Diffusive Sampling of MVOCs by a Solid-Phase Microextraction Device

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Introduction
Indoor Air Quality (IAQ)

- 75%~90% stay in indoor environment
- significant sources for human exposure to organic air contaminants
- biological hazards - molds, plants, etc.
- asthma, infection, toxic reaction, SBS
- metabolites of Molds - MVOCs (bad odors)
- Microbial Volatile Organic Compounds
Mold gives off spores, cellular debris and MVOCs*

*http://www.wbdg.org/design/env_iaq.php
The pathway of producing MVOCs and toxic metabolites by molds*

Molds vs. MVOCs

- traditional fungi sampling methods—impactor, impinger, centrifugal samplers, filter cassette
  - molds growing but not produce spores yet
  - specific molds will grow on the agar
  - underestimate, can’t know total amount of molds clearly

- Molds $\Rightarrow$ MVOCs
  - as indicators of active growth of molds inside buildings
  - know potentially biological hazards in indoor air in advance
• **Common Mold Genus**
  - *Cladosporium* spp.
  - *Alternaria* spp.
  - *Penicillium* spp.
  - *Aspergillus* spp.

• **Species-Specific MVOCs**
  - Some are produced by a number of species, but some are not
    - 2-pentylfuran is specific for *Aspergillus fumigatus*
    - 2-methyl-1-propanol, 3-methyl-1-butanol, 2-heptanone are produced by a number of species
Morphological pictures for four mold genus commonly occur in indoor environment

*http://www.virtualmuseum.ca/~mushroom/English/Species/cladosporiumcladosporioides.htm
**http://www.mycology.adelaide.edu.au/gallery/photos/alternaria02.html
****http://www.sciencedaily.com/releases/2005/10/051015093046.htm
Need a New Sampling Method

- low [MVOCs]
- mass collected on the sampling medium
  - high sampling rate
  - analytical instrument’s sensitivity
- appropriate/rapid sampling time
  - 4 hrs ~ 5 hrs
  - [MVOCs] distribution
Objectives

- determination of MVOCs
  - rapid and sensitive
  - by SPME device?
Research Structure

- Standards Solution
  - Optimize Parameters
    - Standard Curve
      - Gas Bag Exposure System
      - Detection Limit
      - GC
        - Adsorption Limit of SPME Fiber
        - Adsorption Time of SPME Fiber
        - Storage Stability of SPME Fiber
      - Calculate Conc. and SR
        - Comparison and Assessment of Results
Passive SPME Sampler
SPME Technique

- diffusion-based Fick’s First Law

\[ n(t) = \frac{DgA}{L} \int_0^t C_g(t)dt \]

Schematic of sampling with retracted SPME fiber*

- \( n(t) \) = mass of extracted analyte over extraction time \( t \)
- \( C_g \) = concentration of analyte in air
- \( D_g \) = gas-phase molecular diffusion coefficient
- \( L \) = length of the coated rod = 1 cm
- \( A \) = needle opening area = 0.00083 cm\(^2\)
- \( t \) = sampling time

SPME Sampling Device

- Passive SPME Sampler
  - Fick’s First Law
  - retracted SPME fiber + air bag exposure system
  - long sampling time at low concentration
Materials and Methods

- MVOCs + Mold Species
- Gas Bag Exposure System
- Portable Gas Chromatography, Portable GC
- Solid-phase Microextraction, SPME
  SPME Fiber
## Mold Species and Their Specific MVOCs

<table>
<thead>
<tr>
<th>Mold Species</th>
<th>Microbial Volatile Organic Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Asp. Versicolor</em></td>
<td>1-octen-3-ol, 2-hexanone, 2-heptanone</td>
</tr>
<tr>
<td></td>
<td>2-methyl-1-propanol, 3-methyl-1-butanol</td>
</tr>
<tr>
<td><em>Asp. niger</em></td>
<td>1-octen-3-ol, 3-methyl-1-butanol</td>
</tr>
<tr>
<td><em>Asp. Fumigatus</em></td>
<td>1-octen-3-ol, 2-hexanone, 2-pentylfuran</td>
</tr>
<tr>
<td></td>
<td>2-methyl-1-propanol, 3-methyl-1-butanol</td>
</tr>
<tr>
<td><em>Pen. expansum</em></td>
<td>1-octen-3-ol, 2-hexanone, 2-heptanone</td>
</tr>
<tr>
<td></td>
<td>3-methyl-1-butanol</td>
</tr>
<tr>
<td><em>Pen. chrysogenum</em></td>
<td>1-octen-3-ol, 2-hexanone, 2-heptanone</td>
</tr>
<tr>
<td></td>
<td>2-methyl-1-propanol</td>
</tr>
<tr>
<td><em>Cla. globosum</em></td>
<td>1-octen-3-ol, 2-hexanone, 2-heptanone</td>
</tr>
<tr>
<td><em>Alt. alternata</em></td>
<td></td>
</tr>
</tbody>
</table>
Gas Bag Exposure System

- Air Bag*
  - Teflon + dual stainless steel fittings
  - flexible bag system
  - allow direct insertion of SPME fiber

*http://www.tedlarbag.com/
**Portable GC**

- column: 100% dimethylpolysiloxane
- injector temp.: 250°C
- detector (FID) temp.: 280°C
- carrier gas flow: 10 ml/min
- temp. program: (16.5 min)

\[
\begin{align*}
25°C/\text{min} & \quad 15°C/\text{min} & \quad 3°C/\text{min} & \quad 50°C/\text{min} \\
50°C & \rightarrow 80°C & \rightarrow 120°C & \rightarrow 150°C & \rightarrow 200°C, 1.5\text{min}
\end{align*}
\]
Solid-phase Microextraction, SPME*-

fiber + holder

(1) 70 μm Carbowax/DVB stableflex
(2) 50/30 μm DVB/CAR/PDMS
(3) 100 μm PDMS

Results and Discussions

- SPMS Fiber Selection
- Mass Collected vs. Conc. × Sampling Time
- Theoretical SR vs. Experimental SR
# SPMS Fiber Selection

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>50/30 μm DVB/CAR/PDMS area1</th>
<th>area2</th>
<th>70 μm Carbowax/DVB area1</th>
<th>area2</th>
<th>100 μm PDMS area1</th>
<th>area2</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methyl-1-propanol</td>
<td>5105</td>
<td>-</td>
<td>11715</td>
<td>-</td>
<td>9297</td>
<td>-</td>
</tr>
<tr>
<td>1-butanol</td>
<td>2056</td>
<td>-</td>
<td>4519</td>
<td>-</td>
<td>3551</td>
<td>-</td>
</tr>
<tr>
<td>3-methyl-1-butanol</td>
<td>10926</td>
<td>-</td>
<td>21687</td>
<td>-</td>
<td>19056</td>
<td>-</td>
</tr>
<tr>
<td>2-hexanone</td>
<td>3018</td>
<td>-</td>
<td>4071</td>
<td>-</td>
<td>4843</td>
<td>-</td>
</tr>
<tr>
<td>2-heptanone</td>
<td>15464</td>
<td>-</td>
<td>19123</td>
<td>-</td>
<td>23741</td>
<td>-</td>
</tr>
<tr>
<td>1-octen-3-ol</td>
<td>2221</td>
<td>-</td>
<td>3441</td>
<td>-</td>
<td>3265</td>
<td>-</td>
</tr>
<tr>
<td>2-pentylfuran</td>
<td>26145 269(99%*)</td>
<td>-</td>
<td>29554</td>
<td>-</td>
<td>24311</td>
<td>-</td>
</tr>
</tbody>
</table>

*Desorption Efficiency (%) = (area1/area1+area2)*100
Mass Collected

vs.

Conc. × Sampling Time
MVOCs Exposure Results from Gas Bag (1)

- 2-methyl-1-propanol: 606.30 mg/m³
- 1-butanol: 242.52 mg/m³
- 3-methyl-1-propanol: 1442.13 mg/m³
- 2-hexanone: 163.86 mg/m³
- 2-heptanone: 934.07 mg/m³
- 1-octen-3-ol: 419.53 mg/m³
- 2-pentylfuran: 226.11 mg/m³

[Diagram showing mass collected (ng) vs. conc. * time (mg/cm³ * sec)]
MVOCs Exposure Results from Gas Bag (2)

<table>
<thead>
<tr>
<th>MVOCs</th>
<th>Mass Collected (ng)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methyl-1-propanol</td>
<td>1212.60</td>
</tr>
<tr>
<td>1-butanol</td>
<td>485.04</td>
</tr>
<tr>
<td>3-methyl-1-propanol</td>
<td>2884.25</td>
</tr>
<tr>
<td>2-hexanone</td>
<td>327.72</td>
</tr>
<tr>
<td>2-heptanone</td>
<td>1868.14</td>
</tr>
<tr>
<td>1-octen-3-ol</td>
<td>839.07</td>
</tr>
<tr>
<td>2-pentylfuran</td>
<td>452.22</td>
</tr>
</tbody>
</table>

[MVOCs] (mg/m³)

- 2-methyl-1-propanol: 1212.60 mg/m³
- 1-butanol: 485.04 mg/m³
- 3-methyl-1-propanol: 2884.25 mg/m³
- 2-hexanone: 327.72 mg/m³
- 2-heptanone: 1868.14 mg/m³
- 1-octen-3-ol: 839.07 mg/m³
- 2-pentylfuran: 452.22 mg/m³
MVOCs Exposure Results from Gas Bag (3)

<table>
<thead>
<tr>
<th>MVOCs</th>
<th>[MVOCS] (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methyl-1-propanol</td>
<td>2425.19</td>
</tr>
<tr>
<td>1-butanol</td>
<td>970.08</td>
</tr>
<tr>
<td>3-methyl-1-propanol</td>
<td>5768.51</td>
</tr>
<tr>
<td>2-hexanone</td>
<td>655.44</td>
</tr>
<tr>
<td>2-heptanone</td>
<td>3736.28</td>
</tr>
<tr>
<td>1-octen-3-ol</td>
<td>1678.13</td>
</tr>
<tr>
<td>2-pentylfuran</td>
<td>904.44</td>
</tr>
</tbody>
</table>
## Theoretical SR vs. Experimental SR

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Theoretical Sampling Rate (cm³/s)</th>
<th>Experimental Sampling Rate (cm³/s)*</th>
<th>Experimental Sampling Rate (cm³/s)**</th>
<th>Experimental Sampling Rate (cm³/s)***</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methyl-1-propanol</td>
<td>2.58E-04</td>
<td>(1.27±0.06)E-04</td>
<td>(8.74±0.40)E-05</td>
<td>(7.33±0.35)E-05</td>
</tr>
<tr>
<td>1-butanol</td>
<td>2.58E-04</td>
<td>(2.29±0.11)E-04</td>
<td>(14.60±0.53)E-05</td>
<td>(7.28±0.25)E-05</td>
</tr>
<tr>
<td>3-methyl-1-butanol</td>
<td>2.32E-04</td>
<td>(1.44±0.06)E-04</td>
<td>(12.00±0.60)E-05</td>
<td>(10.90±0.54)E-05</td>
</tr>
<tr>
<td>2-hexanone</td>
<td>2.16E-04</td>
<td>(0.81±0.03)E-04</td>
<td>(6.52±0.24)E-05</td>
<td>(4.45±0.21)E-05</td>
</tr>
<tr>
<td>2-heptanone</td>
<td>1.99E-04</td>
<td>(0.85±0.04)E-04</td>
<td>(8.63±0.42)E-05</td>
<td>(6.77±0.29)E-05</td>
</tr>
<tr>
<td>1-octen-3-ol</td>
<td>1.86E-04</td>
<td>(2.50±0.11)E-04</td>
<td>(7.54±0.30)E-05</td>
<td>(3.05±0.11)E-05</td>
</tr>
<tr>
<td>2-pentylfuran</td>
<td>1.88E-04</td>
<td>(1.13±0.03)E-04</td>
<td>(11.80±1.16)E-05</td>
<td>(7.74±0.34)E-05</td>
</tr>
</tbody>
</table>

* [MVOCs]: 163.86~1442.13 mg/m³
** [MVOCs]: 327.72~2884.25 mg/m³
*** [MVOCs]: 655.44~5768.51 mg/m³
Summary

- passive sampling method is developed
  - SPME Fiber- 70 μm Carbowax/DVB
  - Experimental Sampling Rate
    lower conc. > higher conc.
  - competitive adsorption and displacement effects?
Perspectives

- Know more about the effect of
  - lower [MVOCs]
  - temperature
  - related humidity

- Emission pattern
  - sampling time

- For further applications
  - mold species/concentration vs. their [MVOCs]
  - examining the fingerprints of mold species
Acknowledgement

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