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Portable Headspace Sampling for Field Applications in Forensic Science

Megan E. Harries, Ph.D.
University of Colorado Boulder

Fluid Characterization Group
Applied Chemicals and Materials Division

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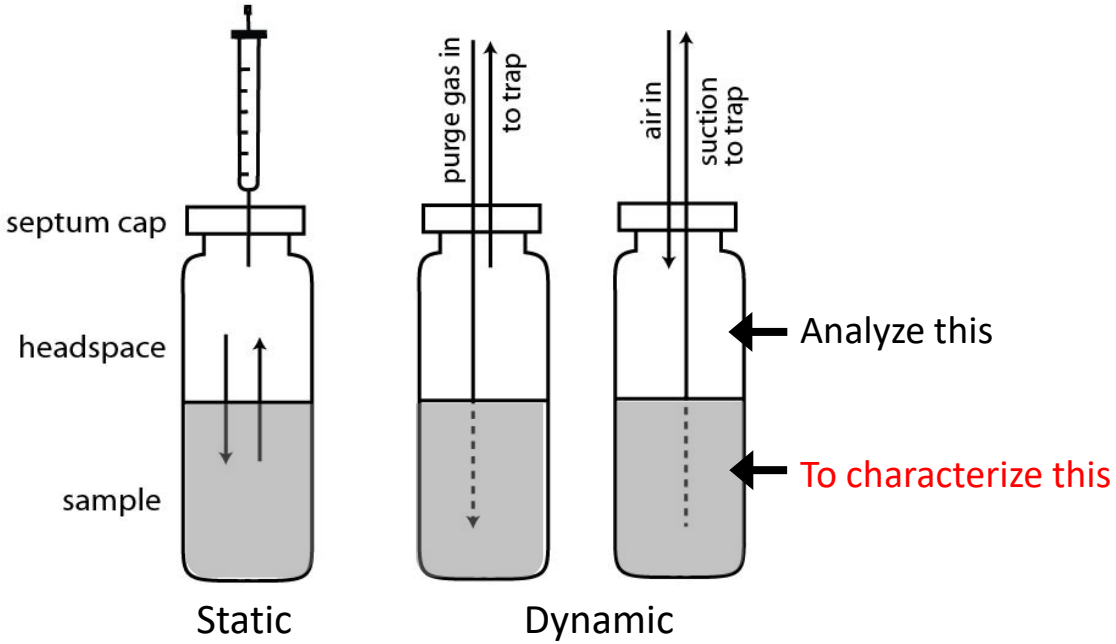
Vapor (= headspace) sampling

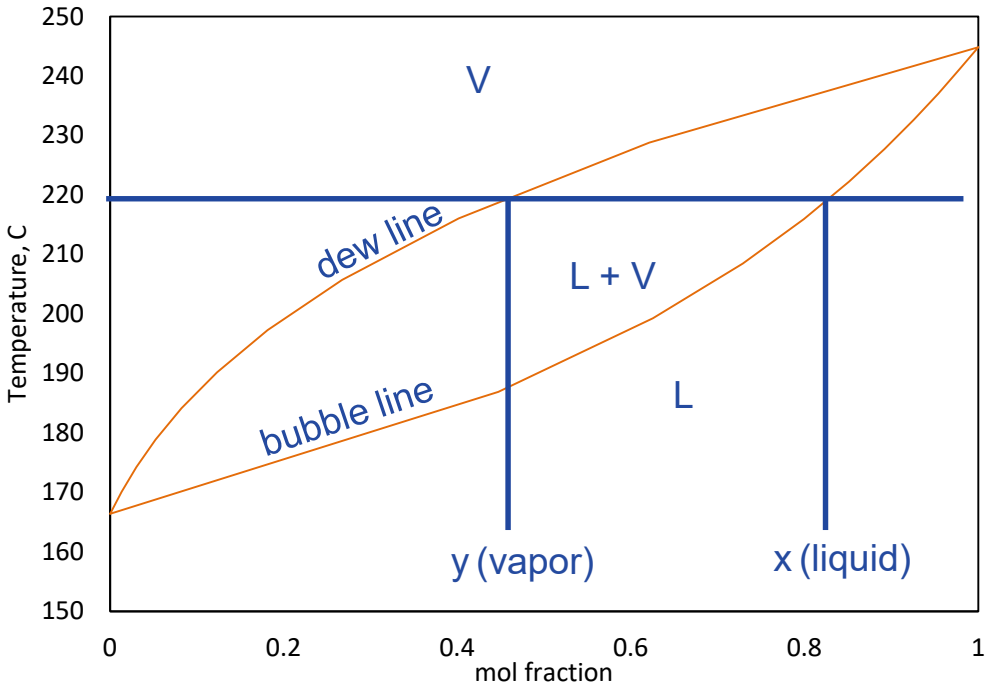
Cleaner: which is why we use it for fire debris analysis and many environmental analyses

Safer: does not require direct contact with sample (like a fentanyl) or even close proximity to a sample, with the right sampling probe

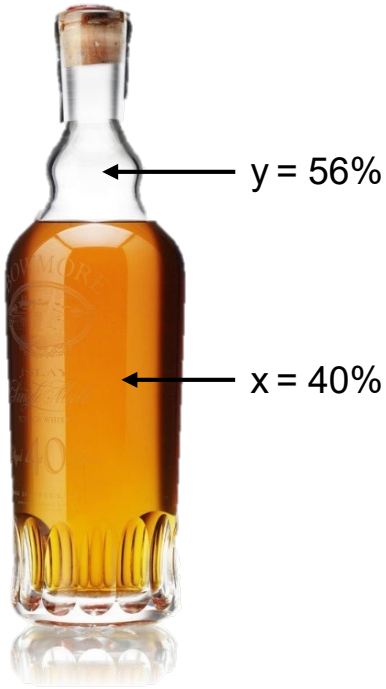
Non-destructive: a big advantage in evidence analysis or when sample availability is limited



Thermodynamics: vapor and liquid phase composition differ



If we have a thermodynamic model and the vapor composition, we can predict the liquid composition.



Example:
An 80-proof spirit is 40% ethanol, by definition, in the liquid.
The *headspace* of an 80-proof spirit is >40% ethanol, because of mixture effects and the variable vapor pressures of the components.

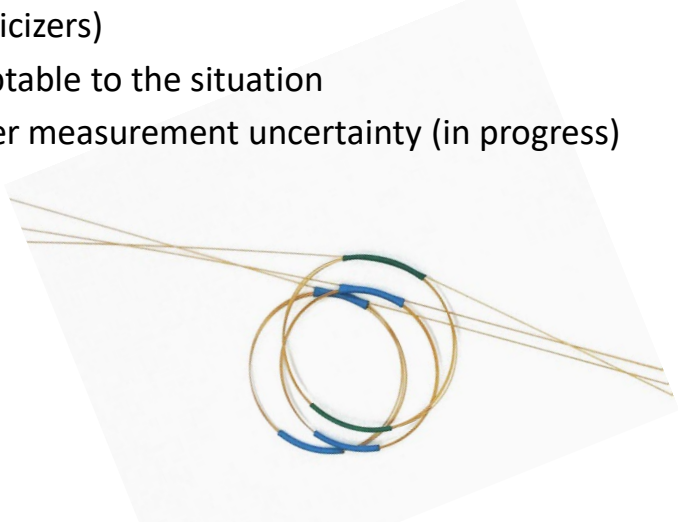
Lab PLOT-cryo and applications

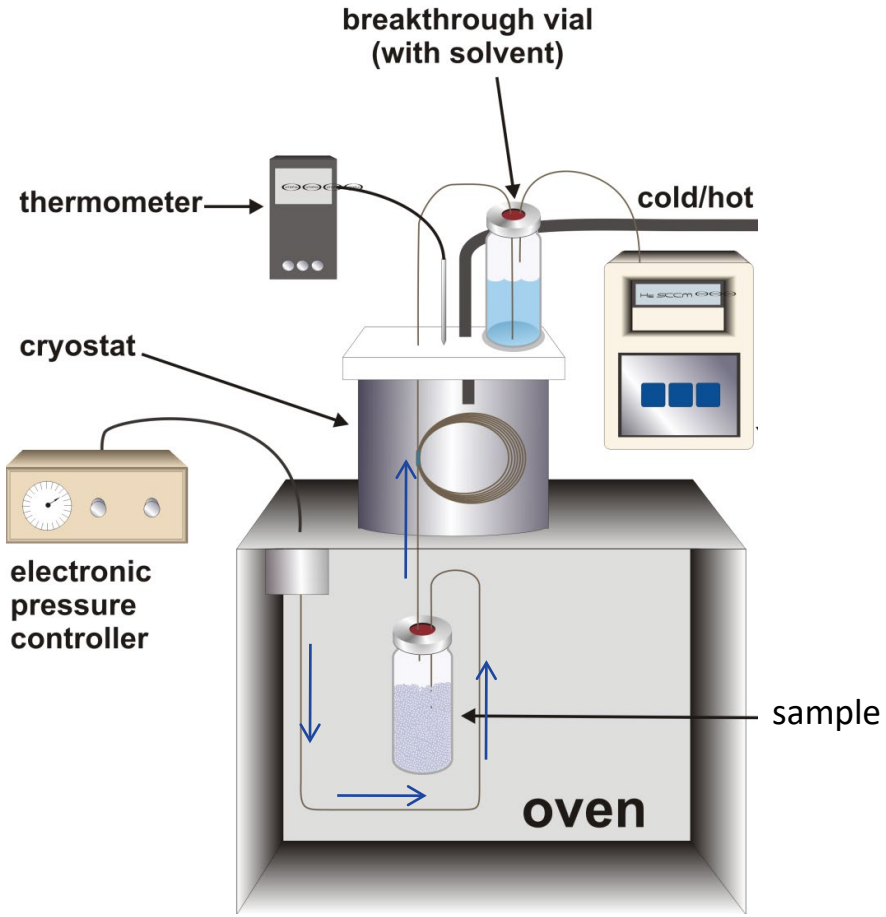
A preconcentration headspace method that uses an adsorbent capillary trap and cryoadsorption to enhance efficiency

Adsorbers are eluted with solvent and analyzed

Advantages

- Small sample quantities (mg)
- Fast
- Temps 30-300 °C
- Fast, cheap, flexible setup
- Good for low-volatility compounds (TNT, plasticizers)
- Adaptable to the situation
- Lower measurement uncertainty (in progress)





Bruno, T.J. *J. Chromatogr. Sci.*, 47, 569-574, 2009.

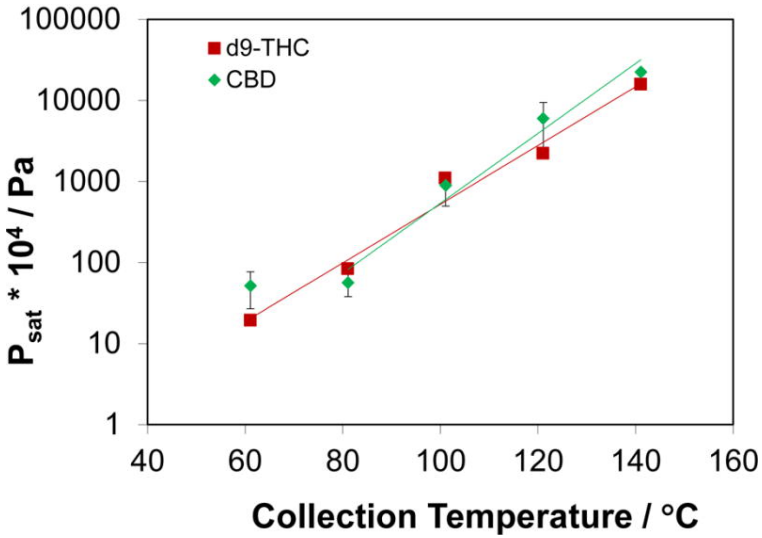
Lab PLOT-cryo and applications

A preconcentration headspace method that uses an adsorbent capillary trap and cryoadsorption to enhance efficiency

Past applications:

- Decomposition (rat graveyard)
- Fire debris
- Spoiled poultry
- Vapor pressure of explosives and cannabinoids

Many unexplored field applications!



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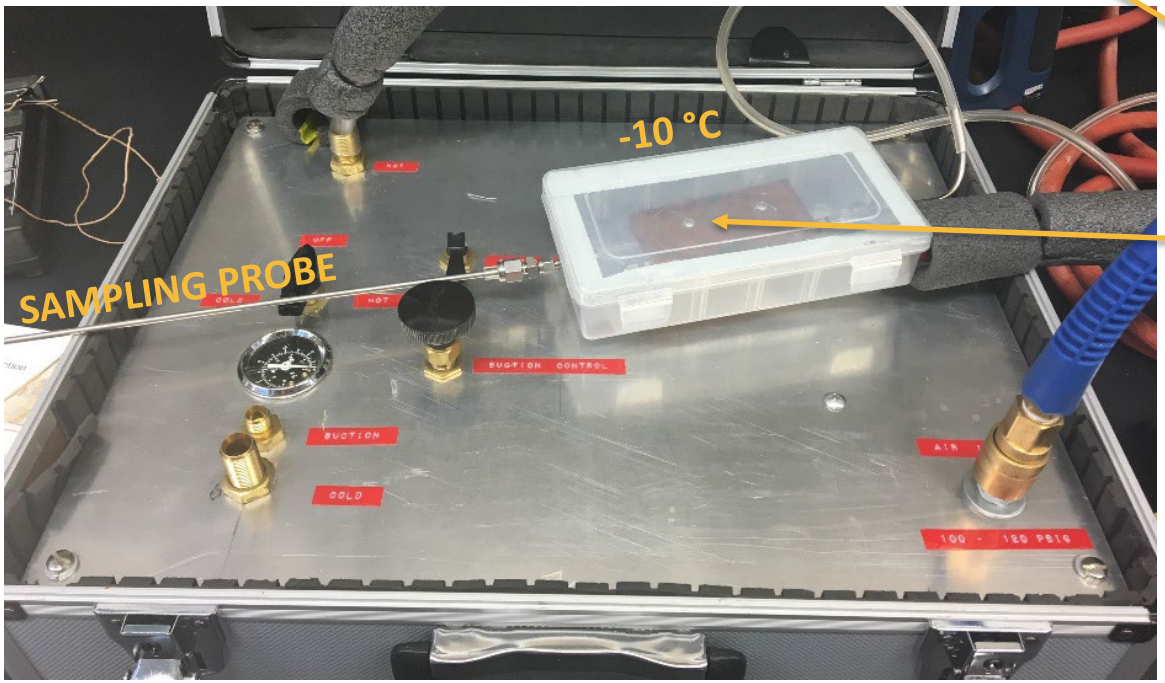
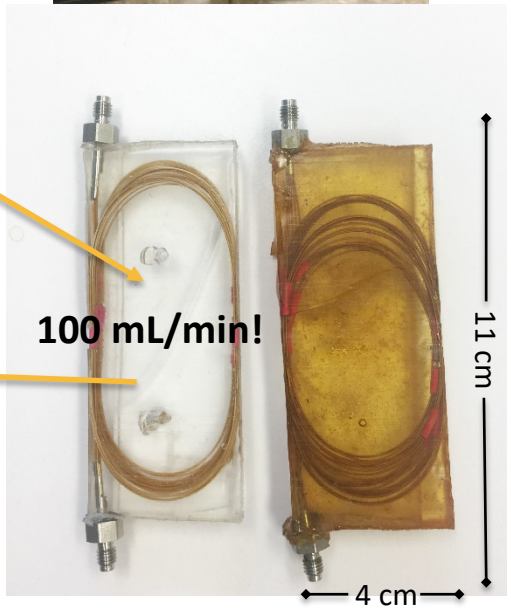
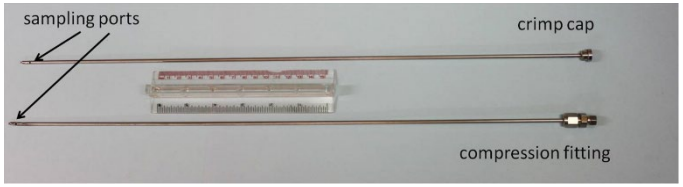
Lovestead, T. M., Bruno, T. J., Detection of poultry spoilage markers from headspace analysis with cryoadsorption on a short alumina PLOT column. Food Chem 2010, 121, 1274-1282.

Portable device development

- Robust, sturdy, hand-portable
- Withstands extreme temperature or humidity
- A probe to enable sampling from a distance
- Capable of rapid sampling times (higher flow rate)
- Field-based sample elution and PLOT reactivation



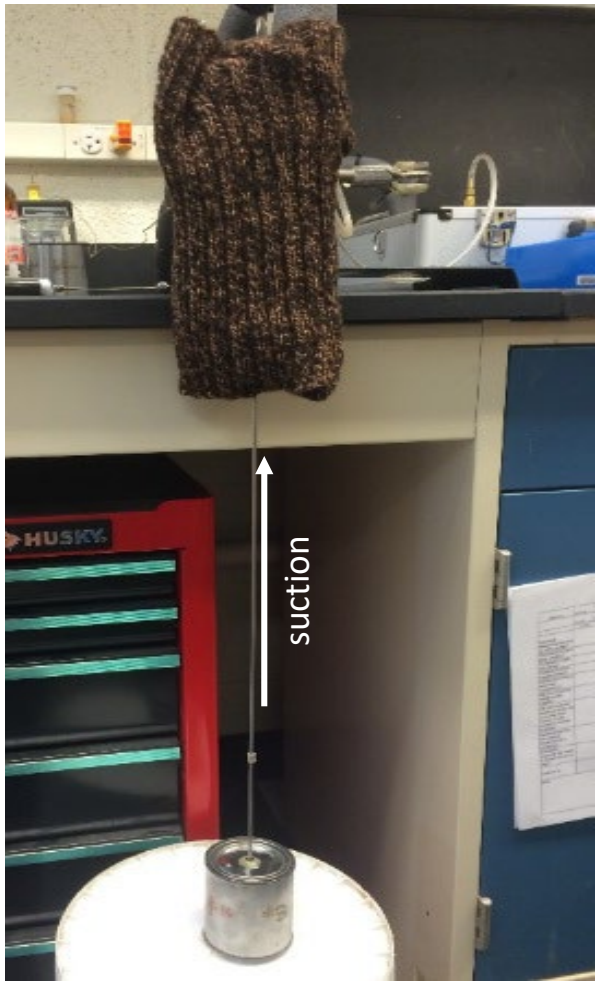


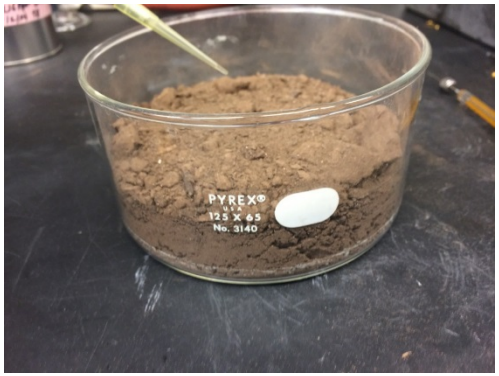


Lab studies

First tested using

- Naphthalene inside a suitcase: 3 sec detection
- Coumarin
- Trinitrotoluene (TNT)
- Low-volatility gas turbine kerosene (JP-5)
- Diesel fuel





Harries, M.E., Bukovsky-Reyes, S., Bruno, T. J., Field portable low temperature porous layer open tubular cryoadsorption headspace sampling and analysis part II: Applications, Journal of Chromatography A, 1429, 72-78, 2016.

Testing the limits with a diesel fuel spill

EPA 40 CFR 136 B: determining a method's detection limit (MDL)

1. Prepare and analyze at least 7 sample replicates at the same concentration
2. Select concentration estimated 2-10x the actual MDL
3. **MDL = s * $t_{n-1, \alpha}$**
   where s is the population standard deviation and t is the Student's t value for the given α-level

PRO: The method is designed to reflect *all* variability from sample prep through analysis… not just the TOF's detection limit.

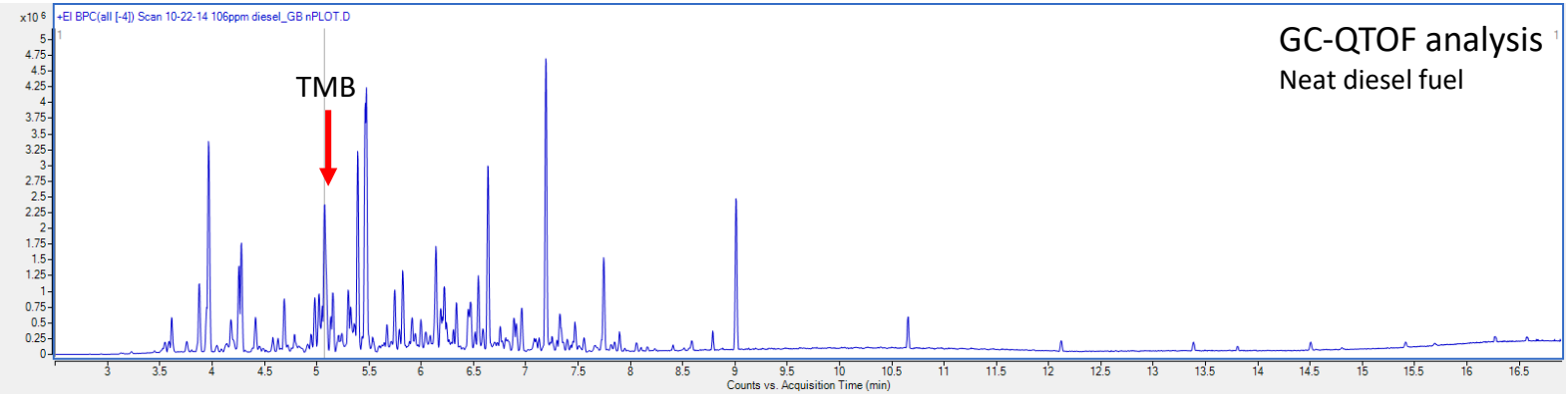
CON: The result is expressed in terms of signal, not concentration, and we can only estimate the MDL in ppm from the signal result.

Result

MDL = 32378 AU

1 ppm = 53997 AU

MDL <1 ppm



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Assessing sampling uncertainty

- 55 gallon (220 L) volume allows multiple headspace samples without changing the overall concentration
- Reduces sample uncertainty and matrix effects (single-phase mixture)
- Isolates variability due to portable vapor collection from variation among individually prepared samples

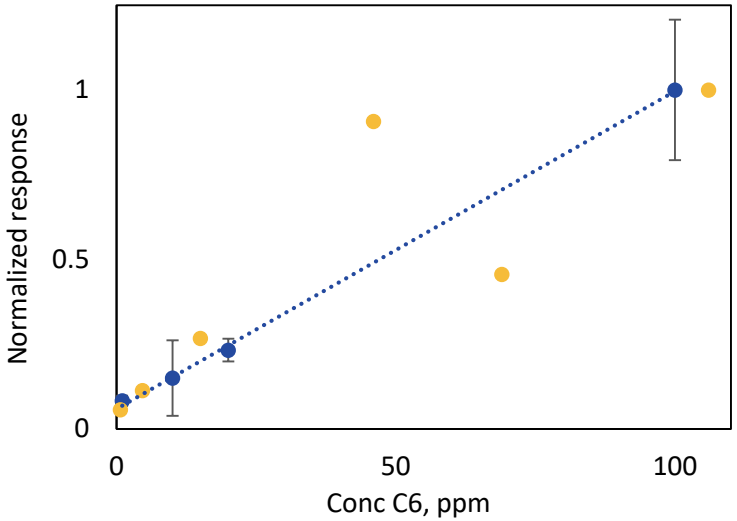
What we found:

In the MDL study, COV ($\sigma/\bar{x}$) included sample variation:

COV = .28 (n=16)

Using the chamber to eliminate sample-to-sample variability:

COV = .05 (n=7)



Bunker study

Bunker exterior

Portable PLOT-cryo setup in the field

Bunker interior

Challenges:

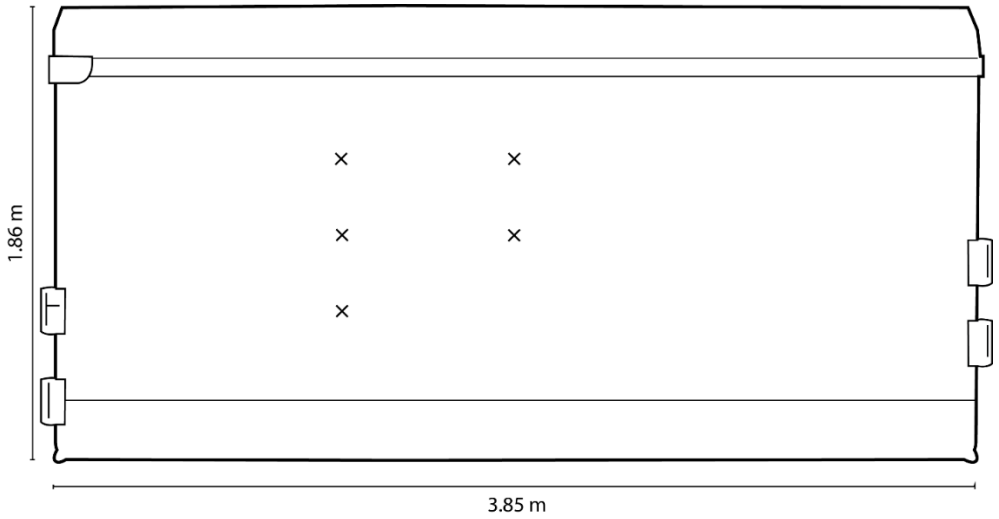
- Mother Nature
- Not well mixed, no guarantee of equilibration
- Open system
- 13600 L = Largest test bed by 100x

Bunker study

Four experiments

Naphthalene	Pure compound	Check device functioning
Explosives-related	4-part mixture	Solvents and plasticizers Vapor pressures 4 x 10^{-3} – 0.63 mm Hg
Gravesoil-related	8-part mixture	Sulfur compounds Diamines putrescine and cadaverine Vapor pressures 3 – 38 mm Hg
Gasoline	Highly complex	≈ ruptured fuel tank

Test compound volatility 5* 10^{-4} kPa to 5 kPa



Test conditions ranging:

$T_{ambient}$ = 3 to 37 °C

T_{bunker} = 2.2 to 43 °C

RH = 9 % to 92 %

Sample times = 30 s – 20 min

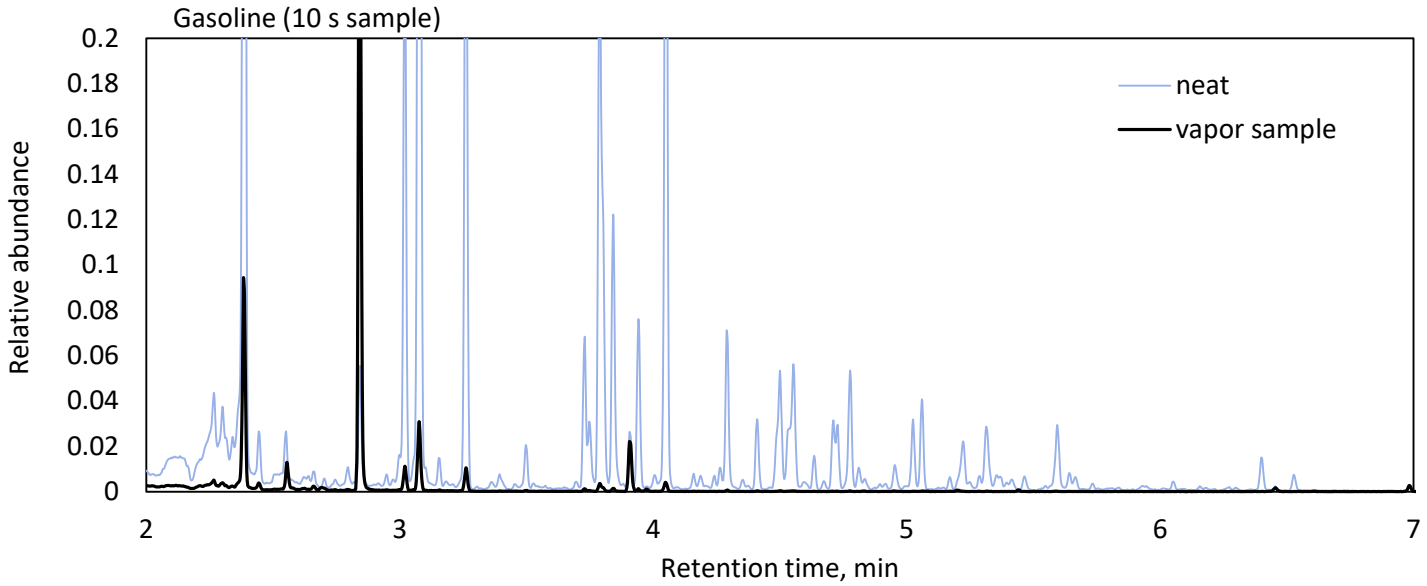
Compressed air testing:

- House air
- Diesel compressors
- Canister from SCBA

Bunker study

Findings

- Strong bunker background signal: degrading polyurethane foam insulation
- Diethyl phthalate (challenge compound)
- Gasoline in 3 s
- Higher temps eased detection
- Humidity > 90% increased sampling time; humid compressed air caused interruption to refrigeration



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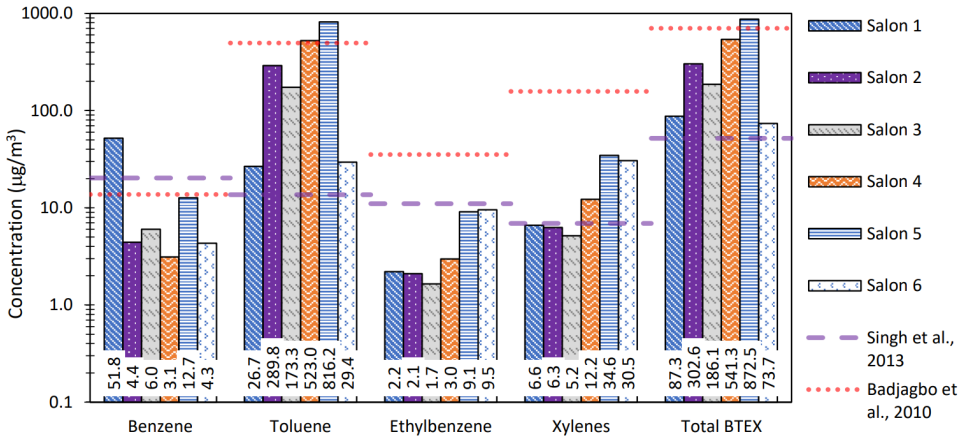
Future work

- Profs. Joost de Gouw and Jose Jimenez (CU Boulder)
  - Online MS and field GC-MS teamed with portable PLOT-cryo preconcentration
  - Breath sampling to detect intoxication
  - Monitoring disease biomarkers in animal agriculture
- Investigating indoor air quality as a route of exposure to occupational hazards

Vocus PTR-TOF



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Platon Science and Technologies
Licensed patents for portable PLOT-cryo

Chris Gray, Ph.D.
platonscitech.com
chris.gray@platonscitech.com

Thank you

ACMD Fluid Characterization Group

Boulder Fire and Rescue Department

NIST Special Programs Office

megan.harries@nist.gov