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Detection of Nitro-aromatic Compound in Soil and Sand using Time Gated Raman Spectroscopy

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ABSTRACT

Laser based time-gated Raman Spectroscopy experiments for detection and identification of nitro-aromatic sample which premixed with soil and sand in different concentrations are conducted. A back-scattered stand-off Raman spectroscopy set-up using a frequency double Nd:YAG pulsed laser (532 nm, 8 ns, 10 Hz) was employed to evaluate samples made up of standard nitro- aromatic compounds, p-nitro Benzoic acid (PNBA) premixed with soil and sand at different concentrations. A sensitive ICCD detector was used to capture the weak Raman signals buried in high background noise at optimised experiments parameters like laser pulse energy, ICCD gate width, background subtraction, number of laser pulses averaging etc. p- nitro benzoic acid up to 5 per cent (v/v) concentration in sand with appreciable signal to noise ratio has been detected. This feasibility study also becomes relevant to evaluate the remnants for post-blast detection of explosives in terrorist attack as most of the explosives used in such attacks contain nitro-aromatic based high energetic explosives.

Keywords: Explosives detection; Nitro aromatic compound; Time gated Raman spectroscopy

1. INTRODUCTION

Detection of explosives has become more important in the last few decades because of the increasing terrorist activities at crowded places in several cities worldwide[1-2]. The growing threats and terrorist activities in last two decades have urged the need for rapid and accurate detection and identification of pre and post-blast samples. The area of explosives detection can be divided into two sub area, pre-blast scanning analysis and post-blast detection analysis. To save the lives and properties from terrorist attack real time pre-blast scanning is required. Analysis of post-blast explosives residues is useful in identification of types of explosives and establishing link to its likely origin. The post-blast detection and identification of explosives residue in soil and sand at blast site is a problem of critical interest for security. It is a technological challenge for rapid detection and identification of explosive materials and hazardous chemicals residues in soil and sand.

Detecting minute quantities of hazards chemicals within the complex background of real world surfaces requires excellent chemical specificity[3]. Sensors for nitro-aromatics has vital importance in national security applications[4]. In our laboratory a prototype for real time pre-blast scanning and identification of explosives material was developed.

Raman technique is a non-invasive instantaneous technique and it provides a 'finger print of the molecule' without any need of tunable laser[5-6]. Because of its ability to provide unique set of vibrational frequencies to identify molecular species, Raman spectroscopy has become an important tool for home land defence applications[7]. Raman spectroscopic technique is non-destructive in nature and it provides high selectivity[7]. The main experimental difficulty in recording the Raman spectra of diluted sample is related to background interference and very low intensity of Raman signal of the diluted sample. To overcome this problem it is necessary to use modern sensitive optical detection. To collect and record the back scattered Raman signal of diluted sample we have used ICCD coupled spectrograph along with 50 mm collection optics.

The main difficulties in detecting the low concentration of the sample are due to weak Raman signature of the sample and interference of the background interference. To minimize the background interference and ambient light, delay and gate width in ICCD were used to open it only during the time when the scattered Raman signal from the sample materials arrived spectrograph. High gain was also used in intensifier to further improve the SNR and to intensify the collected Raman signal of materials. By this method, up to 5 per cent concentration of the sample was successfully detected.

Raman experiments were performed with nitro-aromatic compounds pre-mixed with soil and sand by placing the samples 50 cm away from detection system. Experiments are conducted on nitro-aromatic compounds as most of the commercial explosives are nitro-aromatic in nature. The detection of nitro-aromatic compounds mixed in low concentrations with soil and sand using time gated Raman spectroscopy is demonstrated.

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2. INSTRUMENTATION

Design technique of time gated Raman spectroscopy based laboratory setup for detection of hazardous chemicals or explosives is described. A schematic diagram of the instrumentation for time gated Raman spectroscopy is illustrated in Fig. 1.

This laboratory setup consist of a frequency double Nd: YAG laser (Model: Brilliant B, Make: Quantel laser, wavelength: 532 nm, pulse duration: 8ns, Max Rep rate: 10Hz) source of variable pulse energy and rep rate, lens based optical assembly for collection of back-scattered Raman signal and intensified charged coupled device (ICCD, model number iStar 320) coupled Czerny Turner Spectrograph (ANDOR, Shemrock, SH-303) to record the Raman spectra. Samples were illuminated with pulsed laser and 50 mJ/pulse energy was used to induce the Raman effect. Area of 50 mm^2 of soil sample was illuminated at 50 cm away using green laser of 532 nm wavelength. One 50 mm primary lens based collection assembly is used to collect the back scattered Raman signal of the target materials. Lens based collection assembly comprised of mainly three lenses; a 50 mm biconvex primary lens, 25 mm concave secondary lens and 25 mm bi convex focusing lenses marked as no. 1, 2 and 4 in Fig. 1. The exit of the collection assembly was coupled to the spectrograph with a circular bundle of 19 fibers each with a core diameter of 200 µm to transport the collected signal to the spectrograph. Diameter of fiber bundle was 1.3 mm. Numerical aperture (N.A) of each fiber was 0.22. The 25 mm focusing lens focused the light to the bundle of fiber. A notch filter (Semrok) at laser wavelength (532 nm) marked as serial no.3 was inserted between the focusing lens and concave lens to filter the strong Rayleigh line. Linear end of the fiber bundle is coupled to the f-matcher of the spectrograph. It focused the collected light at the entrance slit of the Czerny-Turner spectrograph with focal length 303mm. Slit size of 20 µm was used to record the Raman spectra of samples. Resolution of the system was around 20cm^{-1} with 20µm slit and diffraction grating having 300 lines /mm. Spectra were recorded using thermoelectrically cooled and gated ICCD camera having 25 mm Gen II Intensifier. CCD array is having 1054 x 256 pixels where each pixel size is 26x26 μm^2. CCD was kept cooled at -20 °C thermoelectrically to reduce the noise of detector. The 256 pixels were binned and acquired on a PC as single spectra to enhance the sensitivity. The gated detection was carried out by triggering the ICCD camera with Q-switched 5V -TTL pulse from the laser. The resulting Raman spectra were acquired on PC attached to ICCD coupled spectrograph using ANDOR Spectrograph Software and analysed using available database.

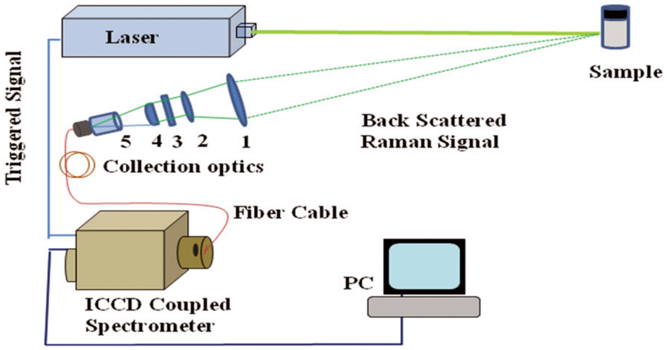

Figure 1. Schematic diagram of time gated Raman technique.

3. EXPERIMENTAL PROCEDURE

Samples of p- nitro benzoic acid (PNBA) were mixed with the soil as well as sand in 5 per cent and 20 per cent v/v (volume/ volume) ratio. P-nitro benzoic acid is yellow colored toxic organic compound with the formula $C_6H_4(NO_2)CO_2H$. Sand and soil were collected from nearby construction site. Samples were put in glass vials and placed at 50 cm away from the lens based collection assembly. Backscattered Raman Signal was collected at an angle of 20° from the laser beam to avoid intense Rayleigh light. Spectra of pure samples of p-nitro benzoic acid (PNBA), 20 per cent v/v PNBA mixed with soil, 5 per cent v/v PNBA mixed with soil, 20% v/v PNBA mixed with sand and 5 per cent v/v PNBA mixed with sand were recorded. Spectra of Sand and soil were also recorded at same experimental condition.

4. RESULTS AND DISCUSSION

Raman spectrum of PNBA, PNBA mixed with sand and soil was recorded from a distance of 50 cm. Figure 2 depicts recorded Raman spectra of pure p-nitro benzoic acid and Sand. Recorded spectra were analysed using available data of nitro-aromatic compounds[7-15]. The principal vibrational signatures for PNBA are around 1,355 cm^{-1} is attributed to NO_2 symmetric stretching vibration.

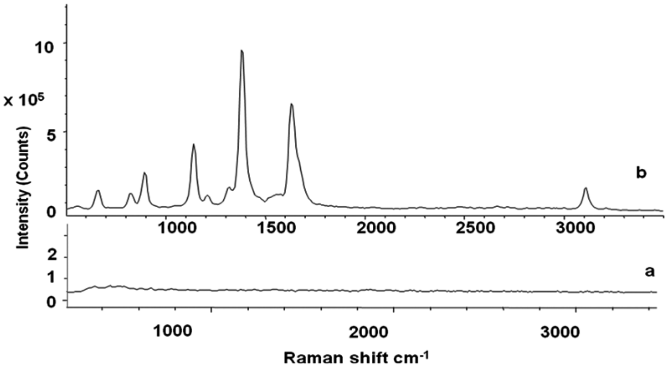

Figure 2. Recorded Raman spectra of (a) p-nitro benzoic acid (PNBA) and (b) Sand.

Raman band at 1,608 cm^{-1} is to C-C stretching of benzene ring present in the PNBA molecule and 1,113 cm^{-1} is assigned to C-H in plane bend/ring breathing. Moderate and low intensity vibrational signatures were observed around 865 cm^{-1}, 635 cm^{-1} and 3085 cm^{-1}. Raman mode at 865 cm^{-1} is assigned to COO^- bending vibration. Band of CH region was observed near 3085 cm^{-1}.

Figures 3 and 4 demonstrated the Raman Spectra of sand, mixture of PNBA and sand with 20 per cent and 5 per cent PNBA in v/v concentration using 532 nm excitation wavelength and gate width of 10 ns.

Raman spectrum of PNBA was achieved in a single pulse. To record the Raman spectra of 20 per cent PNBA mixed with soil or sand 5 s - 10 s integration time was required. For 5 per cent PNBA mixed with sand and soil 20 s - 30 s integration was used to get a proper Raman signal of the sample.

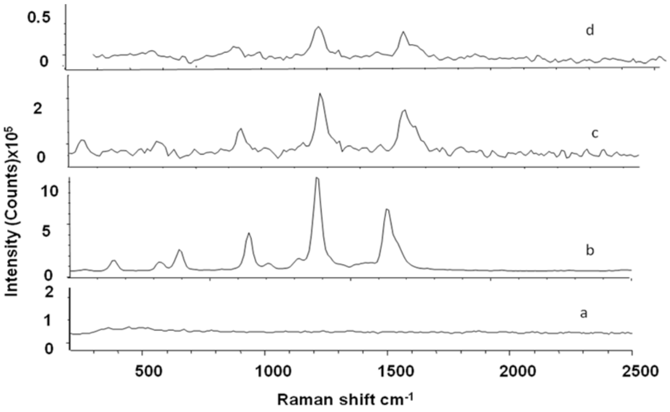

Figure 3. Raman Spectra of (a) Sand (b) PNBA (c) PNBA mixed with sand (20% PNBA + 80% sand (v/v) (d) PNBA mixed with sand (5% PNBA + 95% sand).

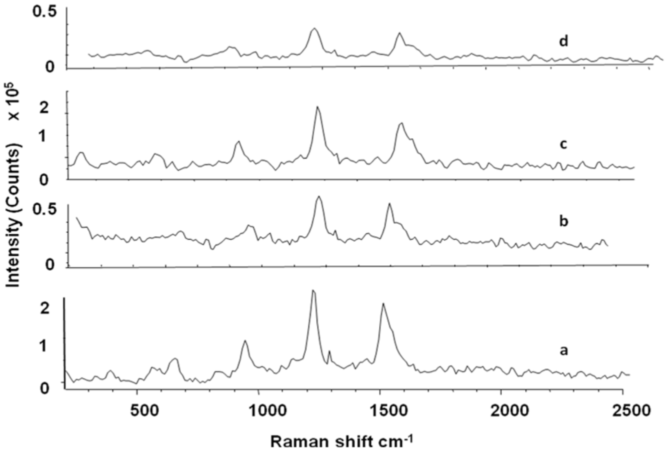

Figure 4. Raman Spectra of (a) 20% PNBA mixed with 80% sand, (b) 5% PNBA mixed with 95% sand, (c) 20% PNBA mixed with 80% soil, (d) 5% PNBA mixed with 95% soil.

5. CONCLUSIONS

Using this system, Nitro aromatic compound, p-nitro benzoic acid up to 5 per cent v/v low concentration in sand and soil are detected. This feasibility study is useful for post-blast detection of explosives because there might be probability to get residues of explosives mixed with sand and soil from blast site. Concludes that time gated Raman technique appear to have the greatest potential for post-blast detection of nitro-aromatic explosives.

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