

Rilevamento di tracce di materiali energetici tramite spettroscopia Raman a fini antiterroristici

Il rilevamento di esplosivi a livello di traccia ha acquisito maggiore importanza negli ultimi decenni, in particolare da quando i terroristi hanno sempre più preso di mira obiettivi civili e alcuni tipi di esplosivi possono essere preparati con ingredienti facilmente reperibili.

Tra le tecnologie di rilevamento attualmente disponibili, la spettroscopia Raman è un potente strumento di analisi per lo studio di materiale forense, in grado di visualizzare e analizzare piccolissime quantità di campioni, dell'ordine di picomoli, con la relativa specificità chimica. Grazie alla capacità di individuare composti organici e inorganici, volatili o non volatili, e spesso di esaminarli in loco, l'interesse circa l'utilità della tecnologia Raman è divenuto ancora maggiore. Nel presente articolo sono illustrate due applicazioni della tecnologia Raman, sviluppate dall'ENEA, per il rilevamento di tracce di esplosivi: il rilevamento prossimale Raman LIDAR (Laser Imaging Detection and Ranging), che permette di individuare tracce di esplosivo con un unico fascio laser UV in condizioni di sicurezza per gli occhi, e la tecnica spettroscopica SERS (Surface Enhanced Raman Spectroscopy), che consente di rilevare tracce di molecole e sostanze in quantità fino a picogrammi.

Raman spectroscopy for detecting trace amounts of energetic materials for counterterrorism issues

The detection of trace levels of explosives has become more important in the last decades as terrorists have increasingly targeted civilians and some type of explosives can be prepared from easily obtainable ingredients.

Among the detection technologies available, Raman spectroscopy is a powerful analytical tool for the study of forensic materials since it can view and analyze small samples down to picomole quantities with chemical specificity. The ability to analyze both organic and inorganic compounds, either volatile or nonvolatile species, and to often examine them in situ has also increased the interest in the utility of Raman. In this work two applications of Raman-based techniques, developed at ENEA, are presented for the detection of trace amounts of explosives: Raman LIDAR (Laser Imaging Detection and Ranging) proximal detection, capable of trace detection of explosives with a single UV laser shot in eye-safety conditions, and Surface Enhanced Raman Spectroscopy (SERS), capable of detecting molecules and substances in trace quantities down to picograms.

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Introduction

In the last decades there have been several terroristic attacks with improvised explosive devices (IED) that have raised the need for new instrumentation and homeland security applications, to obtain a reliable and effective means to fight against terrorism. Public transportation has been around for about 150 years, yet terroristic attacks against buses, trains, subways, etc. are a relatively recent phenomenon [1] that takes on different dimensions, depending on the countries' peculiarities in the global scenario (Fig. 1). Since 1970, transportation has been an increasingly attractive target for terrorists (Fig. 2).

An attack with an IED is performed with a “homemade” bomb and/or destructive device, which can come in many forms, ranging from a small pipe bomb to a sophisticated device. IEDs can be: carried or delivered in a vehicle; carried, placed, or thrown by a person; delivered in a package; or concealed on the roadside. Many commonly available materials, such as fertilizer, gunpowder, and hydrogen peroxide, can be used as explosives, and other materials, such as nails, glass, or metal fragments, can be used to increase the amount of shrapnel propelled by the explosion [3].

Many precursors to IED can be easily purchased without any authorization from chemical supply stores, retail stores selling beauty supply products, groceries, and swimming pool supplies. Most of the

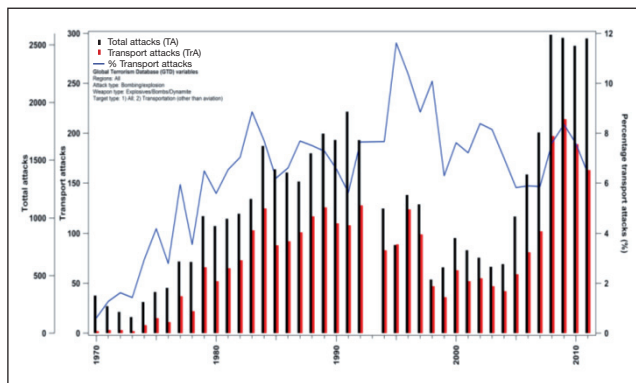


FIGURE 2 Total terroristic attacks and attacks against transportation using energetic material as weapon
Source: [2]

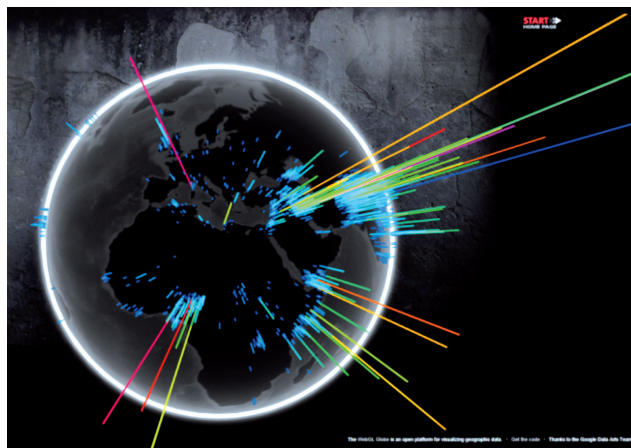


FIGURE 1 Pictorial view of the global scenario of terroristic attacks in Europe and Africa
Source: [2]

substances classified as chemical explosives generally contain oxygen, nitrogen and oxidizable elements, such as carbon and hydrogen. Chemical explosives are generally dense and have high oxygen and/or nitrogen content to react with sufficient rapidity and to maximize the working fluid (i.e., gas) generated in the explosion [3]. The most common functional group in military explosives is NO_2 . That functionality can be attached to oxygen (O-NO_2) in the nitrate esters (PETN), to carbon (C-NO_2) in the nitroarenes (TNT) and nitroalkanes (Nitromethane), and to nitrogen (N-NO_2) as in the nitramines (RDX). Some organic peroxides, such as TATP and HMTD, are popular amongst terrorists as they are powerful initiators that can be easily prepared from ingredients readily available. Azides are also powerful primary explosives commonly used as initiators (commercial detonators) in civilian and military operations, therefore they could be potentially used by terrorists as initiators for IEDs. Elemental ratios for some common basic explosives are reported in Figure 3.

Among the detection technologies available, Raman-based spectroscopy [4] has gained consensus as a potential tool for detecting trace explosives because of its high discrimination capabilities and extremely appealing application in remote sensing [5] and in-situ thanks to the implementation of nanostructured roughened noble-metal substrates [6]. The Diagnostics

and Metrology (DIM) Laboratory have successfully investigated both techniques, developing a proximal LIDAR trace detection of explosives (10 cm – 200 m, NATO classification) and the Surface-Enhanced Raman-Scattering (SERS) [7, 8] technique for a handheld device. While the LIDAR system has the main aim of remotely monitoring trace compounds without any contact with the possible suspect person, the SERS device can be applied to the detection of very low content particles, dispersed in the environment in different contexts as in the bomb factory discovery down to picograms quantities.

Raman LIDAR proximal sensor

The RADEX (RAman Detection of Explosives) system is a Raman-based technology to detect trace explosives considering the constraint of the maximum permissible laser exposure of the human cornea (3 mJ/cm² for a 266-nm laser).

The expected scenario was the monitoring of dispersed explosive compounds on people, either on their accessible clothes or on their personal objects, passing through a high-transit corridor such as, e.g., that in a metro station.

The operational principle of the RADEX system is the following (Fig. 4): an eye-safe laser beam is focused on the target and the Raman scattered radiation, emitted from the illuminated surface, is collected by a telescope and imaged onto the entrance of a Raman spectrometer. The radiation is then analyzed, giving a spectrum suitable for the explosive detection and identification.

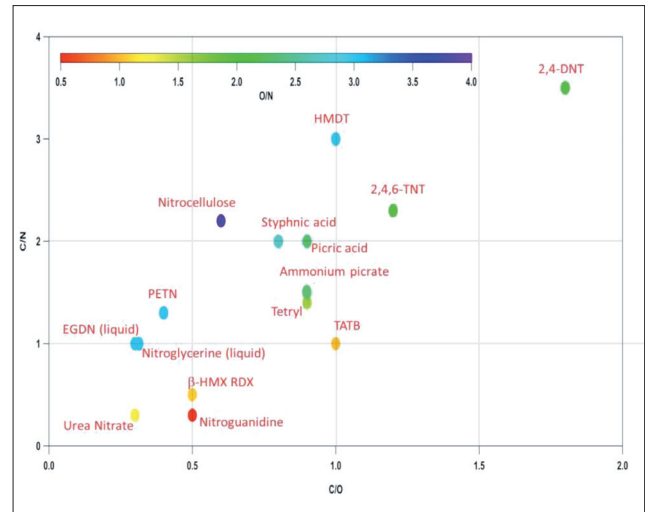


FIGURE 3 Elemental ratios of energetic materials

The apparatus was developed in the context of the STANDEX (STANdoff Detection of EXplosives) program (NATO Science for Peace and Security Program) [9] and it was part of an explosive warning system that includes the fusion of complementary detection sensors, designed to work in a mass transit infrastructure such as a metro station. The main features of the system are the use of technologies without having a physical contact with passengers, and a real time response.

The STANDEX program also included the demonstration of the system ability to automatically and discreetly detect and localize a hidden and mobile explosive in

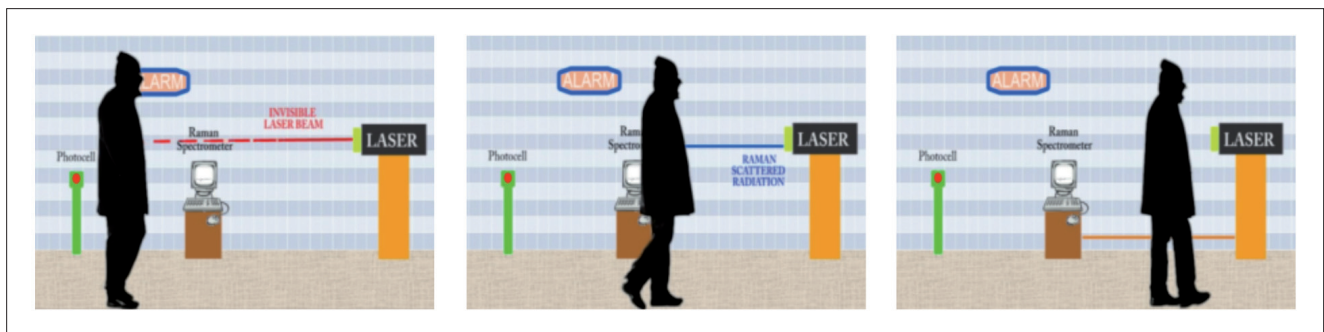


FIGURE 4 The operational principle of RADEX

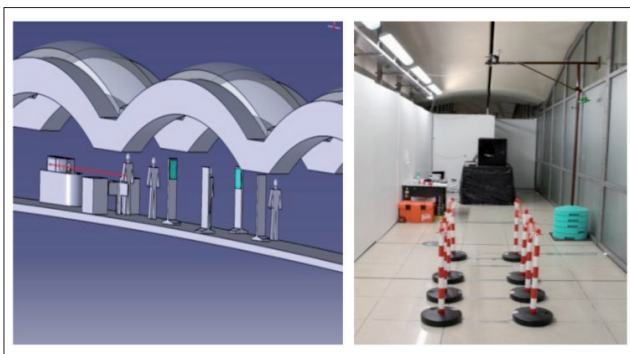


FIGURE 5 3D model of the Layout of the RADEX system on the footbridge and the RADEX set-up during the trials

real conditions of use, during a realistic phase of tests, in the metro station *Bibliothèque François Mitterrand* (the Big City Trials project).

The trials were performed by using real traces of explosive materials and with environmental conditions similar to those of a metro station, to ensure that the technology was compatible with the hard environmental conditions met inside large public transport stations, to validate the detection performances in an operational environment, and to assess the potential capabilities of the prototype to work together with the other instrumentation in a complex alarm system.

The RADEX prototype was placed on the footbridge of the BFM metro station as shown in Figure 5, looking into the direction opposite to the passenger flow with the laser placed at the specified height of 1.15 m from the ground. The corridor was delimited in order to guide the passengers in the direction of the instrument. At the end of the delimited corridor, optical sensors were used to simulate a gate in order to synchronize the laser emission with the transit of a passenger.

An on-line data analysis algorithm was implemented for the acquisition software in order to identify the substances in real time.

The safety requirements of the system demand that the identification of substances be performed on a single shot of low energy (energy density less than 3 mJ per square centimeter) in the UV region. For this reason, along with the fact that the echo is revealed

at about 6 m from the target, the signal is very low although the system was optimized in order to lose as less energy as possible between the mirror and the CCD. Integration over more laser shots is not possible, and the analysis must be performed with sufficient reliability on each shot. The CCD was cooled to $-70\text{ }^{\circ}\text{C}$ in order to minimize the thermal noise and maximize the signal-to-noise ratio. Nevertheless, classical approaches for substance identification - based on multivariate analysis of spectral region - did not work with these noisy data, hence an original and alternative approach to data analysis was chosen. The raw signal is preprocessed to clean the spectra from noise, background and, eventually, fluorescence. The Ricker wavelet (also known as 'Mexican hat') was used as convolution kernel to calculate a special transform of the spectrum. The properties of this wavelet make the transform able to cut off both high frequency noise and low frequency trend, leading to a much easier analysis of the spectrum.

In order to avoid the classical scheme of peak recognition, based on the minimization of a some kind of distance in a suitable space between the spectrum under recognition and a reference database, a fuzzy approach is adopted. At the end of the fuzzy process, the percentage of presence of referenced species is provided, whereas the layout of the acquisition software provides the following information to the operator along with other valuable information acquired (Fig. 6): real time image from the videocamera of the instrument, the camera snapshot of the analyzed person, the acquired Raman spectrum, the logging data and the traffic light showing the analysis results. The developed software is user-friendly for the operator, since only few preliminary steps are needed for the daily calibration, and the response given is "threat" or "no threat", indicated with a red or green signal, respectively.

The implemented software allows to use the apparatus either as stand-alone or in a more complex warning system, where the information provided by several instruments is collected and processed by a Data Merging and Alert System (DAMAS). Each time the DAMAS sent a "shot" command after the identification of a suspect person, the RADEX system automatically

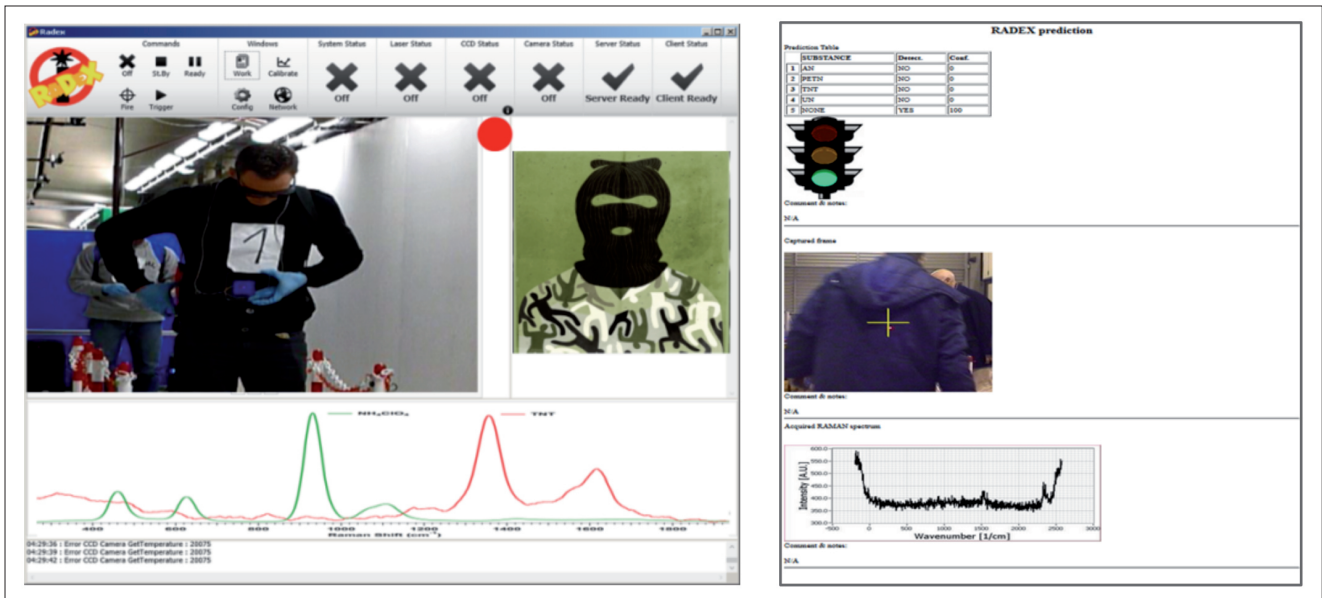


FIGURE 6 Layout of the acquisition software and the first version of the web server with details of an incident report

sent an eye-safe laser shot when the potential bomber passed through the gate. The Raman signals produced by the target area were acquired and compared with those included in the database to figure out the presence of explosive traces. Then, the acquired information and the relevant response, were sent in real time to DAMAS (Fig. 7).

During the trials the following energetic materials were tested: ammonium nitrate, urea nitrate, TNT, PETN. Different fabrics (natural and synthetic) were used as a substrate for the deposition of energetic

materials. Samples of traces of explosives on fabrics were prepared by the Fraunhofer Institute for Chemical Technology ICT using a piezoelectric Nano-Plotter™ (PNP, GeSIM, Germany). The PNP can deliver a precise number of droplets on a well-

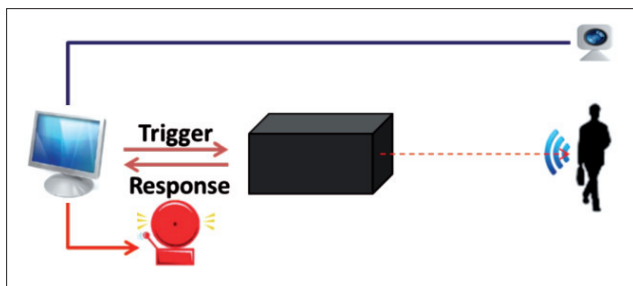


FIGURE 7 The schematic representation of the DAMAS-RADEX communication

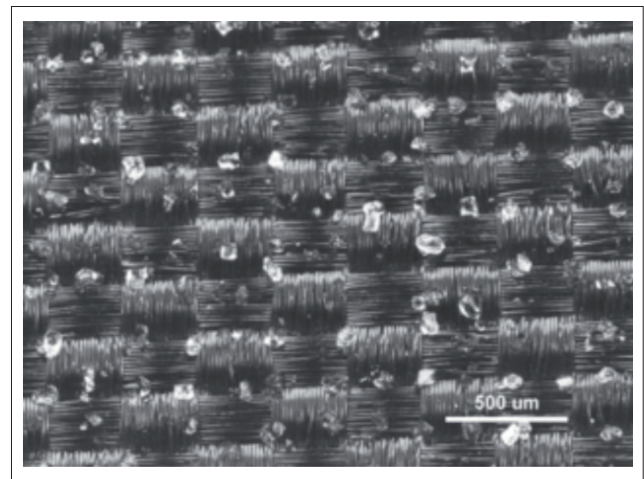


FIGURE 8 Energetic material deposited on the surface of synthetic fabrics with a piezoelectric Nano-Plotter™

defined surface (Fig. 8). This method provides a more uniform surface coverage with the analyte also for low surface densities (down to few $\mu\text{g}/\text{cm}^2$), as requested by the project.

Surface Enhanced Raman Spectroscopy (SERS)

At present the SERS enhancement mechanism appears to derive from two separate contributions: 1) an electromagnetic enhancement and 2) a chemical enhancement. The former comes through the electromagnetic interaction of light with metals, which produces large amplifications of the laser field through excitations generally known as plasmon resonances [10, 11, 12]; the latter corresponds to any modification of the Raman polarizability tensor upon adsorption of the molecule onto the metal surface [8 - 11].

The SERS technique has been implemented in the framework of the EC FP7 BONAS project [13], coordinated by DIM, in order to support the project partner Sersetech to develop a portable device.

Methodology

SERS substrates composed of arrays of inverted pyramidal pits (Klarite, Renishaw UK) have been implemented. A silicon nanostructure, produced by electron beam lithography, has been successively covered by a layer of gold deposited with the sputtering technique [14]. In Figure 9, a sketch and

a Scanning Electron Microscope (SEM) image of the substrate are shown.

Raman spectra were acquired with a table-top Raman system suitable for Raman and NIR measurements. For Raman measurements, it attaches via an optical fiber to an optical microscope, which in turn is attached to a diode laser source emitting at 785 nm. The detector is an un-cooled CCD. NIR excitation strongly reduces the sample fluorescence and the gold plasmonic frequency resonance is located near this spectral region [15]. The laser power was set at 180 mW on the samples while the acquisition time was 10 s. The scanned area, and therefore the sampled quantity depend on the objective used. In the case of the present measures, the laser beam was focused through the 20x objective, that means a laser spot of 90 μm diameter and an energy density of about $11.7 \cdot 10^3 \text{ J}/\text{cm}^2$.

Results

Raman spectroscopy provides a unique spectral ‘fingerprint’ of any molecule, hence each spectrum is molecularly specific and contains key signature bands that can be used for unambiguous identification [16]. The SERS spectra of the explosives PETN, RDX, TNT, EGDN in the spectral region $250\text{--}2500 \text{ cm}^{-1}$ are shown in Figure 10. Also, Table 1 lists the Raman wavenumbers and vibrational assignments of the principal characteristic bands of these explosives, which can be used to uniquely identify each substance [16, 17, 18, 19, 20, 21]. The comparison of the acquired spectra with the reference spectra showed that the

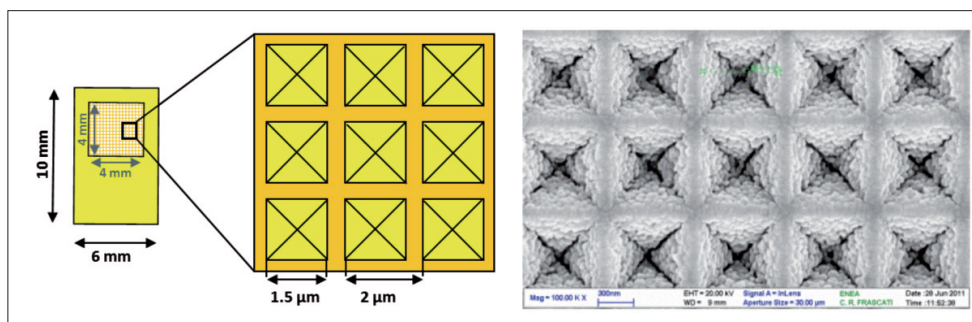


FIGURE 9 (left) Sketch of the SERS substrates. (right) SEM images of a portion of the SERS substrate. It is possible to recognize the inverted pyramidal pits

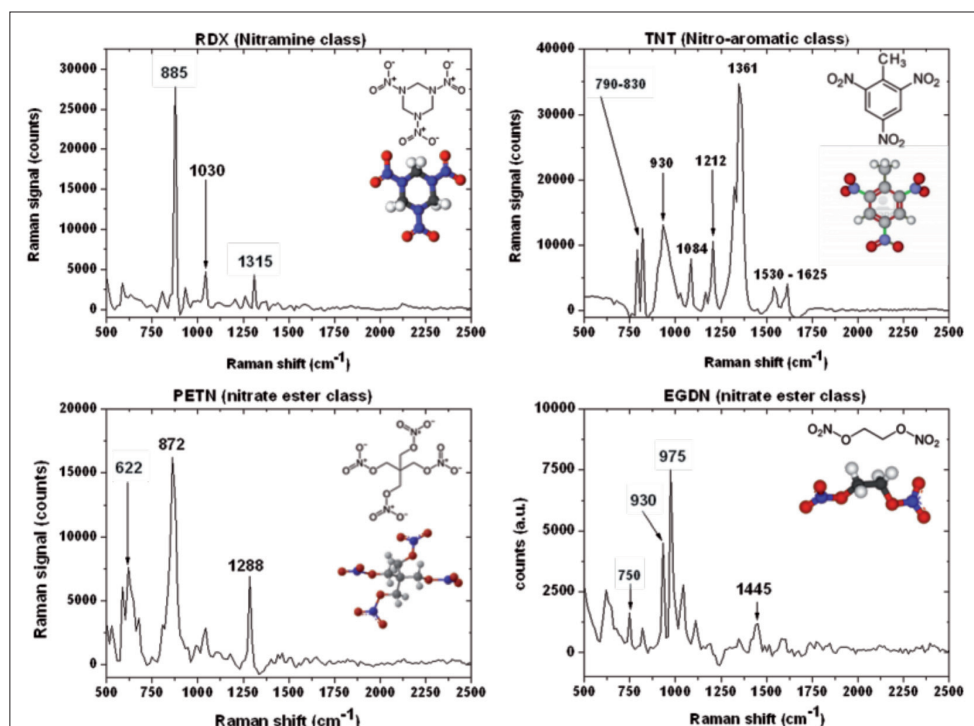


FIGURE 10 SERS spectra of PETN, RDX, TNT, EGDN. The mass probed by laser is about 200 pg for each substance. The acquisition time is 10 s. The laser power is set to 180 mW

Explosive	Wavenumber (cm ⁻¹) vibrational assignments	Reference
PETN	1290, [v_s (NO ₂)] 871, [v_s (O-N)]	[17]
EGDN	1600, [v_{as} (NO ₂)] 979, [C-O stretching] 941, [C-H ₂ vibration] 756, [O-NO ₂ umbrella]	[18]
TNT	1540, [v_{as} (NO ₂)] 1360, [v_s (NO ₂)] 1212, [C-H breathing] 790-822, [(NO ₂) scissor] 796-827, [C-H bending]	[16]
RDX	1584, [v_{as} (NO ₂)] 1361, [v_s (NO ₂)] 1318, [C-H ₂ wagging] 1260, [C-H ₂ scissoring] 887, [C-N-C ring] 592, [O-C-O stretching]	[19, 20, 21]

TABLE 1 Wavenumbers and vibrational assignments of the principal characteristic bands observed in the explosive spectra

substances are easily identified by their main spectral features, which comprise strong sharp peaks.

SEM analysis

A more careful observation of explosive residues on the surface of the SERS substrate has shown that they tend to occupy the individual pits, not covering the surface of the substrate in a homogeneous way but rather completely occupying single sites randomly. In Figure 11, two SEM images of the SERS substrate: the first, acquired in the area covered by the deposited solution at low magnification (reference bar 10 nm, magnification 5000), shows traces of the explosive residues (in this case RDX) filling some pyramidal pits over a large area of the sample; the second, at higher magnification (reference bar 200 nm, magnification $\sim 1.1 \cdot 10^5$) shows details of some pits full of explosive. Through the analysis of Figure 11-a and similar by using the image processing and analysis software "ImageJ", the explosive sampled resulted to be about 155 pg

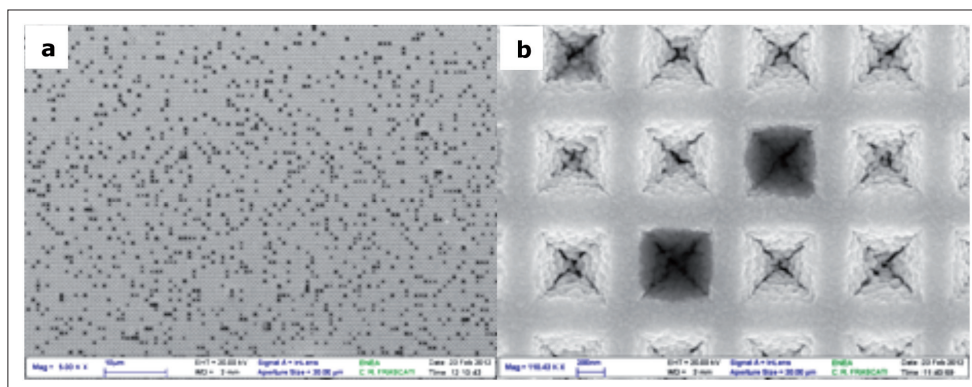


FIGURE 11 SEM images of the same SERS substrate at different magnification: (left) a large area randomly filled with the residual explosive (RDX); (right) a more detailed image of some filled pits

($155 \cdot 10^{-12}$ g). A similar procedure was applied for the other explosives, obtaining comparable quantities (about 200 pg).

Conclusions

The Raman techniques in both RADEX and SERS devices have demonstrated to supply valid and valuable results to the detection of very low trace level of sensitive materials.

In particular, RADEX was able to detect trace amounts of energetic materials using an eye-safe single pulse laser. The detection limit depends on the type of substance (i.e., on the Raman scattering cross section, the resonance frequency, and the stability of the molecules when excited with a 266 nm wavelength).

Detection of low surface densities, in the order of $100\text{-}1000 \mu\text{g}/\text{cm}^2$, was obtained for the analyzed energetic materials respecting the constraint of a single laser pulse with $3 \text{ mJ}/\text{cm}^2$. RADEX seemed to be a robust apparatus since it was able to work inside a challenging environment, such as a metro station, without encountering any type of interference (i.e., dust, temperature, electromagnetic fields, humidity etc.).

Furthermore, SERS was used to detect explosives in quantities of about 150-200 pg. The high signal-to-noise of the spectra suggests the identification of the explosives could be clearly performed by their

characteristic Raman spectra even at such low and, possibly, lower quantities. Spectra have been obtained non-destructively with a 10 s acquisition and 180 mW excitation, for a total fluence of $11.7 \cdot 10^3 \text{ J}/\text{cm}^2$.

Both devices have opened a new possibility to increase the limit of detection of new threats not only for energetic materials but also for biohazards like deadly microorganisms that can be used in bioterrorist attacks.

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