DETERMINATION OF UPTAKE RATES FOR VOCs IN AMBIENT AIR BY USING AXIAL TYPE THERMAL DESORPTION PASSIVE TUBES

Mihriban Yılmaz Civán, Öznur Kuntasal and Gürdal Tuncel
OUTLINE

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  - Passive Tube Theory

- **Material & Methods**
  - Sampling Site and Duration
  - Sample Preparation & Handling
  - Analytical Techniques
  - Performance Evaluation

- **Results & Discussions**
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  - Meteorological Parameters

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INTRODUCTION

- **Uptake rate** for VOCs

- **VOCs**: Organic compounds having vapor pressure $>10^{-4}$ atm @ 25°C and 1 atm
Introduction...

- VOCs are important because:
  - Precursors of photochemical reactions with NO\textsubscript{x}
  - \textit{O}_3\rightarrow\text{adverse health effects (iritation to noise and throat, asthma and bronchitis) and damage vegetation}
Introduction...

- toxic substances
- known or suspected carcinogen

- VOC Conc.

exhaust emissions
industrial process
evaporation
Introduction...

- **Sampling and Analyzing Techniques:**
  - Use near real time instrument (*infrared spectrometers or portable GC*)
  - Sample from air using
    - Canister
    - Adsorption on selective sorbents (*passive and active sampling*)
Introduction...

PASSIVE (DIFFUSIVE) SAMPLING:
taking samples by a physical process (diffusion and permeation)
Introduction...

- **Passive Sampling Theory:**
  - Adsorption of the sample onto adsorbent surface through the air movement

- **Fick’s First Law**

  \[
  \text{Analyte Conc} (\text{ppm}) = \frac{M_a(ng)}{U.R. (ng / ppm \times \text{min}) \times t(\text{min})}
  \]
Introduction...

- **Uptake rate (UR):**

- Experimental U.R (exposure chamber or online GC system)
- Ideal U.R (Diffusion Coefficient (D) is obtained from literature)

\[
\text{Uptake Rate (ng / ppm × min)} = \frac{D \left( cm^2 / s \right) \times A \left( cm^2 \right)}{L \left( cm \right)}
\]
Introduction...
MATERIALS & METHODS

- **Sampling Site**
  - Bursa Station
    - Urban

- **Sampling**
  - Passive Sampling
  - Active Sampling (Hourly measurement)

Continuous and un interrupted data obtained
Sample Preparation and Handling

Thermally desorber stainless steel passive tubes

Advantage:

✓ not require solvent extraction
✓ have chance to select sorbent
✓ leave long term in sampling area without breakthrough
✓ less affected from relative humidity
Sample Preparation and Handling...

- Sorbent: Chromosorb 106 by Supelco

Characteristics:

- suitable analyte volatility range for VOC in concern
- Hydrophobic
- analyte volatility range boiling point 50 °C - 200 °C
- maximum temperature: 250 °C
- specific surface area: 750 m²/g
Sampling Methodology

- **Condition** of tubes
- **Swagelock**-type screw caps with combined PTFE ferrule
- Sealed glass tubes filled with silica gel and charcoal at the bottom
- **Deep-freeze** in the laboratory
- **Glass sealed** jar filled with activated charcoal
Sampling Methodology …

- European Standard (EN) 13528
- Shelters made from aluminum
- Replacing the sampling cap with diffusion part
- placed between 1.6 - 2.0 m from ground level
- Field /Lab Blanks
Methodology...

- Analysis of collected samples on sorbents
- Organics (VOCs) → GC-FID-Unity TD
Methodology...

- GC-FID coupled with Unity Air Server
  - Markes Unity-Air Server Thermal Desorber
  - HP 6890 Dual Column GC coupled to FID with Dean Switch System
Methodology... (GC-FID)
Methodology... (GC-FID)
Methodology...

- **Calibration gas** standard:
  
  148 VOCs ($C_2$-$C_{12}$) from AAQD of Environment Canada
  
  ![5 point calibration](image)

- **Sorrogate** Standard:
  
  1-Bromofluorobenzene
Methodology...

Typical Calibration Standard Chromatogram
Methodology...

Typical Sample Chromotogram
Performance Evaluation

- **Detection Limit**
  0.21 μg m\(^{-3}\) (0.08 μg m\(^{-3}\) - 0.31 μg m\(^{-3}\))

- **Recovery/Desorption Efficiency**
  93.6% (80 - 100%)

- **Precision**
  7.7% (2.6 - 15.7%)

- **Sampling Stability**

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## RESULT

<table>
<thead>
<tr>
<th>Exposure Date</th>
<th>Number of active samples</th>
<th>Number of passive tubes</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-19 Oct.2005</td>
<td>258 (77%)</td>
<td>3</td>
</tr>
<tr>
<td>21-29 Oct.2005</td>
<td>173 (90%)</td>
<td>5</td>
</tr>
<tr>
<td>1-7 Nov.2005</td>
<td>84 (58%)</td>
<td>4</td>
</tr>
<tr>
<td>03-10 Apr.2006</td>
<td>144 (86%)</td>
<td>6</td>
</tr>
<tr>
<td>13-20 Apr.2006</td>
<td>152 (90%)</td>
<td>4</td>
</tr>
<tr>
<td>25 Apr - 03 May.2006</td>
<td>181 (100%)</td>
<td>3</td>
</tr>
</tbody>
</table>
Uptake Rates for BTEX
Uptake Rates for NMHCs
Meteorological Parameters:

- Temperature (°C)
- Relative Humidity (%)
- Wind Speed (m/sec)
<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>UPTAKE RATE (ng ppb(^{-1})min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.323</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.562</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.718</td>
</tr>
<tr>
<td>m&amp;p-xylene</td>
<td>1.535</td>
</tr>
<tr>
<td>o-xylene</td>
<td>1.123</td>
</tr>
<tr>
<td>COMPOUND</td>
<td>UPTAKE RATE (ng ppb⁻¹min⁻¹)</td>
</tr>
<tr>
<td>------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>1-Heptene</td>
<td>0.3219</td>
</tr>
<tr>
<td>3-M-Hexane</td>
<td>0.257</td>
</tr>
<tr>
<td>Heptane &amp; cis-3-Heptene</td>
<td>0.568</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.189</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>0.543</td>
</tr>
<tr>
<td>n-Probylbenzene</td>
<td>0.351</td>
</tr>
</tbody>
</table>
Future Works…

- Long term sampling with canister
- Meterological parameter
- QA/QC complete