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Forensic and security applications of a long-wavelength dispersive Raman system

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A novel dispersive system operating at 1064-nm excitation and coupled with transfer electron InGaAs photocathode and electron bombardment CCD technology has been evaluated for the analysis of drugs of abuse and explosives. By employing near-IR excitation at 1064-nm excitation wavelength has resulted in a significant damping of the fluorescence emission compared to 785-nm wavelength excitation. Spectra of street samples of drugs of abuse and plastic explosives, which usually fluoresce with 785-nm excitation, are readily obtained *in situ* within seconds through plastic packaging and glass containers using highly innovative detector architecture based upon a transfer electron (TE) photocathode and electron bombarded gain (EB) technology that allowed the detection of NIR radiation at 1064 nm without fluorescence interference. This dispersive near-IR Raman system has the potential to be an integral part in the armoury of the forensic analyst as a non-destructive tool for the *in-situ* analysis of drugs of abuse and explosives. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: forensic; dispersive near-IR Raman; 1064 nm; drugs of abuse; explosives

Introduction

The last two decades have seen a significant increase in the utility of Raman spectroscopy in academic, industrial, and governmental laboratories. Recent technological advances have widened the applications of Raman spectroscopy to polymers,[1,2] biological systems,[3–5] process monitoring,[6,7] geological,[8,9] forensic sciences,[10–12] and many other areas. In the forensic arena, Raman spectroscopy is an attractive technique for identifying materials of forensic relevance because of the ease with which fibre-optic probes can be interfaced to small rugged spectrometers that can be used in the field.[13] This has enabled the forensic investigator to deal remotely with potentially dangerous materials that may be sensitive to shock, heat, or light and analyse samples in unlabelled containers, such as those found in clandestine laboratories without the need to open the containers themselves.

The main obstacle in using Raman spectroscopy for the analysis of drugs of abuse and explosives is sample fluorescence.[14] Feasibility studies for the adoption of a portable Raman spectrometer for the identification of drugs of abuse and explosive materials have been investigated by several research groups in an attempt to build an instrument that affords a good compromise between sensitivity to target molecular signals and fluorescence rejection. Explosives have been analysed by both FT- and CCD-Raman spectroscopy in order to determine an appropriate wavelength for constructing a field usable explosive analyser.[14] The authors concluded that 1064-nm excitation eliminates the majority of fluorescence interference although longer data acquisition times are required to attain the desired signal-to-noise ratio (SNR). Also, 785-nm excitation showed a benefit over that at 633 nm for most of the explosives studied, although several samples (e.g. Semtex) suffered from similar fluorescence emission levels with both 785-nm and 633 nm wavelength excitation. A fibre-optic probe equipped with a 633-nm laser has been applied for the detection of traces of explosives in fingerprints using a 4-m fibre-optic probe.[15] A fibre-optic Raman probe equipped with a 532-nm laser has been applied for the *in-situ* detection of illicit drugs; it was possible to differentiate cocaine hydrochloride from free base or crack cocaine using their Raman spectra.[16,17] A standoff Raman system equipped with a 532-nm laser for detecting high explosives at distances up to 50 m in ambient light conditions has been demonstrated.[18] A portable Raman system has been used to monitor hydrocarbons and explosives in the environment.[19] Illicit drugs have been analysed using a portable Raman analyser equipped with a diode laser emitting at 785 nm and a thermoelectrically cooled CCD detector.[20,21]

One of the approaches used to minimize fluorescence is to use longer laser wavelengths and in this respect the most common long wavelength laser is the 1064-nm Nd:YAGlaser. However, Stokes Raman spectra generally cannot be measured with a CCD Raman spectrometer operating at this wavelength because most CCD detectors exhibit significant reduction in response cut-off about this wavelength. Anti-Stokes Raman spectra of explosive materials have been obtained with 1064-nm excitation using fibre-optic probe sampling and a charge-coupled device (CCD) detector.[22] In a later study, the anti-Stokes Raman spectra of the explosives were compared with Stokes Raman spectra obtained using a fibre-optic probe equipped with 830-nm and 785-nm excitation wavelengths and a CCD detector.[23] It was concluded that the anti-Stokes Raman spectra measured with 1064 nm and

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CCD detection is not the optimal approach for the analysis of explosives. The decreased fluorescence background is offset by the decrease in signal intensity caused by the longer excitation wavelength. 830-nm excitation offered a slightly better fluorescence rejection than 785 nm particularly for the analysis of fluorescent samples such as Semtex. An alternative approach to using dispersive spectrometers based on CCD-detectors is to use a longer excitation wavelength coupled to Ge or InGaAs detectors. A dispersive Raman spectrometer with a germanium detector and a 1064-nm laser has been applied to measure the Stokes Raman spectra of explosives.[24] This instrument did not offer any advantage over either 830-nm Stokes or 1064-nm anti-Stokes measurement made with a CCD detector, and the device did not show wide applicability for the forensic applications of Raman spectroscopy due to the high cost of the detector, the need for liquid nitrogen cooling, the low signal-to-noise ratio of the data obtained due to the detector noise characteristics, and the decreased sensitivity related to the v^4 dependence of the near-infrared excitation.

In this work, a portable prototype Raman spectrometer (DeltaNu Advantage 1064) equipped with 1064-nm laser excitation (Fig. 1) has been evaluated for the analysis of drugs of abuse and explosives. The feasibility of the instrument for the analysis of the samples both as neat materials and in plastic and glass containers has been investigated. The analytical potential of the instrument is assessed based on a comparison with portable Raman spectrometers operating with 785-nm excitation.

Experimental

Samples

Drugs of abuse

Pure samples of cocaine hydrochloride, N-methyl-3,4-methylenedioxy-amphetamine HCl (MDMA-HCl), amphetamine sulphate, were supplied by the Sigma-Aldrich Company Ltd., United Kingdom. Seized street samples of cocaine hydrochloride, MDMA, amphetamine, and heroin were supplied by the Home Office Scientific Development Branch.

Explosives samples

Samples of pentaerythritoltetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), trinitrotoluene (TNT), and ammonium nitrate and five plastic explosive samples were supplied by the Home Office Scientific Development Branch. The explosive precursors hexamethylenetetramine (HMTA) and pentaerythritol used in this study were supplied by the Sigma-Aldrich Company Ltd., United Kingdom.

Raman spectroscopic instrumentation

The Advantage 1064 is a prototype[25,26] compact Raman spectrometer supplied by DeltaNu (Laramie, WY, USA). This system measures $12 \times 8 \times 4$ inches (LWH) and weighs 9 kg (Fig. 1). It is equipped with a 1064-nm diode laser giving a maximum laser power of 1000 mW at source. This is a dispersive reflective grating system giving Raman spectra in the wavenumber range 200–2000 cm^{-1}. The output optics provides a laser spot size of approximately 100 microns. The detector is an Intevac Photonics MOSIR 950 camera based on transfer electron (TE) photocathode and electron bombardment (EB) gain technology. Electron-bombardment CCD is a technique that improves the sensitivity and spectral range of a CCD detector. The photons are detected by an InGaAs photocathode placed in front of the CCD detector. The photocathode then releases electrons that are accelerated across a gap and focused onto the CCD detector. These energetic electrons generate multiple charges in the CCD detector, resulting in a modest gain of a few hundred times. The camera has a working range from 950 to 1650 nm and is thermoelectrically cooled to −40 °C. A knee-shaped optical head attached to the instrument allows for the flexible positioning of the sample relative to the instrument (Fig. 1 inset). The instrument is equipped with NuSpec software which

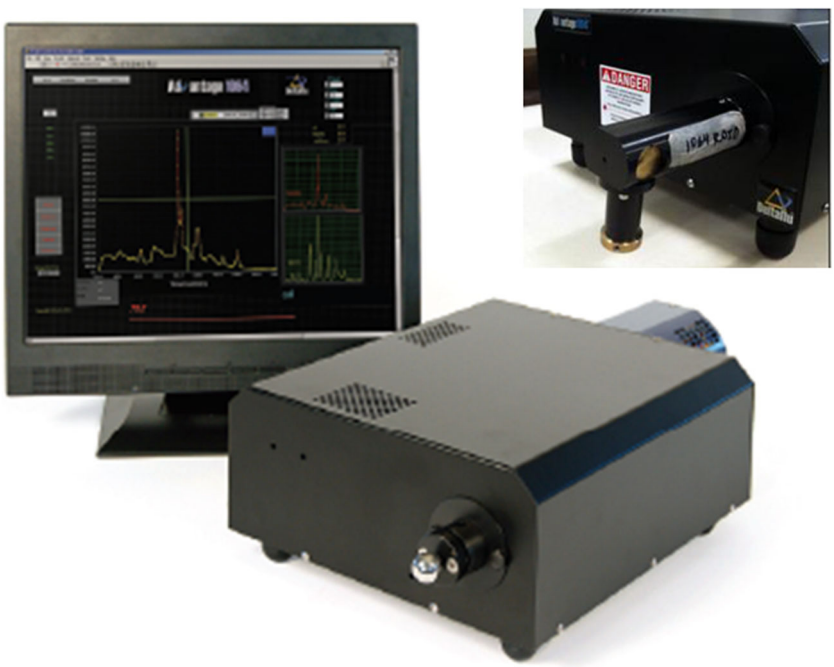

Figure 1. Advantage 1064 system. **Inset**: Knee-shaped optical head. (This figure is available in colour online at wileyonlinelibrary.com/journal/jrs.)

permits the selection of three steps of operable spectral resolution 9–11 cm^{-1}. The Delta Nu software allows a five-stage setup of adjustable laser power from 800 mW to 30 mW. The spectral integration time and the number of accumulations are under the full control of the operator. Raman spectra were acquired from the drugs of abuse and explosives samples both as neat materials and in plastic and glass containers to investigate the penetration power of the laser. To compare the results obtained from the 1064 Advantage system, corresponding measurements on another portable instrument using 785-nm laser wavelength as an excitation source have been performed. The DeltaNu Inspector Raman instrument (Laramie, WY, USA) is equipped with a diode laser emitting at 785 nm, a thermoelectrically cooled (1 × 1024 pixels) CCD detector, and a custom 25-mm-focal-length nose-piece. The spectral range is 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. The spectrometer was controlled by a portable PC with instrument control software (Nu Spec Version 4.75). Also Reference spectra of the drugs of abuse were obtained using a benchtop Renishaw In Via Reflex spectrometer (Renishaw, Wotton-under-Edge, UK) coupled with a 785-nm diode laser to be compared with the spectra collected using the 1064 Advantage system.

Results and discussion

Many drugs and explosives consist of either pure components or mixtures with diluents and additives. Illicit drugs in particular are usually diluted or cut at various levels with other drugs or common household products that exhibit significant fluorescence even under conditions of 785 nm laser excitation. Such excipient compounds include paracetamol, caffeine, aspirin, flour, talc, etc. These cutting agents may complicate the Raman spectrum, making the identification of individual components very difficult. Figures 2 and 3 compare the 1064-nm and 785-nm spectra for street-grade cocaine hydrochloride and an MDMA tablet, respectively. Despite

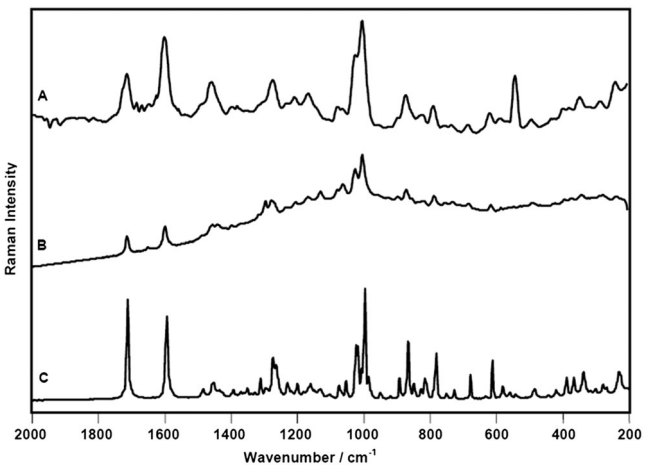

Figure 2. Raman spectra of seized cocaine. HCl. A: Advantage 1064 nm, 10-s exposure, 1 accumulation. B: DeltaNu, 785 nm, 10-s exposure, 1 accumulation. C: Reference cocaine HCl, benchtopInvia Reflex Raman microscope, 785 nm.

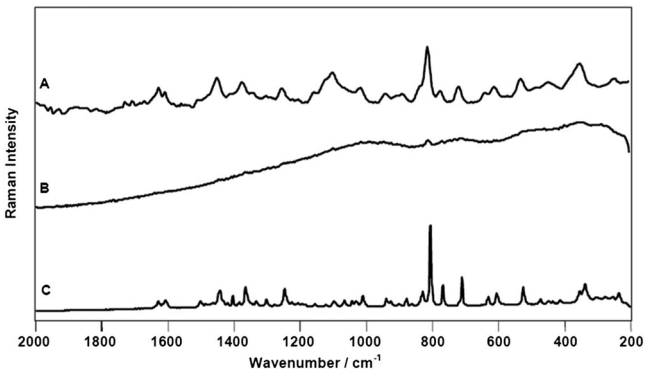

Figure 3. Raman spectra of seized MDMA. A: Advantage 1064 nm, 10-s exposure, 1 accumulation. B: DeltaNu, 785 nm, 10-s exposure, 1 accumulation. C: Reference MDMA, benchtopInvia Reflex Raman microscope, 785 nm.

the presence of some bands attributable to the cutting agent(s), the characteristic bands of cocaine hydrochloride and MDMA can be easily identified and compare favourably with the spectra obtained with benchtop spectrometer. It is observed that excitation with the 1064-nm laser wavelength has resulted in a damping of the fluorescence background emission compared with the spectra achieved with 785-nm excitation. This can also be seen in the spectra obtained from another two street samples of cocaine hydrochloride and MDMA (Fig. 4), where again shifting to the 1064-nm excitation wavelength has resulted in a significant damping of the fluorescence emission. Similar results were obtained from two seized samples of amphetamine (Fig. 5). With the 785-nm excitation, significant fluorescence background can be seen in the Raman spectra of both samples (Fig. 5 B and D) whereas with the 1064-nm excitation fluorescence-free spectra can be obtained and the characteristic Raman features of amphetamine can be clearly observed. It should also be noted that the spectra contain few bands attributable to the cutting agents, and this did not therefore prevent the identification of amphetamine as the active drug constituent of both samples. Further illustration of the applicability of this prototype instrument was demonstrated by the identification of seized heroin samples. Figure 6 shows the Raman spectrum acquired from a seized heroin sample in which the characteristic Raman bands of heroin can be clearly identified and agree well with the reference spectrum of heroin (Fig. 6 C). It

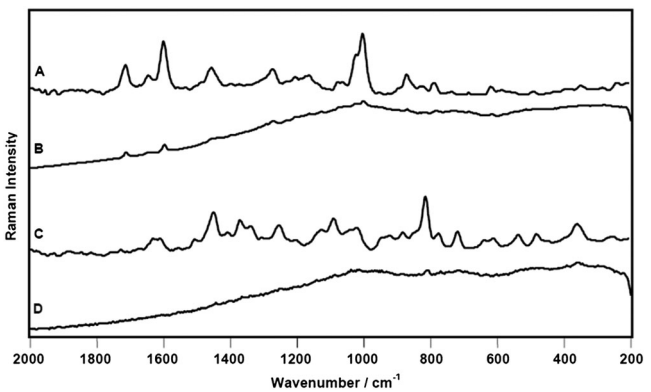

Figure 4. Raman spectra of seized drugs of abuse. A: Cocaine HCl, Advantage 1064 nm, 10-s exposure, 1 accumulation. B: Cocaine HCl, DeltaNu, 785 nm, 10-s exposure, 1 accumulation. C: MDMA, Advantage 1064 nm, 10-s exposure, 1 accumulation. D: MDMA, DeltaNu, 785 nm, 10-s exposure, 1 accumulation.

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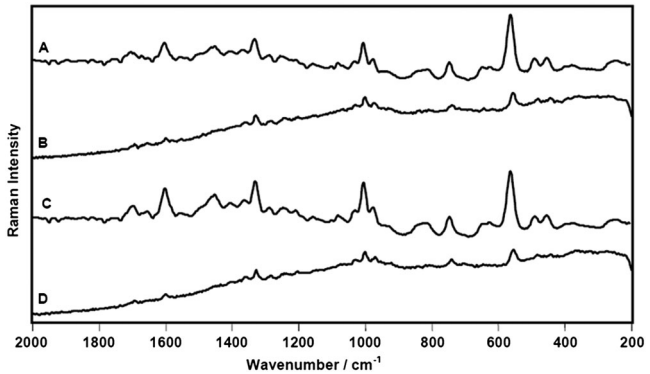

Figure 5. Raman spectra of seized amphetamines. A: Sample 1, Advantage 1064 nm, 10-s exposure, 1 accumulation. B: Sample 1, DeltaNu, 785 nm, 10-s exposure, 1 accumulation. C: Sample 2, Advantage 1064 nm, 10-s exposure, 1 accumulation. D: Sample 2, DeltaNu, 785 nm, 10-s exposure, 1 accumulation.

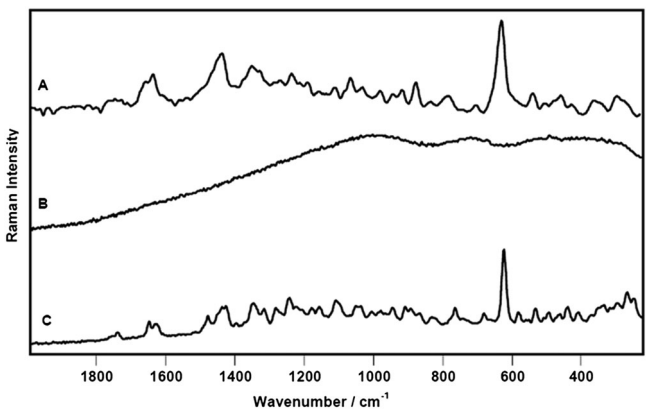

Figure 6. Raman spectra of seized heroin. A: Advantage 1064 nm, 10-s exposure, 1 accumulation. B: DeltaNu, 785 nm, 10-s exposure, 1 accumulation. C: Reference heroin, DeltaNu, 785 nm, 10-s exposure, 1 accumulation.

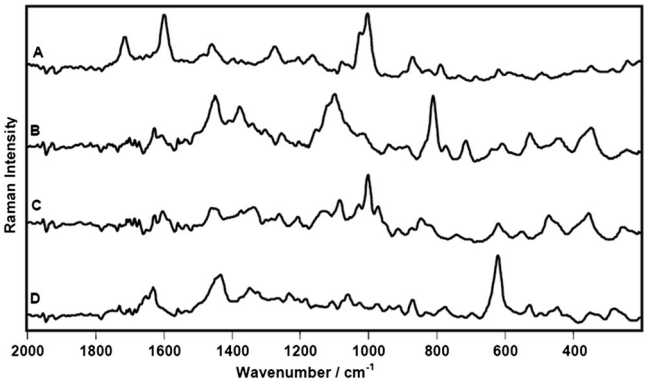

Figure 7. Raman spectra of seized drugs of abuse inside plastic bags. A: Cocaine hydrochloride. B: MDMA tablet. C: Amphetamine. D: Heroin.

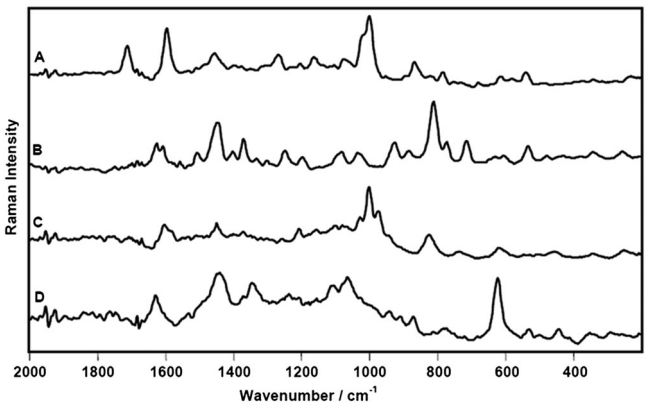

Figure 8. Raman spectra of drugs of abuse inside green-coloured glass containers. A: Cocaine hydrochloride. B: MDMA. C: Amphetamine. D: Heroin.

can also be observed that with the 785-nm excitation the Raman spectrum of heroin in the same samples is completely masked by the fluorescence emission arising from the cutting agents.

The feasibility of the instrument for sampling drugs of abuse which are contained in transparent containers, such as clear plastic bags, that are used by crime scene investigators to store drug evidence and to maintain the chain of custody has also been investigated. Pure and street samples of drugs of abuse were analysed without removing them from their plastic containers. The street samples were analysed inside their sealed plastic containers as received from the Home Office Scientific Development Branch. Raman spectra were obtained from seized samples of drugs of abuse, namely, cocaine hydrochloride, an MDMA tablet, amphetamine, and heroin. The principal characteristic bands of the drugs can be clearly observed (Fig. 7) in all spectra, and the plastic containers did not prevent the identification of the drugs therein. The increased spectral background is attributed to the cutting agents present in the seized samples. Furthermore, Raman spectra were acquired from samples of drugs of abuse inside different-coloured glass containers, i.e. clear, amber–yellow, green, and brown. Coloured containers in which there are drugs of abuse usually fluoresce under visible excitation, which may mask the Raman signals; here, however, from the individual spectra the characteristic features of the drugs are clearly identified, and the coloured glass did not significantly attenuate the illumination laser or prevent the detection of the scattered Raman signals from the drugs (Fig. 8). This clearly demonstrates the ability of this instrument to effectively sample the drugs inside their containers which is of significant importance for field analysis. This can be attributed to the drugs of abuse being relatively good Raman scatterers whereas the glass container is a much poorer Raman scatterer.

The feasibility of the instrument for the analysis of the explosives and explosive precursors was also investigated. Plastic explosives usually exhibit strong fluorescence emission even with the near-infrared excitation at 785 nm. Raman spectra were obtained from four samples of Semtex explosive, and the spectra were compared with the spectra obtained for the same samples with 785-nm excitation. The spectra obtained from the first two samples are shown in Fig. 9 which clearly shows the advantage of shifting the excitation to the 1064-nm laser wavelength. These samples are highly fluorescent and using 785-nm excitation resulted in the Raman signal being completely masked by the fluorescence background. With 1064-nm laser excitation the fluorescence background is significantly reduced, and the characteristic bands of the explosives can be clearly identified. Also Raman spectra were successfully acquired from explosives and explosives precursors whilst held in clear plastic packaging and inside glass containers of various colours (Fig. 10). All the samples can be identified, and the packaging did not interfere with the detection of the explosives. There is

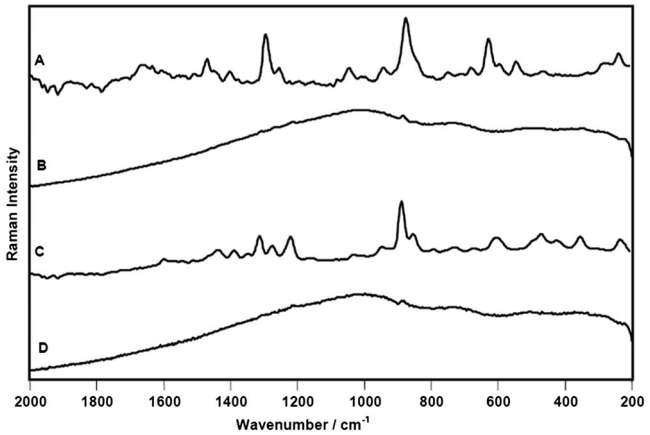

Figure 9. Raman spectra of the plastic explosives. A: Semtex (sample 1), Advantage 1064 nm, 10-s exposure, 1 accumulation. B: Semtex (sample 1), DeltaNu, 785 nm, 10-s exposure, 1 accumulation. C: Semtex (sample 2), Advantage 1064 nm, 10-s exposure, 1 accumulation. D: Semtex (sample 2), DeltaNu, 785 nm, 10-s exposure, 1 accumulation.

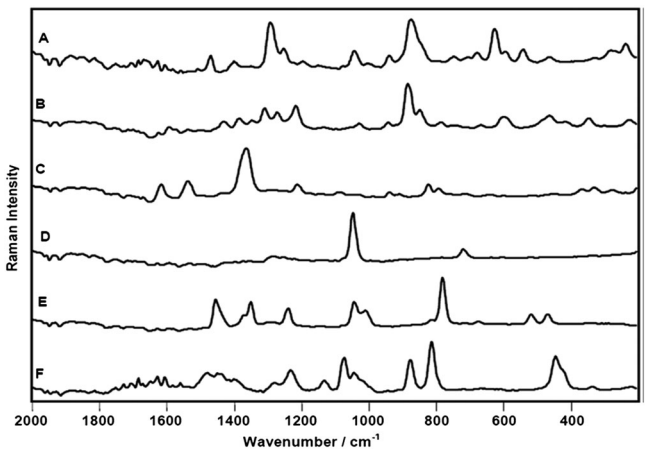

Figure 10. Raman spectra of the explosives and precursors inside plastic bags. A: RDX B: PETN. C: TNT D: Ammonium nitrate. E: Hexamethylenetetramine (HMTA). F: Pentaerythritol.

no significant band in the spectra that can be assigned to the containers neither can any fluorescence background be seen in the spectra. This is significantly important as the ability to identify the explosives while inside their containers eliminates the chance of exposure to possible harmful substances in such containers and prevent evidence contamination.

Conclusions

These results demonstrate that this prototype portable instrument operating with 1064-nm excitation and coupled with transfer electron (TE) InGaAs photocathode and electron bombardment (EB) CCD technology has an excellent potential for the analysis of drugs of abuse and explosives. Street samples of drugs of abuse and plastic explosives which usually fluoresce with visible or 785-nm excitations were successfully analysed without interfering fluorescence backgrounds. Spectra have been obtained for drugs of abuse and explosives, both neat and in plastic and glass containers. Sampling drugs of abuse and explosives through coloured glass, which is highly fluorescent with laser excitation in the visible, was also feasible. The right-angled optical head allows for a flexible positioning of the sample to be analysed. The portability and rapidity of the analysis are significant advantages of the 1064 Advantage system. These criteria are significantly important for law enforcement agencies working in the field and dealing with relatively large numbers of samples on a daily basis. Hence, the prototype tested here brings a new potential to detect compounds which are fluorescing at lower excitation wavelengths and broadens the number of samples that can be analysed by Raman spectroscopy.

Acknowledgements

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