Portable Headspace Sampling for Field Applications in Forensic Science

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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
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)
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!

Lovestead, T. M., Bruno, T. J., Detecting gravesoil with headspace analysis with adsorption on short porous layer open tubular (PLOT) columns. Forens Sci Int 2011, 204, 156-161.
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

100 mL/min!
Lab studies

First tested using

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

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 \( \alpha \)-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

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:

$$\text{COV} = .28 \ (n=16)$$

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

$$\text{COV} = .05 \ (n=7)$$
Bunker study

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

Four experiments

<table>
<thead>
<tr>
<th>Compound Type</th>
<th>Description</th>
<th>Vapor Pressures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>Pure compound</td>
<td>Check device functioning</td>
</tr>
<tr>
<td>Explosives-related</td>
<td>4-part mixture</td>
<td>Solvents and plasticizers</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vapor pressures $4 \times 10^{-3} - 0.63$ mm Hg</td>
</tr>
<tr>
<td>Gravesoil-related</td>
<td>8-part mixture</td>
<td>Sulfur compounds</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diamines putrescine and cadaverine</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vapor pressures $3 - 38$ mm Hg</td>
</tr>
<tr>
<td>Gasoline</td>
<td>Highly complex</td>
<td>≈ ruptured fuel tank</td>
</tr>
</tbody>
</table>

Test compound volatility $5 \times 10^{-4}$ kPa to 5 kPa

**Test conditions ranging:**

- $T_{\text{ambient}} = 3$ to $37$ °C
- $T_{\text{bunker}} = 2.2$ 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

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

Thank you

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Platon Science and Technologies
Licensed patents for portable PLOT-cryo

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