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PORTABLE RAMAN SPECTROSCOPY FOR DETECTION OF AMMONIUM NITRATE–FUEL OIL EXPLOSIVE PRECURSORS

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Abstract: *A handheld Raman spectrometer was used as a sensor for the detection of ammonium nitrate (NH_4NO_3, AN), fuel oil (FO), AN-water solutions, and AN-soil mixtures deposited on materials such as glass and tape to simulate the field conditions of explosive detection. AN is an inorganic oxidizing salt that is commonly used in mining explosives. A significant explosive mixture is Ammonium nitrate–fuel oil (ANFO). However, owing to its widespread accessibility, AN-based explosives are also utilized for the manufacture of improvised explosive devices (IEDs). The portable Raman system with a laser operating at 785 nm wavelength is used to analyze simulated sites manipulated with IEDs. Characteristic Raman bands from AN were found at 710 cm^{-1} and 1050 cm^{-1}, and 1440-1470 cm^{-1} for FO. The relative limit of detection of AN in water was less than 0.1%.*

Keywords: *Raman spectroscopy, Ammonium nitrate, fuel oil, explosive, IEDs.*

1. INTRODUCTION

Global security risks and the threat of terrorism have been growing rapidly in recent decades. Improvised explosive devices (IEDs) are commonly used for this purpose. These devices are not fueled by traditional familiar explosive materials such as 3-Nitrotoluene (TNT) but can be produced from homemade explosives and unexploded military ordinances [1].

Ammonium nitrate–fuel oil (ANFO) is a widely used explosive mixture. This type of explosive is used in coal and metal mining. Since the 1995 ANFO attack on a federal building in Oklahoma City, improvised explosive devices (IEDs) have attracted enormous attention because of concerns regarding their widespread use in terrorism [2]. ANFO explosives are popular among terrorists because of their simplicity of preparation. It can be prepared industrially, or it can also be made at home very easily. From a chemical-technological point of view, it is possible to differentiate three different versions of ANFO explosives: ammonium nitrate and fuel; ammonium nitrate, fuel, and powder metal (usually aluminum or magnesium); and ammonium nitrate, fuel, and wooden powder. They are explosive and decompose via detonation. The main disadvantages of this material are its low water resistance and problems related to non-ideal detonation, which generally requires a booster [3,4].

Rapid and precise identification of explosives is a crucial task for public security and safety, particularly with the recent proliferation of IEDs. Explosives ordnance disposal (EOD) specialists, bomb technicians, forensic scientists, hazardous material (HazMat) technicians, Chemical, Biological, Radiological, and Nuclear Specialist (CBRN) specialists, and first responders meet a broad set of challenges in the course of their missions and consequently require a broad set of tools to assist them in the completion of their duties [5].

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A wide range of instruments can be used in the field to identify various explosives and their precursors rapidly and accurately. One particularly useful technology in the battle against IEDs is Raman spectroscopy. Raman spectroscopy is a technique that measures the frequency shift of inelastically scattered light from the sample when the photon from incident light strikes a molecule and produces a scattered photon. A Raman spectrometer comprises a light source, a monochromator, a sample holder, and a detector. Raman spectroscopy has been used for the analysis of explosives based on ammonium nitrate [6,7].

This study aimed to evaluate a handheld Raman spectrometer for the analysis of ammonia nitrate and fuel oil in combination with several types of substrates to simulate the detection of explosive precursors at high interferences from different materials. The effect of the integration time on the Raman figures of merit is also detailed.

2. EXPERIMENTAL

2.1. Materials and chemicals

Ammonium nitrate (AN, NH_4NO_3) was obtained from Centrohem (Serbia). Pure AN crystals were ground to powder size. Fuel oil (FO, CAS: 68553-00-4) was obtained from NIS (Serbia). Silver Duct tape was obtained from Würth (Germany). To mix the AN and soil, a soil sample was taken from a local site. Soil sample was collected from the upper layer of the soil to a depth of 10 cm. Before mixing AN with soil, the soil sample was cleaned from vegetation and stones and brought to a constant mass by drying in an oven at 105 °C. After that, the sample was homogenized by mechanical mixing and brought to a uniform distribution by sieving through a 0.25 mm sieve.

2.2. Instrumentation and software

The characteristics of the obtained samples were investigated using a handheld Raman spectrometer (Serstech ARX, Sweden) in the optical range 2300–400 cm^{-1} with a resolution of 8 cm^{-1}. The portable Raman system used in this research included a laser operating at 785 nm wavelength. The obtained results were processed using the program software, ChemDash Pro, Excel, and Origin Pro 9.

3. RESULTS AND DISCUSSION

The field conditions are being simulated in this research to identify IEDs. We used a Handheld Raman spectrometer for measurement of the explosive precursors (AN and FO), some substrates commonly present in field and clutter materials (soil, glass, water, and tape), and their mixtures.

The Raman spectra of each explosive precursor and tape are shown in Figure 1. The Raman spectra of soil and glass samples are not shown because there was no useful information on spectra due to the high-intensity fluorescence detected.

Characteristic Raman bands from AN were found at 710 cm^{-1} and 1050 cm^{-1} which are associated with the NO_3^- in-plane deformation and NO_3^- symmetric stretch. Comparison of these spectra with the reference spectra [8] of the AN showed that the AN could be easily identified by Raman spectra. FO, a minor component of ANFO, is readily detected and identified. FO showed several wide bands, with bands at 1440-1470 cm^{-1} detected as CH stretching. The tape shows Raman spectra rich in sharp bands coinciding with the bands of PVC (650 cm^{-1} –CCl stretch, 1300 cm^{-1} –CH rocking, 1450 cm^{-1} –CH_2 bending, and 1620 cm^{-1} –aromatic ring stretch).

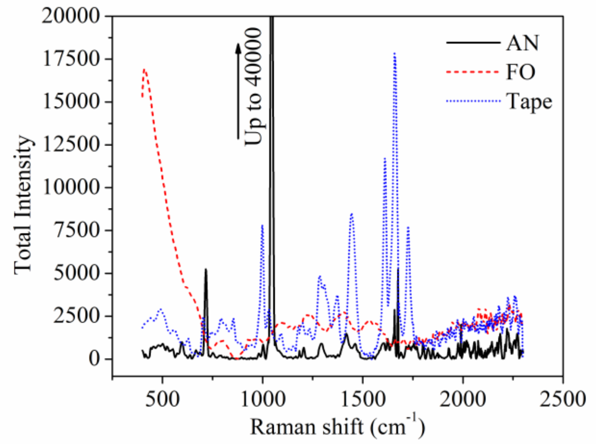

Figure 1. Spectra of explosive precursors (AN and FO) and tape. Integration time: 30 s

Figure 2 shows spectra of a mixture of AN-water which can be found in the area where was manipulated with IEDs. Small amounts of AN could be scattered in the surrounding ponds or leak from the surface of the container due to wet weather conditions.

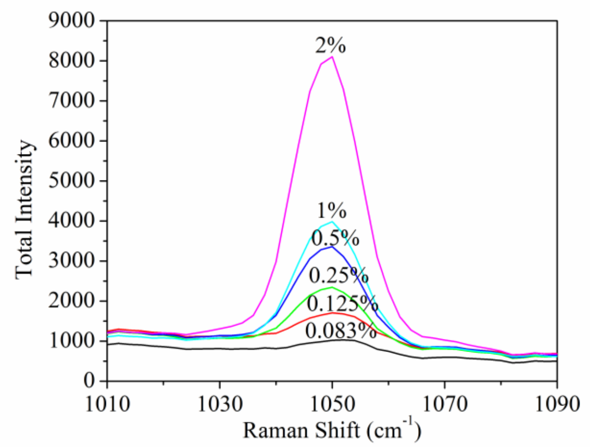

Figure 2. Effect of AN percentage on AN-water solutions. AN Raman band 1050 cm^{-1}. The percentage value represents AN. Integration time: 30 s

With these techniques, we can detect AN in water mixtures in less than 1%. The useable band was at 1050 cm^{-1} and the band at 710 cm^{-1} was not visible for lower concentrations of AN in water.

Figure 2 shows that the intensity of the band at 1050 cm^{-1} decreased as the AN concentration in water decreased. This result is in full agreement with the results obtained by Diaz et al., who used a laser with different characteristics [6].

Soil mixtures with the explosive precursors (AN and FO) were also tested. The useable spectra were obtained only for AN-soil mixtures because these spectra had no characteristic band of the FO due to the high fluorescence emission of the soil [9]. The spectra of the AN, soil, and AN-soil mixtures are shown in Figure 3.

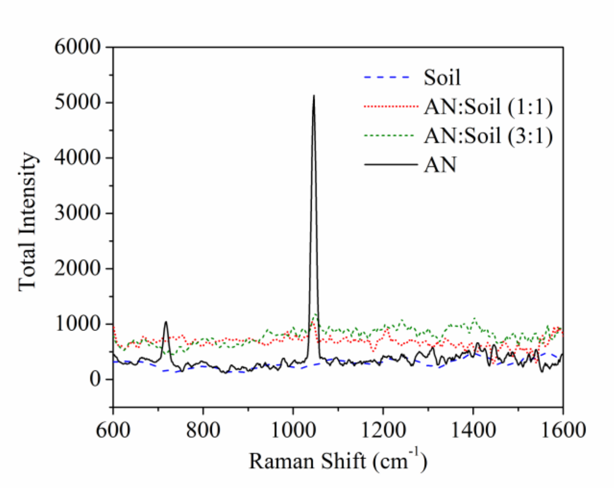

Figure 3. Effect of the relationship between AN and soil. AN Raman band at 710 cm^{-1} and 1050 cm^{-1}. Integration time: 30 s

The characteristic band of AN at 1050 cm^{-1} can be seen for the AN and all investigated AN-soil mixtures and the band at 710 cm^{-1} is visible for the concentrations higher than 90% of AN in the mixture. We detected AN in the 1:1 AN-soil mixture which is also the lowest detectable concentration. The concentration lower than 50% AN in the mixtures cannot be detected due to the high fluorescence emission of the soil. The identification of AN in soil would likely require considerable effort for sample homogenization. Similar allegations were reported by Diaz et al. [6].

4. CONCLUSION

This study shows Raman's capability for the detection and identification of IEDs in field conditions through the investigated potential of the explosive precursors (AN and FO), some substrates commonly present in field and clutter materials (soil, glass, water, and tape) and its mixtures. The portable Raman spectrometer with optimization of device parameters could be a good tool for fast response in real situations in field conditions. In addition to pure substances, this technique can also be used to identify their mixtures with water (a concentration of AN less than 0.1%) and soil (a concentration of AN up to 50%), which can be found in the field in real situations.

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