

Detection of Organic Components of Gunshot Residue on Carbon SEM Stubs

by Raman Spectroscopy

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Abstract

Current methods of GSR analysis concentrate on identification of the inorganic components of ammunition primer. 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. This study introduces early research into the ability to detect and characterize organic residues deposited on the standard 12.7 mm SEM stubs using Raman Spectroscopy, while still allowing for subsequent traditional SEM-EDS analysis. 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.

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. 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 using scanning electron microscopy with energy dispersive x-ray spectrometry (SEM-EDS). SEM-EDS allows for the non-destructive identification of GSR particles based on their characteristic morphology and elemental composition.

The inorganic components of GSR do provide valuable circumstantial evidence. Although, 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. The GSR could have also been transferred from another surface that had come in contact with 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 in question.

Previous research has shown that chromatography coupled with mass spectrometry is very useful in identifying organic components. 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. 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 allow the Raman system to be used as a novel way to detect organic GSR without destroying the sample prior to traditional SEM-EDS analysis.

Materials and Methods

Goals:

1. Reproduce prior research by López-López et al.. (3)
2. Detect a signal from the organic GSR residue on the prepared best case scenario SEM stubs
3. Detect organic GSR from stubs collected from a shooter's hands

Samples

Seven different types of ammunition were used, as can be seen in Table 01.

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

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

Two cartridges from the same boxes of ammunition were used. One cartridge of each pair was opened safely to collect the unfired 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. After each shot, the shooter's hands were sampled in accordance with normal field sampling protocols. 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 suitable caliber firearms without previous cleaning.

Sample Preparation

Approximately 10 mg of unburnt propellant from the cartridge of each type of ammunition was dissolved into methyl ethyl ketone and then placed in an ultrasonic bath for 30 minutes at room temperature. 50 µL was then spotted onto well microscope slides and left to evaporate. 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.

Materials and Methods

Instrumentation

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 laser emitting at 532 nm, with the laser 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 ammunition 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.

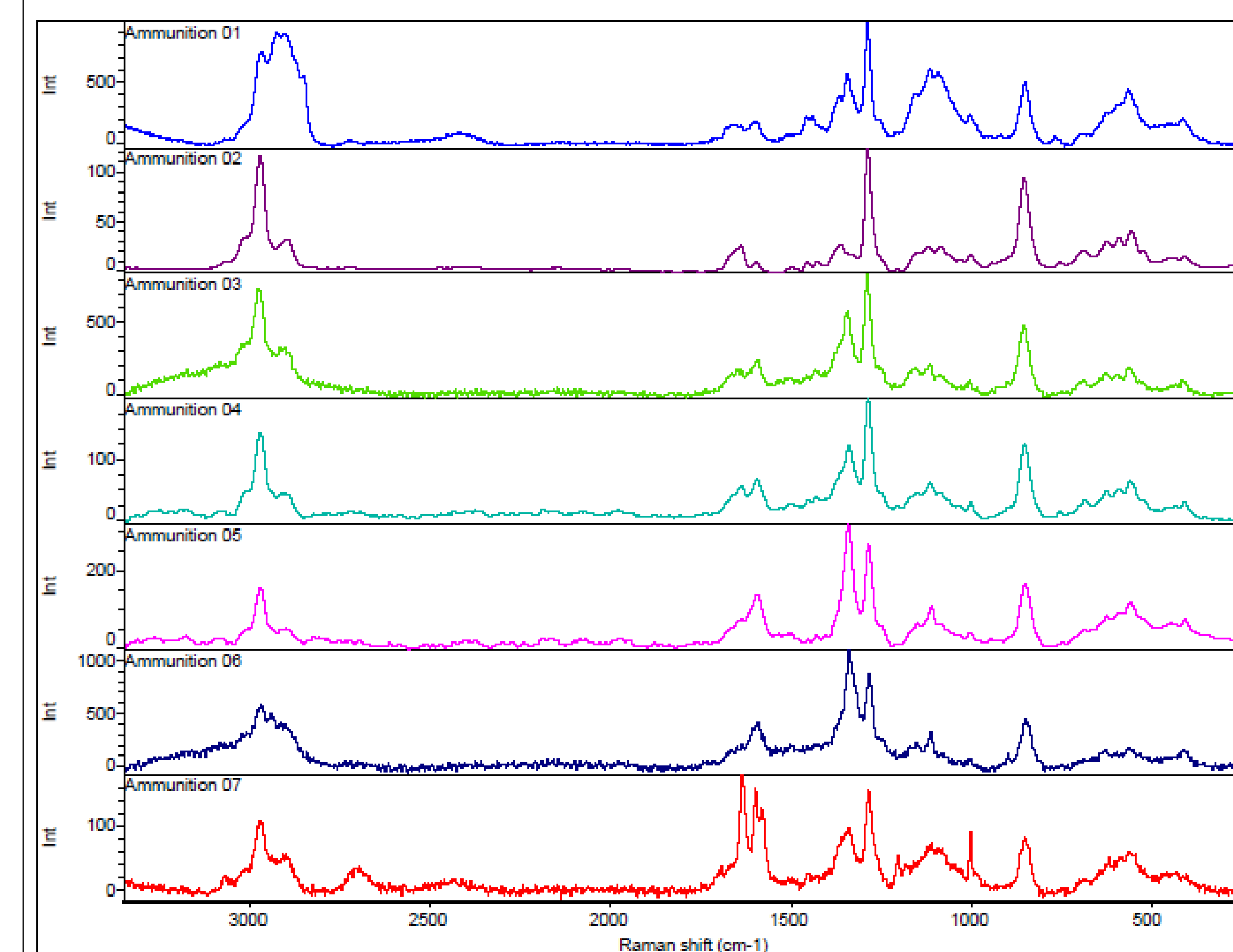


Figure 01. Raman spectra of each of the seven unfired ammunitions.

There were no significant differences between the unburnt and burnt propellants collected. This allowed for target bands to be identified. In Figure 02, bands corresponding to nitrocellulose are seen and this was the first glimpse into the possibility of identifying organic GSR from carbon tabs.

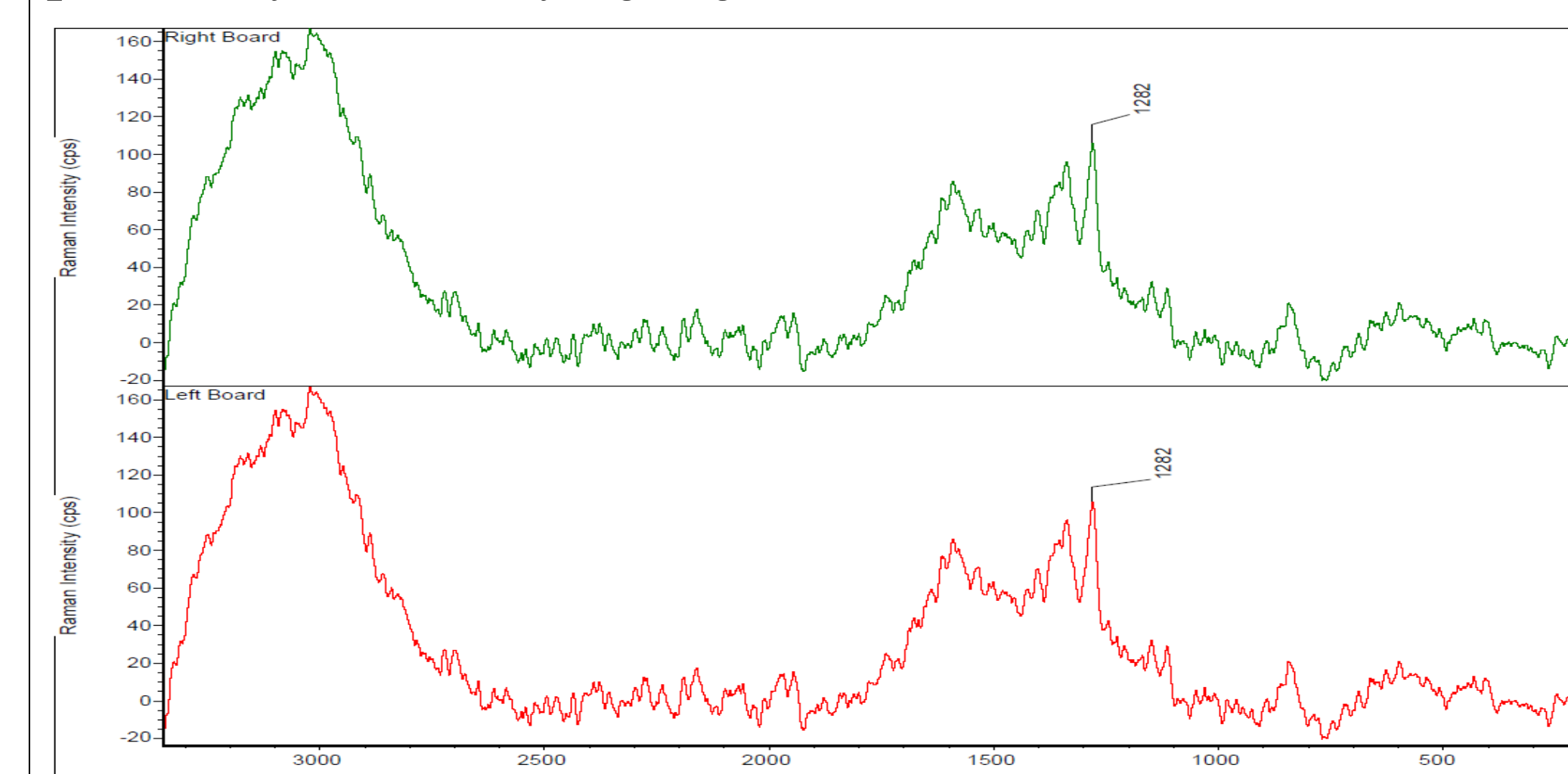


Figure 02. Raman spectra of particles from either side of the backboard. These were collected under ideal conditions to assure there would be GSR on the SEM stubs.

Results

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 (Figure 03) that adequately displayed the characteristic 1282 cm⁻¹ and 853 cm⁻¹ bands which are consistent with the major bands found the unfired ammunition.

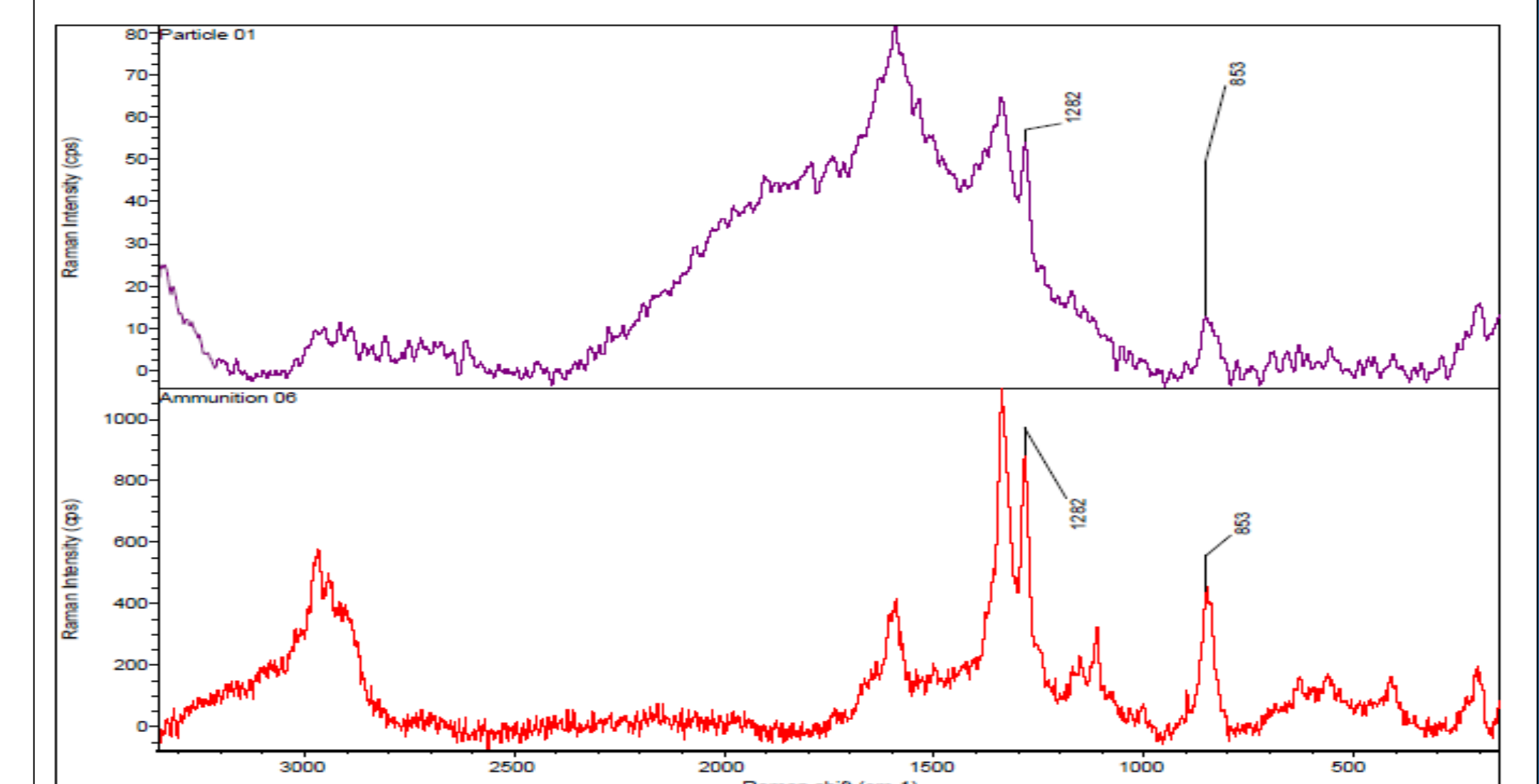


Figure 03. Raman spectrum gained from the singular particle on the left hand GSR stub from ammunition 06 (top) compared with spectrum gained from the corresponding unfired ammunition 06 (bottom).

Conclusions

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. Future research must be done to increase the ability of the instrument to focus on particles, rather than the carbon backbone of the SEM stub.

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