

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

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OUTLINE

■ Introduction

- ☐ Importance and scope of the study
- ☐ Passive Tube Theory

■ Material & Methods

- ☐ Sampling Site and Duration
- ☐ Sample Preparation&Handling
- ☐ Analytical Techniques
- ☐ Performance Evaluation

■ Results & Discussions

- ☐ Uptake Rate
- ☐ Meteorological Parameters

■ Future Works



INTRODUCTION

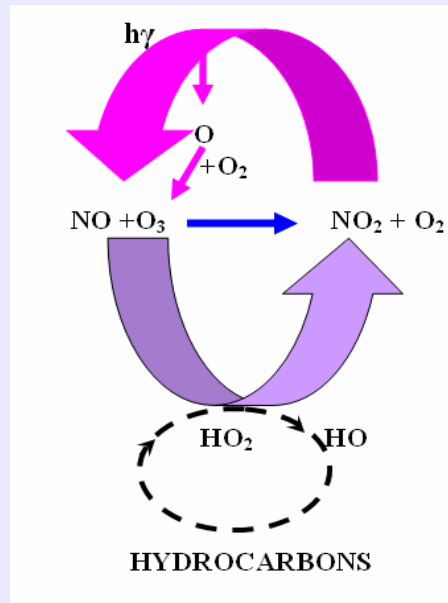
- **Uptake rate** for VOCs
- **VOCs:** Organic compounds having vapor pressure $>10^{-4}$ atm @ 25 C⁰ and 1 atm

Introduction...

❖ VOCs are important because:

■ Precursors of photochemical reactions with NO_x

O_3 \longrightarrow adverse health effects (irritation to nose 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**)

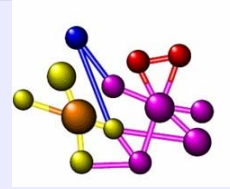
Introduction...

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

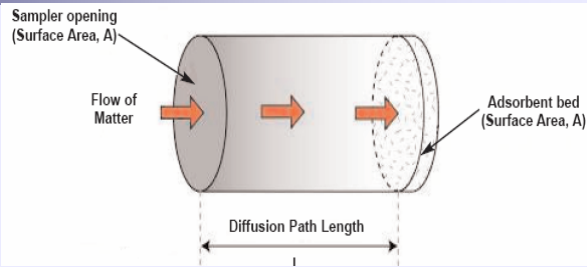
$$\text{Analyte Conc(ppm)} = \frac{M_a(\text{ng})}{U.R.(\text{ng} / \text{ppm} \times \text{min}) \times t(\text{min})}$$

Introduction...

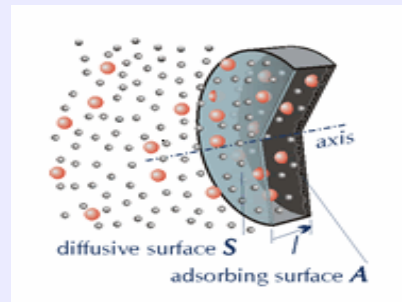
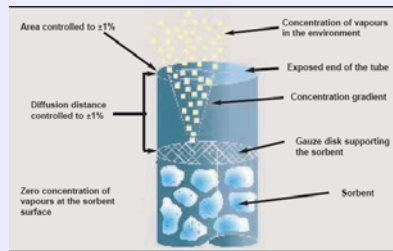
❖ Uptake rate (UR):

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

$$Uptake\ Rate\ (ng / ppm \times min) = \frac{D(cm^2 / s) \times A\ (cm^2)}{L\ (cm)}$$



Introduction...



MATERIALS & METHODS

■ Sampling Site

- Bursa Station

- Urban

■ Sampling

- Passive Sampling

- Active Sampling (Hourly measurement)

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Continuous and uninterrupted 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**

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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**

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Sampling Methodology



- **Condition** of tubes
- **Swagelok**-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**

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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)



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Methodology...

- ☐ Calibration **gas** standard:

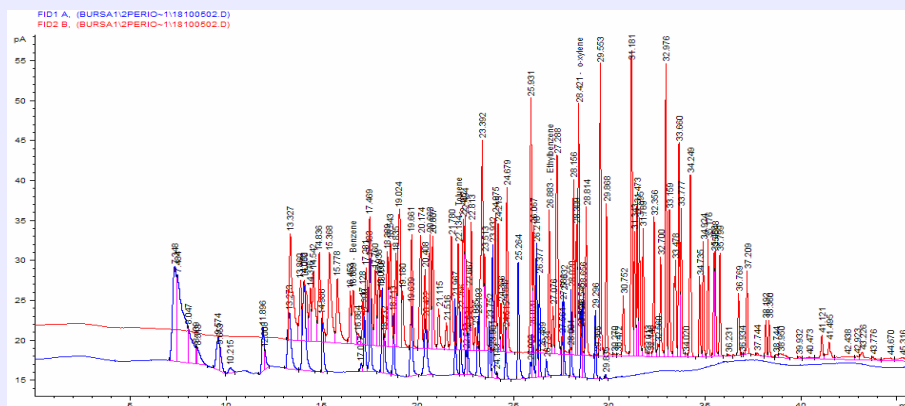
148 VOCs (**C₂-C₁₂**) from AAQD of Environment Canada

✓ **5 point calibration**

- ☐ **Sorrogate** Standard:

1-Bromoflourobenzene

Methodology...



Methodology...

Typical Sample Chromatogram

Performance Evaluation

- ❖ **Detection Limit**

0.21 $\mu\text{g m}^{-3}$ (0.08 $\mu\text{g m}^{-3}$ - 0.31 $\mu\text{g m}^{-3}$)

- ❖ **Recovery/Desorption Efficiency**

93.6% (80 - 100%)

- Precision**

7.7% (2.6 - 15.7%)

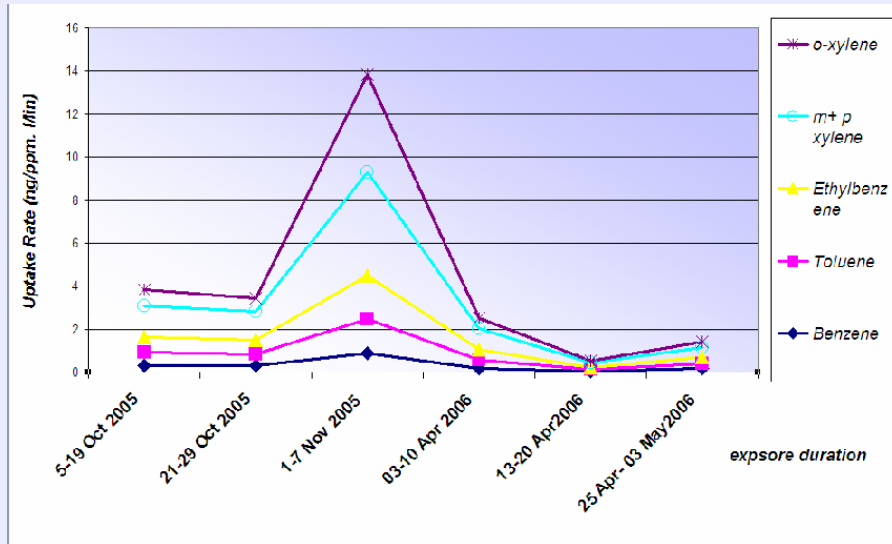
- ❖ **Sampling Stability ??**



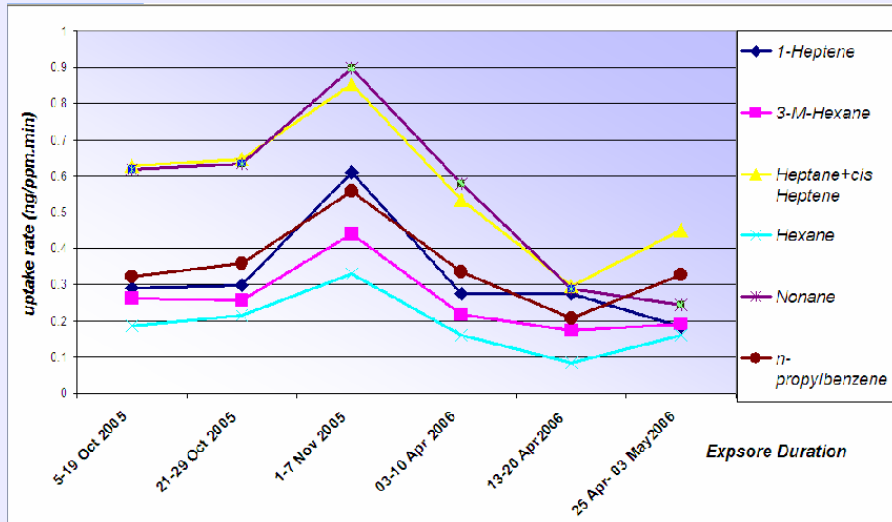
RESULT

Exposure Date	Number of active samples	Number of passive tubes
5-19 Oct.2005	258 (77%)	3
21-29 Oct.2005	173 (90%)	5
1-7 Nov.2005	84 (58%)	4
03-10 Apr.2006	144 (86%)	6
13-20 Apr2006	152 (90%)	4
25.Apr-03 May.2006	181 (100%)	3

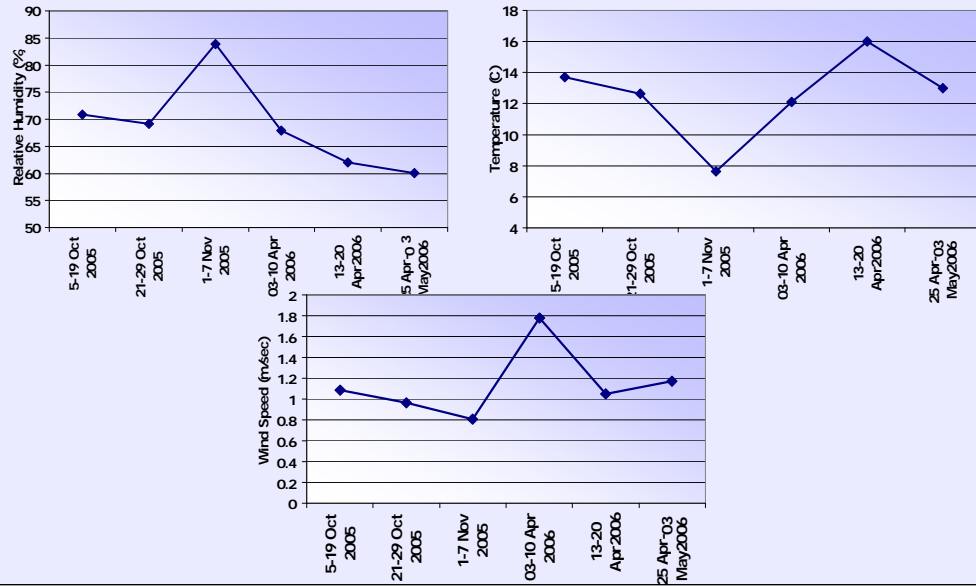
Uptake Rates for BTEX



Uptake Rates for NMHCs



Meteorological Parameters:



UPTAKE RATE

COMPOUND	UPTAKE RATE (ng ppb ⁻¹ min ⁻¹)
Benzene	0.323
Toluene	0.562
Ethylbenzene	0.718
m&p-xylene	1.535
o-xylene	1.123

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UPTAKE RATE...

COMPOUND	UPTAKE RATE (ng ppb ⁻¹ min ⁻¹)
1-Heptene	0.3219
3-M-Hexane	0.257
Heptane& cis-3-Heptene	0.568
n-Hexane	0.189
n-Nonane	0.543
n-Probylbenzene	0.351

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Future Works...

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