Ammonium Nitrate (AN) Detection with Mass Spectrometry

Susan Rose-Pehrsson Lauryn DeGreeff, Braden Giordano, Greg Collins
And F. Lucus Steinkamp*
Naval Research Laboratory, Chemistry Division
Washington, DC 20375-5342

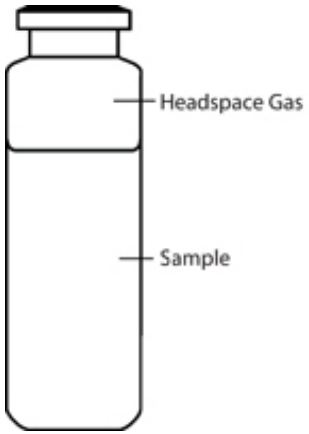
Adam Lubrano, Benjamin Andrews, and G. Asher Newsome
Nova Research, Inc., Alexandria VA, USA

* Former NRC Post Doc

So What/Who Cares?

Need to detect Binary explosives (Ammonium Nitrate + Fuel) in checked luggage/cargo (Baggage)

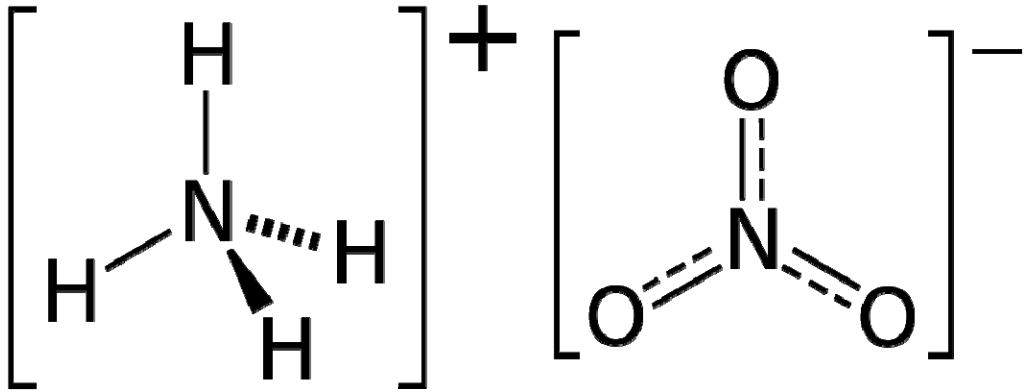
- Binary explosives are salts making them very difficult to detect
- ETD (eg, IMS) relies on particle sampling and is not selective for AN
- Vapor methods are difficult because of low VP.
- One potential solution: sample AN from headspace or gas above a sample and detect with Mass Spectrometry
- Method provides verification of both oxidizer and fuel
- Mass Spectrometry is applicable to other explosives
- Detector is very selective
- False alarms would occur from benign combinations of similar component



Binary Explosives Characteristics

Binary explosives are commonly used as Improvised Explosive Devices (IED)

- Oxidizer and fuel mixture:
  - Ease of detonation depends on fuel:oxidizer ratio
    - Oxidizer Examples: Ammonium nitrate (AN), potassium perchlorate ($KClO_4$)
    - Fuel Examples: Sugar, aluminum powder (Al), fuel oil (FO)
- Vapor detection of AN is challenging
  - Low vapor pressure (VP)
    - Estimated VP = 2.2×10^{-6} mmHg at 25 ˚C
    - Compared to VP of TNT = 2.0×10^{-4} mmHg
  - AN = salt
    - AN is in equilibrium with ammonia and nitric acid



Ammonium Nitrate (NH_4NO_3)

Volatile Emissions of AN

- Characteristics of AN vapor generated from solid sample vary as sample approaches equilibrium inside chamber
- Initially, large quantities of ammonia observed, but as steady state achieved within the laminar flow and a dynamic equilibrium established, the ratio of ammonia to nitric acid in the effluent vapor drops, although never becoming equimolar
- Ratio strongly dependent upon humidity

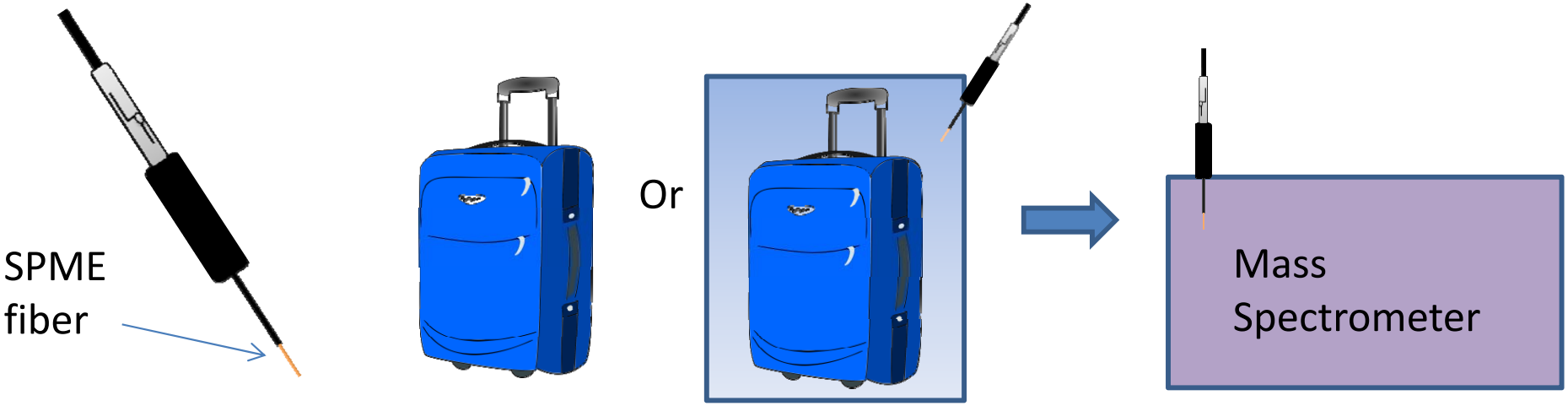
"Volatile Emissions of Ammonium Nitrate Under Flowing Conditions," F.L Steinkamp, B. Giordano, G. Collins, S. Rose-Pehrsson, Propellants, Explosives, Pyrotechniques (2015), 40, 682-687.

SPME Derivatization Method

Detection method for ammonia in the headspace of ammonium nitrate (NH_4NO_3). The method is:

- Easy to use
- Sensitive and selective
- Collect sample on solid phase microextraction (SPME) subtract
- Implement a derivatization method on the SPME
- Thermally desorb SPME into a conventional gas chromatography (GC) mass spectrometry (MS) for analysis

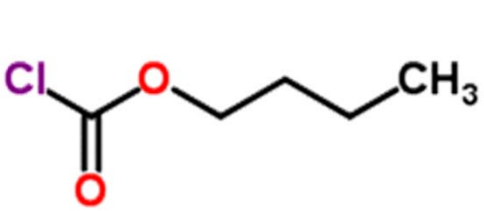
Butyl Chloroformate + Ammonia → Butyl Carbamate



SPME Derivatization Method Advantages

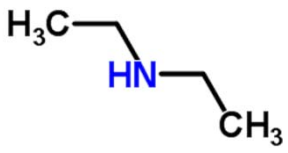
- Direct derivatization of ammonia in a headspace
  - No need for liquid phase
- Use of widely available lab instrumentation
  - GC/MS readily available in most labs
- Quick sampling compared to alternative techniques
  - Approximately 5 minutes
- Rapid analysis
  - Under 10 minutes
- The ability to simultaneously detect fuel among the ammonia

A derivatized externally sampled, internal standard (dESIS) is used to provide fiber to fiber reproducibility with a relative standard deviation of less than 5%.

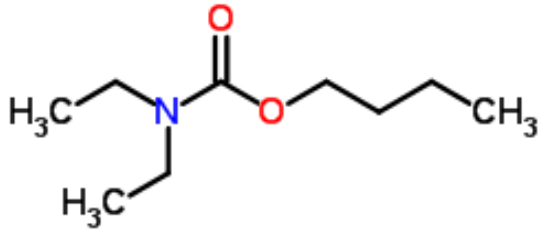


Butyl Chloroformate

+



Diethylamine



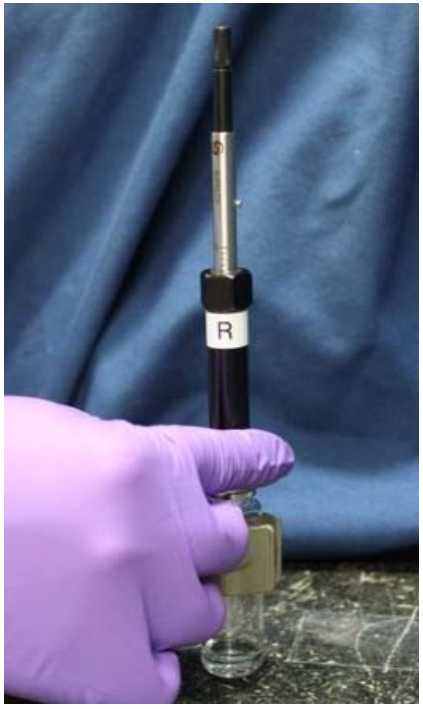
Butyl Diethylcarbamate

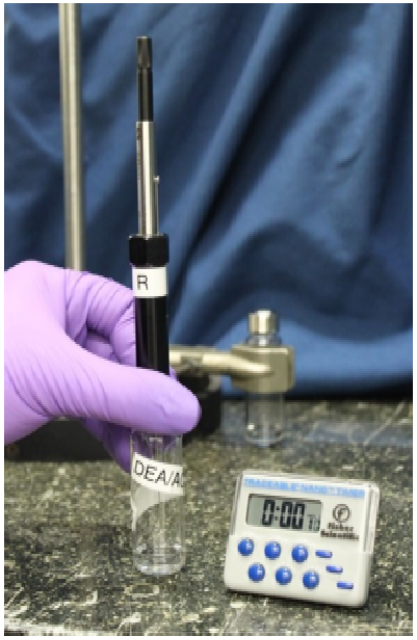
Simple 3 Step Sample Process

Step 1 Derivatization Agent:
Insert a SPME fiber into a 20 mL headspace vial with 2 mL of Butyl Chloroformate for 1 minute

Step 2 Sampling: Insert the SPME fiber into a sample and expose the fiber for 5 minutes

Step 3 dESIS: Immediately after exposing the fiber to the sample, the fiber is exposed to the dESIS headspace: 2mL of 1:10000 dilution of diethylamine in acetonitrile in a 20mL headspace vial for 15 seconds



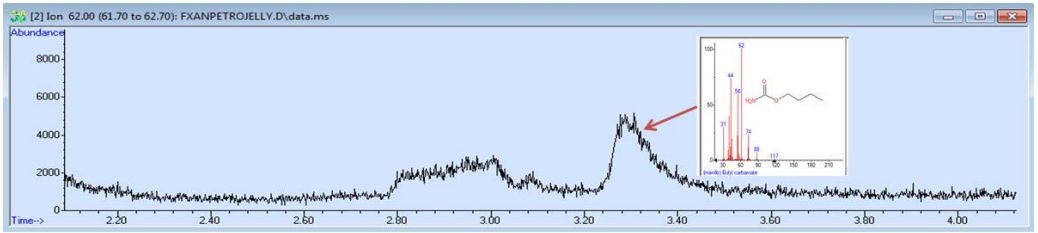


"Analysis of Ammonium Nitrate Headspace by On-Fiber SPME Derivatization with Gas Chromatography Mass Spectrometry," A. Lubrano, B. Andrews, M.H. Hammond, S.L. Rose-Pehrsson, Journal of Chromatography A (2016), 1429, 8-12.

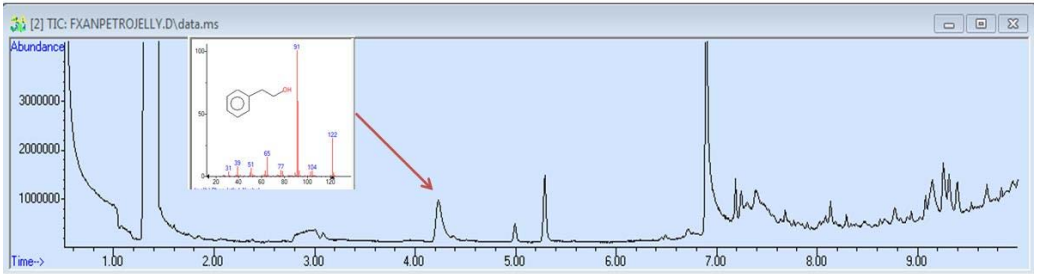
Headspace Samples for Mixtures of AN and Fuel

Headspace Samples of Mixtures of AN and Fuel

AN and Petroleum Jelly



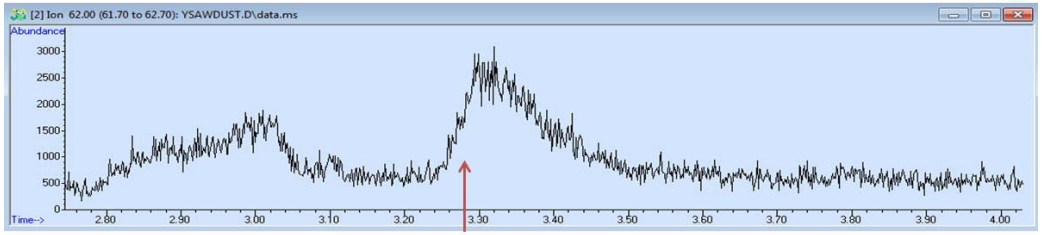
Presence of Butyl Carbamate at 3.25 min , evidence of ammonia in the headspace.



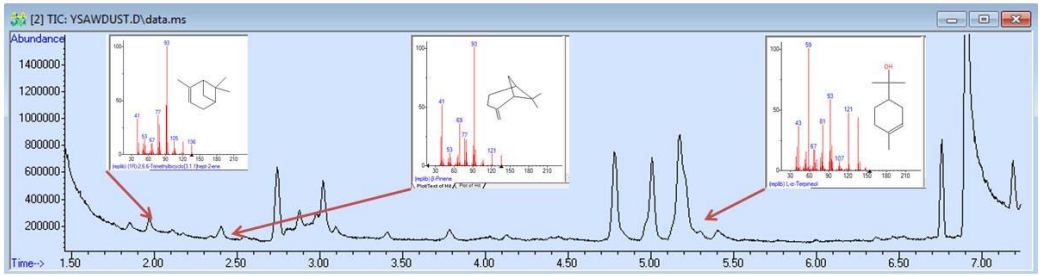
Peak at 4.25 min: library match for Phenylethyl Alcohol, a commonly found cosmetic fragrance.

Headspace Samples of Mixtures of AN and Fuel

AN and Saw Dust



Butyl Carbamate (m/z 62) at 3.25 min



TIC compromised of mainly pinenes and terpenes from sawdust, evidence of fiber degradation

Method provides detection of both the oxidizer (ammonia) and the fuel

Field demonstrations

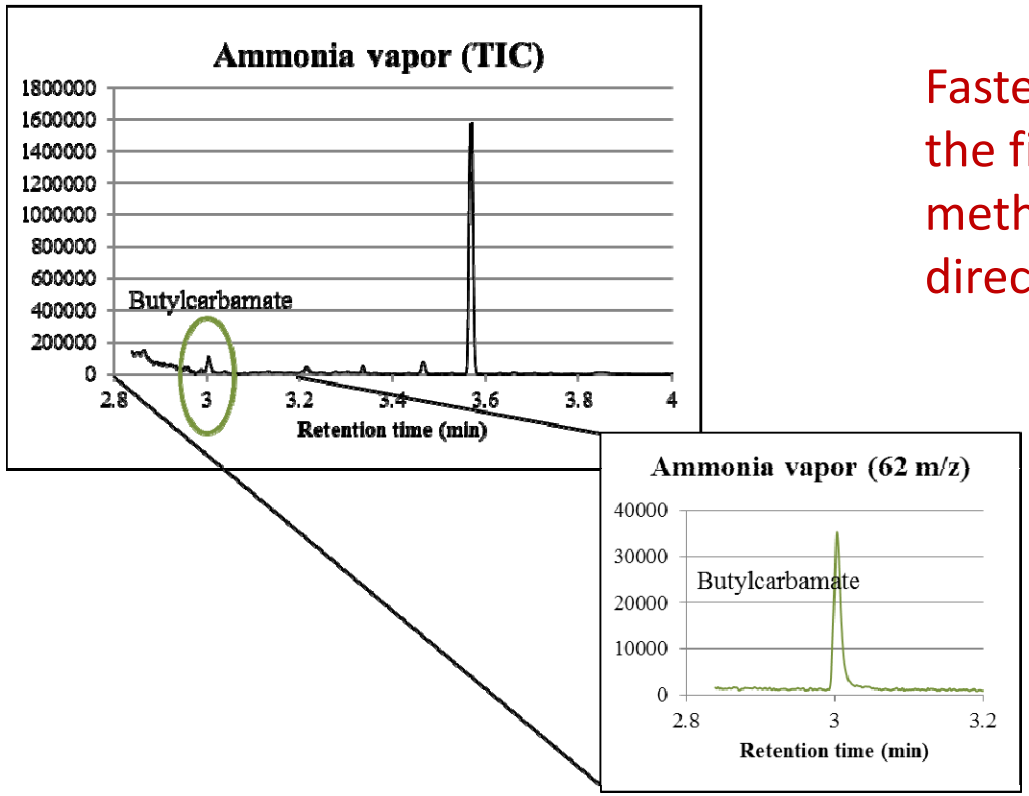
- Sampled the headspace of soil contaminated with ANFO
- Sampled the air in a magazine storing AN
- Can be implemented passively and actively

- The method needs further development before it can be effectively used in an operational environment to determine humidity and temperature effects and to assess the full range of potential interferences.

New Approach Direct Headspace Samples of AN

The derivatizing agent, butylchloroformate vapor, is cryogenically trapped on the CIS liner; ammonia vapor from AN is then collected onto the CIS liner with derivatizing agent. Following collection of the ammonia vapor, the CIS is heated and the vapor analyzed by GC-MS. No internal standard is used.

The estimated limit of detection with this method is sub-ppb ammonia.

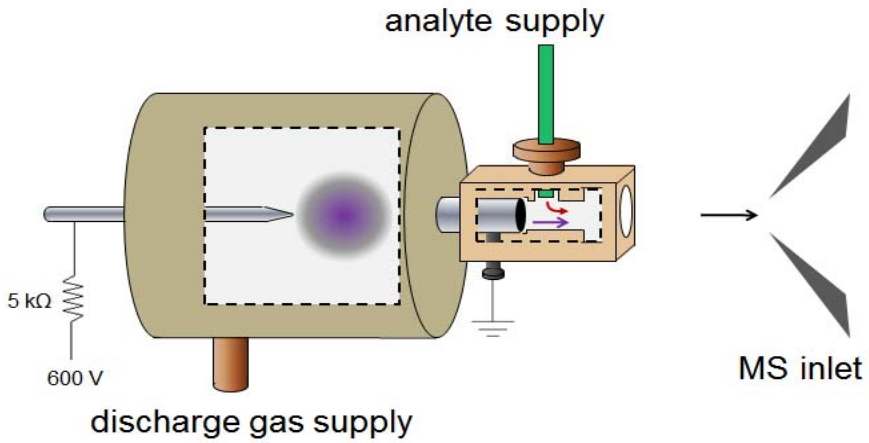


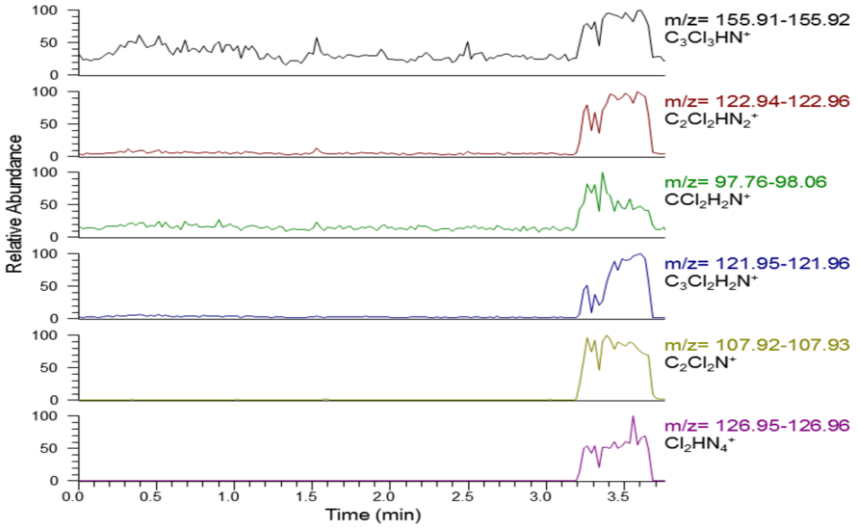
Faster method eliminates the fiber and allows the method to be sampled directly

New Ambient Pressure Mass Spectrometric Analysis

Ammonium nitrate produces ammonia and nitric acid in the gaseous headspace above bulk solids

- Both are detected in real time using ambient ionization mass spectrometry with custom-designed ion-molecule reaction techniques using preconcentration method
  - Preconcentration of NH_3 on Tungsten oxide successfully demonstrated





Carbon tetrachloride was selected as the reagent gas for ion-molecule reactions that generate larger ammonia adduct ions in a detectable range.

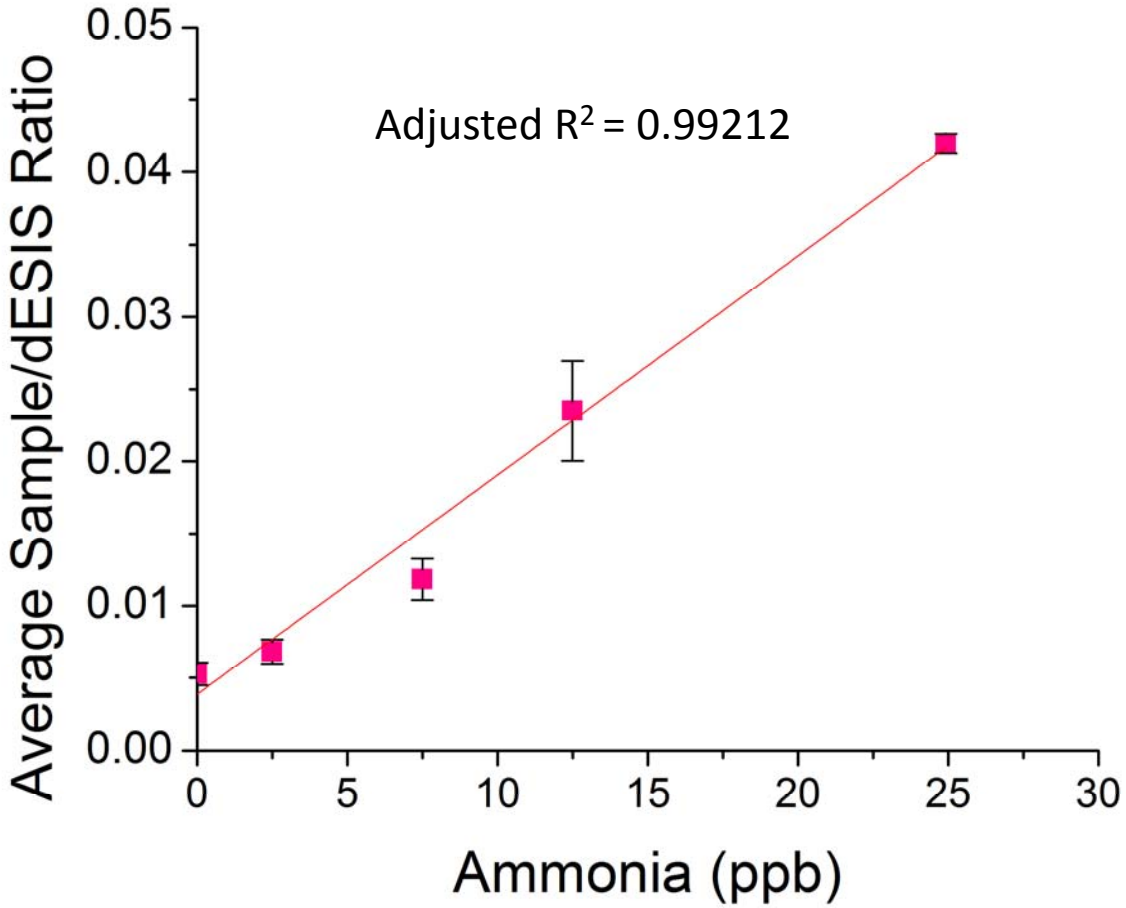
Using preconcentration, the ammonia adduct was observed at *m/z* 98 corresponding to $[CCl_3+NH_3-HCl]^+$

Acknowledgements

The program is funded by
U.S. Department of Homeland Security,
Science and Technology Directorate,
Homeland Security Advanced Research Projects Agency,
Explosives Division

Backup Slides

Calibration Curve Using the dESIS Method

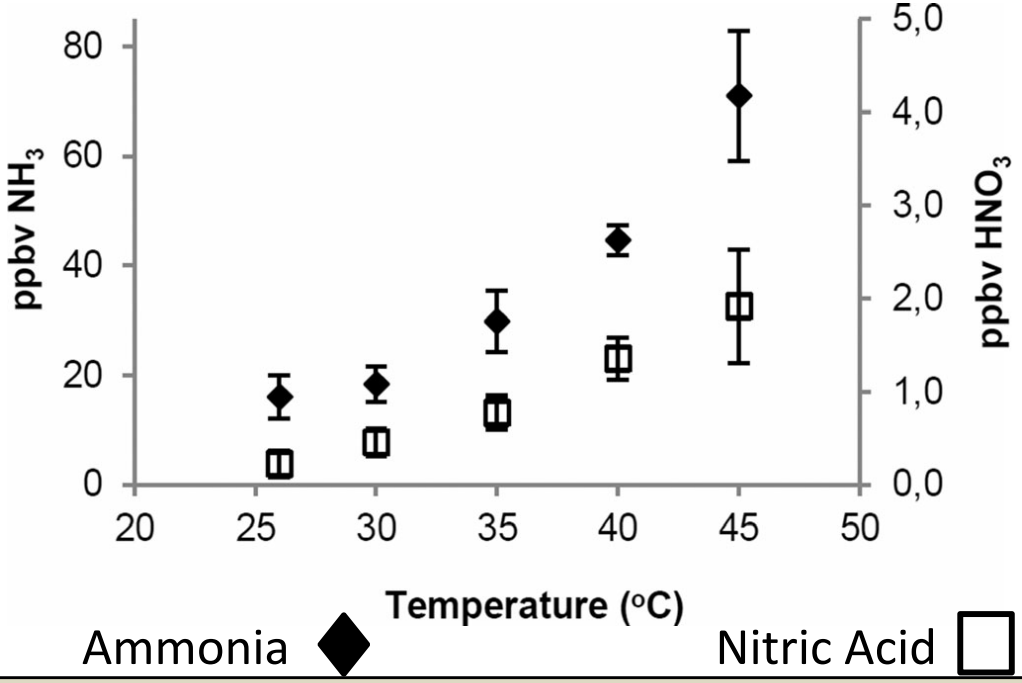


Ammonia (ppb)	Average Sample	Average dESIS	Avg Ratio	STDEV	%RSD
0.00	168212	31736357	0.0053	0.0008	14.96
2.50	166742	24619664	0.0068	0.0008	12.29
7.50	207471	17572558	0.0118	0.0014	12.07
12.49	307666	13353280	0.0235	0.0035	14.76
24.93	469498	11180272	0.0420	0.0007	1.57

Volatile Emissions of AN

- Characteristics of AN vapor generated from solid sample vary as sample approaches equilibrium inside chamber
- Initially, large quantities of ammonia observed, but as steady state achieved within the laminar flow and a dynamic equilibrium established, the ratio of ammonia to nitric acid in the effluent vapor drops, although never becoming equimolar
- Ratio strongly dependent upon humidity

Effect of temperature on AN vapor concentration and composition



Ratio of ammonia to nitric acid at two different humidity levels, dry & elevated

Flow	ppbv NH_3/ppbv HNO_3 (NH_3:HNO_3 ratio) Absolute humidity	
0.6 L/min	5.8/0.42 (14:1) 0 g/m^3 H_2O	8.0/0.43 (19:1) 6.3 g/m^3 H_2O
1.1 L/min	2.5/0.16 (15:1) 0 g/m^3 H_2O	11/nd[a] (--)[b] 14.8 g/m^3 H_2O

[a]not detected, [b]no ratio calculated

"Volatile Emissions of Ammonium Nitrate Under Flowing Conditions," F.L Steinkamp, B. Giordano, G. Collins, S. Rose-Pehrsson, Propellants, Explosives, Pyrotechniques (2015), 40, 682-687.

AN Methods in Literature

Mass Spectrometric detection of sample in liquid

Zhao and Yinon, "Characterization of ammonium nitrate by electrospray ionization tandem mass spectrometry," *Rapid Communications in Mass Spectrometry*, 2001, **15**, 1514-1519

Ammonium Nitrate in methanol/water solution introduced to electrospray by syringe pump produced cluster ions containing entire AN species via positive-ion ESI/MS

IMS detection of vapor from bulk sample

Ewing et al., "A critical review of ion mobility spectrometry for the detection of explosives and explosive related compounds," *Talanta,* 2001, **54**, 515-529

Using IMS, Ammonium Nitrate detection has been reported via the nitrate ion. Ammonia should be detected in positive polarity while nitrate ion is observed in negative polarity. Resolution and specificity problems exist. Nitrate ion is common in background air.

Bulk detection via Nuclear Quadrupole Resonance

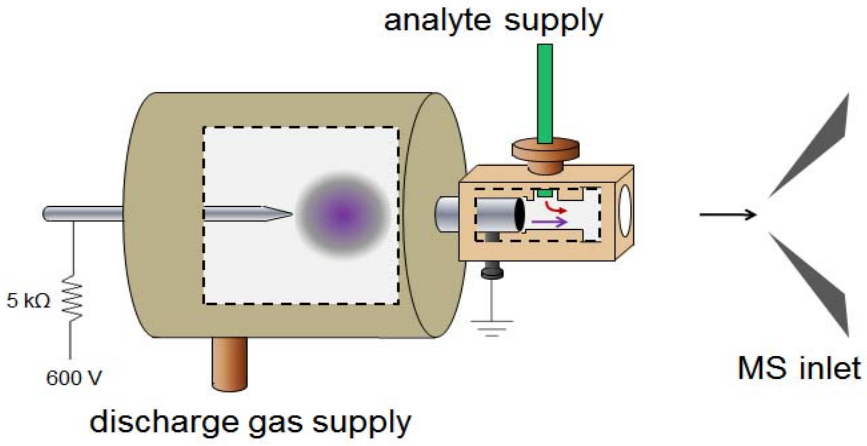
Barras et al., "Detection of Ammonium Nitrate inside Vehicles by Nuclear Quadrupole Resonance," *Applied Magnetic Resonance,* 2004, **25**, 411-437

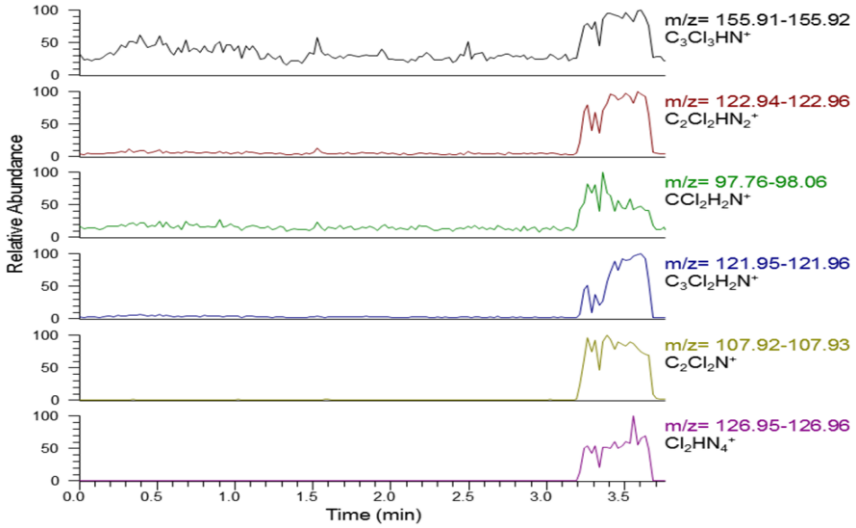
Using NQR, concealed Ammonium Nitrate detection has been demonstrated in vehicles.

Ambient Pressure Mass Spectrometric Analysis

Ammonium nitrate produces ammonia and nitric acid in the gaseous headspace above bulk solids

- Both are detected in real time using ambient ionization mass spectrometry with custom-designed ion-molecule reaction techniques
  - Insufficient sensitivity for real time detection of headspace concentrations
  - Preconcentration of NH_3 on Tungsten oxide successfully demonstrated
  - The methodology to accurately measure ammonia and nitric acid above bulk ammonium nitrate was resolved, but lacked a sufficiently-developed tungsten oxide preconcentrator.





Carbon tetrachloride was selected as the reagent gas for ion-molecule reactions that generate larger ammonia adduct ions in a detectable range.

Using preconcentration, the ammonia adduct was observed at *m/z* 98 corresponding to $[CCl_3+NH_3-HCl]^+$