Videira-Quintela, Diogo; Zapata, Félix & García-Ruiz, Carmen, 2018. Detection of microscopic traces of explosive residues on textile fabrics by Raman spectroscopy. Journal of Raman Spectroscopy, 49(10), pp. 1668-1677.

Available at https://doi.org/10.1002/jrs.5455

Detection of microscopic traces of explosive residues on textile fabrics by Raman spectroscopy

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Abstract

Direct or cross-contamination of explosive residues on clothing is of high occurrence when handling explosive materials, leading to physically trapped particles between the fibres. In this work, the detection and identification of trace amounts of organic explosives, inorganic explosives, and oxidizing salts trapped between the fibres of dyed and undyed synthetic and natural textile clothing fabrics were studied using two (desktop and portable) confocal Raman microscopes. The results show that, despite the contribution of the textile fabric in terms of fluorescence and vibrational bands coming from the fibres and dyes, detection and identification of the explosive/oxidizing salt particles trapped on highly interfering surfaces was possible. Limits of detection (LOD) were estimated in the nanogram/picogram range depending on the explosive and fabric. However, problems involving the burning of either some explosive particles or dark cloth textiles were verified, what can cause a destruction of the sample. Also, the analysis of improvised homemade explosives (potassium nitrate mixed with ten different fuel substances) was studied to evaluate possible interferences.

Keywords: confocal Raman microscopy, trace detection, homemade explosives (HMEs), clothing textiles.

1. Introduction

In the manufacture, handling or transportation of Improvised Explosive Devices (IEDs), there is a possibility of explosive traces (trace amounts of microscopic particles) to be easily transferred to the surrounding materials such as suit cases, human fingerprints, textile fabrics, etc.[1–3] Particularly, in the case of clothing, microscopic particles of the explosives get physically trapped between the fibres.

Different techniques have been investigated for the detection of explosive particles in textile fabrics, including HPLC and TLC[4], hyperspectral imaging (visible and/or near infrared range)[5,16–18], terahertz spectroscopy[6–10], and Raman spectroscopy[11–15]. In brief, spectroscopic techniques are the most used, probably because of being rapid, non-destructive and solvents-free, where no sampling and separation methods are required.[19] Confocal Raman microscopy can be highlighted as one of the most suitable techniques to this aim, since the Raman signal from the analyte (i.e., explosive particle) can be remarkably enhanced and separated from the background signal (i.e., textile fabric) by exclusively focusing the microscope spot onto the explosive particle. For instance, post-blast explosive residues (in the order of microns) of different organic and inorganic explosives have been easily detected on white cotton fabric by confocal Raman microscopy.[11] In other studies[12–14], organic explosives (PETN, TNT) and other energetic particles (ammonium nitrate, hexamethylenetetraamine (HMTA), pentaerythritol, urea nitrate (UN), ammonium perchlorate), with a range between 5 – 150 μm, were detected on dyed (orange coloured T-shirt, blue denim jeans, black polyester, brown leather) and undyed natural (wool, silk, white cotton) and synthetic (white polyester) textile fabrics. However, despite the general assumption that explosive particles can be perfectly focused to obtain the explosive spectrum avoiding the background spectral interference, this depends on many factors such as the composition and size of the explosive particle, the composition and colour (dyes) of the textile fabric or the type of Raman instrument and acquisition parameters.

The kind of explosive that may be found on IEDs might be military, commercial or homemade explosives.[20,21] Nowadays, homemade explosives are becoming an emergent situation, since they are easily manufactured in illicit homemade conditions using readily available chemicals (i.e. fertilizers, kitchen and household products). They are usually the mixture of an oxidizing compound (e.g., oxidizing salts) with fuels (e.g., charcoal, sugars, gasoline, etc.).[22] The analysis of homemade explosives usually poses a hard detection, since the spectra usually display multiple bands from both the fuel and the oxidizing compound, which makes the correlation with the individual components very difficult. Raman spectroscopy has shown a high efficiency in the differentiation of oxidizing salts mixed with certain fuels, present in military and commercial explosives such as black powder, dynamite, ammonal or chloratite.[11,23–25]

In this study two main objectives can be highlighted. First, the detection capability of confocal Raman microscopy using a desktop and a portable Raman instrument to identify explosive residue particles on a wide variety of different fabrics (including different colored cotton, polyester, jeans and wool fabrics). Second, the oxidizing component detection in explosive mixtures with various fuels, was performed in order to determine to what extent the different fuels interfered and hindered the positive identification of the oxidizing compound.

2. Experimental section

2.1. Explosives, fabrics and interferent substances

Different oxidizing salts and explosives were analysed in this study. Oxidizing salts, including ammonium, sodium, potassium and barium nitrates, sodium and potassium chlorate and potassium perchlorate were purchased from Sigma-Aldrich (Germany) at ACS grade (purity over 98%). Explosives, including ammonal (ammonium nitrate (85%) + aluminium (15%)), black powder (potassium nitrate (75%) + charcoal (15%) + sulfur (19%)), chloratite (sodium chlorate (80%) + sugar (10%) + sulfur (10%)), TNT (2,4,6-trinitrotoluene (100%)), RDX (hexogen, Cyclotrimethylene trinitramine (91%) + bis(2-ethylhexyl)phthalate (5.3%) + polyisobutylene (2.1%) + motor oil (1.6%)), PETN (penthrite, Pentaerythritol tetranitrate (100%)), and HMTD (Pentaerythritol tetranitrate (100%)) were provided by TEDAX, the Spanish Explosive Ordnance Disposal (EOD). Flash powder (potassium perchlorate (85%) + aluminium (15%)), was extracted from commercial firecrackers. For the explosive mixture study, the following interferent fuels were used: talc powder, wheat flour (and corn starch), chocolate cocoa powder, sugar (white, powdered and brown sugar), charcoal and aluminium powder. These were acquired from the closest supermarket, except charcoal and aluminium powder, which were purchased from Sigma-Aldrich (Germany) at ACS grade. These explosive mixtures were prepared by mixing 70 mg of potassium nitrate with 30 mg of the corresponding interfering substance using a pestle and mortar. These quantities were selected in order to obtain mass percentages of 70% of potassium nitrate and 30% of interfering substance/fuel (similar to the percentage usually found in black powder). The textile fabrics used to disperse the explosive residues were: wool (beige colour), cotton (white, green, red, blue, and black), polyester (white, black, and blue), blue denim jeans, latex gloves, nitrile gloves, and polyskin.

Textile fabrics were cut into approx. 8 cm × 8 cm square pieces, large enough to cover a circle area of dispersion of 23.8 cm^2. In order to handle these textile pieces carefully, they were held into cardboard supports wrapped with aluminium (which is not Raman active). Then, they were contaminated with the respective explosives and oxidizing salts, through the dispersion of fixed quantities of explosives within the range 3-30 mg, weighed using an Ohaus DV215CD (Parsippany, NJ, USA) analytical balance. The dispersion of the initial amount of explosive was accomplished using an air dryer, with the air traveling through a cardboard roll (length 40 cm, diameter 5.5 cm) whose end was in contact with the fabric (area 23.8 cm^2). This methodology was proposed in order to homogeneously distribute the explosive residues along the fabric, and partially simulate the blowing and dispersion undergone by explosive residues after an explosion.

2.2. Instrumentation for Raman analysis

Raman measurements were performed with two commercial instruments: (1) a desktop Thermo Scientific DXR Raman microscope using the Thermo Scientific Omnic for dispersive Raman 8 software (Waltham, MA, USA), and a 780-nm excitation wavelength, 10x, 20x, 50x, and 100x magnification objectives (depending on the particle size), 400 lines mm^{-1} grating, and 50 μm slit, from 3200 to 200 cm^{-1}; and (2) a portable Raman BWTEK i-Raman Pro (BWTEK Inc., Newark, Delaware) instrument coupled with a portable confocal microscope using a 785-nm excitation wavelength, 20x, and 40x magnification objectives, from 3200 to 200 cm^{-1}. These two instruments were used in their standard conditions with no proper modification in terms of instrumental components, and only the spectral features (power of laser, exposure time, and number of accumulations) were modified accordingly. The spectra acquisition options, in both instruments, which varied for each explosive and textile fabric, are summarized in Table 1.

Table 1. Raman acquisition conditions used in the (Desktop) Thermo Scientific DXR Raman microscope and (Portable) BWTEK i-Raman Pro depending on the compound studied.

Compound	Laser power (mW)*	Accumulations (scans)	Acquisition time (seconds)	Total acquisition time (seconds)
Oxidizing salts	Desktop:14, 5**, 1** Portable: 64*, 3.2***	Desktop: 8 Portable: 10	Desktop: 5 Portable: 0.3	Desktop: 40 Portable: 3
Inorganic explosives	Desktop:10, 5**, 1** Portable: 3.2*	Desktop: 5 Portable: 10	Desktop: 6 Portable: 1	Desktop: 30 Portable: 10
Organic explosives	Desktop:10, 5**, 1** Portable:16*, 3.2***	Desktop: 5 Portable: 5	Desktop: 6 Portable: 3	Desktop: 30 Portable: 15

* Adjustable power in the range 1% to 100% of a maximum power of 320 mW.
** Black cotton and polyskin textiles were analysed with 5 mW and 1 mW, respectively, due to their sensitivity to the laser.
***Laser power for the textiles black cotton, blue cotton, jeans 1, and jeans 2.

2.3. Particle size and limit of detection determination

The particle sizes of explosive residues, were calculated using a program called ImageJ (Wayne Rasband, USA), that allows the determination of the distance in pixels of a certain marked line. This marked line was drawn in the image of the collected particle, in order to match the wider diameter of the particle.

Then, knowing the scale of the collected image and the distance in pixels of the wider diameter of the particle, the size was determined.

According to previous studies[11], the limit of detection (LOD) was estimated by multiplying the density of the explosive substance (oxidizing salt, organic or inorganic explosive) by the volume of the particle detected, assuming always a range since the volume of the particle might be between spherical (minimum size) or cubic shape (maximum size). Although, the thickness of the particle will also affect the estimated volume, it is expected that most particles will be laying on the fabric through their largest area (largest diameter), in such a way that the thickness is expected to be lower than the longitudinal observed diameter. Thus, the volume might be even smaller than the estimated one, and the LOD overestimated.

3. Results and discussion

3.1. Explosives detection on dyed and undyed textile fabrics

The preliminary detection of particles was made through visual inspection combined with microscopic detection. The time spent in searching each particle (overall time of 1 – 3 min) depended on both the size of explosive particles and their contrast with cloth fibres (i.e. the colour differences between particle and background). Sometimes, visual searching and location of the particles trapped within the cloth fibres posed difficulties (mostly with white explosives on white coloured textiles), increasing the time for spectra scanning (10 – 18 min).

After finding microscopically the alleged explosive/oxidizing salt particles trapped on the surface of the cloth fabrics (Fig. 1), the laser was focused on it, and the Raman analysis was performed, obtaining the characteristic Raman spectrum of the explosive. Each Raman spectrum was compared with the standard spectra of the explosives/oxidizing salts, and the textile fabrics (See Fig. S1 (Supporting Information)), analysed previously. In order to show the differences and difficulties when identifying microscopic explosive particles for different explosives and textile fabrics, Raman spectra did not undergo any pre-processing method: neither baseline correction, nor smoothing, nor fluorescence correction.

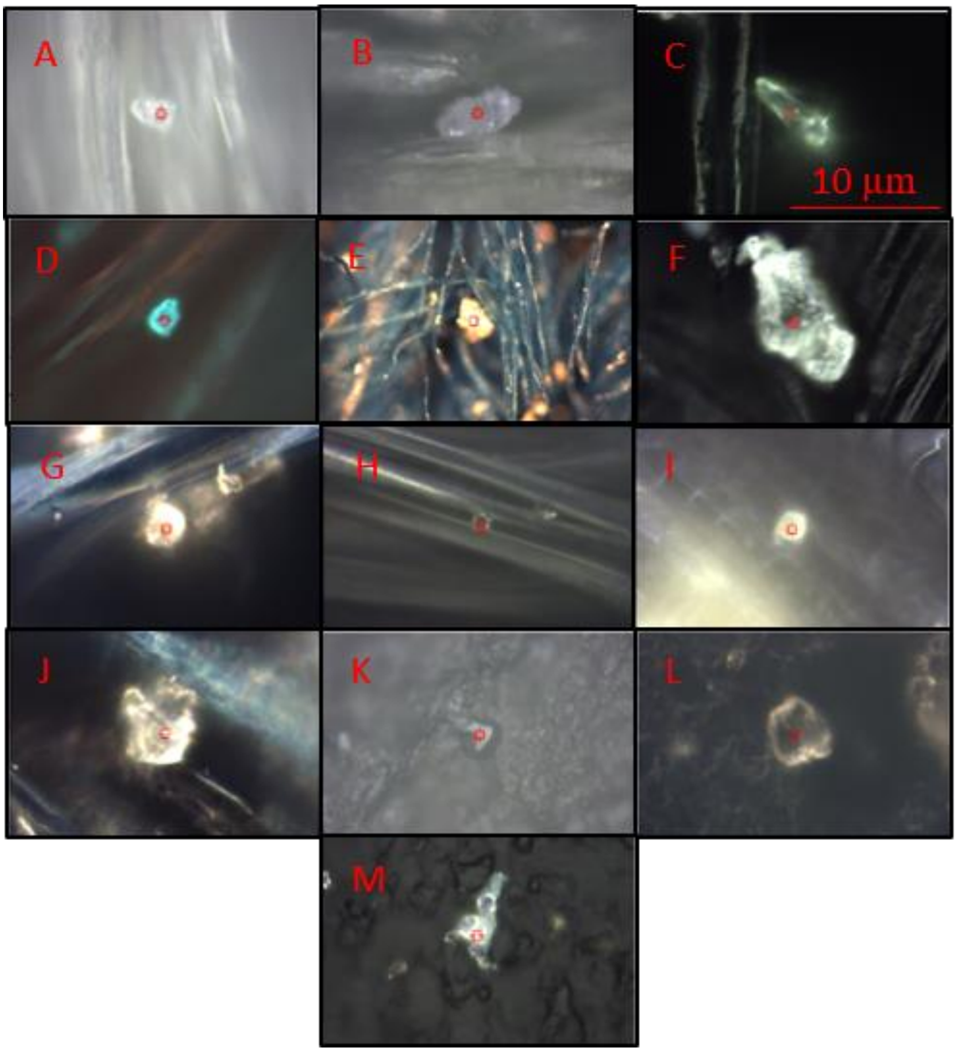

Figure 1. Explosive particles trapped in the various textiles (100x microscope objective): (A) barium nitrate on white cotton; (B) chloratite on green cotton; (C) HMTD on black cotton; (D) potassium perchlorate on red cotton; (E) flash powder on blue cotton; (F) potassium nitrate on black polyester; (G) RDX on blue polyester; (H) potassium chlorate on white polyester; (I) TNT on wool; (J) sodium chlorate on blue denim jeans; (K) PETN on nitrile; (L) ammonium nitrate on latex; (M) sodium nitrate on polyskin

As an example, Fig. 2 and Fig. 3 display the Raman spectra of HMTD and potassium chlorate, respectively, trapped in the various textile fabrics studied. HMTD is a peroxide organic explosive characterized by peroxide O-O bonds. In fact, the Raman spectrum of HMTD was dominated by the bands located at 773 and 414 cm^{-1}, corresponding to O-O stretching and N-C-O deformation vibrations, respectively (Fig. 2). The Raman spectrum of potassium chlorate (Fig. 3) was characterized by the ClO_3^- vibrations, at 979 cm^{-1} (antisymmetric stretching {ν_3(E)}), 940 cm^{-1} (symmetric stretching {ν_1(A$_1$)}), 620 cm^{-1} (symmetric deformation {ν_2(A$_1$)}) and 488 cm^{-1} (antisymmetric deformation {ν_4(E)}).[11,26]

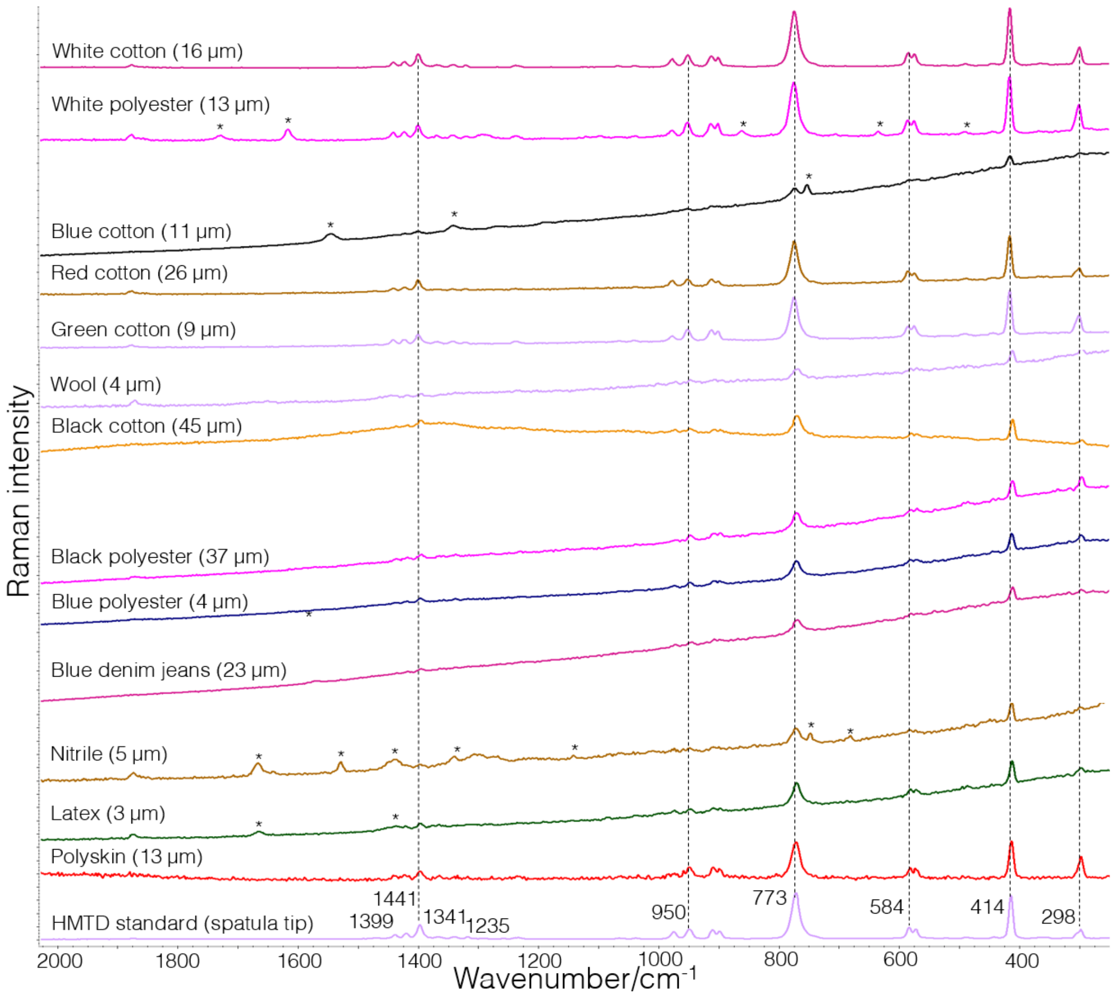

Figure 2. Raman spectra of HMTD particles (the diameter size of the explosive particle providing each Raman spectrum is indicated in brackets) trapped in the various textiles fibres. Asterisks indicate textile fibres bands. Spectra were collected using Thermo Scientific DXR Raman Microscope, 780 nm, 10 mW, 6 s exposure, 5 accumulations

except for black cotton (5 mW, 6 s exposure, 5 accumulations) and polyskin (1 mW, 6 s exposure, 5 accumulations)

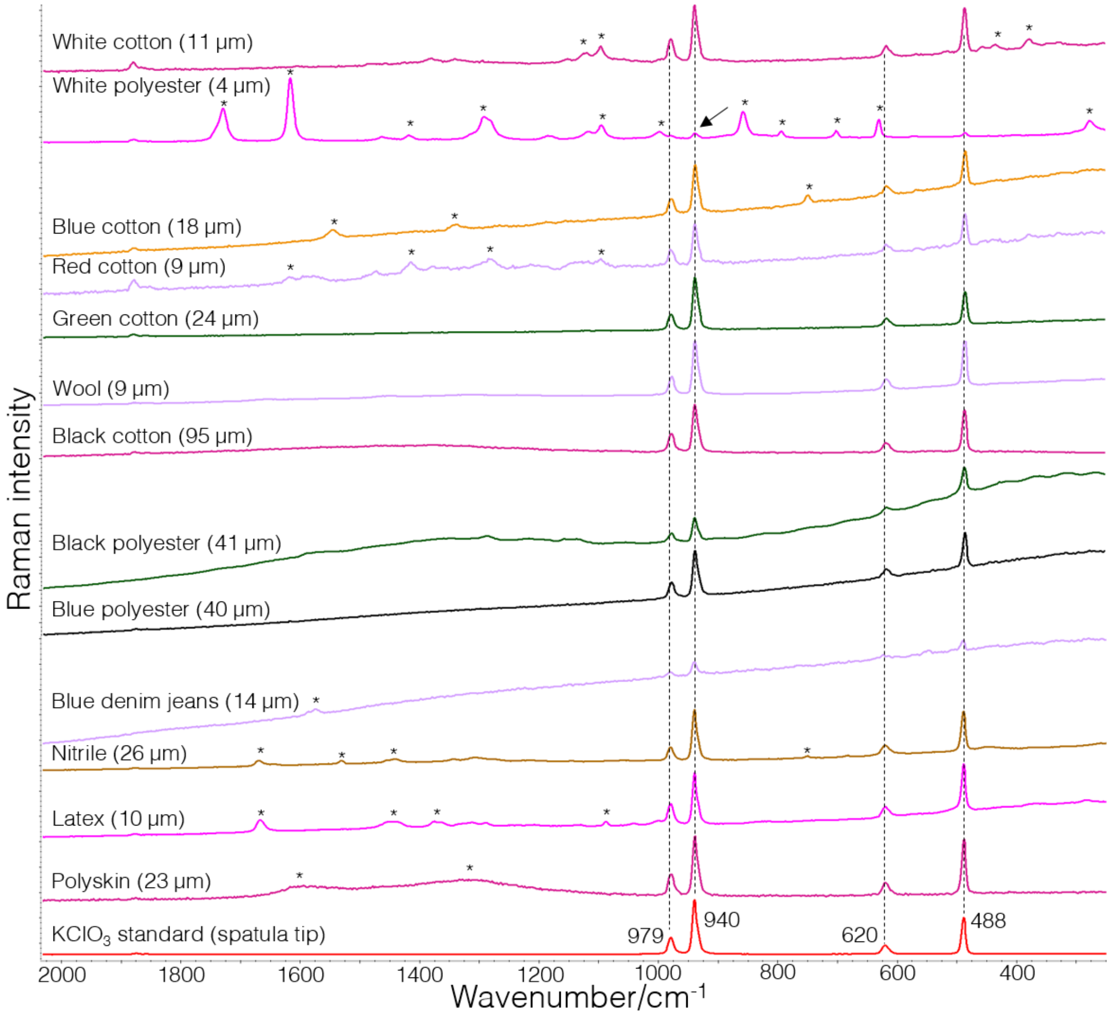

Figure 3. Raman spectra of potassium chlorate particles (the diameter size of the explosive particle providing each Raman spectrum is indicated in brackets) trapped in the various textiles fibres. Asterisks indicate textile fibres bands. Spectra measurements as in Figure 2.

In general, particles of explosives and oxidizing salts trapped in white cotton and white polyester (See Fig. S2 (Supporting Information)) were easily identified because of the absence/ low overlapping of bands from the cloth compared to the intense Raman bands of explosives. With regards to blue, red, and green cotton textiles, they provided bands that may correspond to the dye (marked with asterisks) superimposed on a fluorescence background. Positively, these bands did not overlap with the bands of the explosives/oxidizing salts, thus their identification was also successfully accomplished.

Regarding wool, black cotton, black and blue polyester fibres, and blue denim jeans, most spectra (mostly from HMTD spectra, Fig. 2) displayed high levels of background fluorescence that hindered the visualization of the bands corresponding to the dye and/or the textile material. It was necessary to carefully focus the laser spot directly on the particle to obtain the Raman spectral bands from explosives over the background. In the case of blue denim jeans, one band located at 1570 cm^{-1} was observed over the fluorescence that corresponded to the "blue indigo" dye, generally present in blue denim textiles.[12,13]

For nitrile, latex and polyskin materials, since they are smooth surface materials (Fig. 1), rapid visualization of the particles was possible. Positive identification of the oxidizing salts/explosive particles was possible by matching the characteristic bands to the standards. The most intense bands do not interfere with the bands of the inorganic explosives and oxidizing salts, but in the HMTD particle trapped on nitrile, they partially overlapped (see Fig. 2).

The analysis of trapped particles by the portable Raman showed similar results, but an increase in background fluorescence for most of the fabrics. Fig. 4 displays the Raman spectra of HMTD, TNT, potassium chlorate, and sodium nitrate particles (with approximately similar diameter sizes) using both Raman instruments. An increase in background fluorescence is clearly seen in the Raman spectra collected with the portable Raman, which in some cases overlapped the Raman bands of the energetic particles. These results were obtained using a 40x maximum microscope objective.

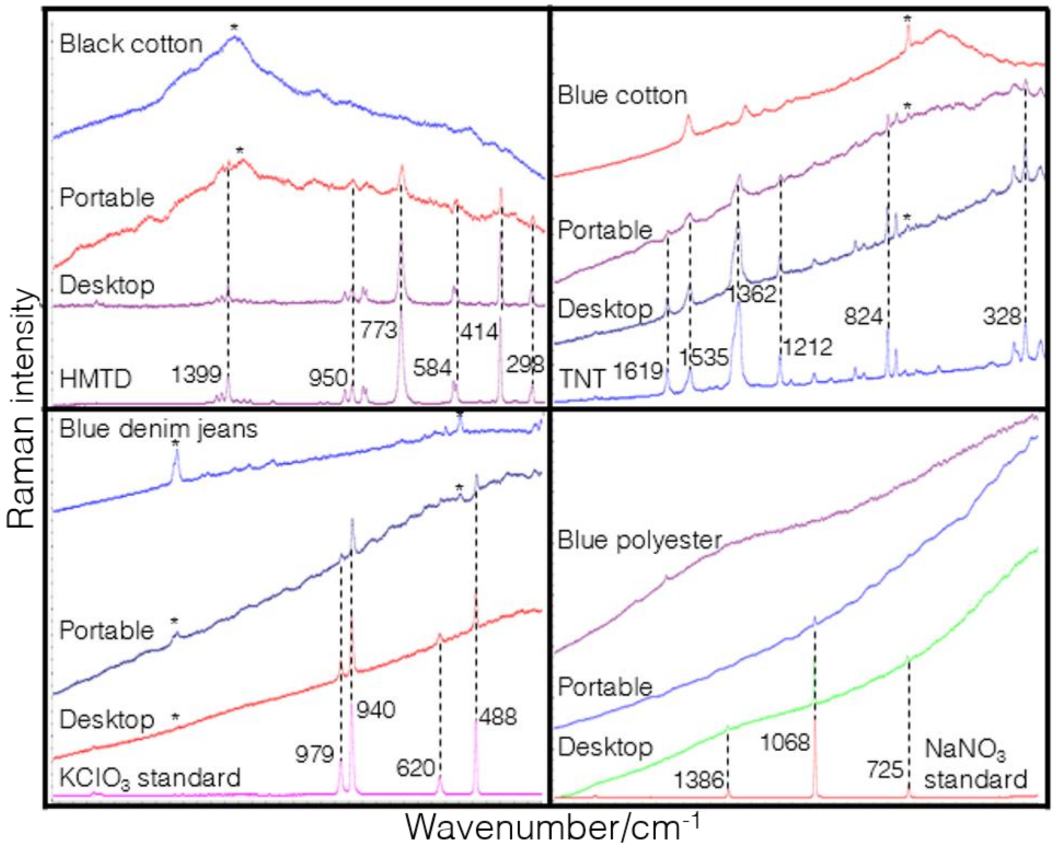

Figure 4. Comparison of Raman spectra taken by the Thermo Scientific DXR Raman microscope 100x and Portable BWTEK i-Raman pro 40x of similar diameter size particles: 62µm - 53µm (HMTD), 67µm - 32µm (TNT), 109µm - 107µm (Potassium Chlorate), 38µm - 37µm (Sodium Nitrate). Raman measurements conditions in table 1.

The analysis of polyskin, black cotton, blue denim jeans, and blue cotton textiles posed some additional problems. In some cases, the textile burned when subjected to the Raman laser. This was observed more frequently when using the portable Raman instrument, due to the power of the laser (See Fig. S3 (Supporting Information)). Portable instruments tend to have more powerful lasers to compensate the lack of resolution in comparison to desktop Raman instruments. Even so, by reducing the laser power, and focusing the laser at big particles (>40 µm), positive identification was possible. However, explosive particles on polyskin were not detected by the portable Raman since it burned even when using the minimum laser power (1%). Thus, sensitivity trials for the different textiles regarding the Raman laser have to be made, on order to prevent the destruction of the material and leave it intact for further analysis.

The solution of analysing bigger particles to avoid high background fluorescence will also depend on their thickness. Analysed particles with high diameter sizes that give high levels of fluorescence, are probably characterized as thin particles. In Fig. 5, is shown as the thickness of the particles could influence the travelling distance of the Raman laser, resulting in high or less fluorescence.

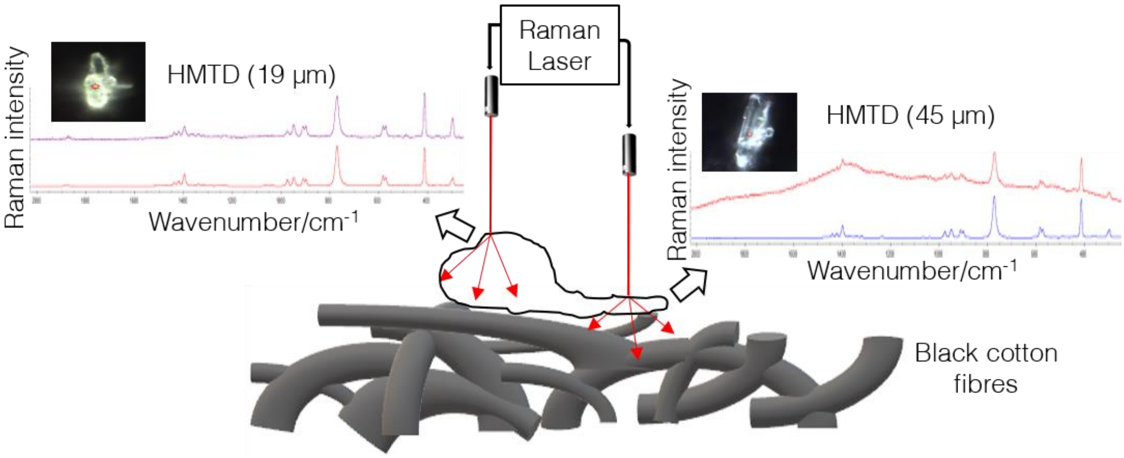

Figure 5. The background fluorescence will also depend on the thickness of the energetic particle analyzed, that automatically influences the travelling distance of the Raman laser. A small particle may be distinguished by having a greater or small thickness that will influence the level of background fluorescence observed in the corresponding Raman spectra. This difference in thickness may be inside the same particle. Explosive analyzed: HMTD with 19 µm and 45 µm diameter size. Spectra taken by the Thermo Scientific DXR Raman microscope, 780 nm, 5 mW, 6 s exposure, 5 accumulations.

The analysis of inorganic explosives (i.e., ammonal, chloratite, black powder, and flash powder) is characterized by the presence of high-sensitive substances (i.e., aluminium and charcoal), which resulted in the destruction of the energetic particle when target by the Raman laser (See Fig. S4 (Supporting Information)). In most cases, the search for bigger particles was strictly necessary (and even more when trapped on the cloth textiles with higher background fluorescence), in order to have the explosive bands intense enough for providing a positive identification.

Once detected the microscopic traces of explosives on the different textile fabrics studied, a key analytical aspect is to determine the limit of detection of that explosive traces. Prior to determine the LOD, the particle size (i.e., particle diameter) was studied. Interestingly, some tendencies were observed (see Fig. 6). For example, the diameter size of the smallest particles detected on blue cotton, black cotton, blue polyester, and polyskin by desktop Raman (particle size interval from 0 to 50 μm) was larger than for the rest of fabrics. The same was observed for the portable Raman (particle size interval from 0 to 200 μm), including also the blue denim jeans. For both instruments, white polyester was the one that provided less fluorescence, thus smaller particles were detected.

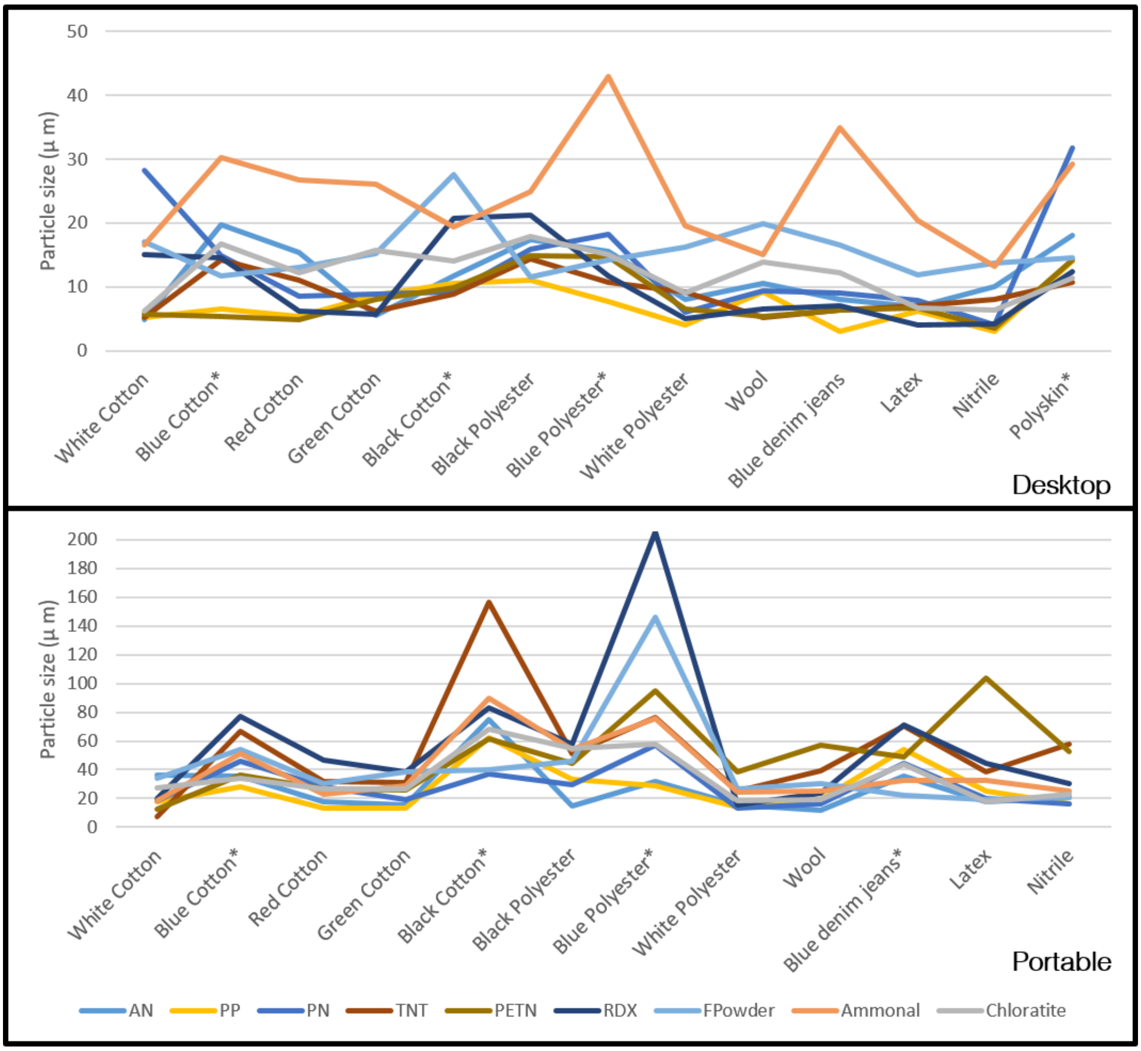

Figure 6. Graphics representing the minimum diameter size encountered for the oxidizing salt (ammonium nitrate (AN), potassium perchlorate (PP), potassium nitrate (PN)), organic (TNT, PETN, RDX) and inorganic (flash powder (FPowder), ammonal, chloratite) explosives particles, for each textile fabric by the desktop Thermo Scientific DXR Raman microscope and the portable BWTEK i-Raman pro.

Once determined the particle sizes, the LOD values were calculated as explained in section 2.3. As summarized in Figure 6, the Thermo Scientific DXR Raman microscope enabled the identification of particles with diameter size about 2 µm for the oxidizing salts (barium nitrate), 3 µm for the organic explosive particles (HMTD), and 6 µm for the inorganic explosive particles (black powder and chloratite). In the knowledge that barium nitrate, HMTD, black powder (potassium nitrate), and chloratite (sodium chlorate) have a density of 3.24 g/cm^3[27], 1.57 g/cm^3[28], 2.11 g/cm^3[11], and 2.50 g/cm^3[11], respectively, the mass of the smallest detected particles using the Thermo Scientific DXR Raman microscope was approximately 26 pg, 42 pg, 0.5 ng and 0.5 ng if cubic particles, and approximately the half if spherical particles (without considering the lowering effect of thickness).

For the portable BW&TEK i-Raman Pro, particles sizes about 7 μm for the oxidizing salts (barium nitrate), 7 μm for the organic explosive particles (TNT), and 18 μm for the inorganic explosive particles (chloratite and ammonal) were identified as the smaller ones. Considering that barium nitrate, TNT, chloratite (sodium chlorate), and ammonal (ammonium nitrate) have a density of 3.24 g/cm^3[27], 1.654 g/cm^3[29], 2.50 g/cm^3[11], and 1.725 g/cm^3[11,29], respectively, the mass of the smallest particles determined using the portable BW&TEK i-Raman Pro was 1.1 ng, 0.6 ng, 14.6 ng, and 10.1 ng if cubic particles, and 0.6 ng, 0.3 ng, 7.6 ng, and 5.3 ng if spherical particles.

Thus, the estimated LOD values were in the nanogram/picogram range, depending on the explosive and portable/desktop Raman, even in the presence of high interfering surfaces, which proves the analytical performance of Raman microscopy, comparable with other high sensitive and selective analytical techniques. The use of a portable Raman (maximum microscopic objective of 40x), limited the search for smaller particles, but even so, and giving the larger laser spot, smaller particles in the LOD range of ng were detected which empathizes the performance of this portable instrument coupled to a microscope.

3.2. Oxidizing component detection in explosive mixtures with various fuels

Regarding the analysis of energetic mixtures, a well-known forensic challenge involves the identification of the oxidizing component in explosive mixtures. In fact, the positive identification of potassium nitrate strongly depends on the fuel compound in which is mixed, since the fuel can be an interferent in Raman identification. The potassium nitrate was chosen since it is a common oxidizing salt used in the manufacture of inorganic explosives, such as black powder.

In Fig.7 the Raman spectra of mixtures, pure oxidizing salt and pure interfering substances are displayed. Regarding the detection of potassium nitrate in mixtures with sugar (white, powdered and brown sugar), despite of the numerous bands that sucrose spectra contains, the bands of potassium nitrate (1050 cm^{-1} and 715 cm^{-1}) were positively identified, even with some close overlapping bands of the interfering substance spectrum. In the mixtures involving wheat flour (and corn starch), the Raman bands of the oxidizing salt are superimposed on the Raman spectra of the interfering substance, giving a positive identification. The presence of talc powder did not present any difficulty in the identification of the potassium nitrate, since the bands of the interfering substance did not overlap. Similar results were observed in a previous study[14], in which the authors used a table-top microscope-based Raman system (i-Raman from BWTEK Inc., Newark, Delaware) with a excitation wavelength of 785-nm, to positively identify ammonium nitrate in mixtures with only talc powder, white sugar and wheat flour. Although similar results were verified, the performance of the Raman equipment was not evaluated at full capacity, that is by analysing the smallest particle to check the equipment performance. In this study, not only the positive identification of the oxidizing salt within those fuels was accomplished, but also was demonstrated the capability of a desktop confocal Raman microscope on the analysis of small particle sizes.

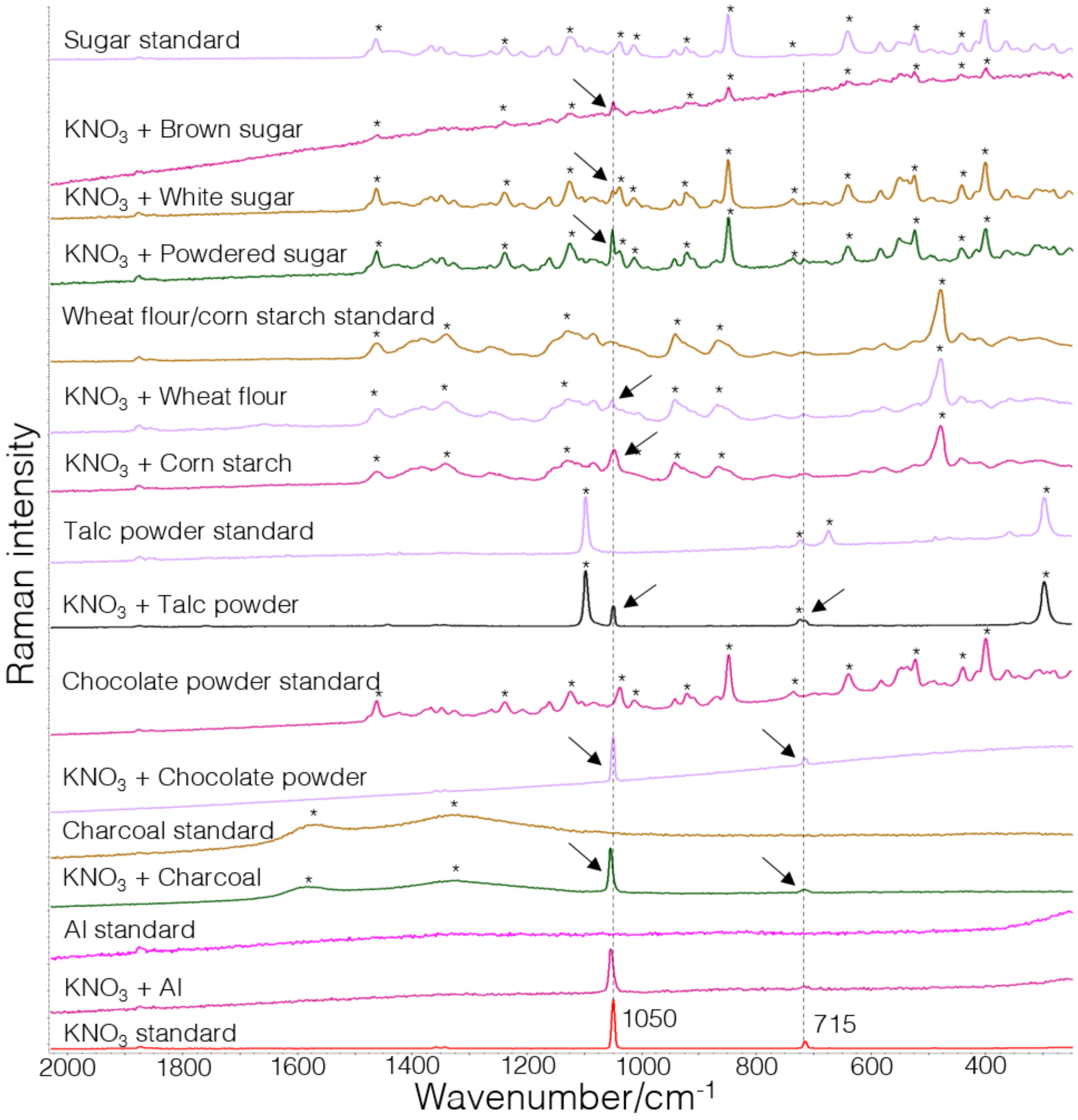

Figure 7. Raman spectra of mixtures of potassium nitrate (PN) with sugar (white sugar, powdered sugar, and brown sugar), wheat flour (and corn starch), charcoal, aluminium, chocolate powder, and talc powder taken by the Thermo Scientific DXR Raman Microscope, 780 nm, 8 accumulations, 5 seconds, 14 mW.

Despite the positive identification demonstrated in Fig. 7, when analysing the mixtures with chocolate cocoa powder, aluminium, and charcoal, the potassium nitrate particles can be totally covered by the fuel substance (See Fig. S5 (Supporting Information)), which gives rise to high levels of fluorescence in the spectra. This fluorescence might hinder the spectroscopic identification of the fuel itself (see Fig. 7 for the chocolate powder mixture), and of the oxidizing salt, increasing (making poorer) the LOD.

4. Conclusions

The detection of explosive particle residues trapped on highly fluorescence interfering surfaces (i.e. textile fabrics) was evaluated by two confocal Raman microscopy instruments. Considering the right focus, the type of explosive particle and clothing, and the fluorescence coming from the textile background, a high discrimination was obtained for each confocal Raman instrument, giving positive identifications of the explosive residue. Calculated limits of detection (LOD) considering the smallest particle size diameter were in the range of picogram, for the Thermo Scientific DXR Raman microscope, and nanogram, for the portable BW&TEK i-Raman Pro. It was demonstrated that the background fluorescence coming from the textile fabric influence the particle size detection, and that the particle thickness also plays a role when analysing in high fluorescent surfaces. In addition, it was shown that for inorganic explosives and for some textiles (such as black cotton, blue cotton, blue denim jeans and polyskin), burning of the sample was observed when subjected to the Raman laser. The detection of potassium nitrate in mixtures with interfering substances that act as fuels was also demonstrated with no significant interferences from the fuel (charcoal, aluminium, talc powder, wheat flour (and corn starch), sugar (white, powdered and brown sugar), and chocolate cocoa powder).

Acknowledgements

Diogo Videira-Quintela thanks the Erasmus+ programme for his “Learning Agreement for Traineeships” grant, and the INQUIFOR investigation group for the assistance and technical support. Félix Zapata thanks the Spanish Ministry of Education for his PhD research fellowship FPU014/00790.

References

[1] F. Zapata, M. Á. F. de la Ossa, E. Gilchrist, L. Barron, C. García-Ruiz, *Talanta* **2016**, *161*, 219.
[2] M. R. Almeida, D. N. Correa, J. J. Zacca, L. P. L. Logrado, R. J. Poppi, *Anal. Chim. Acta* **2015**, *860*, 15.
[3] M. Nordberg, M. Åkeson, H. Östmark, T. E. Carlsson, Proc. of SPIE **2011**, 8017, 80171B-1.
[4] M. A. M. Huri, U. K. Ahmad, *Malays. J. Anal. Sci.* **2014**, *18*, 68.
[5] C. C. Cooksey, J. E. Neira, D. W. Allen, Proc. of SPIE **2012**, 8357, 83570O-1.
[6] C. Baker, T. Lo, W. R. Tribe, B. E. Cole, M. R. Hogbin, M. C. Kemp, *Proc. IEEE* **2007**, *95*, 1559.
[7] W. R. Tribe, D. A. Newnham, P. F. Taday, M. C. Kemp, Proc. of SPIE **2004**, 5354, 168.
[8] M. C. Kemp, C. Baker, I. Gregory, in *Stand-off detection of suicide bombers and mobile subjects,* (Eds: H. Schubert, A. Rimski-Korsakov), Springer, Dordrecht, The Netherlands, **2006**, pp. 151–165.
[9] U. Puc, A. Abina, M. Rutar, A. Zidanšek, A. Jeglič, G. Valušis, *Appl. Opt.* **2015**, *54*, 4495.
[10] M. J. Walczakowski, N. Palka, M. Szustakowski, Proc. of SPIE **2015**, 9651, 96510I-1.
[11] F. Zapata, C. García-Ruiz, *Anal. Chem.* **2016**, *88*, 6726.
[12] E. M. A. Ali, H. G. M. Edwards, I. J. Scowen, *J. Raman Spectrosc.* **2009**, *40*, 2009.
[13] E. M. A. Ali, H. G. M. Edwards, I. J. Scowen, *Talanta* **2009**, *78*, 1201.
[14] S. Almaviva, S. Botti, A. Palucci, A. Puiu, F. Schnürer, W. Schweikert, F. S. Romolo, *Opt. Eng.* **2014**, *53*, 44113.
[15] D. S. Moore, *Rev. Sci. Instrum.* **2004**, *75*, 2499.
[16] C. M. Canal, A. Saleem, R. J. Green, D. A. Hutchins, Proc. of SPIE **2010**, 7838, 78380G-1.
[17] A. Saleem, C. Canal, D. A. Hutchins, R. J. Green, Proc. of SPIE **2011**, 8018, 80181I-1.
[18] G. G. Diamond, R. B. Gohel, Proc. of SPIE **2009**, 7296, 72983S-1.

[19] M. López-López, C. García-Ruiz, *Trends Anal. Chem.* **2014**, *54*, 36.

[20] M. Marshall, J. C. Oxley, Eds., *Aspects of explosives detection*, Elsevier, Amsterdam, **2009**.

[21] J. P. Agrawal, *High Energy Materials: Propellants, Explosives and Pyrotechnics*, Wiley-VCH Verlag, Weinheim, **2010**.

[22] D. Menning, H. Östmark, in *Detection of Liquid Explosives and Flammable Agents in Connection with Terrorism*, (Eds: H. Schubert, A. Kuznetsov), Springer, Dordrecht, The Netherlands, **2008**, pp. 55–70.

[23] F. Zapata, C. García-Ruiz, *Forensic Sci. Int.* **2017**, *275*, 57.

[24] N. Abdul-Karim, C. S. Blackman, P. P. Gill, R. M. Morgan, L. Matjacic, R. Webb, W. H. Ng, *Anal. Chem.* **2016**, *88*, 3899.

[25] B. Zachhuber, G. Ramer, A. Hobro, E. t. H. Chrysostom, B. Lendl, *Anal. Bioanal. Chem.* **2011**, *400*, 2439.

[26] K. Nakamoto, *Infrared and Raman spectra of inorganic and coordination compounds*, John Wiley & Sons, New Jersey, USA, 6th ed., **2009**.

[27] P. G. Zverev, T. T. Basiev, V. V. Osiko, A. M. Kulkov, V. N. Voitsekhovskii, V. E. Yakobson, *Opt. Mater.* **1999**, *11*, 315.

[28] Yin Sun, *Field Detection Technologies for Explosives*, ILM Publications, Hertfordshire, UK **2010**.

[29] J. Hwang, N. Choi, A. Park, J.-Q. Park, J. H. Chung, S. Baek, S. G. Cho, S.-J. Baek, J. Choo, *J. Mol. Struct.* **2013**, *1039*, 130.