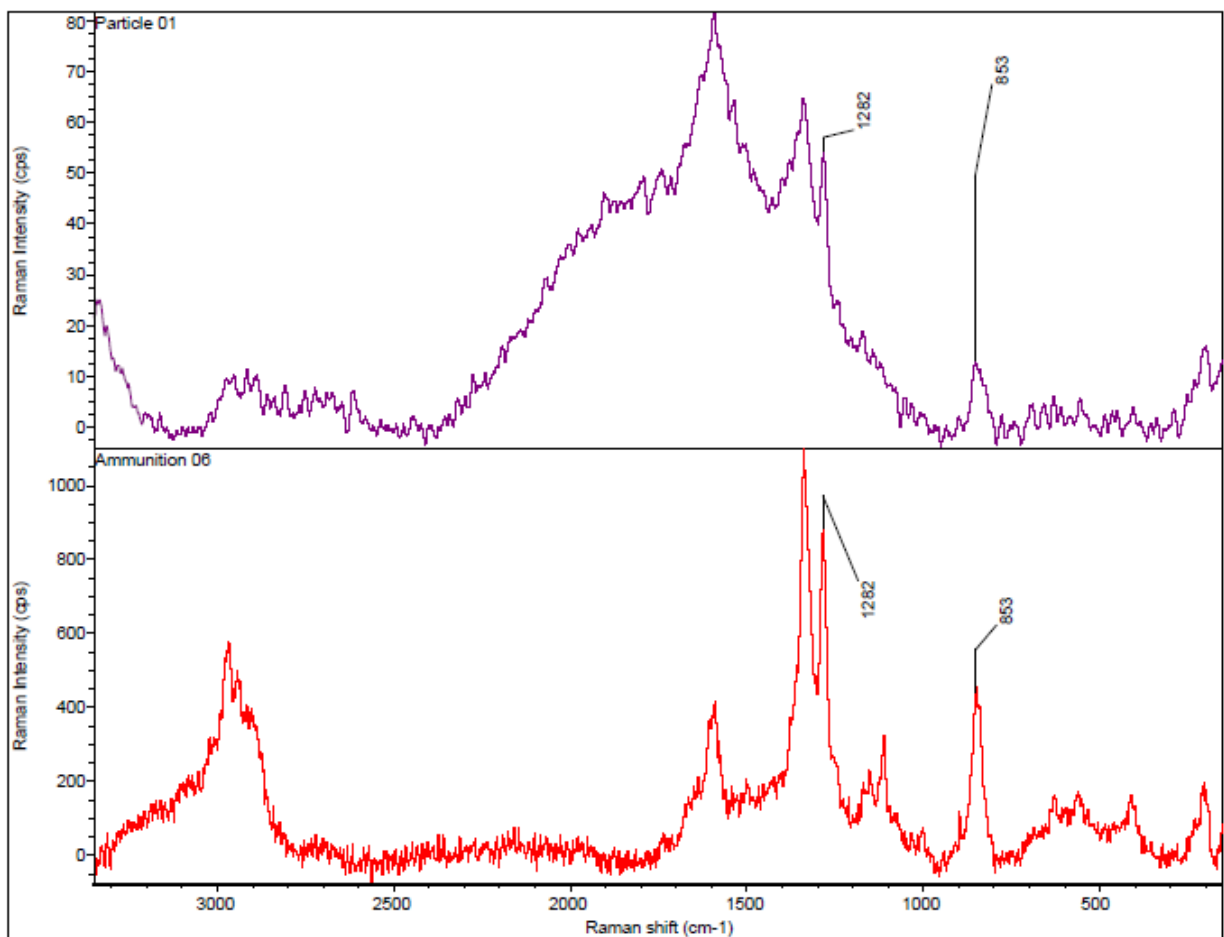

Figure 04. Raman spectrum gained from the singular particle on the left hand GSR stub from ammunition 06 (top) compared with spectrum gained from the corresponding unfired ammunition 06 (bottom).

Although this is not a perfectly clean spectrum, it does clearly show the presence of materials consistent with the known propellants. This is considered a first step in the detection and characterization of individual propellant types on a standard 12.7mm SEM stub with adhesive carbon tab.

Discussion and Conclusions

The results obtained from the SEM stubs have shown that Raman spectroscopy is a useful tool in detecting organic GSR residues. It has been shown that the propellants' organic components do not change much from before and after firing which can provide additional information as to the type of ammunition used. With this instrument, the particles of organic GSR were easily detected and distinguished from other residues that are also expelled from the firearm. The breakthrough of detecting organic residue of GSR on a standard 12.7 mm SEM stub with adhesive carbon tab while still retaining the ability to perform subsequent SEM-EDS analysis for inorganic GSR particles will lead to an increase in the accuracy of a GSR determination and increase probative value of the technique. It is theorized that the combination of the two techniques may eventually be able to distinguish between possible firearms or ammunition types used in gun-related incidents.

Although these results represent a new possibility of gaining more information from the commonly used carbon stubs, more research must follow. Discrimination between the types of ammunition seems to be possible; however research must be performed to determine if it is a viable option with current instrumentation. Development of a library similar to the automotive paints library for FTIR will be required. Testing the limits of the Raman microscope system will also have to be accomplished. More powerful instruments are being developed by manufacturers that will almost certainly be able to expand what has been reported in this study. Software

improvements may also increase the abilities of currently available instruments. Finally, a more realistic scenario should be tested; one that is performed in field conditions. The stubs should be analyzed when there is a higher chance of other organic components being picked up from the shooter's hands such as dirt and oil. Once these studies can be performed, a significant amount of headway can be made into improving the field of firearms identification within the field of forensic science.

Acknowledgements

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