ANALYTICA CHIMICA ACTA 607 (2008) 50–53

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Non-invasive detection of cocaine dissolved in beverages using displaced Raman spectroscopy

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

Central Laser Facility, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0QX, United Kingdom

ARTICLE INFO

Article history:
Received 8 September 2007
Received in revised form
7 November 2007
Accepted 12 November 2007
Published on line 19 November 2007

Keywords:
Raman
Illicit drugs
Cocaine
Spatially Offset Raman
Spectroscopy
Non-invasive

ABSTRACT

We demonstrate the potential of Raman spectroscopy to detect cocaine concealed inside transparent glass bottles containing alcoholic beverages. A clear Raman signature of cocaine with good signal-to-noise was obtained from a ~300 g solution of adulterated cocaine (purity 75%) in a 0.7 L authentic brown bottle of rum with 1 s acquisition time. The detection limit was estimated to be of the order of 9 g of pure cocaine per 0.7 L (~0.04 moles L^{-1}) with 1 s acquisition time. The technique holds great promise for the fast, non-invasive, detection of concealed illicit compounds inside beverages using portable Raman instruments, thus permitting drug trafficking to be combated more effectively.

1. Introduction

Currently, one of the major routes for smuggled cocaine into the UK involves dissolution of the drug in common alcoholic beverages such as rum. Relatively large quantities of the drug (of the order of 100's of grams) can be concealed inside a single bottle and then separated upon arrival at its destination by simple evaporation of the liquid content. A single bottle can be carried by a smuggler across an entry port into the country; larger quantities can be concealed within a consignment of genuine drink bottles. The detection of such items is extremely difficult, particularly in the latter case, as currently there are no simple, effective and rapid means of inspecting such samples without opening each individual bottle. There is clearly an urgent need in this area for a fast, portable non-invasive detector of concealed drugs. In this work, we demonstrate that a variant of Raman spectroscopy, Displaced Raman spectroscopy, fulfils these requirements.

This research builds on our earlier work on the detection of powder and liquid explosives in plastic and other types of packaging, both transparent and diffusely scattering (translucent). In these experiments we used a variant of Spatially Offset Raman Spectroscopy [1–9], we call here Displaced Raman Spectroscopy [10] to distinguish it from standard SORS. A major advantage of the concept is that any interfering Raman and fluorescence contributions originating from the bottle itself are effectively suppressed as demonstrated experimentally in our earlier work on liquid explosives, which also included highly fluorescing glass bottles [10]. Fluorescence emission can be a particularly severe problem to conventional backscattering Raman spectroscopy

* *Corresponding author*. Tel.: +44 1235 445377; fax: +44 1235 445888.
E-mail address: P.Matousek@rl.ac.uk (P. Matousek).
0003-2670/$ – see front matter
doi:10.1016/j.aca.2007.11.023

with coloured bottles (e.g. brown or green) where, in some cases, it can pose an insurmountable obstacle by swamping the weaker Raman signal [11]. An additional advantage is that the Displaced Raman geometry automatically acts, i.e. with no need for reconfiguration, as a standard SORS method when presented with diffusely scattering samples instead of transparent containers as we demonstrated earlier [10]. This feature substantially broadens its applicability. It should also be noted that a 90° Raman collection geometry [12] used with some laboratory Raman instruments, would also result in the effective suppression of surface layer Raman and fluorescence signals when applied to transparent samples. However, such an arrangement would not be suitable for SORS with diffusely scattering samples due to its inability to provide, at least, two SORS spectra of different spatial offsets thus permitting a complete numerical elimination of the surface Raman signal [9].

In the Displaced Raman concept, the basic delivery of the laser radiation into the bottle through its wall is accomplished by sending a narrow, weakly focused laser beam into the sample at an angle, typically ~30–60°, such that the beam intersects the Raman collection zone located within the contents of the bottle as illustrated in Fig. 1. This basic layout was adopted in the experiments presented here. However, other Raman collection and delivery geometries with various benefits are also possible with the Displaced Raman concept [10], notably one where two axicon lenses [13] are used to deliver a convergent laser beam in the shape of a ring, a geometry which benefits from the distribution of the laser power across a larger area on the container surface and the absence of a sharp focus along its propagation axis, thus limiting the potential for laser damage to the sample and minimising the risk of accidental harm to the operator or a bystander.

Raman spectroscopy holds particular promise in this application 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 the conventional Raman technique in chemically characterising both powders and liquids through transparent or semitransparent containers has already been shown [14,15]. Here we demonstrate, for the first time, the technique's viability for the non-invasive detection of cocaine dissolved in alcoholic beverages.

2. Experimental

2.1. *Apparatus*

The experimental apparatus used in the detection of dissolved cocaine 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 using three 830 nm bandpass filters (Semrock). The laser beam was brought onto the

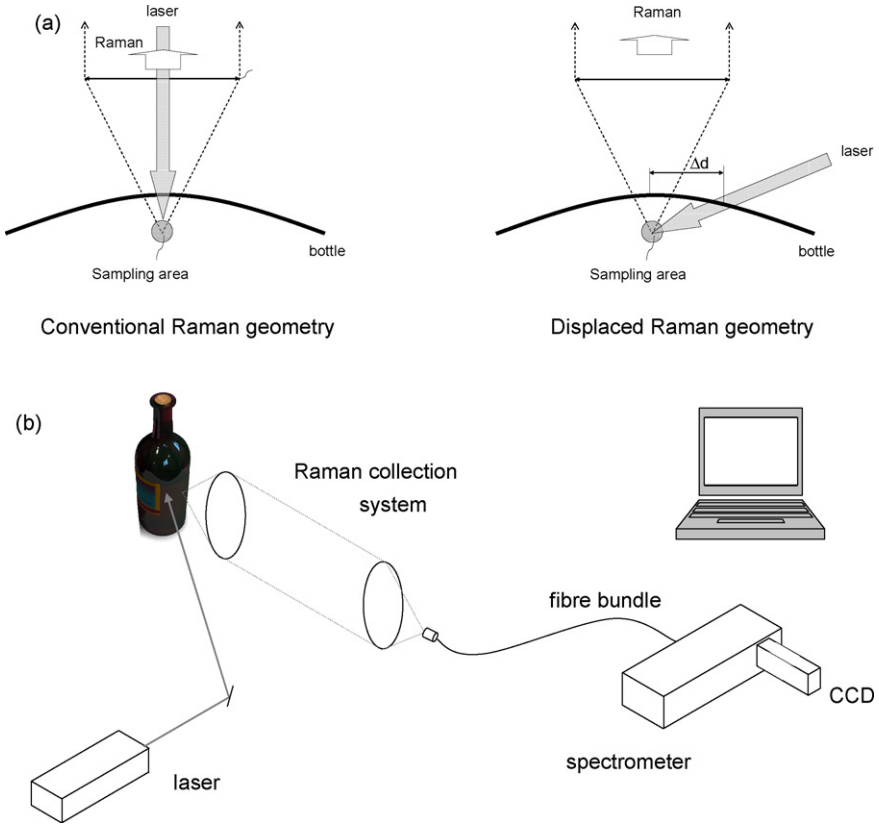

Fig. 1 – (a) Schematic diagrams of the experimental geometries for conventional backscattering Raman and Displaced Raman spectroscopy. (b) Overall experimental layout used in the non-invasive measurements.

sample at a 45° angle with a displacement from the collection axis (Δd) of 10 mm (see Fig. 1a). The collection zone was placed ~10 mm below the surface of the probed bottle.

Raman light was collected 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 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. *Samples*

Samples were prepared by dissolving ~300 g of adulterated cocaine (75% pure cocaine) in 'Havana Club Añejo Especial Golden Rum' beverage (0.7 l, 40% alcohol by volume, ethanol concentration ~7 moles L^{-1}) corresponding to a pure cocaine concentration of ~1 moles L^{-1}. The sample was probed in the original brown glass bottle. An identical bottle with no cocaine was used in control measurements. Experiments were also performed using a bottle containing ~200 g of 75% pure cocaine (data not shown).

2.3. *Data processing*

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 [16]. 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.

3. Results and discussion

The results of the non-invasive probing of the rum bottles with and without cocaine are shown in Fig. 2a. The Raman spectrum without the cocaine is dominated by ethanol; the other principal component, water, is a very weak Raman scatterer. The presence of cocaine results in the appearance of new, intense, Raman bands in agreement with those reported earlier for cocaine in powder form [17]. In particular the intense doublet at around 1000 cm^{-1}, spectrally distinct from the major bands of ethanol, can serve as an easy marker for the presence of this substance. Fig. 2b shows the spectrum of the cocaine content after subtraction of the rum Raman contributions. The high intensity and good signal-to-noise of the bands permitted the use of relatively short acquisition times (1 s). From this data it can be estimated that the cocaine could also be detected under the same experimental conditions even if its intensity was 25-times lower, i.e. 25-times diluted than the solution used. This is based on the measurement of noise

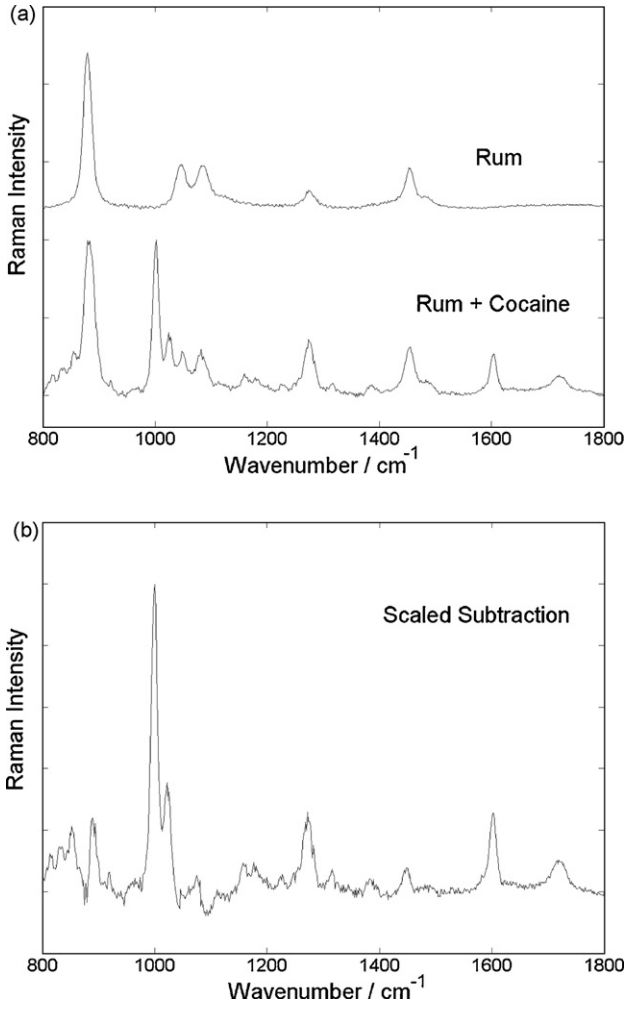

Fig. 2 – (a) The results of the non-invasive probing of bottles containing rum with (bottom trace) and without dissolved cocaine (top trace). The Raman spectrum of pure rum is dominated by ethanol. The presence of cocaine results in the appearance of new Raman bands. (b) A scaled subtraction of the two spectra canceling the ethanol contribution. The spectrum is identifiable as that of cocaine. The spectra were measured using a probe wavelength of 830 nm, laser power of 250 mW and 1 s acquisition time.

in the area where the dominant cocaine band is present and assuming the signal would be detectable down to a level of ~4-times the noise amplitude. This places the detection limit at the level of ~12 g of adulterated cocaine (75% pure cocaine) per 0.7 L corresponding to a pure cocaine concentration of 0.04 moles L^{-1}. Although it should be noted that it is high doses of cocaine that are most likely to be encountered in practical situations when screening bottles at customs check points.

The linear dependence of Raman signal on sample concentration offers the possibility of using measured Raman intensities for the determination of the relative concentration of cocaine in the bottle by simply comparing the intensities of the ethanol and cocaine bands.

It should be noted that highly fluorescent ingredients and/or impurities present within the solution could diminish the sensitivity of this technique as intense fluorescence can potentially swamp the Raman signal. Operating in the NIR region of the spectrum, as in this work, greatly reduces this fluorescence. However, in an extreme case, an unusually high level of fluorescence could be present. If so this, in its own right, could be used as a marker of a suspicious content warranting a more detailed invasive inspection. Alternatively, more specialist methods could be used to suppress fluorescence including Kerr gated Raman spectroscopy which has previously been demonstrated on illicit powder drugs by Littleford et al. [18].

Importantly, the use of displaced Raman spectroscopy also opens a potential for monitoring substances, either in powder or liquid form, concealed in plastic diffusely scattering bottles with the same experimental arrangement as reported earlier for liquid explosives [10]. The simplicity of the concept makes it amenable for adoption in conventional portable Raman instruments permitting deployment of the technique in the field. The combination with automated data processing and band assignment would also eliminate the need for the presence of a specialist to interpret the Raman data. If required, the device could also be incorporated into an automated system with a conveyer belt for rapid inspection of the large quantities of beverage bottles carried in wholesale shipments.

4. Conclusions

We have demonstrated a variant of Raman spectroscopy that is a viable tool for the rapid, non-invasive, detection of cocaine concealed within alcoholic beverages. A ~300 g solution of cocaine (purity 75%) was detected non-invasively in a 0.7 L glass bottle of rum with good sensitivity within 1 s acquisition time. The sensitivity limit for pure cocaine in this application is estimated to be around 9 g per 0.7 L (0.04 moles L^{-1}) with 1 s acquisition time. Other uses of the technique include quality control and the authentication of food and other chemical products through packaging.

Acknowledgements

We wish to thank a UK Government Department for providing advice, arranging samples and for secure transport of the samples to our lab and the Forensic Science Service for the preparation of the test samples in their laboratories. The authors also wish to thank Dr. Darren Andrews and Dr. Tim Bestwick of the CLIK Knowledge Transfer and Professor Anthony Parker and Professor Mike Dunne of the Science and Technology Facilities Council for their support of this work. The financial contribution of CLIK Knowledge Transfer and the EPSRC (grant EP/D037662/1) is also acknowledged.

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