Passive Air Sampling for Ozone by Solid Phase Microextraction

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Outline

- Introduction
- Purpose
- Materials and methods
- Results
- Conclusions
Introduction
### Air Quality Index (AQI) for Ozone

<table>
<thead>
<tr>
<th>Index Values</th>
<th>Levels of Health Concern</th>
<th>Cautionary Statements</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-50</td>
<td>Good</td>
<td>None</td>
</tr>
<tr>
<td>51-100*</td>
<td>Moderate</td>
<td>Unusually sensitive people should consider reducing prolonged or heavy exertion outdoors.</td>
</tr>
<tr>
<td>101-150</td>
<td>Unhealthy for Sensitive Groups</td>
<td>Active children and adults, and people with lung disease, such as asthma, should reduce prolonged or heavy exertion outdoors.</td>
</tr>
<tr>
<td>151-200</td>
<td>Unhealthy</td>
<td>Active children and adults, and people with lung disease, such as asthma, should avoid prolonged or heavy exertion outdoors. Everyone else, especially children, should reduce prolonged or heavy exertion outdoors.</td>
</tr>
<tr>
<td>201-300</td>
<td>Very Unhealthy</td>
<td>Active children and adults, and people with lung disease, such as asthma, should avoid all outdoor exertion. Everyone else, especially children, should avoid prolonged or heavy exertion outdoors.</td>
</tr>
<tr>
<td>301-500</td>
<td>Hazardous</td>
<td>Everyone should avoid all physical activity outdoors.</td>
</tr>
</tbody>
</table>

* Generally, an AQI of 100 for ozone corresponds to an ozone level of 0.08 parts per million (averaged over 8 hours).
Methods of Sampling and Analysis

- Direct instrument
  - UV-light absorption
  - ......

- Personal sampler
  - Active
  - Passive
Active vs. Passive

Active
- Advantage: High accuracy
- Disadvantage: Need pump

Passive
- Advantage: Short term monitoring, Operation easiness, Long term monitoring
- Disadvantage: Low sensitivity, Heavy, Sample storage hard, Not reusable

source, http://www.epa.gov/environment/air/ontheair/outdoor.htm
The advantages of SPME

- Integration of sampling, extraction, concentration, sample injection
- Reduce and simplify the extraction procedures
- Solvent-free
- Good detection and quantitation limit
- Reusable
Purpose

- Develop a passive sampler for ozone based on the technique of SPME
Expected reaction

$$\text{DPE} \xrightarrow{\text{ozone}} \text{other product}$$

$$\text{PFBHA}$$

$$\text{Pyridin-4-aldehyde-PFBHA}$$
Materials and methods
Materials

- 1,2-Di-(4-pyridyl)ethylene (DPE)
- Pyridin-4-aldehyde
- PFBHA
- Ozone
- Oxime
- Exposure system
- SPME diffusion sampler
Chromatogram of oxime

- Synthesize oxime
- Aldehyde and PFBHA form oxime on SPME
Reaction time between PFBHA and pyridin-4-aldehyde
Materials

- 1,2-Di-(4-pyridyl)ethylene (DPE)
- Pyridin-4-aldehyde
- PFBHA
- Ozone
- Oxime
- Exposure system
- SPME diffusion sampler
Materials

- 1,2-Di-(4-pyridyl)ethylene (DPE)
- Pyridin-4-aldehyde
- PFBHA
- Ozone
- Oxime
- Exposure system
- SPME diffusion sampler
SPME diffusion sampler

Perspective view of the passive sampler: (a) SPME fiber assembly, (b) PTFE septum, (c) PTFE tubing, and (d) cap/PTFE tape.
<table>
<thead>
<tr>
<th>Fiber</th>
<th>Oxime*</th>
<th>DPE**</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>455475</td>
<td>-</td>
</tr>
<tr>
<td>PDMS/DVB</td>
<td>1125855</td>
<td>8852208</td>
</tr>
<tr>
<td>CAR/PDMS</td>
<td>nd</td>
<td>-</td>
</tr>
<tr>
<td>CW/DVB</td>
<td>110338</td>
<td>-</td>
</tr>
<tr>
<td>DVB/CAR/PDMS</td>
<td>1168172</td>
<td>872430</td>
</tr>
</tbody>
</table>

*pyridin-4-aldehyde extract 5min and PFBHA extract 2min, GC inject port temperature 250 °C, desorption time 2min
**DPE extract 30min, GC inject port temperature 250 °C, desorption time 5min
### Desorption efficiency of oxime

<table>
<thead>
<tr>
<th>desorption time (min)</th>
<th>area</th>
<th>desorption efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>first</td>
<td>second</td>
</tr>
<tr>
<td>1</td>
<td>16671.055</td>
<td>797.887</td>
</tr>
<tr>
<td>2</td>
<td>15390.997</td>
<td>468.4785</td>
</tr>
<tr>
<td>5</td>
<td>15269.862</td>
<td>398.117</td>
</tr>
<tr>
<td>7</td>
<td>14746.4935</td>
<td>0</td>
</tr>
</tbody>
</table>

# aldehyde adsorption 1 min, PFBHA react 20min, temperature of GC inject port 270 °C

*first area/(first area + second area)*
<table>
<thead>
<tr>
<th>Fiber</th>
<th>PDMS/DVB</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPE loaded method</td>
<td>Direct extraction 30sec</td>
</tr>
<tr>
<td>GC inject port temp</td>
<td>270 °C</td>
</tr>
<tr>
<td>Desorption time</td>
<td>7min</td>
</tr>
<tr>
<td>PFBH reaction time</td>
<td>20min</td>
</tr>
<tr>
<td>GC temperature prog</td>
<td>150 °C $\rightarrow$ 250 °C (15min)</td>
</tr>
</tbody>
</table>
Results
Test on real sample

Ozone concentration: 400 ppb
Exposure for 4 hours
Fick’s First Law: 

\[ n_f = D_g(A/Z) \int C_g(t) \, dt \]

- \( n_f \): Sampling mass of the analyte
- \( Q \): Sampling rate
- \( D_g \): Binary diffusion coefficient of analyte in air, \( \text{cm}^2\text{min}^{-1} \)
- \( A \): Surface area of the needle opening, \( \text{cm}^2 \)
- \( Z \): Retracted fiber path length, \( \text{cm} \)

Sampling method

method 1

Fiber condition → Coating DPE sampling → React with PFBHA → Wait 20min → GC analyse

method 2

Fiber condition → Coating PFBHA → Coating DPE sampling → GC analyse
ozone concentration $\times$ exposure time
vs. oxime mass

$y = (1.10\times10^{-4}\pm0.053\times10^{-4})x + (0.061\pm0.0091)$
$R^2 = 0.975$

$y = (9.80\times10^{-5}\pm0.647\times10^{-5})x + (-0.059\pm0.0131)$
$R^2 = 0.948$
## Pyridin-4-aldehyde storage

<table>
<thead>
<tr>
<th>Day*</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2998.857</td>
</tr>
<tr>
<td>1</td>
<td>2477.574</td>
</tr>
<tr>
<td>4</td>
<td>2160.433</td>
</tr>
</tbody>
</table>

*aldehyde adsorption 1min, storage in 4 °C, PFBHA react 20min
## Compare with other sampler

<table>
<thead>
<tr>
<th>Sampling reagent</th>
<th>Instrument</th>
<th>Detection limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-di(4-pyridyl)ethylene (DPE)</td>
<td>GC-ECD</td>
<td>Method 1, 120 ppb-hr  Method 2, 30 ppb-hr</td>
</tr>
<tr>
<td>1,2-di(4-pyridyl)ethylene (DPE)</td>
<td>Spectrophotometry(422nm)</td>
<td>3 ug/m$^3$ for a one week exposure</td>
</tr>
<tr>
<td>indigo carmine</td>
<td>Spectrophotometry(408nm)</td>
<td>0.7 ppm-hr, 50 ppb for 8 hr</td>
</tr>
<tr>
<td>potassium iodide</td>
<td>Spectrophotometry(575nm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ion chromatography(IC)</td>
<td></td>
</tr>
<tr>
<td>3-methyl-2-benzothiazolinone acetone azine (MBTH)</td>
<td>Spectrophotometer(504nm)</td>
<td>0.09 ppm-hr, 4 ppb for 24 hr</td>
</tr>
<tr>
<td>p-acetamidophenol(p-ATP)</td>
<td>Spectrofluorimeter</td>
<td></td>
</tr>
<tr>
<td>nitrite ion</td>
<td>ion chromatography(IC)</td>
<td>201 ppb-hr, 17 ppb for 12 hr, 8 ppb for 24 hr</td>
</tr>
</tbody>
</table>
Conclusions

- More sensitive
- Reusable
- Solvent-free
- Background noise
- Coated fiber should be prepared before sampling
- Interference
- Field test
Acknowledgement
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