
Standoff Raman Spectroscopy of Explosive Nitrates Using 785 nm Laser

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Abstract: We have demonstrated that standoff Raman spectra of some nitrates could be obtained at distances ranging from 20 meters to 250 meters using an 11-inch reflecting telescope and a continuous wavelength 785 nm laser of 400 mW power coupled with a small portable spectrometer. The measurements were taken during both day and night, indoors and outdoors, for various integration times. Detection and identification of chemical and biological hazards within the forensic and homeland security contexts requires conducting the analysis in field while adapting a non-contact approach to the hazard. In this paper, we report the adequacy of a standoff Raman system with a 785nm laser for remote detection and identification of ammonium, sodium, and magnesium nitrates in bulk form. The results demonstrate that, as the standoff distances increases, there is a discernible attenuation in the intensity of the Raman signatures of the nitrates. To discriminate the background lights, improve the signal-to-noise ratio and trigger the weak characteristic bands, Raman spectra were also acquired using higher integration time. For the measurements taken at a 100 meter standoff distances, we were able to achieve a signal-to-noise ratio of about 10. For greater distances, due to the difficulty of locating the target using IR laser, a 50 mW green laser pointer at 485 nm wavelength is used before the IR laser is used for acquiring the Raman signals.

Keywords: Remote Sensing, Standoff Raman, Measurements of Nitrates, Raman of Explosives

1. Introduction

Raman spectroscopy is a laser-based vibrational technique that provides a unique set of optical signature/fingerprint about a molecule of interest. Due to its chemical specificity, capability in analyzing and identifying organic and inorganic compounds in any state, non-destructive and real time detection and identification of molecules, with little if any sample preparation required, Raman spectroscopy is becoming a promising remote in-situ detection tool for explosives identification and analysis purposes. When trying to analyze unknown chemicals, extreme care is required because of the potential threat that substance could be posing. Some chemicals react violently involving explosion or detonation, others could be sensitive to light, heat or shock. Standoff Raman spectroscopy which is an inelastic scattering of light with the same principles as conventional Raman spectroscopy is a technique that allows the detector to be away from the sample that is being studied. This method is

finding increasing applications in a wide range of issues like criminal forensic analysis, counter terrorism and homeland security where access to the sample can be difficult.

The demand for rapid field detection has led to an increase in development of commercial-portable Raman systems with more sensitive detectors and spectrometers operating with high power lasers. The innovation in technology has made these systems easier to use and smaller. The application of portable standoff Raman system for remote detection monitoring of highly toxic organic and inorganic substances was first reported in 1992 by Angel et al [1] for distances up to 16.7m with excitation sources of 488nm and 809nm lasers. Many commercial-portable systems use the pulsed Nd: YAG laser of 1064nm, frequency doubled to 532 nm for excitation and different research groups have come up with designs for this particular wavelength [2-7] mainly for monitoring environmental pollution, gases on planetary surfaces and explosives. Using a 532nm Nd: YAG laser-based system, Pettersson et al.[8-9] showed that a number of explosives could be detected at 30m in outdoor environment. To the best

of our knowledge, the longest distance of detection achieved is 470m by Pettersson *et al* [10] with this laser. Most of the work done with the 532nm pulse laser can be found in the paper published by Wallin *et al* [11-12].

It is reasonable to assume that shorter wavelength lasers produce more intense Raman signals. However, with these lasers there are generally concerns of absorption, fluorescence, photodecomposition, and ignition when it comes to materials in the forensic context. Photodecomposition and ignition of chemicals are of special concern when using pulsed lasers with high peak powers. For these reasons, lasers in the NIR region are often used. One such laser is the continuous wave (CW) 785nm which is portable and relatively inexpensive and often reduces the risk of signal being interfered with fluorescence but requires a greater power.

The numerous benefits of Raman spectroscopy in forensic analysis [13-17] were first reported in the 1990s. The 785 nm laser has been used in the study of artworks and artifacts [18]. In 2008, Hargreaves *et al* reported the use of Raman spectroscopy to identify illegal narcotics in an airport [19]. In-depth review of the role of portable Raman spectroscopy systems for forensics, archaeometry, geoscience, and other applications are covered elsewhere [20-22].

In this paper, we report the use of a portable standoff Raman system with a 785nm laser to detect three different nitrates of ammonium, sodium and magnesium which are often used as low-grade explosives. This work has been done for distances ranging from 20 meters up to 250m for indoor and outdoor environments. To the best of our knowledge this is the first report of the use of 785 nm CW laser for stand-off detection of these explosive nitrates at such distances.

2. Materials and Methods

Standoff Raman measurements of ammonium, sodium, and magnesium nitrates in powder form (Fisher Scientific) were carried out using a portable standoff Raman system (Enwave Optonics EZRaman, Irvine, CA) with 785 nm diode laser having a maximum power of 400 mW. The system is compact with the laser and spectrometer integrated with a laptop computer for data collection and analysis (Figure 1). The fiber-optic probe shown in the figure consists of two single fibers: a 100 micron excitation fiber and a 200 micron collection fiber with a numerical aperture of 0.22. While the original instrument is coupled to a 2-inch refractive telescope, we have modified it by replacing the refractive telescope with an 11-inch aperture, 110 inch focal length CPC Series Celestron telescope for standoff excitation of the distant target as well as collecting Raman signal from the target.

Due to a number of optical surfaces in the fiber-optic light-coupling assembly to the telescope, most of the laser power is lost and the actual output laser power reaching the target is just 80 mW. Further, the collection efficiency of Raman light from the target falls down with standoff distance by inverse-square law. To compensate for this loss, for standoff

measurements at distances greater than 100 meters, a second 785 nm laser was used close to the target. Thus, for distances greater than 100 meters, a total light-power of 480 mW is incident on the target. Clearly, this second laser will not be required with a better optical design of the input light coupling device or with a higher power lasers which are available commercially. An additional factor which limits the stand-off measurement at increasing distances is the spot size of the focused 785 nm laser on the target. With the 11-inch reflecting telescope used here, the laser spot-size on a target 250 meters away is about 6 inch. For standoff distances less than 100 meters, both the daytime and nighttime measurements were done indoors in a long straight corridor. Residual lighting due to diffuse sunlight contributed to the background in the daytime measurements. Measurements for distances greater than 100 meters were made outdoors in a vacant field. Background light signal in these measurements was mostly due to the city lights. Since 785 nm light is barely visible to the eye, a challenge in these experiments was to ensure that light from the telescope was falling on the target for standoff distances of greater than 100 meters. This was accomplished with a 50 mW green laser-pointer at 485 nm wavelength that could be fitted in the same input assembly as the 785 nm fiber-coupled laser. Once the telescope is aligned to the target with green light, the 785 nm laser is put back for standoff Raman measurements. The Raman signal was analyzed with a mini-spectrometer coupled to a CCD detector. The detector is thermoelectrically cooled to -50°C and the spectrometer records the scattered Raman signals in the spectral range of $250 - 2350\text{ cm}^{-1}$ and with a resolution of 6 cm^{-1} . For the standoff Raman measurements of nitrates, the samples were put in a large transparent glass container at specified distances in the range of 20 meters to 250 meters away from the telescope. The measurements reported here in this paper were made at an integration time as low as 1 second to 60 seconds. As indicated earlier, for distances below 100 meters, all the measurements were made indoors inside a long straight corridor.

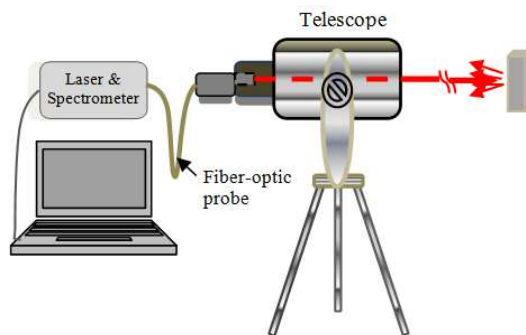


Figure 1. Schematic representation of the portable standoff Raman system used in the detection of ammonium nitrate, sodium nitrate and magnesium nitrate.

3. Results and Discussions

Figures 2-5 represent measurements taken during daytime but with the corridor lights off. The only background light in

these measurements was the diffuse sunlight through doors in the corridor opening to outside the building. It was found that repeating measurements in figures 2-5 under nighttime conditions gave results with similar signal-to-noise ratio. Figure 2 shows the spectra of sodium nitrate, ammonium nitrate and magnesium nitrate measured for the samples kept at 20 meters from the telescope and the spectrometer with an exposure time of one second with 80 mW laser power. As shown in the figure, it is possible to record the distinctive symmetric stretching (v1) bands of sodium nitrate, ammonium nitrate, and magnesium nitrate at 1065cm^{-1} , 1041cm^{-1} , and 1061cm^{-1} respectively, which agree well with literature values [23]. It is known that [24,25], in-phase symmetric stretching (v1), the out-of-phase stretching (v3), and the in-plane bending (v4) modes of nitrate ion are Raman active.

To improve the signal-to-noise ratio, and observe the other bands of the nitrates, the measurements were repeated at the same distance but with an integration time of 60 seconds. As can be seen in Figure 3, in addition to the enhancement in the prominent peaks described above, the higher integration time triggers additional intense characteristic Raman bands of sodium nitrates at 1386 and 725cm^{-1} , which are attributed to degenerate stretching (v3), and degenerate bending (v4) of nitrate ion. Similarly, an intense in-plane bending (v4) band of ammonium nitrates is observed at 715cm^{-1} . However, for this measurement conditions, the in-plane deformation (v4) does not appear for the magnesium nitrate.

Figures 4 and 5 show the spectra of the three nitrates stated above for an exposure time of 60 seconds for distances of 40 and 60 meters respectively. These measurements were taken with 80mW power on the target from a 400 mW diode laser.

Figures 6, 7 and 8 show the Raman spectra of the three nitrates of interest at 100 and 250 meters standoff distances. These measurements were taken in the field during the nighttime. The source of background signal was streetlights, building lights and the vehicle lights. As mentioned earlier, for these measurements, a second 400 mW laser was used close to the target to excite Raman spectra apart from the 80 mW of laser power through the telescope. Thus a total laser power of 480 mW was incident on the target. The decrease in the signal-to-noise ratio with increasing standoff distance is found to be mainly due to two factors: (1) Increase in spot size of the focused 785 nm laser beam through the telescope on the target and (2) Inverse square fall-off of the Raman signal with the standoff distance. Focused 785 nm laser beam through the telescope has a spot size of 2.5 inch for a standoff distance of 250 meters as compared to a spot size of 0.1 inch for a distance of 20 meters. Raman-light collection efficiency of the telescope is generally seen to deteriorate as the excitation point on the target moves away from the telescope axis. Clearly, for the modest laser power used in these experiments and with the home-built optical-fiber-to-telescope light coupling device used, the standoff distance is limited to 100 meters for a signal-to-noise ratio of around 10. However, as we have shown with an auxiliary second laser close to the target, the standoff distance can be easily

increased to greater than 250 with a more powerful pump laser and a better light coupling assembly. In addition, to acquiring characteristics Raman bands at greater standoff distances, higher integration time and laser power improve the signal-to-noise ratio of the Raman spectra.

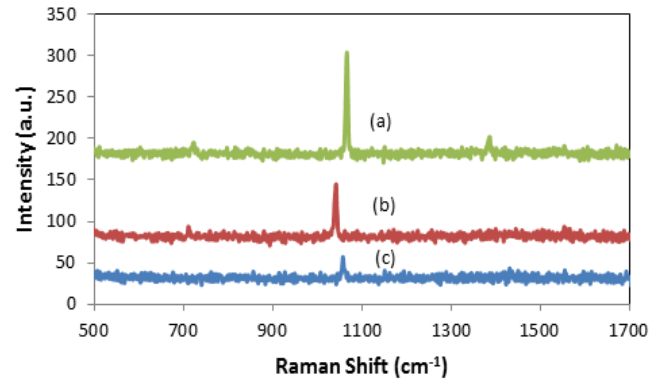


Figure 2. Raman Spectra of sodium nitrate (a), ammonium nitrate (b), and magnesium nitrate (c) measured at a distance of 20 meters, with an integration time of 1 second using 80 mW laser power on the target from a 785 nm CW diode laser.

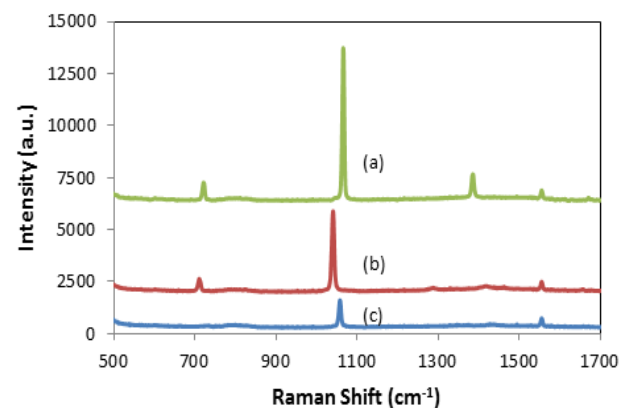


Figure 3. Raman Spectra of sodium nitrate (a), ammonium nitrate (b), and magnesium nitrate (c) measured at a distance of 20 meters, with an integration time of 60 seconds using 80 mW laser power on the target from a 785 nm CW diode laser.

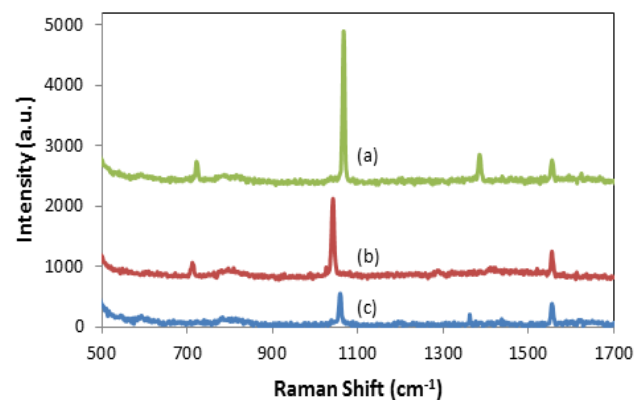


Figure 4. Raman Spectra taken at a distance of 40 meters, with an integration time of 60 seconds. Curves (a), (b), and (c) represent the spectra of Sodium Nitrate, Ammonium Nitrate, and Magnesium Nitrate, respectively. A 785 nm CW diode laser with 80 mW of power on the target was used.

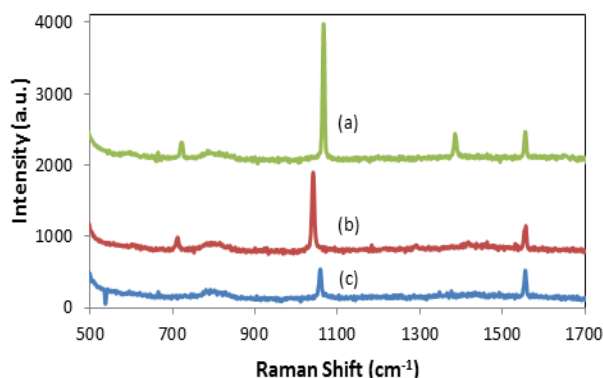


Figure 5. Raman Spectra taken at a distance of 60 meters, with an Integration Time of 60 seconds. Curves (a), (b), and (c) represent the spectra of Sodium Nitrate, Ammonium Nitrate, and Magnesium Nitrate, respectively. A 785 nm CW diode laser with 80 mW of power on the target was used.

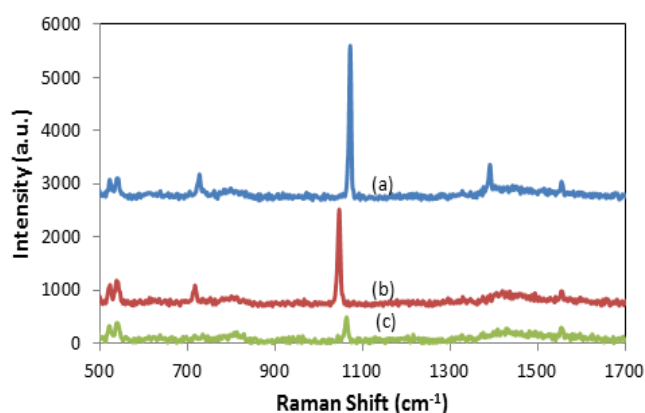


Figure 6. Raman Spectra taken at a distance of 100 meters, with an Integration Time of 60 seconds. Curves (a), (b), and (c) represent the spectra of Sodium Nitrate, Ammonium Nitrate, and Magnesium Nitrate, respectively. Two 785 nm CW diode lasers with a total of 480 mW of power on the target were used. Measurements were taken outside at nighttime in the presence of street lights, vehicle headlights, and building lights.

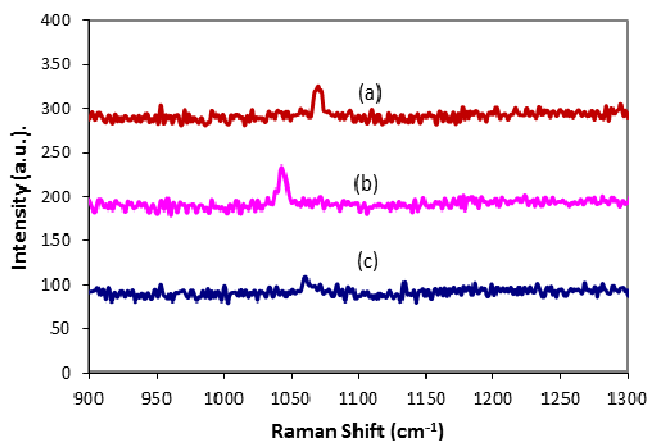


Figure 7. Raman Spectra of sodium (a), ammonium(b), and magnesium (c) nitrates taken at a distance of 250 meters with an exposure time of 10 seconds. Measurements were taken outside at nighttime in the presence of street lights, vehicle headlights, and building lights. Two 785 nm CW diode lasers with a total of 480 mW of power were used.

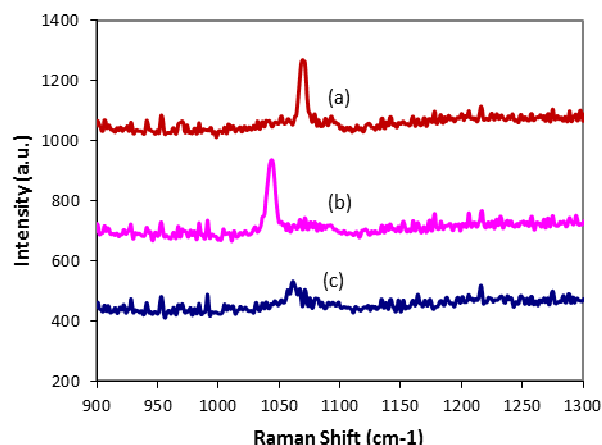


Figure 8. Raman Spectra of sodium (a), ammonium (b), and magnesium (c) nitrates taken at a distance of 250 meters with an exposure time of 60 seconds. Measurements were taken outside at nighttime in the presence of street lights, vehicle headlights, and building lights. Two 785 nm CW diode lasers with a total of 480 mW of power were used.

4. Conclusions

Raman spectroscopy has potential benefits for forensic science for many different reasons. One of which is a no contact requirement between the sample under investigation and the investigator, which minimizes the risk of contamination to the sample or harm done to the investigator. Daytime-indoor and nighttime-outdoor detection of bulk sodium, ammonium, and magnesium nitrates chemicals used in explosives have been demonstrated for distances 20, 40, 60, 100, and 250m using a portable Raman system with a 785nm laser.

Depending on the standoff distance separating the laser source and the chemical target, good signal-to-noise ratio was obtained for modest integration time between 1-300 seconds. Even though the standoff Raman technique with an infrared pump-laser wavelength of 785 nm is not ideal for daytime-outdoor measurements, we believe that these measurements show a potential for several forensic applications involving either nighttime-outdoor or day and nighttime-indoor measurements. With some improvements in light-coupling optics and increased laser-power, this relatively inexpensive setup is amenable to field measurements of up to several hundred meters.

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