Detection of Organic Explosive Residues from Outdoor Explosions Using Confocal Raman Microscopy

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ABSTRACT

The present study evaluates the ability of Raman microscopy to detect post-blast organic explosive residues from two simulated improvised explosive devices (IEDs) containing a mixture of TNT/RDX and two IEDs containing smokeless powder (SP). Various witness materials contained in the IEDs were swabbed and extracted with acetone to create post-blast liquid extracts. The extracts were dried and examined using Raman microscopy, which enabled the determination of optimal sampling locations of post-blast analytes within the dried extracts. TNT, RDX and smokeless powder constituents were successfully identified on most substrates.

INTRODUCTION

While identifying the explosive type used in an IED after an explosion is a challenge, it is an essential step that can have positive effects on the ensuing investigation. Literature regarding the analysis of organic post-blast explosive residues using spectroscopic techniques, specifically Raman spectroscopy, is limited [1,2]. Typically, no microscopically visible unreacted particles remain after the explosion. The present study demonstrates the successful detection of smokeless powder constituents, including ethyl centralite (EC), diphenylamine (DPA), di-n-butyl phthalate (DBP) and nitroglycerin (NG) in post-blast dried extracts using confocal Raman microscopy and a software mapping function without the presence of unreacted particles. TNT and RDX were also successfully identified in the extracts, with RDX crystals observed in certain dried extracts following solvent evaporation.

MATERIALS & METHODS

Standards and Materials – A standard reference mixture containing 50 ppm each of EC, DPA, DBP, nitrocellulose (NC), and NG was created using standards purchased from Accustandard. Hodgdon BL-C® (2) smokeless powder, as well as authentic TNT and RDX was provided by the TX Montgomery County Fire Marshal's Office (MCFMO).

Figure 1. Witness materials placed in each IEDs.

Construction, Detonation, and Collection of Explosive Devices – Four simulated IEDs (two utilizing smokeless powder and two utilizing a TNT/RDX mixture) were constructed. The explosive charges were placed in an orange toolbox with witness materials commonly found in IEDs, including electrical tape, two paint sticks, a cell phone, electric wiring, nuts and bolts, four AA batteries, a 9V battery, and a rocker switch (**Figure 1**). The devices were detonated, and the debris was collected in unlined aluminum paint cans.

Preparation of Post-Blast Extracts - Swabs were prewetted with acetone, then used to swab the debris, avoiding collection of unburned particles. Each swab was placed in 1 mL of acetone and extracted for 3 minutes. The swabs were squeezed to remove the absorbed acetone and discarded. Swabs for each substrate were collected in triplicate. Following ASTM E3329–21, the liquid extracts were prepared for Raman analysis by drying a 10 µL aliquot of the extract onto a steel slide.

Instrumental Setup - A Renishaw InVia™ Inspect confocal Raman microscope (Renishaw, Wotton-under-Edge, UK) was used for the Raman data collection. Spectra for the analytical standards were collected using the 785 nm laser at 1 mW at the source. Spectra for the 50-ppm smokeless powder reference mixture and the authentic post-blast extracts were collected using the 785 nm laser at 10 mW at the source. Raman point mapping was used as screening tool to rapidly determine the optimal location of post-blast analytes within the dried extracts (**Figure 2**).

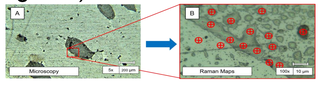

Figure 2. Developed methodology for location indentification of explosive residues using microscopy.

RESULTS & DISCUSSION

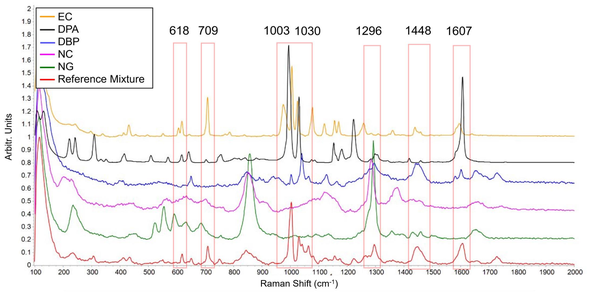

Figure 3. Comparison of spectra from the individual constituents of SP standards to the 50-ppm reference mixture (red).

Table 1. Positive identifications of smokeless powder constituents per witness materials. 3 swabs were analyzed per witness material: Green = 3/3, Yellow = 2/3, Orange = 1/3 and Red = 0/3.

Substrate	*DPA*		*EC*		*DBP*		*NG*		*NC*	
	Det. 1	*Det. 2*	*Det. 1*	*Det. 2*	*Det. 1*	*Det. 2*	*Det. 1*	*Det. 2*	*Det. 1*	*Det. 2*
Orange toolbox	1	3	1	1	1	2	1	2	1	3
Wood	0	3	0	2	0	3	0	3	0	3
Tape	2	3	2	1	1	3	1	2	1	2
Wire	3	3	2	3	2	3	1	3	1	3
Cell phone	1	2	2	2	1	2	2	2	2	2
Switch	1	3	1	3	2	3	1	3	1	3
Shrapnel	1	3	1	2	1	2	1	1	1	1
9V battery	2	3	2	3	2	3	2	3	2	3
AA battery	2	3	2	3	2	3	2	1	2	1

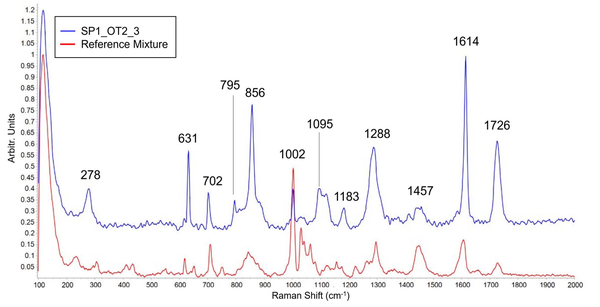

Figure 4. Comparison of a SM post-blast extract spectrum (blue) and a spectrum for the 50-ppm reference mixture (red).

- Raman bands observed in the dried mixture were identified by attributing potential Raman scattering contributions to the individual components of smokeless powder (**Figure 3**), such as the band at 618 cm^{-1}, which can be attributed to a combination of the in-plane ring bending vibration from the EC as well as the in-plane ring bending vibration from the DPA.
- Several bands were absent when comparing the individual standards to the dried reference mixture. For example, the DPA band located at 1250 cm^{-1} (black spectrum) is missing in the dried reference mixture (**Figure 3**).
- All smokeless powder constituents were identified from the post-blast residue when compared to the 50-ppm smokeless powder reference mixture (**Figure 4)** on most substrates, except for the paint sticks (wood) (**Table 1**).
- Minor bands were observed in the authentic post-blast sample, such as the bands at 795 cm^{-1} and 1095 cm^{-1} (**Figure 4**), that were not present in the dried reference mixture. These bands could be due to the presence of an unknown contributor, such as partial decomposition products resulting from the explosion, or variations in concentrations of constituents when compared to the reference mixture.

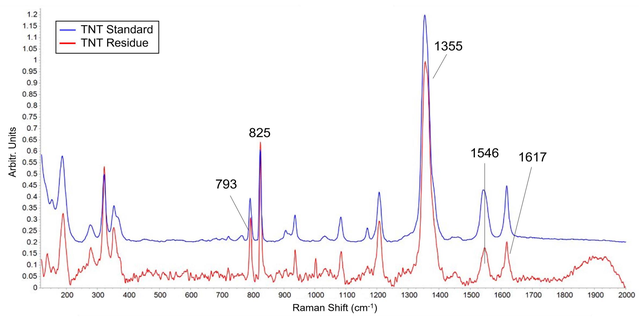

Figure 5. Comparison between the spectrum from TNT post-blast explosive residue (red) and the spectrum from TNT standard (blue).

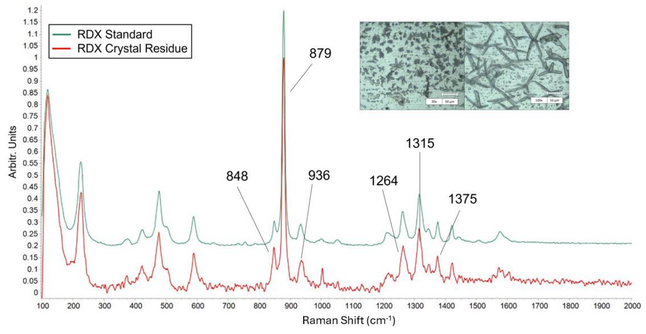

Figure 6. Comparison between the spectra from RDX post-blast explosive residue (red) and RDX standard (green).

- TNT dried liquid post-blast extract showed characteristic bands for TNT at 793 cm^{-1}, 825 cm^{-1} (NO2 scissoring modes), and 1355 cm^{-1} (symmetric NO2 stretch) (**Figure 5**).
- RDX dried liquid post-blast extract displayed characteristic bands for RDX at 848 cm^{-1} (CH2 rocking and C-N-C deformation) and 879 cm^{-1} (ring breathing). Raman bands at 936 cm^{-1} (ring stretching and N-O deformation), 1264 cm^{-1} (CH2 scissoring and N-N stretch), and 1315 cm^{-1} (CH2 wagging) (**Figure 6**).
- RDX crystals were observed after allowing the solvent to evaporate from the liquid extract (**Figure 6 inset**)

CONCLUSIONS

- The developed methodology allowed for the successful identification of organic explosives in post-blast residue extracts, including TNT, RDX and several smokeless powder constituents using confocal Raman microscopy.
- The microscopical capabilities of the instrument allowed to rapidly determine the optimal location of post-blast analytes within the dried extracts, as well as the observation of crystals being formed in the drying extracts, subsequently identified as RDX.
- This study provides a framework for practitioners evaluating post-blast debris without the presence of unburned or partially burned particles when using Raman microscopy.
- The small quantity of extracts used with Raman microscopy allows for their subsequent analysis with GC-MS or HPLC-MS.

REFERENCES

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