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In situ detection of cocaine hydrochloride in clothing impregnated with the drug using benchtop and portable Raman spectroscopy

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This study describes the application of benchtop and portable Raman spectroscopy for the *in situ* detection of cocaine hydrochloride in clothing impregnated with the drug. Raman spectra were obtained from a set of undyed natural and synthetic fibres and dyed textiles impregnated with the drug. The spectra were collected using three Raman spectrometers: one benchtop dispersive spectrometer coupled to a fibre-optic probe and two portable spectrometers. Despite the presence of some spectral bands arising from the natural and synthetic polymer and dyed textiles, the drug could be identified by its characteristic Raman bands. High-quality spectra of the drug could be acquired *in situ* within seconds and without any sample preparation or alteration of the evidential material. A field-portable Raman spectrometer is a reliable technique that can be used by emergency response teams to rapidly identify unknown samples.

Keywords: cocaine impregnated textiles; *in situ* detection; Raman spectroscopy; forensic

Introduction

Drug trafficking and smuggling is an ongoing battle facing law enforcement agencies. Cocaine smuggling is a high-value pursuit for smugglers and has been attempted by a wide diversity of concealment methods including the use of bottled liquids,[1] canned milk,[2] wax and book bindings,[3] wicker baskets and bamboo sticks[4] and suspensions in cans of beer.[5] Smuggling of illicit drugs 'starched' into cloth[3] and dissolved in rubber-like material has also been identified,[6] and, in particular, traffickers have used clothing impregnated with cocaine for smuggling. These materials are prepared by pouring cocaine solutions onto the clothing and allowing the solvent to evaporate.[7,8] The main laboratory procedures used for identifying the drugs of abuse in these cases included gas chromatography with flame ionization detection (GC-FID),[2] gas chromatography mass spectrometry (GC-MS)[3] and Fourier-transform infrared-attenuated total reflectance (FT-IR-ATR).[4] These analytical techniques require preparation steps in which the sample to be analysed is extracted into an organic solvent before injection into GC. Also, each of these approaches requires isolation and/or destruction of the analyte and these techniques therefore alter or destroy the evidential material during analysis.

Raman spectroscopy has been shown to be an effective technique for forensic screening of drugs of abuse.[9–15] Raman spectroscopy produces molecular-specific spectra and, in most cases, sample preparation is minimal, allowing for the non-destructive analysis of tablets, powders and liquids *in situ*. This is particularly important with regard to the speed of analysis, prevention of sample contamination and preservation of evidential material.[16] Raman instrumentation has been traditionally restricted to the laboratory due to the sophistication required to analyse the inherently weak scattering process. However, recent advances have allowed the production of compact and field portable Raman systems that are commercially available. Principle developments allowing this technological advancement are the advent of compact, powerful, stable and reliable near-infrared solid-state laser sources along with the use of high-resolution charge coupled device (CCD) detectors.[17] These developments in addition to spectral identification software have facilitated the commercial availability of portable fibre-optic Raman probes for in-field applications. Several studies have appeared in the literature addressing the application of portable Raman spectroscopy to the *in situ* detection and the identification of drugs of abuse[18–20] and explosives.[21–23]

In this study, we have investigated the application of fibre-optic Raman spectroscopy to the *in situ* identification of cocaine hydrochloride on a variety of fibres and textiles impregnated with the drug. In such situations, we demonstrate that fibre-optic Raman spectroscopy can be applied effectively for the acquisition of Raman spectra of the drugs of abuse. The spectra were readily obtained *in situ* non-destructively without necessitating sample extraction or pre-treatment. The spectra obtained were identified by searching against an identification library, which is desirable for automated database recognition algorithms; an important consideration for future application with non-spectroscopist

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evaluation of data. Furthermore, the non-destructive and non-contact character of the technique offers a special role for Raman spectroscopy in the first-pass evaluation screening of materials of forensic relevance.

Experimental

Samples

Drugs

Pure cocaine hydrochloride was obtained from Sigma-Aldrich and was used without further purification. Four hundred and fifty milligrams of the drug were dissolved in 1 ml of an ethanol/water mix.

Fibres and textiles

A set of natural and synthetic fibres was used in this study in an attempt to cover the wide range of textile materials found in real life. Natural fibres included wool, silk and cotton. Polyester fibres were used as a representative of synthetic fibres. Also, pieces of blue denim and an orange-coloured T-shirt were used in this study as representatives of dyed clothing commonly found on an everyday basis. A bundle of fibres and textile pieces about 0.5 cm in length were soaked with the solution of cocaine hydrochloride. Then the fibres bundles and textile pieces were left overnight to dry by evaporation of ethanol prior to spectrometric examination.

Spectroscopic instrumentation

Raman spectra were collected from the cocaine-impregnated fibre bundles and textile pieces using three different spectrometers; one benchtop spectrometers, a Renishaw *InVia* Reflex dispersive spectrometer and two portable spectrometers; a Renishaw RX210 'Raman-in-a-suitcase' (RIAS) portable Raman analyser and a Delta Nu Inspector Raman FSX instrument.

Renishaw InVia reflex spectrometer

Raman spectra were obtained using a Renishaw *InVia* Reflex spectrometer (Wotton-under-Edge, UK), operating with a high-power NIR diode laser emitting at 785 nm and thermoelectrically cooled CCD (400 × 575 pixels) detector, coupled to a Renishaw compact fibre-optic probe with a 25-mm-focal-length lens. The diffraction grating (1200 lines mm^{-1}) gave the spectral range 3200–100 cm^{-1} with a spectral resolution of 2 cm^{-1}. Daily calibration of the wavenumber axis was achieved by recording the Raman spectrum of a silicon wafer (1 accumulation, 10 s) in static mode. If necessary, an offset correction is performed to ensure that the position of the silicon band is calibrated at 520.5 ± 0.1 cm^{-1}. Spectra were recorded from cocaine-impregnated clothing with the accumulation of one scan, 10-s exposure and 28-mW laser power at the sample. Spectra were not corrected for instrument response. The spectrometer was controlled by PC with instrument control software (Renishaw WiRE 2 Service Pack 9).

Using the instrument in the microscopic mode (Renishaw *InVia* dispersive Raman microscope), reference Raman spectra of cocaine hydrochloride, fibres and textiles were obtained to be compared with the spectra collected from the three spectrometers. The Raman scattering was excited with a 785-nm near-infrared diode laser and a 50× objective lens giving a laser spot diameter of 2 µm. Spectra were obtained for a 10-s exposure of the CCD detector in the wavenumber region 100–3200 cm^{-1} using the extended scanning mode of the instrument. With 110 mW laser power, one accumulation was collected for cocaine hydrochloride and five accumulations were collected for the fibres and textiles.

Renishaw portable Raman analyser RX210 'RIAS'

The RIAS (Wotton-under-Edge, UK) was equipped with a diode laser emitting at 785 nm and a thermoelectrically cooled (400 × 575 pixels) CCD detector, with a coupled Renishaw compact fibre optic probe, equipped with a 20× (NA 0.35) Olympus objective lens. The diffraction grating (1000 lines/mm) afforded the spectral range 2100–100 cm^{-1} with a spectral resolution of 10 cm^{-1}. The power of the diode laser was 49 mW at the sample. Daily calibration of the wavenumber axis was achieved by recording the Raman spectrum of a silicon wafer (one accumulation, 10-s exposure) for static modes. If necessary, an offset correction is performed to ensure that the position of the silicon band is 520.5 ± 0.1 cm^{-1}. Spectra were recorded with the accumulation of one scan, 10-s exposure. Spectra were not corrected for instrument response. The spectrometer was controlled by a portable PC with instrument control software (Renishaw WiRE 2 Service pack 8).

Delta Nu inspector Raman FSX

The Inspector Raman instrument (Laramie, WY, USA) was equipped with a diode laser emitting at 785 nm and a thermoelectrically (1 × 1024 pixels) CCD detector and a custom 25-mm-focal-length nose piece. The spectral range was 2000–200 cm^{-1} with a spectral resolution of 8 cm^{-1}. The laser power at the sample was 37 mW. Daily calibration of the wavenumber axis was achieved by recording the Raman spectrum of polystyrene within the calibration routine built into the software. Spectra were recorded with the accumulation of one scan, 10-s exposure. Spectra were not corrected for instrument response. The spectrometer was controlled by a portable PC with instrument control software (Nu Spec Version 4.75).

Results and Discussion

For these studies, drug-impregnated clothing was simulated by treating a piece of denim with a methanolic solution of cocaine hydrochloride. After the cloth was left to dry, a scanning electron micrograph (Quanta 400, FEI Company, Cambridge, UK) was taken (Fig. 1). The image clearly shows that microcrystals of the drug molecules form between the denim fibres.

Cocaine hydrochloride–impregnated undyed natural fibres

Raman spectra were collected from the cocaine hydrochloride–impregnated cotton bundle using the three spectrometers (Fig. 2). Comparison of these spectra with the reference spectrum of cocaine hydrochloride showed that the drug could be easily identified by its Raman spectrum. The Raman spectrum of pure cocaine hydrochloride has several characteristic features that can be used to identify the drug, such as the benzoate ester (–C═O–) stretch at 1711 cm^{-1}, the aromatic ring (–C═C–) stretch at 1594 cm^{-1}, the aromatic ring breathing mode at 998 cm^{-1}, the pyrrolidine ring (–C–C–) stretch at 866 cm^{-1} and the piperidine ring (–C–C–) stretch at 784 cm^{-1}.[24] It is clearly observed that these key signature bands are clearly observed in the spectra collected from the three spectrometers and the results compare

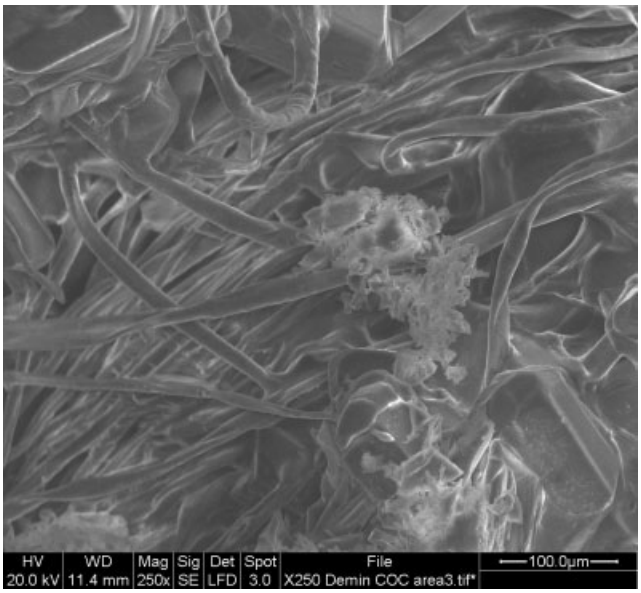

Figure 1. Scanning electron micrograph of a piece of denim impregnated with cocaine hydrochloride.

favourably with the reference cocaine hydrochloride. The total acquisition times were 25, 20 and 60 s for data collected from the Delta Nu Inspector Raman FSX, the RIAS portable spectrometer and the Renishaw *InVia* Reflex Spectrometer coupled to a fibre-optic probe respectively. Also, the spectra collected from cocaine impregnated wool show the characteristic features of cocaine hydrochloride (Fig. 3). Although the spectrum obtained from cocaine-impregnated wool using the Delta Nu inspector Raman FSX instrument contains two bands assigned to the wool; the amide I ν(C═O) mode at 1654 cm^{-1} and the δ (CH_2) mode at 1445 cm^{-1}.[25] The presence of these bands (marked with asterisks in Fig. 3(a)) did not prevent the identification of the characteristic signature bands of the drug. Similarly, the characteristic Raman features of cocaine hydrochloride could be clearly observed in the Raman spectra collected from cocaine-impregnated silk (Fig. 4). The spectra are of a high quality with a good signal/noise ratio and no appreciable background due to fluorescence. The NIR laser at 785 nm gave excellent spectra for the drug and there was no detectable background fluorescence. There were no significant bands that could be assigned to the fibre substrate; the Raman scattering from the drug is usually relatively intense compared to that from the fibres allowing ready differentiation from interference from the fibres' substrate bands.

Cocaine hydrochloride–impregnated undyed synthetic fibres

Figure 5 shows the spectra obtained from cocaine hydrochloride–impregnated polyester fibres. In addition to the bands arising from the drug, the resulting spectra also contain several peaks assigned to the polyester fibres (marked with dashed lines in Fig. 5): these appear at 1724 cm^{-1} [ν(C═O)], 1610 cm^{-1} (aromatic ring stretch) and 854 cm^{-1} [ρ (CH)].[26,27] The polyester bands at 1724 and 1610 cm^{-1} overlap with the drug bands at 1711 and 1594 cm^{-1} respectively. While the overlapped bands at *ca.* 1600 cm^{-1} are clearly resolved, the polyester feature at 1724 cm^{-1} appears as a shoulder at a higher wavenumber on the cocaine benzoate ester band at 1711 cm^{-1}. However, in each case, the identity of cocaine hydrochloride was readily established and the drug characteristic features at 1711, 1594, 998, 866 and 784 cm^{-1} could be clearly identified.

Cocaine hydrochloride–impregnated dyed textiles

The previous data were acquired from cocaine hydrochloride–impregnated natural and synthetic undyed fibres. Of course, many real textile samples are dyed and it is necessary to determine how this will affect the Raman spectra obtained from the drug-impregnated clothing. In particular, fluorescence background and the functional group features, arising from the dye molecules, may conceal diagnostic Raman spectral features of the drug. The spectra obtained from cocaine-impregnated denim show the characteristic Raman features of cocaine hydrochloride. While a band corresponding to the strongest band in the Raman spectrum of the denim substrate (attributable to blue indigo dye) at 1570 cm^{-1} is also present in the spectra, this band did not interfere with the identification of the drug (Fig. 6). Also, Fig. 7 shows the Raman spectra collected from cocaine hydrochloride–impregnated orange-coloured T-shirt specimens. It is observed that the reference Raman spectrum of the T-shirt contains a few cotton

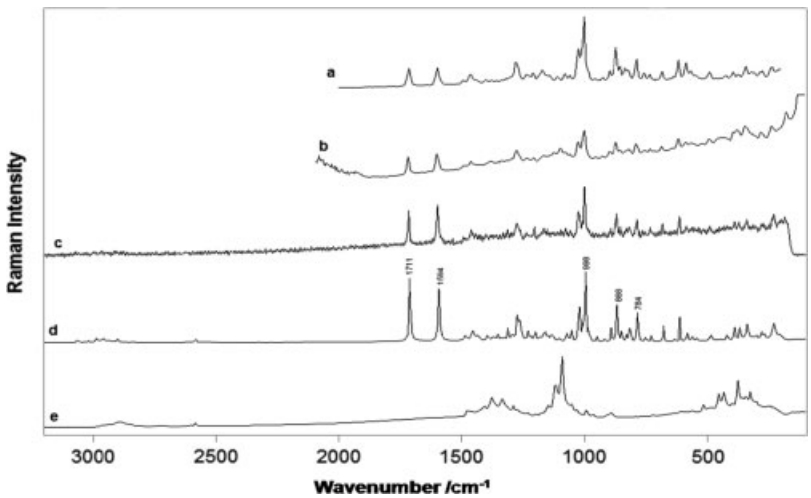

Figure 2. Raman spectra of cocaine-impregnated cotton collected using (a) Delta Nu portable, (b) RIAS portable, (c) benchtop Renishaw *InVia* Reflex dispersive spectrometer coupled to a fibre optic probe, (d) reference cocaine HCl and (e) reference cotton fibres.

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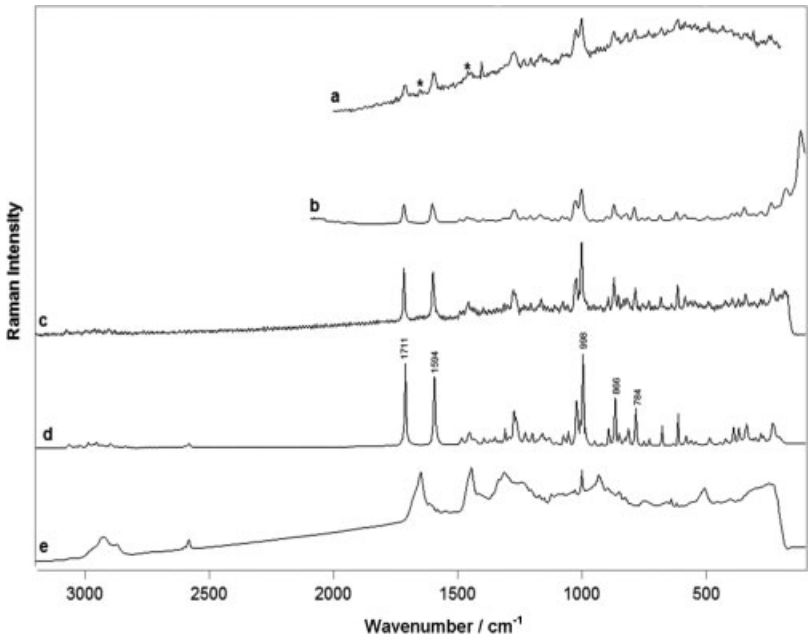

Figure 3. Raman spectra of cocaine-impregnated wool collected using (a) Delta Nu portable, (b) RIAS portable, (c) benchtop Renishaw *InVia* reflex dispersive spectrometer coupled to a fibre optic probe, (d) reference cocaine HCl and (e) reference wool fibres.

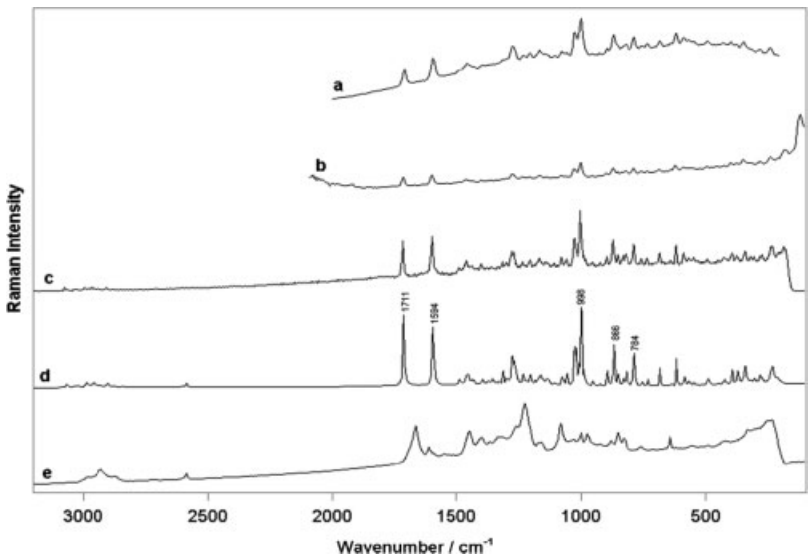

Figure 4. Raman spectra of cocaine-impregnated silk collected using (a) Delta Nu portable, (b) RIAS portable, (c) benchtop Renishaw *InVia* reflex dispersive spectrometer coupled to a fibre optic probe, (d) reference cocaine HCl and (e) reference silk fibres.

bands superimposed on a fluorescence background, which may swamp the Raman signals from the drug. A broad fluorescent background could be seen in the spectra collected from the three spectrometers but in all the cases the diagnostic Raman features of cocaine hydrochloride were usually clearly visible above the background and the characteristic drug bands were clearly observed.

Data comparison and library searching

Raman spectra from all instruments were exported to the Galactic *.SPC format. Spectra were then compared using GRAMS AI (Version 8.0, Thermo Electron Corp, Waltham, MA, USA); the Raman spectra were not subjected to any data manipulation or processing techniques and are reported as collected. We have used the spectral ID function of GRAMS AI to construct instrument-specific libraries, which contain spectra of a range of narcotics and explosives. This allows the user to rapidly identify unknown compounds by searching a database held on the spectrometer computer. Once the spectral data has been collected from each spectrometer, a library search was carried out. The search algorithm provided by GRAMS AI software involves using double-sided peak matching (with shoulder detection), non-baseline corrected, 32-bit data construction and using the first derivative least squares. Essentially, the software compares the peaks-position search data with data in the constructed libraries for the highest number of peak position matches. Table 1 presents the percentage matches for peaks searches of the constructed libraries. The data show

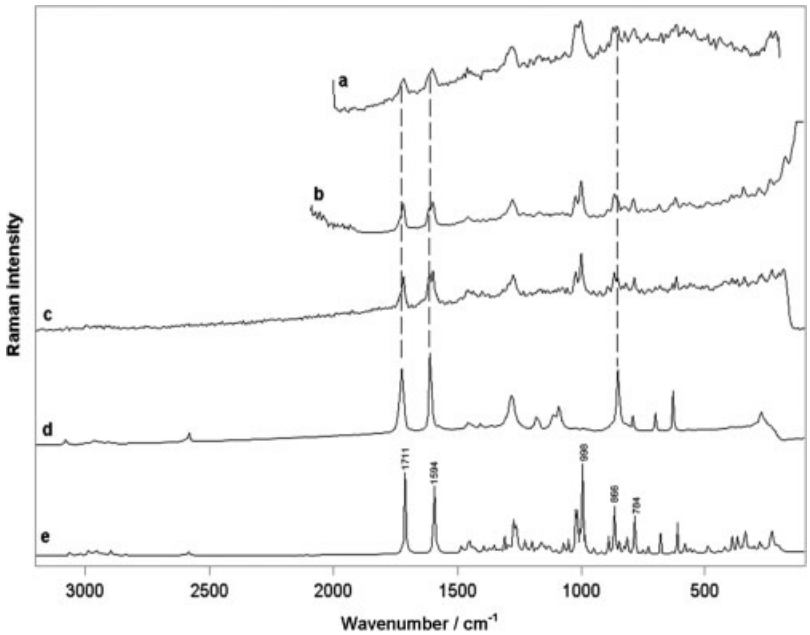

Figure 5. Raman spectra of cocaine-impregnated polyester collected using (a) Delta Nu portable, (b) RIAS portable, (c) benchtop Renishaw *InVia* reflex dispersive spectrometer coupled to a fibre optic probe, (d) reference polyester fibres (dashed lines indicate polyester bands) and (e) reference cocaine HCl.

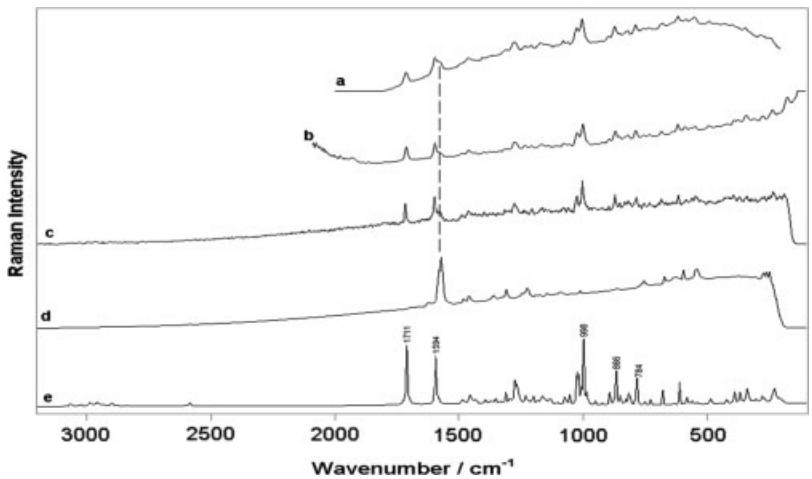

Figure 6. Raman spectra of cocaine-impregnated denim collected using (a) Delta Nu portable, (b) RIAS portable, (c) benchtop Renishaw *InVia* Reflex dispersive spectrometer coupled to a fibre optic probe, (d) reference denim fibres (dashed line indicates denim band and (e) reference cocaine HCl.

that in all the cases a positive identification can be made, with the highest match being cocaine hydrochloride in all the cases.

These results show a clear application of portable Raman spectroscopy as a primary screening technique for drugs-of-abuse in live situations. Data could be obtained rapidly and, using a library search, unambiguous identification of unknown contaminants could be made. Identification can be readily obtained, for example, in a port of entry using the portable spectrometers and, on taking the sample to the laboratory, identification can be confirmed using the benchtop Raman spectrometer coupled to a fibre-optic probe or other hyphenated analytical techniques. In addition, our approach leaves the drug unaltered and in its original environment without risking operator exposure or evidence contamination. Furthermore, the rapid acquisition of Raman spectra *in situ* in the field offer a reliable method for forensic scientists and police agencies that has the potential for rapidly identifying unknown samples.

Conclusions

This is the first study that illustrates the use of portable Raman spectroscopy for the detection and identification of cocaine hydrochloride in clothing impregnated with the drug. The presence of spectral bands arising from the fibre polymers and/or dyes presented no difficulty in establishing the identity of the drug, which could be clearly identified by its characteristic Raman bands. Raman spectra of the drug could be readily obtained *in situ* non-destructively, within 20–60 s and without sample preparation. These results demonstrate the implementation of Raman spectroscopic techniques to emergency field situations

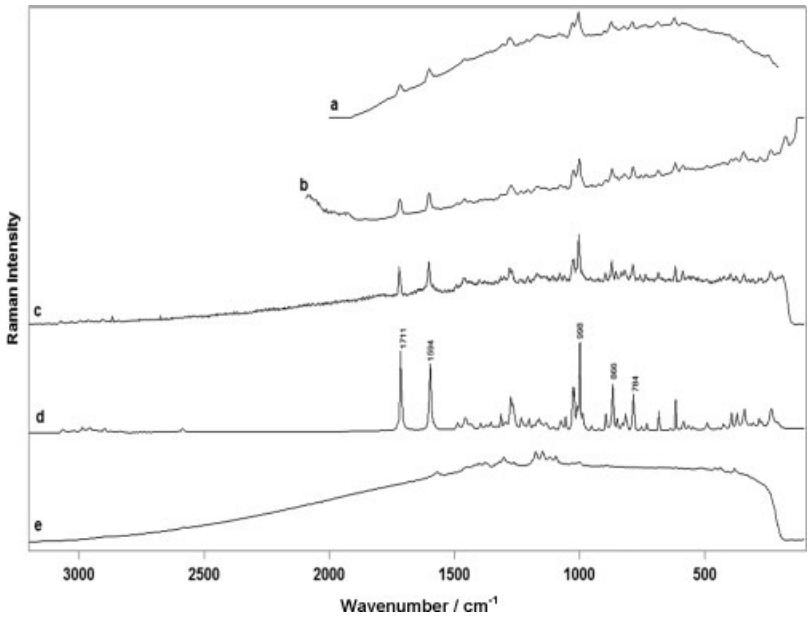

Figure 7. Raman spectra of cocaine-impregnated T-shirt collected using (a) Delta Nu portable, (b) RIAS portable, (c) benchtop Renishaw *InVia* reflex dispersive spectrometer coupled to a fibre optic probe, (d): reference cocaine HCl and (e) reference T-shirt fibres.

Table 1. Library searching matches of the spectra obtained from the cocaine-impregnated clothing using three spectrometers

Instrument Cocaine-impregnated sample	Renishaw *InVia* Library match (%)	RIAS Match (%)	Delta Nu Match (%)
Cotton	77	92	89
Wool	82	98	79
Silk	74	93	74
Polyester	80	97	76
Denim	67	94	78
T-shirt	67	89	79

and indicate a high level of performance that should extrapolate to actual field application.

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