Practical Investigation of Direct Analysis in Real Time Mass Spectrometry for Fast Screening of Explosives

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Abstract

While the direct analysis in real time (DART) ionization source coupled with mass spectrometry (MS) is viable for the screening of trace explosives, current and previous methods have significant disadvantages for screening of explosives. This work demonstrates novel methods using DART-MS for the high-throughput and sensitive detection of nineteen organic explosive residues in four different categories deposited on several substrates. Explosive residues were selected based on their use in historical bombings that have tragically claimed the lives of civilians and the armed forces of many nations. To combat the threat of explosives to national security, several methods were investigated using DART-MS. The Quickstrip™ sample card method was used to optimize DART gas heater temperature as well as dopants. Four sample introducing strategies for DART-MS including transmission, thermal desorption, closed mesh, and direct-insert methods were implemented to analyze liquid and dried samples deposited on five substrates. Fabric, leather, metal, plastic, and synthetic skin were selected to simulate realistic matrices for explosive residues. It was found that representative explosives from each category could be detected with nanogram sensitivity and in less than ten seconds. Therefore, the proposed methods using DART-MS provide prompt analysis of explosives to improve explosive trace detection strategies.

Materials and Methods

- The explosive samples were analyzed using QuickStrip™, Transmission, Thermal Desorption, along with home-made Closed Mesh and Direct-Insert modules of the DART-MS with helium as the ionization gas. The mass spectra were collected in an *m/z* range of 50-400 in negative-ion or positive-ion mode
- To observe the effect of helium gas stream temperature, samples were analyzed on quick strip sample cards at three different temperatures: 150°C, 200°C, and 250°C
- To observe the effect of dopants, three solutions of 50 µL explosive with 1 µL dopant (acetic acid, acetone, or nitric acid) were prepared for sampling
- To observe the effect of substrates, neat liquid samples of explosives were spiked onto leather, metal, plastic, fabric, or synthetic skin and then swabbed with a polymer swab or foam-tipped swab moistened with a methanol and acetic acid solution
- To observe the effect of thermal desorption heating stage temperature, a neat liquid sample of explosive was pipetted onto a polymer swab
- For Closed-Mesh and Direct-Insert modules, methanol was used to dilute explosives and samples were allowed to dry for 5 min before swabbing with foam-tipped swab

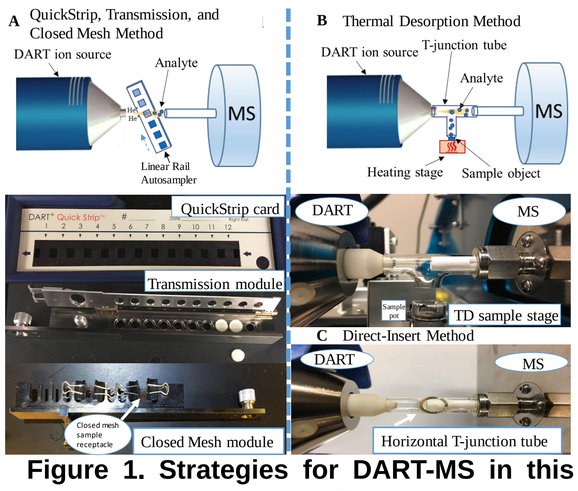

Figure 1. Strategies for DART-MS in this study. A: QuickStrip, Transmission, and Closed Mesh methods. B: Thermal desorption (TD) method. C: Direct-insert method.

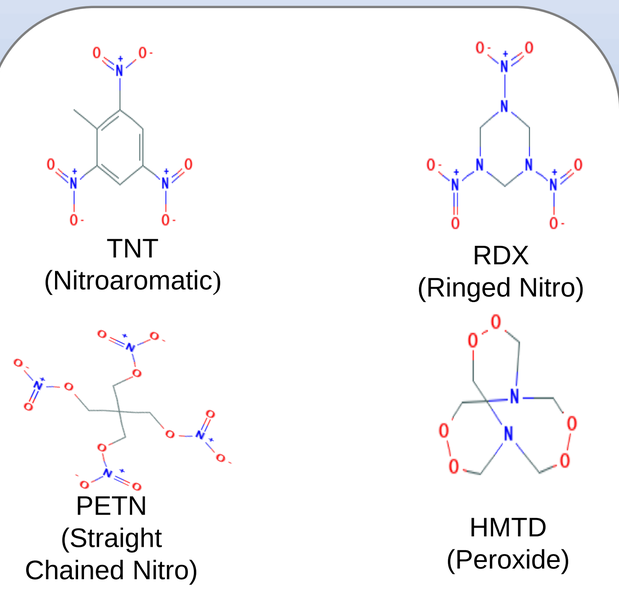

Figure 2. Examples of Chemical Structures of Explosives by Category.

Results

#	Explosive Name	Mass	Ion
	Nitroaromatic		
1	2,4,6-trinitrotoluene (TNT)	227.018	$[M-2NO]^-$, $[M-NO]^-$ $[M-H]^-$
2	2,4-dinitrotoluene (2,4-DNT)	182.033	$[M-H]^-$, $[M-H+O]^-$
3	2,6-dinitrotoluene (2,6-DNT)	182.033	$[M-2NO]^-$, $[M-CH_3]^-$, $[M-H]^-$
4	2,4,6-Trinitrophenylmethylnitramine (Tetryl)	287.014	$[M-N_2O_2CH_3]^-$, $[M-N_2O_2CH_3+O]^-$
5	Ammonium picrate (AP)	246.024	$[M-NH_4]^-$
6	Picric acid (PA)	228.997	$[M-H]^-$
7	Nitrobenzene (NB)	123.032	$[M]^-$,$[M+CH_3]^-$
8	1,3-dinitrobenzene (1,3-DNB)	168.017	$[M-H-NO]^-$, $[M-NO]^-$, $[M]^-$
9	1,3,5-trinitrobenzene (1,3,5-TNB)	213.002	$[M-2NO]^-$, $[M]^-$, $[M-NO_2]^-$, $[M-NO]^-$
10	2-nitrotoluene (2-NT)	137.048	$[M+CH_3]^-$, $[M-H]^-$
11	3-nitrotoluene (3-NT)	137.048	$[M+CH_3]^-$, $[M-H]^-$
12	4-nitrotoluene (4-NT)	137.048	$[M+CH_3]^-$, $[M-H]^-$
13	2-amino-4,6-dinitrotoluene (2-A-4,6-DNT)	197.044	$[M]^-$, $[M-H]^-$
14	4-amino-2,6-dinitrotoluene (4-A-2,6-DNT)	197.044	$[M]^-$, $[M-H]^-$
	Ringed Nitros		
15	Cyclotrimethylenetrinitramine (RDX)	222.035	$[M+NO_2]^-$, $[M+NO_3]^-$
16	Cyclotetramethylenetetranitramine (HMX)	296.047	$[M+NO_2]^-$, $[M+NO_3]^-$
	Straight Chained Nitros		
17	Pentaerythritol tetranitrate (PETN)	316.014	$[M]^-$, $[M-H]^-$, $[M+NO_2]^-$
18	Erythritol tetranitrate (ETN)	301.998	$[M+H+O]^-$
	Peroxide		
19	Hexamethylene triperoxide diamine (HMTD)	208.070	$[M+H]^+$

Table 1. Identification Results for Explosives by DART-MS. Only ions which could be detected in at least two of the three method optimization modules (Quickstrip, Transmission, and Thermal desorption) were included.

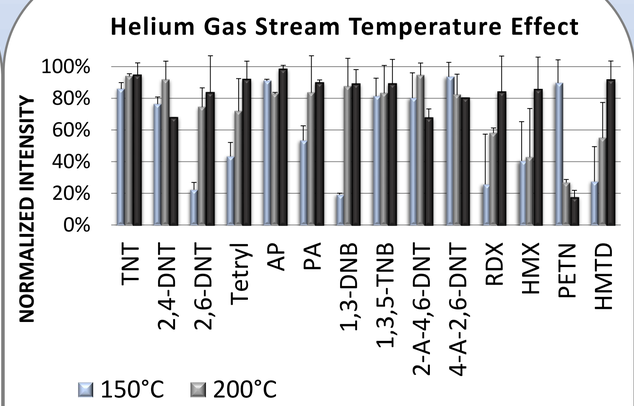

Figure 3. DART ionization source helium gas stream temperature and its effect on explosives' signal intensity.

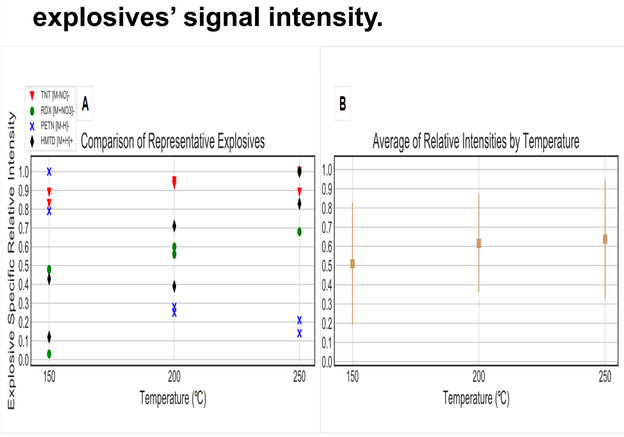

Figure 4. Simplified DART temperature optimization figure. (A) Plot of each representative explosive. (B) Average of explosive signal intensity by temperature.

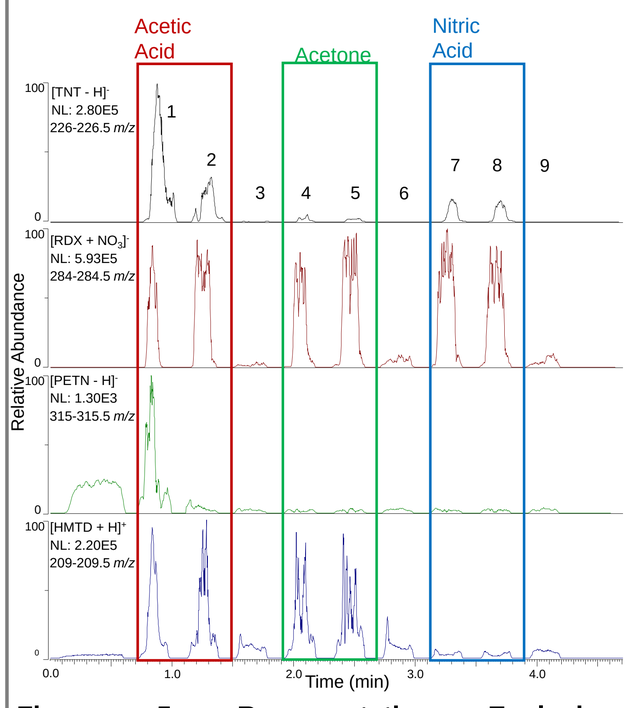

Figure 5. Representative Explosives with QuickStrip Method at 200 °C with Acetic Acid, Acetone, and Nitric Acid dopants. Note: The boxed peaks are explosive+dopant; peaks 3, 6, and 9 are MeOH+dopant blanks for mass spectral background subtraction.

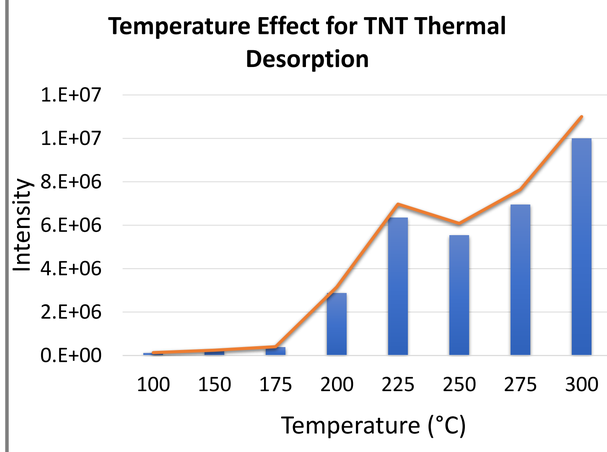

Figure 6. Thermal desorption heating stage temperature and its effect on signal intensity of TNT pipetted directly onto a polymer swab placed on the sample stage

Table 2. Summary of **detection limits in nanograms (ng) by method.**
*Explosives were not diluted for this method because the analysis time was too long to be considered for fast screening of explosive residues
**Estimated lowest detectable mass
nt = not tested; nd = not detected

Name	Material	Method: Transmission*	Thermal Desorption*	Closed Mesh**	Direct-Insert
TNT	Leather	5000	5000	25	25
	Metal	5000	5000	25	2.5
	Plastic	5000	5000	nt	nt
	Fabric	nt	nt	25	25
	Skin	nt	nt	50	50
RDX	Leather	5000	5000	250	25
	Metal	5000	5000	250	2.5
	Plastic	5000	5000	nt	nt
	Fabric	nt	nt	500	25
	Skin	nt	nt	250	25
PETN	Leather	500	nd	500	25
	Metal	500	nd	25	25
	Plastic	500	nd	nt	nt
	Fabric	nt	nt	50	25
	Skin	nt	nt	500	25
HMTD	Leather	500	nd	250	5
	Metal	500	nd	250	5
	Plastic	nd	nd	nt	nt
	Fabric	nt	nt	250	5
	Skin	nt	nt	nd	5

Conclusions

- Characteristic ions of explosives were identified using DART-MS
- 200°C was selected as the optimal helium gas stream temperature as many of the explosives have very high vapor pressures and the difference in signal intensity compared to 250°C is not large
- Acetic acid is the optimal dopant as for some explosives it helped decrease background noise and increase signal intensity
- Some volatile explosives could not be detected
- Direct-insert method, in which a foam-tipped swab with explosive residue is placed directly into the ionization gas stream, had the most rapid analysis time of only 6-9 seconds with the highest sensitivity
- DART-MS is demonstrated as a potential tool for the fast detection of explosives

References

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Acknowledgements

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