

DEEP UV RAMAN SPECTROSCOPY OF EXPLOSIVES PRECURSORS ON TEXTILES

Emanuela Gallo, Anja Köhntopp, Christoph Kölbl, Arne Walter, Frank Duschek

German Aerospace Center, Institute of Technical Physics, Im Langen Grund 1, 74239 Hardthausen, Germany

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 (μg 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 ~ 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 ν_1 mode ($\text{NH}_2\text{-CO-NH}_2$ planar) for urea was detected at 1007 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 cm^{-1} , $\text{NH}_2\text{-CO-NH}_2$ planar vibrational mode). For concentrations above 1 mg three main peaks can be distinguished: 1465 cm^{-1} (asymmetric NCN stretch), 1536 cm^{-1} (NH_2 bend) and the close 1578 cm^{-1} , and 1646 cm^{-1} (CO stretch) [6]. For sodium perchlorate (Figure 2, upper right) a main Raman vibrational ν_1 mode (Cl-O symmetric stretch [7]) at 948 cm^{-1} can be noticed for all the concentrations tested. A secondary double peak (ν_3 antisymmetric stretch) at 1087 cm^{-1} and 1148 cm^{-1} is distinguishable above 0.5 mg. A weak ν_4 (antisymmetric band) peak placed on the left hand side of the strong ν_1 at 630 cm^{-1} is barely noticeable. Ammonium nitrate (Figure 2, lower left) shows a characteristic ν_1 band (symmetric stretch) at 1041 cm^{-1} for all the samples. Above 0.5 mg some secondary vibrational modes appear respectively from left to right at 1285 cm^{-1} (ν_3), a double peak at 1408 cm^{-1} and 1452 cm^{-1} , and finally at 1651 cm^{-1} . In the region between 1400 cm^{-1} and 1500 cm^{-1} those vibrational modes are related to the NH_4 deformation and the NO_3 stretching [6]. Figure 2 (lower right) shows two vibrational modes for sodium nitrate at 1064 cm^{-1} (ν_1 [8]), and 1383 cm^{-1} (ν_3). The vibrational mode at 1668 cm^{-1} vanishes at the background noise level; however both ν_1 and ν_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.

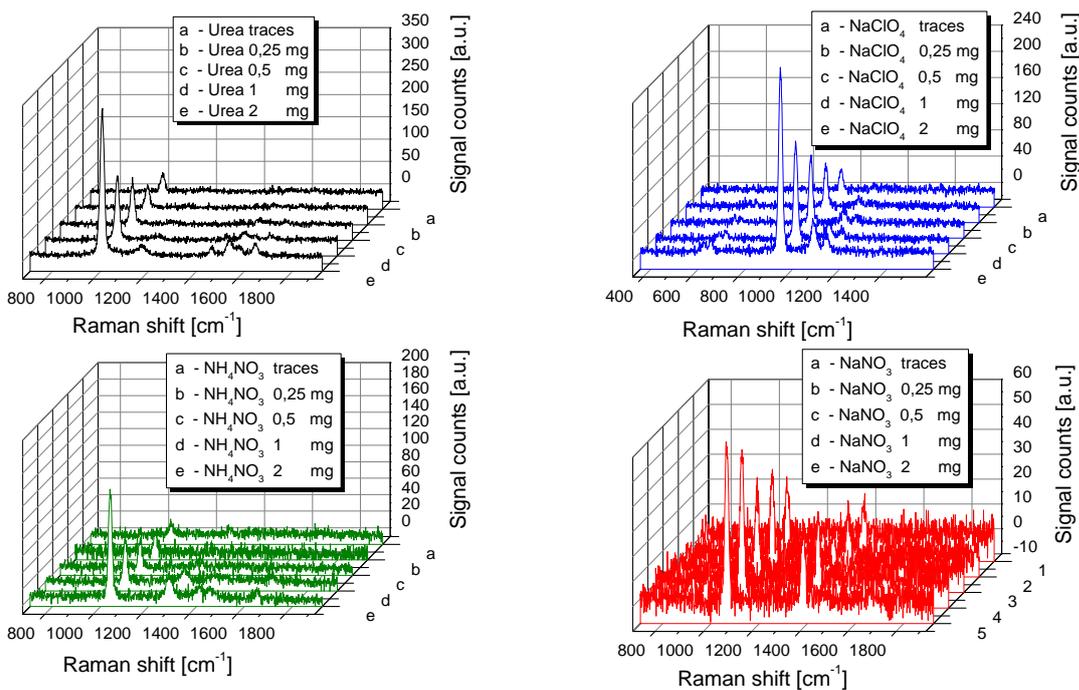


Figure 2 Raman spectra of urea, sodium perchlorate, ammonium nitrate, and sodium nitrate samples at different nominal concentrations. a. traces (μg) on a textile, b. 0.25 mg, c. 0.5 mg, d. 1 mg, e. 2 mg on a textile sample

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 mJ/cm^2 . In this experiment, the laser energy was kept below the maximum permissible skin and eye exposure limits of 3 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.

REFERENCES

- [1] Chirico R, Almaviva S, Colao F, Fiorani L, Nuvoli M, *Proximal Detection of Traces of Energetic Materials with an Eye-Safe UV Raman Prototype developed for Civil Applications*, Sensors, 2015, vol: 16, page 8.
- [2] Gulia S, Gulati KK, Gambhir V, Sharma R, Reddy MN, *Trace Detection of Explosive and their Derivatives in Stand-off mode using Time Gated Raman Spectroscopy*, Elsevier Vibrational Spectroscopy, 2016, vol: 87, pages 207-214.
- [3] Skvortsov LA, *Laser Methods for Detecting Explosive Residues on Surfaces of Distant Objects*, Quantum Electronics, 2012, vol: 16, page 8.
- [4] Almaviva S, Chirico R, Nuvoli M, Palucci A, Schnuerer F, Schweikert W, *A New Eye-Safe UV Raman Spectrometer for the Remote Detection of Energetic Materials in Fingerprints Concentrations: Characterization by PCA and ROC analyzes*, Elsevier Talanta 2015, vol: 144, pages 420-426
- [5] Aggarwal RL, Farrar LW, Di Cecca S, Jeys TH, *Raman Spectra and Cross Sections of Ammonia, Chlorine, Hydrogen Sulfide, Phosgene, and Sulfur Dioxide Toxic Gases in the Fingerprint Region 400-1400 cm^{-1}* , American Institute of Physics 2016, Vol: 6, page 025310.
- [6] Acosta-Maedar TE, Misra AK, Muzangwa LG, Berlanga G, Muchow D, Porter J, Sharma SK, *Remote Raman Measurements of Minerals, Organics and Inorganics at 430 m Range*, Applied Optics 2016, vol:55, pages 10283-10289.
- [7] Ruan C, Wang W, Gu B, *Surface-Enhanced Raman Scattering for Perchlorate Detection Using Cystamine-Modified Gold Nanoparticles*, Analytica Chimica Acta 2016, vol: 567, pages 114-120
- [8] Ben Mabrouk K, Kauffmann TH, Fontana MD, *Abilities of Raman sensor to probe pollutants in water*, Journal of Physics 2013, Vol: 450