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The Advanced Spectroscopic Analysis of Organic Gunshot Residue and Explosives

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THE ADVANCED SPECTROSCOPIC ANALYSIS OF ORGANIC GUNSHOT RESIDUE AND EXPLOSIVES

by

JENNIFER MARIE LEONARD

A dissertation submitted to the Graduate Faculty in Criminal Justice in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

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Jennifer Marie Leonard

This manuscript has been read and accepted for the Graduate Faculty in Criminal Justice in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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ABSTRACT

THE ADVANCED SPECTROSCOPIC ANALYSIS OF ORGANIC GUNSHOT RESIDUE AND EXPLOSIVES

by

Jennifer Marie Leonard

Advisor: Thomas A. Kubic, M.S., J.D., Ph.D.

With the prevalence of shooting cases and terrorist attacks/or threats that plague the current state of the criminal justice system, it is of paramount importance to be able to detect, identify and interpret the presence of gunshot residue or explosives material. This concern is seen in law enforcement agencies and the media throughout the United States and abroad.

Currently, the typical method of analyzing gunshot residue in most crime laboratories serves to identify the inorganic constituents of the primer residue, namely lead, barium and antimony. However, it is possible that the organic matter from the propellant could provide different information to help detect the presence of gunshot residue or maybe even classify which kind of ammunition was used. There have been a few studies that have attempted to use vibrational spectroscopy to do so, however, the majority of these studies focused on a limited number of components or lack real-life samples. The additional benefits of the surface enhanced Raman technique explored in this study could offer a more successful method for analysis. In addition, the methods developed herein for organic gunshot residue are also applied to the analysis and identification of explosive compounds.

This research focused upon the use of Raman spectroscopy and surface enhanced Raman spectroscopy to analyze the chemical makeup of organic gunshot residue. In addition, this analysis scheme was expanded to include the analysis of some common explosive materials and
was considered successful for a large number of standard chemicals and “real-world” samples. Different substrates and methods for analysis (such as agar gels, agar gels made with silver colloids, TLC-SERS, etc.) are also presented herein. Several suggestions for implementation and improvement on these findings are also reported.

There is a substantial need in the criminal justice system for a systematic approach to the analysis of organic gunshot residue and explosives. There is an obvious benefit to this rapid and non-destructive method that can detect both oGSR and explosives in a variety of circumstances. This project will have an impact on the criminal justice system and state of forensic science as it offers novel and straightforward means of analyzing gunshot residue and explosives.
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CHAPTER 1 - INTRODUCTION

Statement of the problem

Forensic analysis of gunshot residue or explosive materials can prove extremely valuable in criminal investigations or circumstances in which a gun may have been used or improvised/home-made explosives may be present or have been detonated. This may involve casework ranging from illegal possession of firearms to homicide and suicide cases and have even larger implications in crimes of suspected terrorism or to more broad issues involving threats to homeland security. There is a common need in forensic science for a non-destructive and sensitive method that is capable of rapidly analyzing these types of evidence.

When a firearm is discharged, several different materials are released along with the heat and explosion. Gunshot residue refers to the burned and partially or unburned particles deposited after a firearm has fired. Lead, barium and antimony are three of the major components found in the primer of ammunition that is responsible for setting off the explosion when the firing pin of the gun strikes it. Modern smokeless powder contains various components in its’ propellant, including large amounts of nitrocellulose, as well as oxidizing plasticizers (nitroglycerine), fuel plasticizers (such as phthalates), stabilizers (such as diphenylamine, dinitrotoluene, and centralites), inorganic additives (such as graphite), and others. Single base powders contain nitrocellulose as the sole oxidizer and double base powders contain both nitrocellulose and nitroglycerin (Romolo & Margot 2001).

Typically, gunshot residue (GSR) is analyzed in crime laboratories by evaluating its inorganic constituents using Scanning Electron Microscopy (SEM) (Wallace 2008). This technique usually involves characterizing lead, barium and antimony particles left on a shooter’s
hands or clothing or particles deposited on a target such as a victim’s clothing. In addition, atomic absorption spectroscopy (AAS) has been used to perform the same tri-component elemental analysis (Newton, 1981), (Krishnan, 1974), (Koons & Peters, 1987). There have also been studies that suggest gas chromatography/mass-spectrometry (GC-MS), inductively coupled plasma-mass spectrometry (ICP-MS), neutron activation analysis (NAA), and others can also be used to study lead, barium and antimony in suspected gunshot residue (Krishnan 1974), (Vanini et al 2014) (Rudzitis et al 1973). Many of the methods for this bulk particle analysis involve multiple extractions, specialized chemical swabs and stubs, and very expensive equipment with a highly trained analyst determining if gunshot residue is present. However, this analysis only determines if a person was in the vicinity of a recently discharged weapon. It does not give information as to which kind of ammunition or weapon was used.

Organic gunshot residue (oGSR) refers to burned and unburned components from gunpowder and it refers to the many different compounds that may be detected. Routinely, these components are not used to determine if a person has been in the vicinity of a recently fired weapon or if residue on an object is consistent with gunshot residue (though oGSR may sometimes be used in a small number of laboratories in the case of reconstruction) (Wallace 2008). Studies on organic elements of gunshot residue involve detection via capillary electrophoresis (CE) or micellar electrokinetic capillary electrophoresis (MECE) and high performance liquid chromatography/photodiode array detection (HPLC-PDA) or gas chromatography-mass spectroscopy (GC-MS) (Northrop 2001) (Northrop et al 1991). Whereas there have been a few studies that involve Infrared or Raman spectroscopy and oGSR, none are completely exhaustive. These studies involve characterizing some of the components of oGSR, such as diphenylamine and nitrocellulose (Lopez-Lopez et al 2013), (Lopez-Lopez et al 2012a)
(Eliasson et al 2007). In literature, it has been noted that organic gunshot residue (oGSR) is rarely used in casework. In research laboratories, however, studies have been done concerning the ability to test oGSR using ion mobility spectrometry and swabs from shooters’ hands (Arndt et al 2012). Though these studies are not particularly relevant to the project at hand, it is useful to note that some research groups are concerned with the utility of oGSR as a critical piece of forensic evidence.

Explosives analysis can vary widely depending on the type of evidence involved. Of special consideration with explosive analysis is the evaluation of a potential threat pre-explosion, as well as analysis of the molecular constituents after an explosion. Common techniques employed for explosive analysis include microscopy (particularly stereo and polarized light microscopy) ion mobility spectroscopy (IMS), GC-MS, LC-MS, X-Ray diffraction (XRD) (Wallace 2008). Some work has been done to highlight the use of normal Raman and surface enhanced Raman spectroscopy for the detection of nitro-based explosives and some components of gunshot residue (Lopez-Lopez et al 2013a) (Lopez-Lopez et al 2012a), (Lopez-Lopez et al 2013b). However, most of these lack real-world samples or are only based on a small number of constituents on a macro scale and have lacked the added benefits of employing a surface enhanced Raman technique.

**Significance of the Problem**

There is a need for a systematic approach to the analysis of organic gunshot residue and explosives. A unified approach of separation techniques such as TLC and CE as well as analysis via normal Raman and surface enhanced Raman spectroscopy could prove invaluable in the analysis of organic gunshot residue.
There is a definite requirement for the evaluation of methods used to detect oGSR. It has been shown that there is a great value in oGSR analysis as there may be recovery of organic matter such as nitroglycerin, 2,4-dinitrotoluene and methyl and ethyl centralite when relatively few inorganic particles are recovered, especially on suspects’ clothing (Wallace 2008). It has been noted that “organic detection appears to be more sensitive than the detection of inorganics” and many of these particles can be found on clothing, hands and so forth of persons in the vicinity of a firearms’ discharge (Wallace 2008). Thus, when evidence is only analyzed for inorganic gunshot residue it may be falsely classed as negative; techniques for oGSR may be more sensitive than those used to detect lead, barium and antimony.

This research is a preliminary step in exploring the significance of the analysis of organic gunshot residue and explosives via Raman spectroscopy. As Raman analysis is becoming more commonplace and more portable units are being developed and utilized in the field, this work could potentially lead to more rapid analysis of this evidence type. In addition, this technique is concerned with constituents of gunshot residue that are not routinely studied at crime laboratories. It is possible that more discriminating information and lower limits of detection can be obtained for samples of important evidentiary value.

Furthermore, there is certainly a lack of comprehensive studies of many explosives and their spectral features. This lack of knowledge leads to inconsistencies amongst standard operating procedures in agencies across the country as well as in the field. A large study with several samples of both explosives and organic gunshot residue has proven very meaningful as it could lead to a database of spectral information that could be used by law enforcement agencies. This could be useful both for routine crimes and for on-site evaluation of scenes involving the presence of firearms or threats of terrorism. Additionally, having this information in one place
allows for quicker reliable analysis that could be important for providing investigative leads and aiding in successful prosecutions. Considering the prevalence of shooting cases and terrorist concerns in the United States, it is projected that this project will have a significant impact.

**Past Work – Literature Review**

**THEORY:**

Raman Spectroscopy:

Raman spectroscopy is often employed as an analytical technique due to its ability to give a “fingerprint,” or molecularly specific information by detecting characteristic vibrations in molecules. Raman spectroscopy relies upon measuring the difference in energy from incident light and scattered light that is offset in energy. This results in a spectrum containing sharp signature vibrations (Skoog et al 1998).

Raman scattering is a technique in which an incoming photon interacts with a molecule and scatters from it. Raman spectroscopy uses a single frequency source of radiation, often a high-powered laser, to excite the molecule to the virtual state. This means that a photon from the incident light interacts with a molecule such that it is promoted to a short-lived virtual state (or a level in which there may not be a discrete energy level) and immediately comes back down to the ground state, at a different vibrational level compared to its original. The vibrational modes of molecules are often described based on the motions between the bonds, such as (symmetrical or asymmetrical) stretching, bending, wagging, scissoring, twisting or rocking. The energy of the incoming photon does not have to be equal to the energy difference between two electronic levels of the molecule in order for scattering to take place (as it does for absorption to occur).
The incident light polarizes, or distorts, the cloud of electrons around a molecule so that there is a small change in frequency. A short-lived virtual state is formed. The molecule does not get promoted to another discrete state but does return to one of the discrete vibrational states. This state is not stable so the photon is quickly re-radiated (or scattered) and the molecule usually returns back to its original state (Skoog et al 1998), (Smith & Dent 2005). These vibrational levels of interest are usually in the range of about 200-4000 cm\(^{-1}\) and are thus far less energetic than ultraviolet and visible light.

Scattering can occur in an elastic or inelastic manner. Elastic scattering involves a molecule being promoted to a higher virtual state and then immediately returning to the original and scattering a photon of equal energy. Known as Raleigh scattering, it is very intense and happens much more frequently than inelastic scattering. Inelastic scattering means the molecule
is located in a different vibrational state compared to where it started (either of higher or lower energy) so a photon with different energy from the incident photon is emitted/scattered (Skoog et al 1998). Inelastic scattering can be described as either Stokes or Anti-stokes. Stokes scattering is seen when a molecule begins at a level of lower energy and ends at a higher energy vibrational state. The resulting scattered photon has less energy than the incident photon. Anti-stokes means that a molecule that is already in a higher energy vibrational state, perhaps due to thermal energy, and travels back to the ground state after excitation. The resulting scattered photon has more energy than the incident photon (Smith & Dent 2005).

Only one out of every $10^6$-$10^8$ photons that is scattered is inelastic or Raman, the rest are elastic or Rayleigh (Smith & Dent 2005). In Raman spectroscopy, a filter is used to block out Rayleigh scattering and usually, Stokes scattering is detected and analyzed. Anti-stokes may be preferred if there is strong fluorescence masking the Stokes signal. The Anti-stokes part of the spectrum looks identical to Stokes but is often a weaker signal due to a smaller number of molecules already existing in an excited state (Smith & Dent 2005).
Figure 2: A comparison of the vibrational modes, dipole moments, and polarizability in IR and Raman Spectroscopy (Reprinted from Smith & Dent 2005)

The difference in energy between the original vibrational state of the molecule and the resulting state is measured as a shift in the photon’s frequency. The value of this shift gives information about the types of bonds and atoms in a molecule and thus a structure and identity can be deduced (Skoog et al 1998), (Ingle & Crouch 1988), (Smith & Dent 2005). In order for a molecule to be Raman active, there must be an induced dipole, also known as a change in the polarizability of the molecule. This is different than IR absorption, for example, in which a change in the permanent dipole moment must occur (Birke & Lombardi 1988). An induced
dipole means that there is a dipole or slight separation of charge due to the introduction of an electric field (Birke & Lombardi 1988). Raman selection rules can be understood by describing the normal modes, or characteristic vibrational frequency of the molecules of interest. For example, molecular oxygen ($\text{O}_2$) is not considered to be IR active as the dipole moment does not change during vibration or excitation of the molecule. However, there is an induced dipole and therefore Raman activity (Smith & Dent 2005). Some molecules, such as $\text{CO}_2$, are both Raman and IR active. In IR spectroscopy, it is the asymmetrical stretch and in Raman spectroscopy the symmetrical stretch that are larger contributors in the spectrum (Smith & Dent 2005). Raman activity is often synonymous with symmetry, as the most symmetrical molecules typically yield the most intense Raman peaks as they are responsible for the largest amount of Raman scattering (Lombardi & Birke 2008). Density functional theory uses a computer logarithm to characterize the vibrational modes of a molecule and then predict where their Raman activity would be seen in a spectrum. This is particularly valuable for complex molecules (Smith & Dent 2005).
Figure 3: Group Frequencies: an outline of common chemical groups, and their positioning on a Raman spectrum (Reprinted from Smith & Dent 2005)
Raman instrumentation can vary quite a bit depending on the way in which the instrument is used, the wavelength of excitation desired and the samples planned for analysis. Typically, the source is a laser and the intensity of the Raman scattering is dependent both on the power and frequency of the laser. Thus, an energetic UV source may seem desirable. However, many compounds absorb in the UV and these high-energy photons may degrade the sample (Smith & Dent 2005). Thus, visible lasers are most common, such as 488nm (blue), 514nm (green), or 633nm or 785nm (red) (Birke & Lombardi 1988). Typically, lasers with excitation wavelengths of 488nm or 514nm are argon lasers, 532nm is usually a krypton laser, 633nm is usually a helium-neon laser, and 785nm is usually a diode laser (Skoog 198). There is a problem with the use of visible light in scattering techniques, however. Excitation with a visible light can cause major fluorescence which can overwhelm the spectrum. There are also near-infrared lasers, such as 1064nm. This is often chosen by an operator who desires to look at the largest array of samples possible (Smith & Dent 2005).

Filters are necessary in Raman instrumentation to eliminate any Rayleigh scattering and to block out any other or ambient light in the system. A notch filter is used to absorb the frequency of the laser light and then any scattered light is collected through this filter and focused onto a monochromator. Some Raman instruments employ more than one monochromator (where the first separates the Raman scattering from other light and the second increases dispersion and further separates out the peaks). Many systems are dispersive, utilizing a visible laser and charged couple device detector. However, Fourier transform instruments are popular for excitation lasers in the near-IR and include an interferometer and typically an InGaAs detector (Smith & Dent 2005).
Many Raman instruments also employ the use of a microscope to make the system confocal. In other words, the laser is focused through a pinhole and collected as an expanded parallel beam. This means that very small samples can be studied, and very small amounts of material may be detected. In addition, because the operator is focusing on the area of interest, he/she can choose an appropriate spot to discriminate fluorescence issues from the sample matrix (Smith & Dent 2005). In addition, many companies are exploring the use of fiber optics to create flexible, portable and robust systems (Lombardi & Birke 2008). These characteristics are of distinct interest in this proposal to ensure that this work remains relevant in the forensic science field.

Figure 4: A simple schematic of a Raman microscope system $\lambda_o = 785$nm (Reprinted from: Andor; Oxford Instruments)

Raman spectroscopy is characterized by high spectral resolution and thus can be used to deduce the chemical structure of a substance for purposes of identification or even quantification. The technique is quick, non-contact, involves minimal preparation, and may even give the analyst options because several methodologies and systems are available. As opposed to Infrared Spectroscopy, Raman analysis can be readily conducted on aqueous substances, making this technique far more practical for many samples. Raman spectroscopy has been used to study a wide variety of samples such as drugs, fibers, dyes and pigments, biological molecules, explosives and many more (Bartick 2002).
Surfaced Enhanced Raman Spectroscopy (SERS):

Normal Raman is usually described as having a low intensity which has precluded its broad use as a sensitive spectroscopic probe. In addition, fluorescence interferences at high energy (visible and ultraviolet sources) excitations often overwhelm a spectrum, which allows little information to be gained. Surfaced enhanced Raman spectroscopy presents a solution to these issues.

![Pyrazine](image)

**Figure 5:** Peaks seen in NR vs. SERS
NOTE: These spectra show that peaks not seen in normal Raman may become apparent in SERS and that their modes (and thus structures) can be calculated via DFT (Lombardi & Birke 2008).

Surfaced enhanced Raman spectroscopy involves enhancement of the Raman signal in the order of $10^6$-$10^{14}$ (Chang & Furtak 1982) (Moskovits 1985). This technique involves the alignment of the molecule of interest on a metal with high surface area to increase the probability of scattering. Typically, this means silver or gold nanoparticles are combined with the analyte of interest. These nanoparticles may be a metallic colloid made via microwave synthesis, or commercially made nanoparticles often designed for field use (Uehara et al 1990) (Birke & Lombardi 1988).
There are three contributions to this SERS effect and together, they act as multipliers. They are: surface plasmon resonance, charge transfer (metal to molecule), and molecular resonance. The surface plasmon resonance is defined by the collective oscillations of conduction electrons at the surface of the metal which is formed at the substrate’s surface (Ag or Au) upon excitation with the laser source. The surface plasmon resonance is due to the fact that the surface is thin and is not smooth (i.e. a spherical and uneven colloid) and when the frequency of the incident light matches the natural frequency of the electronic vibrations, a resonance occurs. This causes an electric field to form on the surface of the Plasmon (Le Ru & Etchegoin 2008). When these oscillations are excited with the incident light, they couple with the vibrational modes of a molecule. Charge transfer involves an electronic transfer from either the HOMO (highest occupied molecular orbital) of the molecule to the Fermi level of the metal substrate, or a transfer from the metal’s Fermi level to the LUMO (lowest unoccupied molecular orbital) of the molecule. Molecular resonance is electronic transitions taking place within the molecule (Le Ru & Etchegoin 2008). All three of these resonances must be simultaneously non-zero in order to see this enhancement. The enhancement gives information about the normal modes and the Raman activity of the molecule (Smith & Dent 2005).

These enhancements are especially large in areas in which the molecule of interest lies in a narrow gap between the nanoparticles, resulting in “hot spots.” Also, the fact that the analyte of interest is in such close proximity to the surface establishes a non-radiative pathway for relaxation from the excited state, which successfully quenches the fluorescence. With the aid of density functional theory calculations, the vibrational modes (or the bonds symmetrical and asymmetrical stretching, bending, and so forth) and thus the structures of molecules can be
predicted given their spectral features. This can be extremely useful for identification in forensic cases.

Separation Techniques:
Various separation techniques may be utilized to separate mixtures so that the individual components can be analyzed. These include thin layer chromatography and capillary electrophoresis. Thin layer chromatography involves the separation of a mixture due to its affinity for a mobile (solvent) or stationary phase in the system. This is achieved via the capillary action of a solvent moving up a plate, usually a glass or plastic plate coated in silica, though other adsorbent materials such as aluminum oxide or cellulose may be used as a stationary phase (Ingle & Crouch 1988). Capillary electrophoresis performs separation via inducing an electric field along a capillary tube in which analytes are located and all ions and even neutral molecules are pulled through the capillary via electroosmotic flow and charge and analytes are separated due to their differences in motility down the tube (Miller 2004). Both TLC and CE have been paired with Raman and Surface enhanced Raman spectroscopy so that both separation and spectroscopic analysis can occur in tandem (He et al 2000), (Geiman et al 2009), (Leona et al 2011), (Leona & Tague 2008).

ORGANIC GUNSHOT RESIDUE, EXPLOSIVES AND FORENSIC SCIENCE:
Research into organic gunshot residue and explosives dates back a few decades and mostly involves the use of capillary electrophoresis. In fact, capillary electrophoresis has been studied, somewhat extensively, in relation to separation and detection of oGSR constituents and explosives.
The U.S. National Institute of Standards and Technology (NIST) developed a reference material, RM 8107 Additives in Smokeless Rifle Powder, to be used as a standard. It contains some key additives seen in oGSR: nitroglycerin, diphenylamine, N-nitrosodiphenylamine and ethylcentralite. NIST also established micellar electrokinetic capillary electrophoresis as a successful method for the detection of oGSR from the hands of a shooter (MacCrehan et al 2006). This reference material was evaluated in 2006 by MacCrehan and Bedner via capillary electrophoresis and liquid chromatography. Though not an exhaustive list of additives in organic gunshot residue and residues found in improvised explosive devices (IEDs), this work was a good start at recognizing that potential evidentiary value exists in these components. There still exists the need for a development of a standard methodology or procedure in which spectral information about these standards are available for comparison.

Northrop, Martire and MacCrehan (1991) explored the separation and identification of organic gunshot and explosive constituents by micellar electrokinetic capillary electrophoresis. They were able to rapidly separate and identify twenty-six different constituents in which the peaks exhibited clear separation, or were completely resolved. They studied a variety of different parameters, such as the addition of a detergent, pH, concentration and hardware specifications and also evaluated their method on spent cartridge cases. This work represents an important step in developing a systematic way to study all of the different constituents found in oGSR and explosives, and to test the lower limits of detection and sensitivity of the methodology. Though capillary electrophoresis is not the main focus of the project at hand, this kind of work is still important for this proposal. This work illustrates that there is a large and diverse number of molecules that can be researched in relation to oGSR.
Sampling protocols were developed to detect smokeless powder residues using capillary electrophoresis by MacCrehan, Smith and Rowe (1998). This group investigated the use of micellar electrokinetic capillary electrophoresis (MECE) after recovering organic components from different substrates and under diverse sampling conditions. These included samples in the presence of blood or grease, via a tape lift and a solvent extraction method followed by supercritical fluid extraction. Around fifty smokeless powders were investigated, and it was determined that tape lifts presented an accurate method for positive identification of oGSR. Yet, due to their chemical and physical properties, certain tapes are not suitable for MECE (MacCrehan et al 1998). In addition, it was found that most contaminants found in the environment did not interfere with the ability of the method to detect the oGSR molecules. But, in some cases, blood was problematic in the analysis scheme, especially if decomposition of the blood had been noted. A database of MECE results for several powders was also developed, which is certainly important for future research. The work by MacCrehan et al was one of the most complete in terms of investigating several different factors and reiterating that capillary electrophoresis is, indeed, a very suitable method of identifying oGSR in forensic cases.

The same laboratory determined, in a subsequent study, that in cases in which there is sequential firing of two different ammunition types, they could only detect slight traces of the residue from the previous shot. In all subsequent shots, there was no trace detected of the first ammunition type (MacCrehan et al 2001). This work was also done via capillary electrophoresis and sheds light on an important aspect that was investigated in the work presented, namely weapon cleaning and mixed samples.

Many studies on capillary electrophoresis and forensic oGSR and explosive concerns did appropriately address some of the types of evidence that would be important for those in the
criminal justice field. Pipe bombs were constructed in the laboratory, used to represent improvised explosive devices (IEDs) that could be found in the field, and were the subject of a MECE study in 1999. It was found that pipe bombs, filled with different types of smokeless gun powder, could be detonated and samples collected from the post-blast fragments could be analyzed. Residue could be classified as to which of the powders was used (Smith et al 1999). Dr. David M. Northrop evaluated the application of MECE of oGSR to casework in a two-part series of published studies. He set guidelines for sample preparation and collection methods and determined limits of detection (which he found to be in the picogram range). In addition, he investigated false positives in the environment, of which he found none, and attempted to quantify the number of constituents in commercially available ammunition (2001). Such studies are meaningful in that they establish a foundation for the types of relevant and thorough studies needed to make a significant impact on forensic science.

Although these techniques offered a sort of breakthrough in terms of meaningful research into the organic components of GSR, most forensic laboratories shifted their focus greatly to the inorganic components: lead, barium and antimony via SEM/EDX analysis as some continued to consider the advantages of CE. One study conducted focused upon detecting inorganic ions in post-blast explosive residues with a portable capillary electrophoresis (Hutchinson et al 2008). Another looked at a way to analyze explosives by detecting anions and cations via capillary zone electrophoresis (Hopper at al 2005). Though these works are important in showing the ever-evolving research involved in explosives research, it is not particularly relevant to a discussion on organic gunshot residue and Raman spectroscopy. Additionally, with Raman spectroscopy becoming more common in laboratories, it is important to focus upon these types of studies.
There have some studies conducted that involve the use of Raman spectroscopy and the analysis of gunshot residue. Typically, gunshot residue is analyzed per its inorganic components. This may involve color tests (bulk analysis) such as the dermal nitrate (or paraffin) test, which were used for some time, yet widely discontinued due to the many false positives that exist. Thus, neutron activation, atomic absorption and scanning electron microscopy (for particle analysis) methods were developed. Additionally, some statistical analysis has been explored to determine if there is a capability to gain more information about the gunshot residue from these tests (Romolo & Margot 2001). Vibrational spectroscopy methods have not always been the most widely used for gunshot residues, but some studies have appeared in the last fifteen years (Sylvia et al 2000).

One concern regarding the study with Raman spectroscopy of organic gunshot residue and explosives is safety. Often, the lasers in most Raman systems are strong enough to heat the samples, causing them to burn slightly or deflagrate, which can be both harmful for the analyst if the fumes are toxic and impractical if it uses up a sample at hand. Thermography experiments as well as analysis of the potential hazards of many of these samples (both bulk and in mixtures) have been published, and guidelines are recommended for under which conditions certain explosives should be studied by Raman analysis (Harvey & Wright 2002). It is important to note that there are specific precautions that must be taken during the conduction of the experiments performed herein.

Lopez-Lopez (2010) and her group in Spain have conducted several experiments concerning the use of Raman spectroscopy for the analysis of organic gunshot residue. In one, they have developed a protocol to isolate nitrocellulose from gunpowder samples. Their goal was to establish this method and determine its value in identification of the specific molecules
found in their oGSR samples. They developed a system in which they used a series of solvent extractions to purify nitrocellulose and FTIR spectra were then collected. Though it is not particularly exhaustive and samples utilized were purposefully quite different, this research was valuable in that it highlights a preliminary method to differentiate different ammunition types and to show the necessity of extraction in certain cases.

In another study, six different types of ammunition were used to fire at cloth targets and the oGSR was analyzed via Raman spectroscopy. Analysis was also conducted on unfired ammunition and the group noticed similarity between the pre- and post-shot spectra. In addition, sand, blood and ink were analyzed to show the discriminatory power of Raman spectroscopy for forensic purposes. In all, it appears as this was a good beginning for the development of Raman spectroscopy for the analysis of oGSR. The main conclusion drawn was that gunshot residue could be easily distinguished from other samples (i.e. sand, blood and ink). Additionally, it was shown that ammunition with different stabilizers, of which the investigators were aware before analysis, could be differentiated (Lopez-Lopez et al 2013a). However, this work was certainly preliminary, and more work on similar ammunitions and other substrates is necessary before a large impact on the field can be realized.

The Lopez-Lopez group also conducted research on the use of Raman spectroscopy to assess weapon memory effect. In this experiment, twenty shots were fired consecutively with two different ammunition types, both 9mm NATO parabellum cartridges. Shots one, three, nine and twenty were conducted with the first type of ammunition and the others with the second type. oGSR was analyzed macroscopically with Raman spectroscopy (2012a). The ammunition was successfully identified from the first shot by looking for the presence or absence of the peak at 1342cm⁻¹ (corresponding to the absence or presence of a diphenylamine derivative called 2-
nitrodiphenylamine) at an excitation wavelength of 532nm. Afterwards, they found a range of 1.5-7.5% of particles identified in shots three, nine and twenty that corresponded to the second type of ammunition. They then performed this analysis by looking for discriminating bands in the range of 1800-800cm$^{-1}$. This was much less successful compared to the presence/absence of the single band at 1342 cm$^{-1}$ (2-nitrodiphenylamine). Whereas the work presented was quite interesting, it neglected to talk about any visual features that may differentiate these particles. It was not a truly comprehensive and comparative study in which the same stabilizers are present in both ammunition types. The reliance on one band, or component of oGSR, is useful only to class ammunitions into two groups: those that do or do not have that particular stabilizer. That information is useful but it is certainly not sufficient to identify a true unknown sample, though exclusions (or to say that two samples of gunshot residue are certainly different) could be possible.

Some of the studies involving Raman spectroscopy and organic gunshot residue focus upon the analysts’ ability to predict where certain vibrational modes that appear in a spectrum, based on the vibrational modes and structure of the analyte. This is done through a calculation called density functional theory (DFT) and has proven important in many studies on the reliability of Raman and surface enhanced Raman spectroscopy research (Lombardi & Birke 2008). In one such study, density functional theory calculations were conducted for some typically seen high explosives, such as HMX, PETN, RDX and TNT using the software Gaussian09®. Predicted IR spectra of HMX, PETN, RDX and TNT were also presented (Huang et al 2011). In another study, the ionization potential and electron affinity of six explosive compounds were calculated. These include RDX, HMX, TATP, HMTD, TNT, and PETN (Cooper et al 2012). These calculations are important figures used for DFT calculations and
predicting spectra. These studies are important because there are research groups that recognize the potential importance of the determination of explosives via vibrational spectroscopy and subsequent data analysis. This information can be used to match theoretical predictions to experimental results and can certainly be an important facet of the proposal herein.

A study was also conducted that involved the analysis of solid cross sections of explosives and explosives in solution via Raman spectroscopy. It was found that both visible and near-IR Raman laser excitation (at 532 and 785nm) were useful to find identifying spectral bands in explosive samples such as RDX, HMX, TNT, 2-4DNT, 2,6-DNT and ammonium nitrate. In this paper, the mode frequencies were calculated and vibrational modes involved in each explosive were identified, and these results were compared to data gathered at different excitation wavelengths. This was valuable in showing that it is possible to obtain spectral features and judge if they match with the theory (Emmons et al 2012). Though solid state Raman analysis is done rarely, this study is still a meaningful look at the vibrational modes found in common explosives, and the frequency values found were compared to values obtained in the research in this work.

Lastly, a comparison of Fourier Transform-Infrared and Raman spectroscopy was conducted in relation to smokeless gunpowder. It was found that a visual inspection of spectra obtained from either technique provided useful information to make an identification of powders containing dinitrotoluene, one of the key constituents found in many oGSR samples. It was also found that Raman spectroscopy was more useful in providing a discriminatory spectral feature for another constituent, 2-nitro-diphenylamine, that was not seen with FTIR. Discriminant analysis, a statistical analysis tool was also performed to show that together, both FTIR and Raman spectra of oGSR prove valuable in identification (Lopez-Lopez et al 2012b).
Dynamite has been used as an analyte to show the efficiency of Raman spectroscopy as a tool for explosives analysis. Confocal Raman spectroscopy was used to study two different samples of made of ethylene glycol and ammonium nitrate; with other minor contributors that the authors referred to as dynamite (though dynamite is typically defined as a combination of nitroglycerin and diatomaceous earth). It was found that the individual components of the “dynamite”, namely the ethylene glycol and ammonium nitrate could be identified, and that these components could be distinguished from other material that may be collected along with explosives evidence, such as sawdust, calcium carbonate and flour (Lopez-Lopez et al 2013a). This research, though limited to only one explosive that may contain a complex mixture of minor components, shows that Raman spectroscopy has the potential to be a very useful tool in the analysis of explosives and pointing out characteristic spectral features so that other research laboratories can replicate it and use it as an identifier. Though much further research is needed, this is certainly a step in the right direction because it focuses upon common explosive materials and seeks to develop a method for samples that are forensically pertinent.

In 2007, a group studied a method of Raman spectroscopy as a non-invasive way to detect liquid explosives that were concealed in bottles or some sort of packaging. This group used spatially offset Raman spectroscopy (SORS) that uses diffuse scattering. This allows for the analysis of material inside different containers, even colored or scattering plastic, without affecting the geometry of the experiment. This group claims that their experimental setup allows for increased sensitivity by suppressing fluorescence and Raman scattering from the walls of the container (Macleod & Matousek 2007). Though not immediately pertinent to the study at hand, such a study may have a future impact in expanding this project to work for arenas such as homeland security, airport security, and others. In other words, modifications on the typical
Raman spectroscopy setups can prove to be important in the future when researchers are attempting to make their methods the most practical and straightforward. In this way, their results can be easily used with the criminal justice system.

Some research has been conducted concerning the use of surface enhanced Raman spectroscopy for the detection of explosives. Though none of these studies are exhaustive, they are important steps that have helped lead to the development of this proposal.

For example, Botti’s group in Italy (2010) has had some success with the study of SERS and explosives. In one study, trace-level explosive detection was studied using samples of TNT and nitroglycerin and TATP, all in acetonitrile. Small quantities of the standards were evaporated and absorbed onto industrially made SERS substrates, consisting of gold particles on silicon, and analyzed with a compact Raman system with excitation at 785nm. In most cases, high signal to noise spectra were generated and detection and identifications were made with a detection limit of approximately a few hundred picograms. The total time for analysis was thirty seconds and visually different spectra were seen. In another study, this group looked for trace-level detection of nitro-based explosives, such as PETN, EGDN, RDX and TNT. A similar methodology was used yet spectrum acquisition time was lowered to ten seconds. In addition, statistics (PCA) was used to prove that the spectra generated were different enough to aid in classifying an unknown into one of the types of explosives discussed and 76% of the variation was accounted for in the first three principle components (Botti et al 2013). No true test samples were used after the statistical analysis to test the efficacy of this model. Again, though these studies lack extensive depth and field samples that mimic forensic casework, they are valuable in showing that SERS is an effective method for explosives analysis.
Some studies conducted focused upon vapor concentrations and detection via SERS. Though not directly relevant here, these studies still show the efficiency and discriminatory values of SERS. In 2000, a study was conducted on the SERS detection of 2,4-dinitrotoluene as an “impurity vapor” in an effort to locate landmines (Sylvia 2000). Another combined a free-surface microfluidic apparatus to conduct real-time vapor detection of 2,4-dinitrotoluene (Piorek 2012). Both studies were able to detect 2,4-dinitrotoluene down to the ppb level. The limit of detection of specific components in oGSR could be an interesting topic for future study.

One SERS experiment focused upon the ability to detect perchlorate with a portable SERS system. This is of particular interest here, as the ease in which a method can be introduced into the criminal justice field and crime laboratories (or at crime scenes) is of paramount importance. This portable system had an excitation wavelength at 785nm and industrial grade emulsions of perchlorate were used as the samples, which were first analyzed by ion chromatography. These samples were prepared by pentane extraction or a combustion technique in which a small amount of explosive was burned in an open flame in an alcohol burner for thirty seconds; then, residue of both the extraction and combustion techniques were re-dissolved in purified water. SERS substrates were prepared with an in-lab sputtering system to make a silver surface deposited on silicon. Portable SERS was compared to a laboratory Raman system and the ion chromatography analysis. It was found that the portable SERS instrument was sufficient for rapid and on-site detection of trace perchlorates (Nuntawong et al 2013). Whereas such research is exciting in terms of potential impact in the field, it also involved a significant amount of time and equipment used to prepare samples in the laboratory. This would not be the most realistic for all crime scene units. A goal explored in this study was to limit some of the time-
consuming preparation work that requires extra supplies. Thus, time and supplied were
minimized or eliminated to allow for quicker and more realistic on scene analysis.

The combination of capillary electrophoresis and surface enhanced Raman spectroscopy
has been reported in previous studies. For example, in 2000, a group at The Pennsylvania State
University determined that eluents straight from a capillary electrophoretic system could be
detected via an interface between the column and the SERS apparatus. They determined that the
retention times obtained agreed well with the more common UV-visible detection and that the
added benefit of the vibrational spectrum provides a higher degree of discrimination (He at al
2000). Although this 2000 study focused primarily upon biological and environmental
applications, the general scheme is certainly something relevant for this project as both silver and
gold SERS colloids were utilized.

Additionally, there have been some controversial and flawed publications regarding the
use of Raman spectroscopy and its role in the examination of gunshot residue. There has been
research published that makes claims about the abilities of the Raman spectroscopic analysis
gunshot residue to point to a specific caliber of the weapon used (Bueno et al 2012). However,
this study by Bueno et al involved the use of two different types of ammunition, distributed by
different manufacturers, so their claims seem overzealous and misleading to those without a keen
sense of the nuances of forensic science. That is certainly not a goal herein as the conclusion
seems to be an incorrect and premature judgment on the part of the aforementioned study.
However, it is plausible that characteristic components of gunshot residue can help to
differentiate ammunitions of different manufacturers, brands or types. Thus, the objective is not
to differentiate caliber type, but aims to work alongside other methods (i.e. microscopy) to
narrow down types (manufacturers or brands) of ammunition used or chemically determine if a
firearm has been discharged. For this reason, it is of the utmost importance to focus upon careful understanding of any Raman data, and assigning the appropriate weight to any results deemed significant.
Figure 6: A schematic of the general research design of this study
INSTRUMENTATION

Spectrometers:

Several Raman spectrometers were used throughout the course of this research. For all measurements, unless otherwise noted, samples were focused upon and photographed using a 10x objective lens (and occasionally a 100x objective lens) and all spectra were collected via 5 acquisitions for 10s each for a total acquisition time of 50s.

Horiba

A Horiba XploRA confocal Raman imaging system equipped with 532nm and 785nm lasers was used to collect spectra. It was equipped with a full confocal light microscope (with 10x, 50x and 100x Nikon objectives) set with a pinhole setting of 300 and a slit setting of 100, video camera, and high resolution and range for spectroscopic measurements. Horiba’s LabSpec v.6 software© was used to set measurement parameters and collect spectral data. A grating was set at 600T and data was collected for 10s for 5 acquisitions, for a total of 50s collection time. A laser power setting of 1% (~0.57mW for 10x objective, ~0.36mW for 100x objective) was used for both the 532nm and 785nm lasers for detection with an electron multiplying charged couple device.
Figure 7: A photograph of the Horiba XploRA instrumentation

Figure 8: A screen-grab of the Horiba Lab Spec 6 © software
City College Spectrometer

A laboratory grade spectrometer system built at CUNY City College of New York was used to collect data at 488nm, 514nm and 633nm. It is equipped with a liquid nitrogen cooled CCD (charge coupled device) detector at -114°C, a diffraction grating set at 1200 BLZ (=500nm), set at a speed of 100nm/min, and various notch filters and bandpass filters that were aligned and set separately for each laser. An Olympus BS2 microscope with a pinhole of 50μm attached to the spectrometer to allow for confocal Raman measurements that ranged from about 200-2000cm⁻¹. Q-Cap Pro camera software© was used to focus the laser on the sample that is laid on the microscope stage, and Win-Spec software is used for the collection of spectral data. For the 488nm and 514nm laser, the power was set on the lowest power setting, which produced a power of about 1.15mW whereas the 633nm laser produced a power on the sample of about 6.72mW.

WITec

A WITec Alpha300r+ confocal Raman imaging system was used for much of this experimentation. It was equipped with a research grade optical microscope with a confocal pinhole of 50μm, video camera, ultrahigh-throughput spectrometer set with a 600l/mm BLZ grating and CCD (charge coupled device) detection. WITec software (WITec control and WITec Project©) was used for both instrument and measurement control. An excitation laser was 532nm (calibrated and fixed at 532.374nm) and a spectral center of 2050cm⁻¹ was chosen to acquire a spectrum from about 0-3700cm⁻¹. An excitation of 785nm (calibrated and fixed at 784.695cm) and a spectral center of 1050cm⁻¹ was chosen to acquire a spectrum from about 0-1800cm⁻¹. All spectra were collected maximum laser power, (~29.3mW for 532nm and
~11.8mW 785 power) unless noted otherwise. Often, at 532nm a lower laser power of 1.5mW or 0.5mW was used to prevent sample burning/incineration.

Figure 9: A photograph of the WITec instrumentation (note: microscope, spectrometer on bottom bench and the alternate beam splitter and a laser source on the top bench)
Calibration and Wavelength Accuracy

A silicon wafer (Ted Pella, Inc. 3-inch Si wafer) was used as a reference standard at the start of each day of experimentation to ensure proper calibration. The WITec spectrometer was calibrated daily. The two lasers were calibrated with the software such that the exact wavelength of the exciting laser was changed slightly on the software controller so that the intense standard silicon peak was narrow and centered at about 520-521 cm\(^{-1}\). For all other spectrometers, spectral data for a silicon standard was collected at the start of each day, to ensure the silicon peak was narrow and centered around 520-521 cm\(^{-1}\).

Additionally, 4-Mercaptophenol, crystal violet, and rhodamine 6-G were often used as standards for SERS as their spectra are well known and they are very strong scattering agents with various nanoparticle substrates. These solutions were diluted in distilled water at about 1mM concentration and were stored in the refrigerator in an Eppendorf tube in between use.
SAMPLE PREPARATION

Solvents Used

The following solvents were used throughout different procedures in this study; their structures were included in case there were any spectral features that could be attributed to the solvent.

Table 1: List of solvents used throughout the experiment

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Manufacturer</th>
<th>CAS/Lot #</th>
<th>Structure</th>
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</thead>
<tbody>
<tr>
<td>Acetone</td>
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<tr>
<td>Acetonitrile</td>
<td>Fisher Chemical</td>
<td>75-05-8</td>
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<tr>
<td>Chloroform (stabilized with Ethanol)</td>
<td>Acros Organic</td>
<td>67-66-3 / Lot # A0357593</td>
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<td>Ethyl Alcohol</td>
<td>Pharmco-AAPER</td>
<td>64-17-5 / Lot # C15129002</td>
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<tr>
<td>Hexane</td>
<td>Fisher Chemical</td>
<td>110-54-3 / Lot # 161730</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>Fisher Chemical</td>
<td>67-56-1 / Lot # 142422</td>
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<tr>
<td>Methyl Ethyl Ketone</td>
<td>Fisher Chemical</td>
<td>78-93-3 / Lot # 154876</td>
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</tr>
<tr>
<td>Petroleum Ether</td>
<td>Pharmco-AAPER</td>
<td>8032-32-4 / Lot # PL001116</td>
<td>*Mixture of aliphatic hydrocarbons; AKA Light ligroin</td>
</tr>
</tbody>
</table>
Silver Colloids

NOTE: All sodium citrate solutions herein were made with Sodium Citrate Dihydrate (Fisher Chemicals, CAS 6132-04-3.68-04-2) solid that was dissolved in ultrapure water.

Microwave Synthesis Procedure:

Ag$_2$SO$_4$ was precipitated by reacting 0.1g of AgNO$_3$, dissolved in 5ml cold Millipore water, with 20-25 drops of 10% H$_2$SO$_4$. The Ag$_2$SO$_4$ precipitate was centrifuged for about 10 minutes, and then dried overnight on filter paper. The Ag$_2$SO$_4$ was then dissolved in tri-distilled water to make a 5x10$^{-4}$M solution. 12.5ml of this Ag$_2$SO$_4$ solution was combined with 900µl of 1% glucose solution and 503.5µl of a 1% sodium citrate solution in a microwavable Teflon vessel. A counter weight vessel was placed opposite the solution in the vessel holder. The microwave (Anton Paar Multiwave 3000) was set via a temperature/pressure program to 120°C, and allowed to ramp for 30s and hold for 30s. The silver colloid solution was then chilled in an ice bath and stored in a falcon tube that is covered with aluminum foil to avoid light exposure. Before use, the colloids were centrifuged for 20minutes, and 900µl of supernatant was removed and replaced with 900µl of deionized water. Various dilutions of these colloids (from full concentration: 50% concentration, and 25% concentration) were made.

NOTE: This procedure was adapted from a procedure used at the Metropolitan Museum of Art, under the directions of Dr. Marco Leona (Leona 2009).
Figure 11: (a) Photo of the Anton Paar Multiwave 3000 Microwave Sample Preparation System used to make silver colloids; (b) a photo of the microwave vessel with the solution and temperature-pressure sensor; (c) a photo of Ag nanoparticles after microwave synthesis; (d) a photo of Ag nanoparticles after the centrifugation/concentration step
Lee-Meisel Method:

90mg of AgNO₃ was dissolved in 500ml of ultrapure H₂O and brought to boiling. A 10ml aliquot of 1% sodium citrate solution (in H₂O) was added and allowed to boil for ~1 hour. A color change was noted as the solution turned to a deep green-yellow. The colloids referred to herein as “modified Lee-Meisel” colloids were allowed to boil just until a color change occurred (less than 1 hour, about 35-40 mins boiling) (Lee & Meisel 1982).

Figure 12: A photograph of the silver colloids during the boiling phase (NOTE: the color change to a light green then a dark green, which indicated the synthesis was complete)
Gold Colloids

Lee-Meisel Method:

240mg of HAuCl$_4$ was dissolved in 500ml of water and the solution was brought to boiling. A 50ml aliquot of a 1% sodium citrate solution (in H$_2$O) was added and allowed to boil for about 1 hour. A color change occurred in which the solution turned a deep red wine color. The colloids referred to herein as “modified Lee-Meisel” colloids were allowed to boil just until a color change occurred (less than 1 hour, about 35-40 mins boiling) (Lee & Meisel 1982).

Diagnostic AnSERS, Commercial Gold Nanoparticles:

Gold nanoparticles were obtained commercially from Diagnostic AnSERS. They are concentrated at 0.35mg/ml and a 100ml container was obtained (SKU SERS-nanoparticles).

Figure 13: A photograph of Diagnostic anSERS nanoparticles, obtained commercially on February 2nd, 2015
Silver Nanosheet Synthesis

The synthesis of silver nanosheets was adapted and modified from the procedure presented by Gao et al (2013). Copper tape (Ted Pella, Inc.) was cut into small pieces and then washed with acetone, methanol and ethanol for five minutes each in a standard lab sonicator. The pieces were rinsed with water and ethanol and dried with a kimwipe. A CuSO4 solution was prepared (100mg in 12.5ml Millipore water) and 25mg of SDS was added to form a sudsy, clear, light blue solution. Scotch tape was applied to one side of the copper tape and cut such that some hung below the surface for sample handling (see Figure 14). The copper tape soaked in the CuSO4 solution for 1 hour. When removed, a white precipitate was noted and the exposed copper surface was slightly more reddish in color. The tape was rinsed with ethanol and distilled water three times each. Next, the copper tape was placed into a sodium citrate solution (44mg in 17.5ml H2O) and allowed to stir mechanically on a low setting for about thirty minutes. Next, an AgNO3 solution (38mg in 1.25ml H2O) was added and the solution immediately turned a milky white color and exposed copper surfaces began to turn black and flake. 10 minutes later, 2.5µL of 2mM HNO3 was added to the solution and the surface soaked for thirty minutes. Lastly the surfaces were rinsed with water and ethanol three times, soaked in ethanol and then dried. All nanosheets were stored in Eppendorf tubes wrapped in aluminum foil, to avoid exposure to light.

Figure 14: A photograph of synthesized nanosheets, with standard solutions deposited on the center two sheets
Ultraviolet/Visible Spectroscopy

Nanoparticles synthesized in this study were analyzed via a Shimadzu uv-2450 in absorbance mode. The spectrometer was set at a medium scan speed and a slit width of 0.1nm. It is equipped with a high-performance blazed holographic grating monochromator and a photomultiplier detector. 1cm silica cuvettes were used for analysis in the range of 200-750nm and Shimadzu’s UVProbe software was used for data collection and its “peak picking” capabilities to determine the wavelength of maximum absorbance. A holmium oxide standard glass filter was used to check proper wavelength accuracy (within 2-3nm of the literature value) before each day of measurement.

Scanning Electron Microscopy

Nanoparticles and nanosheets synthesized in this project were also analyzed using a Tescan Scanning Electron Microscope. 15µl of the Ag and Au nanoparticle solution was deposited on a standard carbon SEM stub, and allowed to fully dry. A nanosheet was deposited onto the sticky side of carbon tape on a standard SEM stub for analysis. The SEM’s detector was situated in back scatter electron (BSE) mode, and accelerating voltage was either 10, 15 or 20 kV, and magnification varied from ~80x-850x depending upon which produced the highest quality image. The instrument was controlled via the Vega3 Control Software (Version 4.2.17.1 build 4174, Tescan USA Inc.). Next, X-Ray energy dispersive spectroscopy was performed on selected areas (multiple spots per image) on the image to analyze the chemical makeup of the surface. The area was scanned for 30s, with an amp time of 96µs and a resolution of 128eV. Element identification results were obtained. These functions were performed with TEAM Enhanced software (Version V4.2.2, Tescan USA Inc.).
Standard Solutions

For all mass measurements conducted in this study, one of two analytical balances was used. Both were calibrated on a yearly basis by Scitech Instruments or Metler-Toledo technicians (See Appendix I). One balance was a Denver Instrument SI-114 (maximum capacity 110g, d=0.1mg) tagged CUNY: JJC-002419 #561A. The other was an Ohaus Analytical Plus (Model number AP250D-0, Serial Number 1115290056, capacity 210g/20g x 0.1g/0.01mg).

Obtained Commercially:

Reference materials for organic gunshot residue constituents and/or explosives were obtained in either a solid or liquid form. All liquid samples were diluted from 1mg/ml to 100µg/ml and 10µg/ml solutions. Some standards were obtained at a concentration of 100µg/ml so only one further dilution to 10µg/ml was made. All dilutions were made in the same solvent used by the manufacturer. Solid standards were weighed and diluted to a final concentration of 1mg/ml in acetonitrile and then diluted to 100µg/ml and 10µg/ml.
Table 2: Table of standard chemicals, obtained commercially

<table>
<thead>
<tr>
<th>NAME, Formula</th>
<th>Manufacturer</th>
<th>CAS &amp; LOT</th>
<th>Size OR Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>4-Amino-2,6-dinitrotoluene</strong>&lt;br&gt; C₇H₇N₃O₄</td>
<td>SPEX CertiPrep</td>
<td>CAS S-226 Lot: EN151112002</td>
<td>1ml 1mg/ml in MeOH</td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>1,3,5-Trinitrobenzene</strong>&lt;br&gt; C₆H₃N₃O₆</td>
<td>SPEX CertiPrep</td>
<td>CAS S-3770 Lot: Lk15102301</td>
<td>1ml 1mg/ml in MeOH</td>
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<td></td>
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<tr>
<td><strong>Tetryl</strong>&lt;br&gt; C₇H₅N₅O₈</td>
<td>SPEX CertiPrep</td>
<td>CAS S-2178 Lot: T1140613011</td>
<td>1ml 1mg/ml in ACN:MeOH</td>
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<tr>
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</tr>
<tr>
<td><strong>HMX</strong>&lt;br&gt; C₄H₈N₈O₈</td>
<td>SPEX CertiPrep</td>
<td>CAS S-2229 Lot: E1140918009</td>
<td>1ml 1mg/ml in ACN:MeOH</td>
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<td><img src="image" alt="HMX" /></td>
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<tr>
<td><strong>N-Nitrosodiphenylamine (N-nDPA)</strong>&lt;br&gt; C₂H₆N₂O</td>
<td>Crescent Chemical</td>
<td>CAS 33118-10 Lot: 0900058</td>
<td>1ml 1mg/ml in CH₂Cl₂</td>
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<tr>
<td><strong>2-Amino-4,6-dinitrotoluene</strong>&lt;br&gt; C₇H₇N₃O₄</td>
<td>AccuStandard</td>
<td>CAS M-8330-13-01 Lot: 212111083</td>
<td>1ml 0.1mg/ml MeOH:ACN</td>
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<tr>
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<td>Supplier</td>
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<td>Lot Number</td>
</tr>
<tr>
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</tr>
<tr>
<td>Nitroglycerin</td>
<td>Accustandard</td>
<td>CAS M-8330-ADD-1</td>
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<td>Lot: AO113373</td>
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<td>Dibutyl phthalate</td>
<td>Aldrich</td>
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<td>Aldrich</td>
<td>CAS 85-98-3</td>
<td>Lot: 05107LFV</td>
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</table>
Donated:

Other reference standards were donated from various agencies/colleagues. The identity of those donated from John Jay College faculty members were verified via GC-MS. If in a solid form, standards were weighed and diluted to a final concentration of 1mg/ml in acetonitrile and then diluted to 100µg/ml and 10µg/ml. Liquids were presumed to be of a 1mg/ml concentration so were all diluted in the same manner in acetonitrile.

21 explosive samples were received from a colleague’s casework. They were all of unknown concentration and dissolved in ethanol. Their identities and any information known about them are included in Table 4 below.
### Table 3: Standard chemicals donated to this project

<table>
<thead>
<tr>
<th>NAME, FORMULA</th>
<th>Any other information known</th>
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<tbody>
<tr>
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<td>2-Nitrodiphenylamine*&lt;br&gt;(2-nDPA)&lt;br&gt;C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CAS 119-75-5&lt;br&gt;Sigma Aldrich, Batch: 07505BS</td>
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<tr>
<td>4-Nitrodiphenylamine*&lt;br&gt;(4-nDPA)&lt;br&gt;C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
<td>2,3-Dinitrotoluene*&lt;br&gt;(2,3-DNT)&lt;br&gt;C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>2,4-Dinitrotoluene*&lt;br&gt;(2,4-DNT)&lt;br&gt;C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>CAS 121-14-2&lt;br&gt;Supelco&lt;br&gt;1mg/ml (ACN)</td>
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<tr>
<td>2,6-Dinitrotoluene*&lt;br&gt;(2,6-DNT)&lt;br&gt;C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>CAS 606-20-2&lt;br&gt;Supelco&lt;br&gt;1mg/ml (ACN)</td>
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<td><strong>Diethyl phthalate</strong></td>
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<td><strong>Trinitrotoluene (TNT)</strong></td>
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<td><strong>Pentaerythritol Tetranitrate</strong></td>
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<tr>
<td>(PETN)</td>
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<tr>
<td><img src="image" alt="Pentaerythritol Tetranitrate" /></td>
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</tbody>
</table>
| **RDX**<sup>+</sup>  
| $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$ | Small, round colorless crystals |

| **C-4**<sup>+</sup>  
| (mainly RDX $\text{C}_7\text{H}_5\text{N}_5\text{O}_6$) | Sticky white/yellow gummy substance |

| **1,2-Dinitrobenzene**<sup>+</sup> (Herein referred to as dinitrobenzene)  
| $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$ | CAS: 528-29-0  
| Small, white, rod-like crystals  
| LOT: 7724212 |

| **Urea Nitrate**<sup>+</sup>  
| $\text{CH}_5\text{N}_3\text{O}_4$ | CAS: 124-47-0  
| Soft, white chunks |

| **2,4,6-Trinitrobenzoic Acid**  
| $\text{C}_7\text{H}_3\text{N}_3\text{O}_8$ | CAS: 129-66-8  
| Fine, white powder |

| **Trinitroanisole**  
| $\text{C}_7\text{H}_5\text{N}_3\text{O}_7$ | CAS: 606-35-9  
| Flat, shiny, white crystals |

| **2,4-Dinitrophenetole**<sup>+</sup>  
| $\text{C}_8\text{H}_8\text{N}_2\text{O}_5$ | CAS: 610-54-8  
| Fine, shiny, rod-like crystals |
| **Ammonium Nitrate**<sup>*</sup> | CAS: 6484-52-2  
Fisher Scientific, Lot: 120879  
Sticky, white, shiny crystals |
| (NH₄)(NO₃) |   |
| **Trinitrotoluene**<sup>+</sup> (TNT) | CAS: 118-96-7  
Flat, white, crystals |
| C₇H₅N₃O₆ |   |
| **2,4-Dinitrodiphenylamine**<sup>^</sup> | CAS: 961-68-2  
Yellow crystals |
| C₁₂H₉N₃O₄ |   |
| **Nitroglycerin**<sup>^</sup> | Synthesized by John Jay staff members, dissolved in acid at unknown concentration |
| C₃H₅N₃O₉ |   |

**KEY:**
*Donated by faculty at John Jay, CUNY & verified identify via GC-MS
+Donated as a standard solid from a personal contact courtesy of NYPD crime laboratory
^Donated by a faculty at John Jay, CUNY – donated from a crime laboratory or ordered commercially for a classroom laboratory exercise
Table 4: List of explosive samples donated from Smiths Detection

<table>
<thead>
<tr>
<th>NAME of main explosive</th>
<th>Any other information known</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – Semtex Type II</td>
<td>IRA</td>
</tr>
<tr>
<td>2 – Semtex Type II</td>
<td>IRA – labeled “home office Semtex-H Type 2 Dec 92 IRA Explosives)</td>
</tr>
<tr>
<td>3 – Semtex-H</td>
<td>IRA</td>
</tr>
<tr>
<td>4 – Semtex-H</td>
<td>RCMP</td>
</tr>
<tr>
<td>5 – Semtex-H</td>
<td>MNT</td>
</tr>
<tr>
<td>6 – Semtex-H</td>
<td>Para-MNT 0.1%</td>
</tr>
<tr>
<td>7 – Semtex-1A</td>
<td>Spanish EGDN</td>
</tr>
<tr>
<td>8 – Semtex-A</td>
<td>Spain 600µl taggant</td>
</tr>
<tr>
<td>9 – C-4</td>
<td>Regular</td>
</tr>
<tr>
<td>10 – C-4</td>
<td>MNT</td>
</tr>
<tr>
<td>11 – C-4</td>
<td>DMNB 0.1%</td>
</tr>
<tr>
<td>12 – Hexageno</td>
<td>Spanish C-4</td>
</tr>
<tr>
<td>13 – Dynamite</td>
<td>IRA</td>
</tr>
<tr>
<td>14 – Dynamite</td>
<td>Forcite 40</td>
</tr>
<tr>
<td>15 – Dynamite</td>
<td>Giant Coalition</td>
</tr>
<tr>
<td>16 – Detasheet</td>
<td>NAX</td>
</tr>
<tr>
<td>17 – Detasheet</td>
<td></td>
</tr>
<tr>
<td>18 – Pentex</td>
<td></td>
</tr>
<tr>
<td>19 – Tetryl</td>
<td></td>
</tr>
<tr>
<td>20 – TNT</td>
<td>Flake</td>
</tr>
<tr>
<td>21 - TNT</td>
<td>Crystals</td>
</tr>
</tbody>
</table>

NOTE: All are of unknown concentration, but were known to be dissolved in ethanol prior to donation. No further dilutions were made.

Some notes on explosives donated/purchased for this experiment:

RDX, TNT and PETN are military secondary high explosives, so they are detonated by a primary explosive (primer) and are relatively insensitive to heat, shock and friction but are used for commercial and military blasting. Common taggants used include EGDN (ethylene glycol dinitrate), MNT (mononitrotoluene/toluene), PMNT (para-nitrotoluene), and DMNB (dimethyl dinitrotoluene). Semtex is a plastic explosive that contains RDX and PETN that fits into several classifications such as 1A, H (hardening), 2P (hexagonal booster charges that contains PETN and wax), and they are often composed of PETN, RDX, binder, plasticizer, antioxidant, and a dye.
C-4 is usually composed of about 90% RDX plus a plasticizer such as dioctyl sebacate or dioctyl adipate (~5%), a binder such as butyl rubber (~2%), and an oil (~1%). Dynamite is typically made with a nitroglycerin base, combined with some diatomaceous earth and a small amount of sodium carbonate. However, dynamite has often been used as a bit of a generic term thus it may contain nitrate esters and carbon based fuels, though the original formulation was nitroglycerin based. Detasheet is a flexible rubberized explosive that commonly contains PETN, nitrocellulose and a binder. Pentex typically is composed of either TNT and RDX and PETN. Tetryl is a booster, or an explosive charge that provides detonation linkages between a main charge and a primary explosive. TNT usually comes in two forms, flakes and crystals that appear different in morphology. The crystal form is more common (Urbanski 1964), (Dobratz 1972).

Gas Chromatography/Mass Spectrometry:

An Agilent 5975C GC-MS (inert MSD with triple axis detector) was used to verify the identity of any standards donated to the researcher in this study (i.e. any standards lacking certification documents). Agilent MSD Chemstation (G1791EA E.02.00.493) software was used to set up a method that entailed a 0.5µl injection, a 50:1 injection split on a HP-5MS 5% phenylmethylsilox column that was 30m x 250µm x 0.25µm with a 2ml/min flow and an oven programming set from 70° (hold 4 minutes) - 220° (hold 5 minutes), ramping 8°/minute. The quadrupole was set to have a solvent delay of 1.50min, a gain factor of 2, a scan time of 1.5, start/end mass of 50-500.0, a scan speed of 1,562u/s and a step size of 0.1m/z. Agilent’s Chemstation Masshunter© software was used to evaluate the retention and spectral data and compare to an internal database.
Salt Solutions

Solutions of 0.5M NaCl and 0.5M KNO₃ were made by weighing out an appropriate amount of solid (~0.0506g/ml KNO₃ in dH₂O and ~0.02922g/ml NaCl in dH₂O) and diluting in deionized water.

GENERAL RAMAN SCHEME

Note: Before a silicon wafer was used for any experimentation, it was cleaned using ethanol and/or methyl ethyl ketone with a kimwipe, then the solvent was allowed to completely evaporate. This cleaning was done before any new sample was deposited onto the wafer.

Normal Raman Samples

About 0.1mg solid (bulk) sample were deposited onto a silicon slide with a clean spatula. If the sample was a liquid, 20µl of liquid samples were pipette onto a silicon slide. They were allowed to dry completely prior to analysis. At least three, but usually more than five separate data collection trials were obtained for each sample.

Surface Enhanced Raman Samples

To validate the effectiveness of the nanoparticles synthesized or purchased, SERS studies with standard solutions were utilized to judge which methodology was the most useful for further studies. In terms of the silver nanoparticles, three types were compared; those made via the microwave synthesis (“Ag NPs”), Lee-Meisel synthesis (“LM”) and Modified Lee-Meisel synthesis, with a shorter boiling time (“Mod-LM”). For the gold nanoparticles, the variations compared were commercial Nanoparticles (“Commercial”), Lee-Meisel Synthesis (“Au LM”), and Modified Lee-Meisel synthesis, with a shorter boiling time (“Au Mod-LM”). These validations made use of a combination of nanoparticles, sample (analyte) and salt in a 16:4:2
ratio and their spectra were acquired for 50s at various laser powers. Based on previous reports, a 16:4:2µl ratio of nanoparticle:analyte:salt was chosen for a standard method for preliminary investigations.*CITE The nanoparticles were also used in different concentration ratios (100%, 50% and 25% concentration) to assess which combination of variables produced the most useful spectrum, in terms of number of counts and lack of sample burning.

For the SERS experimentation at 532nm excitation, using silver nanoparticles, 4µl or 8µl of sample was combined with 16µl of silver nanoparticles prepared via Lee-Meisel method or a modified microwave procedure and 2µl of 0.5M KNO₃. For SERS experimentation at 785nm excitation, 4µl or 8µl of sample was combined with 16µl of gold nanoparticles prepared via Lee-Meisel method or acquired from Diagnostic AnSERS and 2µl of 0.5M NaCl (Pozzi et al 2012). 15-20µl spots of this mixture were pipetted onto a silicon wafer. The mixture was allowed to dry completely before analysis. For SERS experimentation at 532nm excitation using the silver nanosheets, 5-10µl of sample was pipette upon the sheet and allowed completely prior to analysis. At least three, but usually more than five separate data collection trials were obtained for each sample.

Various trials in which different variables were changed were performed. For example, standard solutions were analyzed with or without salt, at different laser powers, and with different substrates. The combination of variables that produced the highest quality spectra was selected for a set of experiments, though any general trends were noted and utilized throughout the experimentation.
**Figure 15**: Typical set-up of silicon wafer with various 15µl samples dried on it

**SHOOTING PARAMETERS/GUNSHOT RESIDUE**

**Firearms:**

All the firearms used in this portion of experimentation were 9mm semi-automatic pistols. The make and model of the firearms used were a Glock 19, a Smith and Wesson 5946 a Ruger p95, a Walther p38. All of them were cleaned with methyl ethyl ketone (Fisher, Lot 154876) by use of a cotton-tipped applicator forced down the barrel of the firearms until no residue appeared on a clean applicator tip. Firearms were cleaned before shooting and between different brands of ammunition to avoid any contamination/crossover in the same thorough manner. Additionally, shooters’ hands were washed thoroughly with soap and water before shooting and between different brands of ammunition to avoid any contamination/crossover.
Ammunition:

Five different types of ammunition were used. They were Winchester 9mm Luger (Centerfire, 115gr FMJ, Lot: HPO2N), Remington UMC 9mm Luger (Centerfire, 115gr, Lot: L9MM3), Aguila 9mm Luger (Centerfire, 115gr FMJ, Lot: 30CG3193), CCI Blazer 9mm Luger (115gr, FMJ, Lot: FO5X37), and Speer Lawman 9mm Luger (Centerfire, 115gr, TMJ, Lot: F22036). All cartridges were disassembled with a standard kinetic bullet pull and their powders were photographed and collected in an Eppendorf tube (Figure 17).
These five ammunition types (pulled via a kinetic bullet pull) were each weighed (~1.5mg) and combined with 50µl of methyl ethyl ketone in separate labeled Eppendorf tubes. These solutions were sonicated (Branson 1800 Ultrasonic Bath, Bransonics Series, Model M1800, Serial number BGA0412572440B) for 30 minutes at about 35°C, and then excess graphite was removed via a centrifugation at 3500g for 5 minutes. These solutions would be analyzed via normal Raman and SERS. This procedure was adapted from Lopez-Lopez et al (2010).

Figure 17: Photographs of disassembled cartridges, manufacturers used in this study: Winchester, Remington, Aguila, Speer Lawman, CCI Blazer (clockwise from top left)
General Shooting Scheme:

Four different 9mm handguns were used to shoot five different types of ammunition into various substrates. The substrates included 8 ½ x 11-inch white copy paper, approximately 8x10 inch “cotton cloth fabric” and approximately 8x8 inch “denim fabric” (both obtained from a local fabric store). The firearms were held on a hand mount, to stabilize the firearm, about 12 inches from the target, and casings were collected as well as the substrate.

Scotch brand double-sided permanent tape was also used to collect GSR from shooters’ hands. Separate pieces of tape were gently applied to the webbing of the shooters’ hands after shots one and two, and the stored on a piece of paper lined with packing tape for easy removal.

Agar gel plates were made in a ratio 2 grams of agarose: 100mL of dH2O. A total of 20g of agarose was carefully weighed and combined with 1L of distilled water, and the solution was heated until it was near boiling, with occasional stirring. The solution was then poured into small petri dishes, allowed to cool and harden, and then covered and parafilmed and stored in the refrigerator before and after experimentation. The agar plates were gently pressed upon the webbing a shooters’ hands after the third shot for each firearm/ammunition combination.

Mixed ammunition studies were also conducted. Two sets of cloth substrates were used to collect residue from firearms in which there was no cleaning of the firearm’s barrel or the shooters’ hands in between shots. Set 1 consists of four shots, all from the S&W firearm. The first shot fired CCI Blazer ammunition, while the next three fired Speer Lawmakers ammunition. Set 2 consists of three shots, all from the S&W firearm. The first shot fired Speer Lawmaker ammunition, while the next two fired Remington ammunition. All mixed shots were shot upon the cotton cloth substrate at a distance of approximately 12-14 inches.
All substrates were analyzed via normal Raman and SERS, with both 532nm and 785nm excitation lasers (Ag nanoparticles used for 532nm, Au for 785nm).

Agar gel plates impregnated with silver colloids were made in a ratio 2 grams of agarose: 100mL of silver colloidal suspension solution (made via the Lee-Meisel method). A total of 1.8g of agarose was carefully weighed and combined with 90mL of the silver solution and the solution was microwaved for a few seconds (~40s) until it was near boiling, with occasional stirring. The solution was then poured into six separate small petri dishes, allowed to cool and harden, and then covered and parafilmed and stored in the refrigerator before and after experimentation. The agar gels were cut into eighths with a clean scalpel, and the piece of gel was gently pressed upon the cotton cloth of “mixed shooting” samples (in which cotton cloth was used as the substrate and different shots were fired without cleaning). Raman analysis was performed before and after the addition of 2µl of KNO₃ pipetted directly onto the gel. The gel was placed upon a slide, wrapped in aluminum foil, to prevent the laser from penetrating through it and reaching the microscope stage. These gels were analyzed with the 532nm excitation laser.
Figure 18: (a) A photograph of an agar gel (blanks) with gold and silver colloidal solutions dried on its surface vs. (b, c) agar gel impregnated with silver colloidal solution ((b) before and (c) after cutting)
Figure 19: The setup used to fire all of the shots in this experiment. Here, a cloth substrate is the target.

THIN LAYER CHROMATOGRAPHY

TLC analysis was conducted on mixtures of standard samples. The first contained Diphenylamine, 2-Nitrodiphenylamine, 4-Nitrodiphenylamine and 2,4-Dinitrodiphenylamine (all in acetonitrile, 1mg/ml in equal parts). The next contained TNT, PETN, RDX and C-4 (all in acetonitrile, 1mg/ml in equal parts), and the last contained Tetryl, HMX and Urea Nitrate (all in acetonitrile and/or methanol, 1mg/ml in equal parts). The same three mixtures were also analyzed, but with all standards at a concentration of 100µg/ml. In subsequent trials, the mixtures were as follows (all at a concentration of 100µg/ml): Mixture 1: Diphenylamine, 2-
Nitrodiphenylamine, 4-Nitrodiphenylamine; Mixture 1A: 2,4-Dinitrodiphenylamine and N-Nitrosodiphenylamine; Mixture 2: TNT, PETN, RDX and C-4; Mixture 3: Tetryl, HMX and Urea Nitrate.

Standard TLC plates (TLC Silica Gel, MERCK, 10x20cm) were washed in methanol and dried in an oven for twenty minutes at 120°C. Plates were marked with pencil ~10mm from the bottom and 16µl of the mixture was placed on the line (~0.5µl at a time). Two different mobile phases were used, petroleum ether:acetone (3:1) and hexane:acetone (3:1), and ~40ml of mobile phase was used, to develop separate plates that were configured in the exact same manner.

Analysis was conducted in two identical glass TLC chambers that were closed with glass lids, and sealed with vacuum grease (Lutonska et al 2015), (Nam 1997). Plates were visualized under an ultraviolet light source, both short and long wavelengths, and 16µl of a mixture of silver colloid and KNO₃ was pipetted onto each separated spot and allowed to dry for at least thirty minutes. SERS spectra were then collected via the WITec instrument with a 532nm. The same was repeated at 785nm excitation, with a gold colloid and NaCl mixture.

Figure 20: A typical design for a TLC plate in this experimentation (This plate is labeled for three standard mixtures, each at a 1mg/ml concentration and a 100ug/ml concentration; it was used to study the Raman spectrum before introduction of a mobile phase)
CHAPTER 3 - RESULTS & DISCUSSION

Preliminary Salt Studies

Preliminary studies concerning the appropriate ratios and components in the mixture for SERS analysis were conducted. It was found that there was very little normal Raman response for 4-mercaptophenol alone. However, in the presence of silver nanoparticles, spectral features became apparent and there was an increase in the relative peak heights/detector counts when salt was added. Additionally, for the silver nanoparticles, KNO₃ seems to provide a greater enhancement than NaCl, whereas NaCl was found to provide a better enhancement with gold nanoparticles (Figure 21, 22 and 24). The predictable relationship between laser power and overall peak intensity was confirmed. As the laser power increased, the intensity of the peaks did as well (Figure 23). It must be noted that the apparent focus of each sample, via the BH-2 microscope varies from trial to trial. Thus, quantitation of an overall enhancement based on one trial could be misleading. The overall trends, however, were of significance for proceeding forward. It also confirmed, as suggested by the literature, silver colloids provide more spectral information when a laser closer to the green color of the colloids is used (higher energy, shorter wavelength), whereas the gold nanoparticles were better suited for excitation lasers closer to their reddish color (lower energy, longer wavelength) (Figure 24). Different objective lenses were also investigated. Although the 100x objective did provide greater peak intensities, samples could be harder to focus at such a great magnification with its lesser depth of focus. It was determined the best conditions for SERS analysis involved a combination of silver colloids and KNO₃ with the analyte, whereas gold colloids should be combined with NaCl and the analyte.
**Figure 21**: A comparison of spectra of 4-mercaptophenol in the presence of silver nanoparticles (SERS), and with and without salt (SERS)

**Figure 22**: A comparison of spectra silver nanoparticles (alone), combined with 4-mercaptophenol (SERS), and with the addition of salt (SERS)
Figure 23: A comparison of spectra of 4-mercaptophenol at different laser powers.

Figure 24: A comparison of silver vs. gold nanoparticles in the study of 4-mercaptophenol SERS.
Photomicrograph Salt Studies

![Image](image_url)

**Figure 25**: Examples of structures seen in a gold “blank” sample – 10x objective, Horiba Instrument (Sample: Au, NaCl and ethanol)

NOTE: The center of the image is the region in which the laser interacts with the sample.

As documented in photomicrographs of both silver and gold colloidal solutions, crystalline structures were observed. A simple X-Ray diffraction analysis confirmed that these structures were due to the KNO₃ or NaCl added to the solutions (Appendix IV). For this reason, it was decided that all samples, which typically dried in a circular spot, should be sampled five times in varying places within the spot: one in the approximate center, and one each towards the top, bottom, left and right of this sample. The goal was to sample an assortment of crystalline structures, which is any dark or light places as seen through the microscope.

WITec Laser/Focusing Studies

All three spectrometers systems were evaluated to ensure that the proper focus was used to photograph the sample, and then adjusted so that the maximum Raman signal, in terms of counts, was obtained. After proper visual focus was realized, the signal was maximized using the oscilloscope mode and adjusting the visual image so that the laser looked as small and sharp a circle as possible. For all the spectrometers, this involved a significant change in the distance...
between the lens and the stage. Figure 26 (A and B) shows the difference seen when the image was focused upon versus when the laser was focused via oscilloscope mode. This process was completed each time that an analysis was conducted for each.

**Figure 26a:** A comparison of different methods of focus and their spectral intensities; images of silicon surface and laser spot via WITec confocal instrumentation and software (532nm)
Figure 26b: A comparison of different methods of focus and their spectral intensities; images of silicon surface and laser spot via WITec confocal instrumentation and software (785nm)

It is evident in Figure 26 (A and B) above, that there was a marked increase in the intensity of the silicon peak when the laser was re-focused and the oscilloscope mode was used for both the 532nm and 785nm excitation laser. Although this lead to a poorer quality of image in terms of the photomicrograph, the change in intensity of the spectral features was of the utmost value. For that reason, all experiments that followed involved a visual focus and a photomicrograph being saved, and then a re-adjustment of the focus using the laser image, and then the oscilloscope mode until the maximum spectral intensity was reached.
Nanoparticle Validation Studies

In terms of the silver colloids, three types were compared; those made via the microwave synthesis (“Ag NPs”), Lee-Meisel synthesis (“LM”) and Modified Lee-Meisel synthesis, with a shorter boiling time (“Mod-LM”). For the gold colloids, the variations compared were commercial nanoparticles (“Commercial”), Lee-Meisel Synthesis (“Au LM”), and Modified Lee-Meisel synthesis, with a shorter boiling time (“Au Mod-LM”). UV-Visible absorption data was used to compare the spectra obtained to literature values for the wavelength of maximum absorbance ($\lambda_o$) for silver and gold colloid solutions. The silver nanoparticles were found to have a wavelength of maximum absorption value at approximately 409-412nm and the gold nanoparticles at approximately 526-528nm. These numbers show that the silver or gold was synthesized correctly, and at a suitable concentration, as this $\lambda_o$ and level of necessary dilution is consistent with the literature values for the maximum wavelength values for the respective colloids.

UV/Vis

Wavelength Accuracy – Holmium Oxide Glass Filter

The spectrum of a standard reference material, a holmium oxide glass filter, was compared to literature values to ensure the instrument was properly calibrated in terms of wavelength. This procedure was repeated each time UV/Vis Spectroscopy was performed in these sets of experiments. Representative data and spectrum obtained for this calibration verification appear in Figure 27.
Figure 27: The UV/Visible spectrum of a standard holmium oxide glass filter
Figure 28: Absorption spectra of different concentrations of a silver colloid solution (microwave synthesis)

Figure 29: Absorption spectra of different concentrations of a gold colloid solution (Lee-Meisel synthesis)

Note: The [Full], [50] and [25] denotation above refers to the concentration/dilution of the nanoparticles. [Full] refers to an undiluted nanoparticle formulation, [50] is diluted 50% with deionized water, and [25] is a 25% solution, diluted with deionized water.
Nanoparticle Validation Studies II: SERS

Silver:

**Figure 30:** A comparison of crystal violet SERS spectra using different concentrations of silver colloids (microwave synthesis)

**Figure 31:** A comparison of crystal violet SERS spectra using different silver colloid preparations
Gold:

**Figure 32:** A comparison of crystal violet SERS spectra using different concentrations of gold colloids (Lee-Meisel method)

**Figure 33:** A comparison of crystal violet SERS spectra using different concentrations of gold colloids (Modified Lee-Meisel method)
Raman experiments were used to verify the proper formulations that should be used for subsequent SERS studies. It was found that, in general, the colloid solutions diluted to 25% of the original concentration of silver gave rise to the best spectral data and resulted in the least amount of burning with the high-energy laser (532nm). This burning is observed as two large bands, appearing at approximately 1350 and 1580 cm\(^{-1}\) which is described by Alvarez-Puebla as “the amorphous carbon background due to the photocombustion of the sample” (2012), herein, it is referred to as burning or burning as carbon bands. All formulations produced an enhancement, but the original Lee-Meisel formulation produced the most intense spectra (Figure 31). The 100% concentrated gold colloids produced the most intense spectral data and did not suffer from photocombustion. There was not a large difference between the Lee-Meisel and Modified Lee-Meisel formulations, so either could be used for future experimentation (Figure 32). The comparison of several trials was necessary to result in the highest quality spectrum as a different image, or focus upon a hot spot could lead to a difference in spectral intensity.

**Nanoparticle Validation Studies III: SEM**

Based on the scale in the photomicrograph, an estimation of the size of colloidal particles was conducted. It was determined that the silver nanoparticles ranged in size from dimensions of about 12.29x14.64 \(\mu\text{m}\) to particles that were approximately 26.82 \(\mu\text{m}^2\). The gold nanoparticles varied in size, the smallest particle was about 25.64 \(\mu\text{m}^2\) whereas the large particles were approximately 25.64x38.64 \(\mu\text{m}\). Some of these particles appeared clustered or oblong, and therefore a true estimation of one single nanoparticle proved quite difficult from just these images. However, for the purposes of this research, an estimation of approximately 25 \(\mu\text{m}^2\) was sufficient.
Ag Nanoparticles:

Figure 34: A photomicrograph of the silver nanoparticles (SEM) with the areas highlighted for EDX analysis and EDX results for each spot; NOTE: EDX Results for “Free Draw 1” and “Free Draw 2” were very similar and thus only one is included here
Au Nanoparticles:

**Figure 35:** A photomicrograph of the gold nanoparticles (SEM) with the areas highlighted for EDX analysis and EDX results for each spot

NOTE: EDX Results for “Free Draw 1-4” were all very similar and thus not all were included herein
Ag Nanosheets:

Free Draw 1
Figure 36: A photomicrograph of the silver nanosheets (SEM) with the areas highlighted for EDX analysis and EDX results for each spot. NOTE: EDX Results for “Free Draw 1 and 4” were similar and thus only one was included here.
Based on the elemental analysis of the silver nanoparticles, it was concluded that in the X-ray analyzed area of silver nanoparticles, elements of sodium, sulfur, and silver were present. The silver was important here as it is this colloidal particle to which the analyte will attach for SERS analysis. Sodium, carbon and oxygen were present due to the sodium citrate used to prepare and store the colloidal solution, and sulfur is present due to the silver sulfate used to prepare the colloids. There could be a contribution of carbon in the spectrum from the substrate, which was a high purity carbon tape on an aluminum stub used to mount the nanoparticles for analysis. It can be seen in Figure 34 that certain areas (“Free Draw 3”) seemed to contain only a small amount of silver, which could be due to a lack of homogeneity in drying.

Based on the EDX analysis of the gold nanoparticles, it was concluded that the gold nanoparticles consisted of gold, with sodium and chlorine also present. The gold was important here because it is the colloidal particle the analyte will attach to for SERS analysis. Sodium, carbon and oxygen were present due to the sodium citrate used to prepare and store the colloidal solution, and chlorine was present due to the chloroauric acid used to prepare the colloidal solution. There could be a contribution of carbon from the substrate, which was a high purity carbon tape on an aluminum stub used to mount the nanoparticles for analysis.

Based on the EDX analysis of the silver nanosheets, it was concluded that the nanosheets consisted of silver and copper. The silver was important here as it is the substrate to which the analytes will attach for SERS analysis. Copper was present since copper tape was used as the substrate in preparation of the nanosheets, thus any area that was not fully coated in silver would still generate copper X-Rays from the surface (see “Free Draw 1 and 2 vs. Free Draw 3 in Figure 36; this could be useful in determining the extent of nanosheet synthesis). Lastly, carbon and oxygen is present due to the sodium citrate used in the preparation of the nanosheets.
NANOPARTICLE VALIDATION IV: SERS; “Anomalous Bands”

Figure 37: A comparison of silver nanoparticle blanks

Figure 38: A close-up view of the anomalous bands seen in silver nanoparticle blanks
Figure 39: A SERS spectrum of the colloidal solution presented by Teslova et al; It shows several bands that can be attributed to the citrate in the colloidal mixture (Teslova et al 2007).

\[ \text{Au + NaCl} \]

Au + NaCl Blanks

Figure 40: A comparison of gold nanoparticle blanks
For both silver and gold nanoparticle “blank” solutions, it was typical to not see very many discernable spectral features. Sometimes, burning was noted based on the appearance of carbon bands appear at approximately 1350 and 1580cm\(^{-1}\). Yet, at certain locations in the sample spot, small features that look like significant spectral features were noted. It was postulated by Sanchez-Cortes and Garcia-Ramos that citrate, nitrate and perchlorate bands were often seen in SERS experimentation. They note that this is both due to the way in which the colloids were prepared and because every laboratory that conducts SERS analysis has at least a low level of contaminants originating from the atmosphere, lab bench, etc., and due to the extreme sensitivity of the SERS technique there are these “anomalous bands” that appear in even the most meticulous experiments. Thus, it is of the utmost importance to pay attention to the interpretation of results and careful experimental design (Sanchez-Cortes & Garcia-Ramos 1998). In work presented by Teslova et al., it is noted that many of these bands were due to the citrate ions present in the colloid solution, in which citrate is the stabilizer (Figure 39). The bands were observed often in this work, and were especially obvious in the overlaid spectra in Figure 38, though their intensities were quite low compared to bands in SERS spectra. It appears that the unassigned bands seen in this work were due both to the citrate present in the solution, as well as some of these reported “anomalous bands.” For simplicity, these will all be referred to as anomalous bands in this study. It is possible that the instruments used in these experiments are so sensitive that bands which may not be noted with other systems were apparent here. This was an important result because it was deemed essential to analyze “blank” samples before every day of experimentation so that the difference between blank spectral bands and important bands for the analyte could be discerned. Furthermore, the intensity was important to note as the intensity
in these bands in blank samples was usually only a few hundred counts, whereas actual SERS bands showed intensities in the range of thousands to tens of thousands of counts.

STANDARD SAMPLES

Validation

GC-MS:

The donated standards were validated using a GC-MS and a database search. The typical output from the database showed the total ion chromatogram (TIC), the mass spectrum labeled with the selected ions, a table with the mass to charge ratio values of the ten largest peaks, as well as the database information (spectrum, identity, match quality etc.) for the chemical. The GC-MS data of diphenylamine is shown as an example in Figure 41. The other standards can be seen in Appendix II. The results of this validation confirmed the identity of diphenylamine, 2-nitrodiphenylamine, 4-nitrodiphenylamine, 2,3-dinitrotoluene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 3,4-dinitrotoluene, diethyl phthalate, 2-nitrotoluene, and 4-nitrotoluene standards.
GC-MS Results:

File: D:\MassHunter\Data\Che320 Instrumental Anal\2014 1028 30 JL DPA Nist NO delay.D
Misc Info: Date Acquired: 28 Oct 2014 15:27
Method File: JLC03SR.m Operator: GCMS-HP\admin
Sample Name: Abundance: 29701 TIC: 2014 1028 30 JL DPA Nist NO delay.Ddata.ms 18966

Time-> 3.00 3.20 3.40 3.60 3.80 4.00 4.20 4.40 4.60 4.80 5.00 5.20 5.40 5.60 5.80 6.00 6.20 6.40 6.60 6.80
Abundance 123 Ion range 271.85 to 271.95: 2014 1028 30 JL DPA Nist NO delay.Ddata.ms 0
72 Area
S/N (rms) = 123

Time-> 3.00 3.20 3.40 3.60 3.80 4.00 4.20 4.40 4.60 4.80 5.00 5.20 5.40 5.60 5.80 6.00 6.20 6.40 6.60 6.80
Abundance Scan 579 (3.092 min): 2014 1028 30 JL DPA Nist NO delay.Ddata.ms 207.0

m/z-> 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500
Mass 189.7

m/z-> 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500
Mass 182.7

The noise interval was from 2.692 to 2.992 min. and contained 59 scans

Noise: Avg Min Max RMS PkCalc PkTrue Signal-Avg Noise
S/N : 123.0 26.4 0.6
Hit 1: Diphenylamine

(replib) Diphenylamine

Name: Diphenylamine
Formula: C12H11N
Other DBs: Fine, TSCA, RTECS, EPA, HODOC, NIH, EINECS, IRDB
Contributor: Japan AIST/NIMC Database- Spectrum MS-NW- 486
10 largest peaks:

| 169 999 | 168 358 | 51 224 | 167 190 | 77 153 | 39 131 | 170 130 | 66 121 | 65 105 | 50 65 |

Synonyms:
1. Benzenamine, N-phenyl-
2. Anilinobenzene
3. Benzene, (phenylamine)-
4. DFA
5. DPA
6. N-Phenylaniline
7. N-Phenylnbenzeneamine
8. Aniline, N-phenyl-
Figure 41: GC-MS data and database output for Diphenylamine standard
UV/Vis:

Ultraviolet/visible spectroscopy was used to determine the wavelength of maximum absorbance ($\lambda_0$) for some of the standards. It was postulated that most standards would absorb in the ultraviolet region of the spectrum, and thus the higher energy laser would be best to produce the most detailed Raman spectrum. Figure 42 is the UV/Vis spectrum of diphenylamine, used here as an example of the data obtained. Its wavelength of maximum absorbance is located at 282.5nm, which is in the ultraviolet region. All other standards tested also had a $\lambda_0$ located in the ultraviolet region. This data is presented in Appendix III.
Figure 42: UV/Vis data for Diphenylamine Standard
Normal Raman & SERS Results

NOTE: For any of the spectral results presented herein, any band assignments (to specific structural groups) are tentative. In other words, no quantum mechanical calculations or density functional theory was conducted to assign these bands. Rather, group correlation tables were used to associate the spectral information to the specific functional groups in the sample.

Blanks:

Silicon

![Silicon Standard](image)

**Figure 43**: A comparison of Silicon blanks with an excitation laser of 532nm and 785nm. A silicon standard was analyzed and verified for calibration at least three times at the beginning of each day of experimentation. In any of the spectra that follow, a peak at approximately 521 cm\(^{-1}\) and a small band at about 936 cm\(^{-1}\) represent spectral lines from silicon. This results in the spectra because the samples were dried upon a silicon wafer.
The Acetonitrile standard was analyzed each day in which a standard dissolved in acetonitrile was analyzed. Often, certain bands/burning features were noted (photocombustion bands). Often, a sharp band at about 1047-1050 cm\(^{-1}\) appeared which was attributed to the acetonitrile itself. In the analysis of the standards, a band at 1047-1050 cm\(^{-1}\) would be interpreted as being contributed from the acetonitrile solvent, not from the standard’s chemical makeup, itself.
**H$_2$O SERS**

![H$_2$O SERS Blank](image)

**Figure 45**: A comparison of H$_2$O SERS at full and lower laser ($\lambda_o = 532$nm)

The SERS spectra from a water blank (Ag nanoparticles, KNO$_3$ and H$_2$O) does not indicate that there were any noteworthy spectral features. However, there is a great possibility for burning as the carbon bands were especially noticeable with a full power laser, and even seen with a lower laser power. This is important during further experimentation because sample burning must certainly be of concern to the analyst.

**Methanol SERS**

![Methanol SERS Blank](image)

**Figure 46**: A comparison of methanol SERS at full and lower laser ($\lambda_o = 532$nm)
Anomalous bands were also noted in some methanol solvent blanks, as well as some slight burning. Most methanol samples, however, show very few spectral features which make it a suitable solvent for analytes of interest.

The explosives donated by a colleague were all diluted in ethanol, so analysis by SERS of a blank ethanol standard was of utmost importance to ensure that bands from ethanol were not observed in the standards. The Ethanol blank can be seen in Figure 151.
STANDARDS: Results & Discussion

Note: Both normal Raman and the SERS of the liquid samples [100µg/ml] were analyzed via both the Horiba and WITec instruments with excitation lasers 532nm and 785nm. The nanosheets data was collected using the WITec (at 532nm) and the City College Instrument (488nm). Select representative spectra are shown, the rest can be found in Appendix V. In some spectra, a peak is visible at approximately 521cm⁻¹ and a small broad peak at about 936cm⁻¹ which represent spectral lines from silicon. These occur because the samples were dried and analyzed on a silicon wafer. On certain spectra, the y-axis was truncated so the intense citrate peaks and the silicon peaks were no longer completely visible; thus, allowing for the enhanced viewing of less intense spectral features.

Photomicrographs were used to determine where spectral data should be collected. Large crystalline structures were noted due to the salt (KNO₃ with the silver colloids appeared to have a leaf-life or multiple rod-like structures, NaCl with the gold colloids appeared to look cubic in structure). The overall yellow or purple appearances of the photos are due to the specific filters located in the beamsplitter setup for each of the WITec wavelengths (yellow corresponds to the 532nm’s filter; purple corresponds to the 785nm’s filter). The photos from the Horiba system were pink or pale yellow in appearance as they were captured under low white light, without the presence of the filter (the filter was inserted via a sliding mechanism before spectral data collection). The spectral data was collected from the approximate center of each image (as that is where the laser was aligned to interact with the sample).
Diphenylamine

**Figure 47**: A comparison of normal Raman ($\lambda_o=532$nm) and SERS spectra ($\lambda_o=532$nm and 785nm) of a Diphenylamine standard [100µg/ml]

Spectral features were observed for diphenylamine (with the 785nm SERS analysis only) at 603, 808, 1248, ~1375, 1438 and 1605 cm$^{-1}$. The band at 808 cm$^{-1}$ is assigned as the stretching modes between two carbons, or an out of plane vibration between a carbon and hydrogen and the band at 1248 cm$^{-1}$ correlates to C-N stretch seen in aromatic amine compounds. The band observed at 1375 cm$^{-1}$ correlates to the symmetric stretch between a C-NO$_2$ whereas the band at 1605 cm$^{-1}$ is due to aromatic chain vibrations between the carbon atoms. The normal Raman at both wavelengths and SERS spectra at 532nm wavelength did not reveal any spectral features, other than the massive silicon peak.

**Figure 48**: Photomicrographs of diphenylamine SERS samples, 10x objective, WITec; 532nm (left) and 785nm (right)
2-Nitrodiphenylamine

![2-Nitrodiphenylamine Standard](image)

**Figure 49**: A comparison of normal Raman ($\lambda_0=532$nm) and SERS spectra ($\lambda_0 =$532nm and 785nm) of a 2-Nitrodiphenylamine standard [100µg/ml]

Spectral features were noted for 2-nitrodiphenylamine in the SERS spectra at 1188, 1315, 1383, 1554 and 1663cm$^{-1}$ with a 785nm wavelength excitation. The band at 1188cm$^{-1}$ is due to the C-N stretching mode in the aromatic amine. The doublet located at 1383 cm$^{-1}$ is due to the symmetric stretching mode between carbon and the nitro functional ground (C-NO$_2$); the band at 1554cm$^{-1}$ correlates to the asymmetric stretching mode (between C-NO$_2$). The band at 1663cm$^{-1}$ is due to stretching between two carbons sharing a double bond. There is a change in relative peak intensities when the two excitation wavelengths were compared. In the 532nm spectrum, the doublet at 1334/1354cm$^{-1}$ was the most prominent feature; it correlates to the symmetric stretching mode between carbon and the nitro group. No spectral features were observed in the normal Raman spectrum, which proves the utility of a SERS technique with this analyte.

![Photomicrographs of 2-Nitrodiphenylamine SERS samples](image)

**Figure 50**: Photomicrographs of 2-Nitrodiphenylamine SERS samples, 10x objective, WITec; 532nm (left) and 785nm (right)
4-Nitrodiphenylamine

**Figure 51:** A comparison of normal Raman (λ₀=532nm) and SERS spectra (λ₀ =532nm and 785nm) of a 4-Nitrodiphenylamine standard [100µg/ml]

Spectral features were observed via both normal Raman and SERS analysis, with the 532nm laser, for 4-nitrodiphenylamine at 847 (doublet), 992, 1101, 1180, 1283/1318 (large doublet), 1397, 1501 and 1598 cm⁻¹. The band at 992 cm⁻¹ correlates to aromatic chain vibrations between carbons. The bands at 1180 and 1283/1318 cm⁻¹ are due to the stretching mode between carbon and nitrogen seen in aromatic amines. The peak at 1397 cm⁻¹ is due to the symmetric stretch between C-NO₂ whereas the peak at 1598 cm⁻¹ is due to the asymmetric stretching mode. The peak at 1501 cm⁻¹ is due to CC stretching seen in ring structures. The SERS spectrum analyzed via an excitation wavelength of 785nm showed weakly intense features, and mostly bands due to citrate.

**Figure 52:** Photomicrographs of 4-Nitrodiphenylamine SERS samples, 10x objective, WITec; 532nm (left) and 785nm (right)
The above figure is a comparison of the SERS analysis of three diphenylamine standards analyzed with Diagnostic anSERS commercial gold colloids, and via the Horiba instrument. The bands observed for the DPA standard are the most obvious, though many of the features discussed above are seen for the 2-nDPA and 4-nDPA standard as well.
2,3-Dinitrotoluene

![2,3-Dinitrotoluene Standard](image)

**Figure 54**: A comparison of normal Raman ($\lambda_o=532\text{nm}$) and SERS spectra ($\lambda_o=532\text{nm}$ and 785nm) of a 2,3-Dinitrotoluene standard [100µg/ml]

No major spectral features were observed in the analysis of 2,3-dinitrotoluene. In fact, most features present in the above figure were due to the citrate ions or other “anomalous bands” that may have been present in the solution. In the SERS spectrum with a 785nm excitation laser, there were bands at 435 and 1193cm$^{-1}$ and these bands correlate to a stretching mode between a carbon and nitrogen in an aromatic ring, but neither of these bands were completely convincing as they were of low intensity and lacked reproducibility during separate days of experimentation.

![Photomicrographs of 2,3-Dinitrotoluene SERS samples](image)

**Figure 55**: Photomicrographs of 2,3-Dinitrotoluene SERS samples, 10x objective, WITec; 532nm (left) and 785nm (right)
2,4-Dinitrotoluene

No major spectral features were observed during the analysis of 2,4-dinitrotoluene. Again, most features present were due to the citrate ions that were due to the citrate in the colloidal solutions. In the SERS spectrum with an excitation wavelength of 785nm, there was a large band noted at 1193 cm\(^{-1}\) but it probably correlates to citrate ions.

**Figure 56:** A comparison SERS spectra (\(\lambda_0=532\text{nm and } 785\text{nm}\)) of a 2,4-Dinitrotoluene standard [100 \(\mu\text{g/ml}\)]

**Figure 57:** Photomicrographs of 2,4-Dinitrotoluene SERS samples, 10x objective, WITec; 532nm (left) and 785nm (right)
2,6-Dinitrotoluene

Figure 58: A comparison of SERS spectra ($\lambda_0 = 532\text{nm}$ and 785nm) of a 2,6-Dinitrotoluene standard [100µg/ml]

No distinguishing spectral features were observed for the 2,6-dinitrotoluene standard. Any features present were most likely due to the citrate ions or other “anomalous bands” that were due to the citrate and salt in the colloidal solutions. In the SERS spectrum with an excitation wavelength of 785nm, there was a band observed at about 1193cm$^{-1}$ that corresponds to citrate ions.

Figure 59: Photomicrographs of 2,6-Dinitrotoluene SERS samples, 10x objective, WITec; 532nm (left) and 785nm (right)
3,4-Dinitrotoluene

![3,4-Dinitrotoluene Standard](image)

**Figure 60:** A comparison of normal Raman ($\lambda_o=532$nm) and SERS spectra ($\lambda_o = 532$nm and 785nm) of a 3,4-Dinitrotoluene standard [100µg/ml]

No prominent spectral features were observed in any of the analyses conducted for the 3,4-dinitrotoluen standard. Most of the features that were present were due to the citrate ions, as noted in the literature. There was a large band at 1193cm$^{-1}$ that correlates to citrate ions that was noted in the analysis conducted via SERS with a 785nm excitation wavelength.

Based on this work, the dinitrotoluene samples do not appear to be significant Raman scatterers.

![Photomicrographs of 3,4-Dinitrotoluene SERS samples](image)

**Figure 61:** Photomicrographs of 3,4-Dinitrotoluene SERS samples, 10x objective, WITec; 532nm (left) and 785nm (right)
Diethyl phthalate

**Figure 62:** A comparison of normal Raman ($\lambda_o=532$nm) and SERS spectra ($\lambda_o=532$nm and 785nm) of a Diethyl phthalate standard [100µg/ml]

No distinguishing features were observed in the analysis of diethyl phthalate. Any of the features that were observed were most likely due to the citrate ions that were present in the SERS solution. In the SERS spectrum with a 785nm excitation wavelength, there is a fair amount of photocombustion that was represented by the presence of carbon bands located approximately at 1315 and 1609cm\(^{-1}\).

**Figure 63:** Photomicrographs of diethyl phthalate SERS samples, 10x objective, WITec; 532nm (left) and 785nm (right)
2-Nitrotoluene

**Figure 64:** A comparison of normal Raman ($\lambda_o=532nm$) and SERS spectra ($\lambda_o=532nm$ and 785nm) of a 2-Nitrotoluene standard [100µg/ml]

No major spectral features were observed in any of the analyses of the 2-nitrotoluene standard. Most of the minor bands observed were due to the citrate ions, because citrate was used to create the colloidal solutions.

**Figure 65:** Photomicrographs of 2-Nitrotoluene SERS samples, 10x objective, WITec; 532nm (left) and 785nm (right)
4-Nitrotoluene

**Figure 66:** A comparison of normal Raman ($\lambda_o=532\text{nm}$) and SERS spectra ($\lambda_o=532\text{nm}$ and 785nm) of a 4-Nitrotoluene standard [100µg/ml]

No major spectral features were observed in any of the analyses of the 4-nitrotoluene standard. It seemed that any features noted were due to the citrate ions, they were particularly apparent in the SERS spectrum with a 532nm excitation wavelength. Many small bands are observed throughout the spectrum; they correlate to bands due to citrate.

**Figure 67:** Photomicrographs of 4-Nitrotoluene SERS samples, 10x objective, WITec; 532nm (left) and 785nm (right)
Note: For the following four samples (TNT, PETN, RDX and C-4), the bulk (solid sample), liquid and SERS samples were analyzed via both the WITec instrument with full excitation laser powers and the Horiba instrument with 1% laser at 532nm and 785nm. Only one trial for each sample type is shown herein, the rest may be seen in Appendix V.

**TNT**

![TNT Raman spectra](image)

**Figure 68:** A comparison of normal Raman of a solid sample, a liquid sample ($\lambda_o=532$nm) and SERS spectra ($\lambda_o=532$nm) of a TNT standard [100$\mu$g/ml]

![TNT Raman spectra](image)

**Figure 69:** A comparison of normal Raman of a solid sample, a liquid sample ($\lambda_o=785$nm) and SERS spectra ($\lambda_o=785$nm) of a TNT standard [100$\mu$g/ml]
Major spectral features were observed for the analysis of TNT at 791, 820, 1209, 1361, 1610 and 2955 cm$^{-1}$. These bands were consistent between both excitation wavelengths within a few wavenumbers. The bands at 791 and 820 cm$^{-1}$ correlate to a scissoring mode in the NO$_2$ groups. The band at 1209 cm$^{-1}$ is due to interplanar bending mods between C-H. The band at 1361 cm$^{-1}$ is due to a symmetric stretch between carbon and nitro groups, whereas the band at 1610 cm$^{-1}$ is due to the vibrations of the aromatic rings. Lastly, the band at 2995 cm$^{-1}$ is due to a stretching mode between carbon and hydrogen. The bulk (solid sample) certainly provided the most intense spectral features at both excitation wavelengths. The liquid sample only revealed some burning features for the 532nm excitation wavelength. SERS was unsuccessful with the 532nm laser, but some of the major bands were seen with the 785nm laser, such as the 1361 cm$^{-1}$ band, at a low intensity (which was not surprising because there was a lower concentration of analyte used to prevent burning).

**Figure 70**: Photomicrographs of TNT samples, 10x objective. From left: NR WITec 532nm; NR Horiba 785nm; SERS Horiba 785nm; SERS WITec 785nm
Figure 71: A comparison of normal Raman of a solid sample, a liquid sample ($\lambda_o=532\,\text{nm}$) and SERS spectra ($\lambda_o=532\,\text{nm}$) of a PETN standard [100 $\mu$g/ml].

Figure 72: A comparison of normal Raman of a solid sample, a liquid sample ($\lambda_o=785\,\text{nm}$) and SERS spectra ($\lambda_o=785\,\text{nm}$) of a PETN standard [100 $\mu$g/ml].
Many intense spectral features were observed for the PETN standard at both excitation wavelengths, such as bands at 145, 586, 626, 871, 1289 and 2979 cm\(^{-1}\). The band at 145 cm\(^{-1}\) is due to some lattice vibrations or an interaction between oxygen and the metal surface in SERS analysis, so it is not very important for discrimination. The band at 626 cm\(^{-1}\) is due to a rocking mode between oxygen and the NO\(_2\) groups. The band at 871 cm\(^{-1}\) is due a stretching mode between oxygen and nitrogen. The 1289 cm\(^{-1}\) band is due to the symmetric stretch of the nitro groups (NO\(_2\)), whereas the band at 2979 cm\(^{-1}\) is due to a stretch between carbon and hydrogen.

The solid/bulk sample had the most intense bands noted, but the liquid sample at 532 nm was a successful normal Raman analysis, in which all the major bands, plus a silicon peak, were noted at a lower intensity. SERS analysis did not reveal distinguishing spectral features, and only peaks due to the citrate were noted.

**Figure 73:** Photomicrographs of PETN samples, 10x objective. From left: NR WITec 532nm; NR Horiba 785nm; SERS Horiba 785nm; SERS WITec 785nm
**Figure 74:** A comparison of normal Raman of a solid sample, a liquid sample ($\lambda_o=532\text{nm}$) and SERS spectra ($\lambda_o=532\text{nm}$) of a RDX standard [100µg/ml].

**Figure 75:** A comparison of normal Raman of a solid sample, a liquid sample ($\lambda_o=785\text{nm}$) and SERS spectra ($\lambda_o=785\text{nm}$) of a RDX standard [100µg/ml].
RDX had many characteristic spectral features observed, such as bands at 880, 1209, 1270, 1309, 2943, 2997 cm\(^{-1}\). The band at 880 cm\(^{-1}\) corresponds to a ring breathing mode between carbon-nitrogen-carbon. The bands at about 1209 and 1309 cm\(^{-1}\) correlates to a C-N stretching mode, whereas the band observed at 1270 cm\(^{-1}\) corresponds either to a CH\(_2\) scissoring mode or a N-N stretching vibration. The peaks observed at approximately 2943 and 2997 cm\(^{-1}\) correlate to stretching modes between carbon and hydrogen. It appears that these spectral features were most apparent when the 532nm excitation wavelength was used, those bands could be seen with the 785nm excitation as well. There was a strong SERS enhancement with the 532nm, given the fact that the analyte used was a lower concentration, and a lower laser power to prevent burning. SERS was also successful at 785nm excitation. The SERS spectrum is at least as intense as the normal Raman, which is of important note considering that the analyte in that sample is ten times less concentrated. Citrate peaks were also quite intense in both SERS samples.

**Figure 76:** Photomicrographs of RDX samples, 10x objective. From left: NR WITec 532nm; NR Horiba 785nm; SERS Horiba 785nm; SERS WITec 785nm
**Figure 77**: A comparison of normal Raman of a solid sample, a liquid sample ($\lambda_0=532\text{nm}$) and SERS spectra ($\lambda_0=532\text{nm}$) of a C-4 standard [100µg/ml]

**Figure 78**: A comparison of normal Raman of a solid sample, a liquid sample ($\lambda_0=785\text{nm}$) and SERS spectra ($\lambda_0=785\text{nm}$) of a C-4 standard [100µg/ml]
Since C-4 is largely comprised of RDX, it was unsurprising that many of the same Raman spectral features were observed. Spectral features were observed at 880, 1215, 1306 and 2943 cm\(^{-1}\). These bands correlate to the aforementioned modes for RDX (C-N-C ring breathing, interplane C-H bending, aromatic C-N stretch, and stretching between C-H, respectively). However, a major difference between C-4 and RDX was observed; it was difficult to note any of the intense Raman bands in the liquid NR sample, and SERS analysis only revealed bands due to citrate. Whereas it is possible that RDX was a more suitable sample for Raman and SERS analysis, it is also possible that the sticky, gum like composition of C-4 made it harder to dissolve the actually explosive in the solution, and thus much less of it was present in a liquid or SERS samples compared to the solid explosive samples.

**Figure 79:** Photomicrographs of C-4 samples, 10x objective. From left: NR WITec 532nm; NR Horiba 785nm; SERS Horiba 785nm; SERS WITec 785nm
Figure 80: A comparison of RDX SERS and C-4 SERS
(Horiba Instrumentation, 785nm 1% laser)

The above figure highlights that there are many similarities, and some differences noted between the RDX and C-4 standard samples. Their analyses via SERS proved that this technique can be utilized for these samples, although it appears as though RDX is more suitable for SERS analysis than C-4. Both samples were reproducible in producing quality spectra, and thus are great candidates for SERS analysis (see Appendix V).
4-Amino-2,6-dinitrotoluene

Figure 81: A comparison of normal Raman (\(\lambda_o\)=532nm and 785nm) and SERS spectra (\(\lambda_o\)=532nm and 785nm) of a 4-Amino-2,6-dinitrotoluene standard [100\(\mu\)g/ml]

4-Amino-2,6-dinitrotoluene sample seemed to burn slightly during the normal Raman analysis, though there may have been a useful feature present at 858 cm\(^{-1}\), as this was seen in more than one replicate. The SERS analysis did not appear to be successful, though a peak at 1350 cm\(^{-1}\) was apparent in both the 532nm and 785nm wavelengths. Note: the feature at 1050 cm\(^{-1}\) is attributed to the acetonitrile solvent, and can be seen in several “blank” acetonitrile trials.

Figure 82: Photomicrographs of 4-amino-2,6-dinitrotoluene samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
1,3,5-Trinitrobenzene

Figure 83: A comparison of normal Raman ($\lambda_o=532$nm and 785nm) and SERS spectra ($\lambda_o=532$nm and 785nm) of a 1,3,5-Trinitrobenzene standard [100$\mu$g/ml]

Relatively low intensity spectral features of 1,3,5-Trinitrobenzene were observed at 820, 1180, 1357, and 1533cm$^{-1}$ via the NR analysis at 532nm. The band at 820cm$^{-1}$ is due to ring breathing. The band at 1180cm$^{-1}$ is due to C-N stretching modes seen in aromatic amines, and the bands at 1357 and 1533cm$^{-1}$ are due to stretching between C-NO$_2$ (symmetric, and asymmetric, respectively). The SERS spectrum collected with the 532nm excitation revealed many of the same features, but at a much lower intensity. A lower laser power and concentrations of analyte were used to prevent burning. A band at 1353cm$^{-1}$ (the band due to the symmetric C-NO$_2$ stretching) was the only band noted with the 785nm excitation. It is important though because no spectral features were observed for the normal Raman analysis at a wavelength of 785nm.

Figure 84: Photomicrographs of 1,3,5-Trinitrobenzene samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
Figure 85: A comparison of normal Raman ($\lambda_o=532$nm and 785nm) and SERS spectra ($\lambda_o=532$nm and 785nm) of a Tetryl standard [100µg/ml]

Spectral features were observed for the Tetryl standard only via the SERS methodology at 532nm; the major peaks were at 1247, 1327, 1401, and a broad band at approximately 1600 cm$^{-1}$. The features noted at 1247 and 1327 cm$^{-1}$ are due to stretching modes between carbon and nitrogen, reported for aromatic amine assignments. The band at 1401 cm$^{-1}$ correlates to bending modes of the CH$_3$ functional group. Lastly, the broad peak at about 1600 cm$^{-1}$ is due to asymmetric stretching between carbon and nitro groups. These spectral features were not observed for either normal Raman experiments or the SERS experimentation with 785nm excitation.

Figure 86: Photomicrographs of Tetryl samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
Figure 87: A comparison of normal Raman ($\lambda_o=532$nm and 785nm) and SERS spectra ($\lambda_o=532$nm and 785nm) of a HMX standard [100$\mu$g/ml].

Spectral features for the HMX standard were solely observed with the 532nm excitation at 619, 841, 1217, 1313 cm$^{-1}$ (Normal Raman) and a slightly shifted 612, 1186, 1279, 1504, and 1643 cm$^{-1}$ (SERS). The bands noted at about 1217 and 1313, or 1186 and 1279 cm$^{-1}$ are due to C-N stretching in the ring structure, and the band at 1643 cm$^{-1}$ are due to modes in the C-N ring structure as well. Note the SERS peak at 1051 cm$^{-1}$ corresponds to the acetonitrile solvent and the peaks at 841 and 1355 cm$^{-1}$ are attributed to citrate.

Figure 88: Photomicrographs of HMX samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
**N-nitrosodiphenylamine**

**Figure 89**: A comparison of normal Raman ($\lambda_o=532\text{nm}$ and 785nm) and SERS spectra ($\lambda_o=532\text{nm}$ and 785nm) of a N-nitrosodiphenylamine standard [100µg/ml]

NOTE: The NR (532nm, full laser) saturated the detector, so the lower laser power is shown

Spectral features for the n-nitrosodiphenylamine standard were observed only via SERS methodology. Unfortunately, most the bands seemed to correlate to the citrate ions. The bands at approximately 839, 1392 and 1593 cm$^{-1}$ correlate to the citrate ions. The bands at 1392 and 1593cm$^{-1}$ correlates to the symmetric and asymmetric stretching modes between carbon and nitro groups, but their intensities were quite low and these bands could be easily confused with the background and citrate ions.

**Figure 90**: Photomicrographs of N-nitrosodiphenylamine samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
2-Amino-4,6-Dinitrotoluene

Figure 91: A comparison of normal Raman ($\lambda_o=532$nm and 785nm) and SERS spectra ($\lambda_o=532$nm and 785nm) of a 2-Amino-4,6-Dinitrotoluene standard [100µg/ml]

Major spectral features were not observed for the 2-amino-4,6-dinitrotoluene standard. Upon very close inspection, the SERS spectra with both excitation wavelengths only revealed minor peaks attributed to the citrate ions and the acetonitrile solution.

Figure 92: Photomicrographs of 2-Amino-4,6-Dinitrotoluene samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
Nitroglycerin

Figure 93: A comparison of normal Raman ($\lambda_0=532\text{nm}$ and 785 nm) and SERS spectra ($\lambda_0=532\text{nm}$ and 785 nm) of a Nitroglycerin standard [100µg/ml].

No distinguishing spectral features were observed in any of the analyses conducted on this nitroglycerin standard. Review of the SERS spectra seemed to reveal minor peaks attributed to the citrate in the colloidal solution and the acetonitrile that the standard was dissolved in.

Figure 94: Photomicrographs of Nitroglycerin samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
Nitrobenzene

![Nitrobenzene Standard](image)

**Figure 95:** A comparison of normal Raman ($\lambda_0=532$nm and 785nm) and SERS spectra ($\lambda_0=532$nm and 785nm) of a Nitrobenzene standard [100µg/ml]

No major spectral features were observed during the normal Raman analysis of nitrobenzene. However, the SERS analysis with the 532nm excitation revealed spectral features at 1198, 1279, 1355, 1504(doublet), and 1643cm$^{-1}$. The band at 1198cm$^{-1}$ corresponds to a C-N stretch whereas the band at 1279cm$^{-1}$ is due to a CH$_2$ scissoring mode. The band observed at 1355cm$^{-1}$ and the small bands after it (such as 1566cm$^{-1}$) correlate to the stretching modes between carbon and a nitro group (symmetric and asymmetric). Lastly, the band at 1643cm$^{-1}$ is due to a stretching mode between two carbons that share a double bond. Though the SERS via the 532nm laser seemed successful, there was some burning with the SERS via the 785nm laser.

**Figure 96:** Photomicrographs of Nitrobenzene samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
3-Nitrotoluene

**Figure 97:** A comparison of normal Raman ($\lambda_o=532$nm and 785nm) and SERS spectra ($\lambda_o=532$nm and 785nm) of a 3-Nitrotoluene standard [100 µg/ml]

There were not many spectral features generated for the 3-nitrotoluene standard. But, both SERS spectra (with 532nm and 785nm excitation wavelengths) revealed a distinct peak at 1287 and 1267 cm$^{-1}$, respectively. This band correlates to a carbon-nitrogen stretching mode. The normal Raman did not reveal any pertinent spectral information, and any other minor peaks seen in the SERS analysis were attributed to the citrate ions.

**Figure 98:** Photomicrographs of 3-Nitrotoluene samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
1,3-Dinitrobenzene

**Figure 99**: A comparison of normal Raman ($\lambda_0=532\text{nm}$ and $785\text{nm}$) and SERS spectra ($\lambda_0=532\text{nm}$ and $785\text{nm}$) of a 1,3-Dinitrobenzene standard [100µg/ml]

There were not many bands noted in the spectra for the 1,3-dinitrobenzene standard, yet both normal Raman spectra revealed a peak at $299\text{cm}^{-1}$ that correlates to some interaction between a metal and oxygen, or the silicon itself. The SERS analysis appeared to be unsuccessful, as it only revealed bands due to citrate and acetonitrile.

**Figure 100**: Photomicrographs of 1,3-Dinitrobenzene samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
Figure 101: A comparison of normal Raman ($\lambda_o=532$nm and 785nm) and SERS spectra ($\lambda_o=532$nm and 785nm) of a Dibutyl phthalate standard [100µg/ml]

There were no major spectral features resulting from the analysis of the dibutyl phthalate standard with the normal Raman methodology, but some features were noted during SERS analysis at excitation wavelengths of 532nm and 785nm. Features were noted at 1133, 1240, 1319, 1394, 1449 and 1582cm$^{-1}$. The band at 1133cm$^{-1}$ corresponds to the asymmetric stretching of C-O-C. The band at 1394cm$^{-1}$ corresponds to a CH$_3$ bending, and the band at 1449cm$^{-1}$ is due to the asymmetric bending of CH$_3$ and CH$_2$ groups. The band at 1582cm$^{-1}$ is due to the aromatic ring chain vibrations. There was also a slight difference in the relative intensities of the bands seen in the two different spectra, but the features appeared at around the same frequency.

Figure 102: Photomicrographs of Dibutyl phthalate samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
1,3-Diethyl-1,3-diphenylurea

**Figure 103**: A comparison of normal Raman (\(\lambda_o=532\text{nm}\) and \(785\text{nm}\)) and SERS spectra (\(\lambda_o=532\text{nm}\) and \(785\text{nm}\)) of a 1,3-Diethyl-1,4-diphenylurea standard [100\(\mu\text{g/ml}\)]

There were no spectral features noted for the 1,3-Diethyl-1,3-diphenylurea standard when a normal Raman analysis was conducted. However, the SERS spectrum revealed features at 1182, 1362 and 1616 cm\(^{-1}\) (532nm), whereas features were noted at 1144, 1270, 1351, 1450 and 1503 cm\(^{-1}\) (785nm). The bands at 1182 and 1362 cm\(^{-1}\) is due to the C-N stretching and the band at 1616 cm\(^{-1}\) is due to aromatic ring chain vibrations. The band viewed at 1270 cm\(^{-1}\) is due to the \(\text{CH}_2\) scissoring mode, whereas 1351 cm\(^{-1}\) is due to C-N stretching modes. A band at 1450 cm\(^{-1}\) is due to the bending modes of \(\text{CH}_2\) or \(\text{CH}_3\) modes, whereas the band at 1503 cm\(^{-1}\) is due to a C=C stretching mode. There was a quite large shift in peak positions and a change in relative intensities with the different excitation lasers.

**Figure 104**: Photomicrographs of 1,3-Diethyl, 1-3-diphenylurea samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
Dimethyl phthalate

**Figure 105**: A comparison of normal Raman (λ<sub>o</sub>=532nm and 785nm) and SERS spectra (λ<sub>o</sub>=532nm and 785nm) of a Dimethyl phthalate standard [100µg/ml]  

Spectral features were observed solely via SERS analysis for dimethyl phthalate, which were a mixture between analyte features and citrate peaks. The SERS spectrum collected via the 532nm excitation wavelength revealed significant bands at 1231, 1358 and 1410 cm<sup>-1</sup>. For 785nm excitation, the significant bands were located at 675, 1231, and 1480 cm<sup>-1</sup>. The band located at 1231 cm<sup>-1</sup> corresponds to stretching modes between carbon and nitrogen in aromatic amines. The feature at 1480 cm<sup>-1</sup> corresponds to vibrational modes in aromatic rings whereas a feature at 1410 cm<sup>-1</sup> is due to asymmetric bending in CH<sub>3</sub> groups. In some replicates, these spectral features were hard to distinguish from some intense citrate peaks, however. So although these results were reproducible, not too much weight was put on their significance.

**Figure 106**: Photomicrographs of Dimethyl phthalate samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
There were not many spectral bands observed in the analyses of the 3,5-dinitroaniline standard, yet both the normal Raman with a 532nm excitation and the SERS with a 785nm excitation showed an intense peak at about 1342-1345 cm$^{-1}$. This band correlates to a symmetric stretch between a carbon and nitro group. The normal Raman spectrum at 532nm also generated small peaks at 547, 813 and 976 cm$^{-1}$. However, none of these peaks were noted in any of the other wavelengths or with SERS methodology and were thus deemed rather insignificant.
Note: For the following standards (Dinitrobenzene, Urea Nitrate, 2,4,6-Trinitrobenzoic Acid, Trinitroanisole, 2,4-Dinitrophenetole, Ammonium Nitrate, Trinitrotoluene, and 2,4-Dinitrodiphenylamine), both the bulk (solid sample) and the liquid sample [1mg/ml] were analyzed via the WITec instrument at full power laser; with excitation lasers 532nm and 785nm. SERS were performed via the WITec instrument at a lower power for 532nm wavelength to avoid sample burning, but full laser power for 785nm wavelength.

**Dinitrobenzene**

**Figure 109**: A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power vs. SERS of a liquid sample at 1.5mW [100µg/ml] (λ₀=532nm) of Dinitrobenzene

**Figure 110**: A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] (λ₀=785nm) of Dinitrobenzene
Spectral features were observed for the dinitrobenzene standard at 837, 1002, 1142, 1348, 1531, and 1598 cm\(^{-1}\) for the 532nm excitation. The feature at 1000 cm\(^{-1}\) is due to a stretching C-C mode seen in aromatic ring chain vibrations. The feature noted at 1348 cm\(^{-1}\) is due to the symmetric stretching mode between carbon and nitro groups, and the 1531 cm\(^{-1}\) peak is due to the antisymmetric stretching mode of the carbon to nitro groups. Lastly, the peak at 1598 cm\(^{-1}\) is due to vibrations seen in rings between carbons or between a carbon and nitrogen. In terms of a comparison of spectral features seen at different excitation wavelengths, at 785nm, major bands were observed at 1002, 1352, 1537 and 1610 cm\(^{-1}\). Those these wavenumbers were slightly offset from the bands for the 532nm laser, they correlate to the assignments listed for the 532nm excitation. The bands in the normal Raman spectra compared to the features noted in the SERS spectra were much more intense. Some of the bands were observed in the NR for the liquid sample, but they were of much lower intensity, and not all bands were observed. The SERS spectra at both 532nm and 785nm excitation did contain some of the distinguishing bands for dinitrobenzene. Since a lower laser power and concentration was used to prevent burning the bands do not seem as significant in the figure above, but were obvious when the y-axis is truncated. In all SERS spectra, the citrate peaks were much more intense than the features of interest.

*Figure 111*: Photomicrographs of Dinitrobenzene samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
**Figure 112a:** A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] (\(\lambda_0 = 532\text{nm}\)) of a Urea Nitrate standard.

**Figure 112b:** A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] (\(\lambda_0 = 532\text{nm}\)) of a Urea Nitrate standard.
Figure 113: A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] (λ₀ = 785nm) of a Urea Nitrate standard.

For the urea nitrate standard, spectral features were observed at 533, 714, and a doublet at 1014/1050cm⁻¹ for the 532nm wavelength excitation, and at very similar frequencies for the 785nm wavelength excitation. The bands noted at 533, 714 and 1050 cm⁻¹ result from internal stretching modes of the NO₃⁻ anion. The peak at 1014 cm⁻¹ is due to a symmetric stretch between carbon and nitrogen. The spectral features in the normal Raman spectra for both the solid and liquid sample compared to the features noted in SERS spectra seem much more intense.

However, the SERS spectrum at 532nm wavelength certainly shows most of the main peaks of the urea nitrate standard, and a lower concentration and laser power was used, indicating that an enhancement was present. This can be seen in Figure 112b and slight changes in relative intensities were also noted.

Figure 114: Photomicrographs of Urea nitrate samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
2,4,6-Trinitrobenzoic Acid

Figure 115: A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] ($\lambda_o = 532$nm) of 2,4,6-Trinitrobenzoic Acid

Figure 116: A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] ($\lambda_o = 785$nm) of 2,4,6-Trinitrobenzoic Acid
Distinguishing spectral features were noted for the 2,4,6-trinitrobenzoic acid standard at 331, 340, 825, and 1355 cm\(^{-1}\) and they were very similar for both 532 nm and 785 nm excitation. The features at 331 and 340 cm\(^{-1}\) are due to the stretching modes between two carbons. The feature at 825 cm\(^{-1}\) is due to the stretching mode of C-O-C, whereas the peak at 1355 cm\(^{-1}\) results from the symmetric stretching mode between carbon and nitro groups. The spectral features in the normal Raman spectra were much more significant compared to the features noted in the SERS spectrum at 532 nm excitation because even at a low laser power and lower concentration, there was significant burning. In terms of a comparison of spectral features seen at different wavelengths, the liquid sample revealed many more spectral features via normal Raman at 785 nm versus 532 nm, but neither excitation provided a significant SERS enhancement.

Figure 117: Photomicrographs of 2,4,6-Trinitrobenzoic acid samples, 10x objective, WITec. From left: NR 532 nm; NR 785 nm; SERS 785 nm; SERS 785 nm
Trinitroanisole

Figure 118: A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] \( (\lambda_o = 532\text{nm}) \) of a Trinitroanisole standard

Figure 119: A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] \( (\lambda_o = 785\text{nm}) \) of a Trinitroanisole standard
Distinct spectral features for the trinitroanisole standard were observed at about 330, 829, 1257, 1347, 1531, and 1610 cm\(^{-1}\) for the normal Raman analysis at 532nm wavelength. The band at 330 cm\(^{-1}\) probably correlates to the stretching in between carbon atoms, whereas the peak at 829 cm\(^{-1}\) is probably due to stretching between two carbons and oxygen. The peak at 1275 cm\(^{-1}\) is due to the stretching between carbon and nitrogen in an aromatic amine. The peaks at 1347 and 1531 cm\(^{-1}\) are due to the stretching between the carbon and nitro groups (symmetric and asymmetric, respectively). Lastly, the feature at 1610 cm\(^{-1}\) is a result of stretching modes in rings from carbons. With the 785nm wavelength excitation, bands were slightly shifted but were close to the values for the 532nm wavelength excitation. The normal Raman spectral features were much more intense in the solid sample versus the liquid sample for the 785nm excitation. The SERS spectra do not show any overwhelming enhancement for any of the peaks, though the citrate peaks were quite intense with the 785nm analysis.

**Figure 120:** Photomicrographs of Trinitroanisole samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
2,4-Dinitrophenetole

Figure 121: A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] (λ₀ = 532nm) of a 2,4-Dinitrophenetole standard.

Figure 122: A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] (λ₀ = 785nm) of a 2,4-Dinitrophenetole standard.
The most intense spectral features observed for the 2,4-dinitrophenetole standard at 831, 1150, 1286, 1337, 1605cm\(^{-1}\) for both excitation wavelengths. The peak at 831cm\(^{-1}\) is attributed to the stretching between C-O-C. The peak at 1286cm\(^{-1}\) is a result of the stretching between carbon and nitrogen in an aromatic amine. The peaks at 1337cm\(^{-1}\) is due to the symmetric stretching between the carbon and nitro groups. Lastly, the feature at 1605cm\(^{-1}\) is present because of stretching modes in rings from carbon-carbon. These bands were also seen with both the bulk sample and the liquid sample via the normal Raman analysis. However, the SERS analysis did not prove fruitful as only bands due to citrate were present in the 532nm SERS spectrum, and some slight burning is the only notable feature observed in the 785nm SERS spectrum.

**Figure 123:** Photomicrographs of 2,4-Dinitrophenetole samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
**Ammonium Nitrate**

**Figure 124:** A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] ($\lambda_o = 532$nm) of an Ammonium Nitrate standard.

**Figure 125:** A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] ($\lambda_o = 785$nm) of an Ammonium Nitrate standard.
Spectral features were discerned for the ammonium nitrate standard at 174, 710, 1040 and 1282 cm\(^{-1}\). The band at 174 cm\(^{-1}\) correlates to lattice vibrations. The band at 1282 cm\(^{-1}\) corresponds to stretching with the ammonium ion. The band at 710 cm\(^{-1}\) correlates to an internal asymmetric vibration of the NO\(_3^-\) ion while the 1040 cm\(^{-1}\) results from its symmetric vibrations. The bands at 713 and 1042 cm\(^{-1}\) were the only major ones noted with the 785 nm wavelength analysis, but correlate closely to two of the bands from the 532 nm wavelength analysis. Both the solid/bulk sample and the liquid sample had similar features observed for normal Raman analysis, though the solid sample provided much more intense spectra. The SERS spectra collected with a 532 nm laser revealed some small bands, as well as peaks due to citrate, whereas with the 785 nm laser, the SERS spectrum only presents some citrate bands and the major band due to silicon.

**Figure 126**: Photomicrographs of Ammonium nitrate samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
Figure 127: A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] ($\lambda_o=532$nm) of a Trinitrotoluene standard.

Figure 128: A comparison of NR of a solid and a liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] ($\lambda_o=785$nm) of a Trinitrotoluene standard.
Distinguishing spectral features were observed for the trinitrotoluene at 819, 1203, 1355, 1531, and 1610 cm$^{-1}$. The band at 819 cm$^{-1}$ corresponds to a NO$_2$ scissoring mode, whereas the band at 1203 cm$^{-1}$ is due to an interplanar C-H bend. The bands at 1355 and 1531 cm$^{-1}$ are due to the stretching modes between carbon and nitro groups (symmetric and asymmetric modes). The band at 1610 cm$^{-1}$ is the result of the stretching of C-N and C-C reported in aromatic rings.

These bands were observed at both 532 nm and 785 nm excitation wavelengths for the solid sample, but only at 785 nm for the liquid sample. It appears that the liquid sample burns at the 532 nm excitation. No features were noted in the SERS trial with this method, though TNT SERS enhancement was noted using the Horiba instrumentation and commercial nanoparticles. This can be seen in the section entitled “Explosive Materials: Real Samples.”

**Figure 129**: Photomicrographs of Trinitrotoluene samples, 10x objective, WITec. From left: NR 532nm; NR 785nm; SERS 785nm; SERS 785nm
2,4-Dinitrophenylamine

**Figure 130**: A comparison of NR liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] (λ₀ = 532nm) of a 2,4-Dinitrophenylamine standard

**Figure 131**: A comparison of NR liquid sample [1mg/ml] at full laser power and SERS of a liquid sample at 1.5mW [100µg/ml] (λ₀ = 785nm) of a 2,4-Dinitrophenylamine standard
Spectral features for the 2,4-dinitrodiphenylamine standard were observed at 843, 1002, 1141, with a triplet centered about 1332, 1515 and a doublet with the larger peak at approximately 1615 cm\(^{-1}\), but only for the 785 nm wavelength excitation. The band at 1002 cm\(^{-1}\) is due to C-C stretching modes in a ring structure. The large triplet corresponds the symmetric stretching of the carbon-nitro group, whereas the peak at 1515 cm\(^{-1}\) is because of the asymmetric stretching of the same bonds. The peak at 1615 cm\(^{-1}\) is due to the C-N or C-C stretching modes seen in ring structures. There was significant burning of the liquid and SERS sample at 532 nm excitation, but the SERS spectrum at 785 nm shows quite evident enhancement, considering a lower concentration and volume of the analyte was used to prevent burning.

**Figure 132:** Photomicrographs of 2,4-Dinitrodiphenylamine samples, 10x objective, WITec. From left: NR 532 nm; NR 785 nm; SERS 785 nm; SERS 785 nm
Nitroglycerin (in acid – DONATED)

Note: The following liquid sample [unknown concentration, in acid] was analyzed via the WITec instrument with excitation lasers 532nm and 785nm. Even after a full twenty-four hours, the sample did not dry so it was analyzed as a liquid. SERS was also performed, in which the samples dried slightly, but still had some areas in which the sample remained a liquid. Full laser power was used for 785nm laser, but 0.5mW for 532nm.

**Figure 133:** A comparison of normal Raman liquid sample SERS of a liquid sample at 1.5mW ($\lambda_o$= 532nm) of a donated Nitroglycerin standard

**Figure 134:** A comparison of normal Raman liquid sample SERS of a liquid sample at 1.5mW ($\lambda_o$= 785nm) of a donated Nitroglycerin standard
For the donated sample of nitroglycerin, spectral features were noted at 230, 851, 1283, 1642 and 2968 cm$^{-1}$ for 532nm, and slightly shifted at 231, 855, 1289 and 1645 cm$^{-1}$ with a 785nm excitation. There is also a band from silicon seen on all nitroglycerin spectra around 518-521 cm$^{-1}$. The peak at 230 cm$^{-1}$ corresponds to an interaction between the colloid and analyte. The peak at 855 cm$^{-1}$ correlates to a stretching seen in C-O-C bonds. The peak at 1283 cm$^{-1}$ is due to a stretching mode between carbon and nitrogen. Lastly, a band at 1645 cm$^{-1}$ is because of the scissoring mode between carbon and hydrogen or due to the double bond vibration. Although spectral features were discernable via both NR and SERS, it seems as though the normal Raman spectrum is the only one seen at both wavelengths of excitation. In other words, no enhancement was noted due to the presence of the metal colloid and salt.
Select Nanosheets Results

Nanosheet Blank

![Nanosheet Blank Graph]

**Figure 135:** A comparison of a nanosheet blank at two different excitation wavelengths ($\lambda_o = 488\text{nm}$ and $532\text{nm}$)

The nanosheets suffered from significant burning, which is deduced from the “carbon bands” (photocombustion), at approximately $1350$ and $1580\text{cm}^{-1}$, no matter what excitation laser wavelength or laser power is used. This is significant because even when spectral features were apparent on a nanosheet, a burning “background” may have to be subtracted to clearly identify the bands of interest in the analyte.

![Photomicrograph of blank Nanosheet sample]

**Figure 136:** Photomicrograph of blank Nanosheet sample, 10x objective, WITec
Standards

As with the SERS (nanoparticle) experiments conducted, standard samples were analyzed to verify that the nanosheets performed properly. Both 4-mercaptophenol (~1mM) and Rhodamine 6-G (~1mM) were used to verify that there was an enhancement seen with each batch of nanosheets synthesized. Examples of enhanced detection of each standard are shown below, though these analyses were conducted several times and with both 488nm and 532nm excitation values. The spectral features seen in each matched well with published literature values and previous nanoparticle experimental results.

**Figure 137**: A mercaptophenol standard sample (top) and a Rhodamine 6G standard (bottom) spectrum on a nanosheet; WITec 532nm (1.5mW laser)
The analysis of diphenylamine was successful with the nanosheet substrate. Spectral features were noted at 1103, 1155, ~356, 1403, and 1602 cm\(^{-1}\). Some of these values were shifted slightly from those seen at 785 nm wavelength SERS experiments with gold nanoparticles, but correspond to the same vibrational modes. Slight burning of the nanosheets complicates some of the data interpretation.
2-Nitrodiphenylamine

**Figure 139**: A spectrum of a 2-Nitrodinitrophenylamine standard sample on a nanosheet; WITec instrumentation 532nm (1.5mW laser)

The analysis of 2-nitrodiphenylamine was successful with the nanosheet substrate. Spectral features were noted at 1155, 1332/1344 (doublet), 1446 and 1517 cm\(^{-1}\). Some of these values were shifted slightly from those seen with the SERS experimentation conducted at 785nm with gold nanoparticles; but the doublet and large peak in the 1500s proves that the overall pattern agrees. Burning of the nanosheets complicates some of the data interpretation.
**4-Nitrodiphenylamine**

*Figure 140:* A spectrum of a 4-Nitrodinitrophenylamine standard sample on a nanosheet; WITec instrumentation 532nm (1.5mW laser)

The analysis of 4-nitrodiphenylamine was also successful with the nanosheet substrate. Spectral features were noted 840, 1110, 1155, 1280, 1348, 1395, 1493 and a large doublet at 1587/1594 cm\(^{-1}\). Some of these values were shifted slightly from those seen with the SERS experimentation conducted at 785nm wavelength with gold nanoparticles but were very close to those seen with the 532nm SERS experiments with silver nanoparticles. There also seems to be a slight shift in relative intensities, but the same vibrational modes were certainly apparent. There also seemed to be very little burning with this sample.
N-Nitrosodiphenylamine

Figure 141: A spectrum of an N-nitrosodinitrophenylamine standard sample on a nanosheet; WITec instrumentation 532nm (1.5mW laser)

N-nitrosodiphenylamine was successfully analyzed via the nanosheet experiments. Spectral features were noted at 1147, 1348, 1395, 1579/1594 (doublet) cm\(^{-1}\). Not only do these features agree very well with the previous SERS experimentation performed at an excitation wavelength of 532nm, but the features were more prominent and easier to distinguish. The bands at 1395 and 1594 cm\(^{-1}\) correlate to the symmetric and asymmetric stretching modes between carbon and nitro groups, and their intensities were much higher than the bands seen in the nanoparticle analysis.
Diphenylamine Comparison

**Figure 142**: A comparison of the spectra of diphenylamine standard samples on a nanosheet; CCNY instrumentation 488nm

The nanosheets showed a great deal of reproducibility in terms of the replication of analyses, as well as comparing the spectral features to the NR and SERS spectra seen in other experiments performed in this study. The nanosheet analysis was particularly successful for the diphenylamines, although some burning is noted, characteristic spectral features were still apparent.

**Figure 143**: A comparison of the spectra of diphenylamine standard samples on a nanosheet; CCNY instrumentation 488nm; Y-Axis Zoom
The nanosheet analysis of the dinitrotoluene standards revealed some spectral features, though they were hard to decipher due to the overall burning phenomenon observed. Compared to analysis at 532nm and 785nm, this method certainly showed more detail. For example, 2,4-dinitrotoluene revealed peaks at 1315 and a broad peak at 1595 cm\(^{-1}\) which could correspond to the stretching modes of a carbon/nitro vibrational mode. However, similar bands were seen in some of the other nanosheet results with a 488nm wavelength excitation, so it is not the most meaningful result. The other DNTs all look similar to each other and few intense spectral features were distinguishable.
The nanosheets analysis of the 1,3,5-Trinitrobenzene standard produced some spectral features, though they were hard to identify due to the overall burning phenomenon and high background. However, when compared to analysis with 532nm and 785nm wavelengths, this method showed more details. Bands were present at 762, 800, 1295/1320 (large doublet), 1546, and 1610 cm\(^{-1}\). However, some of the other bands were seen in some of the other nanosheet results with a 488nm wavelength excitation; thus, these were the bands of the greatest significance.
The analysis of the phthalate standards on nanosheets appeared to reveal minute spectral features, though they were hard to interpret because of the overall burning phenomenon. Compared to analysis at 532nm and 785nm with colloidal solutions, this method certainly seemed to show more detail, yet the features revealed were not reproducible. Similar bands were seen in some of the other nanosheet results with a 488nm excitation. Nonetheless, it appears as though bands at about 1306 and 1581 cm\(^{-1}\) may have been revealed. Further investigation (such as higher concentrations or a different laser wavelength) is needed to verify this.
1,3-Diethyl, 1,3-Diphenyl Urea

Figure 147: A spectrum of a 1,3-Diethyl, 1,3-Diphenyl Urea standard sample on a nanosheet; CCNY instrumentation 488nm

The analysis of the 1,3-diethyl,1,3-diphenyl urea standard on a nanosheet substrate indicated some spectral features, though there was slight burning. Bands were present at 1165, 1310, 1488 and 1584 cm\(^{-1}\). These bands were comparable to the bands seen with 532nm and 785nm analysis, with slight shifts in frequency (which was to be expected with a change in excitation wavelength). Thus, these bands were tentatively assigned in the same manner as previous analysis (C-N stretching, CH\(_2\) and CH\(_3\) bending and C=C or ring stretching modes) and nanosheet analysis was considered successful for this standard.
Explosive Mixtures – Real Samples

NOTE: The following mixed samples of explosives were analyzed via a 785nm excitation laser with the Horiba instrument and Diagnostic AnSERS gold nanoparticles. Though they were all analyzed using 1% laser power, both the 10x and 100x objectives were used. The spectra with the most detailed features are shown here, though other trials are displayed in Appendix V. Furthermore, the spectral features and tentative assignments were compared to the constituents of the explosives, and are tabulated in Table 5.

Silicon Standard

![Si Std - Horiba](image)

**Figure 148**: A comparison of normal Raman ($\lambda_o=785\text{nm}$) of a Silicon standard with 10x and 100x objective

The silicon standard had a large, narrow peak at 517 cm$^{-1}$ (slightly deviated from the standard of 520-521 cm$^{-1}$) as well a small broad feature noted at approximately 950 cm$^{-1}$ for both the 10x and 100x objective ($\lambda_o=785\text{nm}$).
Diagnostic AnSERS Blanks

Figure 149: A comparison of normal Raman and SERS ($\lambda_o=785\text{nm}$) of Diagnostic anSERS with and without salt, 10x and 100x objective.

The most notable spectral feature observed in the commercial nanoparticles ($\lambda_o=785\text{nm}$) was the citrate peak, in the region of $\sim179\text{cm}^{-1}$. Also, interaction between the metal (gold) and the substrate (salt) resulted in a peak at $\sim279\text{cm}^{-1}$.

Figure 150: Photomicrographs of Au AnSERS Blanks, Horiba 785nm, 10x (left) and 100x (right)
Figure 151: A comparison of normal Raman and SERS ($\lambda_o=785\text{nm}$) of an EtOH standard with 100x objective.

The most notable spectral feature seen in the ethanol standard ($\lambda_o=785\text{nm}$) was the silicon peak located at 520 cm$^{-1}$. When the 100x objective was used, some small peaks were seen along the spectrum that mostly resembled spectral noise; no significant bands were noted.

Figure 152: Photomicrographs of EtOH Blanks, Horiba 785nm, 10x (left) and 100x (right)
No significant bands were noted in the normal Raman analysis ($\lambda_0=785\text{nm}$) of Semtex Type II IRA, with either the 10x or 100x objectives. The SERS spectrum ($\lambda_0=785\text{nm}$) revealed spectral features at 1140, a broad peak between 1339-1350 and 1559/1590 cm$^{-1}$ which is due to stretching modes, both symmetric and asymmetric, of a carbon to a nitro group, respectively (these two features could also indicate burning, but probably not intense enough to do so).

**Figure 153:** A comparison of normal Raman and SERS ($\lambda_0=785\text{nm}$) of Semtex II IRA, 10x and 100x objective

**Figure 154:** Photomicrographs of Semtex II IRA samples, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
**Semtex Type II IRA** – labeled “home office Semtex-H Type 2 Dec 92 IRA Explosives)

![Semtex II IRA HO](image)

**Figure 155:** A comparison of NR and SERS ($\lambda_o=785$nm) of Semtex II IRA Home Office, Semtex-H Type 2 Dec 92 IRA Explosive, 10x and 100x objective.

There were no major spectral features noted in the normal Raman spectrum ($\lambda_o=785$nm) of Semtex Type II IRA “home office” sample, with either the 10x or 100x objectives. Spectral features were seen in the SERS analysis ($\lambda_o=785$nm) at 1002, 1231-1237, 1378-1381, 1580-1590 and 1794cm$^{-1}$. The band at 1002cm$^{-1}$ is due to a C-C stretch seen in aromatic chain rings. The features at 1378-81 and 1580-90cm$^{-1}$ are due to the symmetric and asymmetric stretching modes seen between carbons and nitro groups (C-NO$_2$).

![Photomicrographs of Semtex II IRA HO samples, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective](image)
Significant spectral features were not identified in the normal Raman spectrum (λ₀=785nm) for the Semtex H IRA sample, with either the 10x or 100x objectives. Yet, the SERS analysis (λ₀=785nm) revealed spectral features at 665, 707, 881, 1010, 1236-1242, 1315, 1385, and 1792-1794 cm⁻¹. The band at 881 cm⁻¹ is tentatively assigned as the stretching mode between oxygen and nitrogen, whereas the peak at 1010 cm⁻¹ correlates to the stretching mode between two carbons. The feature at 1385 cm⁻¹ corresponds to the symmetric stretching between carbon and a nitro group.
The normal Raman analysis ($\lambda_o=785\text{nm}$) of Semtex H RCMP did not prove successful, with either the 10x or 100x objectives. The SERS spectrum ($\lambda_o=785\text{nm}$), however, displayed spectral features at 428, 888, and 1276-1281 cm$^{-1}$. It is possible the band at 888 cm$^{-1}$ is due to C-N-C ring breathing, and the band at 1276-1281 cm$^{-1}$ resulted from the scissoring mode seen in the CH$_2$ functional group. There also appears to be some slight burning in the sample studied with the 100x objective leading to bands at approximately 1350 and 1590 cm$^{-1}$.

Figure 160: Photomicrographs of Semtex H RCMP samples, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
Semtex H MNT

Figure 161: A comparison of normal Raman and SERS (\(\lambda_o=785\)nm) of Semtex H MNT, 10x and 100x objective

No significant bands were noted in the normal Raman spectrum (\(\lambda_o=785\)nm) of the Semtex H MNT sample, with either the 10x or 100x objectives. The SERS spectrum (\(\lambda_o=785\)nm) showed spectral features at 717-721, 1152-1160, 1223-1230, 1509, 1591-1594 and 1792 cm\(^{-1}\). The band at 1591-1594 cm\(^{-1}\) corresponds to the asymmetric stretching mode between a carbon and a nitro (NO\(_2\)) group.

Figure 162: Photomicrographs of Semtex H MNT samples, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
Semtex Para-MNT 0.1%

Figure 163: A comparison of normal Raman and SERS ($\lambda_o=785\text{nm}$) of Semtex A PMNT, 10x and 100x objective

The Semtex Para-MNT 0.1% sample did not display any significant bands noted in the normal Raman spectrum, with either the 10x or 100x objectives ($\lambda_o=785\text{nm}$). However, bands were present in the SERS spectrum at 430, 1585 and 1794 cm$^{-1}$ ($\lambda_o=785\text{nm}$). The band at 1585 cm$^{-1}$ is due to the asymmetric stretching mode between carbon and a nitro group.

Figure 164: Photomicrographs of Semtex A PMNT samples, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
No distinguishing spectral features were observed in the normal Raman analysis of Semtex 1A Spanish EGDN, with either the 10x or 100x objectives ($\lambda_o=785\text{nm}$). The SERS spectrum ($\lambda_o=785\text{nm}$) did reveal features at 1140 and 1792-1794 cm$^{-1}$.

**Figure 165:** A comparison of normal Raman and SERS ($\lambda_o=785\text{nm}$) of Semtex 1A Spanish EGDN, 10x and 100x objective

**Figure 166:** Photomicrographs of Semtex 1A Spanish EGDN samples, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
Semtex A Spain 600µl Taggant

**Figure 167:** A comparison of normal Raman and SERS ($\lambda_o=785$nm) of Semtex Spain 600µl Taggant, 10x and 100x objective.

No significant spectral bands were noted for NR analysis of Semtex A Spain 600µl taggant, with either the 10x or 100x objectives ($\lambda_o=785$nm). Spectral features were observed in the SERS spectrum ($\lambda_o=785$nm) at 858, 1005-1010, 1126-1129, 1238-1242, 1315, 1381 and 1451-1455 cm$^{-1}$. The feature at 858 cm$^{-1}$ is from the stretching mode between oxygen and nitrogen. The feature seen around 1005-1010 cm$^{-1}$ is due to the stretching between C-C. The peak at 1381 cm$^{-1}$ is due a symmetric stretching mode between carbon and NO$_2$, whereas the peak at 1451-1455 cm$^{-1}$ corresponds to a symmetric stretch between an oxygen and nitro group.

**Figure 168:** Photomicrographs of Semtex Spain 600µl Taggant, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective.
**Figure 169**: A comparison of normal Raman and SERS ($\lambda_o=785\text{nm}$) of C-4 Regular, 10x and 100x objective.

Significant bands were not observed in the normal Raman analysis of C-4, with either the 10x or 100x objectives ($\lambda_o=785\text{nm}$). Distinguishing spectral features were observed via SERS analysis ($\lambda_o=785\text{nm}$) at 611, 1017-1019, 1149-1153, 1544-1546, 1561-1563 cm$^{-1}$. The features at 1544-1546 and 1561-1563 cm$^{-1}$ correlates to an asymmetric stretching mode between carbon and nitro group.

**Figure 170**: Photomicrographs of C-4, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
C-4 MNT

**Figure 171**: A comparison of normal Raman and SERS ($\lambda_o=785$nm) of C-4 MNT, 10x and 100x objective

Significant bands were noted in the normal Raman spectrum of the C-4 MNT sample, with either the 10x or 100x objectives ($\lambda_o=785$nm). The SERS spectrum displayed spectral features at 855, and 1507-1512 cm$^{-1}$ ($\lambda_o=785$nm). The feature at 855 cm$^{-1}$ corresponds to a stretching mode between an oxygen and nitrogen.

**Figure 172**: Photomicrographs of C-4 MNT, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
C-4 DMNB 0.1%

**Figure 173**: A comparison of normal Raman and SERS ($\lambda_o=785\text{nm}$) of C-4 DMNB 0.1%, 10x and 100x objective.

For the C-4 DMNB sample, no major spectral features were noted in the normal Raman analysis, with either the 10x or 100x objectives ($\lambda_o=785\text{nm}$). The SERS spectrum ($\lambda_o=785\text{nm}$), however, did reveal spectral features at 847-851, 1155, 1270-1281, and 1509-1513 cm$^{-1}$. The feature at 847-851 cm$^{-1}$ is due to a stretching mode between oxygen and carbon.

**Figure 174**: Photomicrographs of C-4 DMNB, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective.
Hexageno (Spanish C-4)

**Figure 175**: A comparison of normal Raman and SERS ($\lambda_o=785\text{nm}$) of Hexageno, 10x and 100x objective

No significant bands were noted in the normal Raman spectrum of the Hexageno sample, with either the 10x or 100x objectives ($\lambda_o=785\text{nm}$). The SERS spectrum presented significant bands at 838, 1166, and 1313-1317 cm$^{-1}$ ($\lambda_o=785\text{nm}$). The peak at about 1313-1317 cm$^{-1}$ correlates to a stretch in C-N aromatic amines.

**Figure 176**: Photomicrographs of Hexageno, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
Dynamite IRA

**Figure 177:** A comparison of normal Raman and SERS ($\lambda_o=785$nm) of Dynamite IRA, 10x and 100x objective

There were no major bands noted for the analysis of the Dynamite IRA sample with normal Raman spectroscopy, with either the 10x or 100x objectives ($\lambda_o=785$nm). The SERS spectrum, however, revealed important features at 610-614, 750-754 and 1699-1704 cm$^{-1}$ ($\lambda_o=785$nm). The peaks at 610 and 750 cm$^{-1}$ are results of the stretching C-C modes seen in the aliphatic chain of nitroglycerin.

**Figure 178:** Photomicrographs of Dynamite IRA, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
Dynamite Forcite 40

**Figure 179**: A comparison of normal Raman and SERS ($\lambda_o=785\text{nm}$) of Dynamite Forcite 40, 10x and 100x objective

No major spectral features were observed for the Dynamite Forcite 40 sample via normal Raman spectroscopy, with either the 10x or 100x objectives ($\lambda_o=785\text{nm}$). The SERS spectrum presented spectral features at 610-611, 750-754, and 1699-1700 cm$^{-1}$ ($\lambda_o=785\text{nm}$). Features at 610 and 750 cm$^{-1}$ result from the stretching C-C mode seen in the aliphatic chain of nitroglycerin.

**Figure 180**: Photomicrographs of Dynamite Forcite 40, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
Dynamite Giant Coalition

Figure 181: A comparison of normal Raman and SERS (λ_o=785nm) of Dynamite Giant Coalition, 10x and 100x objective.

No significant bands were noted in the normal Raman spectrum (λ_o=785nm) of the Dynamite Giant Coalition, with either the 10x or 00x objectives. The SERS spectrum (λ_o=785nm), however, presented spectral features at 607-610 and 746-750 cm⁻¹. Peaks at 607 and 746 cm⁻¹ are due to a stretching C-C mode seen in the aliphatic chain of nitroglycerin.

Figure 182: Photomicrographs of Dynamite Giant Coalition, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
Figure 183: A comparison of normal Raman and SERS ($\lambda_o=785$nm) of Detasheet NAX, 10x and 100x objective.

No meaningful spectral data was obtained from the normal Raman analysis ($\lambda_o=785$nm) of Detasheet NAX, with either the 10x or 100x objectives. The SERS analysis ($\lambda_o=785$nm) presented spectral features at 450-460, 1150-1160, 1166, and 1281-1285 cm$^{-1}$. Features at 1281-1285 cm$^{-1}$ are present because of the stretching mode between carbon and nitrogen seen in aromatic amines.

Figure 184: Photomicrographs of Detasheet NAX, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
No significant bands were observed in the normal Raman spectrum of Detasheet, with either the 10x or 100x objectives ($\lambda_{o}=785\text{nm}$). Many were observed in the SERS spectrum ($\lambda_{o}=785\text{nm}$), however, at 1006-1010, 1126, 1150-1160, 1237-1240, and 1455 cm$^{-1}$. The band at 1006 cm$^{-1}$ corresponds to stretching between carbon atoms in a ring.

**Figure 185**: A comparison of normal Raman and SERS ($\lambda_{o}=785\text{nm}$) of Detasheet, 10x and 100x objective.

**Figure 186**: Photomicrographs of Detasheet, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
Significant bands were not displayed in the normal Raman spectrum of Pentex, with either the 10x or 100x objectives ($\lambda_o=785\text{nm}$). The SERS analysis of Pentex ($\lambda_o=785\text{nm}$) was more successful; bands were noted at 863-866, 1168, and a broad peak at 1339-1347 cm$^{-1}$. The peak at 863 cm$^{-1}$ correlates to stretching between oxygen and nitrogen, and the peak at approximately 1339 cm$^{-1}$ is caused by the stretching between carbon and nitro group.

**Figure 187:** A comparison of normal Raman and SERS ($\lambda_o=785\text{nm}$) of Pentex, 10x and 100x objective.

**Figure 188:** Photomicrographs of Pentex, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective.
No significant bands were seen in the normal Raman spectrum of the Tetryl sample, with either the 10x or 100x objectives ($\lambda_o=785$nm). The SERS spectrum presented spectral features at 1331-1335 cm$^{-1}$ ($\lambda_o=785$nm).

**Figure 190**: Photomicrographs of Tetryl, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
Normal Raman analysis, with either the 10x or 100x objectives did not reveal any important spectral information for TNT flakes ($\lambda_o=785\text{nm}$). In the SERS spectrum, spectral features were observed at 653, 1079, 1188-1195, 1341-1350 and 1606-1610 cm$^{-1}$ ($\lambda_o=785\text{nm}$). The band noted around 1188 cm$^{-1}$ correlates to a carbon-nitrogen stretch seen in aromatic amines. The feature at 1341 cm$^{-1}$ is due to a symmetric carbon-NO2 stretch whereas the feature around 1606 cm$^{-1}$ is caused by the stretch between C-C or C-N seen in ring structures.

Figure 192: Photomicrographs of TNT Flakes, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective.
TNT Crystals

Figure 193: A comparison of normal Raman and SERS ($\lambda_o=785\text{nm}$) of TNT Crystals, 10x and 100x objective.

No significant bands were noted in the normal Raman spectrum of the TNT crystal sample, with either the 10x or 100x objectives ($\lambda_o=785\text{nm}$). The SERS spectrum ($\lambda_o=785\text{nm}$), however, revealed spectral features at 653, 1079, 1192-1195, 1347-1350, 1536-1544 and 1610$\text{cm}^{-1}$. The band at 1188$\text{cm}^{-1}$ correlates to a carbon-nitrogen stretch seen in aromatic amines. The feature at 1341$\text{cm}^{-1}$ is due to a symmetric carbon-NO$_2$ stretch whereas the feature at about 1536$\text{cm}^{-1}$ is due to the asymmetric stretch between the same molecules. The feature at 1606$\text{cm}^{-1}$ is caused by the stretch between C-C or C-N seen in ring structures.

Figure 194: Photomicrographs of TNT Flakes, Horiba 785nm. From left: NR 10x, SERS 10x, SERS 100x objective
The significant bands of the above mixed explosives samples are tabulated below. The characteristic bands were compared among the separate standards and to TNT, PETN, RDX and C-4 standards; these standards were also in agreement with literature values; this proves that the spectral bands seen in this experiment is consistent with previous work (Lewis et al 1997), (Botti et al 2013). Any bands that may be used to differentiate one explosive from another is noted.

Table 5: Experimental spectral data of four major explosives, compared to literature

<table>
<thead>
<tr>
<th>Compound</th>
<th>Normal Raman Bands (cm(^{-1})) Experimental</th>
<th>Normal Raman Bands (cm(^{-1})) Literature *Lewis et al 1997</th>
<th>SERS Bands (cm(^{-1})) Experimental</th>
<th>SERS Bands (cm(^{-1})) Literature * Botti et al 2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>266-270, 322, 788, 819, 1013-1020, 1207, 1358-1360, 1532, 1618</td>
<td>~1360 - NO(_2) Symmetric Stretch Broad ~1540 - AntiSym NO(_2) Stretch 830 - Nitro group scissoring</td>
<td>1346-1350</td>
<td>790 - NO(_2) Scissor 820 – NO(_2) Scissor 1360 – NO(_2) Stretch</td>
</tr>
<tr>
<td>RDX</td>
<td>329-341, 600, 628, 843, 879-81, 939-44, 1028, 1211-14, 1269, 1306, 1381-85</td>
<td>887 – C-N-C Ring Vibrations 755-775 – NO(_2) Scissor</td>
<td>567, 596, 862, 1014, 1129, 1248, 1319, 1392, 1457, 1576 (D)</td>
<td>480 – In plane ring bend 870 – C-N-C ring breathing 1080 – C-H ring in plane bend 1258 - CH2 scissor</td>
</tr>
<tr>
<td>C4</td>
<td>341, 458, 600, 843, 881, 944, 1028, 1214, 1307, 1385</td>
<td>SAME as RDX + Spectral Subtraction bands for plasticizers</td>
<td>797, 931, 1151, 1297, 1474, 1523</td>
<td>Same as RDX</td>
</tr>
<tr>
<td>Compound</td>
<td>Significant Bands (cm(^{-1}))</td>
<td>Identifying Bands (cm(^{-1}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>----------------------------------</td>
<td>----------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Semtex II IRA</td>
<td>1140, 1339-1350, <strong>1559/1590</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Semtex II IRA HO</td>
<td><strong>1002, 1231-1237, 1378-1381, 1580-1590</strong>, 1794</td>
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<td></td>
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<tr>
<td>Semtex H IRA</td>
<td>665, 707, <strong>881, 1010, 1236-1242, 1315, 1385</strong>, 1792-4</td>
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<td></td>
<td></td>
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<tr>
<td>Semtex H RCMP</td>
<td>428, <strong>888, 1276-1281</strong></td>
<td><strong>Bold</strong> indicates possible consistency with RDX Std</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Semtex H MNT</td>
<td>717-721, <strong>1152-1160</strong>, 1223-1230, 1509, <strong>1591-4</strong>, 1792</td>
<td><em>Italicics</em> indicates possible consistency with PETN Std</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Semtex A PMNT</td>
<td>430, <strong>1585</strong>, 1794</td>
<td></td>
<td></td>
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<tr>
<td>Semtex 1A Spanish EGDN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Semtex A Spain 600ul Taggart</td>
<td>858, <strong>1005-10</strong>, 1126-9, 1238-42, <strong>1315, 1381, 1451-5</strong></td>
<td></td>
<td></td>
<td></td>
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<td>C4 Regular</td>
<td>611, 1017-1019, <strong>1149-1153</strong>, 1544-1546, 1561-1563</td>
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<td></td>
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<tr>
<td>C4 MNT</td>
<td>855, 1507-1512</td>
<td><strong>Blue</strong> indicates possible consistency with C4 Std</td>
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<td>C4 DMNB</td>
<td>847-851, <strong>1155</strong> (1149-72), 1270-1281, 1509-1513</td>
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<td>Hexageno</td>
<td>838, 1166, 1313-1317</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Dynamite IRA</td>
<td>610-614, 750-754, 1699-1704</td>
<td><strong>610, 750</strong>, maybe 1700 &amp; no other peaks</td>
<td></td>
<td></td>
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<tr>
<td>Dynamite Forcite 40</td>
<td>610-611, 750-754, 1699-1700</td>
<td><strong>610, 750</strong>, maybe 1700 &amp; no other peaks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dynamite Giant Coalition</td>
<td>607-610, 746-750</td>
<td><strong>610, 750</strong>, maybe 1700 &amp; no other peaks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detasheet NAX</td>
<td>450-460, 1150-1160, 1166, 1281-1285</td>
<td>1150-1160</td>
<td></td>
<td></td>
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<td>1150-1160</td>
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<tr>
<td>Pentex</td>
<td>863-866, 1168, 1339-1347</td>
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<tr>
<td>Tetryl</td>
<td>1331-1335</td>
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</tr>
<tr>
<td>TNT Flakes</td>
<td>653, 1079, 1188-1195, 1341-1350, 1606-1610</td>
<td>653, 1079, 1195, 1350, 1610 = TNT Standard</td>
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<tr>
<td>TNT Crystals</td>
<td>653, 1079, 1192-1195, 1347-1350, 1536-1544, 1610</td>
<td>653, 1079, 1195, 1350, 1610 = TNT Standard</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Multi-variate statistical analysis of “Real Explosives” Samples

R© statistical software was utilized to conduct a multivariate statistical analysis on the 21 samples of “real explosives” discussed above. Because the majority of the Semtex explosives could not be distinguished from each other based on the appearance of the spectra alone, it was hoped that statistics may be able to differentiate different sample types, or perhaps establish different groups or classifications. However, since the spectra of many of the Semtex explosives did not reveal many distinguishing features, it was decided that statistical analysis likely would not reveal good discrimination between all of the samples. Principal component analysis (PCA) was first employed to examine if any major outliers or groupings appeared. It was fairly simple to differentiate explosives with distinct spectra (i.e. dynamite vs. TNT). Some apparent distinguishability for intra-group samples (i.e. Dynamite IRA vs. Dynamite Forcite 40) appeared within the PCA scores plots. Thus it was decided to pursue intra-group exploration further.

NOTE: The R-Script for the data presented herein can be seen in Appendix VI.
Samples 1-8 (8 trials of each explosive, all recorded via 100x objective, 785nm, Horiba)

Figure 195: 2D PCA Model of “Real Explosives” Samples 1-8 (Semtex Samples)

Figure 196: 3D PCA Model of “Real Explosives” Samples 1-8 (Semtex Samples)

The principal component analysis of these samples revealed that 99.6% of variance was accounted for within the first three principal components; 2-D and 3-D PCA scores plots are shown above. It was apparent in the 2D model that Sample 8 (Semtex A, Spain 600µl Taggant) was an “outlier,” that is statistically different than the other Semtex samples. This certainly made sense as it was the sample that melted, even under white light, yet produced spectral features more often than the other samples. Some grouping was observed of certain trails from
sample 1 (Semtex II IRA) and sample 7 (Semtex 1A Spanish EGDN), yet due to the lack of convincing evidence in the spectral data, it is not believed that this apparent discrimination would persist in a larger sample. The same overall trends were noted in the 3D PCA scores plot. It was not surprising there was a not large amount of classification for most the samples as many of them did not reveal significant spectral features following a SERS analysis and only a small amount of variance was added with the third PC.

Samples 9-21 (8 trials of each explosive, all recorded via 100x objective, 785nm, Horiba)

![Figure 197: 2D PCA Model of “Real Explosives” Samples 9-21](image-url)
The principal component analysis of these samples revealed that 98.6% of variance was contained in the first three principal components, and the 2-D and 3-D PCA models are shown above. It was apparent in the 2D model that there was a possible difference between some trials of samples 11 (C-4 DMNB) vs. samples 12 (Hexageno, Spanish C-4). Additionally, there seemed to be some grouping of sample 13 (Dynamite IRA) and some separate grouping of sample 14 (Dynamite Forcite 40). This indicates a possible difference between the two. This
was important, as there were not major differences noted via the spectral features. However, the statistical analysis and subsequent analysis via hold-one-out linear discriminant analysis did not present convincing information that this method provided unequivocal differentiations. Lastly, it appeared that trials from sample 16 (Detsheet NAX), sample 19 (Tetryl) and sample 21 (TNT Crystals) appeared to group separately from the other samples. This correlated with the spectral data as these samples were differentiated based on the major bands present in the spectra. The same overall trends were noted in the 3D PCA model. It was not surprising to see a general clustering in the model of most the samples as many of the trials showed large features due to silicon, for example, which could dwarf the other spectral features and confuse the statistical model. Though, since many of the different types of explosives were easily discerned via distinguishing spectral bands, differentiation via multivariate statistical analysis was not the primary concern.
GUNSHOT RESIDUE – Results

NOTE: Only the spectra highlighting important findings are documented in this section, they have all been collected via WITec instrumentation (10 seconds, 5 accumulations).

CARTRIDGES ON SILICON SUBSTRATE:

Methyl Ethyl Ketone Blanks

![Figure 199 a-c: Different variation of MEK + Ag + KNO₃; All 532nm excitation, Full laser](image)

Methyl ethyl ketone was used as a solvent for the gunshot residue samples, and thus an analysis of the blank was essential to differentiate the difference between actual, significant spectral features from GSR molecules, and bands due to the methyl ethyl ketone. During some replicates, no significant spectral features were noted in the spectrum, but during others, significant bands were observed ($\lambda_o = 532$nm). These bands were important to note so not confused with spectral features. In the above figure, specifically spectra a and b, several
features, though low in intensity, were apparent. Some of these bands were noted at ~200-300cm\(^{-1}\) (citrate), 1046, 1240, 1318, 1386, 1575 and 2925cm\(^{-1}\) and probably represent a mixture between citrate ions and scattering from the methyl ethyl ketone.

**Winchester Ammunition**

**SERS**

![Graph](image)

**Figure 200**: Cartridge of Winchester Ammunition + MEK, Pre-Shot SERS; 785nm, Full Laser

In the SERS spectrum of the Winchester ammunition (pre-shot, \(\lambda_0 = 785\)nm), some small spectral features were noted. These peaks were located at 120 (due to citrate), 641, 1286cm\(^{-1}\), with a large contribution from the silicon peak as well.
In the SERS spectrum of the Winchester ammunition (post-shot $\lambda_o = 785\text{nm}$), spectral features were observed in the analysis of cartridges 1a and 1b. The analysis of cartridge 1a, shot from the Glock firearm, revealed spectral features due to citrate and silicon, as well as peaks at approximately 1139, 1269 and 1577 cm$^{-1}$. For the cartridge shot from the Smith and Wesson firearm, peaks were observed due to citrate and silicon, as well as small peaks at approximately 1270 and 1501 cm$^{-1}$. Features were observed at about 1575 cm$^{-1}$, attributed to the methyl ethyl ketone blank, so it is possible that some of the minute features noted for the Winchester samples are due to the SERS effect on the MEK solvent.
Remington Ammunition

SERS

Figure 202 a-b: Cartridges of Remington Ammunition + MEK, Pre-Shot SERS; 785nm, Full Laser

In the SERS spectrum of the Remington ammunition (pre-shot, $\lambda_0 = 785$nm), some small spectral features were noted. The largest feature was due to silicon, but other bands were also observed in both spectra at 1311 and 1569cm$^{-1}$, as well as bands due to citrate ions and MEK in spectrum B. There was a fair amount of burning noted in the analysis of the Remington pre-shot samples.

Figure 203: Cartridge (a) 2c Shot with Ruger vs. (b) 2d Shot with Walther, Both Remington Ammunition; 785nm, Full Laser
In the SERS spectrum of the Remington ammunition (post-shot, $\lambda_o = 785\text{nm}$), spectral features were observed in the analysis of cartridges 2c and 2d. The analysis of cartridge 2c, shot from the Ruger firearm, revealed spectral features due to citrate and silicon, as well as peaks at approximately 609, 1349, 1583 cm$^{-1}$. For the cartridge shot from the Walther firearm, peaks were observed due to citrate and silicon, as well as small peaks at approximately 608, 1349 and 1585 cm$^{-1}$. A slight overall burning phenomenon could have been responsible for the uneven background and a large peak at about 1350 cm$^{-1}$ observed in both spectra. Features were observed at 1575 cm$^{-1}$ for the methyl ethyl ketone blank, so it is possible that some of the minute features noted for the Remington samples are due to the SERS effect on the MEK solvent.

**Speer Lawman Ammunition**

*Normal Raman*

![Figure 204 a-b](image)

**Figure 204 a-b**: Cartridges of Speer Lawman Ammunition + MEK, Pre-Shot Normal Raman; 532nm, Full Laser

In the normal Raman spectrum of the Speer Lawman ammunition (pre-shot, $\lambda_o = 532$nm) with the 532nm excitation laser, some spectral features were noted. The largest feature was due to silicon, but other bands were also noted in both spectra at 1276 and 1336 cm$^{-1}$, as well as other small bands due to silicon, citrate ions and MEK. There was a large doublet noted around
2900cm$^{-1}$ that may be due to some overtone band, but was apparent in each of the spectra for the multiple trials.

![Graph](image1)

**Figure 205 a-b: Cartridges of Speer Lawman Ammunition + MEK, Pre-Shot Normal Raman; 785nm, Full Laser Power**

In the normal Raman spectrum of the Speer Lawman ammunition (pre-shot, $\lambda_0 = 785$nm) with the 785nm excitation laser, some spectral features were noted. The largest feature was due to silicon in spectrum B, though it is quite small in spectrum A. Bands were also noted in both spectra at 845, 1306 and 1571cm$^{-1}$. Small features between 100 and 300 cm$^{-1}$ are due to the citrate ions.

SERS

![Graph](image2)

**Figure 206 a-b: Cartridges of Speer Lawman Ammunition + MEK, Pre-Shot SERS; 532nm, 1.5mW laser**
In the SERS spectrum of the Speer Lawman ammunition (pre-shot) with the 532nm excitation laser, some spectral features were observed. The largest features were due to silicon and the MEK solvent in spectrum B, though they were much smaller in spectrum A. Other bands were also noted at 1283, 1328 and 1509 cm\(^{-1}\). It is probable that the two large peaks observed in spectrum A are due to photocombustion, even though a lower powered laser was employed.

![Figure 207: Cartridge 3d, Shot from Walther; Speer Lawman Ammunition, SERS; 532nm, 1.5mW laser](image)

In the SERS spectrum of the Speer Lawman ammunition (post-shot, \(\lambda_0 = 532\)nm), spectral features were observed in the analysis of cartridges 3d, shot from the Walther firearm. Spectral features were noted due to citrate and silicon, as well as peaks at approximately 638, 1046 and 1204 cm\(^{-1}\). Additionally, it is probable that there were peaks seen as a result of burning, around 1350 and 1590 cm\(^{-1}\). Peaks due to citrate ions were also apparent.
In the SERS spectrum of the Speer Lawman ammunition (post-shot, $\lambda_0=785\text{nm}$), spectral features were observed in the analysis of cartridges 3b and 3c. The analysis of cartridge 3b, shot from the Smith and Wesson firearm, revealed spectral features due to citrate and silicon, as well as peaks at approximately 1185, 1289, and 1503 cm$^{-1}$. For the cartridge shot from the Ruger firearm, peaks were observed due to citrate and silicon, as well as small peaks at approximately 1084, 1280 and 1502 cm$^{-1}$. It is possible that some of these features noted for the Speer Lawman are due to the SERS effect on the MEK solvent as the MEK seemed to vary and included several small peaks.

**Aguila Ammunition**

**Normal Raman**

**Figure 209 a-b:** Cartridges of Aguila Ammunition + MEK, Pre-Shot Normal Raman; 785nm, Full Laser
In the normal Raman spectrum of the Aguila ammunition (pre-shot) with the 785nm excitation laser, some spectral features were noted. The largest feature was due to silicon, yet other bands were noted at 1309 and 1571 cm\(^{-1}\). The peak at about 1571 cm\(^{-1}\) had a shoulder present around 1600 cm\(^{-1}\). No other bands were observed in any of the replicates.

SERS

![Figure 210: Cartridges of Aguila Ammunition + MEK, Pre-Shot SERS; 532nm, 1.5mW laser](image)

In the SERS spectrum of the Aguila ammunition (pre-shot, \(\lambda_0 = 532\text{nm}\)), spectral features were observed in the analysis of the cartridge, after a methyl ethyl ketone extraction. Peaks were observed in the spectrum due to citrate and silicon, as well as peaks at approximately 1283, 1335, 1583 and 2969 cm\(^{-1}\). Some of the other small features were due to the SERS effect on the MEK solvent as the MEK seemed to vary and included several small peaks, and there were bands due to citrate ions. The peak observed at \(\sim1050\text{cm}^{-1}\) was most likely due to the solvent or the colloidal solution.
In the SERS spectrum of the Aguila ammunition (post-shot, 785nm), spectral features were observed in the analysis of cartridges 4a and 4c. The analysis of cartridge 4a, shot from the Glock firearm, revealed spectral features due to citrate and silicon, as well small peaks that were due to the MEK solvent. Peaks were observed in the spectrum of the cartridge shot from the Ruger firearm due to citrate and silicon, as well as peaks at approximately 1267 and 1503cm\(^{-1}\). Some of these features noted were due to the SERS effect on the MEK solvent as the MEK seemed to vary and included several small peaks.

**Blazer Ammunition**

**Normal Raman**

![Blazer Cartridge Normal Raman](image)
No major spectral features were observed in the normal Raman spectrum of the Blazer ammunition (pre-shot) with the 532nm excitation laser. There was a large band due to silicon, as well as a peak around 1049cm\(^{-1}\) (due to the solvent or colloidal solution), and the background was not flat. Yet, none of these features were distinguishing or significant.

**SERS**

![Figure 213: Cartridge 5A (Blazer Ammunition, Shot with Glock)]

(a) 532nm (0.5mW laser) vs. (b) 785nm (Full laser power)

In the SERS spectrum of the Aguila ammunition (post-shot), spectral features were observed in the analysis of cartridge 5A with the 532nm and 785nm excitation lasers. The cartridge was discharged from a Glock firearm. In the 532nm spectrum, peaks were observed due to citrate and silicon, as well as peaks at 1353, 1579, 2095 and a large peak around 3000cm\(^{-1}\). The features around 1350/1580cm\(^{-1}\) may be due to burning, but are repeatable enough to be due to distinguishing features. For the 785nm analysis, most peaks, other than the ones due to citrate and silicon, were quite minute. Peaks were observed around 1282 and 1505cm\(^{-1}\), but these features are due to the SERS effect on the MEK solvent as the MEK seemed to vary and included several small peaks.
Varied Substrates

CLOTH

Blanks

The only peak that was observed in the blank cloth sample was a doublet at approximately 1096 cm\(^{-1}\) (\(\lambda_o = 785\) nm). Compared to the other substrates, the cloth substrate had the fewest number of background bands, and thus was focused upon for future SERS and SERS gel studies.

Normal Raman

Figure 214: Blank Cloth Sample; 785nm excitation, Full laser

Figure 215: Ruger, Remington Ammunition (NR); 785nm excitation, Full laser
In the above spectrum ($\lambda_o = 785$nm), the Ruger firearm was discharged and residue was deposited on a cloth substrate. The feature that was noted in the blank cloth samples, at approximately $1094\text{cm}^{-1}$, was present in this sample as well. Features were also apparent around $379$ and $412\text{cm}^{-1}$, and smaller peaks were observed at approximately $1355$ and $1402\text{cm}^{-1}$.

![Figure 216](image)

Figure 216 Smith & Wesson, Speer Law Ammunition (NR) vs. Aguila, Speer Lawman (NR); Both 785nm, Full laser

In both the above spectra ($\lambda_o = 785$nm), the major feature, a peak at approximately $1096\text{cm}^{-1}$, was due to the cloth substrate, because it was seen in the blank cloth NR analysis. However, other small features were noted at about $400\text{cm}^{-1}$, so it is possible that further Raman analysis may reveal information about the residue deposited on the cloth.
In the SERS spectrum of the sample produced from Remington ammunition being discharged from a Walther firearm, several features were apparent due to citrate. Additional features were noted at approximately 541, 620, and 1571 cm\(^{-1}\) (spectrum A). In spectrum B, residue collected from Blazer ammunition, discharged via a Ruger firearm was analyzed. A burning phenomenon was observed. Peaks were observed at 968, 1469, 1533 and 2914 cm\(^{-1}\). For both spectra, there did not seem to be a major contribution from a burning of the colloids, nor a large feature due to the cloth substrate. Thus, it appeared the features noted were due to the presence of the gunshot residue.
In the above spectra, Speer lawman ammunition was deposited upon cloth substrates, and a SERS analysis was performed ($\lambda_o = 532\text{nm}$). Citrate features were observed in both spectra, but other peaks due to the residue was present as well. In spectrum A, there was some burning that contributed to the overall background and large features noted around 1350 and 1590 cm$^{-1}$. Additional features were noted at approximately 644, 1046, and 2913 cm$^{-1}$. In spectrum B, no major burning phenomenon was noted, and features were observed at approximately 1423 (doublet), 1538 (broad peak), 2075, and 2911 cm$^{-1}$.

![Figure 219: Smith & Wesson, Blazer Ammunition (SERS); 532nm, 0.5mW laser](image)

In the SERS spectrum of the sample produced from Blazer ammunition upon a cloth substrates ($\lambda_o = 532\text{nm}$), features were observed that were due to the presence of citrate in the colloidal solutions. A peak around 1045 cm$^{-1}$ was present, and it could be attributed to the cloth, as this peak was seen in several trials of the blank cloth analysis. There were small features noted in this spectrum, such as a peak at about 376 cm$^{-1}$, but most were quite small and thus deemed insignificant.
DENIM Blank

**Figure 220**: Denim Blank Sample; 785nm excitation, Full laser

Due to the presence of several relative intense peaks, seen at 532nm and 785nm excitation wavelengths, denim was not chosen for subsequent SERS analysis.

PAPER Blank

**Figure 221 a-b**: Two examples of a Blank Paper Sample; Both 785nm excitation, Full laser
Due to the presence of several peaks and a significant amount of noise and a high background, which varied throughout the blank sample but was seen with both excitation lasers, paper was not chosen for subsequent SERS analysis.

**Agar Gel**

**Normal Raman**

![Blank Agar Gel (785nm)](image)

*Figure 222: Blank Agar Gel; 785nm excitation, Full laser*

The normal Raman analysis ($\lambda_o = 785\text{nm}$) of the blank agar gel did not reveal any major spectral features. This made it a suitable substrate for subsequent Raman analysis. The same was noted with the analysis conducted at 532nm excitation wavelength.

![Graphs of Remington ammunition shot from a Glock 9mm (a) macro gunpowder particle vs. (b) residue, both collected from a shooter’s hands; Both 532nm excitation, 0.5mW laser](image)

*Figure 223: Remington ammunition shot from a Glock 9mm (a) macro gunpowder particle vs. (b) residue, both collected from a shooter’s hands; Both 532nm excitation, 0.5mW laser*
On the agar gel substrate, features due to both macro gunpowder particles and residue on the gels were observed in spectra at both excitation wavelengths.

SERS

![SERS spectrum](image)

**Figure 224**: Blank Agar Gel + Au + NaCl; 785nm excitation, Full laser

A SERS spectrum of a blank agar gel with Au nanoparticles and NaCl ($\lambda_0 = 785$nm). The only spectral information noted were the bands from citrate around 100 and 250cm$^{-1}$. The same was noted with the analysis conducted at 532nm excitation.

![SERS spectra for different bullets](image)

**Figure 225**: Agar Gel, SERS (a) Glock, Remington Ammunition vs. (b) Smith & Wesson, Remington Ammunition; Both 532nm, 0.5mW laser
The above spectra were produced following the SERS analysis of agar gels pressed upon shooters’ hands ($\lambda_o = 532\text{nm}$). In spectrum A, bands were observed at approximately 1190, 1385, a triplet with the largest peak at about 1510cm$^{-1}$, and a broad peak around 2941cm$^{-1}$. In spectrum B, many peaks were observed, with larger peaks noted at about 611, 1030, a doublet centered at 1350, a broad peak at approximately 1430, and several narrow peaks in between 1500 and 1750cm$^{-1}$. There was certainly some overlap in the features noted in the two Remington samples, but also a fair amount of difference in between them. It is possible that some of the differences are due to a lack of homogeneity in the samples, and because different features are observed depending on the area chosen for analysis. It is also possible that there are differences (i.e. the amount or type of deposit) depending on the firearm used for analysis.

![Image](image.png)

**Figure 226:** Agar Gel, SERS (a) Walther, Blazer Ammunition vs. (b) Glock, Blazer Ammunition; Both 532nm, 0.5mW laser

The above figure depicts a comparison of two gels with GSR after SERS analysis ($\lambda_o = 532\text{nm}$). In the first spectrum (a), major features were observed at approximately 1199, 1445, a doublet with the largest peak at 1598m and a broad peak centered at about 2975cm$^{-1}$. In (b), the largest peaks were observed at approximately 1099, 1533, 2241, 2699 and a large broad peak centered at about 2950cm$^{-1}$. Many of the features in these two samples appeared quite similar,
indicating that there may be chemical signatures for each type of ammunition that can be detected upon an agar gel via SERS analysis.

![Figure 227: Agar Gel, SERS (a) Smith & Wesson, Winchester Ammunition vs. (b) Glock, Winchester Ammunition; Both 785nm, Full laser](image)

The above figure shows that burning was a major concern in the analysis of the agar gels with SERS ($\lambda_o = 785\text{nm}$; though this was also observed with ($\lambda_o = 532\text{nm}$). The Winchester brand ammunition, specifically, seemed to suffer burning more often than the other types of ammunition. For this reason, other lasers, concentrations and so forth were explored.

**Tape**

![Figure 228: Tape blank, placed on top of aluminum foil vs. Aguila Ammunition shot from Ruger on Tape, placed on aluminum foil Both: 532nm excitation, 0.5mW laser, Normal Raman](image)
All the spectra obtained from the tape lifts showed much noise, and very few spectral features were identified for any of the samples, even if GSR was present to the naked eye. For this reason, more effort was focused upon the agar gel experiments.

**Mixed Samples**

NOTE: Set 1 consists of four shots, all from the S&W firearm. The first shot fired CCI Blazer ammunition, while the next three fired Speer Lawmakers ammunition. There was no cleaning of the firearm, barrel or hands in between shots. Set 2 consists of three shots, all from the S&W firearm. The first shot fired Speer Lawmaker ammunition, while the next two fired Remington ammunition. All mixed shots were shot upon the cotton cloth substrate at a distance of approximately 12-14 inches.

**On Cloth**

Set 1

**Normal Raman**

![Figure 229: (a) Shot 2 Speer vs. (b) Shot 4 Speer; Both: Normal Raman, 532nm excitation, 0.5mW laser](image)

In this normal Raman analysis, several of the same features are seen in the spectra for shot 2 and shot 4 ($\lambda_0 = 532\text{nm}$). These peaks were observed at approximately 903, 1361, 1412 and a doublet at 3000 cm$^{-1}$. The similarity of these two spectra points to a possible significant chemical signature from the Speer Lawman ammunition.
Certain features were observed in the SERS analysis of the mixed shot samples, directly analyzed after a colloid and salt solution was pipetted onto the cloth target ($\lambda_o = 532\text{nm}$). No major contribution from the cloth was noted. Other features were not observed in every replicate, further complicating this analysis. In the first spectrum (a), features were observed at 789, 1049, 1398 and a broad peak at about 1533 and 2920 cm$^{-1}$, though the overall background may have revealed some burning of the sample. In spectrum (b), large spectral features were observed at 1010, 2098, and 2901 cm$^{-1}$, in addition to features due to citrate and burning. In spectrum (c), peaks were noted due to burning and at 2098 and a broad peak centered around 3000 cm$^{-1}$; they were small in intensity, but certainly more significant than the relatively flat
background of the blank samples. Though there was a lack of reproducibility and repeatability, it seemed there was potential for the mixed samples to reveal distinguishing spectral features. Spectrum b and c have some similar features, indicating distinct features due to the Speer Lawman ammunition.

**Gels Impregnated with Silver**

**BLANKS**

![Figure 231: AgGel Blanks (a) + KNO$_3$, (b) NO KNO$_3$. Both: 532nm excitation, 0.5mW laser](image)

The agar gels impregnated with silver were analyzed via the 532nm laser, and thus the analysis of a blank sample was of the highest importance to ensure that any spectral features observed were due to gunshot residue, and not the substrate itself. No features were noted in any of the blank AgGel samples, with or without salt (KNO$_3$), except when a citrate peak was observed around 190cm$^{-1}$, and a large broad peak at approximately 3400cm$^{-1}$. 
Rhodamine-6-G Standards (without and with KNO₃)

![Rhodamine 6G Standards on AgGel](image1)

**Figure 232**: Rhodamine 6G Standards on AgGel (a) + KNO₃, (b) NO KNO₃
Both: 532nm excitation, 0.5mW laser

Rhodamine 6-G was used as a standard to ensure that the AgGel substrates could perform SERS analysis ($\lambda_0=532$nm). Though there seemed to be significant issues with the background, and some overall burning, several of the distinguishing peaks of Rhodamine-6-G were apparent. Thus, the AgGels were deemed useful for further experimentation.

Mixed Gunshot Residue Samples

SET 1
MACRO PARTICLES

![Shot 2 (oGSR Residue) on AgGel with KNO₃](image2)

**Figure 233a-b**: Shot 2 (oGSR Residue) on AgGel + KNO₃, 532nm excitation, 0.5mW laser
The above figure exemplifies the lack of homogeneity in a sample and via SERS analysis ($\lambda_o = 532\text{nm}$). There are not significant spectral features observed in the first spectrum (a), but quite a few in the second spectrum (b), albeit of low intensity. The spectral features in the analysis of Shot 2 were present at 1344, 1445, 1499, 1599 and a broad peak centered at approximately $3485\text{cm}^{-1}$.

![Figure 234: Shot 3 (oGSR Residue) on AgGel (a) + KNO$_3$ (b) NO KNO$_3$, 532nm excitation, 0.5mW laser](image)

Some very small spectral features were noted in the spectra of shot 3, though the largest contributor was the citrate. The other peaks were present at 1161, 1252, 1350 and 2092$\text{cm}^{-1}$. Though the peaks were quite small in intensity, it is possible that they reveal distinguishing spectral information that was not apparent before a SERS analysis ($\lambda_o = 532\text{nm}$).
SET 2
MACRO PARTICLES

Figure 235a-b: Shot 2 (Macro Particle) on AgGel (a) + KNO₃ vs. (b) NO KNO₃; 532nm excitation, 0.5mW laser

In the spectrum from the analysis of shot 2 (λₒ =532nm), several features were observed in multiple trials. Peaks were observed at approximately 1125, 1392, 1380, 1552, 1587 cm⁻¹, among others, including bands due to citrate ions. Since these peaks were observed in multiple trials, and the bands all appeared at approximate similar frequencies, they exemplify one of the best examples of the potential of this technique. Further studies would be necessary to confirm its value.

RESIDUE (Center Plume)

Figure 236 a-c: Shot 1 (oGSR Residue) on AgGel + KNO₃; All 532nm excitation, 0.5mW laser
Though the major contributors to the features observed in the SERS analysis of the residue of shot 1 were due to citrate, as seen with the AgGel blanks, a few other features were noted (\(\lambda_0=532\)nm). For example, peaks were apparent at approximately 242, 1344, 1575 and 3430cm\(^{-1}\). Though these peaks were of very low intensity, their presence still indicated a possible chemical signature left from gunshot residue.

![Figure 237a-d: (a-b) Shot 2 (oGSR Residue) on AgGel + KNO\(_3\) vs. (c-d) NO KNO\(_3\); 532nm excitation, 0.5mW laser](image)

The spectra produced via the SERS analysis of shot 2 with the AgGel substrate were quite varied (\(\lambda_0=532\)nm). Bands due to citrate were observed in all spectra, as well as some peaks that were due to burning. However, in some spectra (such as spectrum a, and much smaller in spectrum c), peaks were observed at 1161, 1337, 1380 (a doublet), and 1605cm\(^{-1}\). It
was important to note that not all “spots” analyzed on the same sample produced the same spectral result, as it is thus important for multiple replicates to be conducted under all circumstances.

The SERS spectra produced when the AgGel was used to analyze shot 3 were quite reproducible in terms of their overall patterns, as were the position of the major spectral features in each ($\lambda_0 = 532\text{nm}$). Features were observed at approximately 1173, 1364 and 1617 cm$^{-1}$, among many other smaller peaks. Though some of these features are like those seen for other shots or even different brands of ammunition, it certainly confirmed the utility of such a tool for the detection of a chemical via silver impregnated agar gels.

![Figure 238 a-b: Shot 3 (oGSR Residue) on AgGel + KNO$_3$, 532nm excitation, 0.5mW laser](image)
Other Raman results:

There is large variability in the ability to obtain quality spectra with high intensity compared to the portion of the sample that is analyzed. This can be seen in the following figures that were collected via the Horiba instrumentation. As seen, in figures 239-241, depending on where on the sample the laser is focused, there can be a large difference in intensity of the spectral features, or even the ability to detect features. This varied widely from sample to sample and day to day so multiple trials were always conducted.

Figure 239: Different spectral results compared to sampling area of a Hexageno sample (10x objective, Horiba instrumentation).
Differences in Spectra due to Change in Focus [SERS]

- Detasheet NAX 10x
- 785nm Excitation

**Figure 240:** Different spectral results compared to sampling area of a Detasheet NAX sample (10x objective, Horiba instrumentation).
The above Figures 239, 240, and 241 show the utility of careful microscopy combined with spectroscopy. It was often found that, with slight changes in focus, or with variation in the spot in which the laser interacted with the sample, there was a large difference in the overall intensity of the spectral features. In some samples, there were areas in which spectra contained distinguishing spectral features of large intensity, and other areas within the same 15µl sample in which no spectral features were observed. For this reason, it was important to keep detailed records about which photomicrographs correlated to which spectra, and to obtain multiple replicates per sample on the same day and different days.
Figure 242: Different spectral results compared to sampling area of an EGDN sample (10x objective, Horiba spectrometer)

Certain samples exhibited specific problems, unique to their nature. For example, as seen in Figure 242, some samples melted under the white light of the microscope. This means that the sample was hard or impossible to analyze afterwards, depending on the extent of the melting or burning in gunpowder, residue and explosive samples. Note images “1” and “4” in Figure 242 in which a large plastic structure is seen, with a clearing in the center, which indicates the melting that was seen in real time by the analyst under the white light microscope.
**TLC – Results**

The two different mobile phase systems used for developing the plates took approximately the same amount of time (about fifteen minutes and the plates were removed from the chamber, or when the solvent front traveled about 90% of the plate). A visual examination was conducted and it was observed that the first set of components (Mixture #1, diphenylamines) were visible to the naked eye under white light, and four different bands were clear at both the 1mg/ml and 100µg/ml concentration. The components of the other two mixtures (Mixture #2, Mixture #3) were not visible with the naked eye (white light) at either concentration.

**Figure 243:** Two TLC plates after interacting with the mobile phase (Left plate: Petroleum Ether:Acetone (3:1) Right Plate: Hexane:Acetone (3:1)) after being removed from the TLC chamber

Upon examination under an ultraviolet light box, more components were visible in the second and third mixture, at both concentrations. However, only two components were visible in each mixture, though mixture 2 contained four standards (TNT, PETN, RDX and C-4) and mixture 3 contained three standards (Tetryl, HMX and Urea nitrate). Nonetheless, the bands were circled in pencil so that $R_f$ values could be calculated for each band. In the second set of experiments, the mixture contained diphenylmine, 2-nitrodiphenylamine and 4-nitrodiphenylamine revealed three faint yellow spots, though the top two spots were difficult to
completely distinguish. The mixture of 2,4-dinitrodiphenylamine and n-nitrosodiphenylamine (in chloroform) showed five dark bands, and all were yellow except the one that traveled furthest. It was a dark purple. Again, the mixtures of TNT, PETN, RDX and C-4 as well as tetryl, HMX and urea nitrate were visualized under a uv light box, and two bands were apparent. Overall, the bands for the 100µg/ml samples were slightly more narrow and provided better spectral results, so they are the focus herein.

**Figure 244:** Two TLC plates viewed under the short wavelength UV light box after interacting with the mobile phase (Left plate: Petroleum Ether:Acetone (3:1) Right Plate: Hexane:Acetone (3:1)) after being removed from the TLC chamber
Table 7: Tabulated values of Rf values for each component: TLC plate compared vs. literature

**Set of Mixtures I**

<table>
<thead>
<tr>
<th>MIXTURE, Concentration</th>
<th>Band</th>
<th>R&lt;sub&gt;f&lt;/sub&gt; Value (Pet Ether:Acetone)</th>
<th>R&lt;sub&gt;f&lt;/sub&gt; Value (Hexane:Acetone)</th>
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<tr>
<td>#1 – 1mg/ml</td>
<td>A</td>
<td>0.646</td>
<td>0.423</td>
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<td>(Diphenylamine, 2-Nitrodiphenylamine, 4-Nitrodiphenylamine, 2,4-Dinitrodiphenylamine)</td>
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<td>0.523</td>
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<tr>
<td>#2 – 1mg/ml</td>
<td>A</td>
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<tr>
<td>(TNT, PETN, RDX, C-4)</td>
<td>B</td>
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<td>0.492</td>
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<tr>
<td>#3 – 1mg/ml</td>
<td>A</td>
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<td>0.130</td>
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<tr>
<td>(Tetryl, HMX, Urea Nitrate)</td>
<td>B</td>
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<td>0.290</td>
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<tr>
<td>#1 – 100µg/ml</td>
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<td>(Diphenylamine, 2-Nitrodiphenylamine, 4-Nitrodiphenylamine, 2,4-Dinitrodiphenylamine)</td>
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<td>#2 – 100µg/ml</td>
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**Set of Mixtures II**

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<th>R&lt;sub&gt;f&lt;/sub&gt; Value (Hexane:Acetone)</th>
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<td>(Diphenylamine, 2-Nitrodiphenylamine, 4-Nitrodiphenylamine)</td>
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<td>(2,4Dinitrodiphenylamine, N-nitroso-diphenylamine in Chloroform)</td>
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<td></td>
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<table>
<thead>
<tr>
<th>Standard</th>
<th>LITERATURE</th>
<th>LITERATURE</th>
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<tr>
<td></td>
<td>R&lt;sub&gt;f&lt;/sub&gt; Value (Pet Ether:Acetone)</td>
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<tr>
<td>HMX</td>
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(NOTE: the experimental Rf values are an average of at least two trials per mobile phase system)
Though none of the Rf values correlated perfectly with literature values, they were used to predict overall trends on the TLC plates. Thus, it was predicted that RDX (and therefore C-4 and perhaps PETN) should have been the first (or A) spot in for mixture #2, and TNT should have been the second spot (B). Also, HMX should have been a lower spot than Tetryl. It was also predicted that urea nitrate would not separate very well due to the inorganic nitrate ion.

For the spectra presented herein, some are assigned to certain standards in the known mixture. However, the identifications of each bands herein are tentative, and are based on a relatively low number of samples and trials, thus more experimentation is needed to confirm.

**NORMAL RAMAN**

In the normal Raman spectra of all TLC results, no major features were noted, and thus the TLC plate was deemed a suitable substrate for further Raman analysis. However, since none of the “spots” on the TLC plate produced a normal Raman spectrum, SERS was necessary. The negative NR results are not presented herein, for the sake of brevity.

**SERS**

Blanks

![Figure 245: SERS Analysis (532nm, 1.5mW laser) of BLANK (100µg/ml) after development in Hexane:Acetone system]
In the “blank” SERS-TLC experiments, a sample of silver (532nm wavelength excitation) or gold (785nm wavelength excitation) nanoparticles, with the appropriate salt, were pipetted onto the TLC plate after development in the mobile phase and drying. The colloid for the “blank” was placed in an area on the plate such that it would avoid any of the components of the mixtures, but would be before the solvent front. It was then analyzed via the SERS methodology, and no major peaks, other than a large peak from citrate in the range of approximately 200-250cm\(^{-1}\), were seen.

Mixtures I

![Graph](image)

**Figure 246**: SERS Analysis (532nm, 0.5mW laser) of Band “1a” (100µg/ml) after development in Petroleum Ether:Acetone system

The most prominent features observed in the spectrum of Band 1a (\(\lambda_o=532\)nm, petroleum ether:acetone development) were largely due to burning. Peaks were observed at approximately 1222, 1337, 1398, 1447, 1496, and a doublet at 1569cm\(^{-1}\). Additionally, a broad peak was present at approximately 2990cm\(^{-1}\). The large features around 1398 and 1569cm\(^{-1}\) may have been due to burning of the sample, but the other peaks represented the ability to detect distinguishing features of one of the diphenylamine compounds. It was possible to tentatively
this compound as 2,4-Dinitrodiphenylamine, as that compound had peaks observed at 1337, 1515, and a doublet at 1615 cm\(^{-1}\), which are quite close to the ones seen here.

![Figure 247: SERS Analysis (785nm, Full laser) of Band “1a” (100µg/ml) after development in Hexane:Acetone system](image)

The majority of the spectral pattern seen in both of the above spectra for Band 1a (\(\lambda_o=785\text{nm}, \text{hexane:acetone development}\)) is due to significant burning. However, in the leftmost spectrum, bands were observed at 1250 and 1486 cm\(^{-1}\).

![Figure 248: SERS Analysis (785nm, Full laser) of Band “1c” (100µg/ml) after development in Hexane:Acetone system](image)

Bands were observed after the SERS analysis of band 1C at approximately 603, 1346, and a doublet at 1363 cm\(^{-1}\). Because the diphenylamine standard had a peak at about 1375 cm\(^{-1}\), and due to the other bands noted in 1A, B and D, this was the tentative identification of this
band. The spectra produced for band 1B were not the most distinguishing, but in several trials, features were observed at 1278 and 1440 cm\(^{-1}\), which were close in value to some of the peaks observed for the 4-nitrodiphenylamine standard, thus it was tentatively identified as such.

![Figure 249](image)

**Figure 249:** SERS Analysis (785nm, Full laser) of Band “1d” (100µg/ml) after development in Hexane:Acetone system

There were peaks observed in the above spectrum (\(\lambda_o=785\text{nm}\)) at 942, 1380 and 1509 cm\(^{-1}\). Due to the fact that the standard 2-nitrodiphenylamine revealed a spectral feature at 1383 cm\(^{-1}\), and none of the other diphenylamines had a feature at this frequency, a tentative identity of 2-nitrodiphenylamine was assigned.

![Figure 250](image)

**Figure 250:** SERS Analysis (532nm, 0.5mW laser) of Band “1d” (100µg/ml) after development in Petroleum Ether:Acetone system
The SERS spectrum of 1d (λ₀=532nm) revealed features at approximately 888, 1368, and a double at 1520/1563 cm⁻¹. The previous analysis of 2-nitrodiphenylamine revealed spectral features at about 1383 and 1554, thus this combined with the process of eliminations provided a suitable identification.

![SERS Spectrum](image)

**Figure 251**: SERS Analysis (532nm, 0.5mW laser) of Band “2b” (100µg/ml) after development in Petroleum Ether:Acetone system

As seen in the above figure, certain samples resulted in burning, in which characteristic burning peaks were noted at about 1350 and 1580 cm⁻¹. Even with a low laser, this is a problem faced by some of the silver nanoparticle samples. Thus, no major features were noted in the spectra produced for band 2A or 2B (λ₀=532nm or 785nm). However, since TNT routinely suffered from a photocombustion effect in many of the previous analyses, and that the literature noted a larger Rf value for TNT vs. RDX, it was presumed that band A from mixture 2 was RDX (and C-4) and band B was TNT.
Figure 252: A comparison of SERS Analysis (532nm, 0.5mW laser) of Band “3a” (a) vs. “3b” (b) (100µg/ml) after development in Petroleum Ether:Acetone system

The above spectra depict the different features seen in the SERS analysis of bands 3a and 3b ($\lambda_\text{o}=532\text{nm}$). Though both samples suffered from some burning, spectral features were still observed. In the spectrum produced from the analysis of band 3a, peaks were noted at 236 (due to citrate), 1368 and 1532cm$^{-1}$. For 3b, a broad peak was observed at approximately 1359 and 1512cm$^{-1}$. These two spectra were difficult to differentiate.

Figure 253: SERS Analysis (785nm, Full laser) of Band “3a” (a) vs. “3b” (b) (100µg/ml) after development in Hexane:Acetone system

After analysis via the hexane:acetone system with a 785nm excitation, some additional features were noted for mixture 3. For the analysis of band 3a, peaks were observed at 255, 661, 914, 1478 and 1538cm$^{-1}$. For 3b, peaks were observed at 1036, 1185, and 1435cm$^{-1}$. These
spectra appeared quite similar. However, since the literature stated a higher Rf value of tetryl than HMX, it was tentatively presumed that band 3a was HMX and 3b was tetryl.

Mixtures Set II

Spectra that provided additional or confirming information, after the analysis of the first set of mixtures, are included below.

Figure 254: SERS Analysis (785nm, Full laser) of Band “1b” (100µg/ml) after development in Petroleum Ether:Acetone system

For the above spectrum ($\lambda_o=785$nm), spectral peaks were noted at approximately 1199 and 1445 cm$^{-1}$, however their intensities are so low that it was not likely that these features were significant, and were more likely due to noise or stray light.

Figure 255: SERS Analysis (532nm, 1.5mW laser) of Band “1A b” (100µg/ml) after development in Hexane:Acetone system
In the above spectrum ($\lambda_o=532\text{nm}$), though several features were seen, many were assigned as burning or noise. However, larger peaks were noted at approximately 1550 and 2907$\text{cm}^{-1}$. For the second set of mixtures, however, the bands produced for mixture 1A produced confusing and inconsistent TLC results, perhaps because n-nitroso-diphenylamine was not dissolved in the same solvent as the others. Thus, it did not add any further information to the TLC results obtained from the first set.

![SERS Analysis](image)

**Figure 256:** SERS Analysis (532nm, 1.5mW laser) of Band “3b” (100$\mu$g/ml) after development in Hexane:Acetone system

In the spectrum produced following the SERS analysis of band 3b ($\lambda_o=532\text{nm}$), peaks were observed mostly due to burning, but some features were noted at approximately 699, 1392, and 1533$\text{cm}^{-1}$. Because these peaks were present in many of the standards’ spectra, this did not add much information to the analysis of the mixtures. However, a feature at 1392$\text{cm}^{-1}$ could correlate to the peak for the tetryl standard at 1401$\text{cm}^{-1}$.
CHAPTER 4 - CONCLUSIONS

The importance of calibration with standards and the spectral analysis of negative controls cannot be overemphasized. The bands due to citrate ions or the so-called “anomalous bands,” are seen in many nanoparticle formulations and at the different laser excitation values and must be taken into account. These bands, if misidentified or unconsidered as a vibrational mode in a molecule, could preclude the use of SERS as a technique for quick and accurate qualitative analysis.

Differences in spectral features because of the wavelength of excitation are important to consider. Though not entirely surprising, this study confirmed that certain compounds are much more successfully analyzed by SERS using a high energy laser (i.e. 532nm), while others suffer from massive burning, even when the laser is set to a very low power output. Conversely, some compounds did not reveal any spectral features at 532nm, but were successful with SERS analysis via an excitation at a wavelength of 785nm. For example, standards such as nitrobenzene, urea nitrate, dimethyl phthalate, and others did not reveal any spectral information when analyzed via a 785nm laser, but could be easily discriminated and assigned when analyzed via NR and SERS with the 532nm laser. On the other hand, the 2,4-dinitrodiphenylamine standard was not successfully distinguished via NR or SERS at 532nm excitation, but revealed a large number of discriminating peaks via NR and SERS analysis with a 785nm excitation wavelength. The Diagnositc snSERS nanoparticles, used with the Horiba instrument (785nm excitation), proved to be very fruitful for the analysis of the so-called “real world” explosives samples. This means that several replicates under different conditions may be necessary when implementing this kind of analysis on a larger and broader scale (i.e. in case work).
Concerning the real world samples, it was possible to note certain trends in these authentic explosives. In other words, some of the explosives’ main constituents (such as a base of TNT or RDX or PETN) could be identified from characteristic bands that coincided with the bands in the standard samples. Furthermore, it was a goal of this study to determine if the samples could be differentiated via the spectra (visually) and via multivariate statistics. It seems as though there is a definite potential for the application of multivariate statistical analysis. In this work, certain discriminations via principal component analysis, such as differentiating between different sources of dynamite or different types of Semtex, was speculated. Studies on a much larger scale are needed to confirm the utility of such a tool.

Lastly, a goal of this research project was to evaluate the ability of an extraction or separation technique to pair with SERS for the analysis of real gunshot residues. It seems as though both of these are viable options. The silver impregnated gel is especially interesting due to its cheap cost and ease of preparation as well as its quick and simple analysis. Further studies should certainly be conducted before any of these are adopted into routine laboratory work.

CHAPTER 5 – CONTRIBUTIONS TO FORENSIC SCIENCE AND CRIMINAL JUSTICE

Firearms related offenses make up a large percentage of the national crime statistics. The United States is unique in the fact that so many people firearms, nearly 200 million guns were estimated legally owned by NIJ in 1997. As of 2010, the NRA and ATF estimate there are around 80 legal million gun owners, and over 300 million guns in the United States. A large number of violent crimes or incidents, whether intentional or accidental involve firearms. However, gunshot residue evidence is often lost in the time it takes to locate or transport a
suspect. The ability to quickly and accurately detect gunshot residue on the hands, clothing, or in the vicinity of a shooter can be of the utmost importance. Given the fact that most crime labs use the standard particle method (by S.E.M.) to evaluate GSR that involves very expensive equipment, significant sample preparation and a highly trained analyst, a novel approach would be extremely valuable. Although there is limited research, it appears possible that testing for organic gunshot residue is more sensitive than the testing for their inorganic counterparts. This would mean that this approach could detect oGSR in samples even if S.E.M. analysis determines GSR to not be detected. Raman spectroscopy, as well as surface enhanced Raman spectroscopy offers the potential for on-site field testing. Some Raman instrumentation manufacturers are marketing themselves for the purpose of in-field use and some customs and homeland security agencies around the world are exploring the use of Raman for detecting explosives. However, a succinct approach for the separation and analysis of the components of organic gunshot residue analysis could be a great improvement upon any of these methods.

The ability to use the same commercial Raman instrument and sampling/separation technique to detect for the possible presence of explosive material would prove extremely valuable. This dual application could limit the amount of personnel that must specialize in this analysis as the same analyst can look at both oGSR and explosive materials. Raman and SERS analysis could be completed in a very short period of time and could be conducted in the field to identify the components in a specific sample and distinguish it from others.

It is also proposed that in the future, sampling and analysis and identification of oGSR and explosive residues via a library search may become so simple that someone with a limited scientific background may be able to evaluate the potential threat of a piece of evidence. This means that law enforcement officials, customs agents, TSA workers, military personnel and so
forth may be able to quickly and accurately determine if a firearm has been discharged or if there is explosive material present in a sample collected. The impact that this test may have on the criminal justice system both at a local and national level is enormous. It may be used at local and state police departments to add a new type of analysis method for evidence from cases such as homicide, suicide, or assault; it may also be used by state and national agencies to evaluate potential terrorist threats.

Preliminary statistical analysis of data was an important part of this work. It is hoped that eventually, statistics assigned to the quality of an oGSR or explosive analysis may be used to give an appropriate weight to the evidence. When presented in court, confidence intervals and principal component analysis will be able to classify evidence into appropriate groups within a certain figures of significance. This could prove to be important in a criminal justice system in which courts are now demanding that forensic scientists assign an error rate to their work to prove that there is some validity to their work. An analyst that uses this technique could testify a percent value in which they are sure their evidence is truly from a certain class, manufacturer, or a similar evaluated category.

Therefore, a significant goal of this work is to demonstrate that the techniques presented herein provide unique and valuable information that could assist significantly in ascertaining innocence or guilt, provide important investigatory leads in a case, or judge the risk of an unknown substance discovered in terrorism cases. This work was a significant step toward that goal.

In terms of the novel techniques and their introduction into the criminal justice system, it is of the utmost importance to ensure that there is rigorous scientific validation and error analysis to guarantee that it can be successfully introduced into a court of law. Given that some
jurisdictions in the United States are Frye states, and others follow the guidelines set forth in Daubert, it is important that good, rigorous scientific experimentation is conducted so that the method has a wide appeal across jurisdictions that differ in size and resources.

In Frye v. United States, 293 F. 1013 (D.C. Cir. 1923), the decision established what is called the Frye standard. The court held that expert testimony is admissible if it has achieved “general acceptance in the relevant scientific community.” In other words, under the Frye ruling, the burden is incumbent on the expert witness to express that the methods and the principles behind the forensic science as scientifically sound. This is proven under Frye by demonstrating that the work is generally accepted within the relevant field. The Frye standard of general acceptance does carry with it some ambiguities. It is not always entirely clear who the relevant scientific community is that must accept a method or principle before it is admissible as evidence. Furthermore, how can a judge or expert for that matter, truly define what is meant by the “relevant scientific community” (Giannelli 1980)?

In Daubert v. Merrell Dow Pharmaceuticals, Inc., 509 U.S. 579 (1993), the Supreme Court of the United States changed the manner by which expert testimony and scientific evidence is admitted into evidence. The court ruled that this decision would not be based on the Frye standard, but rather on the Federal Rules of Evidence 702. The decision in this case set a precedent for the statute and the basis on which federal judges decide on the admissibility of expert testimony. The court said that the judge would act as a gatekeeper, deciding which testimony can be allowed in court and which must stay out. The Federal Rules of Evidence 702 states that: A witness who is qualified as an expert by knowledge, skill, experience, training or education may testify in the form of an opinion or otherwise if the expert’s scientific, technical or specialized knowledge will help the trier of the fact to understand the evidence or determine a
fact in issue and if the testimony is based on significant facts and data, the testimony is based on reliable methods and practices, and the expert has reliably applied the methods and practices to the facts at issue (Federal Rules of Evidence 1975, Amended 2000). Daubert decided that this should be the standard by which forensic science evidence is admitted into court.

In Daubert, the court set up a neither non-exclusive nor mandatory checklist, which can aid a judge/gatekeeper in determining if expert witness testimony is admissible. The judge should consider if the method/principles are testable (falsifiable), if there are known error rates and standards/controls for the procedure were used, if it has been peer reviewed or publications exist, and lastly, if there is general acceptance. In Daubert II, the issue of litigation driven research versus scientific knowledge followed by testimony was also added (Daubert v. Merrell Dow Pharmaceuticals, Inc., 43 F.3d 1311 (9th Cir. 1995). That is the expert testifying to a conclusion or method that has been naturally born out of his/her research or did he/she conduct these specific experiments for the case and issue at hand. A technique does not have to meet all of these criteria in order to be allowed. For this reason, Daubert and the Federal Rules of Evidence is often looked at a more rigorous rule, but may allow the judge flexibility to allow novel forensic science practices into testimony.

Many scholars have noted that a major issue with Frye could be a difficulty in allowing novel evidence into court. Because of the ever changing and expanding realm of scientific knowledge, it is possible that an expert would be available to testify to scientifically sound methodologies and conclusions that just are not accepted yet by the general scientific community. Daubert, as analyzed by some supporters, is meant to allow novel evidence to see its day in court. However, as has been seen in a variety of cases, this also means that in some decisions, more traditional types of forensic science evidence are subjected to new scrutiny never
felt under the *Frye* standard. Disciplines such as fingerprints, firearms, and many other pattern type evidence (footwear, tire tread marks, blood stain pattern analysis, toolmarks) that have been accepted in courts for decades under the *Frye* standard are now being re-evaluated under the *Daubert* checklist. In *Daubert*, the court commented that with the presentation of contrary evidence, rigorous cross examination and careful instruction to the jury about burden of proof, the adversarial system was equipped to “attack shaky, but admissible evidence.” This further emphasized the flexibility of the gatekeeper in determining what is and is not allowed.

It is important to note, however, that the checklist in *Daubert* was not meant to be treated as a point by point evaluation of an analysis and the ability of the expert to conduct it. It was meant to serve as a guideline for the gatekeeper to consider. This is what leads to the great flexibility of this ruling. “If *Daubert* comes to stand for a stringent gatekeeping function in criminal cases, it will be an improvement over *Frye*. If, however, it comes to stand for nothing more than *Barefoot* (a case widely heralded as a poor decision to allow a psychiatric evaluation that predicted an offender’s future likelihood to commit a crime to sway the jury), junk science will be the winner” (“*Daubert*: Interpreting the Federal Rules of Evidence” Cardoza Law Review, 15 1999). This statement is poignant and reiterates the fact that is up to the judge to recognize valid and meaningful forensic science and have the intelligence and control not to admit “junk science.”

An important purpose of this research is to establish that these techniques could eventually withstand a Daubert or Frye ruling. Simply, the goal was to prove that the SERS analysis of organic gunshot residue and explosives, as well as the various sampling and separation techniques are based upon testable methods, that standards and controls were vigorously scrutinized as required, and in the future, that there are more publications and peer
review regarding these methods and results. Perhaps, in time, this work will lead to reach a level of general acceptance in the relevant scientific community (forensic chemists).

In conclusion, because of the frequency of gun related cases and terrorist concerns, the rapid and non-destructive analysis of gunshot residue, explosives, and their residues could have a grand impact on the criminal justice system. This thorough and meaningful research involving Raman and surface enhanced Raman analysis is an early step to altering the current methods in criminalistics laboratories and law enforcement department laboratories, and may prove valuable as a method for field testing as well.

**CHAPTER 6 – FUTURE STUDIES**

In the future, other types of Raman analysis, and other excitation wavelengths should be explored. FT-Raman used with gold nanoparticles, or excitation at a high energy wavelength, such as 488nm, with silver may offer additional information about these chemicals.

Nanosheets, and other commercial substrates (ex: Diagnostic AnSERS and other companies make “tabs” available for purchase in which a gold or silver substrate lay on a piece of paper or plastic and only about 5µl of sample is pipetted on top of it and dried) should be investigated. This would save a significant amount of time in the laboratory and would present the possibility of sampling in the field so long as a portable Raman system was available for the final analysis. Additionally, if this system had a built in database/statistical analysis, on site identification and “level of certainty” could be determined in seconds.

Several research groups are examining the relationship between an analyte of interest and the SERS substrate. Targeting SERS/substrate interactions to ensure that a limited amount of molecules would be selectively enhanced would prove extremely useful. Researchers are
looking into solid semi-conductor substrates designed with particular parameters to ensure maximum SERS enhancement (Islam et al 2013, for example) (Ji et al 2015).

Other extraction/separation techniques could be researched to evaluate the most useful for several types of explosives and oGSR standards. Alternatively, if there is no singular method that would prove useful for a variety of substances, a standard operating procedure that involves a flow-chart decision tree as an analysis scheme could be developed.

Lastly, a goal of a future study should be to quantitate amounts of different explosive components in mixtures. Although this study confirmed SERS and quantitation may be complicated (due to hotspots, uneven drying of samples, etc.), it would be a useful goal to develop substrate/sample combinations and evaluate them for quantitative purposes.
APPENDIX I – Scale Calibration Information

Figure 257: Record of calibration of scales used at John Jay College, CUNY

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Figure 257: Record of calibration of scales used at John Jay College, CUNY
APPENDIX II: Gas Chromatography-Mass Spectroscopy Data

Figure 258: Acetonitrile Standard; GC-MS Results
Unknown; InLib=265

(Text File) Scan 25 (1.730 min): 2014 1110 ACN STANDARD1.D\data.ms

Name: Scan 25 (1.730 min): 2014 1110 ACN STANDARD1.D\data.ms
MW: N/A ID#: 5391 DB: Text File

10 largest peaks:
54 999 | 52 192 | 55 178 | 51 152 | 53 117 | 50 25 | 56 13 | 69 5 | 70 5 | 91 5 |

52 m/z Values and Intensities:
50 25 | 51 152 | 52 192 | 53 117 | 54 999 | 55 178 | 56 13 | 57 3 | 63 2 | 64 1 |
65 2 | 66 2 | 67 3 | 68 3 | 69 5 | 70 5 | 71 1 | 76 1 | 77 4 | 78 4 |
79 3 | 80 1 | 81 3 | 82 2 | 83 2 | 84 2 | 85 1 | 89 1 | 91 5 | 92 2 |
93 1 | 94 2 | 95 2 | 96 2 | 97 1 | 98 1 | 102 1 | 103 2 | 104 1 | 105 3 |
106 1 | 109 1 | 115 2 | 116 1 | 117 1 | 119 2 | 128 2 | 130 1 | 131 1 | 141 1 |
145 1 | 207 3 |
Figure 259: GC-MS Library Results for Acetonitrile Standard
Figure 260: Diphenylamine (100µg/mL) Standard; GC-MS Results
** Figure 261: GC-MS Library Results for Diphenylamine Standard **
Figure 262: 2-Nitrodiphenylamine (100µg/mL) Standard; GC-MS Results
Unknown; InLib=257

Name: Scan 3714 (22.838 min): 2014 1029 100 2NDPA2.Ddata.ms

MW: N/A ID#: 5284 DB: Text File

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68 m/z Values and Intensities:

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**Figure 263**: GC-MS Library Results for 2-Nitrodiphenylamine Standard
Figure 264: GC-MS Library Results for TNT Standard
Figure 265: 4-Nitrodiphenylamine (100µg/mL) Standard; GC-MS Results
Unknown: InLib=189

Name: Scan 4491 (27.284 min): 2014 1030 100 4NDPA2.Didata.ms
MW: N/A ID#: 5290 DB: Text File

10 largest peaks:
214 999 | 167 971 | 164 356 | 168 259 | 166 172 | 215 144 | 139 83 | 51 87 | 128 78 |

55 m/z Values and Intensities:
51 87 | 52 23 | 62 11 | 63 62 | 64 33 | 65 64 | 66 13 | 69 18 | 70 18 | 74 19 |
75 21 | 76 31 | 77 135 | 78 28 | 80 20 | 82 11 | 84 73 | 86 12 | 89 25 | 90 31 |
91 27 | 92 10 | 102 12 | 103 14 | 107 21 | 113 17 | 114 15 | 115 67 | 116 22 | 117 18 |
118 10 | 127 17 | 128 78 | 129 34 | 130 12 | 139 89 | 140 55 | 141 38 | 154 30 | 155 12 |
156 13 | 166 172 | 167 971 | 168 259 | 169 41 | 181 17 | 182 18 | 183 13 | 164 356 | 185 52 |
198 27 | 207 14 | 214 999 | 215 144 | 281 11 |
Hit 1: Benzenamine, 4-nitro-N-phenyl-
-C12H10N2O2; MF: 222; RMF: 940; Prob 79.4%; CAS: 838-30-6; Lib: replib; ID: 25002.

Figure 266: GC-MS Library Results for 4-Nitrodiphenylamine Standard
Figure 267: 2,3-Dinitrotoluene (100µg/mL) Standard; GC-MS Results
Unknown, InLib=191

(Txt File) Scan 2665 (16.836 min): 2014 1029 100 23DNT1.D/data.ms

Name: Scan 2665 (16.836 min): 2014 1029 100 23DNT1.D/data.ms
MW: N/A ID#: 5258 DB: Text File

10 largest peaks:
165 999 | 135 652 | 77 343 | 99 299 | 63 298 | 52 240 | 51 210 | 78 181 | 64 167 | 134 157 |

60 m/z Values and Intensities:
50 89 | 51 210 | 52 240 | 53 123 | 54 18 | 55 11 | 56 7 | 61 28 | 62 93 | 93 208 |
64 107 | 65 73 | 66 42 | 67 21 | 68 11 | 73 7 | 74 42 | 75 66 | 76 66 | 77 343 |
78 181 | 79 73 | 80 18 | 81 7 | 85 7 | 86 23 | 87 16 | 88 12 | 89 299 | 90 78 |
91 133 | 92 29 | 93 7 | 94 17 | 99 4 | 102 18 | 103 26 | 104 28 | 105 134 | 106 37 |
107 28 | 108 61 | 116 6 | 117 11 | 118 22 | 119 16 | 120 5 | 121 21 | 134 157 | 136 652 |
138 64 | 137 19 | 150 6 | 152 27 | 165 969 | 168 87 | 167 12 | 182 99 | 183 6 | 207 8 |
Figure 268: GC-MS Library Results for 2,3-Dinitrotoluene Standard
Figure 269: 2,4-Dinitrotoluene (100µg/mL) Standard; GC-MS Results
Figure 270: GC-MS Library Results for 2,4-Dinitrotoluene Standard
**Figure 271**: 2,6-Dinitrotoluene (100µg/mL) Standard; GC-MS Results
Figure 272: GC-MS Library Results for 2,6-Dinitrotoluene Standard
Hit 1: Benzene, 2-methyl-1,3,5-trinitro-
C7H6N3O6, MF: 227, RMF: 954; Prob 96.0%; CAS: 118-96-7; Lib: replib; ID: 24810.

(replib) Benzene, 2-methyl-1,3,5-trinitro-

Name: Benzene, 2-methyl-1,3,5-trinitro-
Formula: C7H6N3O6
MW: 227 CAS#: 118-96-7 NIST#: 79713 ID#: 24810 DB: replib
Other DBs: Fine, TSCA, RTECS, HODOC, NIH, EINECS
Contributor: USAF ACADEMY, COLORADO SPRINGS, COLORADO 80840; J LLOYD PFLUG
10 largest peaks:
210 999 | 89 335 | 63 265 | 134 151 | 62 149 | 180 144 | 193 141 | 76 128 | 149 123 | 30 122 |
993 m/z Values and Intensities:
14 1 | 15 4 | 16 3 | 17 3 | 18 4 | 27 6 | 29 8 | 30 122 | 31 2 | 37 5 |
38 15 | 39 74 | 40 3 | 43 40 | 44 1 | 46 34 | 49 5 | 50 66 | 51 78 | 52 24 |
53 20 | 54 5 | 55 7 | 60 8 | 61 29 | 62 149 | 63 265 | 64 47 | 65 36 | 68 18 |
67 16 | 68 11 | 69 37 | 71 4 | 73 9 | 74 72 | 75 67 | 76 128 | 77 60 | 78 33 |
79 14 | 80 9 | 81 4 | 84 4 | 85 18 | 86 48 | 87 61 | 88 78 | 89 335 | 90 54 |
91 22 | 92 31 | 93 12 | 94 15 | 95 4 | 96 4 | 103 32 | 104 37 | 105 39 | 106 31 |
107 11 | 108 4 | 116 8 | 117 15 | 118 12 | 119 8 | 120 43 | 121 9 | 122 4 | 133 18 |
134 151 | 135 24 | 136 18 | 149 123 | 150 13 | 151 16 | 152 17 | 163 24 | 164 93 | 165 11 |
Hit 1: Benzenamine, 4-nitro-N-phenyl-
C₁₂H₁₀N₂O₂; MF: 222; RMF: 340; Prob 79.4%; CAS: 838-30-8; Lib: replib; ID: 25002.

(replib) Benzenamine, 4-nitro-N-phenyl-

Name: Benzenamine, 4-nitro-N-phenyl-
Formula: C₁₂H₁₀N₂O₂
MW: 214 CAS#: 838-30-8 NIST#: 9964 ID#: 25002 DB: replib
Other DBs: Fine, TSCA, RTECS, HODOC, NIH, EINECS
10 largest peaks:
214 999 | 167 619 | 168 260 | 184 240 | 77 150 | 215 150 | 166 110 | 51 100 | 65 70 | 63 60 |
50 m/z Values and Intensities:
41 10 | 43 10 | 44 50 | 50 50 | 51 100 | 52 30 | 62 10 | 63 60 | 64 40 | 85 70 |
66 10 | 74 20 | 75 20 | 76 30 | 77 150 | 78 30 | 84 20 | 89 20 | 90 30 | 91 30 |
92 10 | 93 10 | 103 10 | 108 20 | 113 10 | 114 10 | 115 50 | 116 10 | 117 20 | 127 10 |
128 40 | 129 20 | 130 10 | 139 60 | 140 40 | 141 30 | 154 20 | 165 10 | 166 110 | 167 619 |
168 260 | 169 40 | 182 10 | 183 10 | 184 240 | 185 40 | 198 10 | 214 999 | 215 150 | 216 20 |
Figure 273: 3,4-Dinitrotoluene (100µg/mL) Standard; GC-MS Results
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*Figure 274: GC-MS Library Results for 3,4-Dinitrotoluene Standard*
Figure 275: Diethyl Phthalate (100µg/mL) Standard; GC-MS Results
Unknown; intLib=273

149

177

100

50

0

51  65  76  93  105  121  132  164  195  222

50  60  70  80  90  100  110  120  130  140  150  160  170  180  190  200  210  220  230

(Text File) Scan 2824 (17.746 min): 2014 1030 100 DIETHYLPHALTALATE1.D/data.ms

Name: Scan 2824 (17.746 min): 2014 1030 100 DIETHYLPHALTALATE1.D/data.ms
MW: N/A ID#: 5283 DB: Text File
10 largest peaks:
149 999  177 210  150 115  105 85  176 79  76 78  65 75  104 64  93 63  121 48

50 m/z Values and Intensities:
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75 14  76 78  77 38  78 4  79 1  91 7  92 6  93 63  94 4  103 3
104 64  105 85  106 14  107 2  119 1  120 1  121 49  122 32  123 2  131 2
132 15  133 6  135 5  147 1  148 4  149 999  150 115  151 12  152 1  184 3
175 1  176 79  177 210  178 44  179 4  194 1  195 2  221 3  222 13  223 2
**Figure 276**: GC-MS Library Results for Diethyl Phthalate Standard
Figure 277: 2-Nitrotoluene (100µg/mL) Standard; GC-MS Results
Unknown; InLib=256

Name: Scan 1528 (10.330 min); 2014 1030 100 2NITROTOluene1.Ddata.ms

M/V: N/A ID#: 5285 DB: Text File

10 largest peaks:

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Page 1 of 3
Figure 278: GC-MS Library Results for 2-Nitrotoluene Standard
Figure 279: 4-Nitrotoluene (100µg/mL) Standard; GC-MS Results
Unknown: InLib=447

(Text File) Scan 1720 (11.429 min): 2014 1030 100 4NITROTOLUENE.D/data.ms

Name: Scan 1720 (11.429 min): 2014 1030 100 4NITROTOLUENE.D/data.ms
MW: N/A ID#: 5289 DB: Text File
10 largest peaks:
91 899 | 137 807 | 65 630 | 107 326 | 63 216 | 77 201 | 106 161 | 89 156 | 79 146 | 51 97 |
33 m/z Values and Intensities:
51 97 | 52 42 | 53 32 | 60 9 | 61 20 | 62 66 | 63 216 | 64 53 | 65 630 | 66 35 |
73 8 | 74 37 | 75 22 | 76 17 | 77 201 | 78 43 | 79 146 | 80 10 | 85 9 | 86 16 |
87 21 | 89 158 | 90 50 | 91 999 | 92 68 | 104 8 | 106 161 | 107 328 | 108 23 | 121 61 |
137 807 | 138 60 | 207 10 |
Figure 280: GC-MS Library Results for 4-Nitrotoluene Standard
Figure 281: TNT (100µg/mL) Standard; GC-MS Results
APPENDIX III – UV/Visible Spectroscopy Data

Spectrum Peak Pick Report

Data Set: Holmium Oxide Std_124152

Figure 282: UV/Vis Spectrum of Holmium Oxide Standard

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Figure 283: UV/Vis Spectrum of Diphenylamine (10µg/mL)
Figure 284: UV/Vis Spectrum of 2-Nitrodiphenylamine (10µg/mL)
Figure 285: UV/Vis Spectrum of 4-Nitrodiphenylamine (10µg/mL)
Figure 286: UV/Vis Spectrum of 2,3-Dinitrotoluene (10µg/mL)
Figure 287: UV/Vis Spectrum of 2,4-Dinitrotoluene (10µg/mL)
Figure 288: UV/Vis Spectrum of 2,6-Dinitrotoluene (10µg/mL)
Figure 289: UV/Vis Spectrum of 3,4-Dinitrotoluene (10µg/mL)
Spectrum Peak Pick Report

Data Set: 2-Nitrotoluene JL_141100

**Figure 290**: UV/Vis Spectrum of 2-Nitrotoluene (10µg/mL)
Figure 291: UV/Vis Spectrum of 4-Nitrotoluene (10µg/mL)
Figure 292: UV/Vis Spectrum of Silver Nanoparticles (Ag NPs – Microwave Synthesis)
Figure 293: UV/Vis Spectrum of Diphenylamine with Ag NPs
Figure 294: UV/Vis Spectrum of 2-Nitrodiphenylamine with Ag NPs
Figure 295: UV/Vis Spectrum of 4-Nitrodiphenylamine with Ag NPs
Figure 296: UV/Vis Spectrum of 2,3-Dinitrotoluene with Ag NPs
Figure 297: UV/Vis Spectrum of 2,4-Dinitrotoluene with Ag NPs
Figure 298: UV/Vis Spectrum of 2,6-Dinitrotoluene with Ag NPs
Figure 299: UV/Vis Spectrum of 3,4-Dinitrotoluene with Ag NPs
Figure 300: UV/Vis Spectrum of 2-Nitrotoluene with Ag NPs
Figure 301: UV/Vis Spectrum of TNT
**Figure 302**: UV/Vis Spectrum of PETN
**Figure 303:** UV/Vis Spectrum of RDX
Figure 304: UV/Vis Spectrum of C-4
### APPENDIX IV – X-Ray Diffraction Data

**Figure 305**: Structure viewed in photomicrograph of SERS experiment (Photomicrograph 10x, Horiba Instrumentation)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si, Au with Bi @BiOCl3</th>
<th>X-ray</th>
<th>Counter</th>
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</thead>
<tbody>
<tr>
<td>File</td>
<td>LBC/Si@BiOCl3</td>
<td>100 kV/15 mA</td>
<td>Miniflex goniometer</td>
</tr>
<tr>
<td>Comment</td>
<td>Si, Au with Bi@BiOCl3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Date</td>
<td>Nov-10-15 12:46:23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operator</td>
<td>JL</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Memo            | Au NaCl on Si + LBC/Sample Holder 3 |

<table>
<thead>
<tr>
<th>Raw data</th>
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<tbody>
<tr>
<td>Sample</td>
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<td>X-ray</td>
<td>Counter</td>
</tr>
<tr>
<td>File</td>
<td>LBC/Si@BiOCl3</td>
<td>100 kV/15 mA</td>
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<td>Si, Au with Bi@BiOCl3</td>
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<td>Operator</td>
<td>JL</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Memo            | Au NaCl on Si + LBC/Sample Holder 3 |

**Graph**: Intensity (cps) vs. 2θ (deg.)

Nov-09-2015 12:46:23 Page 1
**Figure 306**: XRD Results of Au, NaCl Sample

<table>
<thead>
<tr>
<th>#</th>
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<th>Height</th>
<th>Height%</th>
<th>Phase ID</th>
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<th>I% (hkl)</th>
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</table>

Line Shifts of Individual Phases:
- 90-030-0059: Halite - NaCl <2T(0) = 0.0, d/d(0) = 1.0>
APPENDIX V – Additional Raman Spectroscopy Data

NOTE: The following data shows several different trials for each standard listed. Some are analyzed under varying conditions (usually at a concentration of 100µg/ml, unless noted otherwise), which are noted on the key of the specific spectrum.

NOTE: In any of the following results, a symbol of $\lambda_o=$ indicates the excitation wavelength of the laser source.

NOTE: Unless noted, the laser power used in full power; “LL” refers to a lower laser power of 1.5mW for the 532nm excitation, and “0.5laser” refers to a 0.5mW power for the 532nm excitation.

Diphenylamine

![Figure 307: Additional Spectral Data of Diphenylamine (785nm, Horiba)](image)

![Figure 308: Additional Spectral Data of Diphenylamine (785nm, Horiba)](image)
Figure 309: Additional Spectral Data of Diphenylamine (532nm, WITec)

Figure 310: Additional Spectral Data of Diphenylamine (785nm, WITec)

2-Nitrodiphenylamine

Figure 311: Additional Spectral Data of 2-Nitrodiphenylamine (785nm, Horiba)
Figure 312: Additional Spectral Data of 2-Nitrodiphenylamine (785nm, Horiba)

Figure 313: Additional Spectral Data of Diphenylamine (532nm, WITec)

Figure 314: Additional Spectral Data of Diphenylamine (785nm, WITec)
4-Nitrodiphenylamine

**Figure 315**: Additional Spectral Data of 4-Nitrodiphenylamine (785nm, Horiba)

**Figure 316**: Additional Spectral Data of 4-Nitrodiphenylamine (785nm, Horiba)

**Figure 317**: Additional Spectral Data of 4-Nitrodiphenylamine (532nm, WITec)
**Figure 318**: Additional Spectral Data of Diphenylamine (532nm, WITec)

**Figure 319**: Additional Spectral Data of 4-Nitrodiphenylamine (785nm, WITec)
2,3-Dinitrotoluene

2,3-Dinitrotoluene; SERS
\( \lambda_0 = 785 \text{nm}, 1\% \text{ laser, Horiba} \)

![Graph 1](image1)

**Figure 320:** Additional Spectral Data of 2,3-Dinitrotoluene (785nm, Horiba)

2,3-Dinitrotoluene; SERS
\( \lambda_0 = 785 \text{nm}, 1\% \text{ laser, Horiba} \)

![Graph 2](image2)

**Figure 321** Additional Spectral Data of 2,3-Dinitrotoluene (785nm, Horiba)

2,3-Dinitrotoluene; SERS
\( \lambda_0 = 532 \text{nm, WiTec} \)

![Graph 3](image3)

**Figure 322** Additional Spectral Data of 2,3-Dinitrotoluene (532nm, WiTec)
Figure 323: Additional Spectral Data of 2,3-Dinitrotoluene (785nm, WITec)

2,4-Dinitrotoluene

Figure 324: Additional Spectral Data of 2,4-Dinitrotoluene (785nm, Horiba)

Figure 325: Additional Spectral Data of 2,4-Dinitrotoluene (785nm, Horiba)
Figure 326: Additional Spectral Data of 2,4-Dinitrotoluene (532nm, WiTec)

Figure 327: Additional Spectral Data of 2,4-Dinitrotoluene (785nm, WiTec)

2,6-Dinitrotoluene

Figure 328: Additional Spectral Data of 2,6-Dinitrotoluene (785nm, Horiba)
**Figure 329**: Additional Spectral Data of 2,6-Dinitrotoluene (785nm, Horiba)

**Figure 330**: Additional Spectral Data of 2,6-Dinitrotoluene (532nm, WITec)

**Figure 331**: Additional Spectral Data of 2,6-Dinitrotoluene (785nm, WITec)
3,4-Dinitrotoluene

**Figure 332**: Additional Spectral Data of 3,4-Dinitrotoluene (785nm, Horiba)

**Figure 333**: Additional Spectral Data of 3,4-Dinitrotoluene (785nm, Horiba)

**Figure 334**: Additional Spectral Data of 3,4-Dinitrotoluene (532nm, WiTec)
**Figure 335**: Additional Spectral Data of 3,4-Dinitrotoluene (785nm, WiTec)

**Diethyl phthalate**

**Figure 336**: Additional Spectral Data of Diethyl Phthalate (785nm, Horiba)

**Figure 337**: Additional Spectral Data of Diethyl Phthalate (785nm, Horiba)
Figure 338: Additional Spectral Data of Diethyl Phthalate (532nm, WITec)

Figure 339: Additional Spectral Data of Diethyl Phthalate (785nm, WITec)

2-Nitrotoluene

Figure 340: Additional Spectral Data of 2-Nitrotoluene (785nm, Horiba)
**Figure 341**: Additional Spectral Data of 2-Nitrotoluene (785nm, Horiba)

**Figure 342**: Additional Spectral Data of 2-Nitrotoluene (532nm, WITec)

**Figure 343**: Additional Spectral Data of 2-Nitrotoluene (785nm, WITec)
4-Nitrotoluene

**Figure 344:** Additional Spectral Data of 4-Nitrotoluene (785nm, Horiba)

**Figure 345:** Additional Spectral Data of 4-Nitrotoluene (785nm, Horiba)

**Figure 346:** Additional Spectral Data of 4-Nitrotoluene (532nm, WITec)
**Figure 347**: Additional Spectral Data of 4-Nitrotoluene (785nm, WITec)

**TNT**

**Figure 348**: Additional Spectral Data of TNT (Bulk, WITec)

**Figure 349**: Additional Spectral Data of TNT (785nm, Horiba)
Figure 350: Additional Spectral Data of TNT (785nm, Horiba)

Figure 351: Additional Spectral Data of TNT (532nm, WITec)

Figure 352: Additional Spectral Data of TNT (532nm, WITec)
Figure 353: Additional Spectral Data of TNT (785nm, WITec)

PETN

Figure 354: Additional Spectral Data of PETN (Bulk, WITec)

Figure 355: Additional Spectral Data of PETN (785nm, Horiba)
Figure 356: Additional Spectral Data of PETN (785nm, Horiba)

Figure 357: Additional Spectral Data of PETN (532nm, WiTec)

Figure 358: Additional Spectral Data of PETN (532nm, WiTec)
**Figure 359:** Additional Spectral Data of PETN (785nm, WITec)

**RDX**

**Figure 360:** Additional Spectral Data of RDX (Bulk, WITec)

**Figure 361:** Additional Spectral Data of RDX (785nm, Horiba)
Figure 362: Additional Spectral Data of RDX (785nm, Horiba)

Figure 363: Additional Spectral Data of RDX (532nm, WiTec)

Figure 364: Additional Spectral Data of RDX (532nm, WiTec)
**Figure 365**: Additional Spectral Data of RDX (785nm, WITec)

**C-4**

**Figure 366**: Additional Spectral Data of C-4 (Bulk, WITec)

**Figure 367**: Additional Spectral Data of C-4 (785nm, Horiba)
**Figure 368:** Additional Spectral Data of C-4 (785nm, Horiba)

**Figure 369:** Additional Spectral Data of C-4 (532nm, WITec)

**Figure 370:** Additional Spectral Data of C-4 (532nm, WITec)
Figure 371: Additional Spectral Data of C-4 (785nm, WiTec)

4-Amino-2,6-dinitrotoluene

Figure 372: Additional Spectral Data of 4-Amino-2,6-Dinitrotoluene (532nm, WiTec)

Figure 373: Additional Spectral Data of 4-Amino-2,6-Dinitrotoluene (785nm, WiTec)
1,3,5-Trinitrobenzene

**Figure 374**: Additional Spectral Data of 1,3,5-Trinitrobenzene (532nm, WiTec)

**Figure 375**: Additional Spectral Data of 1,3,5-Trinitrobenzene (785nm, WiTec)

Tetryl

**Figure 376**: Additional Spectral Data of Tetryl (532nm, WiTec)
Figure 377: Additional Spectral Data of Tetryl (785nm, WiTec)

HMX

Figure 378: Additional Spectral Data of HMX (532nm, WiTec)

Figure 379: Additional Spectral Data of HMX (785nm, WiTec)
N-nitrosodiphenylamine

Figure 380: Additional Spectral Data of N-nitrosodiphenylamine (532nm, WiTec)

Figure 381: Additional Spectral Data of N-nitrosodiphenylamine (785nm, WiTec)

2-Amino-4,6-Dinitrotoluene

Figure 382: Additional Spectral Data of 2-Amino-4,6-Dinitrotoluene (532nm, WiTec)
Figure 383: Additional Spectral Data of 2-Amino-4,6-Dinitrotoluene (785nm, WiTec)

Nitroglycerin

Figure 384: Additional Spectral Data of Nitroglycerin (532nm, WiTec)

Figure 385: Additional Spectral Data of Nitroglycerin (785nm, WiTec)
Nitrobenzene

**Figure 386**: Additional Spectral Data of Nitrobenzene (532nm, WITec)

**Figure 387**: Additional Spectral Data of Nitrobenzene (785nm, WITec)

3-Nitrotoluene

**Figure 388**: Additional Spectral Data of 3-Nitrotoluene (532nm, WITec)
Figure 389: Additional Spectral Data of Nitrobenzene (785nm, WiTec)

1,3-Dinitrobenzene

Figure 390: Additional Spectral Data of 1,3-Dinitrobenzene (532nm, WiTec)

Figure 391: Additional Spectral Data of 1,3-Dinitrobenzene (785nm, WiTec)
Dibutyl phthalate

**Figure 392:** Additional Spectral Data of Dibutyl Phthalate (532nm, WiTec)

**Figure 393:** Additional Spectral Data of Dibutyl Phthalate (785nm, WiTec)

1,3-Diethyl-1,3-diphenylurea

**Figure 394:** Additional Spectral Data of 1,3-Diethyl-1,3-Diphenylurea (532nm, WiTec)
Figure 395: Additional Spectral Data of 1,3-Diethyl-1,3-Diphenylurea (785nm, WiTec)

Dimethyl phthalate

Figure 396: Additional Spectral Data of Dimethyl Phthalate (532nm, WiTec)

Figure 397: Additional Spectral Data of Dimethyl Phthalate (785nm, WiTec)
3,5-Dinitroaniline

Figure 398: Additional Spectral Data of 3,5-Dinitroaniline (532nm, WiTec)

3,5-Dinitroaniline; SERS
\( \lambda_o = 532\text{nm}, \) WiTec

Dinitrobenzene

Figure 400: Additional Spectral Data of Dinitrobenzene (Bulk, WiTec)

Dinitrobenzene; Solid NR
\( \lambda_o = 532, 785\text{nm}, \) WiTec

Dinitrobenzene
Figure 401: Additional Spectral Data of Dinitrobenzene (532nm, WiTec)

Figure 402: Additional Spectral Data of Dinitrobenzene (785nm, WiTec)

Urea Nitrate

Figure 403: Additional Spectral Data of Urea Nitrate (Bulk, WiTec)
Figure 404: Additional Spectral Data of Urea Nitrate (532nm, WiTec)

Figure 405: Additional Spectral Data of Urea Nitrate (785nm, WiTec)

2,4,6-Trinitrobenzoic Acid

Figure 406: Additional Spectral Data of 2,4,6-Trinitrobenzoic Acid (Bulk, WiTec)
Figure 407: Additional Spectral Data of 2,4,6-Trinitrobenzoic Acid (532nm, WITec)

Figure 408: Additional Spectral Data of 2,4,6-Trinitrobenzoic Acid (785nm, WITec)

Trinitroanisole

Figure 409: Additional Spectral Data of Trinitroanisole (Bulk, WITec)
Figure 410: Additional Spectral Data of Trinitroanisole (532nm, WITec)

Figure 411: Additional Spectral Data of Trinitroanisole (785nm, WITec)

2,4-Dinitrophenetole

Figure 412: Additional Spectral Data of 2,4-Dinitrophenetole (Bulk, WITec)
Figure 413: Additional Spectral Data of 2,4-Dinitrophenetole (532nm, WiTec)

Figure 414: Additional Spectral Data of 2,4-Dinitrophenetole (785nm, WiTec)

Ammonium Nitrate

Figure 415: Additional Spectral Data of Ammonium Nitrate (Bulk, WiTec)
Figure 416: Additional Spectral Data of Ammonium Nitrate (532nm, WITec)

Figure 417: Additional Spectral Data of Ammonium Nitrate (785nm, WITec)

Trinitrotoluene

Figure 418: Additional Spectral Data of Trinitrotoluene (Bulk, WITec)
**Figure 419**: Additional Spectral Data of Trinitrotoluene (532nm, WiTec)

**Figure 420**: Additional Spectral Data of Trinitrotoluene (785nm, WiTec)

2,4-Dinitrophenylamine

**Figure 421**: Additional Spectral Data of 2,4-Dinitrophenylamine (532nm, WiTec)
**Figure 422:** Additional Spectral Data of 2,4-Dinitrodiphenylamine (785nm, WITec)

**Semtex Type II IRA**

**Figure 423:** Additional Spectral Data of Semtex II IRA (785nm, Horiba)

**Semtex Type II IRA Home Office**

**Figure 424:** Additional Spectral Data of Semtex II IRA HO (785nm, Horiba)
Figure 425: Additional Spectral Data of Semtex H IRA (785nm, Horiba)

Figure 426: Additional Spectral Data of Semtex H RCMP (785nm, Horiba)

Figure 427: Additional Spectral Data of Semtex H MNT (785nm, Horiba)
**Semtex Para-MNT 0.1%**

**Figure 428**: Additional Spectral Data of Semtex Para-MNT 0.1% (785nm, Horiba)

**Semtex 1A Spanish EGDN**

**Figure 429**: Additional Spectral Data of Semtex 1A Spanish EGDN (785nm, Horiba)

**Semtex A Spain 600µl taggant**

**Figure 430**: Additional Spectral Data of Semtex Spain 600µl Taggant (785nm, Horiba)
C-4 Regular

Figure 431: Additional Spectral Data of C-4 Regular (785nm, Horiba)

C-4 MNT

Figure 432: Additional Spectral Data of C-4 MNT (785nm, Horiba)

C-4 DMNB 0.1%

Figure 433: Additional Spectral Data of C-4 DMNB 0.1% (785nm, Horiba)
**Hexageno (Spanish C-4)**

![Hexageno Spectral Data](image1)

**Figure 434:** Additional Spectral Data of Hexageno (785nm, Horiba)

**Dynamite IRA**

![Dynamite IRA Spectral Data](image2)

**Figure 435:** Additional Spectral Data of Dynamite IRA (785nm, Horiba)

**Dynamite Forcite 40**

![Dynamite Forcite 40 Spectral Data](image3)

**Figure 436:** Additional Spectral Data of Dynamite Forcite 40 (785nm, Horiba)
**Dynamite Giant Coalition**

*Figure 437*: Additional Spectral Data of Dynamite Giant Coalition (785nm, Horiba)

**Detasheet NAX**

*Figure 438*: Additional Spectral Data of Detasheet NAX (785nm, Horiba)

**Detasheet**

*Figure 439*: Additional Spectral Data of Detasheet (785nm, Horiba)
Figure 440: Additional Spectral Data of Pentex (785nm, Horiba)

Figure 441: Additional Spectral Data of Tetryl (785nm, Horiba)

Figure 442: Additional Spectral Data of TNT Flakes (785nm, Horiba)
TNT Crystals

**Figure 443**: Additional Spectral Data of TNT Crystals (785nm, Horiba)
library(chemometrics)
library(rgl)  # library for interactive 3D-plots
library(pls)  # library with some nice functions for chemometrics

# Load in IR spectral data for explosives
rootd<-"/Users/Owner/Desktop/

dat.exp<-read.csv(paste(rootd,"STATS1002.csv",sep=""),header=F)
dat.exp[1:5,1:5]
X.exp<-dat.exp[-c(1),3:ncol(dat.exp)]
x <- as.numeric(dat.exp[1,-c(1,2)])

plot(as.numeric(X.exp[2,]))
lbl.exp<-factor(dat.exp[,-1,2])

# Come up with some group labels
rownames(dat.exp)
p<-dim(X.exp)[2]  # number of "variables" in the spectra
n<-dim(X.exp)[1]  # number of spectra observed
p
n
# Plot the spectra:
# wn<-seq(from=100,to=3600,by=10)  # Make an x-axis of wavenumbers
wn <- x
drp.idxs <- c(which(wn<=400),which(wn>=1850))
plot(wn,X.exp[2,],type="l",main="Explosives Spectrum",xlab="wavenumbers")
plot(wn[!drp.idxs],X.exp[2,-drp.idxs],type="l",main="Explosives Spectrum",xlab="wavenumbers")
X.exp.old <- X.exp
X.exp <- X.exp[,-drp.idxs]
plot(wn[!drp.idxs],X.exp[2,],type="l",main="Explosives Spectrum",xlab="wavenumbers")

# Plot all spectra against each other:
for(i in 1:n)
{
  plot(wn,X.exp[i,],type="l",col=lbl.exp[i],main="All F.D. Spectra",xlab="wavenumbers",xlim=c(min(wn),max(wn)),ylim=c(min(X.exp),max(X.exp)))
  par(new=TRUE)
}
#Compute PCs
pca.model<-prcomp(X.exp,center=TRUE,scale=T)

#Plot histogram of PC variances:
plot(pca.model)

#Look at numerical values of PC variances:
summary(pca.model)

#Do a 2D PCA "scores" plot:
M<-2  #Pick dimension
Z<-predict(pca.model)[,1:M]  #Grab PCA scores
plot(Z[,1],Z[,2],col=lbl.exp,pch=16,xlab="PC1",ylab="PC2")  #Plot
text(Z[,1],Z[,2],labels=lbl.exp,font=2,adj=1.5)  #Group lables
text(Z[,1],Z[,2],labels=1:nrow(X.exp),font=1,adj=0)  #Obs. lables

#Do a 3D PCA "scores" plot:
M<-3  #Pick dimension
Z<-predict(pca.model)[,1:M]  #Grab PCA scores
plot3d(Z[,1],Z[,2],Z[,3],type="s",radius=1,col=as.numeric(lbl.exp),aspect="iso",xlab="PC1",ylab="PC2",zlab="PC3")
text3d(Z[,1],Z[,2],Z[,3],text=lbl.exp,font=1,adj=1.5)  #Group lables

#Try to numerically identify outliers with these metrics: Orthogonal and Scores
M<-3  #Pick dimension
Z<-predict(pca.model)[,1:M]  #Grab PC scores

#Compute "orthogonal distances" of full data set from PCA model:
Apc<-pca.model$rotation[,1:M]  #Grab PC loadings
X.proj<-Z%*%t(Apc)  #Project scores back up to data space
res.mat<-X.exp-X.proj  #Compute difference between full data set and PCA reduced model
orthag.dists<-sqrt(rowSums(res.mat * res.mat))  #Orthogonal dists. of each obs to PCA model

#Make a bar chart of the Orthogonal distances. Color coded by label:
barplot(orthag.dists, main="Orthogonal Distances", xlab= "Orthogonal Distance",ylab= "Observation Number",names.arg=1:n,beside=TRUE, col=lbl.exp)

#Huber cutoff for OD outliers. Assums ODs are gaussian:
cutoff.od<-(median(orthag.dists^(2/3)) + mad(orthag.dists^(2/3))*qnorm(0.975))^(3/2)
cutoff.od

#Compute Mahalanobis "Score distances"
score.dists<-sqrt(mahalanobis(Z,colMeans(Z),cov(Z)))
# Make a bar chart of the Mahalanobis distances. Color coded by label:
barplot(score.dists, main="Score Distances", ylab="Score Distance", xlab="Observation Number", names.arg=1:n, beside=TRUE, col=lbl.exp)

# Huber cutoff for SD outliers:
cutoff.sd<-sqrt(qchisq(0.975,M))
cutoff.sd

library(MASS)  # This library has the lda functions as well as lots of data sets
library(caret)
library(rgl)

# Compute PCs to de-correlate the data a bit
pca.model<-prcomp(X.exp,center=TRUE, scale=F)

# Look at numerical values of PC variances:
summary(pca.model)

# Prep data for CVA:
Mpc<-40  # Pick dimension
Zpc<-predict(pca.model)[,1:Mpc]  # Grab PCA scores
pairs(Zpc,col=lbl.exp)

# Do CVA and compute HOO-CV classification error rate:
lda.model<-lda(Zpc,lbl.exp,CV=T)
cv.lbs<-lda.model$class
cv.lbs  
# Error rate:
(1-sum(as.numeric(cv.lbs)==as.numeric(lbl.exp))/length(lbl.exp))*100

# Make up random training and test sets
trainobs<-createDataPartition(lbl.exp,p=0.30,list=F)  # Grab random itemsgrp for training
Zpc.tr<-Zpc[trainobs,]
Zpc.te<-Zpc[-trainobs,]
lbltr<-lbl.exp[trainobs]
lblte<-lbl.exp[-trainobs]

# Train a CVA model:
lda.model<-lda(Zpc.tr,lbltr)

# Test CVA model:
pred.lbl<-predict(lda.model,newdata=Zpc.te)$class

# Make a confusion matrix with diagnostics:
confusionMatrix(pred.lbl,lblte)

#Try out HOO-CV on PCA-CVA:

#First reduce the dimension of the data set a bit:
#Compute PCs
pca.model<-prcomp(X.exp,center=T,scale=FALSE)
M<-50                #Pick dimension
Z<-predict(pca.model)[,1:M]               #Grab PCA scores

#Now do HOO-CV with PCA reduced CVA:
#A little tricky but it is a very general formulation:
theta.fit<-function(xdata,lbls){lda(xdata,lbls)}                          #Define a discrimination model
theta.pred<-function(fit,xdata){predict(fit,xdata,diimen=M)$class}       #A function to spit out group label predictions
cv.results<-general.cv(Z,lbl.exp,theta.fit,theta.pred,ngroup=nrow(Z))$cv.fit    #The actual HOO-CV function

#Make a confusion matrix with diagnostics:
confusionMatrix(cv.results,lbl.exp)

#Or compute the HOO-CV error rate this way:
(1-sum(as.numeric(cv.results)==as.numeric(lbl.exp))/length(lbl.exp))*100

#Try HOO-CV with PLS-DA
M<- 135                  #Pick a dimension
theta.fit<-function(xdata,lbls){plsda(xdata,lbls,M)}                        #Define the model
theta.pred<-function(fit,xdata){predict(fit,xdata)}                        #A function to spit out group label predictions
cv.results<-general.cv(X.exp,lbl.exp,theta.fit,theta.pred)$cv.fit            #The actual HOO-CV function
(1-sum(as.numeric(cv.results)==as.numeric(lbl.exp))/length(lbl.exp))*100        #HOO-CV error
**Bibliography**


*Daubert v. Merrell Dow Pharmaceuticals, Inc.*, 43 F.3d 1311 (9th Cir. 1995).


*Frye v. United States*, 293 F. 1013 (D.C. Cir. 1923).


