Low Temperature Vapor Pressures of Ingredients in Explosive Formulations

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Outline

- **Background**
  - Remote detection -- Active vs. passive detection
  - Vapor plume
- **Simultaneous Thermogravimetric Modulated Beam Mass Spectrometer (STMBMS)**
  - Instrument description
  - Capabilities
  - Application to current work
- **Explosives investigated**
- **Results**
- **Conclusions**

Prevention/Deterence relies on accurate and reliable detection of explosives

- **Active Detection**
  - Active energy input to target -- Interrogation
  - Stimulated mass/energy output from target -- Response
  - Remote measurement of response -- Analysis
  - Identification of target -- Detection

  ⇒ Target must be directly 'imaged'
- **Passive Detection**
  - Passive emission of mass/energy from target
  - Dissolution of mass/energy into munition environment
  - Dispersion of mass/energy by environmental carriers
  - Measurement of 'atmosphere' remote to target
  - Identification of target

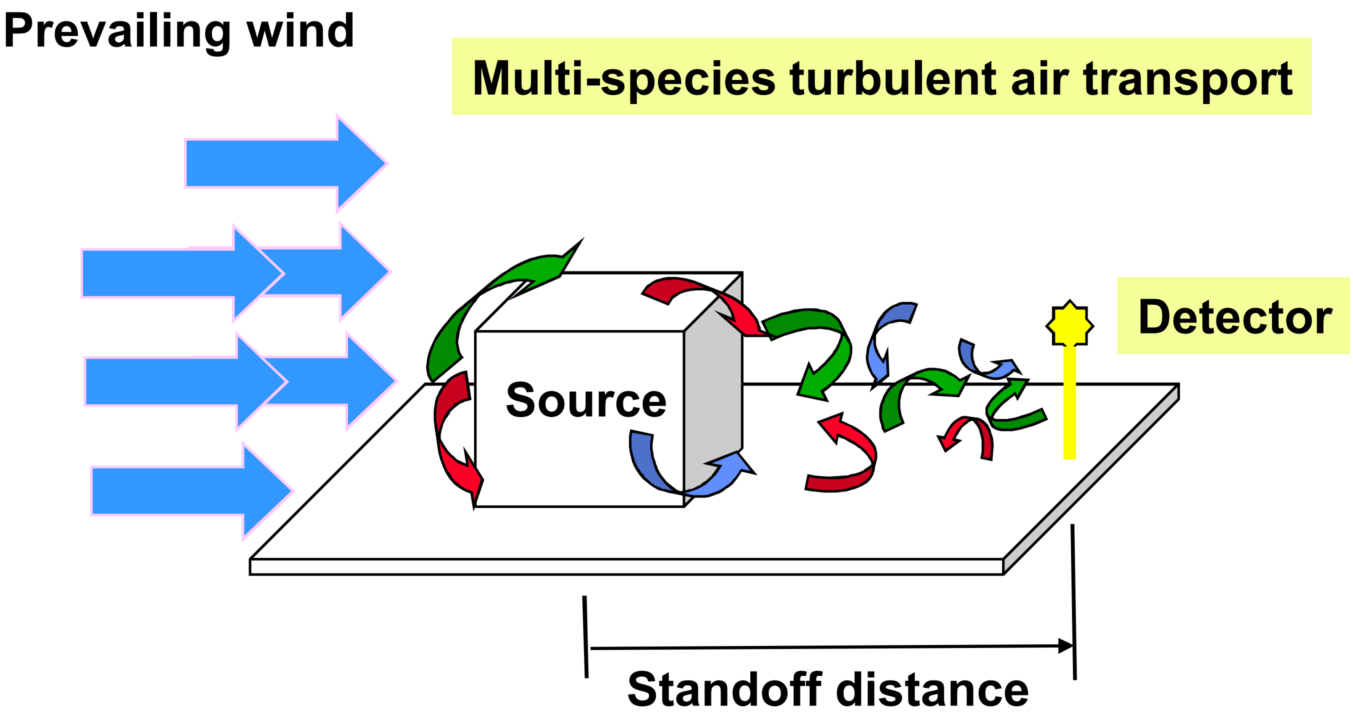
  ⇒ Target can be unknown

Passive canine based systems currently most reliable

Development/Implementation of passive systems require substantial scientific input

- **What information does the target evolve**
  - Gaseous evolution of major/minor constituents
  - Particulate evolution of material
- **What information is unique to the target**
  - Constituents
  - Synthetic impurities
  - Manufacturing/environmental contaminants
- **How does this information 'mix' with the environment**
  - Vapor pressure
  - Sublimation
  - Miscibility/Suspension
- **What is the method of transport of the information through the environment**
  - Diffusivity -- thermal//concentration gradients
  - Convective flow
  - Buoyancy driven flow
- **How is the information measured**
  - Sensitivity/selectivity
- **How are the measured signals analyzed**
  - 'Fingerprinting', information retrieval and pattern matching

Objective: Establish detector sensitivity requirement needed at standoff distance



Computational Fluid Dynamics (CFD) and experimental validation

Collaborative team organized from core expertise necessary to achieve goal

- **Sean Maharrey and Richard Behrens (SNL) -- Source characterization**
  - Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry (STMBMS)
  - High resolution mass spectrometry (FTICR)
  - REaction Modeling and KINetics compiler (REMKIN)
- **Sorin Bastea (LLNL) -- Source/environment coupling**
  - Diffusion and miscible ‘mixing’
- **Rose McCallen and Kambiz Solari (LLNL) -- Transport modeling**
  - CFD
- **Greg Klunder and Marina Chiarappa-Zucca(LLNL) -- Detection**
  - Solid-Phase Micro-Extraction (SPME)

Source Characterization Goal: Identify and quantify chemical species in the immediate atmosphere surrounding an emplaced explosive

Explosive particulates

Explosive vapor

Decomposition products

Impurities
- **solvents**
- **feed-stock chemicals**

Plastic double-wall construction
Set up in 30 minutes
Hasp for padlock
1000 - 2000 lb explosive

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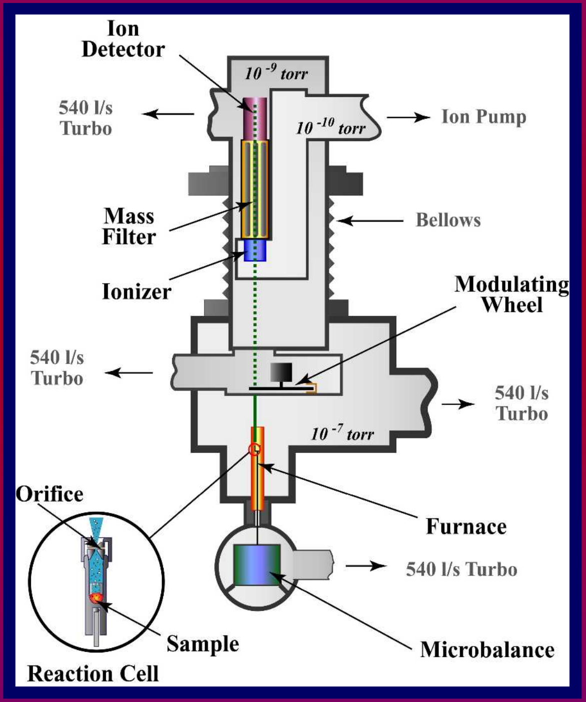
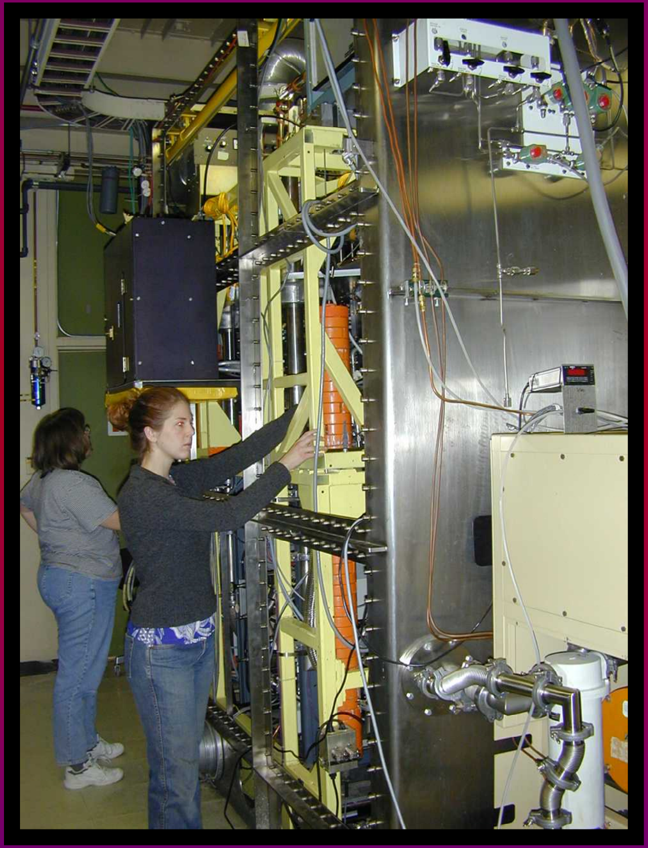
STMBMS provides detailed information on thermal desorption process

- Combines TGA thermal analysis with MS ion detection
- Gas evolution rates of all species evolved from sample
- Develop accurate decomposition/ degradation models
- Vapor pressure of all constituents



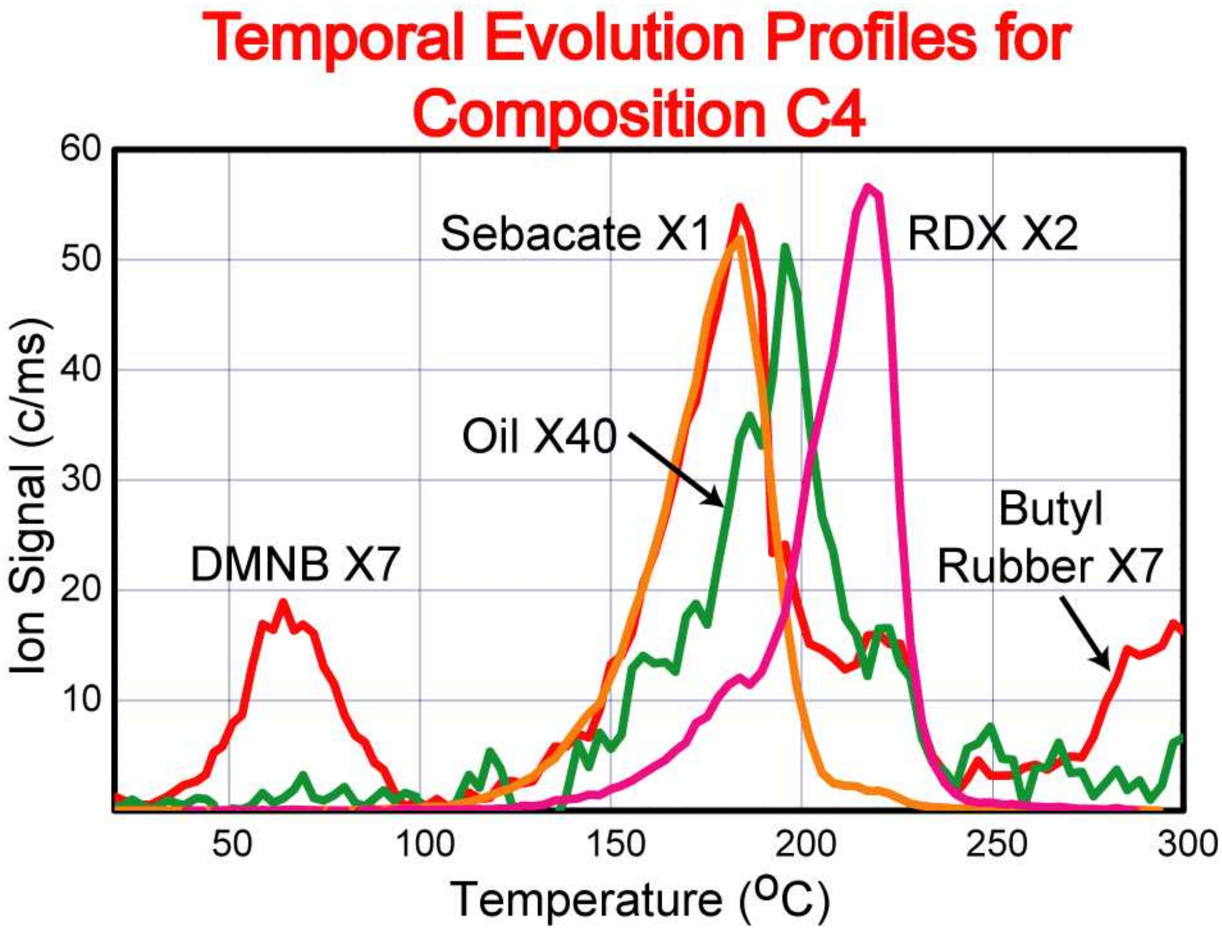


STMBMS: Simultaneous Thermogravimetric Modulated Beam Mass Spectrometer

STMBMS measures vapor pressure of each volatile constituent

STMBMS thermal ramping experiments show the temperature evolution of each constituent

- **All manufacturing compounds identified**
- **Petroleum oil constituent <u>NOT</u> well characterized during manufacturing process**
  - Not considered for low temperature vapor signature
- **Binder material <u>NOT</u> significantly volatile below 250°C**
  - Poor marker for low temperature vapor detection



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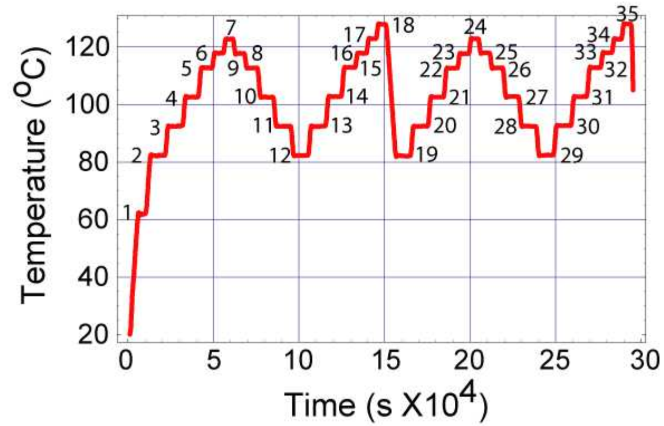
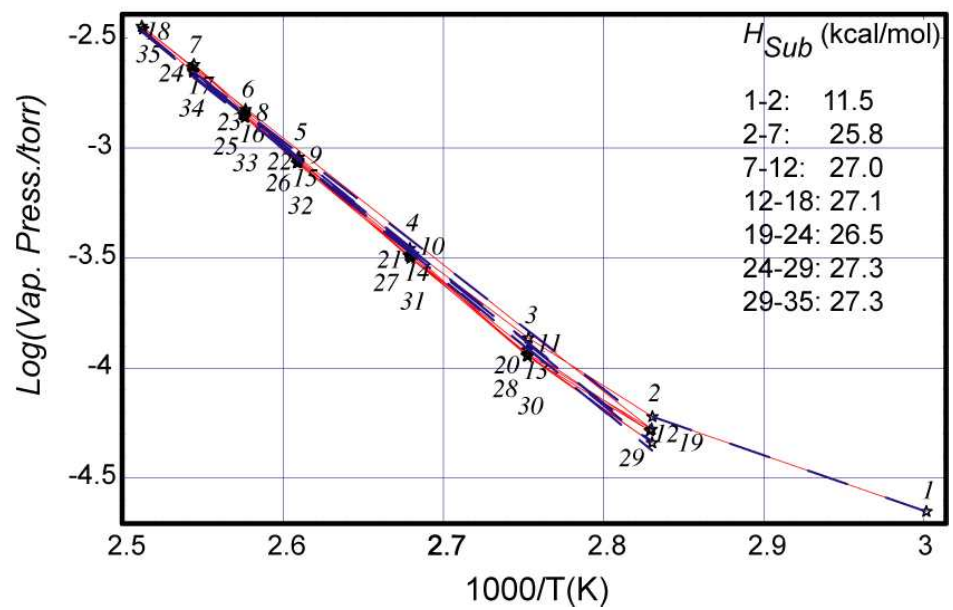
Thermal cycling detects variations caused by ingredient interactions or compositional changes

- **Thermal cycling provides information on variation in ingredient vapor pressures as composition changes**
- **Each constituent analyzed over isothermal step to extract sublimation enthalpy and vapor pressure**
- **25°C vapor pressure calculated to characterize low temperature vapor plume**
- **Data can be used to measure changes in vapor pressures due to aging of explosives or manufacturing process modifications**





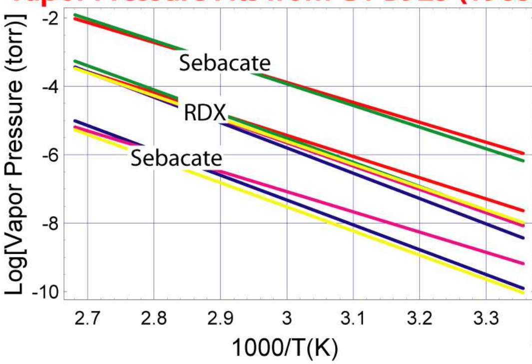
Current study focused on commonly available explosives

- **Composition C4 -- RDX based formulation**
  - RDX: 91%, Di-(2-EthylHexyl)-Sebacate: 5.3%, Butyl Rubber: 2.1%, Petroleum Oil: 1.6%, and DMNB: <0.2%
    - Petroleum oil NOT measured -- Too generic
    - Butyl Rubber NOT measured -- Not volatile at low temperatures
- **Composition B/B3 -- RDX/TNT based formulation**
  - RDX: ~58-61%, TNT: ~39-42%, Synthetic Wax (B3): ~0.7-1.3%
    - Wax NOT measured -- Too generic
- **SemTex 1H -- RDX/PETN based formulation**
  - RDX: 50%, PETN: 35%, Binder: 14.8%, Taggant (DMNB?): <0.2%
    - Styrene-Butadiene binder NOT measured -- Not volatile at low temperatures

Vapor pressure of three different manufacturing lots of C4 showed same general behavior for main ingredients

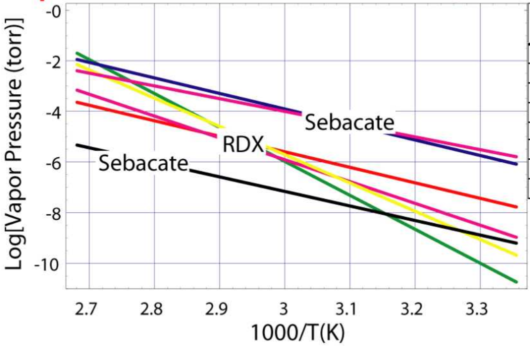
- **Sebacate plasticizer shows two distinct vapor pressure regions**
  - Early VP data indicates Sebacate possibly adsorbed to RDX surface
    - RDX has slightly higher VP in same region
  - Late VP data indicates 'free' Sebacate evolving normally
- **RDX shows VP similar to that for pure RDX powder**
- **Variation of RDX VP in early thermal segments for the C442 lot of C4 as yet unidentified**
  - Features reproduce
  - Seems to be characteristic of this sample
  - Need to characterize the volatiles evolution from this material

Vapor Pressure Fits from C4-B923 (1985)



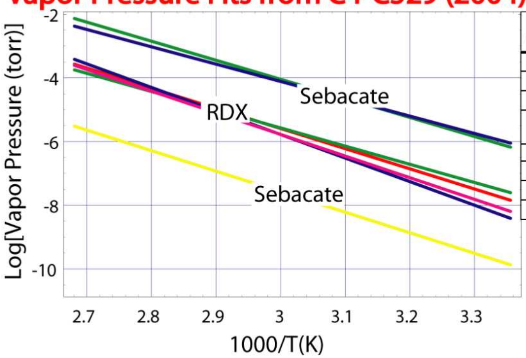
Constituent	Temperature Segments (°C)	H_{Sub} (kcal/mol)	$Log_{10}(P_V)$	$P_V(25°C)$ (torr)
RDX	Red (50-70) ↑	28.38	13.14 - 6192	2.31×10^{-8}
	Green (70-50) ↓	32.34	15.66 - 7057	9.40×10^{-9}
	Blue (50-100-80) ↑↓	33.92	16.40 - 7402	3.70×10^{-9}
	Magenta (80-110) ↑	31.24	14.80 - 6818	8.41×10^{-9}
	Yellow (110-90) ↓	30.59	14.42 - 6676	1.04×10^{-8}
Sebacate	Red (50-70) ↑	26.72	13.61 - 5831	1.10×10^{-6}
	Green (70-60) ↓	28.97	15.03 - 6321	6.60×10^{-7}
	Blue (90-80) ↓	33.26	14.44 - 7257	1.23×10^{-10}
	Magenta (80-110) ↑	27.10	10.66 - 5914	6.56×10^{-10}
	Yellow (110-90) ↓	32.32	13.64 - 7053	9.25×10^{-11}

Vapor Pressure Fits from C4-C442 (2001)



Constituent	Temperature Segments (°C)	H_{Sub} (kcal/mol)	$Log_{10}(P_V)$	$P_V(25°C)$ (torr)
RDX	Red (50-70) ↑	28.06	12.78 - 6124	1.67×10^{-8}
	Green (70-50) ↓	61.38	34.21 - 13395	1.80×10^{-11}
	Magenta (80-50) ↓	39.47	19.92 - 8613	1.06×10^{-9}
	Yellow (50-60) ↑	51.13	27.76 - 11157	2.07×10^{-10}
Sebacate	Blue (70-50) ↓	28.06	14.46 - 6123	8.24×10^{-7}
	Magenta (50-70) ↑	23.07	11.10 - 5034	1.61×10^{-6}
	Black (100-70) ↓	26.30	10.06 - 5739	6.24×10^{-10}

Vapor Pressure Fits from C4-C529 (2004)



Constituent	Temperature Segments (°C)	H_{Sub} (kcal/mol)	$Log_{10}(P_V)$	$P_V(25°C)$ (torr)
RDX	Red (50-70-50) ↑↓	29.00	13.40 - 6330	1.44×10^{-8}
	Green (50-70) ↑	26.18	11.57 - 5713	2.48×10^{-8}
	Blue (70-80-60) ↑↓	33.89	16.41 - 7396	3.89×10^{-9}
	Magenta (60-100-70-110) ↑↓	31.14	14.61 - 6795	6.40×10^{-9}
Sebacate	Green (70-40) ↓	27.43	13.91 - 5986	6.65×10^{-7}
	Blue (40-70) ↑	24.93	12.20 - 5440	8.91×10^{-7}
	Yellow (100-70) ↓	29.55	11.77 - 6448	1.35×10^{-10}

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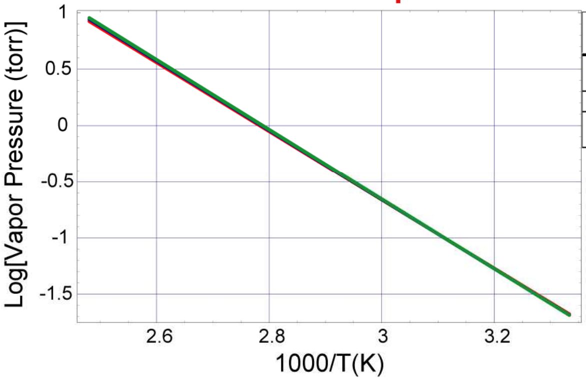
DMNB vapor pressure significantly greater than that of RDX or Sebacate

- **RDX and Sebacate not measureable under temperatures used for more volatile DMNB**
- **DMNB first measured as pure material, then measured from a C4 sample**
  - No measureable differences -- DMNB evolves without interacting with any other ingredients
- **25°C VP over 7 orders of magnitude greater than the RDX or Sebacate constituent**

Vapor Pressure Fits for DMNB



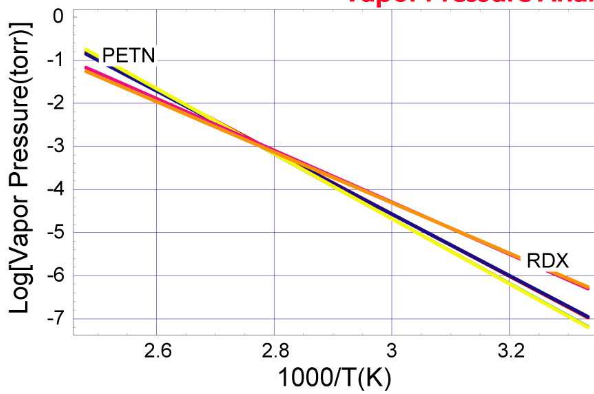
Constituent	Temperature Segments (°C)	H_{Sub} (kcal/mol)	$Log_{10}(P_V)$	P_V(25°C) (torr)
DMNB	Red (40-45-0-55-60)	13.97	8.49 - 3048	1.80 X10^{-2}
	Blue (60-40)	14.11	8.58 - 3078	1.77 X10^{-2}
	Green (40-45-50-55-60)	14.18	8.63 - 9094	1.76 X10^{-2}

DMNB taggant forms one component in a fingerprint ID for C4

SemTex 1H will require a chemical fingerprint based on signatures from the non-explosive manufacturing impurities

- **RDX and PETN vapor pressures not detectable at low temperatures by current technologies**
- **DMNB taggant not detectable in this lot**
  - Possibly EGDN used as taggant
    - Need to characterize pure EGDN
  - Could have different volatility than DMNB in C4
    - Need to try different gas confinements
- **SemTex 1H impurities need to be generalized to manufacturing process to provide useable information**

Vapor Pressure Analysis of SemTex 1H



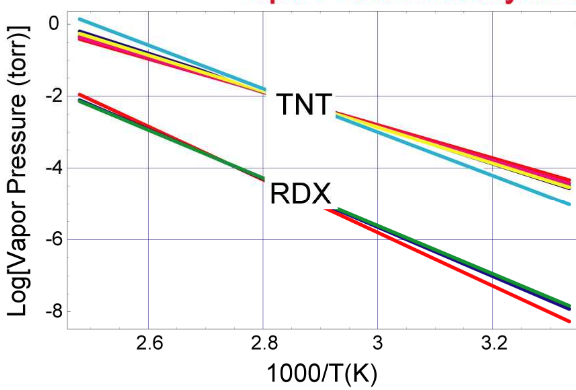
Constituent	Temperature Segments (°C)	H_{Sub} (kcal/mol)	$Log_{10}(P_V)$	P_V(25°C) (torr)
PETN	Red ↓ (80-70-60-50)	33.04	17.07 - 7211	7.38 X10^{-8}
	Blue ↑ (50-60-70-80-90-100)	32.75	16.87 - 7147	7.73 X10^{-8}
	Green ↓ (100-90-80-70)	34.5	17.91 - 7530	4.42 X10^{-8}
	Yellow ↑ (70-80-90-100-110)	34.62	17.98 - 7554	4.33 X10^{-8}
RDX	Magenta ↓ (100-90-80-70)	27.53	13.73 - 6008	3.70 X10^{-7}
	Orange ↑ (70-80-90-100-110)	26.89	13.30 - 5868	4.04 X10^{-7}

Low temperature vapor fingerprint for SemTex 1H as yet undetermined ⇒ absent a taggant, must rely on manufacturing ingredients to provide fingerprint

TNT provides a single-component source for identification of CompB/B3 explosives

- **TNT VP measured from CompB, Comp B3, and pure TNT**
  - No significant variation in TNT VP from the three different sources
  - Indicates no significant interaction between TNT and RDX or synthetic wax (Comp B)
- **Vapor pressure of main ingredients not effect by addition of wax**
- **RDX VP shows no affects from mixing with TNT**

Vapor Pressure Analysis for CompB/B3 Formulations



Constituent	Temperature Segments (°C)	H_{Sub} (kcal/mol)	$Log_{10}(P_V)$	$P_V(25°C)$ (torr)
CompB3:				
TNT	Magenta (40-50-60-70)	21.80	11.44 - 4758	2.96 $X10^{-5}$
	Yellow (70-60-50)	22.95	12.16 - 5009	2.26 $X10^{-5}$
CompB:				
TNT	Red (50-60-70)	21.04	10.98 - 4592	3.69 $X10^{-5}$
	Blue (70-60-50)	23.42	12.48 - 5110	2.13 $X10^{-5}$
	Green (50-60-70)	22.25	11.71 - 4856	2.57 $X10^{-5}$
Pristine TNT:				
TNT	White (40-50-60-70)	26.98	14.55 - 5842	8.84 $X10^{-6}$
	Cyan (70-60-50-40)	27.69	15.13 - 6043	7.09 $X10^{-6}$
RDX:				
RDX	Red (50-100-90-80)	33.92	16.41 - 7402	3.69 $X10^{-9}$
	Blue (80-90-100-110)	31.24	14.80 - 6818	8.41 $X10^{-9}$
	Green (110-100-90)	30.59	14.42 - 6676	1.03 $X10^{-8}$

TNT is best candidate for CompB/B3 chemical signature

1. Provides direct detection of explosive
2. Does not interact with other ingredients

Conclusions

- **Low temperature vapor pressures of high volatility ingredients in several common explosives have been determined**
- **Energetic solids (RDX, PETN) generally not the most volatile component in the formulation**
  - Not currently amenable for fingerprint ID of explosive
- **Common waxes and oils used for phlematizing formulation too generic for use as key signature**
  - Could be used as part of low level cursory inspection of environment
- **Binders do not produce a significant vapor signature at low temperatures to be useful**
- **TNT provides a two-tier signature where present:**
  - Direct detection of an explosive
  - Vapor signature not affected by other ingredients
- **Taggants, if available, would make a key signature for any explosive fingerprint**
- **Minor constituents (plasticizers, manufacturing reagents, solvents, etc.) are a necessary form for the vapor-phase chemical fingerprint of some explosives**

Continuing Work

- Measure vapor pressure of TNT synthetic impurities (DNB, DNT)
- Develop 'multipoint' vapor-phase chemical fingerprint for characterized explosives
- Expand chemical characterization to other common explosives (small arms propellants, commercial explosives, homemade explosives -- TATP)
- Measure specific sublimation rates of each explosive
- Characterize particle evolution from explosives and explosive contaminated surfaces