Two Techniques, One Goal: An Analysis of Intact Explosives Using Confocal Raman Microscopy and Direct Analysis in Real Time-High Resolution Mass Spectrometry (DART-HRMS)

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INTRODUCTION

Homemade explosive devices (HMEs) have increased in prevalence within domestic casework and pose a particular challenge to forensic investigators: they are often difficult to classify since they are frequently constructed from common household materials, may fall under multiple explosives categories, and may contain organic and/or inorganic components[1, 2]. Thus, when analyzing HMEs, it is critical for forensic analysts to use a methodology effective for identifying a diverse array of explosives.

The current primary techniques for explosive analysis are gas chromatography-mass spectrometry (GC-MS) and liquid chromatography tandem mass spectrometry (LC-MS/MS). However, these methods require extensive sample preparation, are time-consuming, and destroy the sample. Confocal Raman microscopy and DART-MS are two instrumental techniques that have shown promise for identifying explosives and are quick, non-destructive, and require minimal sample preparation.

This study examines three classes of explosives (high explosives, inorganic oxidizers, and smokeless powder stabilizers and deterrents) by combining data gathered from standards and authentic intact samples using confocal Raman microscopy and DART-MS.

MATERIALS & METHODS

Sample Preparation for Standards
High Explosives: Diluted to 50 ppm with methanol
Inorganic Oxidizers: <20 mg dissolved in 50:50 methanol and deionized water, then diluted to 50 ppm
Smokeless Powder: Diluted to 50 ppm with methanol

Sample Preparation for Authentic Samples
TNT: A flake (<10 mg) was dissolved into 1 mL acetone, then diluted to 100 ppm
ANFO: A single grain was dissolved in 1 mL of 50:50 methanol and deionized water
Smokeless Powder: 10 mg was crushed, put in a microcentrifuge tube and extracted with ethyl acetate

Table 1: Explosives standards analyzed

Explosive Category	Standard
High Explosives	2,4,6-Trinitrotoluene (TNT) Pentaerythritol tetranitrate (PETN)
Inorganic Oxidizers	Ammonium Nitrate (AN) Ammonium Perchlorate (APC) Potassium Chlorate (PC) Potassium Perchlorate (PPC) Potassium Nitrate (PN) Sodium Chlorate (SC) Sodium Nitrate (SN)
Smokeless Powder Stabilizers, Deterrents	Diphenylamine (DPA) Ethyl Centralite (EC) Methyl Centralite (MC) 2,4-Dinitrotoluene (2,4-DNT)

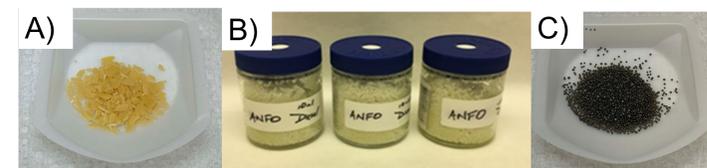*Figure 1: Authentic TNT (A), ANFO (B), and smokeless powder (C) analyzed in this study*

Raman Sampling and Instrumental Parameters
Instrument: Renishaw inVia™ InSpect confocal Raman microscope coupled with Leica DM 2700 M research microscope
Specifications: 20x objective, 785 nm laser (50 mW for high explosives, 1 mW for inorganic oxidizers), 532 nm laser (25 mW for smokeless powder), from 100 cm^{-1} to 2000 cm^{-1}. All wattages were measured at the source for the laser power.
Sampling: Placed on steel slide (10 μL dried solution for standards, pinhead quantity for authentic samples). Smokeless powder samples were organically extracted to prevent combustion

DART-MS Sampling and Instrumental Parameters
Instrument: DART JumpShot® ionization source coupled to Agilent 6530 quadrupole time-of-flight (Q-TOF) mass spectrometer with a Vapur® pressure interface
Specifications: Helium as source gas, 350 °C with temperature hold of 30 s and pulse of 3 s
Sampling: 5 μL of all samples were pipetted onto QuickStrip™ cards and allowed to partially dry before being analyzed in positive mode; 5 μL solvent blank aliquots were run between each sample, except for AN, which was directly analyzed

RESULTS & DISCUSSION

- Traditionally, inorganic oxidizers have been difficult to analyze with DART-MS analysis due to their low volatility; however, this study successfully obtained spectra for ammonium-based oxidizers.
- Key ions detected for AN are *m/z* 98.0551 (monomer), *m/z* 178.0773 (dimer), *m/z* 258.0980 (trimer), as well as higher order clusters at *m/z* 338.1198, *m/z* 418.1421, and *m/z* 498.1641 (**Figure 2**).
- The ammonium nitrate clusters were highly labile and broke apart during isolation without applying any collision energy.
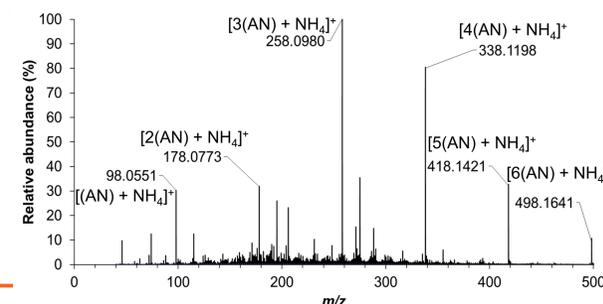
- A DART mass spectrum of the authentic smokeless powder sample was collected in positive mode and showed ions at *m/z* 269.1658 and *m/z* 170.0963, which correspond to DPA and EC (**Figure 4**).
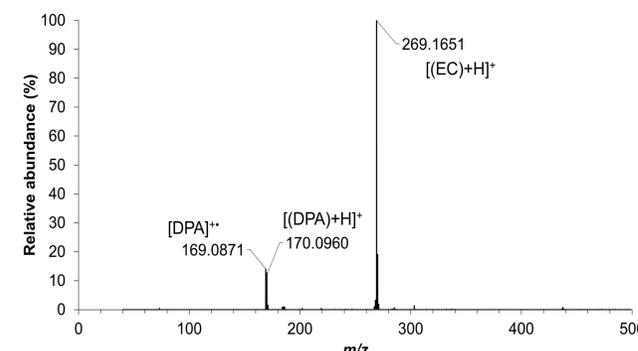

Figure 2: DART mass spectrum for ammonium nitrate collected in positive ionization mode with key ions labeled

Figure 3: Raman spectrum of ammonium nitrate salt illustrating its two characteristic vibrational bands, along with two lattice vibration modes (highlighted in the orange box)

Figure 4: DART mass spectrum of an authentic smokeless powder sample collected in positive ionization mode

- The Raman analysis of inorganic oxidizers, including AN, showed that the spectra were primarily influenced by anions, such as the symmetric N-O stretching vibration at 1043 cm^{-1} and the N-O plane deformation at 714.4 cm^{-1}.
- These results indicates that salts sharing the same anion are likely to exhibit comparable spectra, posing difficulties for their discrimination in a forensic context.
- However, there were enough spectral differences between compounds with the same anions to indicate cation influence.
- Lattice modes of crystalline salts could help with further discrimination and appear in the low-energy region of Raman spectra (10–250 cm^{-1}).
- These vibrations generally result from lattice motions and yield informative details regarding the translational and torsional movements of molecules or ions relative to their lattice sites.
- AN is expected to display several lattice modes at ambient temperature (25 °C).
- In **Figure 3**, two of these lattice modes of AN can be observed, with the *B3g* coupled libration and translation modes at 139.9 cm^{-1} and the *B1g* libration at 169.7 cm^{-1}.

- Nitrocellulose is a well-studied component in smokeless powder, so this study focused on stabilizers and deterrents often added to smokeless powders.
- When comparing the Raman spectrum of an authentic smokeless powder sample and nitrocellulose, a peak at 1598 cm^{-1} was unaccounted for in the nitrocellulose spectrum (**Figure 5**). This peak aligned with a band present in EC and MC associated with C-N stretching.
- These results indicate that Raman spectroscopy is a potential method for detecting smokeless powder stabilizers and deterrents, but more research is necessary.
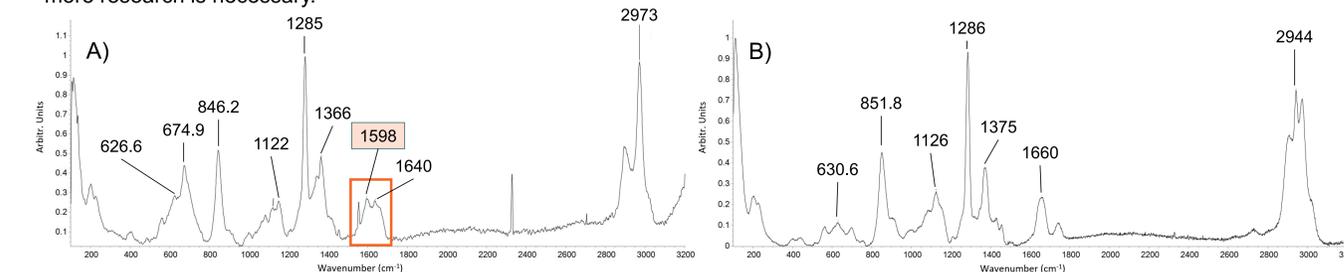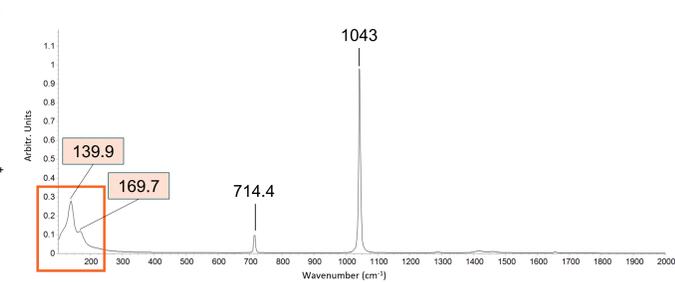

Figure 5: Comparison of Raman spectra for A) an authentic smokeless powder sample and B) nitrocellulose

CONCLUSIONS

- Inorganic oxidizers were more easily identified using Raman than DART-MS, though DART-MS could detect ammonium-containing oxidizers.
- Smokeless powder components could be identified using Raman, though fluorescence was a concern, and DART-MS analysis corresponded with existing literature.
- A proposed analytical scheme was developed for the analysis of suspected intact explosives (**Figure 6**).
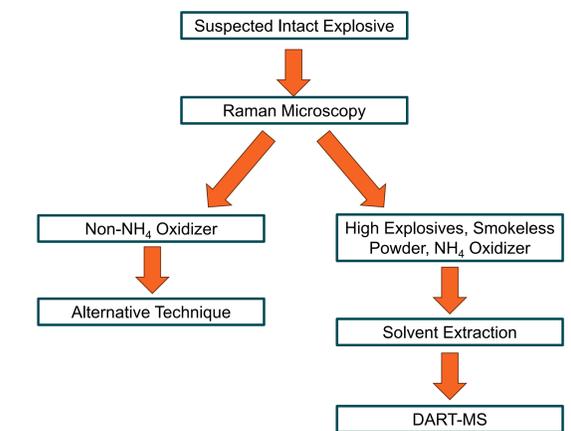

Figure 6: Proposed analytical scheme for explosive compound analysis

REFERENCES

[1]United States Bomb Data Center, United States Bomb Data Center (USBDC) Explosives Incident report (EIR) 2021, Bureau of Alcohol, Tobacco, Firearms and Explosives, Redstone Arsenal, AL (2021).

[2]C. Black, T. D'Souza, J.C. Smith, N.G.R. Hearns, Identification of post-blast explosive residues using direct-analysis-in-real-time and mass spectrometry (DART-MS), Forensic Chem. 16 (2019) 100185, https://doi.org/10.1016/j.forc.2019.100185.

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