

Detection of Trace Explosive Materials by Standoff Raman Spectroscopy System

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Abstract

Standoff Raman spectroscopy SRS technique is one of the most powerful technologies that can identify trace amount of explosive materials. The Raman scattered signal collected by reflective telescope and a spectrograph is used to analyze the Raman scattered light. In order to view the spectrum, the spectrograph is equipped with charge coupled device CCD detector which allows detection of very weak Stokes line. In order to test the capability of SRS system of detecting explosives trace, detection of C4 and AN explosives have been achieved with limit of detection (LOD) about 20 µg for C4 and 40 µg for AN. [DOI: 10.22401/JNUS.20.1.13]

Keywords: standoff Raman spectroscopy, trace amount, explosive materials, CCD detector.

Introduction

In the last decades there have been several terrorist attacks in different cities, which have raised the need for new, reliable and effective instrumentation for the detection of explosives and their precursors at trace levels for homeland security applications. In particular, attacks against buses, trains, subways, etc., are a relatively recent phenomenon [1]. Since 1970, transportation has been an increasingly attractive target for terrorists [2]. A suicide attack is usually performed with an improvised explosive device (IED) which can come in many forms, ranging from a small pipe bomb to a sophisticated device. Many commonly available materials, such as fertilizer, gunpowder and hydrogen peroxide, can be used to prepare an IED [3].

Raman-based technologies are potential tools for the detection of explosives at a certain distance due to recent technical improvements [4]. The instantaneous inelastic scattering of incident photons by target molecules produces Raman spectra that uniquely identify chemical substances. The challenging requirements to deal with in the development of Raman technologies are to achieve high detection sensitivity for trace explosive materials at a certain distance and also a high selectivity for a reliable identification of the substance on an interfering background.

Most solid explosives have low vapor pressures at room temperature (parts per trillion (ppt) to parts per million (ppm)), and

military grade explosives can be detected on persons who have handled explosives even 48 hours after exposure [5]. Fingerprints of contaminated individuals can contain some µg of energetic material [6,7].

Several Raman apparatuses for the detection of energetic materials, either at trace levels or for quantities in the order of mg, have already been developed by different research groups [8,9].

In order to screen passengers and luggage fast and reliably, it is of significant importance to have a good technology for detecting a trace amount of high explosives (HEs) and analyzing the chemical identification accurately [10]. Improvised explosive devices (IED) are common and growing threat to civilian society [11]. To defeat IED, detecting a trace of HEs present in IED from a safe distance is of particular importance. One of the approaches is Raman spectroscopy. Standoff detection using Raman spectroscopy was first proposed by Hirschfield [12].

In this work, the main aims of this study is to determine the limit of detection of C4 and AN for SRS system at fixed standoff distance of 4 m using continuous wave laser of 532 nm in dark condition. The amounts of high explosives detected were of the order of microgram present as traces on test surfaces.

Experimental Work

The setup of prototype standoff system based on Raman spectroscopy is schematically shown in Fig.(1). The ensemble consisted of

Ventana 532-Raman spectrometer with 0.6 nm spectral resolution and grating 1600 L/mm HD VPG equipped with a Hamamatsu S11510 charge-coupled device (CCD) detector (Pixel format 1024 x 64, Pixel size 14 μm square), and the THORLABS notch filter. The Remaining parts were a Cassegrain telescope with 110 mm clear aperture was adopted to collect relatively large area of Raman signals scattered from target sample, Cobolt TorTM laser system operating at 532 nm (frequency doubled Nd:YAG continuous wave laser) used as a excitation source and a fiber optic assembly of (600 μm diameter, NA = 0.39 fiber input).

The telescope was coupled to the Raman spectrometer through fiber optics cable. The notch filter was inserted between the telescope and the fiber optics that is used to block Rayleigh scattered light and reflected light from the sample. The output of the fiber optic bundle was directly coupled to the Raman spectrometer by 5x objective lens. The collimated light from the telescope output passing first through the notch filter and then is collected by fiber optic and finally the light was directed into the CCD detector which is integrated in Ventana Raman spectrometer.

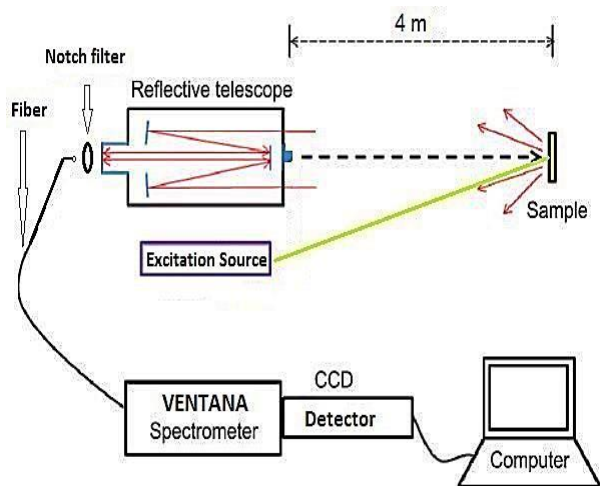


Fig.(1): Design details of the SRS system: (1) laser source; (2) sample; (3) reflective telescope; (4) notch filter; (5) fiber optic coupling; (6) spectrograph.

Before the measurements of explosive materials, a known amount of the ammonium nitrate was wet with distilled water and then the AN was paste onto the glass slides. The C4 was wet with acetone and then the C4

substance was paste onto the glass slides. The primary lasing wavelength for the Nd:YAG laser is 1,064 nm. The Nd:YAG laser can be frequency doubled (half the wavelength) with an intracavity KDP* crystal to lase at 532 nm.

Results and Discussion

Standoff Raman spectrum of Plastic Explosive C4

C4 or Composition C4 is a common variety of the plastic explosive family. The explosive material in C4 is cyclotrimethylene-trinitramine ($\text{C}_3\text{H}_6\text{N}_6\text{O}_6$). Fig.(2) shows standoff Raman spectrum of C4 collected at 4 m distance. This sample was detected using frequency doubled Nd:YAG 532 nm with laser power of 750 mW and the integration time of 8 seconds. The measurements have been performed on mass of 800 μg adhered to a glass slides. The Raman signals were measured in the dark laboratory condition. The most prominent Raman bands of C4 are indicated in the Fig.(2). Standoff Raman spectrum of C4 is in a good agreement with the spectrum obtained by other authors[13-15].

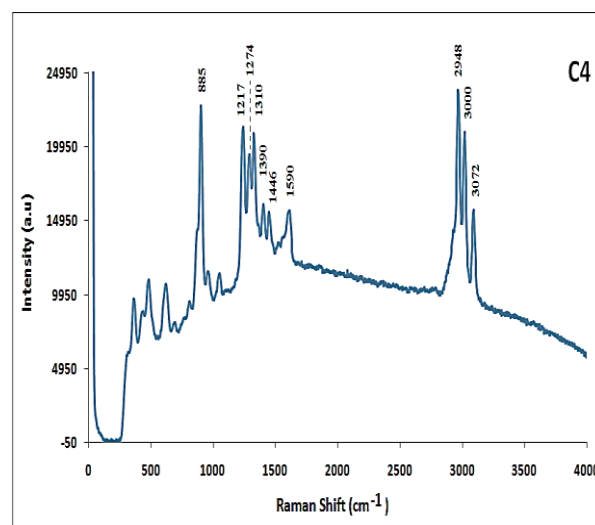


Fig.(2): C4 spectrum at 4 m, 750 mW and integration time of 8 s.

Standoff Raman Spectrum of Ammonium Nitrate (AN)

Ammonium nitrate (NH_4NO_3) is NO_3 containing material. Standoff Raman spectroscopy spectrum of AN collected at 4 m distance is shown in Fig.(3). This sample was detected using frequency doubled Nd:YAG 532 nm laser excitation with laser power of 250 mW and the integration time of 2 seconds. The measurements have been performed on

mass of 2 mg adhered to a glass slides. The most prominent Raman bands of AN are indicated in the Fig.(3).

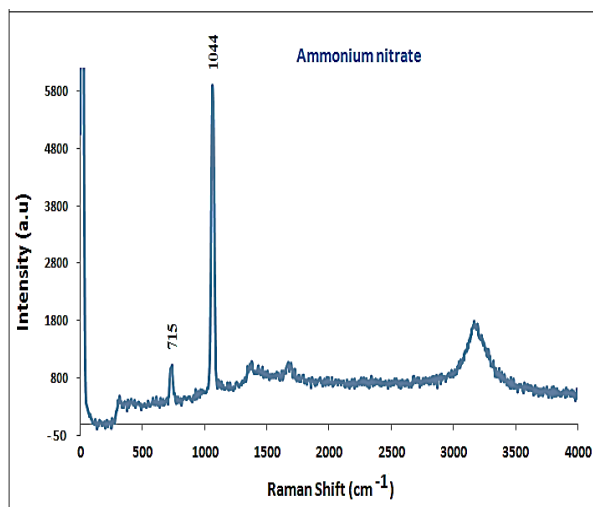


Fig.(3): SR spectrum of AN at 250 mW and integration time of 2 s.

The spectra detected via standoff Raman spectroscopy coincides well with previously reported literature [16-18].

Detection of Trace Explosives

Capability to detect small quantities of explosives is significant in possible “real world” scenarios. People involved in the storage and transportation of mines and IED typically have detectable amounts of explosives traces on their hand, clothes and this traces can be extended to cars, bags, doors, glasses and any other items that can be touched after handling explosives. Explosives are very polar molecules and tend to strongly physisorb to many surfaces. The transfer of explosive residues while handling explosives is typically unavoidable. Most explosives can be identified on persons who handle explosives over 48 hours past the time of exposure even when washing with surfactants is performed [19].

To develop standoff Raman as a field-deployable technique it is important to assess its capabilities for trace detection. The LOD is defined as being the mass which provides a detection signal equal to three times the standard deviation of the noise level in another word, LOD is the limit at which the Signal to noise ratio (S/N ratio) equal to three. The limits of detection of C4 and AN were determined for continuous wave SRS system

used in this work at distance of 4 m using frequency doubled Nd:YAG 532 nm continuous wave laser. The standoff Raman spectra of trace quantities of C4 and AN substances put on glass slides and aluminum plates were obtained in dark room conditions. With respect to the low availability of traces from explosives upon handling of an IED, 1 mg should still be considered as bulk amount [20]; therefore, samples of less than 1 mg have been used in this part of study to be investigated. It is of importance to obtain standoff Raman signal of suspect object with integration time as low as possible that allows to the operator to identify the suspect object very quickly, and to identify suspect objects with laser power as low as possible because lasers with high power are expensive instrument and are not always available.

Signal to noise ratio (S/N ratio) is roughly estimated. The Raman spectrum is magnified and then the peak height of the signal and the peak height of the noise are calculated using a metric ruler. Finally dividing the calculated value of the signal peak height on the calculated value of the noise peak height as a result the S/N ratio is obtained.

Detection of C4 Traces

C4 is a relatively complex mixture and it was actually unanticipated that Raman spectra of this formulation resulted in highly tidy spectra that could be used to detect, identify, and quantify the important military and commercial plastic explosive. Fig.(4) shows photographic image of the glass slides used with samples of 800 μg , 200 μg , 50 μg , 20 μg .

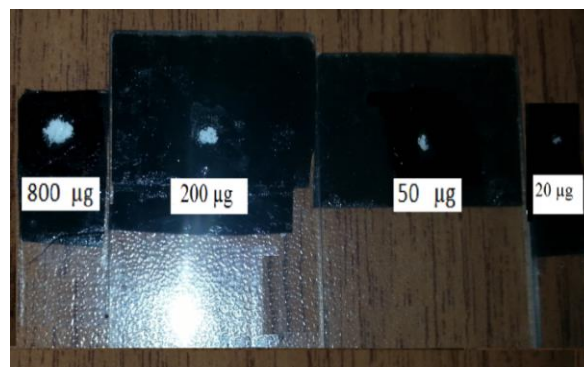


Fig.(4) Photographic image of the glass slides used with samples of 800 μg , 200 μg , 50 μg , 20 μg .

Limit of detection (LOD) of C4 was calculated from detection measurements at fixed standoff distance of 4 m, fixed laser power of 750 mW, fixed integration time of 8 seconds and diameter of laser beam is 5 mm. The standoff Raman measurements were obtained for different trace quantities starting from 800 μg and then we continue reducing quantity until least detectable quantity of C4 is reached. Firstly the standoff Raman measurement of mass of 800 μg results in Raman spectrum with excellent signal to noise ratio which is roughly estimated to be fifty two (S/N ratio =52), after that, the measurement is repeated for same conditions but with mass reduced to 200 μg which results in Raman spectrum with excellent S/N ratio which is roughly estimated to be fourteen (S/N ratio = 14), then the C4 mass is reduced to 50 μg and the Raman spectrum recorded with much lower S/N ratio which was roughly estimated to be five (S/N ratio = 5). Since the S/N ratio is still higher than three. Therefore, it was expected that it is still possible to further reduce the C4 mass to 20 μg which results in spectrum with high background where the Raman bands are barely identifiable and the S/N ratio roughly estimated to be three (S/N ratio = 3) and this ratio represents the limit of detection of C4. Therefore, it was no longer possible to reduce the mass any further, and hence the limit of detection of C4 for the SRS system is determined to be 20 μg .

The LOD obtained in this study is compared to the other author Pacheco-Londono et al. [13]. Their LOD calculated for C4 was 3 mg at standoff distance of 7 meters, using continuous wave SRS system operating at wavelength of 488 nm, integration time of 50 s, laser power of 500 mW and laser spot size is 3.5 mm.

The standoff Raman spectra of C4 are integrated and graphed as a function of mass as shown in Fig.(5).

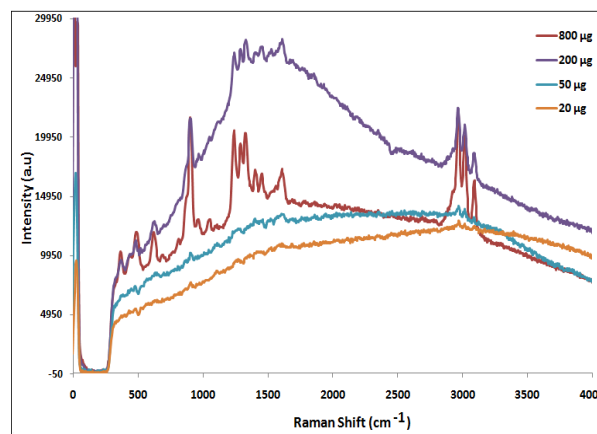


Fig.(5): SR spectra of different masses at fixed conditions: laser power of 750 mW, integration time of 8 s, and distance of 4 m.

The results show, as the mass of C4 substance is decreased the Raman signal is decreased in intensity. Once the mass drops below 100 μg the weak Raman bands are not distinguished and the strong Raman bands are reduced much in intensity. For comparison purposes the four Raman spectra of C4 are integrated in one Fig.(5) but it was not very easy to identify the spectra of little masses (50 μg 20 μg). Therefore, it was necessary to separate the spectra of little masses and illustrate them on separated Fig.(6).

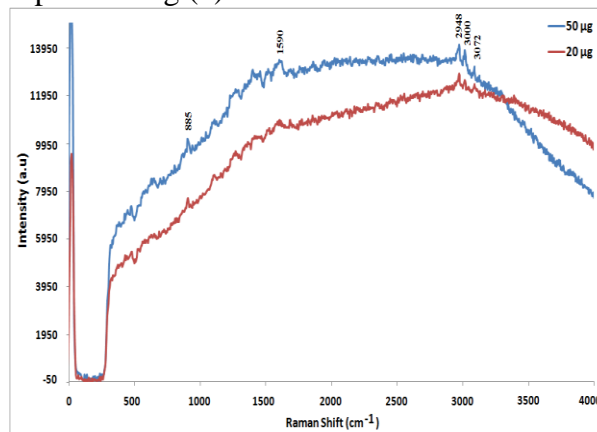


Fig.(6) SR spectra of little masses of 50 μg and 20 μg at integration time of 8 s and laser power of 750 mW.

Fig.(6) can be helpful to get better vision for spectra of low masses of 50 μg and 20 μg . The Raman bands recorded for mass of 50 μg are bit stronger and more clearly defined than Raman bands recorded for mass of 20 μg .

Trace measurements for masses of 800 μg , 200 μg , 50 μg , 20 μg are also studied as a function of various parameters condition (laser power and integration time).

Trace measurements with various laser powers and various integration times at distance of 4 m were studied until the least parameters condition (minimum laser power and minimum integration time) for each quantity is specified. The standoff Raman measurements for masses of 800 μg , 200 μg , 50 μg , 20 μg with minimum laser power and minimum integration time for each trace quantity are indicated in Table (1).

Table (1)
Trace quantities of C4 with minimum parameter conditions.

Mass of C4 (μg)	Min. Integration time (s)	Min. Laser power (mW)
800	0.4	250
200	0.4	500
200	1	250
50	4	750
50	8	500
20	8	750
20	12	500

The information indicated in the Table (1) is extracted from the measurements of Raman spectra. It was found from these measurements that as the C4 masses are reduced; either the laser power or integration time or both must be increased in order to compensate the reduction that is occurred in S/N ratio of Raman spectrum.

It important to mention that, the laser beam diameter at 4m distance was significantly larger than the samples shown in Fig.(4). As the sample mass is reduced, the difference in area between the laser beam spot size at the sample and the sample area is increased which resulted in a reduced energy density that strikes the target and hence lower Raman scattering.

Detection of Ammonium Nitrate Traces

Limit of detection (LOD) of Ammonium Nitrate (AN) is also determined for the SRS system at fixed standoff distance of 4 m, fixed laser power of 250 mW, fixed integration time of 2 seconds and diameter of laser beam is 5 mm. The standoff Raman measurements were obtained for different trace quantities starting from 150 μg and then we continue reducing quantity until least detectable quantity of AN

is reached. Firstly, the standoff Raman measurement of mass of 150 μg results in Raman spectrum with excellent S/N ratio which was roughly estimated to be ten (S/N ratio = 10). The measurement is repeated for same conditions but with mass reduced to 70 μg which results in Raman spectrum with good S/N ratio which was roughly estimated to be seven (S/N ratio = 7). After that, the AN mass is further reduced to 40 μg and the Raman spectrum recorded with lower S/N ratio which was roughly estimated to be five (S/N ratio = 5). The Raman spectra of these three masses are clearly shown in Fig.(7). Since the S/N ratio for mass of 40 μg is still higher than three. It was expected that it is still possible to reduce the AN mass to about 20 μg , but the results for mass of 20 μg showed that the prominent Raman band (1044 cm^{-1}) is disappeared and the Raman spectrum is no longer fingerprint of AN, Therefore the LOD of AN is determined to be 40 μg .

The LOD obtained in this study is compared to the other author Chirico et al. [21]. Their limit of detection calculated for AN is 289 μg at standoff distance of 6.4 meters, using pulsed wave SRS system operating at wavelength of 266 nm, laser pulse energy of 3 mJ/cm^2 and pulse length of 10 ns.

It's worth mentioning that for mass of 20 μg the prominent band was disappeared even after trying higher laser power and higher integration time.

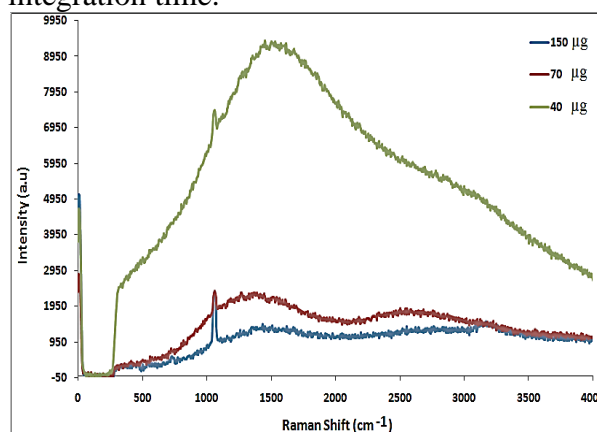


Fig.(7): SR spectra of different masses of AN at power of 250 mW, integration time of 2 s.

These results show that as the mass is reduced the S/N ratio is decreased. The results also show that the weak Raman band at 715 cm^{-1} is absent for all three trace quantities of AN as compared with the results explained in

Fig.(3) that shows the prominent Raman bands.

The trace quantities of 150 μg , 70 μg and 40 μg are also studied as a function of various parameters condition (laser power and integration time) at fixed standoff distance of 4 m.

Traces measurements of AN for the same masses of 150 μg , 70 μg and 40 μg are repeated with laser power of 500 mW and integration time of 4 s as shown in Fig.(8).

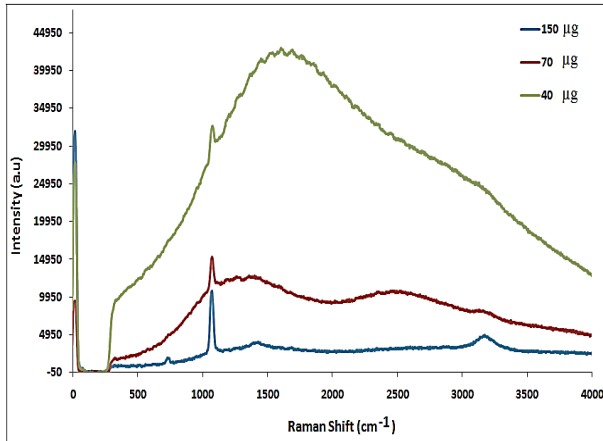


Fig.(8): SR spectra of different masses of AN at laser power of 500 mW and integration time of 4 s.

As clearly shown in Fig.(8), increasing the laser power up to 500 mW and integration time to 4 seconds have almost not enhanced the S/N ratio for mass of 40 μg and little enhanced the S/N ratio for mass of 70 μg and enhanced the S/N ratio for mass of 150 μg as indicated and listed in the Table (2).

Table (2)

The S/N ratio enhancement via laser power and integration time for different masses.

Mass (μg)	Laser Power (mW)	Integration Time (s)	S/N ratio enhancement
40	500	4	Not enhanced
70	500	4	Little enhanced
150	500	4	Enhanced

It means that the spectra for mass of 40 μg has been stopped to be enhanced at specific value of laser power which is 250 mW and specific value of integration time which is 2 s where any further enhancement above these values was not achieved as can be seen when comparing between the Fig.(7) and the Fig.(8).

The specific laser power is the power at which the S/N ratio reaches to its optimum value. The specific integration time is the time at which the S/N ratio reaches to its optimum value where any further enhancement above these specific values are not achieved.

Trace measurements of AN for the same masses of 150 μg , 70 μg and 40 μg are repeated again with increasing the laser power to 750 mW and the integration time to 6 second.

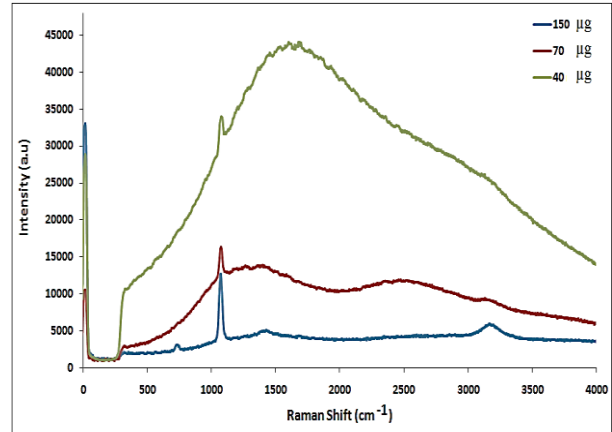


Fig.(9): SR spectra of different masses of AN at laser power of 750 mW and integration time of 6 s.

Fig.(9) shows that, after again increasing the laser power and integration time, the Raman spectrum for mass of 40 μg is still not enhanced. The Raman spectrum for mass of 70 μg is not enhanced. The Raman spectrum for mass of 150 μg is not showing considerable enhancement as indicated in the Table (3).

Table (3)

S/N ratio enhancement via laser power and integration time for different masses.

Mass (μg)	Laser Power (mW)	Integration Time (s)	S/N ratio enhancement
40	750	6	Not enhanced
70	750	6	Not enhanced
150	750	6	Very little enhanced

Since the mass of 70 μg is not enhanced when parameters condition of laser power and integration time are increased to 750 mW and 6 s respectively. It means that the enhancement for mass of 70 μg stopped at specific laser power of 500 mW and specific integration time of 4 s.

Since the mass of 150 μg is little enhanced, any further enhancement above these values is not expected. It means that the enhancement for mass of 150 μg approximately stopped at specific laser power of 750 mW and specific integration time of 6 s.

It can be concluded that increasing the laser power and the integration time will not continue enhancing the S/N ratio, but it will stop enhancing the S/N ratio at specific laser power and specific integration time. The specific laser power and specific integration time for different masses as clearly indicated in the Table (4).

Table (4)

Traces quantity of AN at specific laser power and specific integration time.

Mass (μg)	Specific laser power (mW)	Specific integration time (s)
150	750	6
70	500	4
40	250	2

Therefore, as clearly indicated in the Table (4) the specific laser power and specific integration time are different for different masses. In fact, they differ in a way that as the mass is decreased the specific integration time and the specific laser power is decreased.

Conclusions

For the SRS system at 4 m distance the Limit of detection of C4 substance was determined to be about 20 μg at laser power of 750 mW and integration time of 8s. The Limit of detection of AN substance was determined to be about 40 μg at laser power of 250 mW and integration time of 2s, therefore, it is demonstrated that SRS system used in this study is a promising candidate for trace detection.

It is concluded that, increasing the integration time and laser power will not continuously be enhancing the S/N ratio, but the enhancement via integration time and laser power will be stopped at specific integration time and specific laser power and there will be specific integration time and specific laser power for each mass.

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الخلاصة

تقنية رامان الطيفية هي واحدة من التقنيات الفعالة التي تستطيع ان تكشف المواد المتفجرة ذات المقادير الضئيلة (بقايا المواد). يتم جمع ضوء رامان المستطار بواسطة التيلسكوب العاكس، مطياف رامان يستخدم لتحليل ضوء رامان المستطار. من اجل عرض الطيف، كاشف ضوئي (CCD detector) متضمن في مطياف رامان قادر على كشف الاشارة الضعيفة (خطوط ستوك). لكي يتم التحقق من امكانية منظومة رامان الطيفية ذات المجال البعيد في الكشف عن باقيا المواد المتفجرة، تم كشف بقايا السي فور (C4) و نترات الامونيوم وكانت حدود الكشف الدنيا تقريبا ٢٠ مايكرو غرام الى سي فور و ٤٠ مايكرو غرام الى نترات الامونيوم.