



Review

Forensic and homeland security applications of modern portable Raman spectroscopy

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ARTICLE INFO

Article history:

Received 16 November 2009
 Received in revised form 13 March 2010
 Accepted 17 March 2010
 Available online 14 April 2010

Keywords:

Stand-off detection
 Spatially offset Raman spectroscopy
 Surface enhancement Raman spectroscopy
 Drugs
 Explosives
 Forensics and Homeland security

ABSTRACT

Modern detection and identification of chemical and biological hazards within the forensic and homeland security contexts may well require conducting the analysis in field while adapting a non-contact approach to the hazard. Technological achievements on both surface and resonance enhancement Raman scattering re-developed Raman spectroscopy to become the most adaptable spectroscopy technique for stand-off and non-contact analysis of hazards. On the other hand, spatially offset Raman spectroscopy proved to be very valuable for non-invasive chemical analysis of hazards concealed within non-transparent containers and packaging.

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1. Introduction

Interrogation of different types of chemical and biological hazardous materials requires ascertaining the unknown chemical and biological substances' identity followed by the institution of appropriate countermeasures against the potential harm/toxicity of the substance.

New emerging challenges from organised crime and terrorist groups underline the vital need for sensitive and selective rapid

identification of substances such as drug mixtures, chemical and biological warfare (CBW), explosives and toxic spills in field while adapting a non-contact approach to the hazard. These challenges may also require identifying concealed hazards without opening a suspected packaging in order to minimize harmful exposures.

Several techniques have been utilized for the detection and identification of hazardous substances. These techniques include, HPLC/MS, GC/MS, THZ, ion mobility spectroscopy (IMS), molecularly imprinted polymers (MIP), surface acoustic waves and optical detection via fibre optics. However, all of the above methods require the personnel as well as parts of the instrument to come in contact with the hazardous sample. In addition to placing workers at risk, any time an instrument comes in contact with the

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contaminant; it must either be disposed of in a controlled manner or thoroughly decontaminated. On the other hand, most of these techniques require moving complex laboratory equipment out to the field.

The application of Raman spectroscopy to the above situations has been of great interest especially with the remarkable improvements in the technique's portability. Surface and resonance enhancements of the Raman signal made Raman spectroscopy the most sensitive and portable spectroscopic technique that is adaptable to stand-off and non-contact analysis of unknown chemical and biological hazardous agents.

1.1. Theoretical basis of Raman spectroscopy

When monochromatic light impinges on a sample, much of it passes through the sample unchanged or some may be absorbed, depending upon the wavelength of the light and the nature of the sample. A small fraction ($\sim 0.1\%$) is elastically scattered as light of the same frequency as the incident light (Rayleigh scattering). A smaller fraction of the incident light (~ 1 photon in 10^6 or 10^7) is scattered inelastically (Raman scattering). This scattering can be towards lower frequencies (Stokes scattering), or higher frequencies (anti-Stokes scattering), than the incident light.

Raman is an instantaneous process where some energy is lost to (or gained from) the target molecule. The returning scattered light becomes of a different wavelength. The difference corresponds to an energy shift in the molecule. In this way, Raman spectroscopy probes the vibrational modes of the target molecules. These vibrational modes can be regarded as a fingerprint that uniquely identifies the substance.

A drawback of Raman spectroscopy is that, Raman signal has a weak intensity since spontaneous Raman scattering has a very low cross-section. In addition, at near ultraviolet and visible excitation wavelengths, Raman spectrum can be swamped by the strong fluorescence signal originating from the same target compound or from impurities. This can be avoided using excitation wavelengths in the near infrared (NIR) region (where the lower laser energies required to generate a Raman spectrum do not give rise to fluorescence) or deep UV region (where fluorescence lies outside the Raman spectral range) [1,2].

The Raman spectral intensity is inversely related to the fourth power of the laser wavelength. Therefore, the intensity of a Raman spectrum is much greater when exciting in the UV region than in the NIR region [1,2]. In practical terms, this results in higher sensitivities and shorter data acquisition times when exciting in the UV as compared to the NIR [1,2].

Using a UV laser, therefore, has the advantages of producing both high spectral intensity and being unaffected by fluorescence.

An excitation laser in the UV region below 300 nm has an additional advantage, as the Hartley absorption band of ozone will block solar radiation, meaning that the collection of Raman spectra will not be greatly affected by ambient light. This factor allows UV-based Raman systems to operate with high efficiency in daylight conditions without sophisticated instrumental setups for effective light discrimination.

In comparing Raman scattering versus other screening methods, the Raman approach is advantageous for several reasons:

1. Raman spectroscopy acts as a molecular fingerprint containing, unique, highly reproducible, detailed features, thereby providing the possibility of highly selective determinations.
2. Raman spectroscopy can be applied to any optically accessible sample (i.e. the sample is accessible by the laser excitation beam and the scattered photons can be detected) whether it is organic, inorganic or biological.

3. Solid, liquid and gaseous samples can be measured as well as transparent or non-transparent samples.
4. Aqueous solutions present no special technical problems.
5. No special pre-scanning preparations of the sample are necessary.
6. Scanning can be completely non-invasive and clandestine.
7. Raman spectroscopy offers detection configurations that accommodate different target sizes from $1 \mu\text{m}$ to dm^2 , at ranges from a few millimeters up to several meters.
8. The Raman fingerprint is independent of the excitation wavelength. This allows the use of any laser excitation wavelength.
9. Raman detection can be performed in the ultraviolet (UV) solar-blind region of the spectrum ($\lambda < 300 \text{ nm}$, where stratospheric ozone absorption attenuates the solar background).
10. Detection can be done day and night, without the presence of a large background signal due to ambient light.
11. Raman spectroscopy has completed its transformation into a fully portable technique for field analysis.

The aim of this review is to highlight the current advances in modern field-deployable Raman configurations for forensic and homeland security investigations.

2. Discussion

2.1. Conventional Raman spectroscopy

Different modes of conventional Raman spectroscopy have been used for the detection of drugs and explosives.

Raman spectroscopy with near infrared (NIR) excitation was applied to the forensic analysis of ecstasy and related phenethylamines, including, 3,4-methylenedioxyamphetamine (3,4-MDA); 3,4-methylenedioxyethylamphetamine (3,4-MDEA); *N*-methyl-1-(1,3-benzodioxol-5-yl)-2-butylamine (MBDB) and amphetamine sulfate [3]. Using NIR laser excitation, it was possible to discriminate the spectra of the illicit substances based on differences in the position of vibrational bands, even in the presence of adulterants and diluents. Raman spectroscopy was utilized for profiling and quantification of illicit tablets using multivariate statistical analysis [4].

Modified non-invasive quantitative Raman techniques have been recently reported for the direct determination of active ingredients in pharmaceuticals through plastic bottle packaging [5–9].

The wide area illumination (WAI) Raman scheme permits excitation using a 6 mm laser spot (focal length: 248 mm) that is designed to cover a wide sample area (Fig. 1).

WAI has the potential to improve the reliability of the Raman measurements by significantly enhancing representative sample interrogation, thus improving the reproducibility of sampling. It also decreases the sensitivity of sample placement with regard to the excitation focal plane [5,6]. Samples containing analytes that are sensitive to laser excitation or may experience light-induced degradation (e.g. organic explosives), can be better detected using WAI since the energy density within the illuminated area of the sample as well as light-induced degradation is reduced when compared to those in conventional Raman setup.

Raman spectroscopy has been utilized for the rapid forensic screening, with acquisition time of 1 min, of amphetamine content in street samples of unknown adulterants [10]. Two Raman quantification methods were used: (1) relative peak heights of characteristic signals of the amphetamine and the internal standard and (2) multivariate calibration by partial least squares (PLS) based on the second derivative of the spectra.

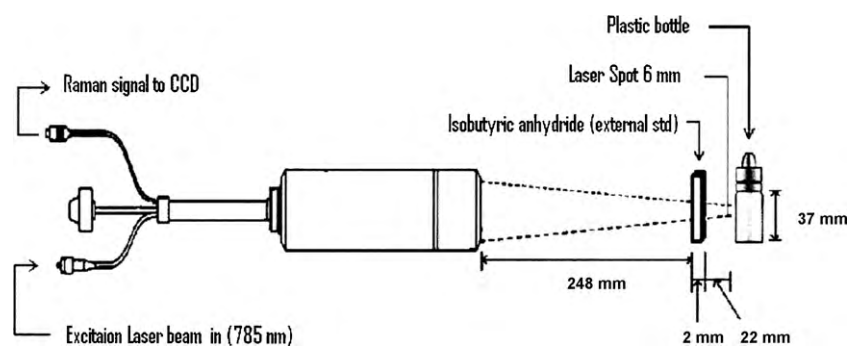


Fig. 1. Schematic diagram of the wide area illumination (WAI) scheme.

Using a combination of principal components analysis (PCA) and hierarchical cluster analysis (HCA), it was possible to design an automated Raman spectroscopy approach to distinguish between genuine and counterfeit tablets. This approach has the potential to be applied by customs or in field to identify counterfeit tablets on the spot without involvement of trained chemists [11].

Recently, confocal Raman spectroscopy has been reported for the detection and identification of ultratrace amounts of illicit drugs particles (average size of 5–20 μm) and their adulterants on the surface of human nail and under the nail varnish coating. Interference-free Raman spectra of the drugs were obtained non-destructively within 3 min with little sample preparation [12].

Raman with NIR excitation has been successful in detecting residual explosives in fingerprint samples [13]. The use of NIR excitation minimized complications due to sample fluorescence.

In a new application, confocal Raman microscopy was used for the detection and identification of explosives and their precursors on un-dyed natural and synthetic fibres as well as coloured textile specimens. Spectra were obtained, in situ within 90 s, from explosives particles trapped between highly fluorescent clothing fibres. The spectra were readily obtained without sample preparation and with no alterations made to the evidential material [14].

In recent years, the development of portable Raman stations equipped with remote sampling probes made it easy to analyse a wide range of sample types at the scene (Fig. 2).

Full range spectra with high spectral resolution and sensitivity can be collected in a few seconds. Portable Raman stations equipped with advanced spectral libraries and chemometric software are now capable of carrying out in-field investigations within a near-real time window.

Raman devices such as “First defender” (from Ahura), and “Inspector Raman” (from Deltanu), are characterized with high resolution and low noise through a variety of packaging materials. These are essential features for unambiguous identification of a wide range of forensic samples including narcotics, explosives and explosive precursors.

The use of portable Raman spectroscopy to discriminate between illegal narcotics in an airport environment has been reported in 2008 [15]. The spectra were obtained from suspected drug samples in less than half a minute. The spectra were of high quality on the provision that the cutting agents did not significantly fluoresce.

2.2. Resonance enhanced Raman spectroscopy

When Raman excitation occurs within an electronic resonance (absorption) band of a material, the scatter cross-section is improved by as much as 10^8 . For biological materials such as nucleic and amino acids these absorption bands are very strong in the deep UV between 220 and 280 nm. Many organic and inorganic

materials, when excited in deep UV, exhibit resonance enhancement of Raman bands. Fluorescence resulting from deep UV excitation occurs in the 280–370 nm wavelength region. Therefore, deep UV Raman does not suffer from fluorescence interferences and is characterized by a very high sensitivity and selectivity for low concentrations of target materials [16].

In the UV range where very energetic photons exist, the Raman lines are very close to the incident exciting frequency, while the luminescence is still very weak. This is due to Stokes shift inherent to this phenomenon (namely luminescent occurs at wavelengths much longer than excitation and, correspondingly, Raman). Besides, for the same reason of very energetic photons, the relatively broad spectral range of Raman shifted lines (from 400 to 5000 cm^{-1}) may be detected simultaneously [17].

Recently, two-dimensional deep UV-resonance Raman was proposed for screening traces of explosives in complex environments containing multiple components and interfering substances. Two-dimensional resonant Raman spectroscopy was

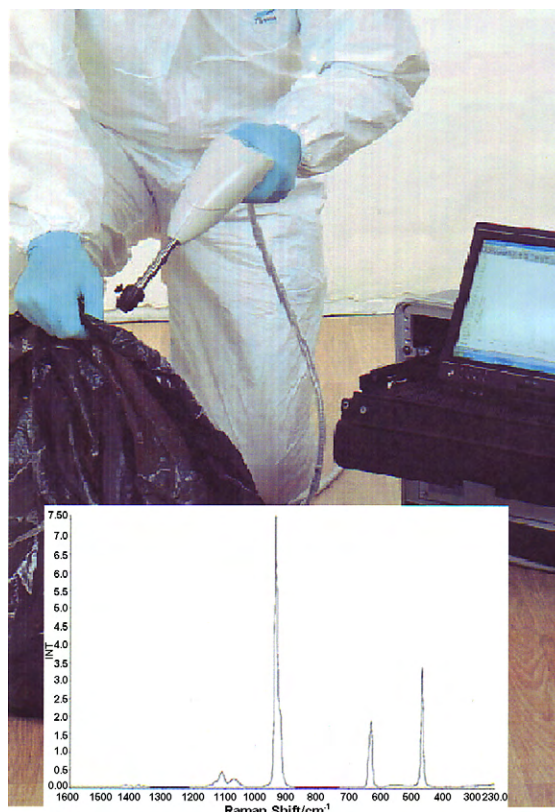


Fig. 2. Raman spectrum of ammonium perchlorate explosive through black plastic bag using a portable Raman station.



Fig. 3. Mobile stand-off Raman detection unit.

also applied to the acquisition and discrimination of microbial signatures. The technique allows the development of devices for robust analysis of real-world samples that include mixtures of explosives, microbes, and contaminants [18,19].

In another new application, automated detection of traces of high explosives in fingerprints by ultraviolet Raman spectroscopy has been reported by Jander and Noll [20]. For real-world applications, a robust algorithm (Fourier filter) has been developed in order to tolerate high levels of fluorescence background and recognize the spectral features of explosives in the sample's spectrum. The authors demonstrated the detection of traces of ANFO (ammonium nitrate, fuel oil) and TNT (2,4,6 trinitrotoluene) explosives at surface coverage levels of $55 \mu\text{g}/\text{cm}^2$ in a blind test experiment.

2.3. Stand-off Raman detection of hazardous substances

Modern Raman spectrometers are of the dispersive type with charged coupled device (CCD) detection. The dispersive/CCD type Raman instruments are made quite portable. The use of NIR excitation minimizes complications caused by sample fluorescence. However, sample heating can be a problem because the $1/\lambda^4$ scattering cross-section dependence on wavelength requires high excitation energies at these longer wavelengths [21–23].

Most stand-off Raman systems utilize non-gated CCD cameras as detectors. However new research demonstrated that using gated intensified CCD (ICCD) enhances the performance of the stand-off system [24,25]. The gating of the detector can be coordinated with the laser pulse to restrict data collection to the time period where Raman-scattered photons are expected to reach the detector, while excluding the ambient light photons outside of this time period. Accurate gating of the laser pulse also allows effective discrimination of the Raman signal from possibly longer-lived fluorescent or luminescent components in the target sample (as these signals will reach the detector after the Raman-scattered photons) [24,25].

Many portable Raman stand-off systems (Fig. 3) utilize a pulsed Nd:YAG laser of 1064 nm, frequency doubled to 532 nm, for the detection of explosives at different ranges between 30 and 100 m [24,26–28], in an outdoor environment.

In 2007, two field-portable directly coupled pulsed remote Raman systems in the oblique and coaxial geometries were reported by Sharma [27]. In the oblique mode the laser is directly aimed at the distant target and the telescope collects the scattered radiation at an oblique angle that is mainly determined by the distance from the Raman system (Fig. 4A). In the coaxial mode, the laser beam is made collinear with the telescope's optical axis (Fig. 4B).

The coaxial geometry allows measurements from samples at different distances without re-alignment of the system. In the coaxial geometry, the laser beam is made collinear with the telescope's optical axis [27].

The oblique geometry ensures that all the laser power reaches the sample, by careful aligning of the laser and the telescope. In the oblique mode the laser is directly aimed at the distant target and the telescope collects the scattered radiation at an oblique angle that is mainly determined by the sample distance from the Raman system [27].

Sharma investigated the range of sample positions at which Raman spectra can be observed was investigated using benzene as target [27]. The results showed that, for the oblique layout, high signal intensities were obtainable at distances between 20 and 50 m. The sample was still detectable at 10 and 65 m. For a coaxial system, a stand-off working distance between 10 and 120 m was achieved.

Johansson et al. developed and tested a close range directly coupled stand-off Raman detection systems for explosives using both the oblique and coaxial geometries [28]. The developed systems were tested in outdoor environments within a range of 55 m. The measurements were conducted in sunshine, at night, in rain as well as during heavy snowfall. Different container materials were also studied (green glass and PET bottles). Measurements were carried out using laser excitation of 532 nm. Using the developed systems, aqueous solutions containing low concentrations of hydrogen peroxide and hexamethylene triperoxide diamine (HMTD) were detected from a stand-off distance of 30 m.

An excitation laser beam of 532 nm is able to transmit through numerous container materials and falls within the visible spectral region where optical components are easily available and affordable. With the use of pulsed lasers and gated detection, the influence from ambient background becomes negligible even during daytime measurements. However, the 532 nm, as the Raman probing wavelength, is prone to fluorescence interference.

Several groups have pursued Raman spectroscopy at UV wavelengths [17,20,29–35]. The reasons for doing so are multiple; the obvious one is the significant enhancement of the Raman signal. Another advantage is the much reduced interference of fluorescence. At wavelengths shorter than 250 nm, the full Raman range, up to 5000 cm^{-1} , is normally free from luminescence allowing for the identification of species in a fluorescent matrix

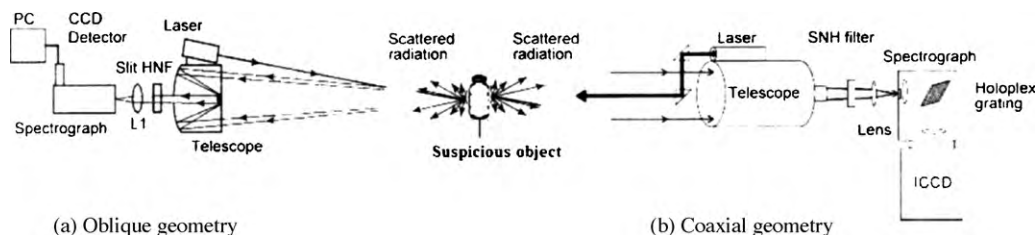


Fig. 4. Schematic diagram of directly coupled pulsed remote Raman system in the oblique geometry (A) and coaxial geometry (B).

[18]. The problem of ambient light background that can be present for longer gating times or continuous measurements disappears if the measurements are done in the solar-blind region, below 300 nm, as the Hartley absorption band of atmospheric ozone will block solar radiation. Since UV laser wavelengths fall outside the visible spectral region, the problem of eye hazards is significantly decreased since the maximum permissible exposure is markedly higher for wavelengths that are not focused by the lens of the human eye onto the retina. For the spectral region between 180 and 400 nm, the international standard allows up to 3 mJ/cm² [36].

Brookhaven National Laboratory developed a mobile Raman LIDAR van for the identification of bulk chemical spills at distances of 0.5 km or more using laser excitation at 266 nm for 60 s. They have also performed UV Raman measurements on some explosives (0.5–1% concentration) using 248 nm laser radiations [37].

Other groups have also studied near resonance Raman spectroscopy of explosives and chemical agents [29,38].

Nagli et al. found that, for the majority of explosives, the signal-to-noise ratio was much better when a 248 nm radiation instead of a 266 nm or a 355 nm radiation was used for excitation. The authors also concluded that for severe luminescence from the sample itself, as is the case for the RDX composition Semtex, 248 nm is the only wavelength (out of 532, 355, 266 and 248 nm) that sufficiently discriminates against fluorescence and allow correct identification [39].

However, UV radiation may cause sample degradation. Ways of countering this phenomenon are to keep the pulse energy at a minimum and to continuously move/rotate the sample [40].

2.4. Spatially offset Raman spectroscopy (SORS)

In the SORS technique, Raman signal is collected from areas that are spatially offset from the point of illumination by distance Δs (where Δs is the spatial distance between the laser illumination and collection areas on the surface of the sample) (Fig. 5). The

spectra collected at each spatial offset contain different relative contributions from sample layers located at different depths due to the wider spread of photons originating from deeper layers on the sample surface. The lateral offset also effectively discriminates against photons propagating sideways within the surface layers as they exhibit a higher loss at the air-to-sample interface than photons propagating through deeper layers. Consequently, the SORS technique suppresses the interfering Raman and fluorescence signals originating from the surface layers and enhances, in relative terms, the Raman signal from the sub-layer. Therefore, the Raman spectra of individual sub-layers within a complex multi-layer system can be isolated with a considerably small and simple experimental approach [41].

SORS has proved to be of valuable practical use in the authentication of pharmaceutical products through non-invasive chemical analysis of products concealed within non-transparent plastic bottles as well as other types of packaging. The need for such inspection has been heightened in recent years by the increase of marketed counterfeit life-saving medicines [42].

SORS has been utilized for probing pharmaceutical tablets in quality control where the active ingredient can be screened directly within its packaging (e.g. Sudafed Dual Relief capsule of shell thickness 150 mm) [43].

In 2008, SORS was utilized for the detection of cocaine dissolved in ethanol [44]. Cocaine was concealed inside brown-coloured glass bottles containing alcoholic beverages.

SORS has demonstrated significant potential for interrogating concealed liquid explosive in. Low concentrations of aqueous hydrogen peroxide concealed within a wide range of plastic and glass containers were successfully detected with fingerprint identification in short time frames without opening the suspected containers [45].

An additional refinement of the SORS concept was achieved through the development of inverse SORS (Fig. 5). In inverse SORS, the collection and laser deposition zones are switched with respect

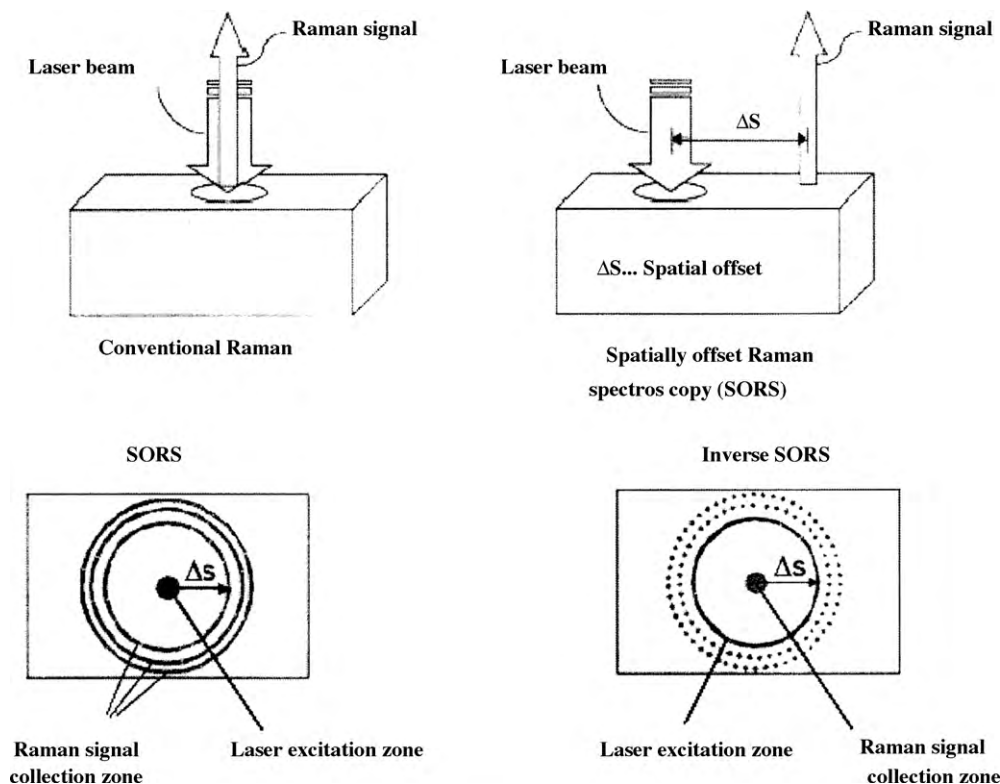


Fig. 5. Schematic diagram of SORS and inverse SORS principle.

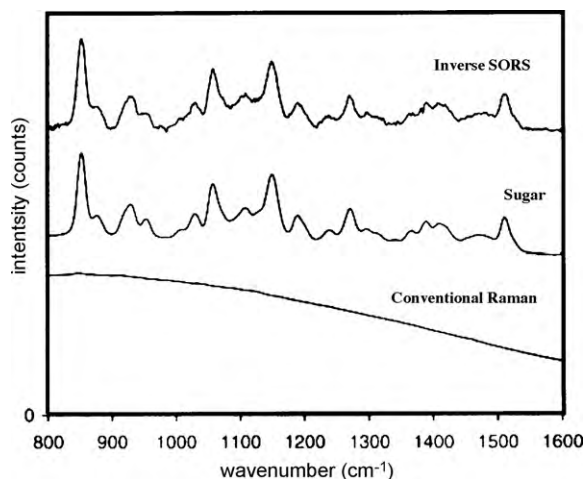


Fig. 6. Demonstration of inverse SORS non-invasive measurement of powder explosives or illicit drugs in envelopes in security screening applications. The powder explosive is mimicked by sugar. The graphs show the background subtracted inverse SORS spectrum (eliminating fluorescence contribution), sugar reference spectrum, and comparative conventional Raman spectrum dominated by fluorescence originating from the envelope.

to standard SORS; Raman light is collected through a group of fibres within the center of a probed area surrounded by a ring shaped laser beam. Inverse SORS reduces the sensitivity to imaging imperfections in the spectrograph and the detector [46]. This causes the spectrum recovered using inverse SORS to be free of subtraction artifacts that are noted in the spectrum obtained using SORS.

The use of inverse SORS for the screening of powders concealed in brown paper envelopes has been demonstrated by Matousek [46]. Comparative conventional backscattering Raman measurements yielded only a massive fluorescence background, originating from the envelope material. Using inverse SORS, the fluorescence background contribution to the overall spectrum was significantly suppressed allowing for the Raman fingerprint of the sugar held within the envelope to be successfully detected (Fig. 6).

A SORS/Inverse SORS probe can be readily utilized into the existing commercial hand-held Raman instruments, thereby, opening the gates for more accurate and sensitive interrogation of concealed drugs and explosives at border security check points without opening a potentially hazardous exhibit [47].

2.5. Surface enhancement Raman spectroscopy (SERS)

Three key features of SERS appear to be a perfect match for the technical specifications required for forensic and homeland security applications. First, SERS furnishes molecular-level, chemical fingerprint-like information and enhances the intensity of the Raman signals by several orders of magnitudes. This enables the detection of many different species and also permits multiplexing, whereby multiple species are detected in a single measurement. Second, the instrumentation meets the needs for point of use measurements. As only short data acquisition times and low incident laser powers are necessary, SERS is capable of investigating samples containing nano-molar to pico-molar concentration levels of drugs, explosives or bio-molecules [48,49]. Third, SERS have the capacity to be used for both direct and indirect detections.

Fluorescence has long been an issue when acquiring Raman spectra, as the resultant background often masks the much weaker Raman scattering bands. Since these problems are most often encountered in the visible light regime, Raman instruments

incorporating NIR laser excitation sources of 785, 830 nm have recently become commonplace. In addition to enhancing the Raman scattering intensity, metal surfaces also have the ability to quench such endogenous fluorescence and produce much higher quality data allowing relatively straightforward analysis (Fig. 7).

Lombardi presented data from a collaborative research effort that utilized SERS for trace identification of the controlled substances, morphine and codeine [50]. In this research, silver nanoparticles were used as SERS substrates providing signal enhancement in the visible and NIR regions. Because the analytes of interest have an intense fluorescence band, NIR SERS allowed for amplification of the analyte signal as well as suppression of the fluorescence interference.

A proof of concept for using SERS in the detection of drugs in saliva has been reported in 2005. Simple SERS syringe capillaries were used for monitoring the concentration of the chemotherapy drug 5-fluorouracil in saliva [51]. The capillaries consisted of a metal-doped sol-gel immobilized in a glass capillary that can be optically accessed along its length to generate and collect surface enhanced Raman spectra (SERS). A simple two-step procedure is followed. In the first step a syringe is used to draw the sample solution through the silver-doped sol-gel to isolate the target drug from potential interfering chemical components of saliva and simultaneously provide SERS activity. In the second step, the Raman optical probe of a Raman analyzer scans the length of the sol-gel. Quality SERS spectra are obtained for samples containing as little as 2 μg of the drug in 1 mL saliva. The separation occurs in a few seconds, while spectra at multiple positions are collected in a few minutes. This allows performing rapid separations or extractions and SERS analyses of drugs at low concentrations.

A quantitative online monitoring of concentration fluctuations of phenothiazine promethazine as well as the anti-cancer agent mitoxantrone via surface enhanced Raman scattering assay based on a microfluidic device has been demonstrated by Ackermann et al. [52]. With the applied liquid/liquid two phase-segmented flow system the authors succeed in preventing the adhesion of nanoparticle aggregates to the channel walls which is necessary for a quantitative analysis.

On-tablet SERS has been demonstrated as a rapid, straightforward, and unambiguous means to distinguish between low dose DOB (2, 5-dimethoxy-4-bromoamphetamine) tablets as well as tablets with no active constituent [53].

Premasiri et al. showed that SERS spectra can be obtained after deposition of bacteria onto a colloidal Au-based substrate, and that these spectra are approximately 10^4 -fold more intense than the corresponding bulk Raman signals [54].

A compact and rugged Raman integrated tunable sensor coupled with surface enhanced Raman scattering substrates has been recently demonstrated for the screening of a wide variety of chemical and biological agents. This portable detection station has been utilized for the detection of various compounds of particular interest for homeland defense applications. These include methyl parathion (a nerve agent simulant) and dipicolinic acid (a biomarker for bacillus endospore), and other chemical warfare simulants such as dimethyl methylphosphonate, pinacolyl methylphosphonate, diethyl phosphoramidate, and 2-chloroethyl ethylsulfide, which are simulants for sarin (GB), soman (GD), tabun (GA), and sulfur mustard (HD), respectively, and intact bacteria such as *Bacillus globigii*, *Erwinia herbicola*, and *Bacillus thuringiensis*, which are simulants for biological warfare agents [55].

A rapid detection protocol suitable for use by first responders to detect anthrax spores using a low cost, battery-powered, portable Raman spectrometer has been developed. The protocol uses surface enhanced Raman spectroscopy on silver film over nanosphere (AgFON) substrates [56].

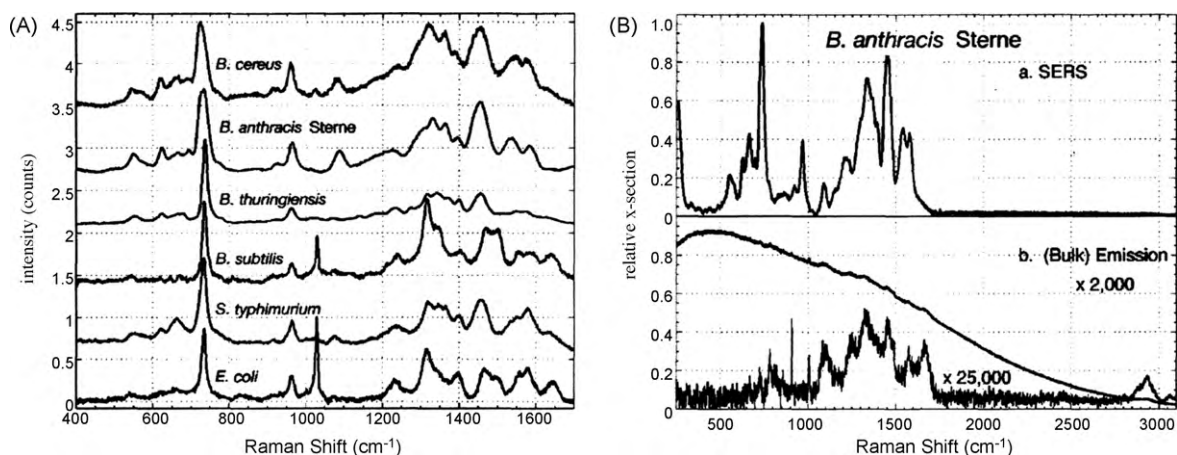


Fig. 7. (A) SERS spectra of six bacterial species obtained under identical conditions. (B) Raman scattering obtained from *B. anthracis* using SERS (top) and bulk Raman (bottom) methodologies. Spectra were acquired using 785 nm excitation. The bottom trace shows the resulting Raman spectrum after subtraction of the broad background associated with the bulk Raman measurement.

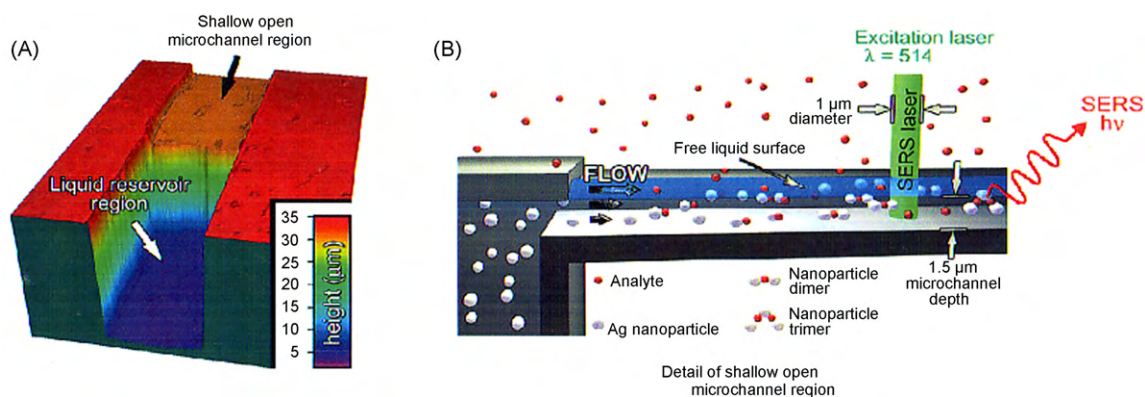


Fig. 8. Spectrafluidics has developed an open-top microfluidic device to collect explosives from the air and detect them using a continuously regenerated SERS surface. A solution of silver nanoparticles flows towards a 514 nm laser for Raman spectroscopy. The nanoparticles aggregate around molecules adsorbed from the nearby atmosphere, causing electromagnetic amplification of the Raman signal and enabling sensitive detection after laser excitation in the fluidic channel.

Direct SERS measurements rely heavily on data analysis. Much effort has recently been devoted to the accurate differentiation of species/strains of bacteria and viruses using principal component analysis (PCA) and hierarchical clustering analysis (HCA) [57,58].

Patel et al. developed clever tactics for automatically processing the spectral fingerprints of pathogens by creating a barcode based on the second derivative of each spectrum [59]. This tactic greatly simplifies the data and allows reliable automated processing. Each of the 50 microbes that he has identified using the developed barcoding has had a distinctive signature.

Moskovits and co-workers developed a field-portable chemical detector that combines free surface microfluidics with SERS [60]. The system draws gaseous analytes onto a SERS substrate. The developed device has been utilized for the detection of explosive and has been licensed by a start-up company, SpectraFluidics. The company is planning to develop a Raman detector, smoke-detector-style, to detect explosives vapours from a distance (Fig. 8).

3. Conclusions

Different modes of Raman spectroscopy continue to emerge as new screening tools for forensic and homeland security applications. The mature portability, selectivity and ease of operation of the current Raman spectroscopic devices make this mode of spectroscopy the most suitable technique for near-real time field

interrogations of different hazards. Raman Remote sensing, spatially offset Raman and surface enhancement Raman spectroscopy proved to be very valuable in obtaining fingerprints of a wide variety of chemical and biological hazards. These techniques have demonstrated noticeable success in conducting high through output field investigations with minimum or no sample preparation.

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