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Point and proximal detection and imaging: Testing of a compact Raman spectrometer coupled with photo-guided sampling

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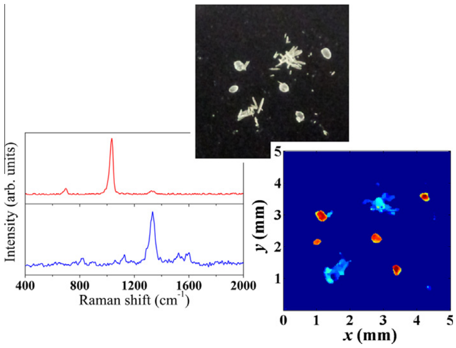
HIGHLIGHTS

- A compact Raman spectrometer for trace detection of explosives was developed.
- Its performance for point and proximal detection was tested.
- Its integration with a smartphone camera enabled photo-guided sampling and mapping at reduced times.

GRAPHICAL ABSTRACT



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ABSTRACT

The need to rapidly detect and identify traces of hazardous materials motivated the development of a modular, compact Raman spectrometer. Its performance for point and proximal detection was tested, while acquiring Raman spectra and Raman spectral maps of different compounds. This system offers high sensitivity and following its combination with photo-guided sampling, its capability for Raman mapping of particles is improved, being faster than raster scanning. The detection capabilities of the spectrometer make it a potential candidate for replacing existing Raman microscopes and for applications to detection of other compounds and under other situations.

Introduction

The necessity to detect and identify chemical and biological hazards, as well as explosive materials are among the major issues that homeland and field security has to deal with. Therefore, many efforts have been recently devoted to provide some solutions to these problems, while developing and improving various detection methods, at least partially related, to laser-based spectroscopic methods [1–6]. In principle, these methods can be used for targets positioned at different distances from the detector, namely for point (<10 cm), proximal (10 cm–200 m) and standoff detection (>200 m) [7] of harmful substances, since they are characterized by high selectivity and sensitivity. Some of these methods were developed for vapors detection, yet, due to the low vapor pressures of explosives [2,3,8], extremely high sensitivities are required. On the other hand, explosive materials and related compounds are known to be very "sticky" and therefore can be readily adsorbed upon surfaces, or incidentally, residues can be left on surfaces, implying that there is a need for spectral methods that are capable to selectively detect particles.

Recently, among other methods, standoff Raman spectroscopy [9–13], or coherent anti-Stokes Raman scattering (CARS) [14–20] were proposed to be used for detection of a variety of bulk

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compounds from distances of tens of meters. This is since, detection at any distance over several centimeters is considered, in the literature, as standoff [7]. These non-destructive vibrational spectroscopies were capable to provide specific spectral signatures of the molecules under study. However, it is to be recalled that these detection methods have to overcome several technical and physical difficulties, which limit their performance. Among these difficulties, the following should be mentioned: the need of free paths for the exciting laser beam and for the signal, the eye safety concern for the former, the wavelength-dependent scattering and absorption losses in air and the decrease in signal intensity with the inverse squared distance [18,21,22]. Nevertheless, at least under some circumstances, standoff detection from long distances is not required, but rather point and proximal detection would be satisfactory. Therefore, it seemed to us that this mode of detection of traces of hazardous materials, positioned at short distances from the detector, might be of great value, reducing somewhat the above mentioned drawbacks.

Indeed, just recently, we have built a compact Raman spectrometer based on a commercial laser pointer, with a 532 nm excitation wavelength [23]. This system operated with an incident beam normal to the sample and served for point detection and imaging of explosives in high order prints of latent fingerprints. The performance of this system was improved even further by using a 532 nm hand held green laser for excitation, which provides higher intensity, and by coupling it with a smartphone camera to allow photo-guided sampling [21]. This enabled to photograph the sample and eventually to selectively measure the Raman spectra and to obtain the Raman images of the particles of interest. The acquirement of the Raman images in much shorter times, than those required by raster scanning of the sample through the focused laser beam, or of the laser beam through the sample, is of great advantage. Here we will further examine the performance of the compact Raman spectrometer and the integrated system for yet untested conditions.

Experimental

The compact Raman system for point and proximal measurements [Fig. 1] is described in our previous articles [21,23]. Briefly, the Raman spectrometer consisted of a handheld green laser at 532 nm, driven by a dc power supply for prolonged operation and for intensity control. The laser beam was turned by a dichroic mirror (DM) and a 90° tiny prism and focused through different focal length (f.l.) converging lenses, or an objective, which served as focusing/collecting/collimating lenses (L_1). The targets were positioned at different distances, R, to fit the f.l. of the used L_1 lenses. The samples were placed on x, y motorized translation stages, computer-controlled by a newly developed LabVIEW software application, combined with a manual z translational stage and positioned in front of the L_1 lenses. The backscattered spontaneous Raman signal was collected and collimated by the same L_1 lenses and filtered by a long wavepass edge filter. Then the signal was focused, using a $f/4$ lens (L_2) onto a pinhole (100 μm), located in front of a slit of a 0.14 m spectrometer with entrance aperture ratio of $f/3.88$, equipped with an air cooled 1024 × 1024 intensified charged coupled device (ICCD). The LabVIEW application controlled the x, y movement of the motorized stages and the ICCD readout, while acquiring the Raman signal at specific points on the sample and allowing to measure the Raman spectra at these positions and eventually to create Raman spectral maps of different samples, either by raster scanning or by photo-guided sampling.

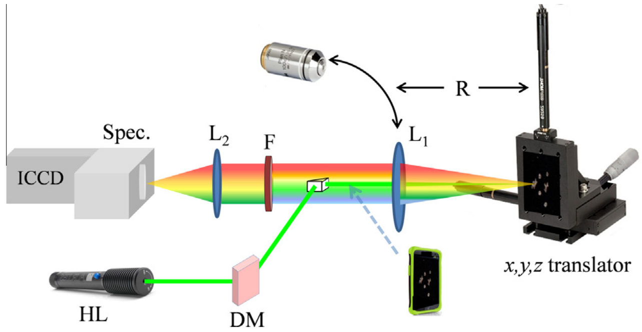

Fig. 1. Schematic of the Raman compact system for proximal and point detection and imaging, including the following components: x, y, z translational stages, focusing/collecting/collimating lens or objective (L_1), long-wavepass edge filter (F), focusing lens (L_2), dichroic mirror (DM), hand-held laser (HL), a spectrometer (spec.) with an intensified charge-coupled device (ICCD) with R, the distance between the target and the focusing/collecting/collimating lens and a smartphone camera.

The performance of the compact Raman spectrometer at proximal distances was tested by measuring Raman spectra of different liquid and solid samples. The liquid samples were held in 1 cm diameter glass vials, while the solid ones were prepared by applying grain particles on glass microscopic slides. The Raman spectra of the liquid samples where measured at a distance of 30 cm and include acetone (C_3H_6O), hydrogen peroxide (H_2O_2), ethanol (C_2H_6O) and cyclohexane (C_6H_{12}), where the former two are precursors for synthesis of triacetone triperoxide (TATP), which is recently used as a material for improvised explosives devices (IEDs) [24,25]. The Raman spectra of the solid samples, i.e., potassium nitrate, KNO_3 and 2,4 dinitrotoluene (DNT), $CH_3C_6H_3(NO_2)_2$ were measured at the same distance. Under these conditions, the roughly estimated laser focal spot size in the lateral (x, y) and axial (z) directions are 66 μm and 4.5 mm, respectively. Raman maps, at proximal distances of 30 and 50 cm, were obtained by raster point to point scanning of a specific area (5 × 5 mm) of the sample, with a step size of 50 μm. The measurements, through this work, were performed with room lights off and under laboratory ambient conditions.

Monitoring of the height of the dominant peaks in the Raman spectra, acquired at each point with respect to the background signal enabled obtaining the corresponding intensity matrices and eventually the Raman maps. For raster scanning at a distance of 30 cm, a 1″ diameter lens was used as the focusing/collecting/collimating lens, while at a distance of 50 cm a 2″ one.

In our previous experiment [20] photo-guided sampling was performed at proximal distances of 10 cm and here point detection was used for this purpose, while photographing by a smartphone camera and measuring the Raman spectra of residues in a fingerprint with an 40× objective (0.65 numerical aperture (NA)). Under these conditions, the full width at half maximum (FWHM) of the beam on the sample in the lateral and axial directions was ∼0.5 and ∼2.5 μm, respectively. The photograph of the sample was processed by a MatLab particle recognition code [20], which provided the positions and areas of the individual particles. By monitoring the Raman spectra of these particles, while scanning the laser beam through their areas, with a step size of 2 μm, a rapid Raman spectral map was acquired.

The fingerprints were prepared according to the procedure of Ref. [26] by cleaning the hands of a volunteer with ordinary soap, rinsed in water and dried and aged in air. The index finger was stained by touching powders of KNO_3 and DNT, spread on a clean microscopic slide. Excessive powder was rubbed off by hitting the contaminated hand with a glove and finally pressing this finger onto a clean slide, which was then positioned in front of the objective.