Investigating the Capability of DART-MS for the Analysis of Intact Explosives and Explosives Residue

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Explosives Background

- U.S. bomb data center estimates there were 334 bombing incidents in 2022[1]
- Fuel/oxidizer mixtures are the second most common explosive charge
- Propellants are the third most common
  - Readily available to civilians
- Organic explosives from discarded military ordinance can fall into the hands of civilian populations
  - TNT, RDX, HMX, etc.

[1] United States Bomb Data Center, United States Bomb Data Center (USBDC) Explosives Incident report (EIR) 2022, Bureau of Alcohol, Tobacco, Firearms and Explosives, Redstone Arsenal, AL, 2022. https://www.atf.gov/resource-center/docs/report/2022-explosives-incident-report-eir/download (accessed January 25, 2024).

Previous Work

- DART has been used successfully for detection of explosives
- Mainly focused on intact organics [2]
    - TNT, PETN, NG, etc.
- Limited post-blast research [3]
    - TATP, HMTD, and MEKP
- Limited inorganic research [4,5]
    - Do not ionize well for DART analysis
        - Infrared Thermal Desorption (IRTD) looks promising

[2] E. Sisco, J. Dake, C. Bridge, Screening for trace explosives by AccuTOF™-DART®: An in-depth validation study, Forensic Sci. Int. 232 (2013) 160–168. https://doi.org/10.1016/j.forsciint.2013.07.006.
[3] 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.
[4] T.P. Forbes, E. Sisco, M. Staymates, G. Gillen, DART-MS analysis of inorganic explosives using high temperature thermal desorption, Anal. Methods 9 (2017) 4988–4996. https://doi.org/10.1039/C7AY00867H.
[5] T.P. Forbes, E. Sisco, M. Staymates, Detection of Nonvolatile Inorganic Oxidizer-Based Explosives from Wipe Collections by Infrared Thermal Desorption—Direct Analysis in Real Time Mass Spectrometry, Anal. Chem. 90 (2018) 6419–6425. https://doi.org/10.1021/acs.analchem.8b01037.

Research Goals

I. Explore use of DART-MS as a rapid and reliable screening technique for intact explosives and explosive residues

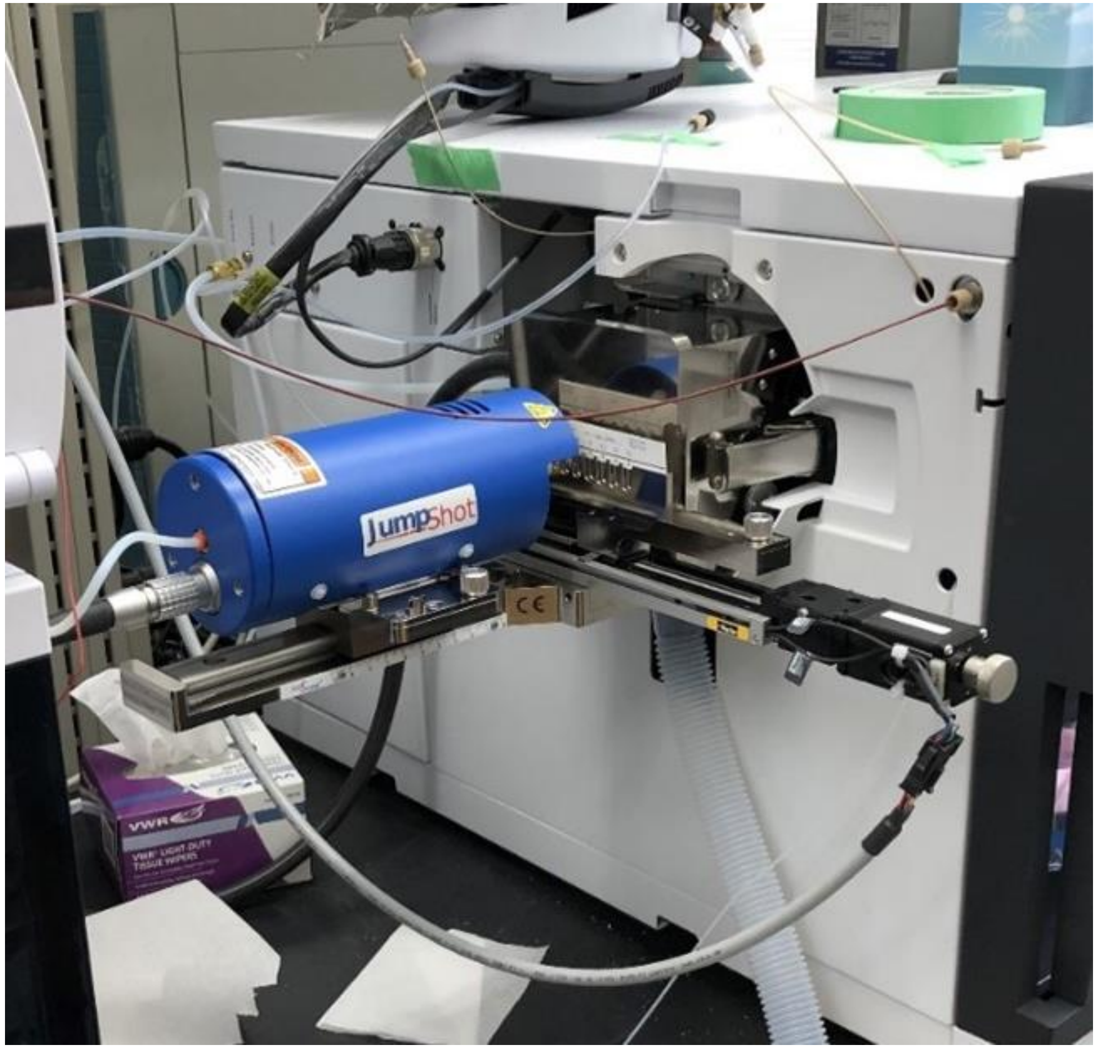
II. Assess challenges as it relates to post-blast analysis

- Debris and interferences

III. Expand range of analytes detected for post-blast with DART-MS

DART-QTOF

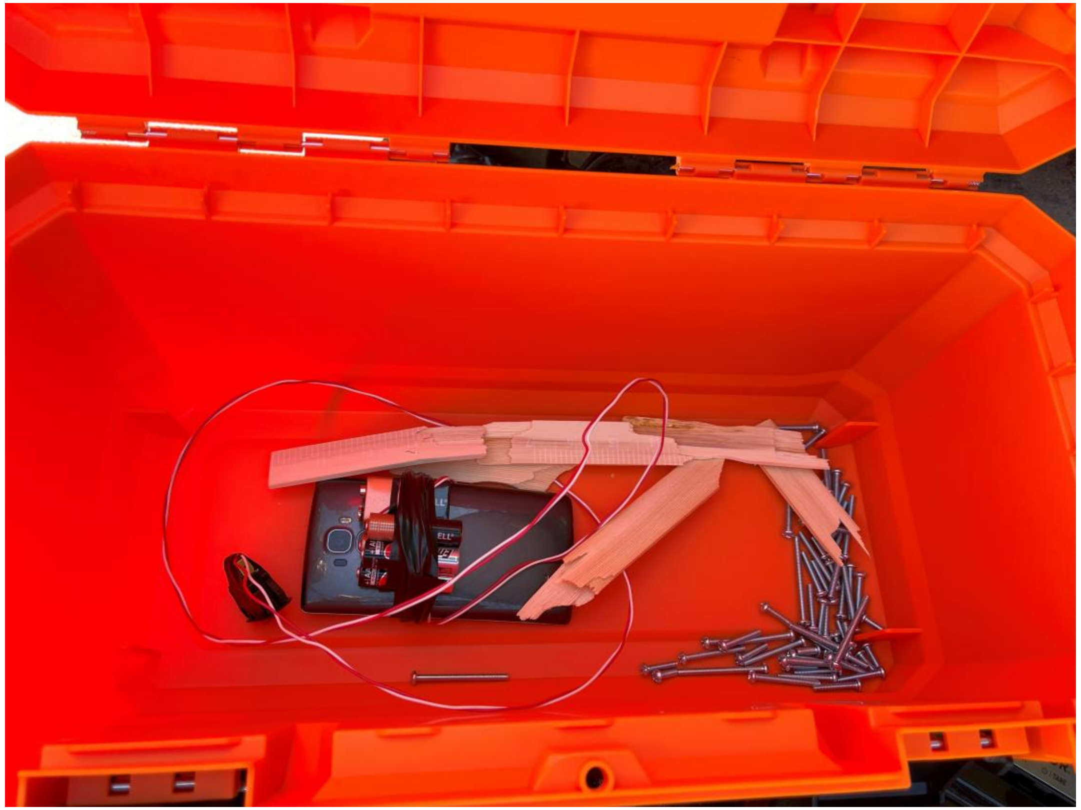
- IonSense DART Jumpshot® ion source
- Agilent 6530 Q-TOF
  - Vapor® pressure interface
- Optimal Parameters
  - 350 °C
  - Positive and negative mode
  - Helium source gas



Post-Blast Field Experiments

- Set up detonations
    - Collaboration with MCFMO
- Detonate explosives and collect debris
- All IEDs were constructed using same components
- Analyze debris with DART-QTOF

Field Experiments



Field Experiments

Field Experiments

Organic Explosives

Smokeless powder, TNT, RDX, Nitromethane

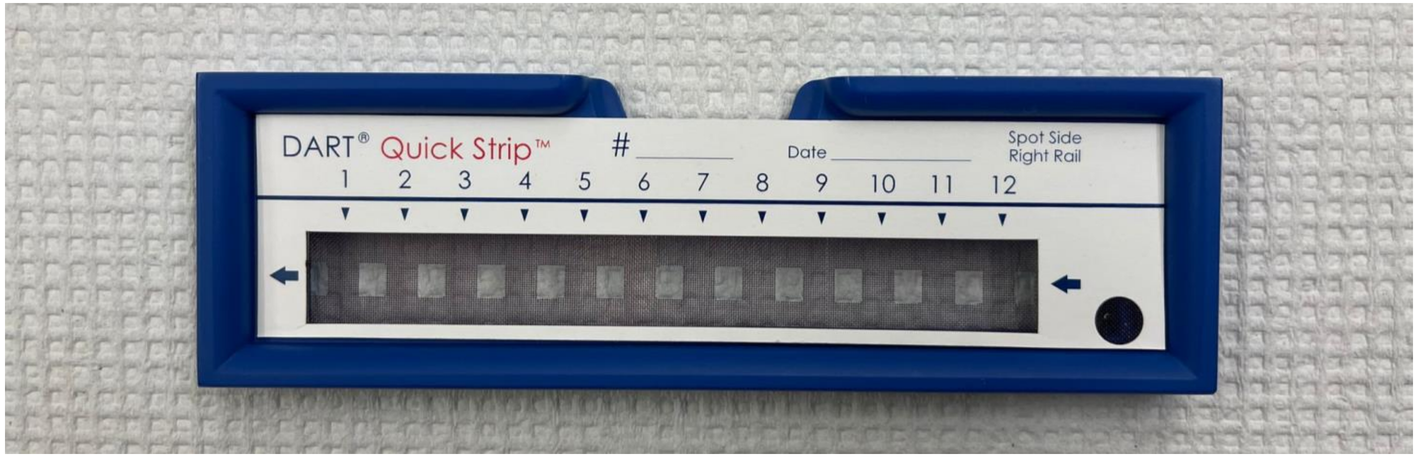
Methods of Analysis

Intact

- Standards were pipetted onto a QuickStrip™
- Introduced into the DART gas stream using a linear rail system

Post-blast

- Explosive residues were introduced via a novel subsampling method
- Held in the DART gas stream for 7 seconds



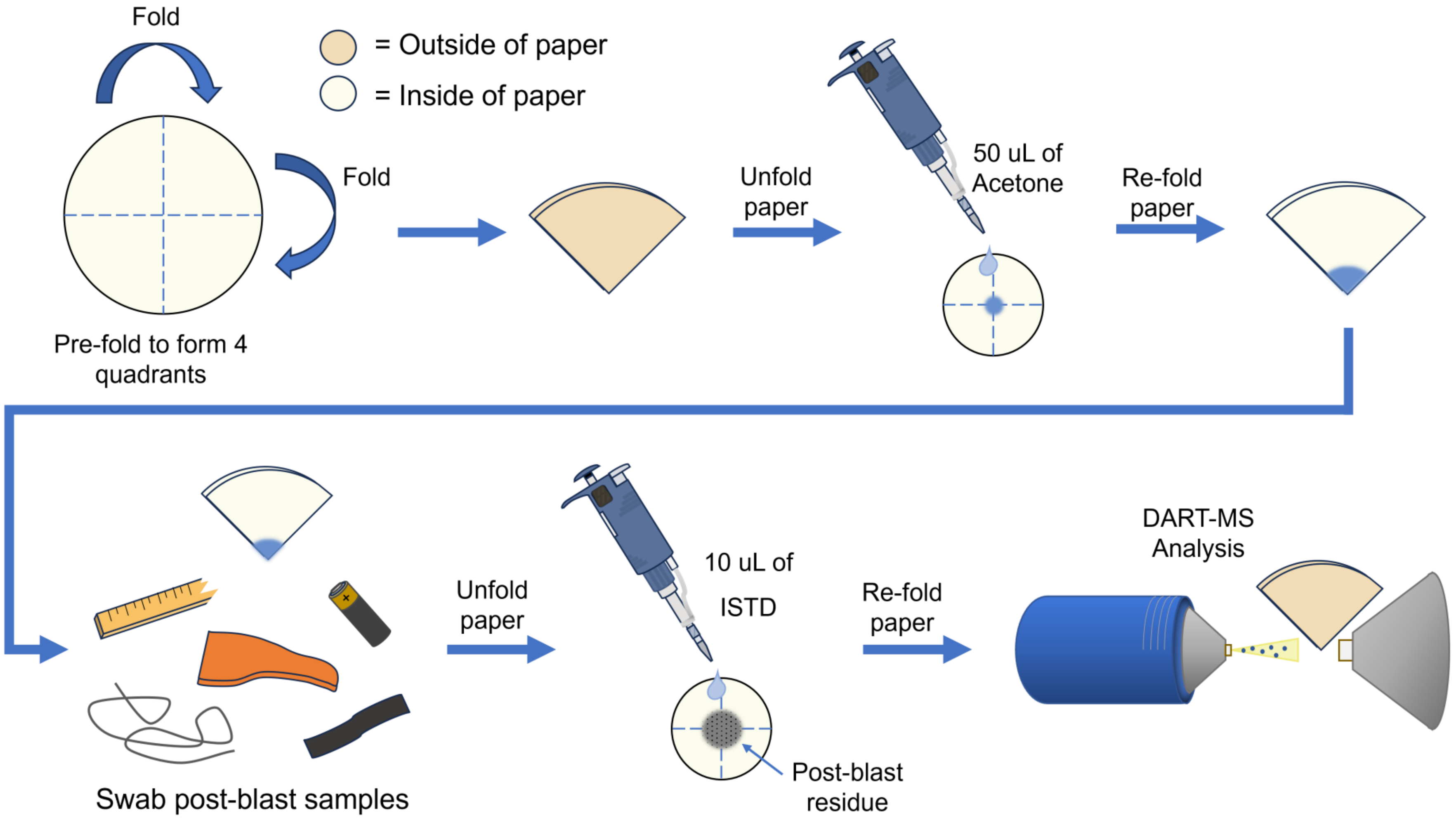
Smokeless powder constituents

Analyte	*Ionization Mode*	*Characteristic Ions*	*Theoretical Exact Mass (m/z)*
Diphenylamine (DPA)	(+)	$[DPA]^{+\bullet}$ $[DPA+H]^{+}$	169.0891 170.0969
Ethyl centralite (EC)	(+)	$[EC+H]^{+}$	269.1653
Di-n-butyl phthalate (DBP)	(+)	$[DBP+H]^{+}$	279.1596
Nitroglycerin (NG)	(-)	$[NG+NO_3]^{-}$	288.9904

Other Organics

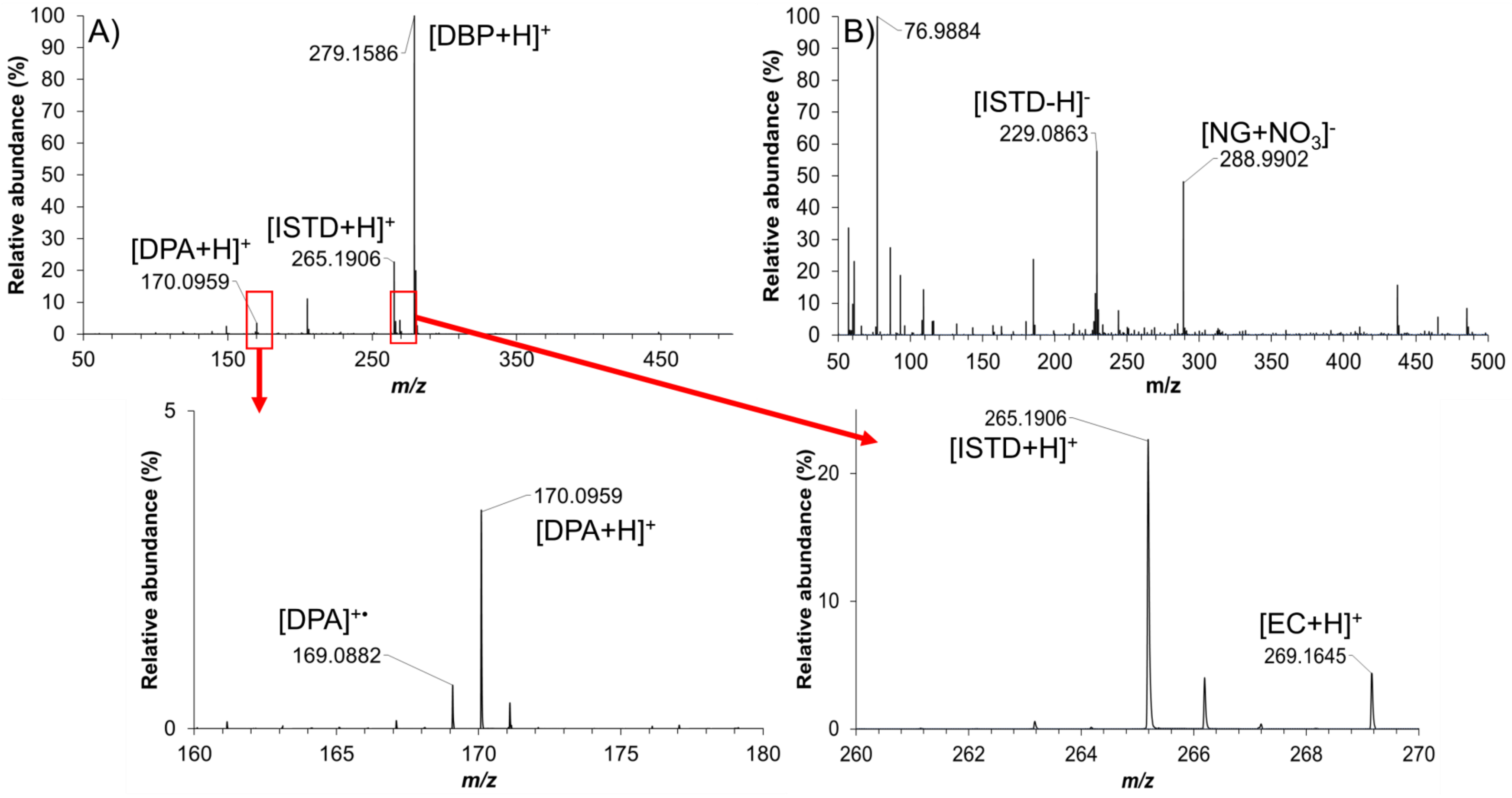
Analyte	*Ionization Mode*	*Characteristic Ions*	*Theoretical Exact Mass (m/z)*
2,4,6-trinitrotoluene (TNT)	(-)	$[TNT-NO]^-$ $[TNT-H]^-$	197.0198 226.0100
1,3,5-trinitro-1,3,5-triazinane (RDX)	(-)	$[RDX+NO_2]^-$ $[RDX+NO_3]^-$	268.0277 284.0227
Nitromethane	X	X	X

Development of a Novel Subsampling Method



Development of a Novel Subsampling Method

Smokeless Powder (SP) Residue Results



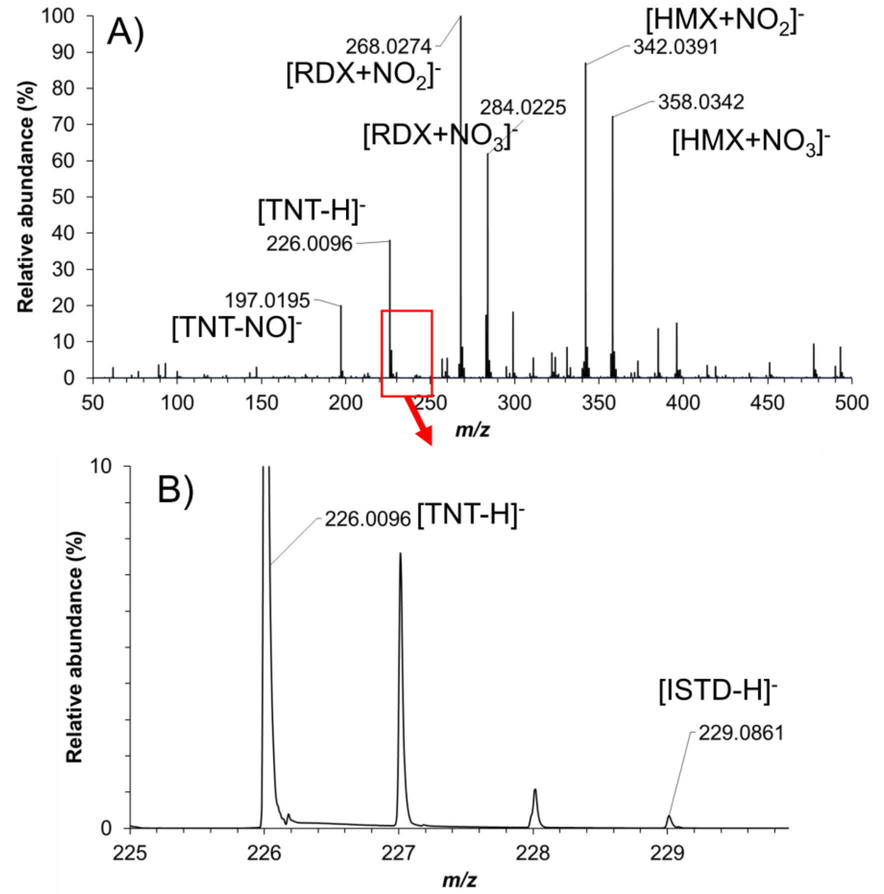
Smokeless Powder Results

Substrate	*DPA*		*EC*		*DBP*		*NG*	
	D.1.	*D.2.*	*D.1.*	*D.2.*	*D.1.*	*D.2.*	*D.1.*	*D.2.*
Orange Toolbox	3	3	3	3	3	3	3	3
Wood	2	1	0	0	3	3	1	1
Electrical Tape	2	2	1	1	3	3	0	3
Coated Wire	3	3	1	0	3	3	0	3
Cell Phone	3	1	2	1	3	2	1	2
Rocker Switch	2	3	0	0	2	3	2	1
Shrapnel	1	0	0	0	3	2	0	0
9V Battery	2	2	1	1	3	3	0	0
AA Battery	3	3	0	0	3	3	0	0

D.1. = detonation 1, D.2. = detonation 2.
Green = 3/3 detections, Yellow = 2/3 detections, Orange = 1/3 detections, Red = 0/3 detections.

TNT/RDX Residue Results

- Additionally detected HMX
- Competitive ionization observed with naproxen internal standard (*m/z* 229.0861)
- Alternative standard needed
- Observed when TNT was present but not with RDX or HMX



TNT/RDX Results

Substrate	*TNT*		*RDX*	
	D.1.	*D.2.*	*D.1.*	*D.2.*
Orange Toolbox	3	0	3	3
Wood	0	1	0	0
Electrical Tape	3	N.R.	3	N.R.
Coated Wire	3	3	3	3
Cell Phone	3	3	3	0
Rocker Switch	3	N.R.	3	N.R.
Shrapnel	3	0	3	0
9V Battery	3	N.R.	3	N.R.
AA Battery	3	1	3	0

N.R.= not recovered.
D.1. = detonation 1, D.2. = detonation 2.
Green = 3/3 detections, Yellow= 2/3 detections, Orange= 1/3 detections, Red= 0/3 detections.

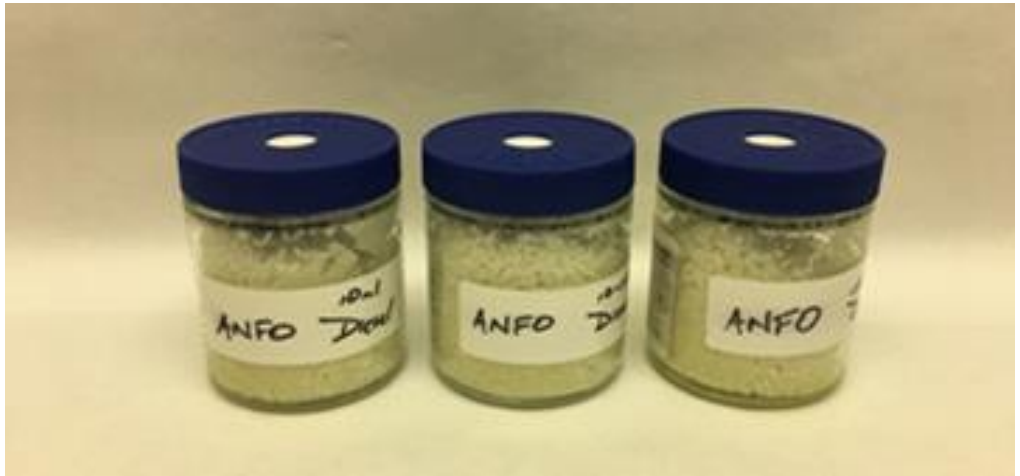
Common Inorganic Oxidizers

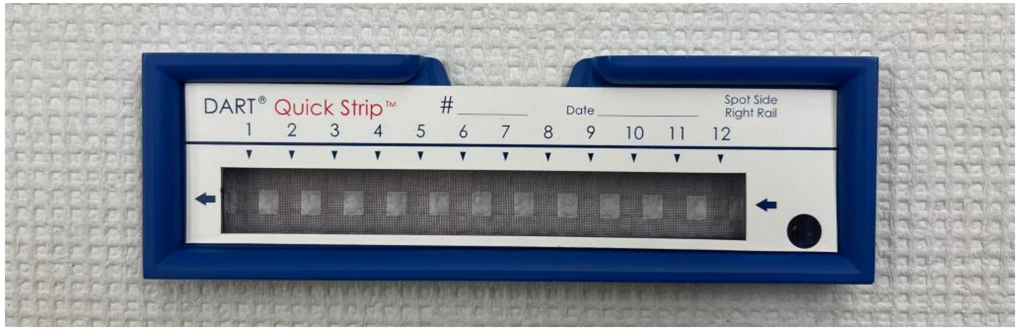
Ammonium nitrate, Ammonium perchlorate

Method of Analysis

Intact

- Dissolved in 50:50 MeOH: deionized (DI) H_2O [6]
- Pipetted onto a QuickStrip™
  - Partially dried
- Allowed the analyte to dissolve but keep ions intact



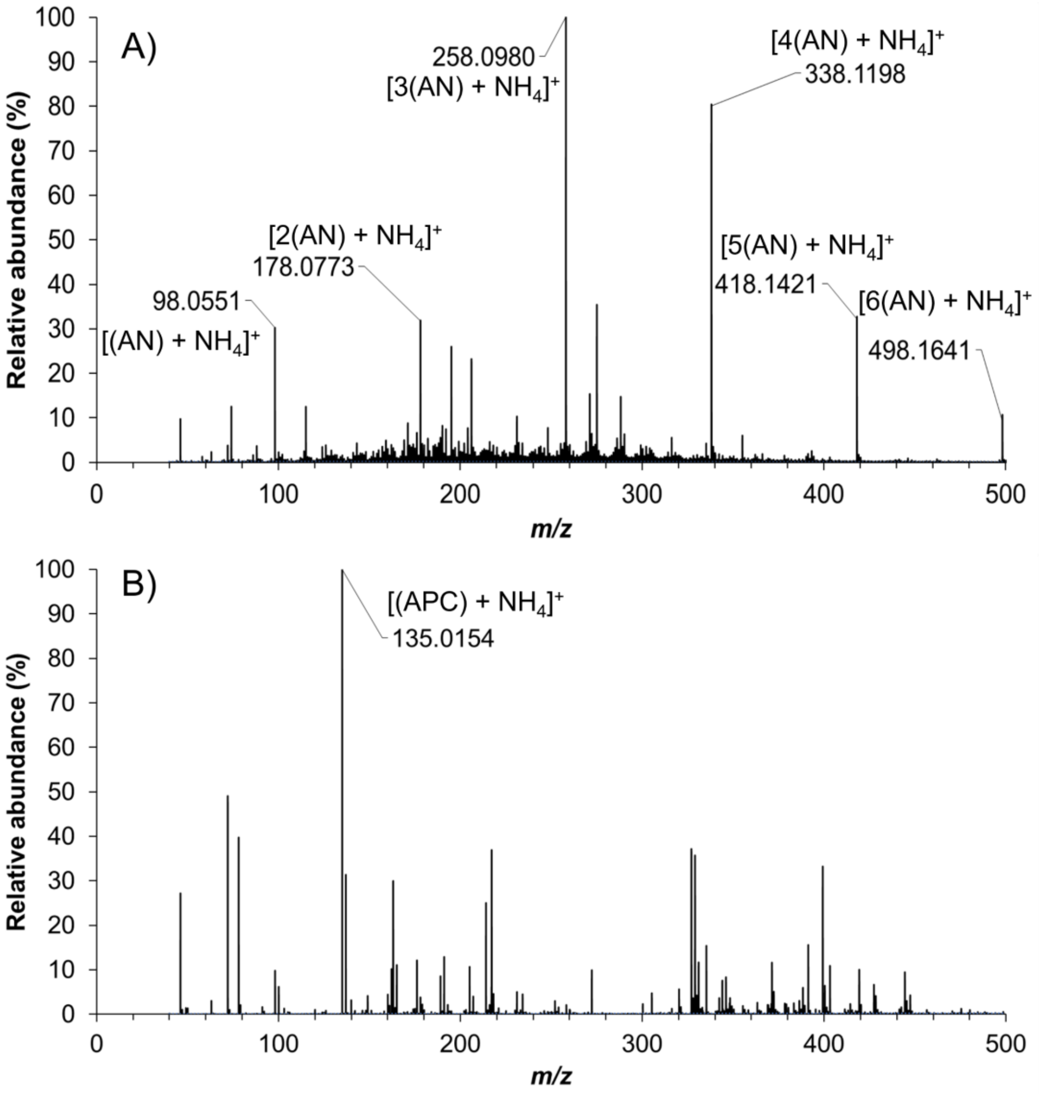


[6] X. Zhao, J. Yinon, Characterization of ammonium nitrate by electrospray ionization tandem mass spectrometry, Rapid Commun. Mass Spectrom. 15 (2001) 1514–1519. https://doi.org/10.1002/rcm.406.

Inorganic Oxidizers

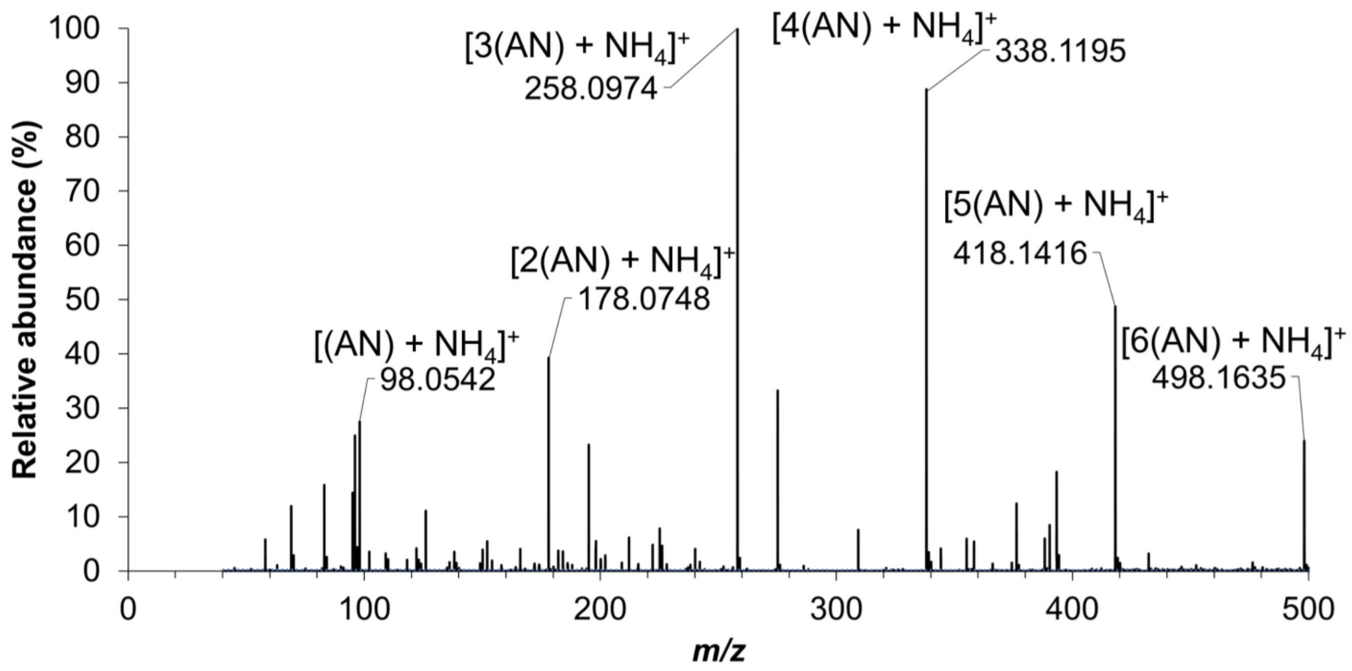
Analyte	*Ionization Mode*	*Characteristic Ions*	*Theoretical Exact Mass (m/z)*
Ammonium nitrate (AN)	(+)	$[AN+NH4]^+$ $[2(AN)+NH4]^+$ $[3(AN)+NH4]^+$	98.0565 178.0787 258.1009
Ammonium perchlorate (APC)	(+)	$[APC+NH_4]^+$	135.0172

Inorganic Oxidizers



- Inorganic oxidizers don't ionize well with DART
- We found that ammonium based inorganic oxidizers can be detected under certain conditions
- Confirmed using ESI-MS/MS
- Other inorganic oxidizers were not successful

Authentic Inorganic Oxidizer − ANFO



- ANFO dissolved in the 50:50 MeOH:DI H_2O solvent
  - Aqueous extract removed
- Successful detection of ammonium nitrate
- Fuel component was problematic

Summary

- Development of a novel subsampling method enabled identification of smokeless powder constituents and TNT/RDX mixtures post-blast
- Organic explosive residues detected more often on plastic compared to wood or metal
  - Positive identifications were greater than 60% on plastic
- Use of internal standard mitigated false negatives
- Intact ammonium-based oxidizers were detected using a custom 50:50 MeOH: DI H_2O solvent

Acknowledgements

- Monjardez Research group
  - Makenzie Kuehn
  - Jose Grijalva
- Department of Forensic Science
  - Students that helped with field collection
- Kevin Bates (MCFMO)
- Lucas Research Grant

Questions?

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References

[1] United States Bomb Data Center, United States Bomb Data Center (USBDC) Explosives Incident report (EIR) 2022, Bureau of Alcohol, Tobacco, Firearms and Explosives, Redstone Arsenal, AL, 2022. https://www.atf.gov/resource-center/docs/report/2022-explosives-incident-report-eir/download (accessed January 25, 2024).

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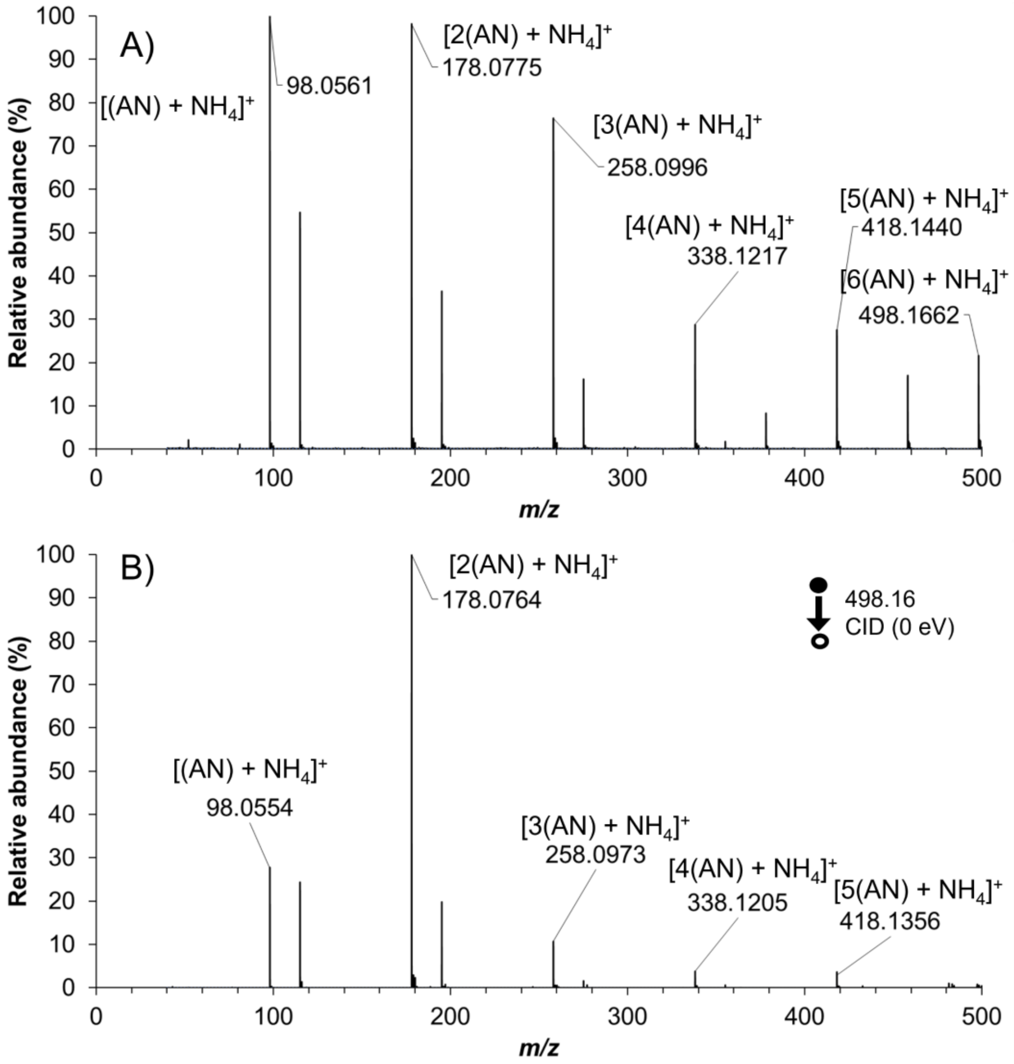
Supplemental

Ammonium Nitrate Confirmation



- Dissolved in 50:50 MeOH: DI H_2O
- Introduced into the instrument via direct injection
- Isolated *m/z* 498.16
  - Isolation energy alone caused cluster to break apart