



A new eye-safe UV Raman spectrometer for the remote detection of energetic materials in fingerprint concentrations: Characterization by PCA and ROC analyzes



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ARTICLE INFO

Article history:

Received 24 March 2015

Received in revised form

25 June 2015

Accepted 27 June 2015

Available online 30 June 2015

Keywords:

Raman spectroscopy

Explosives detection

Eye safe devices

Principal components analysis

ROC curves

ABSTRACT

We report the results of proximal Raman investigations at a distance of 7 m, to detect traces of explosives (from 0.1 to 0.8 mg/cm²) on common clothes with a new eye-safe apparatus.

The instrument excites the target with a single laser shot of few ns (10⁻⁹ s) in the UV range (laser wavelength 266 nm) detecting energetic materials like Pentaerythritol tetranitrate (PETN), Trinitrotoluene (TNT), Urea Nitrate (UN) and Ammonium Nitrate (AN).

Samples were prepared using a piezoelectric-controlled plotter device to realize well-calibrated amounts of explosives on several cm². Common fabrics and tissues such as polyester, polyamide and leather were used as substrates, representative of base-materials used in the production of jackets or coats.

Other samples were prepared by touching the substrate with a silicon finger contaminated with explosives, to simulate a spot left by contaminated hands on a jacket or bag during the preparation of an improvised explosive device (IED) by a terrorist.

The observed Raman signals showed some peculiar molecular bands of the analyzed compounds, allowing us to identify and discriminate them with high sensitivity and selectivity, also in presence of the interfering signal from the underlying fabric.

A dedicated algorithm was developed to remove noise and fluorescence background from the single laser shot spectra and an automatic spectral recognition procedure was also implemented, evaluating the intensity of the characteristic Raman bands of each explosive and allowing their automatic classification.

Principal component analysis (PCA) was used to show the discrimination potentialities of the apparatus on different sets of explosives and to highlight possible criticalities in the detection.

Receiver operating characteristic (ROC) curves were used to discuss and quantify the sensitivity and the selectivity of the proposed recognition procedure.

To our knowledge the developed device is at the highest sensitivity nowadays achievable in the field of eye-safe, Raman devices for proximal detection.

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1. Introduction

Nowadays the detection of explosives has become dramatically important in view of preventing terroristic attacks on civilians, considering that some type of explosives can be prepared from

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easily obtainable ingredients. Among the detection technologies available, Raman spectroscopy [1] has recently gained increasing interest in the forensic science [2] and it has been already applied for the analysis of illicit drugs or medications [3–5] as well as for the characterization of different types of excipients (i.e. adulterants or cutting agents) [6,7]. Because the vibrational modes of the molecules are “fingerprints” that uniquely identify the chemical substance, the technique offers the distinct advantage of chemical specificity and benefits from the ability to generate valid reference Raman spectra under laboratory conditions, comparable with spectra obtained in the field.

Raman spectroscopy also allows the detection of suspicious

substances without any manipulation, so as to avoid close contact with the compound or with a potentially dangerous device or subject.

Recently, the technological evolution of various components (CCDs, optical fibers, monochromators, filters, lasers etc.) has greatly improved the limit of detection of the Raman instruments allowing for proximal (sample-to-device distance of some meters) or stand-off (sample-to device distance of some tenths or hundreds of meters) applications [8–11].

Typically this is accomplished exciting the sample with high power lasers [9,10] or with lasers emitting in the near, middle ultraviolet region of the spectrum (200–400 nm) [11,12]. This wavelength range is chosen because the Raman cross section of a molecule is dependent on the excitation wavelength and scales as λ^{-4} [11–13], therefore, the signal and the signal-to-noise ratio is increased up to some orders of magnitude when exciting in the UV region compared to the VIS excitation [12].

The cost to pay is a series of drawbacks, like possible photo-degradation effects of the sample [14] and a spectrometer with greater resolving power, because the Raman spectrum spans over a restricted wavelength range in the UV region [8].

Low energy is mandatory when laser-based devices are used in public areas, to avoid irreversible damages to the eyes in case the laser is inadvertently or accidentally pointed on the retina or on the skin. To this respect the reference standards to take into account in the US and EU are the ANSI Z136 [15] and IEC 60825-1 [16], that consider and quantify different damages that may be caused to the eye and skin if exposed to laser radiation. The reference quantity to consider is the maximum permissible exposure (MPE) [15,16] that is the highest power or energy density (W/cm^2 or J/cm^2) of a light source that has a negligible probability of creating damage.

MPE levels are determined as a function of laser wavelength, exposure time and pulse repetition and are usually about 10% of the dose that has a 50% chance of creating damage under worst-case conditions. In this regulations MPE is set to $3 \text{ mJ}/\text{cm}^2$ in the case of nanosecond UV laser pulses outdoor. Obviously, this limit is not to be understood as a rigid cut-off but it is an indication based on the best available information from experimental studies.

To our knowledge, stand-off Raman devices meeting this fundamental security criterion are still missing, or under development, so, despite the systems currently developed exhibit high sensitivity, being capable of detect explosives at distances up to hundreds meters [9,10] they cannot be used in public areas such as train stations, subways, airports, or simply outdoor in unrestricted areas, to monitor potential terrorists illegally transporting explosives.

This is actually the context we considered developing our stand-off Raman detector. We also discussed the effect of interfering signals on the data evaluation and we developed and tested a software procedure to automatically check if the Raman signal coming from explosives can be discriminated from these occasional interfering signals.

2. Materials and methods

2.1. Raman apparatus

The Raman apparatus is sketched in Fig. 1 and it is composed of a Nd:YAG laser (ULTRA, Quantel, 20 Hz maximum repetition rate), operating in fourth harmonic (266 nm) with a laser pulse of 8 ns duration and energy density set to a maximum of $3 \text{ mJ}/\text{cm}^2$ per shot, to accomplish the safety requirements previously discussed. The laser has a flat-top beam of 2 mm diameter, expanded up to 10 mm diameter at the target distance of 7 m and directed

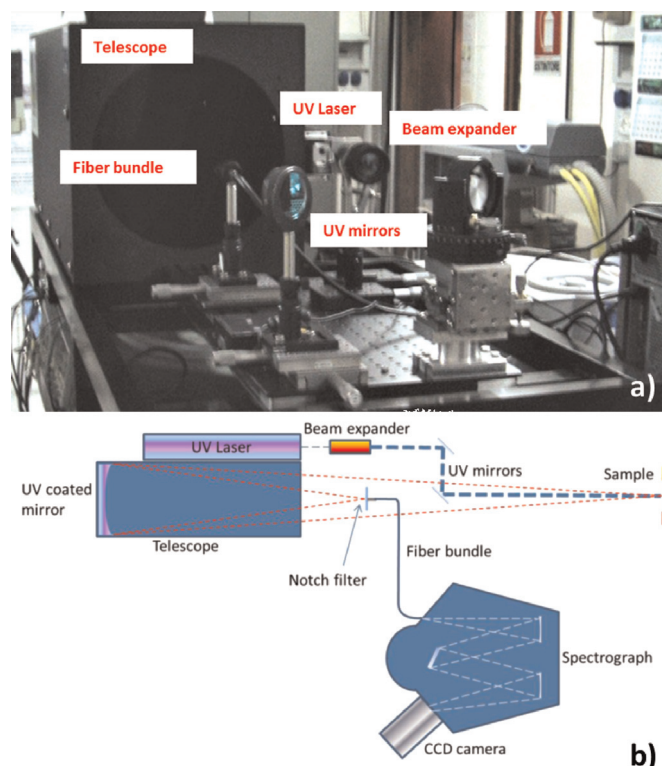


Fig. 1. (a) The stand-off Raman apparatus. (b) Sketch of the whole device.

coaxially to the optical axis of the telescope by using a set of UV flat mirrors.

The Raman signal is collected by a Newtonian telescope and it is focused at the entrance of a circular bundle of optical fibers, placed in the focus of the telescope. This radiation is spectrally decomposed by a 320 mm Czerny–Turner spectrometer and then detected by a low-noise CCD camera.

The telescope mirror (Optical Surfaces, UK, 300 mm diameter, 1004.8 mm focal length) is coated with a high reflectance dielectric (reflectivity $> 98\%$ in the 266–300 nm wavelength range), whereas the reflected laser light is rejected by a high-pass filter (266 nm RazorEdge[®] ultrasteep long-pass edge filter, Semrock) placed in front of the fiber bundle.

The fiber bundle (Leoni fiber, Germany) is 1 m long and it is composed of 49 fibers with an inner diameter of $200 \mu\text{m}$ and a numerical aperture of 0.12.

The filling factor is about 55%, transmittance is about 60%. The fiber bundle is circular at the focus of the telescope with an overall diameter of 2 mm whereas at the entrance of the spectrograph the fibers are vertically aligned to reproduce a slit of $200 \mu\text{m}$ and 1 cm long.

The spectrograph (iHR 320, Horiba, Jobin-Ivon) is equipped with three different blazed holographic gratings (1200, 1800, 2400 line/mm, blaze 250 nm) with a maximum resolution better than 0.06 nm, in order to cover the whole range of interest, the so called “fingerprint region”, in which the peculiar Raman features of each substance are present. For the present measurements we used the 1800 line/mm grating, in the wavelength range from 264 to 286 nm, i.e. up to 2700 cm^{-1} .

An iKon-M934 camera (Andor) was used as detector, with a 65% quantum efficiency at 266 nm, 1024×1024 active pixels and $13 \times 13 \mu\text{m}^2$ pixel size, running with the following optimized settings: temperature $-70 \text{ }^\circ\text{C}$, exposure time 0.00108 s, readout rate 1 MHz. Digital resolution was 2.73 cm^{-1} per pixel.

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