Research article

Drug Testing and Analysis

Received: 9 July 2010 Revised: 27 July 2010 Accepted: 29 July 2010 Published online in Wiley Online Library: 30 September 2010

(www.drugtestinganalysis.com) DOI 10.1002/dta.169

A forensic case study: the detection of contraband drugs in carrier solutions by Raman spectroscopy

A. D. Burnett,[a] H. G. M. Edwards,[b] M. D. Hargreaves,[b] T. Munshi[b]* and K. Page[b]

Recently, cocaine has been concealed by dissolving it in alcohol and then transporting it in solution through ports and airports. At the present time it is very difficult to detect cocaine in this form in these environments. However, it has been shown that Raman spectroscopy can successfully detect the presence of these drugs without removing specimens from their containers. Using two portable 785 nm instruments and a 1064 nm laboratory-based instrument, several common containers used in smuggling were analyzed with varying concentrations of cocaine in ethanol solutions. The presence of cocaine is detectable to about 6% *w*/*v* in most containers. Green glass presents a problem at 785 nm due to fluorescence but by switching to 1064 nm this can be removed. To apply this technique to real samples as met within law enforcement scenarios, cocaine was dissolved in a selection of dark and white rums including Lamb's Navy Rum™, Brugal Añejo™, Bacardi™ and Captain Morgan™; cocaine was detected in all these rum solutions.

Keywords: cocaine; ethanol; limits of detection; Raman spectroscopy; forensic

Introduction

Many attempts are made to transport illegal products into foreign countries through both seaports and airports. Such illegal products include items from endangered species, explosives, and illicit drugs. The smugglers of these illegal materials are constantly trying new and original transport techniques. Therefore, a method of detecting these illegal products is required. It has been shown that it is possible to detect samples through various different plastics and glass with portable instruments using Raman spectroscopy.[1] Further work on explosives samples has identified the ability to remove fluorescence from the spectra obtained and this has implications in identifying interesting material through different coloured glasses, removing background fluorescence emissions.[2]

Another major problem for airports and seaports are illicit drugs. Most of these drugs are solids in plastic bags and therefore identification and detection is relatively easy as they can be seen. Raman spectroscopy can be used for this application. The plastic packaging material of the solid drug is often very thin and so a laser beam can pass through. These materials are often transparent and colourless, meaning that strong fluorescence emission is unlikely to occur and mask the signals of interest.[3] The drug of abuse is usually a mixture of several different additional compounds or diluents (cutting agents), which may occur in far greater quantity than the drug itself and may also be legal substances.[4–6] This makes the detection of the drug more difficult as the legal substances are detected and may mask the signal indicative of the drug. The presence of these additional compounds (cutting agents) may also cause fluorescence. It is possible to distinguish between some drugs such as methamphetamine and related compounds using Raman spectroscopy to a limited degree but only if the main constituents do not fluoresce.[7]

One of the most common illegal drugs smuggled into the United Kingdom is cocaine hydrochloride.[8] Currently, the accepted method for detection is high performance liquid chromatography (HPLC), which is both destructive and requires the container of the substance in question to first be transported to the laboratory and then opened.[9] In its natural form this can be fairly simple; however, when the drug is dissolved in something else detection becomes much more difficult. Often alcoholic solutions such as rum are used to conceal the drug to reduce the chances of the drugs being detected. After successful smuggling operations, the drugs can then easily be recovered by evaporating the alcohol/water solvent. Raman spectroscopy can once again be used for the detection of these drugs as it allows for fast, qualitative data acquisition; it also has the ability to detect materials through their packaging and due to its non-destructive nature. it is a prime choice for forensic identification.[5,10–14] A portable Raman instrument may be the solution to these detection problems as it allows for the fast and effective screening of different solutions over a very short space of time.

Work has been carried out on the detection of alcohol content through glass bottles by Nordon *et al*.[15] to establish whether or not alcohol can be analyzed through glass containers using Raman spectroscopy. In this study, the alcohol content of spirits was measured through the glass container using both near infrared (NIR) and Raman spectroscopy. This technique was developed for

* *Correspondence to: T. Munshi, Division of Chemical and Forensic Sciences, University of Bradford, Bradford, BD7 1DP, UK. E-mail: t.munshi@bradford.ac.uk*

a *School of Electronic and Electrical Engineering, University of Leeds' Leeds, LS2 9JT, UK*

b *Division of Chemical and Forensic Sciences, University of Bradford, Bradford, BD7 1DP, UK*

the spirit-producing industry as a method of monitoring alcoholic content without opening bottles.[15]

The first part of this work shows the detection of cocaine at several concentrations to determine the limit of detection (LOD). The quantities of cocaine usually found in confiscated samples are between 50% and 80% and therefore much greater than any of the lower concentration values and quantities analyzed here. Additionally, most alcohols are not pure ethanol; they contain various different additives and impurities. So, analysis would also need to be carried out to determine whether cocaine can be detected if dissolved in commonly found alcoholic drinks. It is known that a lot of the confiscated samples of cocaine which arrive into the UK are transported in different alcohols, including rum.[16] Based upon this information, several different concentrations of cocaine were analyzed dissolved in several different types of rum and a range of coloured glass and plastic bottles.

Experimental

A Renishaw portable Raman spectrometer (RX210) was used to obtain the spectra of selected cocaine ethanol solutions recorded using a fibre probe attachment operating with 785 nm laser excitation, at 10 cm^{-1} resolution, with a10 s laser exposure time and 1 spectral accumulation. A 20x objective lens was used in all the measurements.

Spectra of the selected cocaine ethanol solutions were additionally recorded on a DeltaNu 'Inspector Raman' spectrometer with 785 nm laser excitation, at 8 cm^{-1} resolution, with a 10 s laser exposure time and 1 spectral accumulation.

FT-Raman spectra were obtained using a Bruker IFS66/FRA 106 instrument using an Nd^{3+}/YAG laser operating at 1064 nm with a 4 cm^{-1} spectral resolution and typically 100 spectral scans. The laser power was set at 200 mW at source, dependent on both the sample type and the colour of the specimen.

Cocaine in ethanol solutions

A 10% w/v dilution was made up by dissolving 1 g of cocaine in 10 cm^3 of ethanol. This concentration was then diluted by adding the required amount of ethanol as to produce a range of concentrations between 0.5% and 10% w/v. Each specimen in this range was analyzed in four different coloured glass containers and two plastic containers. These comprised a clear glass vial, brown glass vial, a light-green glass bottle and a dark-green glass bottle and purple-and-cream-coloured plastic bottles. The samples were analyzed using the FT-Raman, 'Inspector Raman' and the Renishaw RX210 instruments.

Cocaine in rum solutions

Lamb's Navy Rum™, Brugal Añejo™, Bacardi™ and Captain Morgan™ were used as solvents for the cocaine. Both Captain Morgan™ and Lamb's Navy Rum™ are dark rums; Brugal is a pale rum; and Bacardi a white (colourless) rum. Spectra were recorded using both the 785 nm RIAS and DeltaNu portable Raman spectrometers and also at 1064 nm using the laboratory bench-top instrument.

Results and discussion

The application of detection without the need to open a bottle can be transferred to the detection of compounds within the alcohol in glass bottles. Looking at material in glass means that the laser beam must initially travel through the glass once before it reaches the compound and the scattered radiation must also traverse the glass on its way to the detector. This means that the glass has two opportunities to interact with the radiation and affect the spectrum produced. This effect can result in a distortion of the laser beam as the glass acts as a lens that is associated with loss of data as the beam may be absorbed by the glass or by the glass fluorescing and masking signals produced by compounds of interest. Additional factors which affect the spectrum obtained through glass are both the thickness and colour of the container. The surface shape can also affect the resulting spectrum whereby on uneven glass surfaces, the laser may travel through the glass for a longer period of time causing the laser to distort. NIR spectroscopy has been shown to be severely limited by the bottle diameter.[15] The colour of the glass can dramatically affect the spectrum obtained through it as strong absorption/fluorescence can occur.[15] Green glass, for instance, can fluoresce at 785 nm and thus mask a substantial number of important peaks. This means that any spectrum obtained through green glass can be very difficult to identify. Glass colour will also theoretically affect the laser wavelength which can be used as the glass will absorb light at specific wavelengths to give it that colour. Therefore, laser wavelengths which the glass absorbs will produce very poor spectral results. Additional work carried out on explosives has shown that by altering the wavelength of a Raman system, it is possible to obtain the spectrum of different explosive compounds within different coloured glass and plastic containers.[17]

The colourless glass bottles gave good quality results on all the instruments. The glass had relatively little effect on the spectrum of the solution and thus little noise is present. All the major peaks indicative of cocaine at 1730 cm^{-1}, 1603 cm^{-1} and 1003 cm^{-1} were present until 4% w/v on the FT-Raman 1064 nm (Figure 1A) and 6% w/v on the Renishaw RX210 785 nm (Figure 1B) and the 'Inspector Raman' 785 nm (Figure 1C).

Brown glass produced good quality results on the 785 nm instruments but the spectra obtained on the 1064 nm FT-Raman instrument were of a much poorer quality. All the major peaks indicative of cocaine were present on the 785 nm instruments and they remained observable down to a lower limit of 6% w/v on the Renishaw RX210 and the 'Inspector Raman'.

Green glass containers produced good quality results on the 1064 nm FT-instruments compared to the spectra obtained on the 785 nm instruments. Fluorescence of the samples occurred in these containers and so the peaks relating to the ethanol were visible only to a limited degree and the cocaine ethanol peaks were completely masked. After data manipulation it was possible to identify the peaks likely to be caused by the presence of cocaine but these were largely indistinguishable from the noise and fluorescence. The major peaks indicative of cocaine were clearly present on the 1064 nm instrument and remained observable until 6% w/v.

The results obtained through the plastic bottles again gave good results on all the instruments, with a limited degree of noise but peaks representative of cocaine were clearly identified. On the 1064 nm instrument, cocaine was detectable up to 6% w/v in both bottles. At 785 nm using the 'Inspector Raman' cocaine was detectable down to 6% w/v and on the Renishaw RX210 instrument the concentration was 8% w/v in both plastic bottles.

The significant bands of importance at 1730 cm^{-1}, 1603 cm^{-1} and 1003 cm^{-1} are clearly visible at 10% w/v in almost all the

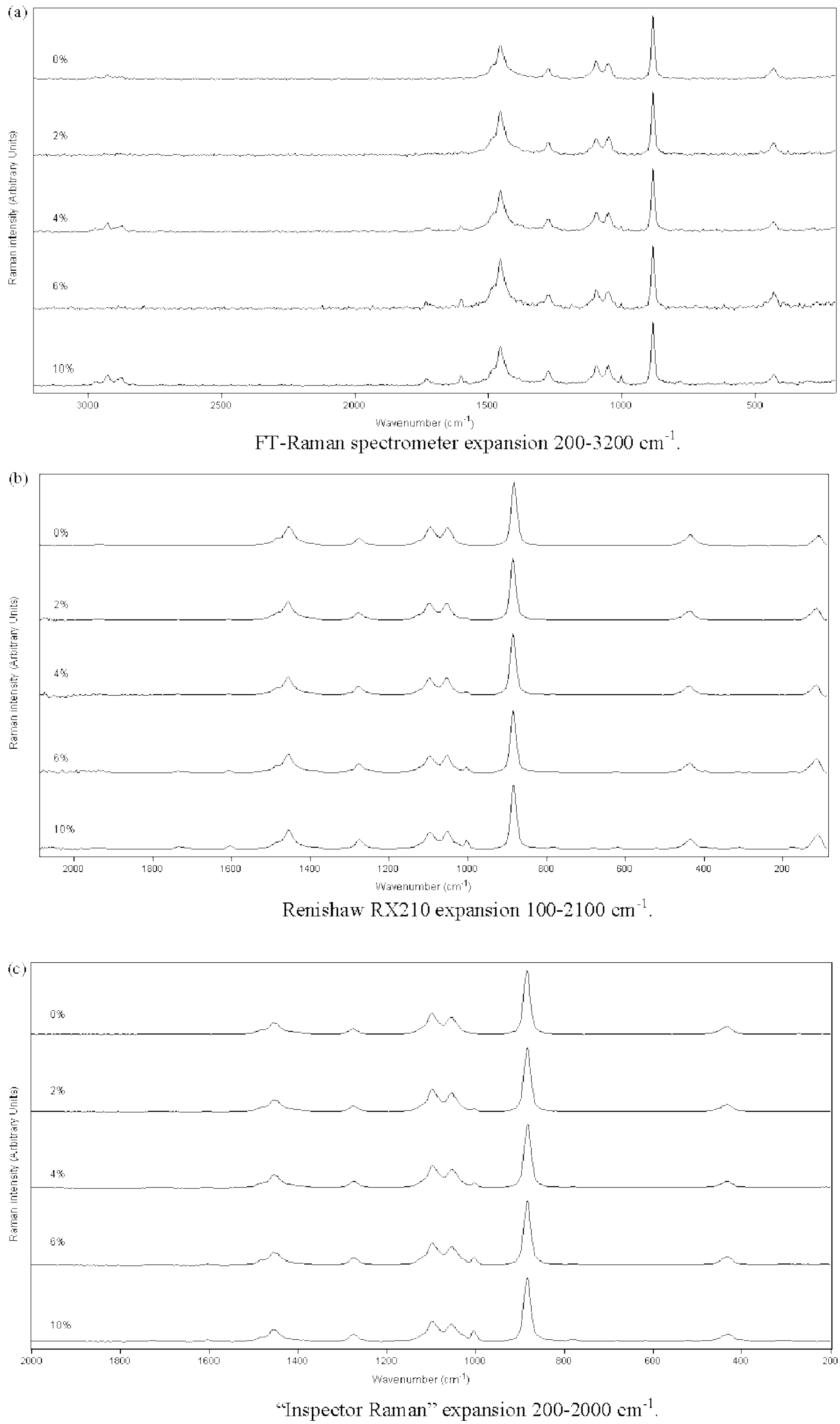
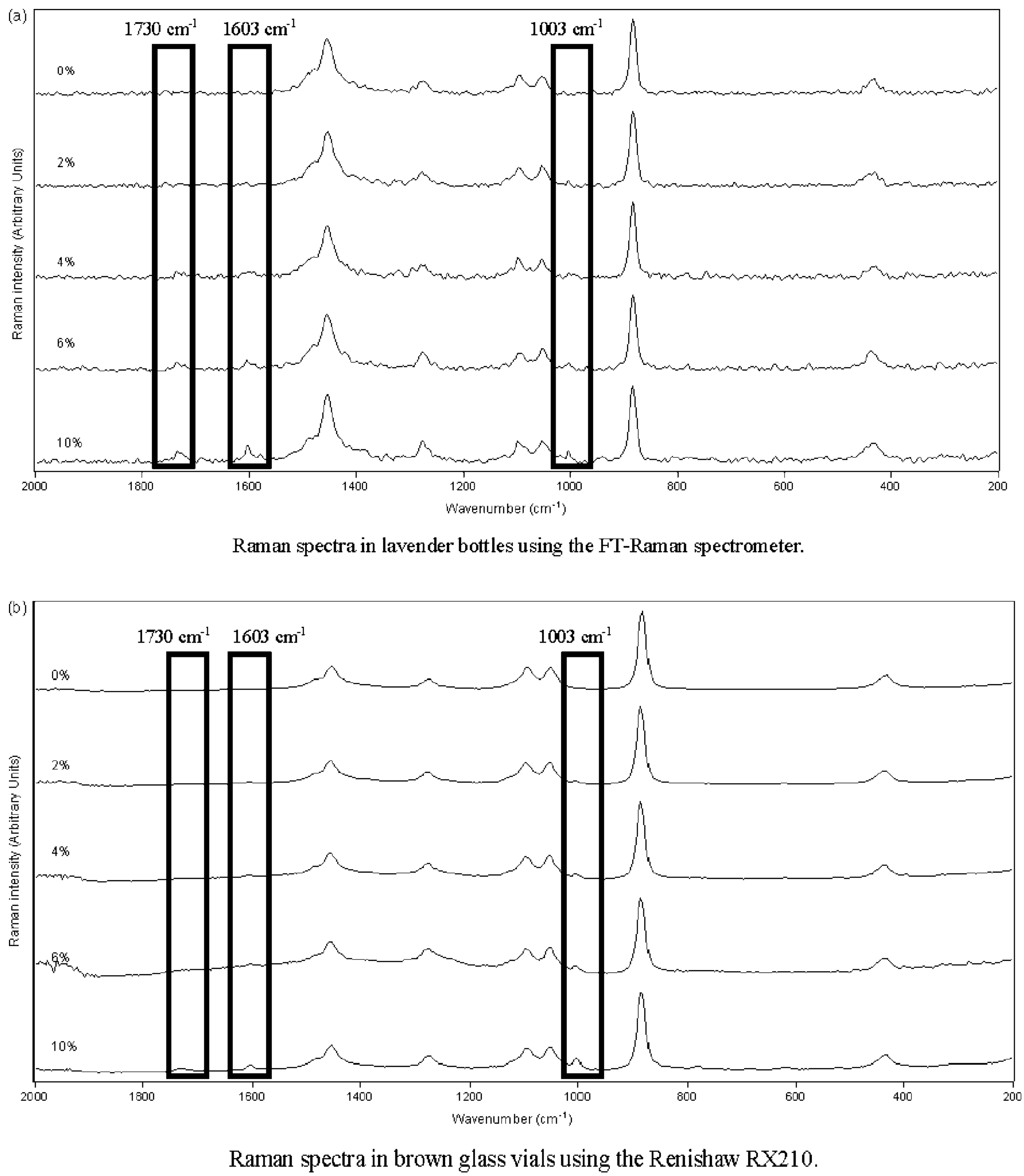


Figure 1. Raman spectra of cocaine ethanol solutions with varying concentrations in clear glass vials obtained using different instruments.



Raman spectra in lavender bottles using the FT-Raman spectrometer.

Raman spectra in brown glass vials using the Renishaw RX210.

Figure 2. Raman spectra of cocaine ethanol solutions with varying concentrations in different containers expansion 200–2000 cm^{-1}.

samples in the range of concentrations studied here. In the majority of instances, they remain visible in a 6% solution. Therefore, it can be stated that cocaine can be detected in the majority of solutions with a concentration of 8% and above. This means that any concentrations of cocaine found in solution in a real-world environment, of between 50% and 80% *w*/*v*, would be easily detectable. To support this conclusion, the LOD for the samples were calculated. Using the band at 1003 cm^{-1} a graph was plotted of the concentration against the intensity. From the linearity equation (y=1.4503x+0.0034) deduced in the graph and using 3σ, from the average of noise over 100 points in the spectrum, an LOD value was deduced of 1.55%. Therefore a real sample containing more than 50% *w*/*v* cocaine would be easily detectable using this experimental scenario.

Different types of glass and plastic had different effects on the spectra produced. Clear glass had little to no effect on the results and brown had very little at 785 nm. Green glass however proved a problem as it fluoresced readily at 785 nm and masked any cocaine peaks within the spectrum. When switching to 1064 nm this fluorescence is removed and peaks can easily be distinguished. The plastic and the brown bottles all produced results of similar quality on all the instruments (Figure 2A and 2B).

At the much higher concentrations of cocaine in rum, the detection of the cocaine was far easier. At 37.5% *w*/*v* the peak at ~880 cm^{-1} in the rum was of similar intensity to that of the peak at 1003 cm^{-1} which corresponds to the presence of cocaine.

Both Brugal and Lamb's Navy Rum™ analyzed at 785 nm fluoresced; this was most likely caused by additional impurities

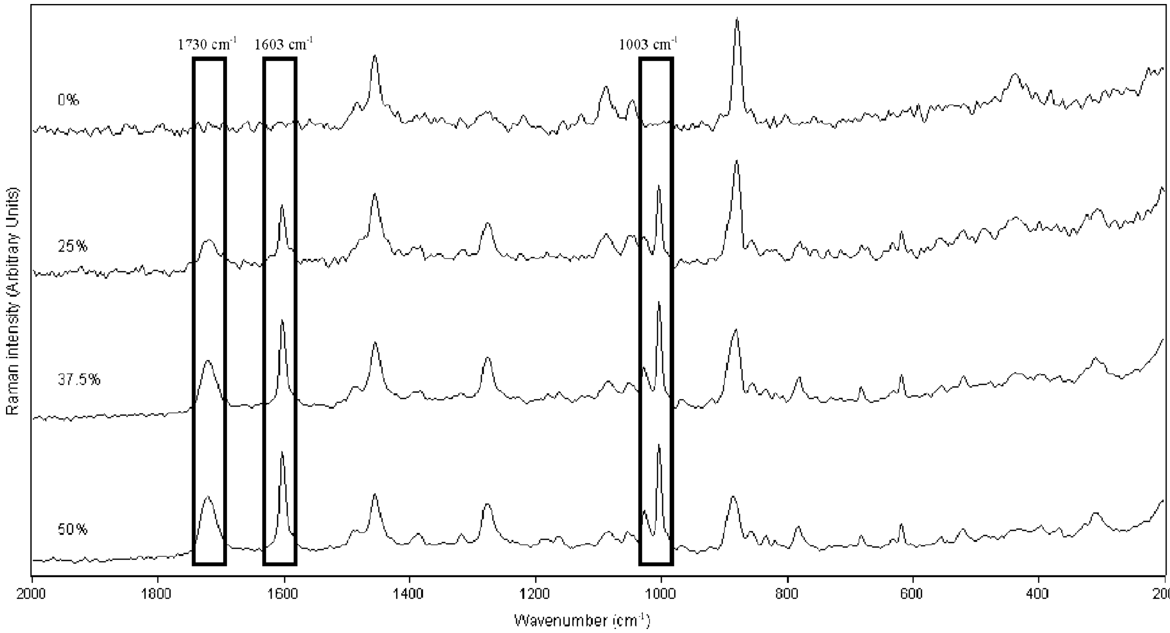


Figure 3. Raman spectra obtained using the FT-Raman spectrometer of cocaine Navy Rum solutions with varying concentrations in clear glass vials expansion 200–2000 cm^{-1}.

within the rum. The major peaks of cocaine at 1730 cm^{-1}, 1603 cm^{-1} and 1003 cm^{-1} were still present but they were partially masked by the fluorescence of the sample. Therefore definitive identification of the peaks could only be obtained via manipulation of the data. At 1064 nm, however, the fluorescence was completely removed and the three expected peaks of cocaine and several smaller additional ones that could be used easily in the identification of the compound (Figure 3).

One additional note is that cocaine does not readily dissolve into rum at these high concentrations. The solution would usually remain cloudy when the cocaine was first added; however within 24 h the cocaine completely dissolved to give a clear solution.

Results have shown that Raman spectroscopy can detect the presence of cocaine in a variety of coloured alcoholic solutions as well as different coloured glass and plastic packaging. It can be used to identify cocaine in rum at concentrations above 8% w/v.

Acknowledgements

We acknowledge the Engineering and Physical Research Council (EPSRC) Grant No. GR/S63052/61, HM Customs and Excise, Her Majesty's Government Communication Centre (HMGCC), the Defence Science and Technology Laboratory (DSTL) and the Home Office Scientific Development Branch (HOSDB).

References

[1] S. D. Harvey, M. E. Vucelick, R. N. Lee, B. W. Wright, *Forensic Sci. Int.* **2002**, *125*(1), 12.

[2] M. L. Lewis, I. R. Lewis, P. R. Griffiths, *Vib. Spectrosc.* **2005**, *38*(1–2), 17.

[3] J. C. Carter, W. E. Brewer, S. M. Angel, *Appl. Spectrosc.* **2000**, *54*(12), 1876.

[4] S. E. J. Bell, D. T. Burns, A. C. Dennis, J. S. Speers, *Analyst* **2000**, *125*(3), 541.

[5] E. Katainen, M. Elomaa, U. M. Laakkonen. E. Sippola, P. Niemelä, J. Suhonen, K. Järvinen, *J. Forensic Sci.* **2007**, *52*(1), 88.

[6] A. G. Ryder, G. M. O'Connor, T. J. Glynn, *J. Raman Spectrosc.* **2000**, *31*(3), 221.

[7] H. Tsuchihashi, M. Katagi, M. Nishikawa, M. Tatsuno, H. Nishioka, A. Nara, E. Nishio, C. Petty, *Appl. Spectrosc.* **1997**, *51*(12), 1796.

[8] K. Edmonds, H. Sumnall, J. McVeigh, M. A. Bellis, *United Kingdom Drug Situation: 2002*. DrugScope and EMCDDA: London, UK, **2004**.

[9] L. Elias, A. H. Lawrence, in *Analysis of Drugs of Abuse*, (Ed. T. A. Gough), Elsevier Science Ireland Ltd **1991**, pp. 373–400.

[10] I. R. Lewis, H. G. M. Edwards, *Handbook of Raman spectroscopy : from the research laboratory to the process line*. Marcel Dekker: New York. **2001**, xiii, 1053 p.

[11] A. H. Kuptsov, *J. Forensic Sci.* **1994**, *39*(2), 305.

[12] C. Cheng, D. N. Batchelder, R. J. Lacey, T. E. Kirkbride, T. G. Sheldon, *J. Forensic Sci.* **1995**, *40*(1), 31.

[13] G. D. Pitt, D. N. Batchelder, R. Bennett, R. W. Bormett, I. P. Hayward, B. J. E. Smith, K. P. J. Williams, Y. Y. Yang, K. J. Baldwin, S. Webster, *IEE Proceedings-Science Measurement and Technology* **2005**, *152*, 241.

[14] N. N. Daeid, R. J. H. Waddell, *Talanta* **2005**, *67*(2), 280.

[15] A. Nordon, A. Mills, R. T. Bum, F. M. Cusick, D. Littlejohn, *Anal. Chim. Acta* **2005**, *548*(1–2), 148.

[16] J. F. Casale, *J. Anal. Toxicol.* **2007**, *31*(3), 170.

[17] I. R. Lewis, N. W. Daniel Jnr, N. C. Chaffin, P. R. Griffiths, M. W. Tungol. *Spectrochim. Acta A* **1995**, *51*(12), 1985.