

Supporting Information

Use of Mass Spectrometric Vapor Analysis to Improve Canine Explosive Detection Efficiency

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Vapor-Analysis Mass Spectrometer Design and Operation

All mass spectrometry measurements were performed on a Sciex 5500 QTRAP mass spectrometer (Sciex; Concord, Ontario, Canada) equipped with Analyst 1.6 build 3773. Custom secondary electrospray ionization (SESI) and dielectric barrier discharge ionization (DBDI) sources were used for vapor ionization. SESI crosses the analyte vapor stream with an electrospray,¹ and DBDI passes the sample through a plasma or reacts the analyte with reactive plasma species.² Source temperature was held at 373 K (100 °C) for most operation. N₂ was provided using a nitrogen generator (ABN2ZA; Peak Scientific; Inchinnan, UK). Q1 scans (m/z 40-350 or m/z 40-400) were taken with 20 V declustering potential (DP) and 10 V entrance potential (EP). Multiple reaction monitoring (MRM) scans were taken for several energetics and cyclohexanone. Instrument parameters in MRM mode (e.g. declustering potential) were optimized for each transition. To make the system deployable to canine training sites, the system was placed on a stainless steel cart that include auxiliary equipment such as vacuum pumps, ion source power supplies, and N₂ generator (Figure S1).

Technical diagrams of our SESI and DBDI sources are shown in Figure S2. For SESI, two ESI needles (Agilent; Santa Clara, CA, USA) flowing separate solvents were used for positive (70:30 methanol: water + 2% acetic acid) and negative (70:30 methanol: water + 0.03% ammonium hydroxide) mode analysis. ESI spray was maintained at ± 4.5 kV, and 1 L/min nebulizer flow. Solvent flow (10 - 20 μ L/min) was maintained using a Series 200 HPLC pump (PerkinElmer; Waltham, MA, USA) or an LD Class HPLC pump (Scientific Systems; State College, PA). Additional N₂ gas flow and vacuum pumping was used to achieve a 1 L/min sampling flow rate into the ionization source.

For DBDI, plasma generation was achieved using a PVM500 power supply (Information Unlimited; Amherst, NH, USA) to supply an AC pulse (± 7.8 kV Vpp, 30 kHz) of 760 μ s in a 19.76 ms cycle. The source was composed of an outer copper electrode (id: 8.6 mm, od: 11.2 mm) held at ground, an inner stainless steel electrode (id: 3.2 mm, od: 6.4 mm), and a Teflon dielectric (length: 31.8 mm, id: 6.4 mm, od: 8.6 mm). N₂ was supplied to the source at 1.5 L/min. The source was connected ~300 mm (12") from the mass spectrometer inlet using a ~13 mm (0.5") ID stainless steel tube and positioned perpendicularly from the sample flow path using a tee. Flow through stainless steel tubing was held at 2.5-4 L/min for typical operation.

The DBDI assembly is based on the work done by Ewing et al., which relies on forming nitrate adduct ions by interacting the analyte with reactive species produced from a corona.³ The DBDI assembly is positioned perpendicularly to the analyte vapor stream (Figure S2(C)). The plasma, containing nitrates, is directed to interact with the analyte through a tee. The sample does not pass through the plasma, allowing plasma characteristics to stay constant during analysis. While sensitive for RDX and PETN, the DBDI set up cannot detect many compounds that do not readily form nitrate adducts. The SESI and DBDI sources are therefore complementary. The SESI and DBDI sources can be quickly swapped (a few minutes) to cover a large range of analytes.

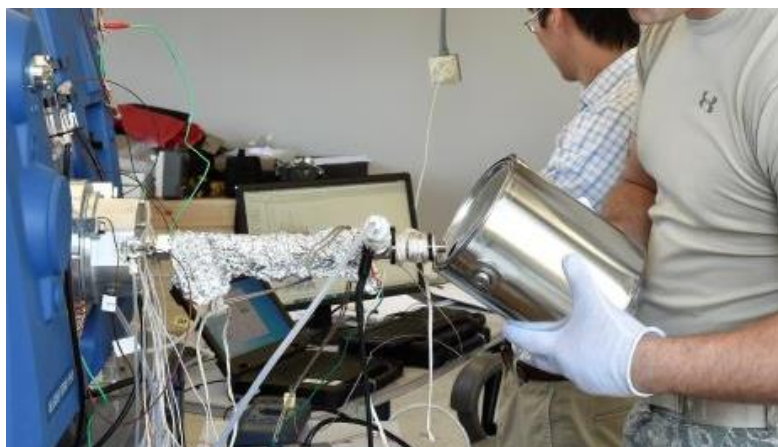


Figure S-1. The developed vapor analysis mass spectrometer was used for in-field analysis of canine training materials.

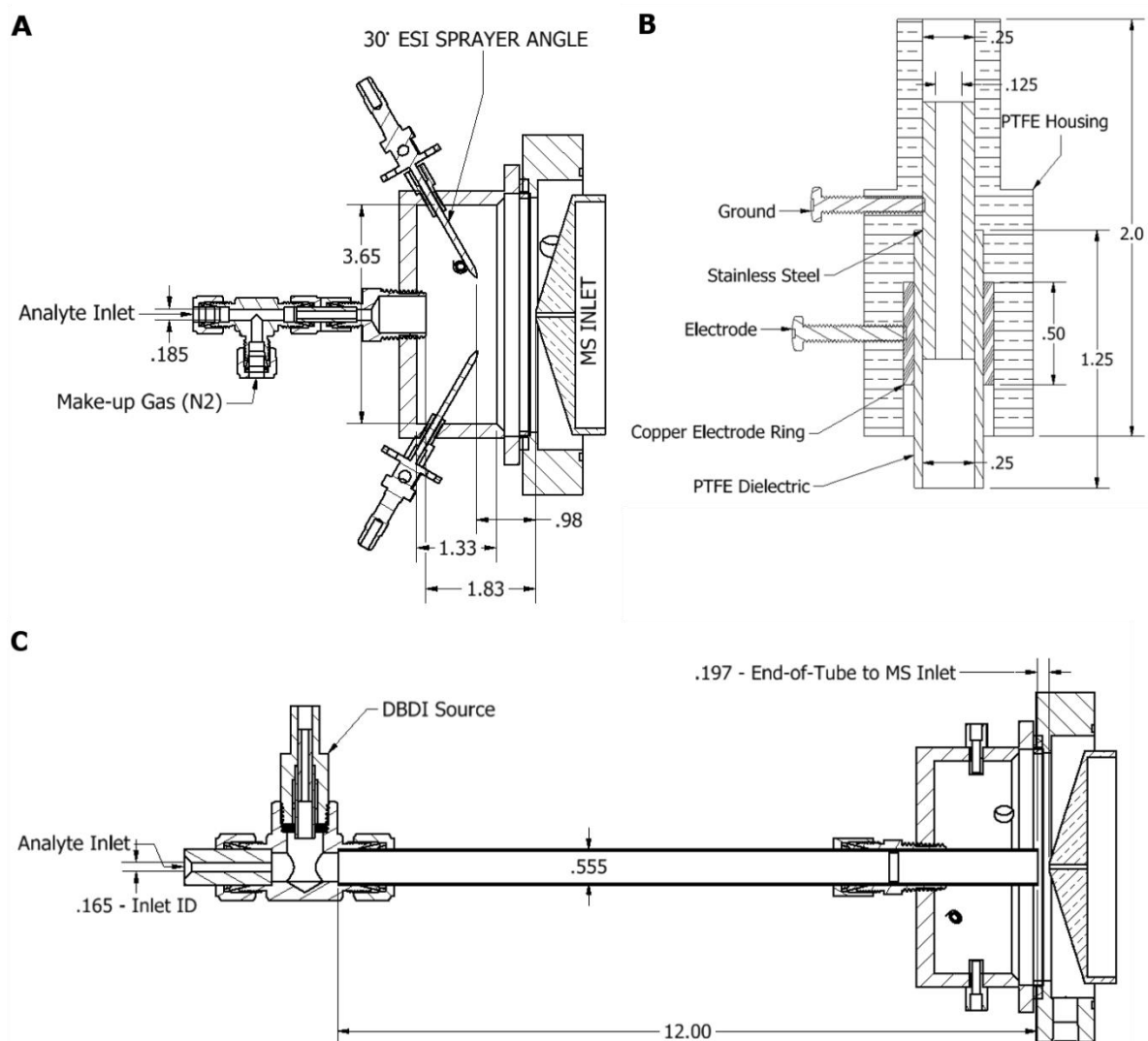
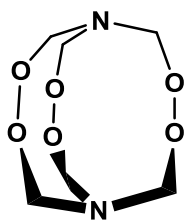


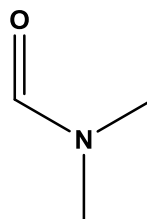
Figure S-2. Ionization sources for vapor detection of several energetics. All measurements are in inches. A. SESI source that uses separate ESI needles for positive and negative polarity analysis. B. DBDI assembly that produces a plasma. C. The DBDI assembly is placed perpendicularly to the analyte gas stream, decoupling plasma generation from sample analysis. After the passing through the tee that connects the DBD, the sample and reactive species from the plasma interact while traveling through a 12" (~300 mm) ionization tube toward the mass spectrometer.



**Hexamethylene Triperoxide Diamine
(HMTD)**

MRM Transition: 209/88

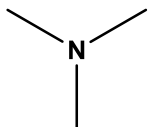
Ion Polarity: Positive



**Dimethyl Formamide
(DMF)**

MRM Transition: 74/46

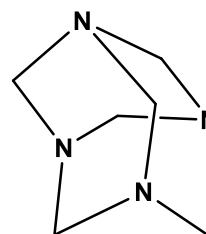
Ion Polarity: Positive



**Trimethylamine
(TMA)**

MRM Transition: 60/44

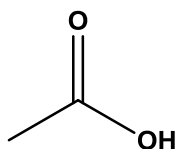
Ion Polarity: Positive



Hexamine

MRM Transition: 141/42

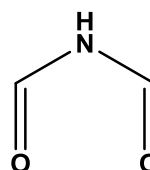
Ion Polarity: Positive



**Formic Acid
(FA)**

MRM Transition: 91/45

Ion Polarity: Negative



**N-Formylformamide
(NFF)**

MRM Transition: 72/42

Ion Polarity: Negative

Figure S-3. HMTD and several associated compounds were monitored in the headspace of HMTD training aids. Analysis covers positive and negative polarities. Masses for the most sensitive MRM transitions are shown.

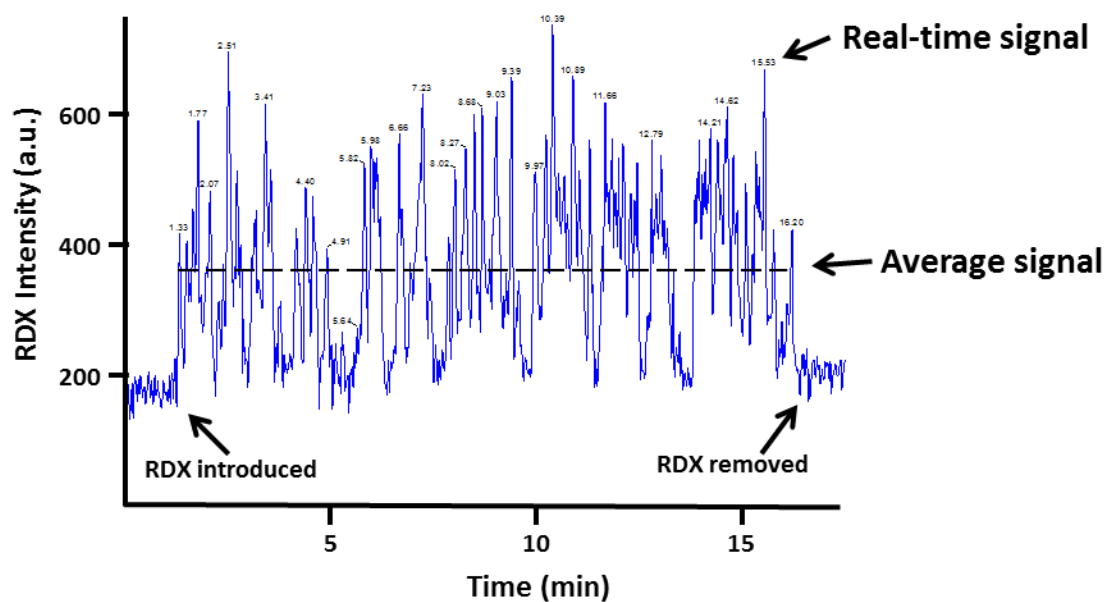


Figure S-4. Signal from RDX placed 30 cm away is observed as pulses on a seconds time scale rather than as a constant, averaged signal (dotted line). This signal pattern is similar across explosives in different chemical classes and vapor pressure (Figure 1).

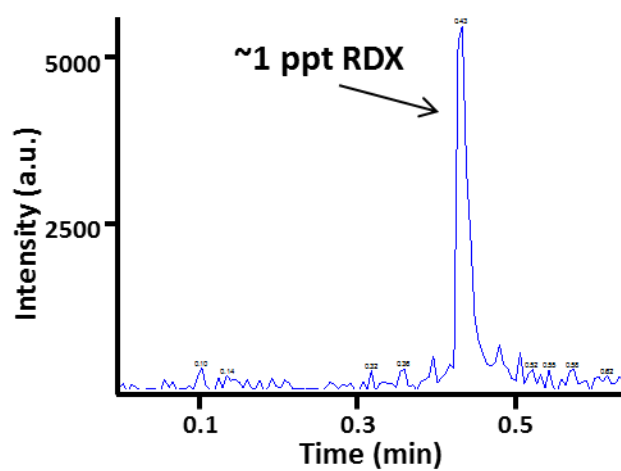


Figure S-5 RDX (~1 ppt) is detected from an empty envelope, turning a blank (ground truth) in to a hide (vapor truth).

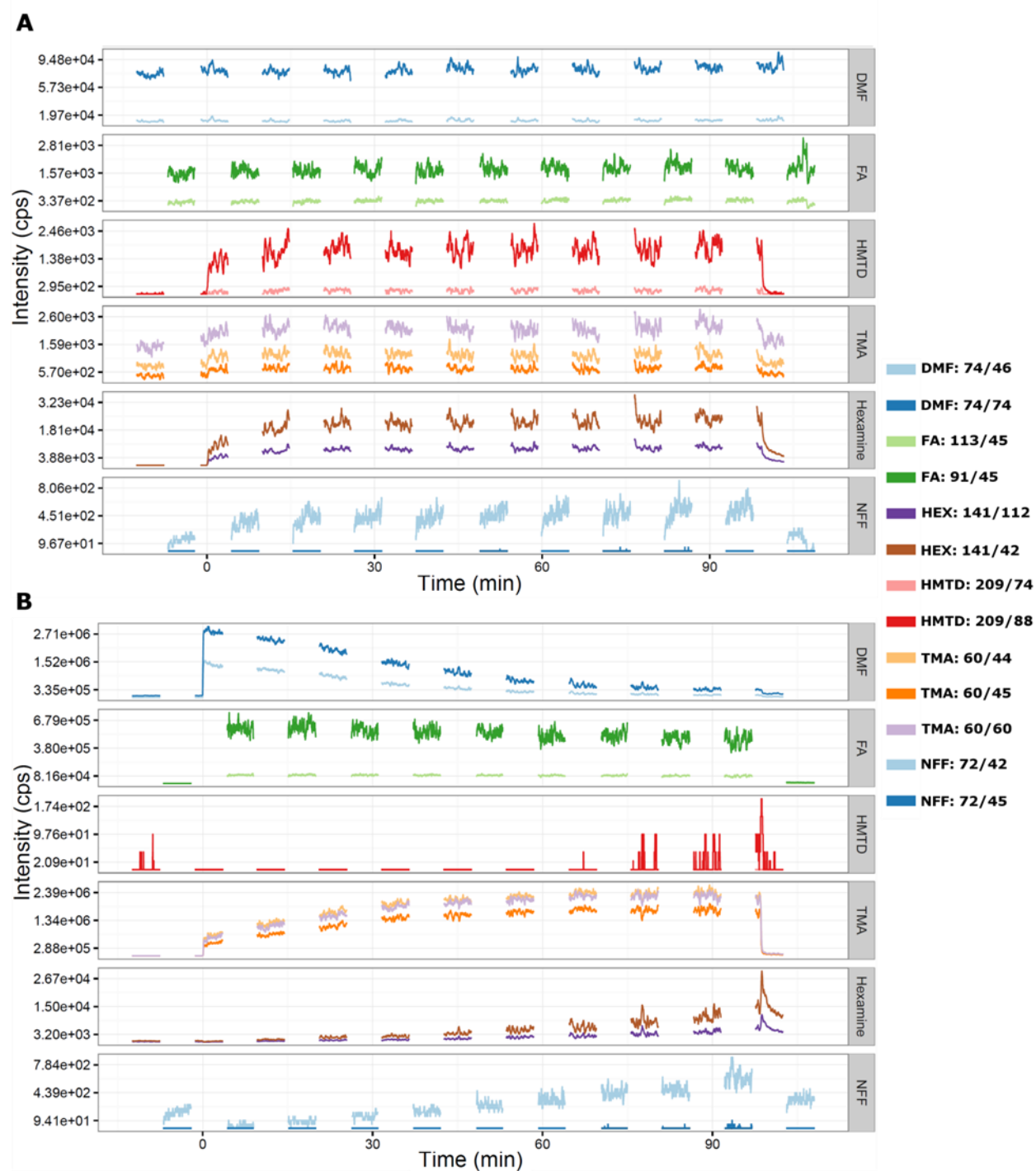


Figure S-6. Two example HMTD training aid measurement traces. A. A training aid with stable signal over the two hour analysis period. B. A training aid with strong formic acid signal and low HMTD signal. DMF signal decreases over time to near baseline, suggesting trapped vapor that is released to the surrounding. DMF: dimethyl foramide, FA: formic acid. HEX: hexamine. HMTD: hexamethylene triperoxide diamine, TMA: trimethyl amine, NFF: N-formyl formamide

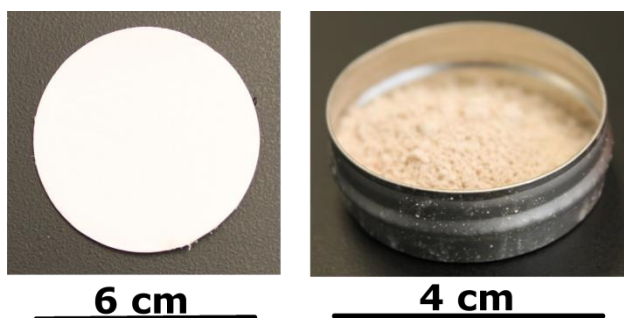


Figure S-7. Training aids were made by distributing HMTD onto inert microfiber or onto powder support.

Table S-1. Expected energetics component in bulk charges.

<u>Bulk Charge</u>	<u>Expected Energetics Component</u>
Ammonium Dynamite	NG
TNT	TNT, DNT
C4	RDX
Smokeless Powder	Nitrocellulose, DNT
Detonation Cord	PETN
Semtex-A	PETN, RDX

Table S-2. Energetics detected in ammunition cans for housing bulk charges. Vapor concentrations are shown in parenthesis for each energetic.

	Expected Energetics (ppt)	Contaminant Energetics (ppt)
Ammonium Dynamite	NG (8)	TNT (<1) PETN (<1)
TNT	DNT (8) ^a TNT (30)	-
C4	-	DNT (<1) ^a
Smokeless Powder	DNT (5) ^a	TNT (<1)
Detonation Cord	-	-
Semtex-A	-	-

^a Assumes only 2,4-DNT as an isomer of DNT

TABLE S-3. Ions (*m/z*) detected in Q1 analysis of training materials

	<u>Bulk Charge</u>	<u>Ammunition Can</u>
Ammonium Dynamite	85.8, 211.9, 285.8	85.8, 166.2, 193.9, 195.9, 210.9, 211.9, 218, 225.9, 227.2, 240.9, 243.9, 262.1, 271.9, 272.9, 285.9, 288.1, 288.9
TNT	100	85.0, 99.9, 165.8, 184.1, 211.0, 225.9
C4	100, 179.1, 194	99.9, 115.9, 130.9, 131.9, 165.9, 173.3, 174.2, 179, 184.2, 194.1, 211.0, 235.0
Smokeless Powder	170.3	99.9, 211.0
Detonation Cord	None Detected	99.9
Semtex-A	100.0, 194.2	158.3, 184.1, 194.1, 235.1

TABLE S-4. Summary statistics of canine performance. All results are aggregates of canine performance in operationally-relevant and non-operationally relevant situations.

They are therefore not reflective of canine capability in operational settings.

Performance when evaluated against trainer intention (ground truth)					Performance when evaluated against vapor analysis (vapor truth)				
	Animal				Animal				
	1	2	3	4	1	2	3	4	
True Negative	89%	88%	89%	97%	97%	87%	92%	97%	
False Positive	11%	12%	11%	3%	3%	13%	8%	3%	
True Positive	43%	83%	26%	31%	53%	74%	27%	24%	
False Negative	57%	17%	74%	69%	47%	26%	73%	76%	

References

- (1) Martinez-Lozano Sinues, P.; Criado, E.; Vidal, G. *Int. J. Mass Spectrom.* **2012**, *313*, 21-29.
- (2) Guo, C.; Tang, F.; Chen, J.; Wang, X.; Zhang, S.; Zhang, X. *Anal. Bioanal. Chem.* **2015**, *407*, 2345-2364.
- (3) Ewing, R. G.; Atkinson, D. A.; Clowers, B. H. *Anal. Chem.* **2013**, *85*, 389-397.