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Raman spectroscopy and security applications: the detection of explosives and precursors on clothing

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This study describes the application of confocal Raman microscopy to the detection and identification of explosives and their precursors *in situ* on undyed natural and synthetic fibres and coloured textile specimens. Raman spectra were obtained from explosives particles trapped between the fibres of the specimens. The explosives pentaerythritol tetranitrate (PETN), trinitrotoluene (TNT), and ammonium nitrate as well as the explosives precursors hexamethylenetetraamine (HMTA) and pentaerythritol were used in this study. Raman spectra were collected from explosives particles with maximum dimensions in the range 5–10 μm. Despite the presence of spectral bands arising from the natural and synthetic polymers and dyed textiles, the explosive substances could be identified by their characteristic Raman bands. Furthermore, Raman spectra were obtained from explosives particles trapped between highly fluorescent clothing fibres. Raman spectra of the explosive and explosive precursor substances on dyed and undyed clothing substrates were readily obtained *in situ* within 90 s without sample preparation and with no alteration of the evidential material.

Supporting information may be found in the online version of this article.

Keywords: explosives; explosive precursors; confocal Raman microscopy; textiles; forensic

Introduction

The development of new, rapid, and direct analytical chemistry methods for detection of explosives is of increasing importance for security and counter-terrorism issues, and for establishing criminal evidence.[1,2] Sensitivity and specificity in the detection of explosives is a crucial attribute, and a number of recent high-profile reports have highlighted the application of desorption mass spectrometric approaches for direct analysis (i.e. without sample preparation) that allow detection of explosive residues down to picogram quantities of analyte.[3–8] In the wider context, a variety of analytical methods have been established for the identification of explosives under various conditions, including gas chromatography,[9] X-ray powder diffraction,[10] thermal neutron analysis,[11] and ion mobility spectrometry.[12,13] However, each of these approaches requires isolation and/or destruction of the analyte, and these techniques therefore alter or destroy evidential material during analysis. Similarly, desorption mass spectrometry although direct is an inherently destructive technique.

Two surveys of high explosives traces in public places were carried out in a number of major cities of the United Kingdom. Samples were collected from taxis, trains, buses, airports, police stations, private houses, privately owned vehicles, and clothing. The results of the surveys indicate that it is unlikely that someone in public areas could accidentally become significantly contaminated with explosives.[14,15] There have been several high-profile cases in the public domain where the identification of minute amounts of particulate matter has formed a significant part of the forensic evidence. So, the detection of explosive residues on clothing can be used as a strong evidence to establish a link between these materials and individuals involved in terrorist activities, because handling, packaging, and transportation of these materials will almost inevitably cause contamination of the premises, clothing, and other possessions of these persons.[16]

Raman spectroscopy is a well-established technique in the field of forensic science.[17–20] Molecular-specific data are produced 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.[21] Several studies have appeared in the literature addressing the application of Raman spectroscopy to the detection and identification of explosives. For example, Fourier-transform Raman spectroscopy was successfully applied for the detection of components of explosives in unknown Semtex samples.[22] Detection and identification of plastic explosives contained in fingerprint samples using Raman microscopy has been reported,[23] and a fibre-optic probe for the detection and identification of explosive materials has been developed allowing Raman spectra to be acquired remotely.[24,25]

A preliminary study in our laboratory addressed the detection of a strictly limited range of explosive materials of potential interest to law-enforcement agencies.[26] The present work represents the first application of confocal Raman microscopy to the identification of explosives and explosive precursor particulates *in situ*. We have investigated the application of confocal Raman microscopy to the *in situ* detection and identification of explosives and their

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precursors on a variety of fibres and textiles contaminated with these hazardous materials. Handling of explosive substances will inevitably leave the clothing and other possessions of the involved persons contaminated with these substances. The contamination of clothing results from microscopic particles of the explosive substance physically trapped between the fibres of the specimens. We will demonstrate that confocal Raman microscopy offers an alternative direct technique with advantageous attributes over other methods for explosives analysis. The Raman technique provides molecular-specific spectra and, when applied with confocal microscopy, non-destructive analysis of minute explosive particulates can be achieved *in situ*. In our study, we establish that, in such situations, confocal Raman microscopy has the ability to provide both speed and specificity for trace identification of explosives on undyed and dyed clothing. Spectra of explosives could be rapidly acquired without significant interference from the substrate matrices. Also, *in situ* analysis of explosives particles from contaminated surfaces without sample handling or preparation is desirable to avoid sample loss or cross-contamination associated with sample manipulation. Furthermore, the non-destructive character of the technique offers a special role for Raman spectroscopy in the first-pass evaluation screening of materials of forensic relevance.

Experimental

Explosives

Pentaerythritol tetranitrate (PETN), trinitrotoluene (TNT), and ammonium nitrate samples were supplied by the Home Office Scientific Development Branch. Hexamethylenetetraamine (HMTA) and pentaerythritol used in this study were supplied by the Sigma-Aldrich Company Ltd., United Kingdom; they are used in the manufacture of high explosives such as RDX and PETN.[27,28]

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 used 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 examples of commonly encountered dyed clothing.

A bundle of fibres, each about 1 cm in length, and textile pieces ($\sim 2 \times 2$ cm) were contaminated with few crystals from each explosive and then presented to the spectrometer. Trapping of the explosive particles between the clothing fibres was achieved by pressing small quantities against the fibre bundles and textile pieces and removing the surface excess of the explosive by gentle brushing.

Raman spectroscopy

Raman spectra were collected using a Renishaw *InVia* Reflex dispersive Raman microscope with a 785 nm near-infrared diode laser (Renishaw, Wotton-under-Edge, UK) and a 50× objective lens giving a laser spot diameter of 5 µm. Spectra were obtained at 2 cm^{-1} resolution for a 10-s exposure of the CCD detector in the wavenumber region 100–1800 cm^{-1} using the extended scanning mode of the instrument. This wavenumber range was chosen as it contains the fingerprint region of the explosive substances. After identification with optical microscopy, Raman spectra were collected from explosive particles with edge dimensions in the range 5–10 µm. With 90.8 mW laser power at the sample, one accumulation was collected for the explosives reference spectra and for confocal experiments with contaminated textiles. Reference spectra for the textile samples were collected with five accumulations. With these parameters, the total acquisition time of the spectra of the explosives on fibres was about 90 s. Spectral acquisition, presentation, and analysis were performed with the Renishaw WIRE (service pack 9) and GRAMS AI version 8 (Thermo Electron Corp, Waltham, MA, USA) software.

Results and Discussion

Explosives on undyed natural fibres

Raman spectroscopy provides a unique spectral ‘fingerprint’ of any molecule, so each spectrum is molecularly specific and contains key signature bands that can be used for unambiguous identification. The Raman spectra of the explosives PETN, TNT, ammonium nitrate, and of the explosive precursors HMTA and pentaerythritol in the spectral wavenumber region 1800–100 cm^{-1} are shown in Fig. 1. Also, Table 1 lists the Raman wavenumbers and vibrational assignments of the principal characteristic bands in the spectra of the explosives, which can be used to identify each substance within the group of the explosives studied.[29–33] The Raman spectra obtained from PETN, TNT, ammonium nitrate, HMTA, and pentaerythritol particles trapped between cotton fibres are shown in Fig. 2. Comparison of these spectra with the reference spectra of the explosives showed that the explosives could be easily identified by their Raman spectra, which comprise strong sharp features throughout the spectral wavenumber region 100–1800 cm^{-1}. It is observed that the characteristic Raman bands of the explosives can be clearly identified and through careful confocal sampling, no significant peaks in the spectra appear from the cotton fibres. The Raman spectra obtained from the explosives PETN, TNT, and ammonium nitrate and from the explosive precursors particles trapped between silk fibres contain some bands attributable to the silk substrate (marked with asterisks in Figs S1 and S2 (Supporting Information)); these are the amide I (C=O) stretch at 1664 cm^{-1}, the δ (CH_2) scissoring at 1445 cm^{-1}, and the (CN)

Table 1. Wavenumbers and vibrational assignments of the principal characteristic bands in the spectra of the explosives

Explosive	Wavenumber (cm^{-1}), vibr. assignment	Reference
PETN	1290, [ν_s (NO_2)] 871, [ν_s (O–N)] 622, [δ (CCC)]	[29,30]
TNT	1532, [ν_{as} (NO_2)] 1357, [ν_s (NO_2)] 822, [(NO_2) scissor]	[30]
Ammonium nitrate	1040, [ν $(NO_3)^-$] 712, [$(NO_3)^-$ bend]	[31]
Hexamethylenetetramine	1040 and 462, [(N–C–N) bend] 777, [ν (N–C)]	[32]
Pentaerythritol	1071, [ν (C–O)] 873 and 810, [δ (CH_2) rock] 439, [δ (C–C–C)]	[33]

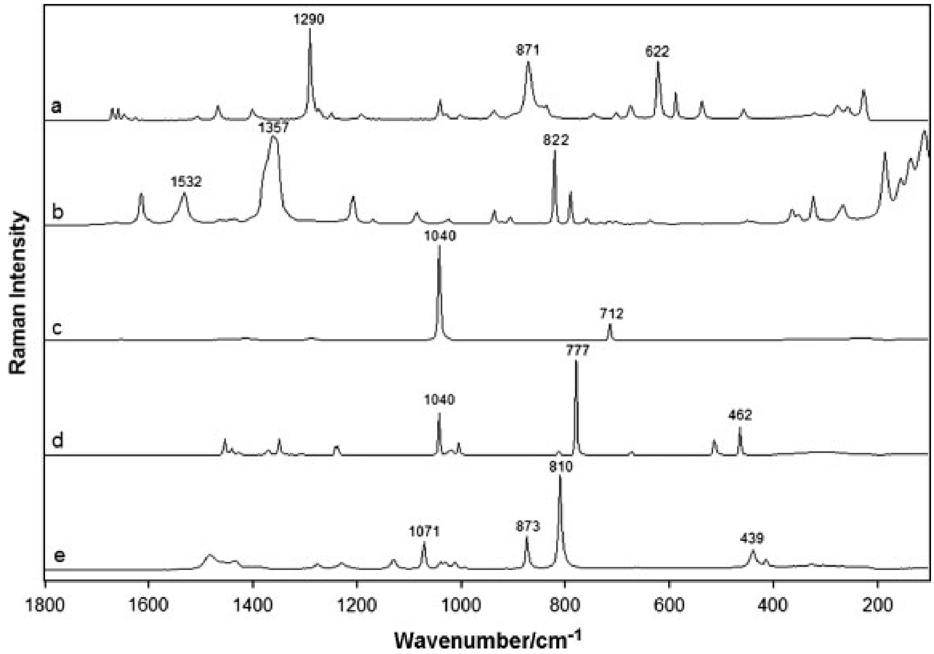

Figure 1. Reference Raman spectra of (a) PETN (b) TNT (c) ammonium nitrate (d) HMTA (e) Pentaerythritol (785 nm, 90.8 mW, 10 s exposure, 1 accumulation).

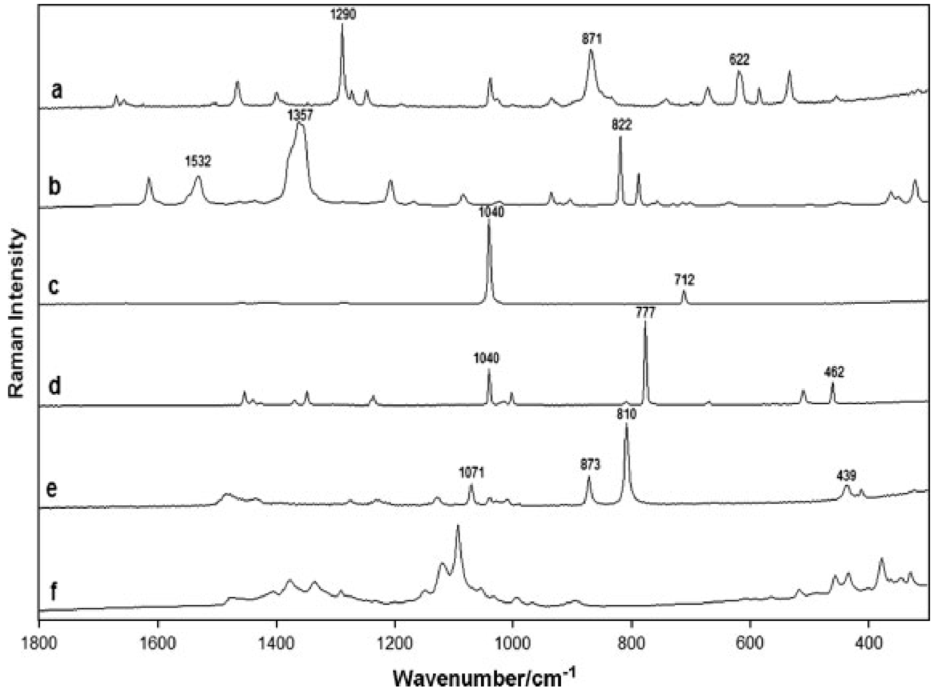

Figure 2. Raman spectra of (a) PETN particle on cotton fibres (b) TNT particle on cotton fibres (c) Ammonium nitrate particle on cotton fibres (d) HMTA particle on cotton fibres (e) Pentaerythritol particle on cotton fibres (f) Cotton fibres (785 nm, 90.8 mW, 10 s exposure, 1 accumulation for (a–e), 5 accumulations for (f).

stretch at 1227 cm^{-1}.[34] The presence of these bands in the spectra of the explosives does not interfere with the identification of the explosives, which can be identified by their characteristic bands. Similarly, the spectra obtained from the explosives and explosives precursors trapped between wool fibres contain some bands (marked with asterisks in Figs S3 and S4 (Supporting Information), respectively) assignable to the wool substrate; the amide I ν (C=O) mode at 1654 cm^{-1}, and the δ (CH$_2$) mode at 1445 cm^{-1}.[35] These bands do not overlap with characteristic features of the explosives, allowing the explosives and the explosive precursors to be readily identified.

Explosives on undyed synthetic fibres

Figure 3 shows an image of a single PETN particle trapped between polyester fibres. The spectra collected from the explosives PETN,

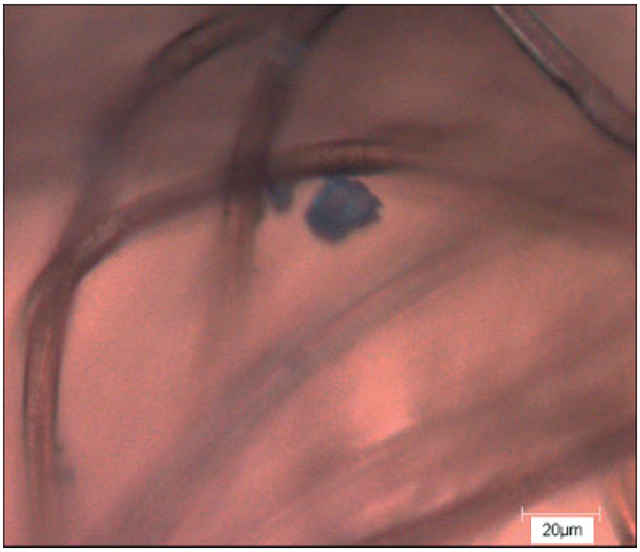

Figure 3. PETN crystal trapped between polyester fibres.

TNT, ammonium nitrate, and from the explosive precursors HMTA and pentaerythritol particles trapped between polyester fibres are shown in Fig. 4, which also allows the presence of the explosive contaminant to be readily established. In addition to the explosives diagnostic bands (*vide supra*), the resulting spectra also contains several peaks assigned to polyester fibre (marked with dashed lines in Fig. 4): these appear at 1724 cm^{-1} ν (C=O), 1610 cm^{-1} (aromatic ring stretch), and 854 cm^{-1} ρ(CH).[36,37] In each case, the strongest bands arising from the polyester fibres do not overlap with the characteristic features of the explosives which can be clearly observed.

Raman spectra could be acquired from explosives particles trapped between the fibres of the specimens of an average size in the range 5–10 µm. The spectra are of a high quality with a good signal/noise ratio and no appreciable background due to fluorescence. Confocal Raman microscopy was applied to focus the laser beam and collect the Raman scattering from the explosive crystals trapped between the fibres of the speciments. The NIR laser at 785 nm gave good-quality spectra of the explosives, and there was no detectable background fluorescence. Interference from the fibres, including background fluorescence, was overcome by careful focusing of the confocal beam, and the resulting spectra allowed ready differentiation from interference from the fibres substrate bands. In addition, the scattering from the explosives is usually relatively intense compared to that from the fibres substrate.

Explosives on dyed textiles

The previous results were acquired from explosives particles trapped between fibres of undyed natural and synthetic fibres. Of course, many real textile samples are dyed, and it is necessary to determine how this will affect the Raman spectra of the explosive particles trapped between fibres of dyed clothing specimens. In particular, fluorescence background and the functional group features arising from the dye molecules may conceal diagnostic Raman spectral features of the explosives. The spectra obtained from explosives and the explosive precursor particles trapped between blue-dyed denim fibres again show the characteristic Raman features of the explosives and their precursors. While a band corresponding with 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 explosives (Fig. 5).

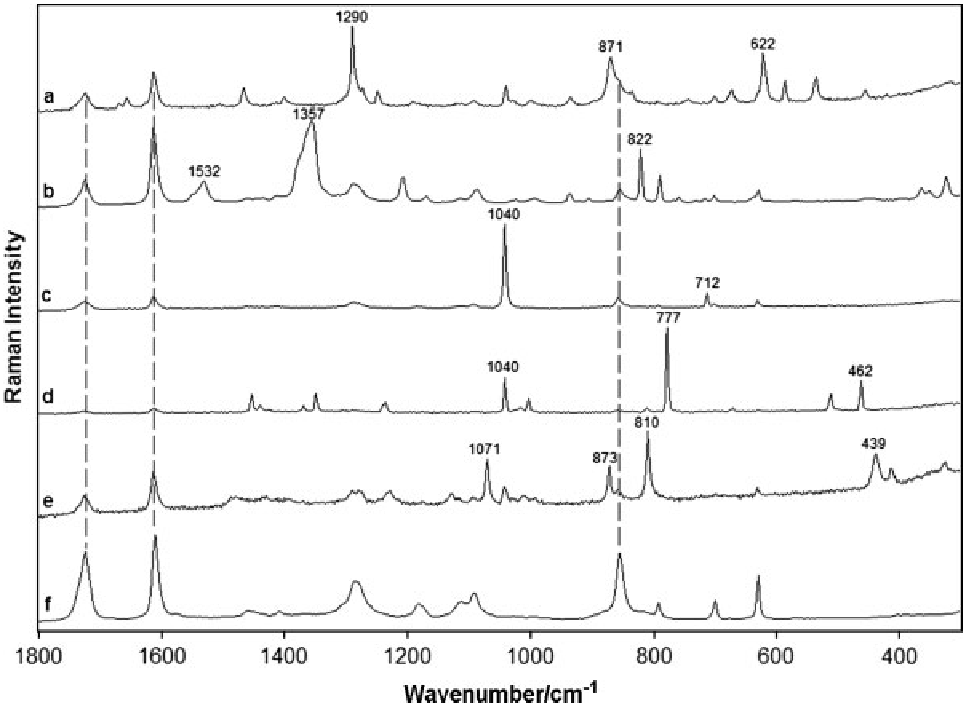

Figure 4. Raman spectra of (a) PETN particle on polyester fibres (b) TNT particle on polyester fibres (c) Ammonium nitrate particle on polyester fibres (d) HMTA particle on polyester fibres (e) Pentaerythritol particle on polyester fibres (f) Polyester fibres 785 nm, 90.8 mW, 10 s exposure, 1 accumulation for (a–e), 5 accumulations for (f).

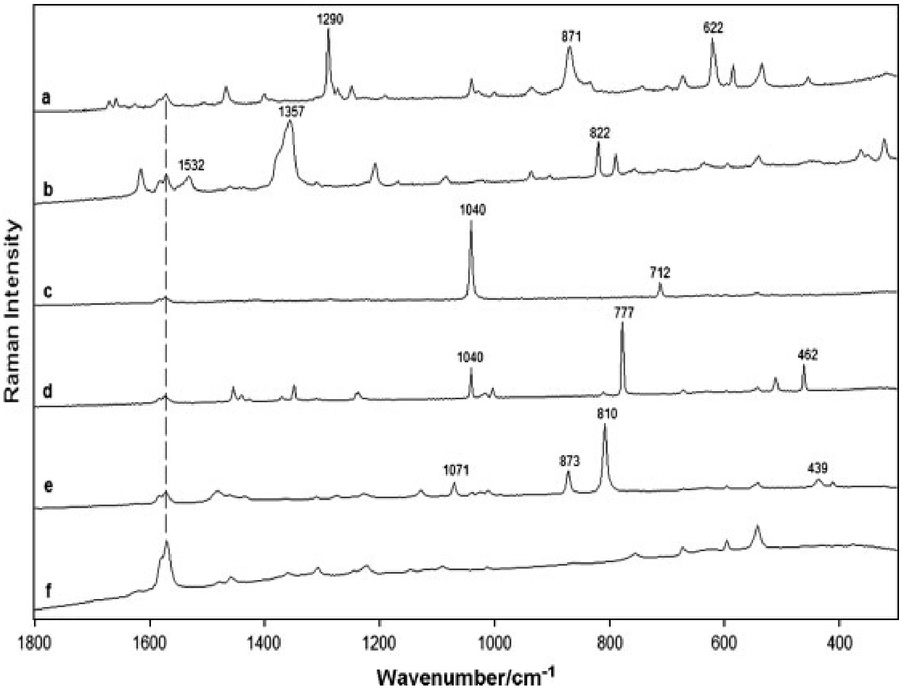

Figure 5. Raman spectra of (a) PETN particle on denim fibres (b) TNT particle on denim fibres (c) Ammonium nitrate particle on denim fibres (d) HMTA particle on denim fibres (e) Pentaerythritol particle on denim fibres (f) Denim fibres 785 nm, 90.8 mW, 10 s exposure, 1 accumulation for (a–e), 5 accumulations for (f).

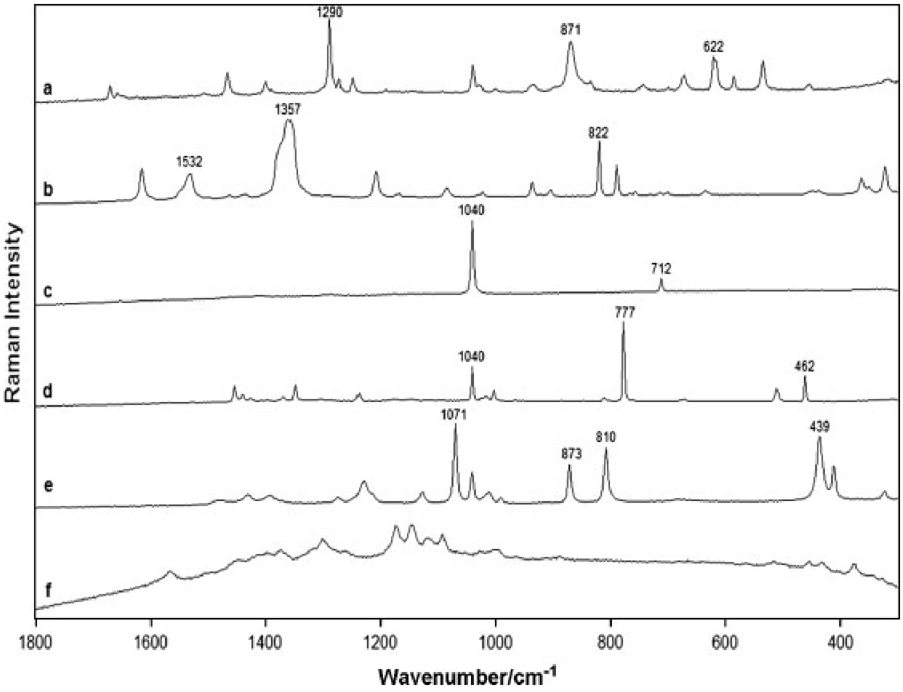

Figure 6. Raman spectra of (a) PETN particle between orange T-shirt fibres (b) TNT particle between orange T-shirt fibres (c) Ammonium nitrate particle between orange T-shirt fibres (d) HMTA particle between orange T-shirt fibres (e) Pentaerythritol particle between orange T-shirt fibres (f) Orange T-shirt fibres 785 nm, 90.8 mW, 10 s exposure, 1 accumulation for (a–e), 5 accumulations for (f).

Raman spectra were successfully collected from the explosives PETN, TNT, and ammonium nitrate as well as from the explosive precursors HMTA and pentaerythritol particles trapped between the fibres of an orange-coloured T-shirt. The Raman spectrum of this substrate contains a few bands of cotton superimposed on a fluorescence background, which may swamp Raman signals from the explosive substances. This gives rise to a slight fluorescence background in the spectra of the explosives. However, the Raman spectral bands of the explosives are clearly identifiable above the background, and in all cases the presence of the contaminants were easily recognised (Fig. 6). The major advantage of confocal Raman microscopy, namely the ability to focus the incident laser radiation onto and collection of Raman scattering from small specimens even when embedded within the interior of a larger highly fluorescent media, is clearly demonstrated in this experiment.

These results show that with the application of confocal techniques, interpretable Raman spectra can be obtained directly from particles as small as 5 μm^3 – approximately 180 pg in mass – and hence the technique has a sensitivity comparable to ionisation desorption mass spectrometric techniques.[3–8] In addition, our approach leaves the particle unaltered and in its original environment. Thus, a clear application of the confocal Raman experiment is as a screening method for identification of particulates during initial inspections of clothing prior to further examination. Furthermore, the rapid acquisition of Raman spectra of explosives *in situ* allows forensic scientists and police agencies to screen the potential of particulates as evidential material during initial inspections of clothing.

The ability for this approach to easily discriminate between the contaminant and the substrate lies in the ability of the confocal system to focus the incident laser radiation directly on the contaminant particles without sampling substantial areas of the substrate. This discrimination is highly desirable for automated database recognition algorithms, as the spectra obtained are relatively simple and are predominantly of a single component in the mixture – an important consideration for future application with 'non-expert' implementation of the technique. Furthermore, confocal Raman microscopy provides an efficient way to obtain Raman spectra of small specimens selectively even when embedded within strong Raman-scattering or highly fluorescent media. The most difficult aspect of the analysis was the visual identification and location of the particles on the fibres prior to the acquisition of the Raman spectra. Raman mapping or chemical imaging could be suitable techniques for this application, which may overcome the difficulty of visual specific location of the particles on the fibres; however, this will also require significant time for spectral scanning.

Conclusion

This the first study that illustrates the use of Raman microscopy for the detection and identification of explosives and their precursors on clothing. Confocal Raman microscopy provides an efficient way for the detection and identification of explosives and explosive precursors on clothing. The presence of some spectral bands arising from the fibre polymers and/or dyes did not interfere with the identification of the explosive substances, which could be clearly identified by their characteristic Raman bands. Also, Raman spectra could be acquired from explosive particles embedded within highly fluorescent specimens. Raman spectra of the explosive and explosive precursor substances could be readily obtained *in situ* non-destructively, within 90 s and without sample preparation.

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Supporting information

Supporting information may be found in the online version of this article.

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