# Standoff Raman Detection of Explosive Materials Using a Small Raman Spectroscopy System

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## Abstract

In this work a standoff Raman spectroscopy SRS system has been designed, assembled and tested for detecting explosives (Ammonium nitrate, Trinitrotoluene and Urea nitrate) in dark laboratory at 4 m target-telescope distance. The SRS system employs frequency doubled Nd:YAG laser at 532 nm excitation with laser power of 250 mW and integration time of 2 second. The Cassegrain telescope was coupled to the Ventana Raman spectrometer using a fiber optics cable, and Notch filter is used to reject Rayleigh scattering light. The Raman scattered light is collected by a telescope and then transferred via fiber optic to spectrometer and finally directed into charge coupled device CCD detector. In order to test SRS system, it has been used to detect the Raman spectra of Toxic Industrial Compounds TIC such as acetone, toluene, and carbon tetrachloride. The SRS results were compared with conventional Raman microscopy results using a bench top Bruker SENTERRA Raman instrument. [DOI: 10.22401/JNUS.20.3.10]

Keywords**:** SRS system, explosives, integration time, ventana Raman spectrometer, CCD detector.

## Introduction

The Raman spectroscopy is a high resolution photonic technique based on analysis of inelastically scattered light after interaction of monochromatic light with material. Raman Spectroscopy provides direct information about the molecular structure and the composition of sample, to identify substances from the characteristic spectral patterns (fingerprinting), and to determine quantitatively or semi-quantitatively the amount of a substance in a sample.

In an international perspective, there are currently much research activities concerning explosives detection, and standoff detection of explosives is in main focus. The reason for this interest is the occurrence of terrorist attacks on the civilian society involving improvised explosives devices IED [1], such as the bombings in London underground in July 2005, bombings occurring in Middle East, and also the situation that armed forces will encounter on international missions, where IED are used against military personnel as well as civilians. Unfortunately, there appear only a limited numbers of techniques to use in standoff detection of HEs. One of the approaches is Raman spectroscopy. Standoff Raman spectroscopy SRS 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. In spite of the Raman scattering is weak phenomenon, the incorporation of powerful laser beams and highly sensitive charge coupled device CCD detectors allow us to detect HEs in a relatively long distance. Therefore, SRS provides a method for identifying chemicals in a sample located meters from the Raman system. Standoff detection using Raman spectroscopy was first theoretically proposed by T. Hirschfield [2]. In general, a Raman spectrum consists of peaks that correspond to the characteristic vibrational frequencies of a material. As a result, one may, for the substances of interest, collect Raman spectra with very high signal to noise ratio (S/N) ratio under laboratory conditions. These "reference" spectra can then be stored in a database as a signature for the particular substance.

The main aim of this work was to design and assemble a continuous wave standoff Raman spectroscopy system and to demonstrate at laboratory scale the capability of SRS system as a tool in remote sensing technology. The standoff Raman system was tested in detection of explosive materials ($NH_4NO_3$, TNT, and UN) and toxic industrial compound TIC (Carbon tetrachloride, toluene

and acetone) as well. Raman measurements of explosives were also acquired using Bruker SENTERRA Raman microscopy for the verification of standoff Raman measurements. The molecular structures of explosive materials are shown in Fig.(1).
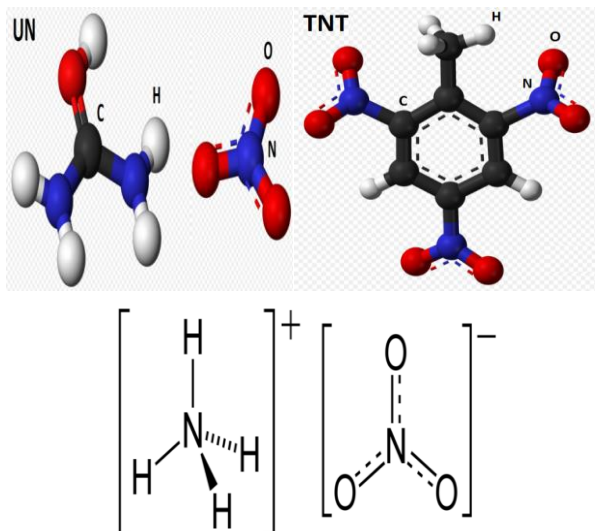


*Fig.(1): Molecular Structures of TNT, UN and AN.*

**Experimental work**

The experimental setup of continuous wave standoff Raman spectroscopy SRS system is schematically represented in Fig.(2). The SRS system consists of a Cassegrain telescope with 110 mm clear aperture was adopted to collect relatively large area of Raman signals scattered from target sample that is being studied, Cobolt Tor$^{TM}$ laser system operating at 532 nm (frequency doubled Nd:YAG continuous wave laser) used as an excitation source for measuring Raman spectra of explosives, Ventana-532-Raman spectrometer with 0.6 nm spectral resolution and grating 1600 L/mm HD VPG, equipped with a charge-coupled device CCD detector (Pixel format 1024 x 64, Pixel size 14 μm square), a THORLABS notch filter was adjusted to attenuate the elastically Rayleigh scattered light and diffuse reflected light from the target, a fiber optic assembly of (600 μm diameter, NA = 0.39 fiber input) and laptop computer.
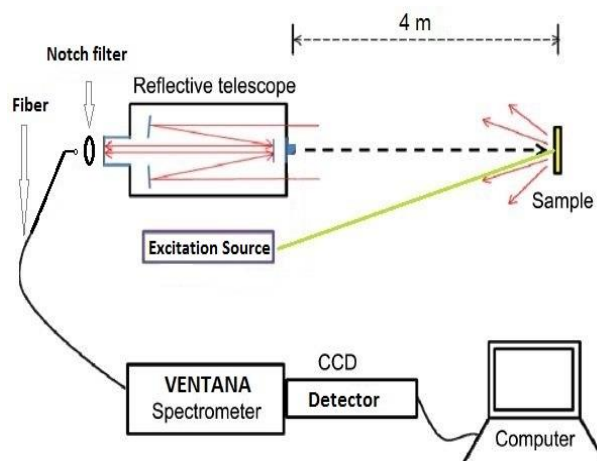


*Fig.(2): Design details of the SRS: (1) laser source; (2) sample; (3) reflective telescope; (4) notch filter; (5) fiber optic coupling; (6) spectrograph (7) detector.*

Once the laser strikes the sample to be identified, at the same time the telescope collects the scattered light from the sample. The collimated light from the telescope output passing first through the notch filter that is located at the back end of telescope tube and then is collected by fiber optic located after the notch filter, the output of the fiber optic assembly was directly coupled to the Raman spectrometer by 5x objective lens, and finally the light was directed into the CCD detector which is integrated in Ventana Raman spectrometer. The major components that make up SRS system are shown in Fig.(3).
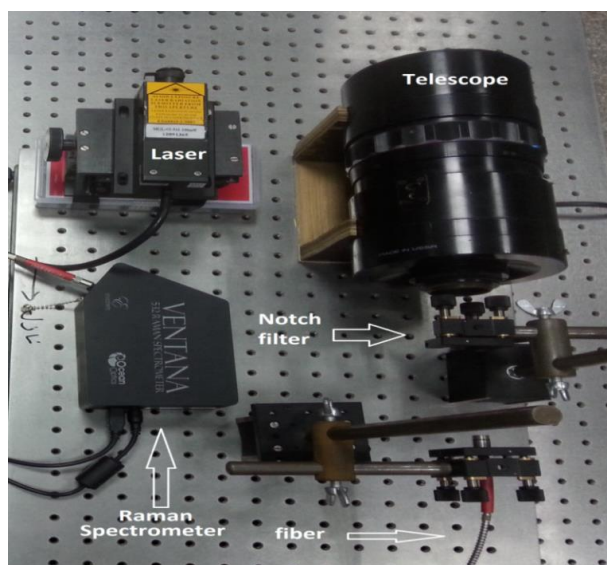


*Fig.(3): Photographic image of SRS system model.*

In order to verify the standoff Raman spectra obtained by Ventana Raman

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spectroscopy system, Raman spectra of the same substances have been recorded using bench top Bruker SENTERRA Raman instrument which are considered as reference spectra. Reference Raman spectra were recorded at 532 nm laser excitation with spectral resolution of 3 cm$^{-1}$, in spectroscopic Raman shift range of 0- 4270 cm$^{-1}$.

For measurements of explosives on surfaces, a known amount of the solid explosives (Urea nitrate and Ammonium nitrate) were wet with distilled water and then each of the substances was ground and pressed by spoon on the glass surface to be spread and paste onto the glass slides. The C4 was wet in acetone and then the substance was ground and pressed by spoon on the glass surface to be spread out and paste onto the glass slides. In order to assess the applicability of SRS system for explosives detection in realistic world scenarios, their detection on different background surfaces (glass slides, aluminum plates and aluminum foil) is achieved. The area that surround the samples were painted in black color in order to diminish the laser beam which is reflected from the area that is surround the explosive samples.

## Results and Discussion
### Standoff Raman Spectra of Toxic Industrial Compounds TIC

Important industrial solvents used for manufacturing in the petrochemical, pharmaceutical, and TIC are highly flammable, toxic, mutagenic or carcinogenic. Some of these compounds are used in amounts that constitute potential threats. Thus, it is vital to find ways of detecting these compounds. The SRS offer new and easy alternatives to carry out these monitoring processes remotely. In addition to significance of detecting TIC: Carbon tetrachloride CCL$_4$, Acetone (CH$_3$)$_2$CO and Toluene C$_7$H$_8$, they are typically used as a calibration standard for the Raman Shift axis in dispersive instruments, therefore the liquid TIC are used to test and evaluate the performance of the SRS system that is used in this study. These toxic compounds were chosen as the first samples to test because of their strong and intensive scattering capability. These compounds were transferred into quartz cuvette of 3.5 mL, 1 cm inside width (path length of 10 mm). As

shown in Fig.(4) standoff Raman spectra of standard samples were collected at a standoff distance of 4 m, in spectroscopic range 0-4270 cm$^{-1}$ using frequency doubled Nd:YAG 532 nm CW laser with laser power of 250 mW and integration time of 2 seconds under dark laboratory conditions to minimize background radiation interference and mercury lines from fluorescent lamps.
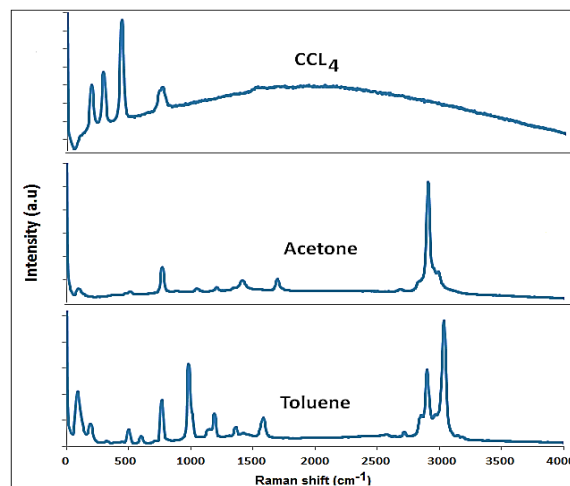


***Fig.(4): Standoff Raman spectra of CCL$_4$, Acetone and Toluene at 250 mW and integration time of 2 s.***

In Fig.(4) CCL$_4$ shows its three main Raman active peaks at (216, 312, 459) cm$^{-1}$. The most important characteristic band of CCL$_4$ was found at 459 cm$^{-1}$. In the case of Acetone, the fingerprint Raman bands are observed at (390, 507, 786, 1067, 1226, 1426, 1709, 2920, 3001) cm$^{-1}$. The most prominent band of Acetone appeared at 786 cm$^{-1}$ and 2918 cm$^{-1}$ as clearly shown in the figure. Finally, the fingerprint Raman bands of toluene are observed at (522, 620, 786, 1000, 1207, 1377, 1600, 2740, 2920, 3054) cm$^{-1}$. All these fingerprint Raman bands of standard compounds are in very good agreement with previously published literature [3-5].

### Standoff Raman Spectroscopy of High Explosives and Comparison with Micro Raman Microscopy

Standoff Raman spectra of high explosive materials were measured for AN, TNT and UN, in the spectral Raman shift region of 0 – 4270 cm$^{-1}$ at a distance of 4 m away from the Raman system using Nd:YAG laser which is frequency doubled to 532 nm excitation lines with laser power of 250 mW (measured

at head) and integration time of 2 second for recording the spectrum. These parameter conditions were enough to easily identify explosives at such distance. Raman spectra detected by normal or micro Raman microscopy considered as a reference data in this study.

Figs. (6), (8) and (10) show typical standoff Raman spectra obtained remotely using standoff Raman spectroscopy in the far field for the HE studied and micro Raman spectra in the near field of corresponding HE samples obtained with a micro Raman microscopy. The measurements have been performed on bulk amount samples, in the amounts of a 2 mg. The Raman signals were measured in the dark condition. Raman spectrum is contributed by background noise due to fluorescence and inherent optical noise of the detection Raman system. Simple background reduction (baseline reduction) technique was applied to suppress these backgrounds of spectrum that is obtained by micro Raman microscopy while spectrum obtained by standoff Raman spectroscopy kept without any modification, it means there is no background reduction. Standoff Raman measurements of explosive substances are indicated below.

### Ammonium Nitrate AN

Ammonium nitrate $NH_4NO_3$ is $NO_3$ containing material. Standoff Raman spectrum of Ammonium Nitrate AN collected at 4 m distance is shown in Fig.(5). This sample was detected using frequency doubled Nd:YAG 532 nm laser excitation with 250 mW and the integration time kept at 2 seconds.
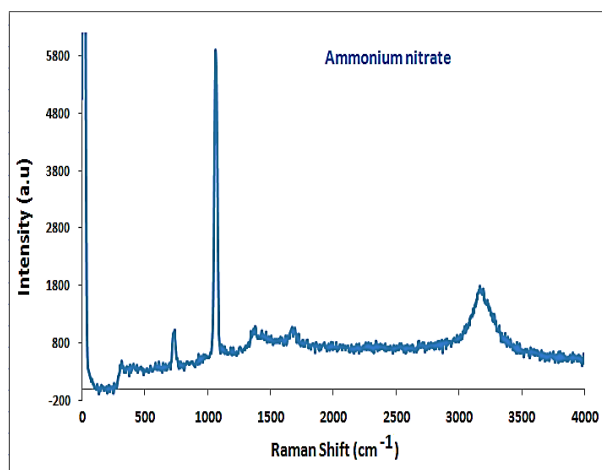


*Fig.(5): Standoff Raman spectrum of AN at 250 mW and integration time of 2 s.*

The reference micro Raman spectrum is compared to the Standoff Raman spectrum of AN in Fig.(6). The very intense Raman bands of AN is observed at 1044 cm$^{-1}$ which is attributed to the symmetric N-O stretching vibration of $NO_3^-$ and the weak Raman band appeared at 715 cm$^{-1}$ is attributed to N-O in-plane bending vibration of $NO_3^-$. The contribution from $NH_4^+$ is negligible.

The spectra detected via standoff Raman spectroscopy coincide well with reference micro Raman spectrum as clearly shown in Fig.(6) as well as our standoff spectrum coincides well with previously reported literature [8-10]. Average difference of peak shift is about 3 cm$^{-1}$ from that of Sandra Sadate et al [9] and in general the average difference of peak shift is about 2 cm$^{-1}$ from that of micro Raman spectroscopy.
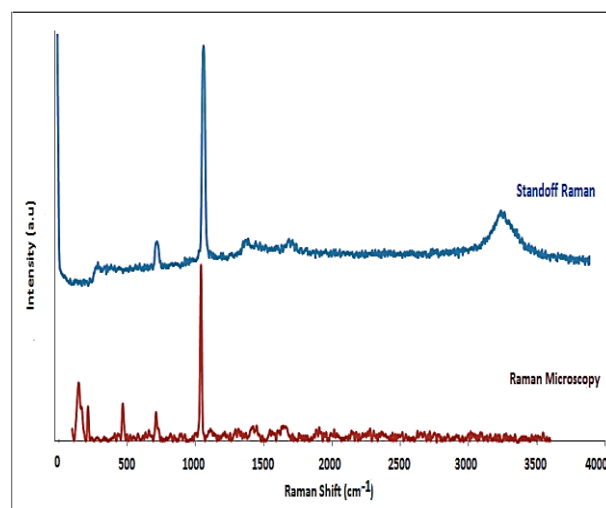


*Fig.(6): Comparison of Standoff Raman and micro Raman spectrum of AN.*

### Trinitrotoluene TNT

Trinitrotoluene $C_7H_5(NO_2)_3$ is another example of an $NO_2$ containing explosive. Standoff Raman spectrum of TNT collected at 4 m distance is shown in Fig.(7). This sample was detected using frequency doubled Nd:YAG 532 nm laser excitation with 250 mW and the integration time is 2 seconds. In addition, Fig.(7) shows an enlarge view of fingerprint region (1150-1700 cm$^{-1}$) to better illustrate the Raman signal and make it easily sensible by reader.
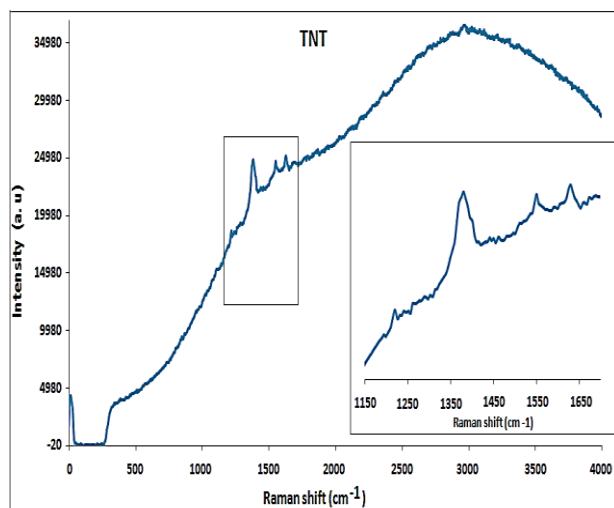
*Fig.(7): Standoff Raman spectrum of TNT at 250 mW and integration time of 2 s.*



*Fig.(8): Comparison of Standoff Raman and micro Raman spectrum of TNT.*

The reference micro Raman spectrum is compared to the Standoff Raman spectrum of TNT as indicated in Fig.(8). The most prominent characteristic Raman bands collected via micro Raman microscopy and Raman bands collected via Standoff Raman spectroscopy as well as the mode of vibrations are indicated and listed in the Table (2). The absent bands which are weak bands are also mentioned in the table.

*Table (1)*
*Assignments of Raman bands measured via micro Raman microscopy and Standoff Raman spectroscopy systems.*

| Standoff Raman $(cm^{-1})$ | Micro-Raman $(cm^{-1})$ | Assignments (mode of vibrations ) |
|---|---|---|
| Absent band | 327 | 2,4,6 C-N in plane torsion |
| Absent band | 366 | Methyl group deformation |
| Absent band | 792 | C-CH3 stretching, 2,4,6 $NO_2$ scissors |
| Absent band | 823 | 2,4,6 $NO_2$ scissors |
| 1211 | 1211 | C-H (ring) in plane bend, ring breathing |
| 1362 | 1362 | $NO_2$ symmetric, C-N stretching |
| 1534 | 1534 | $NO_2$ Asymmetric stretching |
| 1618 | 1618 | 2,6 $NO_2$ Asymmetric stretching |
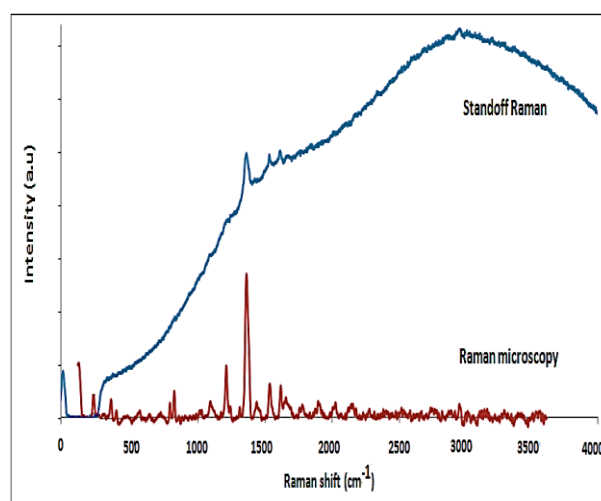
As clearly shown in Fig.(8), for the standoff Raman spectrum of TNT, the signal at 4 m measurement got substantial noise probably due to the interference of fluorescence. However, the standoff Raman bands in the region between 1200 and 1700 $cm^{-1}$, i.e. 1211, 1362, 1534 and 1618 $cm^{-1}$ are clearly identifiable except the band at 1211 $cm^{-1}$ which is barely distinguishable whereas the weak intensity bands in the region between 300 and 1000 $cm^{-1}$ are not observed at all. Those missing bands are overwhelmed by fluorescence interference. Some target materials have large inherent fluorescence which could hamper clear detection of Raman signals, presumably from contamination products of their preparation or from sample decomposition due to exposure to laser. This fluorescence contribution can be reduced by using a new fresh sample (less exposed to laser). The positions of major bands in TNT spectrum detected via standoff Raman spectroscopy consistent with reference micro Raman spectrum as clearly shown in Fig.(8) as well as consistent with previously published experimental data [6,7]. The average difference of peak shift is about 1 $cm^{-1}$ from that of micro Raman spectroscopy and the average difference of peak shift was 2 $cm^{-1}$ from that of Samuel et al [6].

**Urea Nitrate UN**

Urea nitrate (UN) is a 1:1 compound of urea $(NH_2)_2CO$ and nitric acid $HNO_3$, with a formula of $[(NH_2)_2CO] HNO_3$ is an $NO_3^-$ containing material. It is widely used in the

manufacture of fertilizers, but is also known as an easily synthesized homemade explosive. Standoff Raman spectrum of UN collected at 4 m distance is shown in Fig.(9). This sample was detected using 532 nm laser excitation with 250 mW and the integration time was 2 seconds.
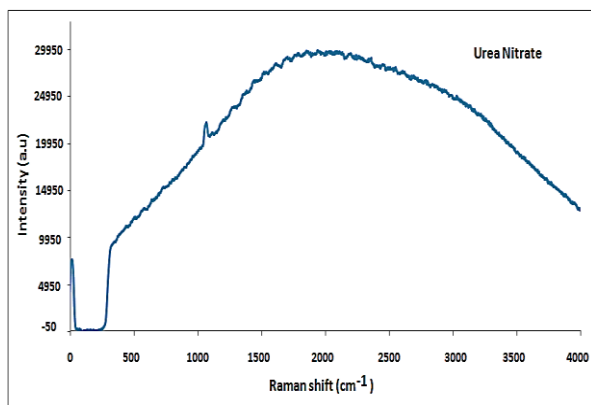


*Fig.(9): Standoff Raman spectrum of UN at 250 mW and integration time of 2 s.*

The reference micro Raman spectrum is compared to the SRS spectrum of urea nitrate in Fig.(10). The most intense Raman line of UN is observed at 1050 cm$^{-1}$ which is attributed to N-O symmetric stretching vibration of $NO_3^-$. As clearly shown in figure below that the weak line in UN (715 cm$^{-1}$) is absent in standoff Raman spectrum but observable in micro Raman spectrum and is attributed to N-O in-plane bending vibration of $NO_3^-$. The spectra detected via standoff Raman spectroscopy coincide well with reference micro Raman spectrum and average difference of peak shift was about 5 cm$^{-1}$. Standoff spectrum in excellent agreement with previously reported literature [11,12] and average difference of peak shift is about 3 cm$^{-1}$.
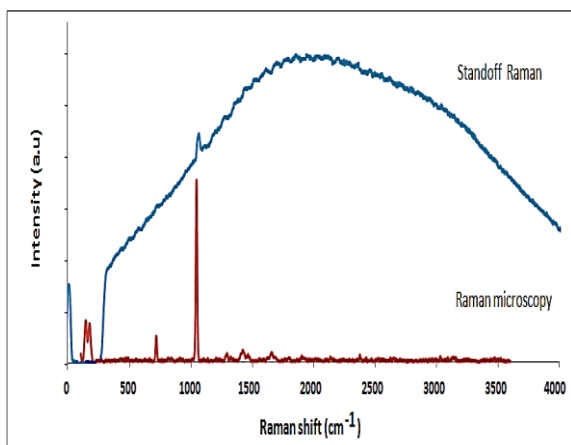


*Fig.(10): Comparison of Standoff Raman and micro Raman spectrum of UN.*

## Conclusions

The results presented here show that continuous wave standoff Raman spectroscopy system designed in this work is capable of detecting explosive materials: AN, TNT and UN under dark laboratory conditions up to a distance of 4 meters. The standoff Raman spectra of standard samples (liquid TIC): Carbon tetrachloride (CCL4), toluene and acetone are measured and verified the performance of Raman system.

In all cases, the spectra show good agreement with the acquired reference spectra, using a bench top Bruker SENTERRA Raman instrument and furthermore, the spectra show good agreement with previously reported literature; most of vibrational features are identifiable in the standoff spectra.

The measurements carried out with relatively low laser power of (250 mW) and low integration time of (2 s) operating in the visible region at 532 nm.

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