From Theory to Practice: Why Thermal Desorption Is the Perfect Solution for Air Analysis

NEMC 2020, Tuesday, August 04th

Lee Marotta, Principal Field Application Scientist, PerkinElmer
Outline

• Introduction
• Thermal Desorption (TD): theory and operation
• Adsorbents and sampling
• Applications / solutions
• Troubleshooting / maintenance / method validation
Introduction
## GC Sample Introduction Techniques

<table>
<thead>
<tr>
<th>Injection Type</th>
<th>Concentrator</th>
<th>Conc compared to 1 µL</th>
<th>Maximum C #</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Liquid Injection Techniques</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Packed</td>
<td>-</td>
<td>x</td>
<td>C44</td>
</tr>
<tr>
<td>Split Capillary</td>
<td>-</td>
<td>x</td>
<td>C44</td>
</tr>
<tr>
<td>Splitless Capillary (pressure pulsed)</td>
<td>-</td>
<td>x</td>
<td>C44</td>
</tr>
<tr>
<td>On-Column Capillary</td>
<td>-</td>
<td>x</td>
<td>C120</td>
</tr>
<tr>
<td>Large Volume Injection</td>
<td>yes</td>
<td>50x+</td>
<td>C60</td>
</tr>
<tr>
<td>Solvent Purge Injection</td>
<td>can be if LV</td>
<td>x</td>
<td>C60</td>
</tr>
<tr>
<td>Liquid Sampling Valve</td>
<td>-</td>
<td>x</td>
<td>C12</td>
</tr>
<tr>
<td><strong>Gas Phase Injection Techniques</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas Sampling Valve</td>
<td>-</td>
<td>x</td>
<td>C7</td>
</tr>
<tr>
<td>Purge &amp; Trap</td>
<td>yes</td>
<td>1000x+</td>
<td>C12</td>
</tr>
<tr>
<td>Headspace</td>
<td>yes</td>
<td>1000x+</td>
<td>C18</td>
</tr>
<tr>
<td>Thermal Desorption</td>
<td>yes</td>
<td>1000x+</td>
<td>C40</td>
</tr>
<tr>
<td><strong>Other Injection Techniques</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Supercritical Fluid Extraction (SFE)/Inje</td>
<td>yes</td>
<td>1000x+</td>
<td>C44</td>
</tr>
<tr>
<td>Solid Phase Microextraction (SPME)</td>
<td>yes</td>
<td>1000x+</td>
<td>C18</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>-</td>
<td>x</td>
<td>C150+</td>
</tr>
<tr>
<td>Thermogravimetric Analysis (TGA)</td>
<td>-</td>
<td>x</td>
<td>C150+</td>
</tr>
</tbody>
</table>
History

• In 1980, introduced first Automated Thermal Desorber

• Model Automated Thermal Desorber 400
  • Portable
  • Ease of use

• Current: TurboMatrix five models to fit your requirements
  • TMX-1 dedicated system for online/and cannister sampling
  • TMX-650 with recollect and many more automated validation features. The standard for the analysis of toxic compounds in air
  • Minimizing plumbing. Optimize inertness. Ease of maintenance

• EPA Collaboration
  • Late 90’s – developed TO-17 toxic compounds in air by ATD/GC/MS
  • Fenceline monitoring and EPA method 325 … 15 years of collaboration with others
Applications besides Environmental …

- Industrial hygiene
- Material or product testing
  - Aromas in air from flavors (i.e. percolated coffee) or in products such as coffee in a tube
  - Fragrances in air or in the material
  - Off – gassing from products in air or in materials
    - Resins
    - Car fabrics
    - Too many to name
- Medical human breath
  - To diagnose possibility of a disease
- Healthy building
- Forensics: Arson investigation
- Semiconductor
- Kinetic studies

... no laborious extractions and no solvent interferences. Saves time / optimizes profits
Environmental Applications

- Indoor/outdoor
- Stack monitoring
- Soil gas
- MGP sites (fenceline monitoring superfund)
- Fenceline monitoring (industrial sites)
- Ozone Precursors

Benefits of Active and Passive Sampling

Benefits of VOC and SVOCs in one sample

Air Monitoring Solution

TurboMatrix 650 Automated Thermal Desorber
Clarus SQ8 GCMS
Thermal Desorption: Operation
Many Ways to Sample

Optional inlet split

Desorb flow

Peltier-cooled trap
(no liquid cryogen)
Sample Tube Desorption

- IS and/or surrogate spike (optional)
- Impedance check (optional)
- Ambient purge (at least 1 min)

Desorption via:
- ✓ Temperature
- ✓ Flow
- ✓ Time

Inert gas

Inlet split (Optional)

Desorb flow

Peltier cooled to -35°C
No need for liquid cryogen
Transfer of Sample to Instrument

Optional ‘outlet’ split or Recollect on same tube or new tube

Typical flows
- Column Flow: 2.5mL/min
- Recollect Flow: 10mL/min
- %Recollected: 80%

The flow is reversed during desorption
Adsorbents

sea sponge
Adsorbent Choice and How It Works

• Choose an adsorbent (s) that will retain and release (recover) the target components of interest in the sample. Active sampling allows for the broadest component range.

• Moisture management
  ◦ When possible, and in most environmental compounds it is, select adsorbent where moisture will not be retained while sampling. Hydrophobic adsorbents.

• How it works
  ◦ Smaller surface areas are for greater boiling point components and larger surface areas are for more volatile components.
Adsorbents: Most Retentive

- Carbon Molecular Sieves
  - Spherical
  - Surface area 400 to 1200 m²/g
  - Retains and releases light components: typically, C₂ – C₅; However, 2016 has a range from C₅ – C₁₂
  - Upper temperature limit: 400 °C
  - Moderate to very hydrophilic. Requires dry purge if sampled in humid conditions environment
Adsorbents: Broad Range

- Graphitized Carbons
  - Granular
  - Surface area 2 to 240 m²/g
  - Retains and releases from C₄ to C₂₆
  - Strongest to weakest X>B>F>C>F
  - For instance; B retains and releases components in the boiling point range from C₄ to C₁₂
  - Upper temperature limit: 400 °C
  - Hydrophobic

Adsorbents: Legacy (old)

- Porous Polymers (legacy)
  - Tenax TA and GR; Porapak N; Chromosorb 106; HayeSep D
    - Surface area 24 to 795 m²/g
    - Retains and releases mid to high boiling point components C₇ to C₃₀
    - Temperature limit: 260 to 350 °C
    - Hydrophobic
    - Tend to produce high backgrounds, adsorbents can pyrolyze and cause significant contamination. Carbon based adsorbents are preferred
    - Let’s move away from legacy and move into new technology
Tube Sampling
Tube Material Used for Thermal Desorption

- Glass – adsorbents held by glass wool or glass frits
- Metal – adsorbents held by screen
- Glass lined metal
- Deactivated metal
Active and Passive Sampling

When used for passive sampling, the uptake of compounds of interest relies on the natural movement of the VOC molecules across the concentration gradient of the air gap in the inlet of the tube.
Tube Sampling

- Air Sampling
  - Adsorbent(s) in the tube, typically multibed, which is selected to trap analytes of interest

Sample the tube in the direction of weak adsorbent to strong adsorbent

Desorb the tube in the direction of strong adsorbent to weak adsorbent

.... analysis of toxic compounds in air
Automated Sample Collection

- Automates sample collection of air matrix
- Unattended sampling of 25 tubes
Applications and Solutions
### EPA Method 325 (passive)

<table>
<thead>
<tr>
<th>Target</th>
<th>Retention Time (min)</th>
<th>Precision (n=7) % RSD</th>
<th>Linearity (range 0.2 to 200 ng)</th>
<th>S/N @ 0.2 ng</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.51</td>
<td>1.80</td>
<td>0.9999</td>
<td>520 to 1</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.93</td>
<td>2.13</td>
<td>0.9999</td>
<td>651 to 1</td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td>2.45</td>
<td>3.01</td>
<td>0.9995</td>
<td>877 to 1</td>
</tr>
<tr>
<td>m,p-Xylene</td>
<td>2.50</td>
<td>2.69</td>
<td>0.9993</td>
<td>1021 to 1</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>2.64</td>
<td>2.84</td>
<td>1.0000</td>
<td>902 to 1</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>3.11</td>
<td>3.69</td>
<td>0.9999</td>
<td>823 to 1</td>
</tr>
<tr>
<td>1,2,3-Trimethylbenzene</td>
<td>3.26</td>
<td>4.01</td>
<td>0.9999</td>
<td>819 to 1</td>
</tr>
</tbody>
</table>

- Chromatography in under four minutes
- Outperformed method criteria
- Can perform TO-17 extended range and 325 on same configuration. When analyzing 325, can backflush unwanted targets through inlet to shorten run times

Chromatogram courtesy of Pace Analytical Services, Minneapolis, MN

Optimized for high throughput

Inlet and outlet splits are enabled
Soil Gas (extended range TO-17)

<table>
<thead>
<tr>
<th>Class of Compound</th>
<th># of analytes per group</th>
<th>Linear range 0.05 to 250 µg/m³</th>
<th>Precision (n=10)</th>
<th>Signal to Noise at Reporting Limit 0.05 µg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases</td>
<td>7</td>
<td>0.9994</td>
<td>7.39</td>
<td>530:1</td>
</tr>
<tr>
<td>Aliphatic Hydrocarbons (halogenated)</td>
<td>35</td>
<td>0.9996</td>
<td>4.80</td>
<td>560:1</td>
</tr>
<tr>
<td>Aromatics (halogenated)</td>
<td>9</td>
<td>0.9997</td>
<td>2.58</td>
<td>1350:1</td>
</tr>
<tr>
<td>Aromatics (non-halogenated)</td>
<td>14</td>
<td>0.9996</td>
<td>1.91</td>
<td>1220:1</td>
</tr>
<tr>
<td>Polynuclear Aromatic Hydrocarbons</td>
<td>7</td>
<td>0.9997</td>
<td>3.56</td>
<td>570:1</td>
</tr>
<tr>
<td>Others</td>
<td>13</td>
<td>0.9996</td>
<td>3.19</td>
<td>560:1</td>
</tr>
</tbody>
</table>

- Compounds were grouped into their classes to make the table easier to read
- The parameters for all compounds in the class had essentially the same results
- Target range: dichlorodifluoromethane to phenanthrene
- Compounds with boiling points nC3 through nC26
Extending to All PAH Concerns in Air

- The polynuclear aromatic hydrocarbons (PAHs) were grouped
- The parameters for all compounds in this class had essentially the same results
- Target range: 1,3 butadiene through benzo(g,h,i)perylene
- Compounds with boiling points nC4 through nC44

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calibration range 0.2 to 50 ng on tube</th>
<th>Reporting Limit μg/m³ (sample)</th>
<th>Precision %RSD (n=6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Butadiene</td>
<td>0.9981</td>
<td>0.0111</td>
<td>1.89</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.9993</td>
<td>0.0044</td>
<td>0.9</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.9994</td>
<td>0.0044</td>
<td>0.94</td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td>0.9991</td>
<td>0.0044</td>
<td>0.77</td>
</tr>
<tr>
<td>m,p-Xylenes</td>
<td>0.9994</td>
<td>0.0044</td>
<td>0.95</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.9998</td>
<td>0.0044</td>
<td>1.57</td>
</tr>
<tr>
<td>Ave 19 PAHs</td>
<td>0.9990</td>
<td>0.0044</td>
<td>1.48</td>
</tr>
</tbody>
</table>
Residue in LPG by TD/FID: $C_6$ through $C_{44}$

Timed Group for calibration
Sum of areas from
1.99 to 28.71 minutes

Quantitative Analysis
XRO – 640 Tube
$C_6$ to $C_{44}$
Troubleshooting / Maintenance / Validation ... not in this order 😊
Retaining Components of Interest

- Validation for the SVI and XRO tubes have been done for 10 liter sample volume
- Laboratories have validated on 50 L sample volumes with concentrated targets successfully
- If additional sample volume is required, this is an easy test to confirm safe sample volume

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SVI Tube</th>
<th>XRO - 440 Tube</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount spiked on Tube</td>
<td>34.6 ug*</td>
<td>8.0 ug**</td>
</tr>
<tr>
<td>Humidity</td>
<td>85%</td>
<td>85%</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>100 mL/min</td>
<td>100 mL/min</td>
</tr>
<tr>
<td>Time</td>
<td>100 minutes</td>
<td>100 minutes</td>
</tr>
<tr>
<td>Total Volume</td>
<td>10 liters</td>
<td>10 liters</td>
</tr>
</tbody>
</table>

*Restek: 300ng 502.2 voa #1; 300ng 1,3-budiene; 300ng 8260 Mega mix; 250 ng 4 PAH; 10ug diesel Total 34.6 ug components

**Custom TD 15 mix and Custom stock mix BTEX and 16 regulated PAHs
New Site

- A secondary tube connected to the primary tube
- Tube background should be confirmed prior to deployment in the field
- A field blank is SOP protocol for all environmental methods
- Fortunately, ATD has excellent recoveries (99.9%) so the tubes are clean with one sampling cycle unlike canisters
Recovery Validation

- **Experiment**
  - Analyze concentrated spiked tube
  - Run trap test
  - Blank tube (no adsorbent)
  - Re-analyzed spiked tube to ensure recovery was achieved from spiked tube

... work courtesy of Roberta Provost, Pace Analytical Services
Instrument Inherent Validation

- Automate spiking internal standard
- Automate surrogate spike
- Automate sample tube and cold trap impedance check to validate trap and tube
- Automate sample recollection on the same or new tube
- Automate leak check of tube and trap prior to each analysis
- Automate water management
Contamination in GC Land … Isolating Components is Crucial for Quick Results

- Schedule acquisition. Select start on GC (no injection from ATD). If clean, have isolated problem to ATD. If not clean, discussion (column may be source).
- Trap test: Setup acquisition. Perform a trap test. This isolates the trap to determine if this may be problem. If “clean”
- Run a blank tube (no adsorbent) to test entire system. If free from contaminants
- Run suspected tube
Cost Savings and Enhanced Performance with ATD

- In addition to better data compared to cans
  - Better recovery and polar recovery
  - In a box: 4 cans or more than 500 tubes.
  - Optimize profits with shipping
  - Space ... cannisters take a lot of space
  - Outstanding recoveries with TO-17 compared to TO-15
  - TO-15 – can’t do SVOCs
  - Don’t have to wait days for a clean can
Questions?

Lee Marotta  
Principal Field Application Scientist  
PerkinElmer  
lee.marotta@perkinelmer.com

Reporting results with confidence

Thank you so much 😊