

# Non-invasive detection of concealed liquid and powder explosives using spatially offset Raman spectroscopy

C. Eliasson, N. A. Macleod and P. Matousek

Central Laser Facility, STFC, Rutherford Appleton Laboratory, HSIC, Didcot, Oxon OX11 0QX, UK

Contact | [pavel.matousek@stfc.ac.uk](mailto:pavel.matousek@stfc.ac.uk)

## Introduction

The non-invasive detection of explosives through containers or packaging represents a considerable analytical challenge, which has attracted particular attention in recent years due to a heightened threat of terrorism. The difficulty in detecting these substances derives from the wide variety of packaging in which they can be readily concealed. Raman spectroscopy holds great potential in this area due to its high chemical specificity, experimental simplicity and its ability to be deployed as a portable battery-powered device. Presently, the key problem preventing its use in this area stems from interfering fluorescence and Raman signals originating from the packaging overwhelming the subsurface Raman signals one aims to recover and analyse. Here we demonstrate an approach, based on an adaptation of Spatially Offset Raman Spectroscopy (SORS)<sup>[1]</sup>, a concept developed through access to the LSF's Ultrafast Spectroscopy Laboratory, which facilitates a dramatic reduction of these interfering signals for a wide variety of packaging types, permitting a much wider applicability than possible before. Details of this work are given in references<sup>[2]</sup> and <sup>[3]</sup>.

The SORS approach relies on the collection of Raman spectra from spatial regions *offset* from the point of illumination on the sample surface (see figure 1). The laterally offset Raman spectra contain different relative contributions from sample layers located at different depths due to the wider lateral diffusion of photons emerging from greater depths<sup>[4]</sup>. Consequently, for larger spatial offsets, a greater suppression of the surface layer signal (relative to the sub-surface layers) is achieved. For a two-layer system such as beverage containers containing liquid, the residual surface signal contribution can potentially remain within the offset (subsurface) spectrum. This can be numerically removed using a scaled subtraction of the Raman spectrum obtained at the zero offset to produce the Raman signature of the liquid within the container. Importantly, the SORS approach is also capable of effectively suppressing interfering fluorescence if it originates from the surface layer of the probed medium. A review of these techniques is given in Ref. <sup>[4]</sup>.

In its standard form, SORS does not permit, automatically, the simultaneous interrogation of diffusely scattering and transparent samples. The proposed Raman geometry satisfies this requirement by utilising the insensitivity of the SORS scheme to the laser beam

incidence angle at the sample surface. This insensitivity stems from the fact that the photon directionality is quickly 'forgotten' as the photons undergo a massive number of scattering events within the diffusely scattering medium upon entering the turbid sample. This enables the angle of incidence to be set such that the laser beam, when presented with a transparent medium, passes *through* the container into the sample to the object plane of the Raman imaging system, which can be placed several millimetres *below* the sample surface within the probed liquid. Such an arrangement is shown to be effective with both transparent and turbid media.

Another key distinction from conventional backscattering Raman spectroscopy is the ability to displace the laser beam incidence point on the sample surface to *beyond* the direct line of sight of the Raman collection system. Consequently, fluorescence or Raman signals emanating from transparent bottle materials, which can often overwhelm the weaker Raman signal of the contained liquid, can be strongly suppressed without compromising the collection efficiency of the Raman system. This permits the sensitive interrogation of challenging samples such as green glass bottles, which can pose an insurmountable obstacle to conventional backscattering Raman spectroscopy<sup>[5]</sup>.

The past development of SORS focused solely on its use with highly scattering media. The study presented here demonstrates that the SORS concept is also applicable with mixed, stratified, samples such as those consisting of a diffusely scattering container with a transparent liquid. In this case, the mechanism of photon transport to the Raman detection region is different from that of standard SORS where photon diffusion dominates<sup>[2]</sup>. The concept also naturally works with the reverse situation where the container is transparent and the liquid diffusely scattering. In this case, the photon propagation mechanism is similar to that utilised in standard SORS, i.e. photon diffusion within the liquid medium. These characteristics make the proposed concept particularly effective and applicable to a wide variety of packaging and samples.

## Experimental

The experiments presented here were performed using an 830 nm laser with 250 mW average power. The Raman spectra were collected using a bundle of optical fibres and dispersed through a spectrograph onto a thermoelectrically cooled CCD camera. The full details of the experimental

setup are given references<sup>[2]</sup> and<sup>[3]</sup>. The acquisition times were 1 s for each spatial offset. The Raman signal was collected at two spatial offsets through two subsequent measurements, at zero offset and at 10 mm. The zero spatial offset Raman spectrum is used to remove the residual Raman spectrum of the surface (container wall) which can potentially contaminate the 10 mm spatially offset spectrum using a scaled subtraction approach to

cancel this residual surface contribution. To demonstrate the potential of the deployment of this technique in the field by a non-specialist, the scaled subtraction of the two offset spectra was performed 'blind' in an automated way with no human intervention. The pure Raman spectrum of the liquid obtained can then be compared with a library data set containing known explosive constituents using standard procedures.

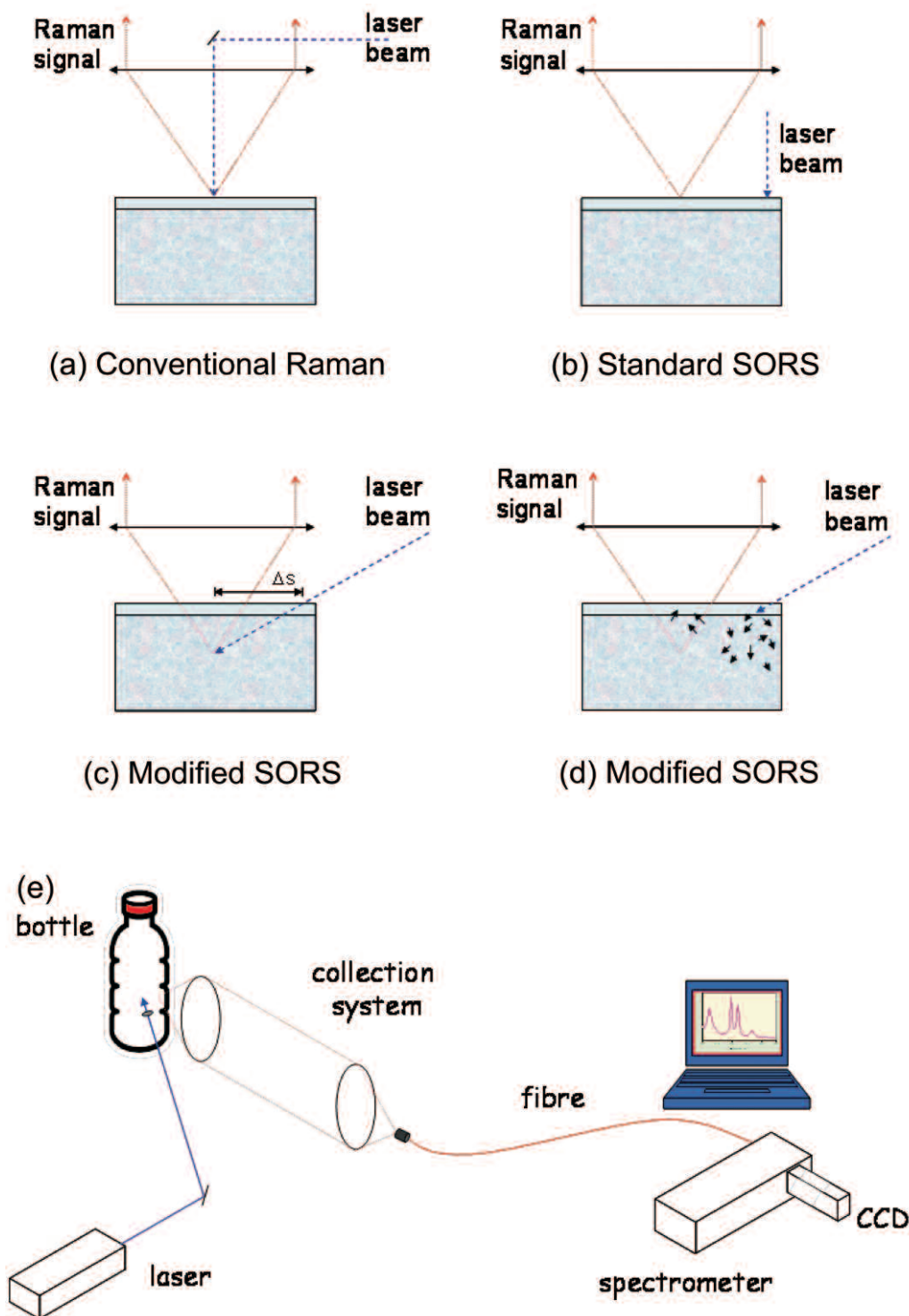


Figure 1. Schematic illustration of (a) conventional backscattering Raman geometry, (b) the standard SORS approach and (c) adapted SORS with transparent and (d) turbid samples. (e) Illustration of the overall experimental setup.

To demonstrate the capability to detect liquid explosives, experiments were performed on a common container typically carried by air-travel passengers in their carry-on luggage with the content substituted with a 30% aqueous solution of hydrogen peroxide ( $\text{H}_2\text{O}_2$  (aq)). Hydrogen peroxide is a critical constituent of a number of liquid explosive mixtures and is readily available as a hair colouring developer to oxidise hair. It can be used, for example, to form the extremely unstable explosive material hexamethylene triperoxide diamine (HMTD)<sup>[6]</sup>. Hydrogen peroxide could be smuggled to the terrorist scene, e.g. on board an aircraft, either premixed with other chemical constituents or as a separate component to be mixed on board. In either case, for the explosive to be effective, a relatively concentrated solution of hydrogen peroxide is required<sup>[6]</sup> such as that used in this study. In a separate experiment sugar was used in the same container to demonstrate the ability of the technique to detect powder explosives concealed in these objects. The same acquisition times were used in both measurements.

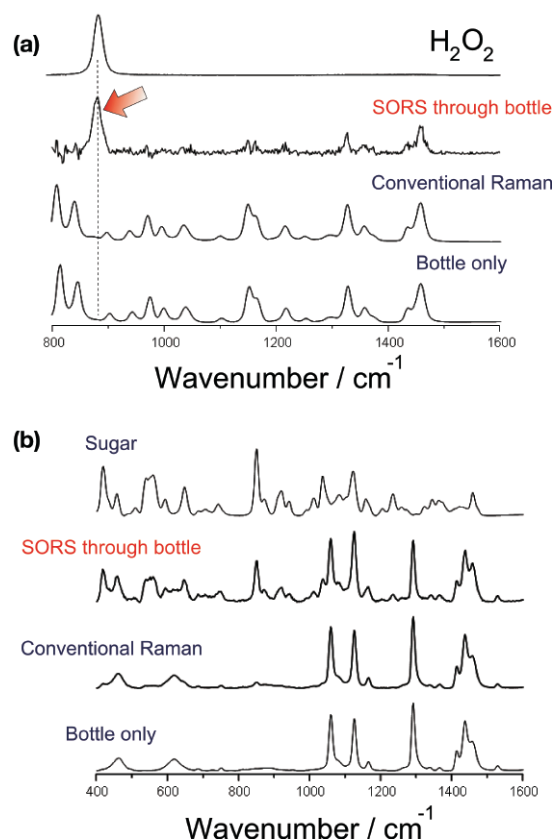
#### Numerical processing of spectra

Raw spectra were processed using MATLAB (version R2006b, The Mathworks, Natick, MA, USA) with the PLS toolbox (version 4.0, Eigenvector Research, Wenatchee, Wash., USA) with both in-built and user-created routines. Fluorescence backgrounds were removed using a polynomial fitting routine with a non-negative spectral peak constraint<sup>[7]</sup>. Corrections were applied using polynomials of order 1 (linear) to 6. The choice of polynomial is assessed through numerical integration of the area under the corrected spectrum; the polynomial order was chosen as the highest order which results in a significant decrease in the area under the spectrum. The spectrum of the subsurface layer was resolved using an automated routine which performs a scaled subtraction of the spatially offset spectrum from that recorded at zero offset. Raw spectra were baseline corrected using polynomials of order 1 to 6 and the resulting spectra were scaled and subtracted. The order of the polynomial was the only variable selected by the operator.

### Results and discussion

The results of probing a white plastic bottle containing  $\text{H}_2\text{O}_2$  solution non-invasively are shown in figure 2. The container is highly diffusely scattering and presents an insurmountable challenge to conventional Raman spectroscopy; the signature Raman band of  $\text{H}_2\text{O}_2$  at  $876\text{ cm}^{-1}$  is completely swamped by Raman signals originating from the container wall. A conventional Raman instrument would therefore be unable to detect its presence. In contrast, SORS, after the 'blind' automated spectra processing using two spectra obtained at the zero and 10 mm spatial offsets ( $\Delta s$  in figure 1c), dramatically suppresses the surface Raman signatures and clearly identifies the  $\text{H}_2\text{O}_2$  marker band.

From the measurement performed it is estimated that the Raman signal could still be detected if the  $\text{H}_2\text{O}_2$  solution was diluted by an order of magnitude, placing the detection limit on  $\text{H}_2\text{O}_2$  concentration in aqueous solution at around a few percent. The Raman technique (in its basic



**Figure 2. Conventional (CR) and SORS Raman spectra of an L'Oréal sun lotion bottle, filled with (a) 30 %  $\text{H}_2\text{O}_2$ .**

form) is clearly not capable of detecting trace quantities of explosive materials; however, since concentrated solutions of  $\text{H}_2\text{O}_2$  are essential for the effectiveness and viability of liquid explosives this does not present a major obstacle for the deployment of the technique.

An example of detecting powder explosives concealed in the same plastic bottle is illustrated in figure 2. The conventional Raman method is again ineffective due to intense Raman bands originating from the container wall swamping the weaker Raman signatures of the content. In contrast, SORS effectively removes this overwhelming signal and permits the sensitive interrogation of the internal content. In both cases, SORS provides Raman spectra of the internal content with sufficient clarity to permit *unambiguous identification* of the chemical composition. The powder identity could also be established when the analysed objects were wrapped in one layer of cotton cloth of a thickness of 0.31 mm (data not shown).

## Conclusions

We have demonstrated an effective Raman spectroscopic approach for the detection of liquid and powder explosives concealed in a wide range of plastic containers. The technique, which has a substantially higher sensitivity than that available from conventional Raman spectroscopy, allows the effective suppression of both the fluorescence and Raman light emanating from the container wall.

## Acknowledgements

The authors wish to thank Dr Darren Andrews, Professor Anthony Parker, Dr Tim Bestwick and Professor Mike Dunne of the Science and Technology Facilities Council for their support of this work. The financial contribution of CLIK Knowledge Transfer, EPSRC (grant number EP/D037662/1), NESTA and the Rainbow Seed Fund is acknowledged. The Home Office Science Branch is thanked for useful discussions.

## References

1. P. Matousek, I. P. Clark, E. R. C. Draper, M. D. Morris, A. E. Goodship, N. Everall, M. Towrie, W. F. Finney and A. W. Parker, *Appl. Spectrosc.* **59**, 393-400 (2005).
2. C. Eliasson, N. A. Macleod and P. Matousek, *Anal. Chem.* **79**, 8185-8189 (2007).
3. C. Eliasson, N. A. Macleod and P. Matousek, Non-invasive Detection of Powders Concealed within Diffusely Scattering Plastic Containers, *Vibrational Spectroscopy*, in press.
4. P. Matousek, *Chem. Soc. Rev.* **36**, 1292-1304 (2007).
5. A. Nordon, A. Mills, R. T. Burn, F. M. Cusick and D. Littlejohn, *Anal. Chim. Acta.* **548**, 148-158 (2005).
6. W. S. Becker and W. M. Dale, *Forensic Science Communications*, <http://www.fbi.gov/hq/lab/fsc/backissu/oct2003/index.htm> (October 2003).
7. C. A. Lieber and A. Mahadevan-Jansen, *Appl. Spectrosc.* **57**, 1363-1367 (2003).