

# DEEP UV RAMAN SPECTROSCOPY OF EXPLOSIVES PRECURSORS ON TEXTILES

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Raman spectroscopy has been used to uniquely identify unknown substances at a safe distance from the examination site [1-4]. Spectroscopic detection of explosive traces and their precursors are important for homeland security applications. A precursor is a commonly available material such as fertilizers, food preservatives, solvents for cleaning agents, fuels, pyrotechnic kits, etc. [Regulation (EU) No 98/2013 on the marketing and use of explosives precursors]. The aim of this work was to remotely detect traces of solid explosive precursors adsorbed on a surface using deep UV Raman. The textile samples prepared simulate the possible amount of a chemical trace adhering on a surface left from a fingerprint which is in the microgram range ( $\sim 10 \mu\text{g}$ ) [3].

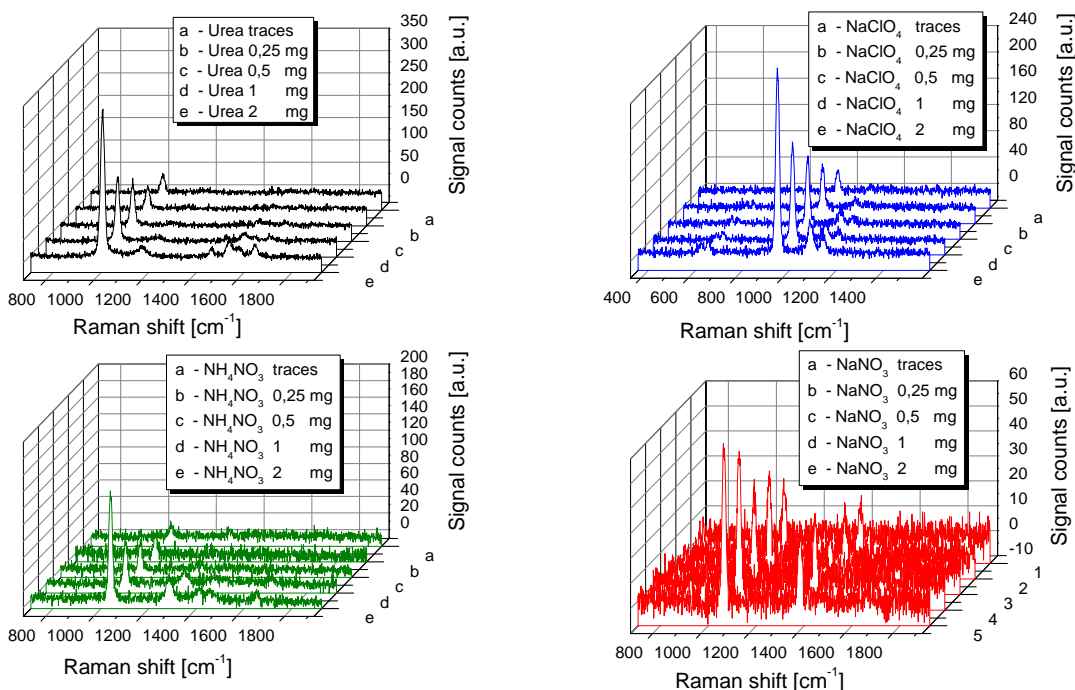


**Figure 1** From left to right, cotton samples with defined amounts of urea, sodium perchlorate, ammonium nitrate, and sodium nitrate

UV Raman spectra of the explosive precursors (urea, sodium perchlorate, ammonium nitrate, and sodium nitrate) were detected over a remote distance of 60 centimeters. All spectra were background subtracted. Standardized samples of 2, 1, 0.5, 0.25 milligrams and traces ( $\mu\text{g}$  range) were weighed and then applied on differently colored cotton textiles (Figure 1). The sample areas were prepared to be below the upcoming laser beam size ( $\sim$ half a centimeter diameter). A type of broad tunable laser was employed to tune a wide range of wavelength from deep UV to IR without employing chemical dyes. A longpass filter was placed in front of the spectrometer to reject incoming UV laser radiation. The signal was collected using a parabolic UV mirror standing  $\sim 60$  cm in front of the sample and then sent through the spectrometer.

A distinct Raman signal peak identifies a chemical in a sample even when the signatures of different substances seem spectrally closer. The strongest Raman vibrational  $\nu_1$  mode ( $\text{NH}_2\text{-CO-NH}_2$  planar) for urea was detected at  $1007 \text{ cm}^{-1}$ . This spectral line is chosen to be the specific signature for urea since it appears for all the concentrations (Figure 2, upper left). Above 0.5 mg a secondary peak appears on the right hand side of to the strongest one and it can be distinguished from the background ( $1172 \text{ cm}^{-1}$ ,  $\text{NH}_2\text{-CO-NH}_2$  planar vibrational mode). For concentrations above 1 mg three main peaks can be distinguished:  $1465 \text{ cm}^{-1}$  (asymmetric NCN stretch),  $1536 \text{ cm}^{-1}$  ( $\text{NH}_2$  bend) and the close  $1578 \text{ cm}^{-1}$ , and  $1646 \text{ cm}^{-1}$  (CO stretch) [6]. For sodium perchlorate (Figure 2, upper right) a main Raman vibrational  $\nu_1$  mode (Cl-O symmetric stretch [7]) at  $948 \text{ cm}^{-1}$  can be noticed for all the concentrations tested. A secondary double peak ( $\nu_3$  antisymmetric stretch) at  $1087 \text{ cm}^{-1}$  and  $1148 \text{ cm}^{-1}$  is distinguishable above 0.5 mg. A weak  $\nu_4$  (antisymmetric band) peak placed on the left hand side of the strong  $\nu_1$  at  $630 \text{ cm}^{-1}$  is barely noticeable. Ammonium nitrate (Figure 2, lower left) shows a characteristic  $\nu_1$  band (symmetric stretch) at  $1041 \text{ cm}^{-1}$  for all the samples. Above 0.5 mg some secondary vibrational modes appear respectively from left to right at  $1285 \text{ cm}^{-1}$  ( $\nu_3$ ), a double peak at  $1408 \text{ cm}^{-1}$  and  $1452 \text{ cm}^{-1}$ , and finally at  $1651 \text{ cm}^{-1}$ . In the region between  $1400 \text{ cm}^{-1}$  and  $1500 \text{ cm}^{-1}$  those vibrational modes are related to the  $\text{NH}_4$  deformation and the  $\text{NO}_3$  stretching [6]. Figure 2 (lower right) shows two vibrational modes for sodium nitrate at  $1064 \text{ cm}^{-1}$  ( $\nu_1$  [8]), and  $1383 \text{ cm}^{-1}$  ( $\nu_3$ ). The vibrational mode at  $1668 \text{ cm}^{-1}$  vanishes at the background noise level; however both  $\nu_1$  and  $\nu_3$  bands can be used to clearly identify the presence of this precursor over the others.

In this work, a UV Raman set up for measuring explosive precursors was tested. The lowest detection limit was in the range of  $40 \mu\text{g}$  for 0.6 meter remote detection. For each precursor at least one vibrational line can be distinguished so that the suspicious compound can be successfully identified over the others.



**Figure 2 Raman spectra of urea, sodium perchlorate, ammonium nitrate, and sodium nitrate samples at different nominal concentrations. a. traces ( $\mu\text{g}$ ) on a textile, b. 0.25 mg, c. 0.5 mg, d. 1 mg, e. 2 mg on a textile sample**

The main disadvantage of UV Raman spectroscopy is usually induced fluorescence and photo degradation of the sample. At an excitation wavelength of 264 nm, fluorescence was not observed and photo degradation was minimized keeping the average laser energy below  $2.3 \text{ mJ/cm}^2$ . In this experiment, the laser energy was kept below the maximum permissible skin and eye exposure limits of  $3 \text{ mJ/cm}^2$  (MPEs) for a nanosecond laser source [4]. Upcoming tests will focus on sensitivity (standoff distance, sample concentrations), and selecting a deeper UV laser wavelength within the fluorescence limit and sample photo degradation limit.

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