

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

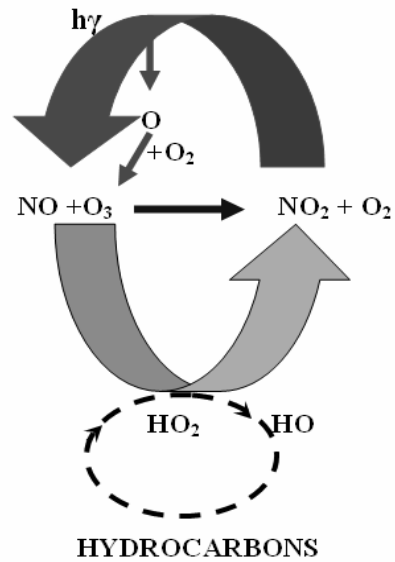
- Uptake rate for VOCs
- VOCs: Organic compounds having vapor pressure $>10^{-4}$ atm @ 25 C⁰ and 1 atm

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)

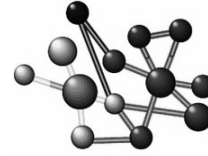
Introduction...

PASSIVE (DIFFUSIVE) SAMPLING:

taking samples by a physical process (diffusion and permeation)



Introduction...



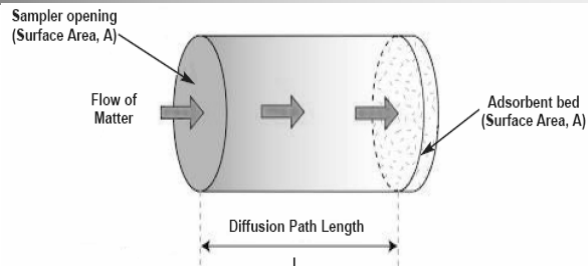
❖ Passive Sampling Theory:

- 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...

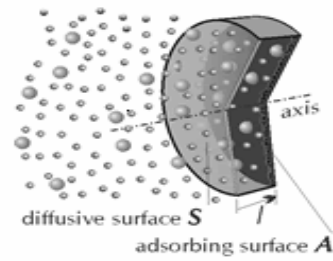
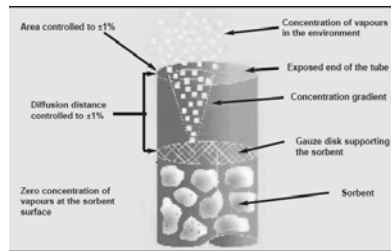


❖ Uptake rate (UR):

- ❑ 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
- **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)



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Methodology...

- ☐ Calibration **gas** standard:

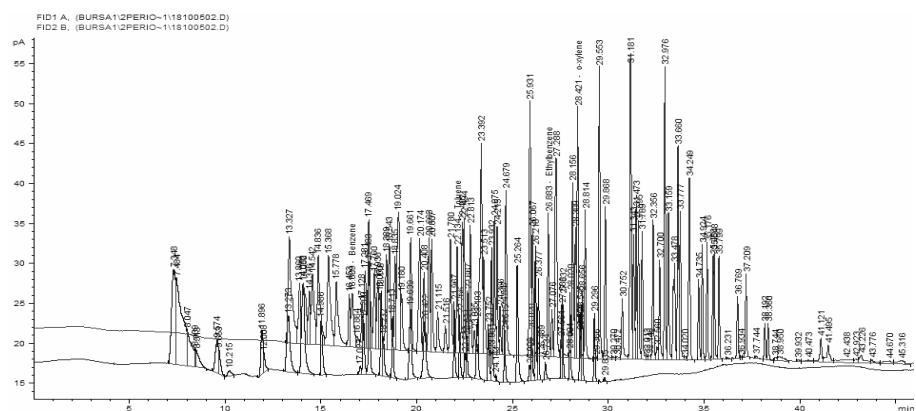
- 148 VOCs (**C₂-C₁₂**) from AAQD of Environment Canada

- ✓ **5 point calibration**

- ☐ **Sorrogate** Standard:

- 1-Bromoflourobenzene

Methodology...



Typical Calibration Standard Chromatogram

Methodology...

FID1 A, (BURSA1\2PERIO-1\21100505.D)
FID2 B, (BURSA1\2PERIO-1\21100505.D)

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%)

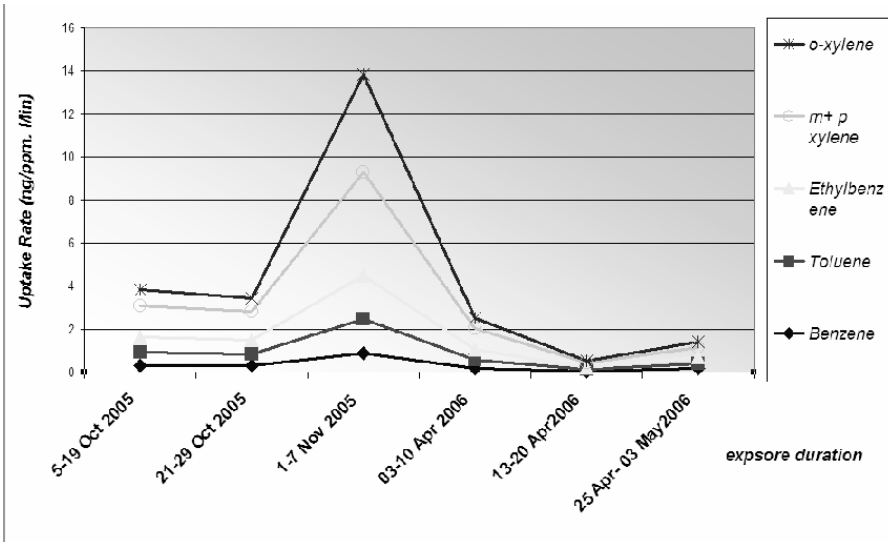
- ❖ **Sampling Stability ??**



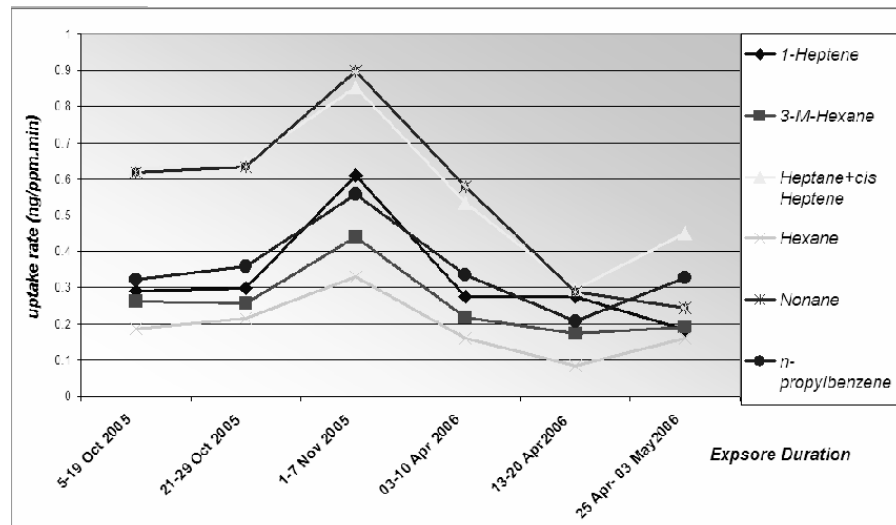
RESULT

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

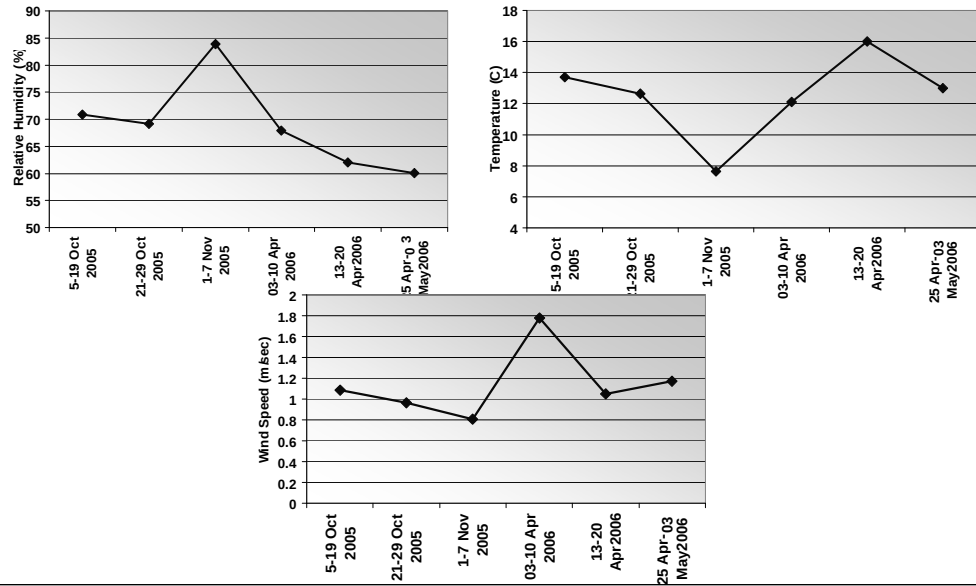
Uptake Rates for BTEX



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