Thermal Desorption combined with dynamic headspace: a versatile tool for miniaturized sample preparation

4th Stir Bar Sorptive Extraction Technical Meeting

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Tutorial lay-out

- Methods for the analysis of volatiles
- DHS principles
- DHS modes
- Examples
- Positioning DHS versus other methods
Sample Preparation Methods for Volatiles

- **Static Headspace (SHS)**
  - Single equilibrium + single injection = classical SHS
    - CTS refocusing
  - Multiple headspace extraction (MHE)
    - Multiple runs (= Kolb method, e.g. Monomers in polymers)
    - Multiple sampling + trapping + single run (eg HIT-SHS, ITEX)

- **Dynamic Headspace (DHS)**
  - Purge & Trap (P&T)

- **Sorptive Extraction**
  - Solid Phase Micro-Extraction (SPME)
    - New: SPME Arrow (increased volume of extraction phase)
  - Stir Bar Sorptive Extraction (SBSE)
Static Headspace (SHS)

Syringe

Head Space Bottle

Injector
Solid Phase Micro-Extraction (SPME)

SORPTION

Pierce sample septum Expose fiber Extract Retract fiber Remove

DESORPTION

Pierce GC Inlet septum Expose fiber Desorb Retract fiber Remove
SHS or SPME

*Analysis of Halides and Haloalkenes in pharmaceuticals*

<table>
<thead>
<tr>
<th>Halide/Alkene</th>
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</tr>
</thead>
<tbody>
<tr>
<td>chloromethane (1)</td>
<td>benzyl bromide</td>
<td>vinyl chloride (2)</td>
</tr>
<tr>
<td>bromomethane</td>
<td>vinyl bromide</td>
<td>4-methylbenzyl chloride (26)</td>
</tr>
<tr>
<td>iodomethane</td>
<td>4-methylbenzyl bromide</td>
<td>1-chloro-2-methylpropene</td>
</tr>
<tr>
<td>1-chloropropane</td>
<td>4-fluorobenzyl chloride</td>
<td>1-bromo-2-methylpropene</td>
</tr>
<tr>
<td>1-bromopropane</td>
<td>4-fluorobenzyl bromide</td>
<td>2-chloroacrylonitrile</td>
</tr>
<tr>
<td>1-iodopropane</td>
<td>2-chloroethanol</td>
<td>4-chloro-butyl ether (28)</td>
</tr>
<tr>
<td>2-chloropropane</td>
<td>2-bromoethanol</td>
<td>cis-1,2-dichloroethylene</td>
</tr>
<tr>
<td>2-bromopropane</td>
<td>2-iodoethanol</td>
<td>trans-1,2-dibromoethylene</td>
</tr>
<tr>
<td>2-iodopropane</td>
<td>2-(2-chloroethoxy)ethanol</td>
<td>benzyl chloride</td>
</tr>
<tr>
<td>3-bromo-2-methyl-acrylonitrile</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Analysis of Halides and Haloalkenes

Conc: 0.5 ppm in API = 25 ppb in solution
HIT-SHS and HIT-SPME option on Gerstel MPS-TDU-CIS
HIT-SHS and HIT-SPME option on Gerstel MPS-TDU-CIS
Dynamic Headspace

- Continuous purging of headspace (sample) at controlled temperature for controlled time at controlled flow.
- Trapping of VOCs (adsorbent, sorbent, +/- cryo)
- Thermal desorption of trap
- Goal: “exhaustive” extraction = highest sensitivity

Tenax
WHY DHS?

60 VOCs in water – 1 ppb – GC-MSD in scan mode

Static headspace (SHS)

Dynamic headspace (DHS)

Sensitivity !!
WHY DHS?

60 VOCs in water – 1 ppb – GC-MSD in scan mode

Solid phase microextraction (SPME) – 65 µm PDMS/DVB

Dynamic headspace (DHS)

Sensitivity for the highly volatiles !!

... and for the other volatiles !!

Complete profile – less selective
Method comparison for fruit drink

Static Headspace

SPME Carbotrap/DVB/PDMS

DHS

C18 – ester (high Mw)
DHS vs SPME: aldehydes/ketones in water

### Counts vs. Acquisition Time (min)

**DHS-GC-MS**

**SPME-GC-MS**

**Zoom: x10**

<table>
<thead>
<tr>
<th>Compound</th>
<th>TIC area in DHS-GC-MS</th>
<th>TIC area in SPME-GC-MS</th>
<th>Fold sensitivity increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>8495390</td>
<td>270432</td>
<td>31</td>
</tr>
<tr>
<td>Hexanal</td>
<td>37701720</td>
<td>3626013</td>
<td>10</td>
</tr>
<tr>
<td>2-Nonanone</td>
<td>122894887</td>
<td>24740844</td>
<td>5</td>
</tr>
</tbody>
</table>
DHS vs SPME: yoghurt aroma

1g yoghurt in the vial

trans-hexenal detected @ 10.45 min by DHS and not by SPME
DHS vs SPME: beef powder

250mg powder with 1mL water in 20 mL vial
DHS vs SPME: Cognac XO

2 mL in 20 mL vial
DHS modes of operation

- Classical mode: single extraction – single run
  - Tenax or Carbotrap adsorption tube
  - without/with dry purge
- FEDHS: full evaporation DHS
- MVM: multi-volatile method
  - Multiple tubes & DHS sampling
  - Desorption & trapping
  - Single GC run
- Derivatization-DHS
- DHS Large
Complementary DHS methods for aroma compounds in food

**DHS on strong Carbotrap at 10 °C**

→ Highly volatiles

- Acetaldehyde
- EtOH

**DHS on Tenax\(^{TA}\) at 70 °C**

- C_{18} – ester (High Mw)

Same scales
DHS parameters

- **Extraction (classical DHS)**
  - Incubation (sample) temperature (as low as possible)
  - Trap:
    - Material
    - Temperature (higher = less water)
  - Time & flow (= x rinses of vial volume)
    example: 500 mL volume, 50 mL/min = 10 min = 25 rinses
  - Dry purge ??? (loss of volatiles) → MVM?

- **TDU: desorption temperature (time, flow)**

- **CIS:**
  - Focusing temperature (w/ packing?)
  - Injection mode (split, splitless)
  - Injection temperature
Full evaporation dynamic headspace (FEDHS)

- 100 μL of aqueous sample is dispensed into a HS vial and purged with inert gas at an elevated temperature (80°C) using DHS.
- Volatile and semi-volatile analytes are transferred into the trap (Tenax).
- After dry purge of water, the trap is thermally desorbed for GC analysis.

*Higher recovery of hydrophilic compounds*
FEDHS method parameters

• **FEDHS conditions**
  - Sample volume: 50 µL
  - Trap: *Tenax*
  - Trap temperature: 40°C
  - Incubation temperature: 80°C
  - Purge: 2500 mL @ 100 mL/min → dry purge 500 mL @ 100 mL/min

• **TDU/CIS conditions**
  - TDU: 30°C, 60°C/min to 270°C (5 min)
  - Transfer temperature: 280°C (splitless)
  - CIS: -100°C, 12°C/sec to 280°C (7 min) using a Tenax liner
DHS vs FEDHS - GC-MS of coffee

Counts vs. Acquisition Time (min)
Selectable $^1$D/$^2$D analysis of allergens in cosmetics in combination with FEDHS

$^1$D chromatogram of a cosmetic sample (body cream)
Selectable $^1$D/$^2$D analysis of allergens in cosmetics in combination with FEDHS

$^1$D/$^2$D chromatogram of body cream
Heart-cut 11.08 – 11.39 min

Co-elution of matrix + heart-cut $\rightarrow$ farnesol 1 & 2 / isoeugenol / hexyl cinnamaldehyde

Target compounds (23 – 25 min)
Selectable $^1$D/$^2$D analysis of allergens in cosmetics in combination with FEDHS

Extracted Ion Chromatograms from $^2$D part

- GLYCERIN ion 61
- Isoeugenol ion 164
- Farnesol 1 & 2 ion 69
- Hexyl cinnamaldehyde ion 216
- Other matrix compound ion 69

Abundance

Time, min
Sequential Dynamic Headspace Sampling incorporating a Multi-Volatile Method (MVM) for Aroma Analysis

Developed by Nobuo Ochiai, Kikuo Sasamoto and Jun Tsunokawa @ Gerstel KK
Dynamic Headspace

Method 1: Very Volatile Analytes

(J. Tsunokawa, N. Ochiai, K. Sasamoto, A. Hoffmann, in preparation)
Dynamic Headspace
Method 2: Volatile or Semi Volatile Analytes

(J. Tsunokawa, N. Ochiai, K. Sasamoto, A. Hoffmann, in preparation)
Dynamic Headspace

Method 3: Volatile, non volatile and hydrophillic analytes

(J. Tsunokawa, N. Ochiai, K. Sasamoto, A. Hoffmann, in preparation)
Dynamic Headspace
Method 4: TDU Multi Desorption

(J. Tsunokawa, N. Ochiai, K. Sasamoto, A. Hoffmann, in preparation)
Dynamic Headspace

Method 4: TDU Multi Desorption

(J. Tsunokawa, N. Ochiai, K. Sasamoto, A. Hoffmann, in preparation)
Dynamic Headspace
Method 4: TDU Multi Desorption

(J. Tsunokawa, N. Ochai, K. Sasamoto, A. Hoffmann, in preparation)
TIC of a brewed coffee by DHS-MVM

Sample: Coffee 100 μL  Incubation Temp.: 80 ºC Purge volume: 3000 mL  Column: DB-WAX 30 m x 0.25 mm i.d., 0.25 μm thickness
Brewed Coffee Extraction

- Acetaldehyde
- Furan
- DMS
- Propanal
- 2-Methylfuran
- Butanal
- 2,3-Butanedion
- Pentanal
- 2,3-Pentanedion
- DMDS
- Pyrrole
- 2,5-Dimethylpyrazine
- Furfural
- cis-3-Hexenol
- 1-Hexanol
- Guaiacol
- Ethyl decanoate
- Indole
- gamma-Nonalactone
- beta-Damascenone
- Coumarin

Recovery [%]

Trap 1
Trap 2
Trap 3

RIC | Research Institute for Chromatography
DHS-Multi-Volatile Method (DHS-MVM ®)*

“MVM option”
(Maestro 1.4.29.21 or later)

Method BXX-X
Shincarbon trap
Top notes

Optimized for enrichment of super VOC and top notes

Method BX
Shincarbon trap
Top to middle note

Optimized for enrichment of remaining top notes to middle notes

FEDHS
Tenax TA trap
Middle to base note

Optimized for enrichment of remaining middle notes to base notes, polar and low boiling compounds

Multiple Tube Desorption

Three TDU tube are sequentially thermal desorbed and cryo-focused on CIS, and then injection into GC-MS

Comparison of BXX-X, BX, FEDHS and MVM for analysis of noodle soup stock

Courtesy: Gerstel KK, Japan
DHS + derivatization
Example: Determination of stale-flavor compounds (aldehydes, ketones) using DHS on PFBHA impregnated PDMS tubes and GC-MS

Derivatization reaction

Pentafluorobenzyl hydroxylamine + aldehyde or ketone → oxime (structural isomers - syn/anti)

Target solutes: octanal, nonanal, decanal, 2-octenal, 2-nonenal, 2,4-decadienal
Impregnation + dry purge

DHS method for impregnation

DHS method for DHS of beer samples
These methods can be put in one sequence consisting of sequential DHS impregnation and (beer) sample analyses
SIM chromatogram (5 ppb in beer)

Method is applicable also for other aldehydes (formaldehyde, acetaldehyde, …)
Overlaid SIM chromatograms for Beer & spike at 1 ppb

**BEER**

2-Octenal (150 ppt)

**SPIKED**

Nonenal (+/-75 ppt)

2,4-Decadienal (25 ppt)

Nonanal (+/-550 ppt)

**Abundance**

**Time, min**
DHS Large option for MPS
Importance of DHS in Flavor Analysis

• Perception: “no technique can deliver the same results as steam distillation (or SAFE)”

• Gerstel DHS:
  • Sensitivity
  • Automation
  • Reduced cross-contamination (e.g. compared to P&T)
  • Flexibility (different modes): DHS > FEDHS > MVM
  • Probably the closest to SDSE & SAFE: “full” profile
Volatiles & Aroma Analysis: “my toolbox”

1. Static headspace (SHS)
2. HS-SPME (headspace)
3. Dynamic Headspace (DHS)
4. Full evaporation DHS (FEDHS)
   FEDHS is only technique that has the potential to provide profiles identical to liquid injection.
5. Multi Volatile Method (MVM)

Remark: more trapping = more difficult desorption and slower injection
Need for additional focussing?
Quid Semi-Volatiles?

- Often other chromatographic conditions required/used.
- **How much enrichment needed?**
- Method selection
  1. (micro-) Liquid-liquid extraction (in-vial extraction)
  2. SBSE (**immersion!!!**)
  3. Solid phase extraction (SPE)
  4. FEDHS ????