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Compound Specific Challenges Associated with Trace Detection

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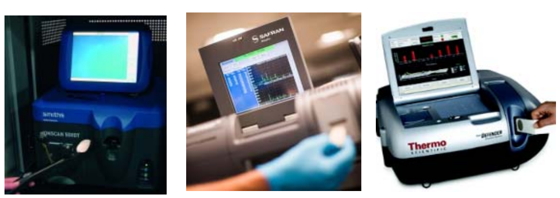
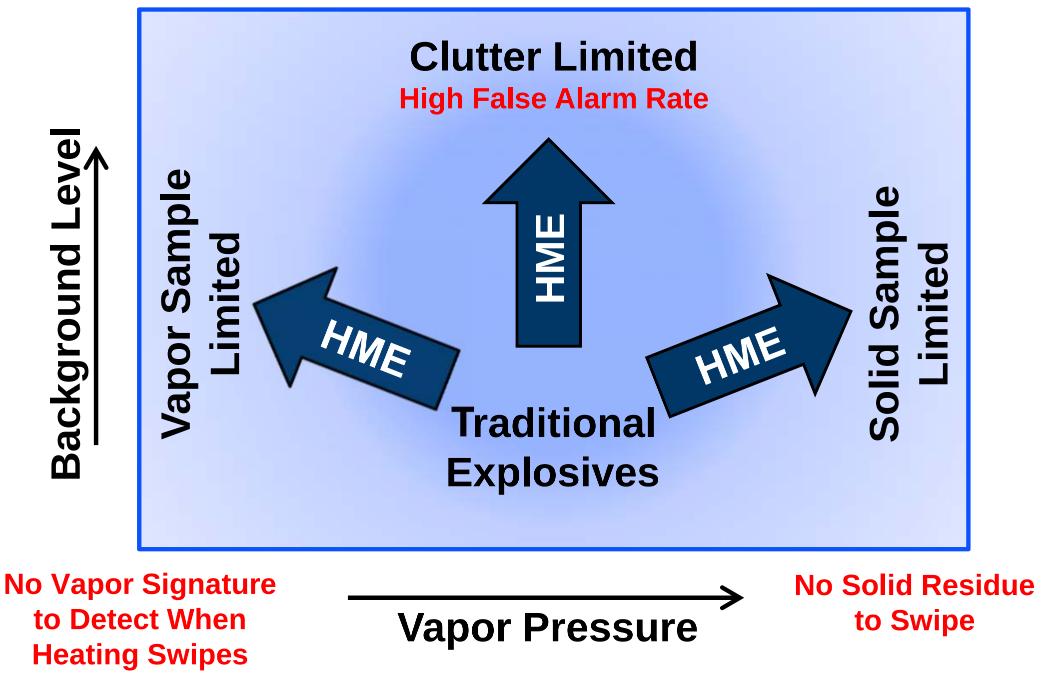
The Evolution of Trace Detection

- **The explosive threat is evolving**
  - **More materials to detect**
- **Trace detection systems are evolving as well…**
  - **Improved sampling methods**
  - **Evolution from IMS to dual-polarity IMS to MS**
  - **See DHS S&T BAA 13-03 titled “Advanced Trace Detection Instrumentation and Methodologies”**



The Challenge for ETD: More / new HMEs



MITLL is providing knowledge to help trace detection systems evolve

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The Growing List of Explosives

- **Widely varying physical properties**
  - **Vapor pressures vary by up to eight orders of magnitude**
  - **Range of morphology (liquids, gels, crystalline solids, moldable plastics, machinable plastics, powders)**

- **Additional challenges**
  - **For some HMEs, their constituents may be present in the background environment**

Focusing on detection of the main charge is not a single detection problem

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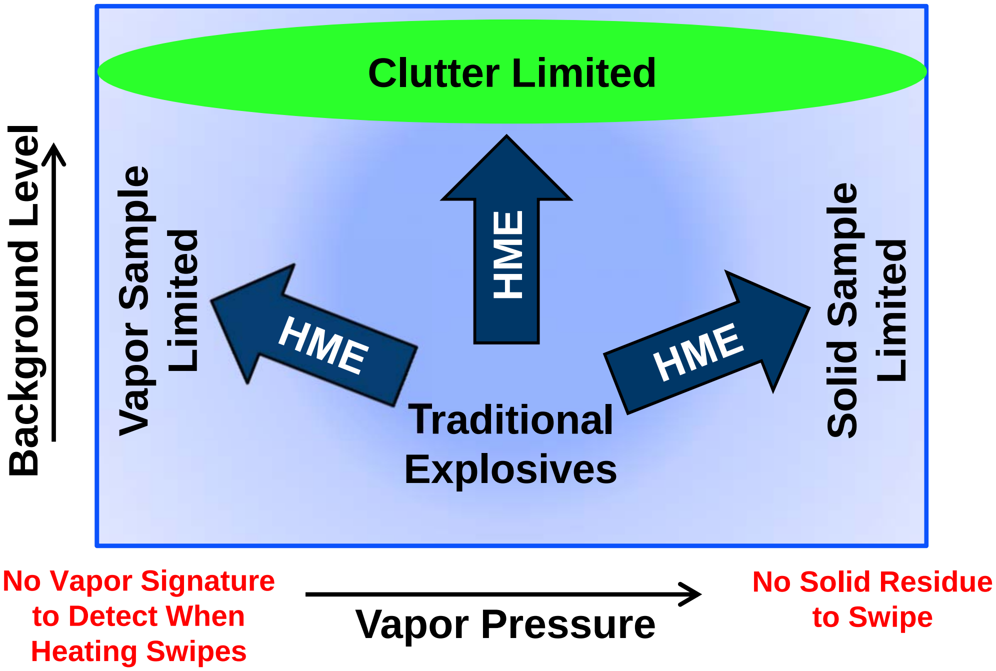
ETD Challenges: Clutter Limited Example

The Challenge for ETD: More / new HMEs



- **Challenge: HMEs constituent chemicals may be common in the background**
- **Case study: Ammonium nitrate**
  - **Common fertilizer**
  - **NH_3 (g) exists at ppb levels and HNO_3 (g) at ppt concentrations in the atmosphere**
- **AN exists in equilibrium with its precursors NH_3 and HNO_3**

$$NH_4NO_3\ (s) \leftrightharpoons NH_3\ (g) + HNO_3\ (g)$$

ETD performance may be background limited

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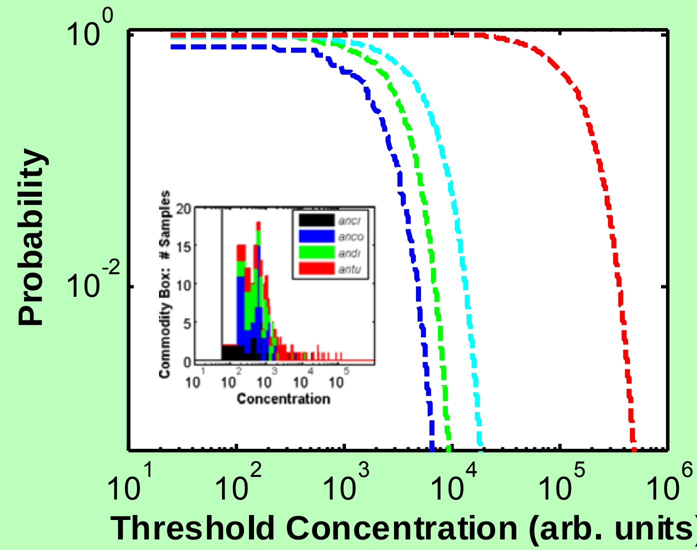
Method for Assessing Impact of Clutter

Background levels

- Background levels of salts similar for all cargo contents, cargo facility locations, seasons
- Simultaneous detection of nitrate and ammonium lowers P_{FA} by an order of magnitude

Threat Signatures



Examine clutter levels relative to signatures to set threshold requirements and identify algorithms/schemes for enhancing detection

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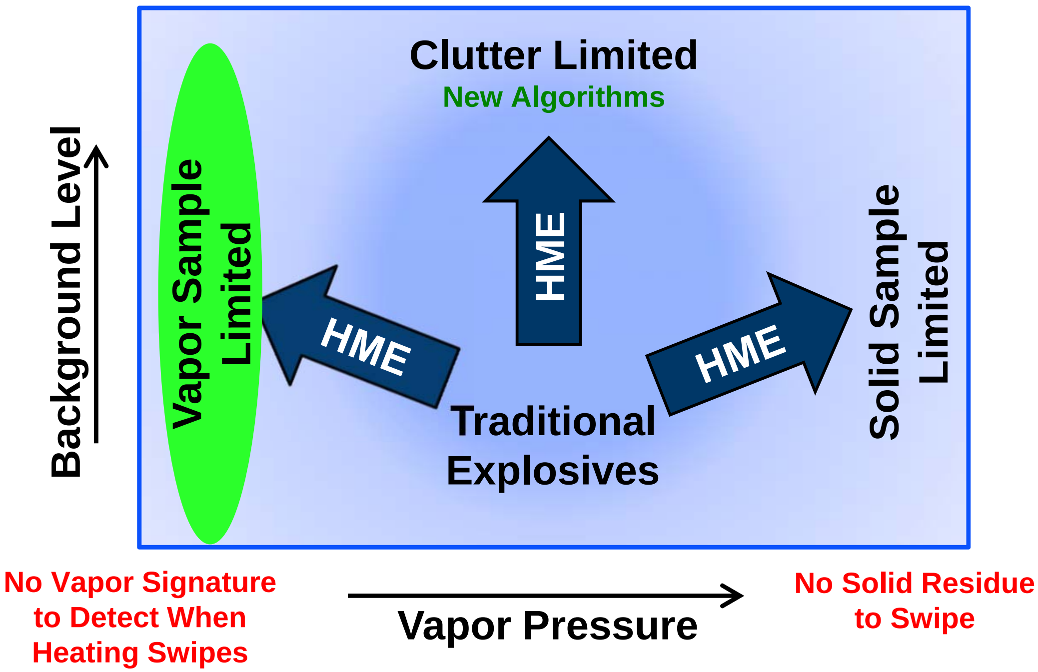
ETD Challenge: Sample Desorption for Chlorates and Perchlorates

The Challenge for ETD: More / new HMEs



Perchlorate and Chlorate Melting and Boiling Points

Compound	M.P. (°C)	B.P. (°C)
Potassium Perchlorate	525	600
Sodium Perchlorate	468	482
Potassium Chlorate	356	400
Sodium Chlorate	248	300
Perchloric Acid	-17	203
Chloric Acid	?	40

Industrial preparation: Salt Metathesis Reactions

$NaClO_4 + HCl \rightarrow NaCl + HClO_4$

$Ba(ClO_3)_2 + H_2SO_4 \rightarrow 2HClO_3 + BaSO_4$

- **High melting and boiling points translate into <u>low</u> vapor pressures at typical thermal desorption (TD) temperatures, 150 – 200 °C**
- **Low vapor pressures of chlorates and perchlorates limits TD based ETD**
- **However, perchloric acid ($HClO_4$) and chloric acid ($HClO_3$) have relatively high vapor pressures**

Convert chlorate and perchlorate salts into chloric and perchloric acids to enable thermal desorption based detection strategies

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ETD Challenge: Sample Desorption for Chlorates and Perchlorates

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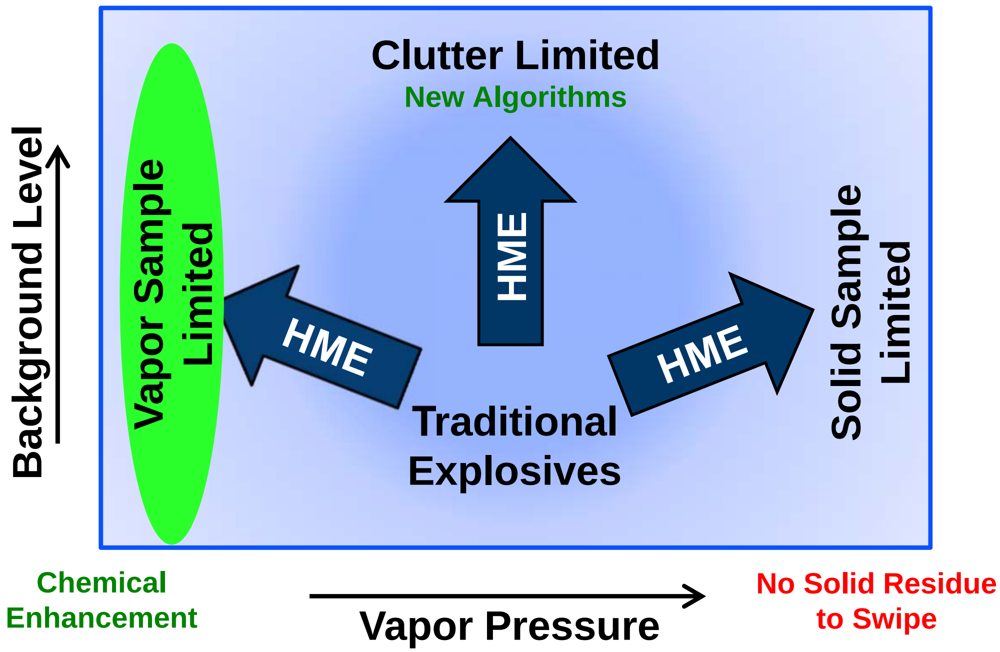

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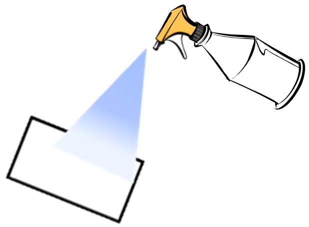
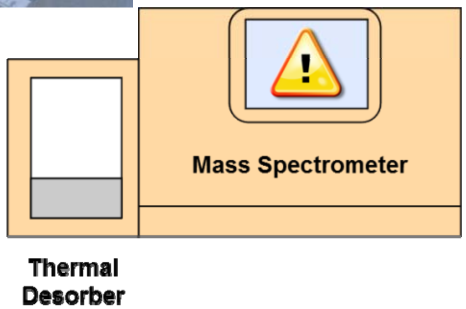
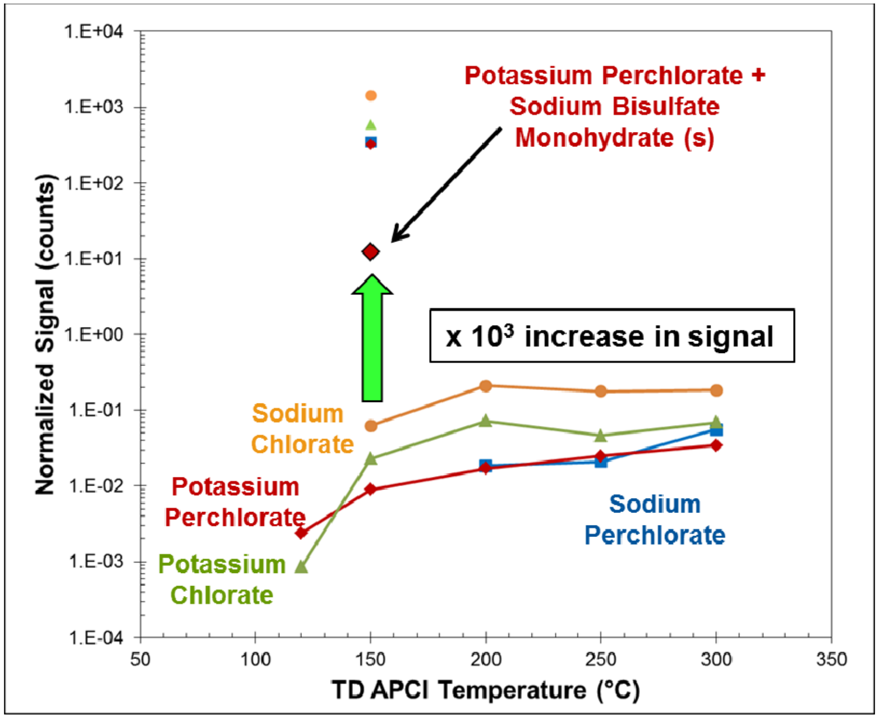
Acid Enhanced Detection of Chlorates and Perchlorates



Swipe:
$NaHSO_4$(s) and $Na_2S_2O_3 \cdot 5H_2O$





- **Solution:**
  - Add sodium bisulfate ($NaHSO_4$(s)); source of acidic protons and the sulfate anion
  - Codeposit sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) as a 'dry' source of water upon thermal desorption
- **Pros:** Easy handling of dry swipes, desired chemistry is thermally activate
  - Sodium bisulfate and thiosulfate are safe

Dry swipe with embedded safe solid compounds will enhance detection of chlorates and perchlorates

Patent Appls. US2014/0030816A1; WO2014/058507A2; US13/832,905; WO2104/058508A3; US61/975,275

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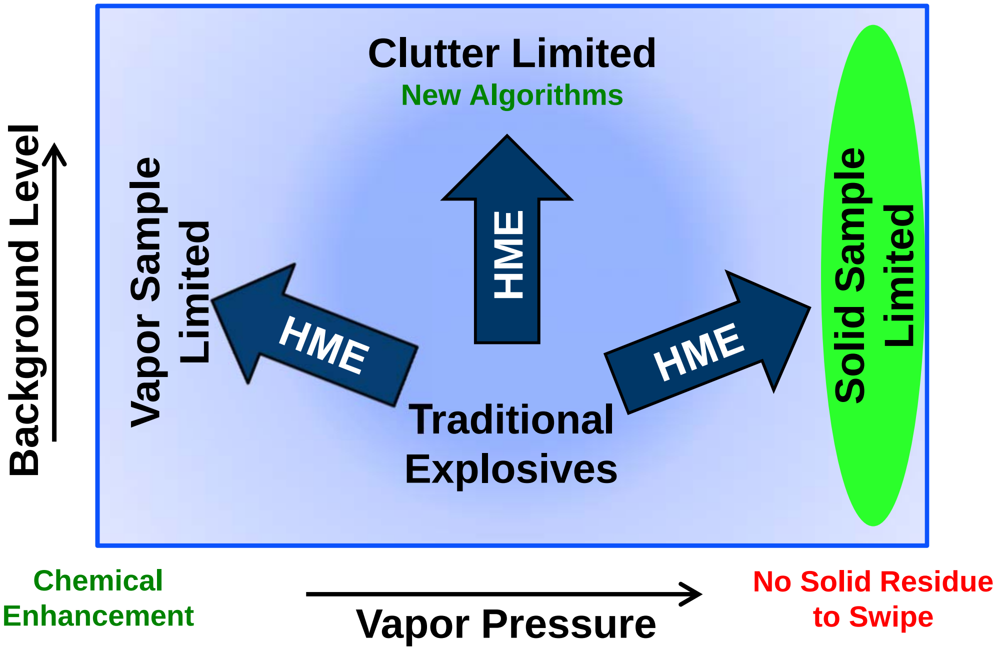
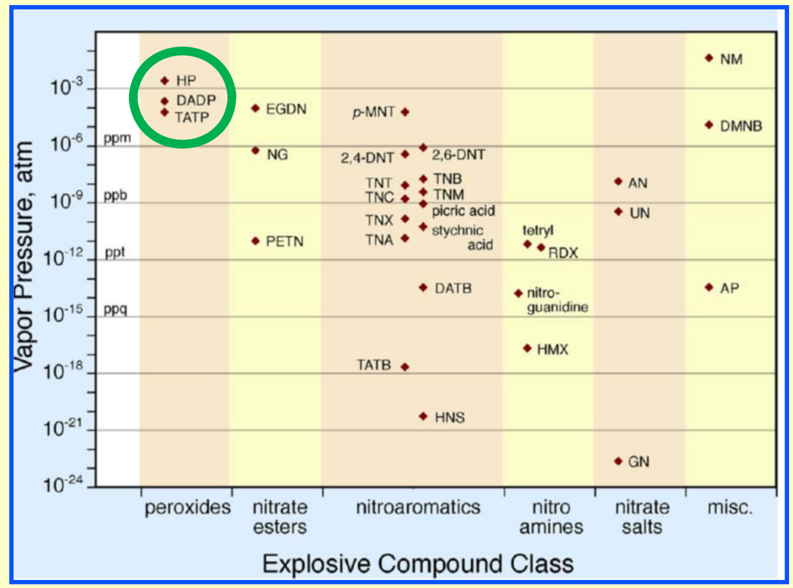
ETD Challenge: High Vapor Pressure Regime

The Challenge for ETD: More / new HMEs



- **TATP has a high vapor pressure**
- **Traditional sampling methods may need to be updated**

Fate, Persistence, Composition



Robert G. Ewing, Melanie J. Waltman, David A. Atkinson, Jay W. Grate, Peter J. Hotchkiss, TrAC Trends in Analytical Chemistry, Volume 42, January 2013, Pages 35-48.

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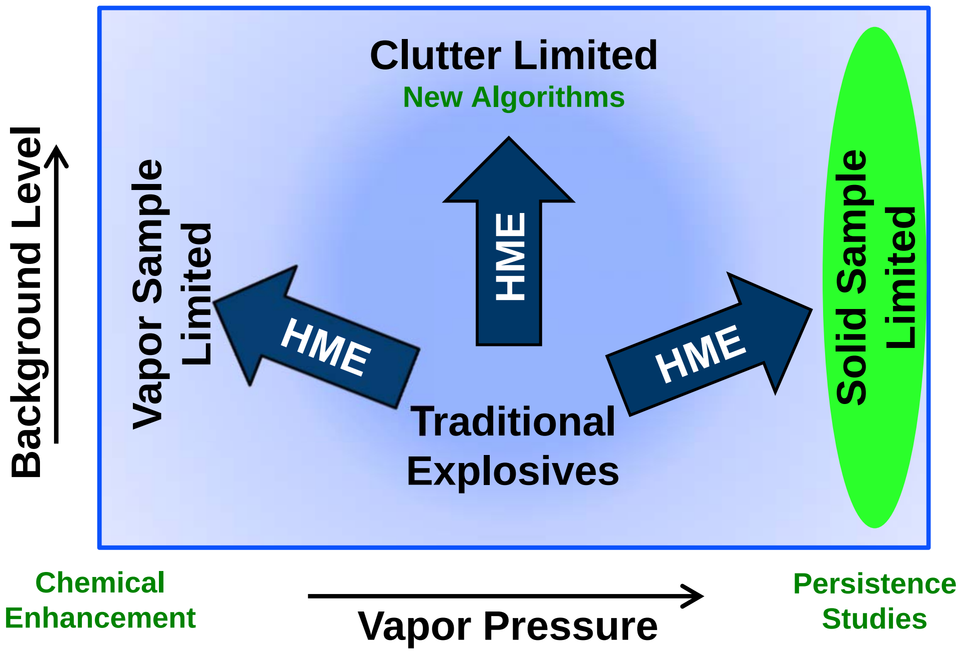

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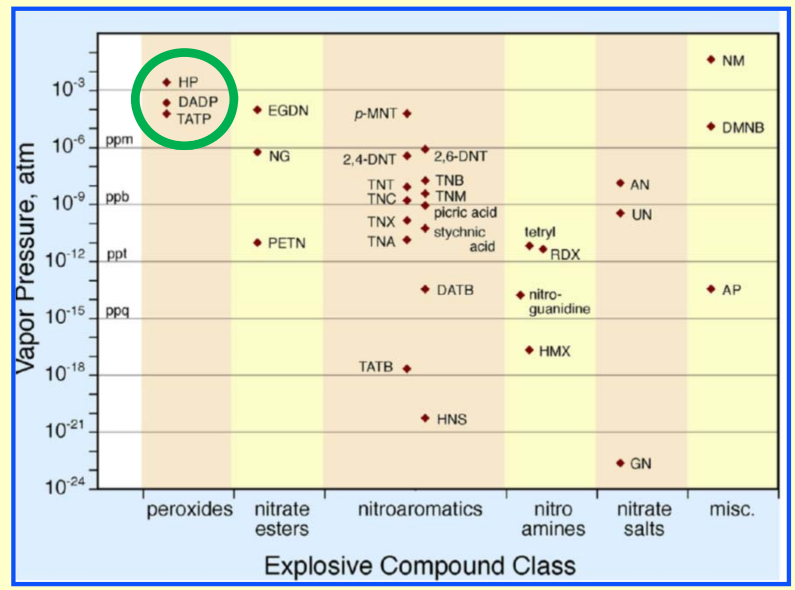

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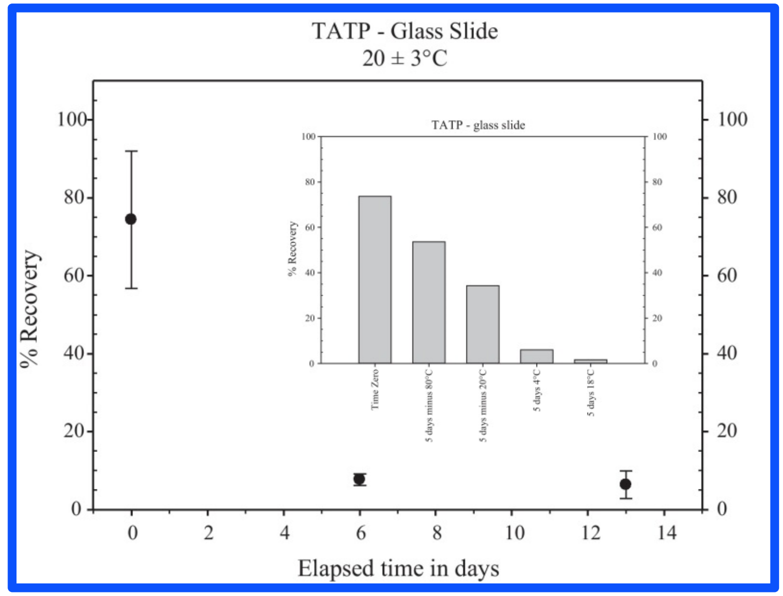
ETD Challenge: Persistence of Residues



Nopporn Song-im, Sarah Benson, Chris Lennard, Forensic Science International, Volume 226, Issues 1–3, 10 March 2013, Pages 244-253

- **TATP residues evaporate/decompose**
  - **Recent study showed that after 12 days at 20°C, 5% of TATP deposited on a glass slide remained (approximately ~1 μg still available for detection)**
  - **Current MITLL work aimed at assessing requisite detection thresholds**
- **Additional Detection Mitigation Measures**
  - **Vapor sensor**
  - **Detect presence of associated chemicals (main charge, or decomposition products)**
  - **Bulk screening**

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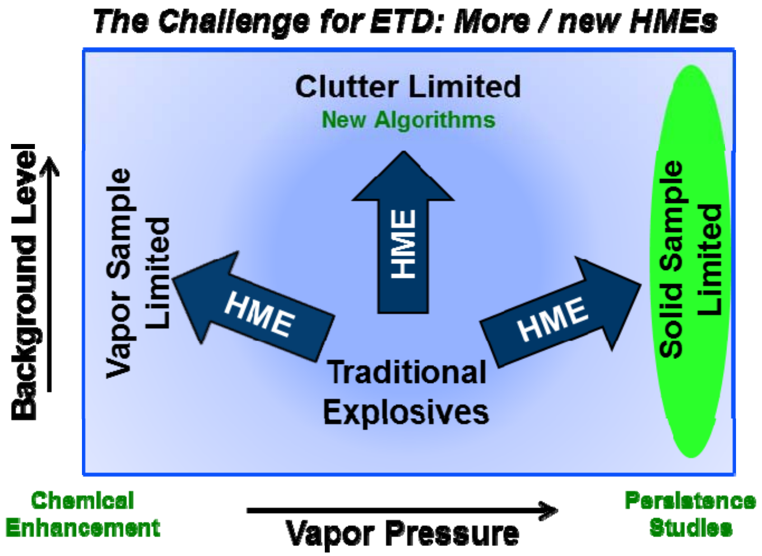
Summary

- **Chemical diversity of IEDs presents challenges for ETDs**
- **These challenges are being met two ways:**
  - **Improved instrumentation (industry focus)**
  - **Increased knowledge of trace phenomenology and background levels, leading to new methods and algorithms (MIT LL focus)**
- **The evolution of ETDs will ensure their future role in our counter-explosives architecture for air cargo security**



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- We would like to acknowledge: Department of Homeland Security, Science and Technology Directorate, Explosives Division and Department of Homeland Security, Transportation Security Administration

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