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Non-invasive detection of powders concealed within diffusely scattering plastic containers

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Abstract

We demonstrate the potential of Spatially Offset Raman Spectroscopy (SORS) for the non-invasive detection of chemicals in powder form (e.g. illicit drugs or explosives) concealed within diffusely scattering containers. The performance of the technique is compared with that of conventional backscattering Raman spectroscopy. Enhanced sensitivity is achieved by the SORS technique's inherent ability to effectively suppress fluorescence and Raman contributions originating from the packaging. The application is demonstrated on the non-invasive detection of sugar hidden in diffusely scattering plastic bottles.

Keywords: Raman; Non-invasive; Illicit

1. Introduction

The non-invasive identification of the chemical constituency of unknown powder substances through transparent and diffusely scattering plastic containers is, naturally, of particular interest to law enforcement agencies. Prime applications include the detection of drugs of abuse or other harmful substances hidden in plastic containers or the detection of powdered explosives in security applications. Raman spectroscopy holds particular promise in this area because of its compatibility with water-containing samples and the large penetration depth of near-infrared (NIR) photons into common materials. The usefulness of this technique in detecting illicit drugs through transparent or semitransparent materials has already been demonstrated [1,2]. The detection of such compounds through diffusely scattering plastic bottles is, however, a much more challenging task; conventional backscattering Raman spectroscopy, in most cases, has insufficient sensitivity to the compounds held within the container due to the intense, and overwhelming, Raman or fluorescence signals emanating from the packaging material. This is due to the excessive bias of the conventional backscattering approach (where light is collected from the same area of the sample surface that is illuminated by the laser) to the surface layers of the probed material.

Recently, several new methods based on Raman spectroscopy capable of probing diffusely scattering samples at much greater depths have been developed. These fall into two basic categories, temporal and spatial. The temporal approach relies on the impulsive excitation of a sample and time resolved detection (on a picosecond timescale) of Raman signals using photon counting [3] or optical Kerr gating [4–8]. The spatial method, Spatially Offset Raman Spectroscopy (SORS) [9,10], is instrumentally much simpler and, in many practical situations, provides higher quality data. The method is based on the collection of Raman signals from spatial regions offset from the point of illumination on the sample surface (see Fig. 1).

Since the first experimental demonstration of the SORS concept on powders [9], the technique has been used in numerous applications including the demonstration of Raman tomography in turbid media by Schulmerich et al. [11], the non-invasive Raman spectroscopy of bones on cadavers by Schulmerich et al. [12] and the first observation of the Raman spectrum of a human bone *in vivo* by our collaborative team [13]. Its potential has also been demonstrated in pharmaceutical

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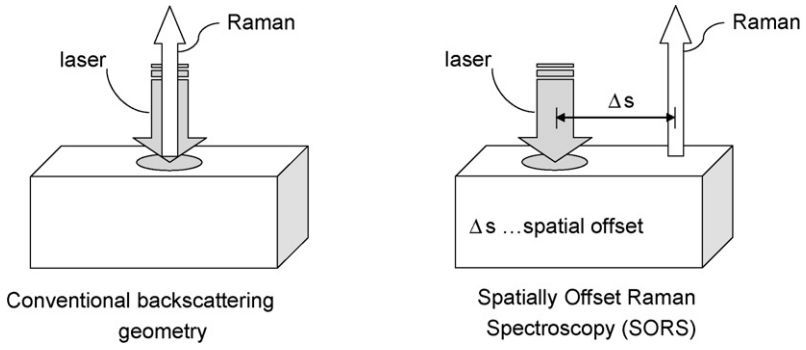

Fig. 1. Schematic diagram of the experimental geometries for conventional backscattering Raman spectroscopy and Spatially Offset Raman Spectroscopy.

applications such as the non-invasive monitoring of counterfeit drugs through packaging [14]. Recently, a more sensitive variant, inverse SORS, has been proposed and demonstrated [15,16].

In parallel research [17,18], it has also been shown that transmission Raman spectroscopy [19,20] can be very effective for probing the *bulk* content of non-absorbing or weakly absorbing pharmaceutical and biological samples at depths well beyond the reach of conventional approaches. The transmission concept has been applied to the non-invasive probing of the bulk content of pharmaceutical tablets [17] and capsules where it effectively suppresses both the Raman and fluorescence components emanating from capsule shells [18]. A similar suppression effect has also been utilised in the probing of calcifications in breast tissue phantoms through a 16-mm slab of tissue [21]. Recent developments in non-invasive Raman methods and their application areas are reviewed in reference [22].

In this work, we demonstrate the ability of the SORS technique to probe common plastic containers, in a non-invasive manner, to permit the detection and identification of the powders held within. As an example we used common table sugar (sucrose) as a model system to represent a chemical in solid form hidden inside common containers carried by passengers through airports.

2. Experimental

2.1. Apparatus

The experimental apparatus used was configured as follows: the probe beam was generated using a temperature stabilised diode laser for Raman spectroscopy operating at 830 nm (Process Instruments Inc., PI-ECL-830-300-FS). The laser power at the sample was 250 mW with a laser spot diameter of ~1 mm. The beam was spectrally purified by removing any residual amplified spontaneous emission components from its spectrum using three 830 nm bandpass filters (Semrock) and brought onto the sample surface displaced from the collection point by an offset (Δs) of up to 8 mm. Conventional Raman spectra were acquired by setting the spatial offset to zero.

Raman light was collected in 180° collection geometry using a 50-mm diameter lens with a focal length of 60 mm. The scattered light was collimated and passed through a 50-mm diameter holographic notch filter (830 nm, Kaiser Optical Systems Inc.) to suppress the elastically scattered component of light. A second lens, identical to the first one, was used to image, with magnification 1:1, the sample interaction zone onto the front face of the fibre probe. The Raman light was propagated through a fibre bundle system of length ~2 m to the linear fibre end which was oriented vertically and placed in the input image plane of a Kaiser Optical Technologies Holospec 1.8i NIR spectrograph. Raman spectra were collected using a NIR back-illuminated deep-depletion TE cooled (−80 °C) CCD camera (Andor Technology, DU420A-BR-DD, 1024 × 256 pixels) by binning the entire chip vertically. The Raman spectra are not corrected for the variation of detection system sensitivity across the spectral range. The acquisition time for each spectrum was 1 s. The fibre bundle collecting the Raman light consisted of 22 active fibres made of silica with a core diameter of 220 μm, a doped silica cladding diameter of 240 μm and a polyimide coating of 265 μm diameter. The fibre numerical aperture was 0.37. The bundle was custom made by CeramOptec Industries Inc.

2.2. Numerical processing of spectra

Raw spectra were processed using MATLAB (Version R2007a, The Mathworks, Natick, MA, USA) with the PLS toolbox (Version 4.0, Eigenvector Research, Wenatchee, WA, 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 [23]. 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. The area under the scaled and subtracted spectrum provided the criteria for optimising the scaling factor. Raw spectra were baseline corrected and the resulting spectra were scaled and subtracted. The order of the polynomial was the only variable selected by the operator.

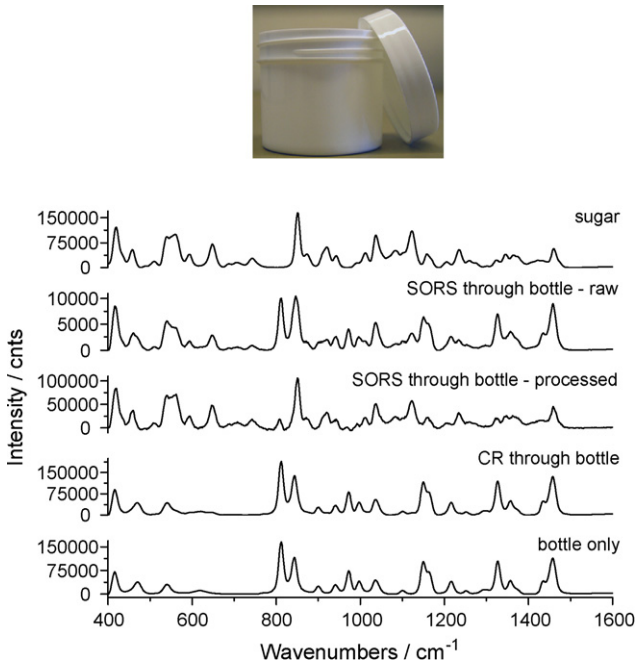

Fig. 2. Conventional (CR) and SORS Raman spectra (raw and processed) of a white plastic bottle (thickness 1.2 mm) containing sugar. The bottom spectral trace is the Raman spectrum of the empty bottle itself and is essentially identical to the conventional Raman spectrum of the bottle containing sugar. The SORS spectrum (processed) after scaled subtraction of two spectra obtained at different spatial offsets (0 and 8 mm) shows a close resemblance to the reference spectrum of sugar (top trace) with some weak, residual, features originating from the bottle. All spectra have been automatically background corrected.

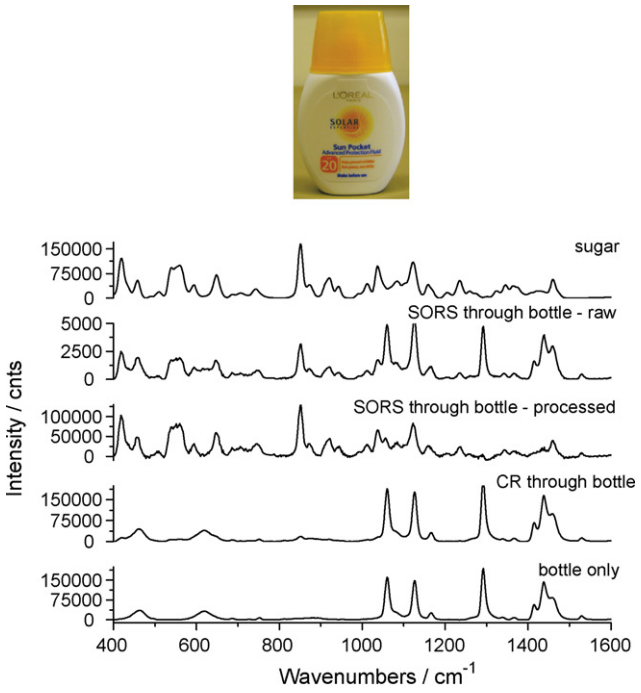

Fig. 3. Conventional (CR) and SORS Raman spectra (raw and processed) of a L'Oréal sun lotion bottle (thickness 1.1 mm) containing sugar. The bottom spectral trace is the Raman spectrum of the empty bottle itself and is essentially identical to the conventional Raman spectrum of the bottle containing sugar. The SORS spectrum (processed) after scaled subtraction of two spectra obtained at different spatial offsets (0 and 8 mm) shows a close resemblance to the reference spectrum of sugar (top trace) with some weak, residual, features originating from the bottle. All spectra have been automatically background corrected.

2.3. Samples

The concealed substance referred to as sugar used in these experiments was sucrose ($C_{12}H_{22}O_{11}$).

3. Results and discussion

Results for a white plastic bottle containing sugar are shown in Fig. 2. Such containers are readily available in drug stores and are commonly used by travellers to transfer a smaller amount of moisturising cream or other products for the purposes of travel to save space in carry-on luggage, or used as a pill bottle to store medication required during the flight. Fig. 2 compares the performance of the conventional backscattering Raman method with the proposed SORS approach. The Raman spectra of the individual components are also shown for comparison. The container is highly diffusely scattering and presents an insurmountable challenge to conventional Raman spectroscopy. A conventional Raman instrument would therefore be unable to detect the presence of sugar (or other powder) in this container.

In contrast, SORS, after the 'blind' automated processing, using spectra obtained at zero and 8 mm spatial offsets with a scaling factor set to cancel the residual surface layer contribution present in the 8-mm SORS spectrum, dramatically suppresses the surface Raman signatures and clearly, and unequivocally, identifies sugar as the content of the container. The raw 8 mm spatial offset SORS spectrum is also shown for illustration. The zero spatial offset SORS spectrum is equivalent to the conventional Raman spectrum. Since only one spectrum is available from conventional Raman spectroscopy, such subtraction is not possible without prior knowledge of the Raman spectrum of the empty container.

Another example is illustrated in Fig. 3 where a plastic bottle, originally containing sunscreen lotion, was probed. 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).

In a number of applications it may be beneficial that the sample does not come into contact with the instrument. In the reported measurements the samples were separated by 6 cm from the nearest optical element. It is possible to increase this distance further, if desired, without sacrificing the performance by scaling the size of the collection optics to maintain the Raman collection solid angle. For example, stand-off distances of 60 cm and 1.8 m would be feasible with 50 cm (f = 60 cm)

and 1.5 m (f = 1.8 m) diameter collection lenses respectively, with no loss in signal quality. The reduction of the lens diameter (and consequently the Raman collection solid angle) leads to a rapid diminishment of the collected signal. For example, a 1.8-m stand-off collection arrangement with a 50-cm diameter collection lens (f = 1.8 m) would require an increase in the acquisition time, or laser power, by a factor of eight to maintain the same spectral quality.

4. Conclusions

We have demonstrated that SORS holds great potential for the detection of illicit or harmful materials concealed in diffusely scattering plastic containers. The technique has a substantially higher sensitivity than that available from conventional Raman spectroscopy. Other uses of the technique include quality control and the authentication of food and other chemical products through packaging.

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