Headspace Technology for GC and GC/MS: Features, benefits & applications

Karima Baudin
Oct 2015
Why use Headspace?

- Very Simple – no to minimum sample prep
- Robust – enhance uptime
- Non-detectable carry-over
- Inert sample path
- Enhance accuracy and repeatability
- Excellent repeatability
- Investigating volatiles in many matrices
  - Avoid extraction
  - Eliminate losses
  - Prevent non-volatiles from entering chromatographic system
- Enables aggressive detection limits
  - Concentrator
  - 1mL, 2mL entire volume.

... enhance productivity and efficiency - saves time and money
Enables the Analysis of Volatiles In Matrices Which Cannot Be Directly Injected
Advantages of using HeadSpace technology...

- Maintenance: is there any?
  - No Septum to change
  - No Liner to change
  - No Glass Wool required (no active sites)
  - No Syringe to clean
Advantages of using HeadSpace technology…

- Saves Time
  - Not changing the above (or forgetting to change them)
  - Analysis time - Shorter runs - analyzing
  - Volatiles not Matrix
Advantages of using HeadSpace technology…

- Saves Money
  - Increase productivity
  - Minimal consumables
  - Extends Column Live
Three sampling methods

• Static (equilibrium) Headspace

• Multiple Headspace Extraction (MHE)

• Total Evaporation
Static or Equilibrium Headspace

ARE YOU IN?

JOIN THE CONVERSATION PERKINELMER INTOURS 2015
Partition equilibrium of analyte “i” between liquid and gas phase

Consider:

- Time
- Temperature

![Solute “i”](image)

![Liquid Sample](image)
Balanced – Pressure Sampling

Standby

Pressurization

Sampling
How Sampling works

HS Trap
Why use Headspace Trap (HS Trap) instead of conventional HS

- Enhance Detection Limits by at least 50
  - Enables injection of entire HS vapor plus more with multiple injections of same vial focusing on a trap
- Dry Purge – remove water excellent water management
- Removes Oxygen
- Enables the use of Narrow Bore Short columns for Fast GC
Sample Vial Thermal Equilibration

Headspace Sampler

- Valve
- Seal
- Trap
- Vial
- Oven

Gas Chromatograph

- Detector
- Column
Vial Pressurization

Headspace Sampler Gas Chromatograph

valve

seal

vial

oven

trap

detector

column
Trap Load

Headspace Sampler Gas Chromatograph

detector

column isolation

column

Gas Chromatograph
Vial Re-Pressurization

Headspace Sampler

Gas Chromatograph
Dry Purge

Headspace Sampler Gas Chromatograph

detector

column

valve

seal

vial

oven

trap
Trap Desorption

Headspace Sampler

Gas Chromatograph

valve

seal

vial

oven

Trap desorbed in Opposite direction
**New USP Residual Solvent Test by Static Headspace Technique**

<table>
<thead>
<tr>
<th>Class 1 Residual Solvents</th>
<th>Class 2 - Mixture B Residual Solvents</th>
<th>Class 3 Residual Solvents (continued)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Dichloroethane</td>
<td>Chloroform</td>
<td>Heptane</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>1,2-Dimethoxyethane</td>
<td>Isobutyl Acetate</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>Hexane</td>
<td>Isopropyl Acetate</td>
</tr>
<tr>
<td>Benzene</td>
<td>Methylbutylketone</td>
<td>Methyl Acetate</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>Nitromethane</td>
<td>3-Methyl-1-Butanol</td>
</tr>
<tr>
<td><strong>Class 2 - Mixture A Residual Solvents</strong></td>
<td>Pyridine</td>
<td>Methylethylketone</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>Tetralin</td>
<td>Methylisobutylketone</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>Trichloroethylene</td>
<td>2-Methyl-1-propanol</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td></td>
<td>Pentane</td>
</tr>
<tr>
<td>C-1,2-Dichloroethene</td>
<td></td>
<td>1-Pentanol</td>
</tr>
<tr>
<td>t-1,2-Dichloroethene</td>
<td></td>
<td>1-Propanol</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td></td>
<td>2-Propanol</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylocyclohexane</td>
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<td></td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td></td>
<td></td>
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<tr>
<td>Toluene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-Xylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Xylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-Xylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Class 3 Residual Solvents</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic Acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
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<tr>
<td>Anisole</td>
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<tr>
<td>1-Butanol</td>
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<td></td>
</tr>
<tr>
<td>2-Butanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butyl Acetate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t-Butylmethyl ether</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cumene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethyl sulfone oxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl Ether</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Blank (bottom) / Class 1 Standard Solution (top)

- HS Conditions
  - Eq. Temp: 80°C
  - Eq. Time: 15min
  - Inj Volume: 1mL
  - Needle Temp: 110°C
  - T Line Temp: 130°C
  - Injector Temp: 140°C

---

Standard Solution

Blank
Class 1: Comparing results on 0.32 id column to 0.53 id column

All method criteria are achieved

PE Elite 624 – 30m x 0.32mm x 1.8um

<table>
<thead>
<tr>
<th>Component</th>
<th>PPB</th>
<th>Area</th>
<th>S/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1,1-Dichloroethene</td>
<td>64.7</td>
<td>14685</td>
<td>34 : 1</td>
</tr>
<tr>
<td>2 1,1,1-Trichloroethane</td>
<td>83.3</td>
<td>14097</td>
<td>35 : 1</td>
</tr>
<tr>
<td>3 Carbon Tetrachloride</td>
<td>33.0</td>
<td>2185</td>
<td>6 : 1</td>
</tr>
<tr>
<td>4 Benzene</td>
<td>17.0</td>
<td>14116</td>
<td>35 : 1</td>
</tr>
<tr>
<td>5 1,2-Dichloroethane</td>
<td>42.2</td>
<td>7546</td>
<td>17 : 1</td>
</tr>
</tbody>
</table>

PE Elite 1301 – 30m x 0.53mm x 3.0um

<table>
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<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>1 1,1-Dichloroethene</td>
<td>64.7</td>
<td>38361</td>
<td>143 : 1</td>
</tr>
<tr>
<td>2 1,1,1-Trichloroethane</td>
<td>83.3</td>
<td>36551</td>
<td>86 : 1</td>
</tr>
<tr>
<td>3 Carbon Tetrachloride</td>
<td>33.0</td>
<td>4658</td>
<td>11 : 1</td>
</tr>
<tr>
<td>4 Benzene</td>
<td>17.0</td>
<td>36528</td>
<td>89 : 1</td>
</tr>
<tr>
<td>5 1,2-Dichloroethane</td>
<td>42.2</td>
<td>14349</td>
<td>36 : 1</td>
</tr>
</tbody>
</table>
Headspace vs Headspace Trap

Residual Solvents Class 1
Conventional Headspace

<table>
<thead>
<tr>
<th>Component</th>
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<td>14097</td>
<td>35 : 1</td>
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<td>33.0</td>
<td>2185</td>
<td>6 : 1</td>
</tr>
<tr>
<td>4 Benzene</td>
<td>17.0</td>
<td>14116</td>
<td>35 : 1</td>
</tr>
<tr>
<td>5 1,2-Dichloroethane</td>
<td>42.2</td>
<td>7546</td>
<td>17 : 1</td>
</tr>
</tbody>
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Residual Solvents Class 1
Headspace Trap

<table>
<thead>
<tr>
<th>Component</th>
<th>PPB</th>
<th>Area</th>
<th>S/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1,1-Dichloroethene</td>
<td>64.7</td>
<td>123689</td>
<td>1021 : 1</td>
</tr>
<tr>
<td>2 1,1,1-Trichloroethane</td>
<td>83.3</td>
<td>230364</td>
<td>969 : 1</td>
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<tr>
<td>3 Carbon Tetrachloride</td>
<td>33.0</td>
<td>38202</td>
<td>156 : 1</td>
</tr>
<tr>
<td>4 Benzene</td>
<td>17.0</td>
<td>184737</td>
<td>816 : 1</td>
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<tr>
<td>5 1,2-Dichloroethane</td>
<td>42.2</td>
<td>81162</td>
<td>377 : 1</td>
</tr>
</tbody>
</table>
Analytical Performance of BTEX acquiring in Full Scan

<table>
<thead>
<tr>
<th>Compound</th>
<th>s/n at 0.02 ppb</th>
<th>Linearity, $r^2$</th>
<th>Precision at 1 ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>370 to 1</td>
<td>0.9996</td>
<td>2.85%</td>
</tr>
<tr>
<td>Toluene</td>
<td>550 to 1</td>
<td>0.9994</td>
<td>2.76%</td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td>578 to 1</td>
<td>0.9993</td>
<td>2.53%</td>
</tr>
<tr>
<td>m,p-Xylenes*</td>
<td>670 to 1</td>
<td>0.9997</td>
<td>1.07%</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>240 to 1</td>
<td>0.9994</td>
<td>3.86%</td>
</tr>
</tbody>
</table>

Chromatogram is 4 ppb...Under four minutes
Amount of Ethanol in Glycerin Soap via Headspace GC

This test was performed via equilibrium HS and total evaporation techniques.

Received same results with both techniques 3% ethanol in soap

3% is a lot of material so dilution and/or using total evaporation works well

Since total evaporation is easier, this would be the recommended technique (both are described)

Soap is a matrix that cannot be directly injected into a GC inlet and extraction is laborious. Headspace provided a quick, precise, accurate means of determining the amount of ethanol in soap while significantly reducing labor time and costs.

**Equilibrium Headspace**

- **Sample**
  - Weigh 0.20g of soap into vial
  - Fill vial with 5mL of water
  - Cap vial and place on autosampler

- **Standard**
  - Prepare a standard of known concentrations in water
  - Add 5mL aliquot of this standard to HS vial
  - Cap vial and place on autosampler and run

- Software calculates results (Std amt and sample weight is entered into appropriate places in software)
  - For single level calibration
  - \( \frac{\text{response unknown}}{\text{response std}} \times \text{std conc.} = \text{amount of unknown} \)

**Total Evaporation**

- **Sample**
  - Weigh 0.2g of soap into vial
  - Cap vial and place on autosampler
  - Thermostat sample at temp that will volatilize ethanol from matrix leaving most matrix in vial

- **Standard**
  - Prepare a known standard in a volatile solvent
  - Add 20uL into HS vial. The amount of ethanol into vial is known

- Software calculates results
Analytes in Paper - Headspace - GC / MS (5g paper)

Sample Temp: 150°C
Th Time: 30 min

2-decenal
Determination of amount of Fragrance in a polymer sphere by Headspace

• Sample Matrix: Fragrance is suspended in a polymeric sphere. The amount of fragrance in this matrix needs to be known for QC purposes. Injecting polymer directly into GC, would have resulted in time consuming maintenance. Extracting fragrance, would have been time consuming and expensive. In addition, the extraction recoveries could be poor and also selective depending upon analyte.

• With Headspace:
  – Easy, fast sample prep.
  – Extremely low maintenance
  – Precise, accurate results

• Sample Preparation: 0.06 g sample in 1mL THF

• Volume in HS vial: 20 uL aliquot in HS vial…cap vial

• Standard Preparation: Prepare fragrance at known concentration in THF

• Volume of Std in vial: 20uL of standard in HS vial…cap vial

• Sample Temp: 120°C (this temperature was enough to completely volatilize the fragrance but not the matrix

• Required detection limits and accurate results were attained. The fragrance amount calculated at 15% which was the expected amount

• Using HS resulted in reduced costs and time

Chromatogram of fragrance in a matrix by HS/GC
Analyzing Beer

"Beer"

Analyzing Beer
Characterizing Flavors in Beer and starting products: HSTrap/GC/MS

- Excellent Chromatography
- Required detection limits
- Repeatable response
- Linear response

Sample Size: 5 mL
Sample Temp: 70°C
Sample Load: 1 cycle
Trap Load Temp: 25°C
Dry Purge: 6 min
Trap high Temp: 300°C
Needle Temp: 160°C
T Line Temp: 180°C
Column Flow:
Pressure Pulse: 2mL/min for 0.4min
Analytical Flow Rate 1mL/min
Blood Alcohol composite

Oven Temp: 70 °C
Needle Temp: 110 °C
T Line Temp: 120 °C
HS psi: 25 psi
Column psi: 21 psi
Column Flow: 3 mL/min dual channel
Columns: BAC 1-30m x 0.32mm x 1.8um
        BAC 2-30m x 0.32mm x 1.2um
GC Oven Temp: 40°C isothermal
Flavors in Green Tea – HS/GC/MS

Sample Size: 1.6488 g
Sample Temp: 130°C
Needle Temp: 180°C
T Line Temp: 180°C
Column Flow: 4 mL/min for 0.2 min then 1 mL/min
Mass Range: 35 to 400 amu
Volatile and Semi-Volatile in High Density Polyethylene
Off odors in Resin – 3.2g in vial – HS/GC/MS

Mal-odor investigation
Off odors in Resin – 0.5g in vial – HS/GC/MS

Scan El+
TIC
4.74e7
Summary – the optimum technique for analyzing residual solvents

- Robust and stable
- Inert
- Excellent analytical results
  - Precision
  - Accuracy
  - Detection Limits
- Minimal Maintenance
- User friendly interface
- Non-detectable carry-over
- Simple sample prep
- Enhance long term productivity and efficiency
- Enhance detection limits and repeatability with the HS Trap