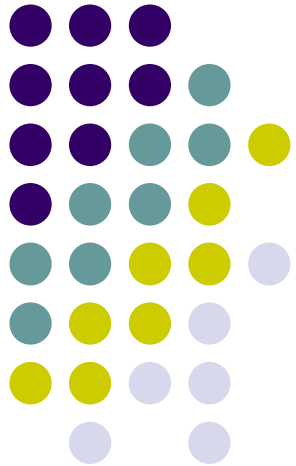
Atmospheric Analysis Gases

Sampling and analysis of gaseous compounds



Introduction

- External environment (ambient air)
  ; global warming, acid rain, introduction of pollutants, etc

- Internal environment (indoor air)

; atmosphere in building
(gases from fuel combustion and cleaning fluids, solvents from cleaning fluids unexpected sources etc)

- concentration

Time-weighted average conc ; avg conc over a period of time
instantaneous concentration
Unit ; ppm (v/v), mg/m3(mass/volumn)

Ex) NO_2 650 mg/M^3 → ppm (v/v)

MW of NO_2 = 46
# of mole of NO_2 in 1m^3 air ; $650 \times 10^{-3}/46 = 14.1 \times 10^{-3}$ mol
Vol occupied by 1mole at 20^{o}C and 1atm ; 24.0 L = 0.024 m^3
Vol of NO_2 in 1m^3 air ; $14.1 \times 10^{-3} \times 0.024\ m^3 = 33.8 \times 10^{-6}\ m^3$ = 338 ppm(v/v)

Conc (ppm) = {conc (mg/m^3) / relative molecular mass} × 24.0

대기환경기준

항 목	기 준	측정방법
아황산가스(SO_2)	연간평균치 0.02ppm 이하 24시간평균치 0.05ppm 이하 1시간평균치 0.15ppm 이하	자외선형광법 (Pulse U.V. Fluorescence Method)
일산화탄소(CO)	8시간평균치 9ppm 이하 1시간평균치 25ppm 이하	비분산적외선분석법 (Non-Dispersive Infrared Method)
이산화질소(NO_2)	연간평균치 0.03ppm 이하 24시간평균치 0.06ppm 이하 1시간평균치 0.10ppm 이하	화학발광법 (Chemiluminescent Method)
미세먼지(PM_{10})	연간평균치 50㎍/㎥ 이하 24시간평균치 100㎍/㎥ 이하	베타선흡수법 (β-Ray Absorption Method)
미세먼지($PM_{2.6}$)	연간평균치 25㎍/㎥ 이하 24시간평균치 50㎍/㎥ 이하	중량농도법 또는 이에 준하는 자동측정법
오존(O_3)	8시간평균치 0.06ppm 이하 1시간평균치 0.1ppm 이하	자외선광도법 (U.V Photometric Method)
납(Pb)	연간평균치 0.5㎍/㎥ 이하	원자흡광광도법 (Atomic Absorption Spectrophotometry)
벤젠	연간평균치 5㎍/㎥ 이하	가스크로마토그래프법 (Gas Chromatography)

• Absorption trains

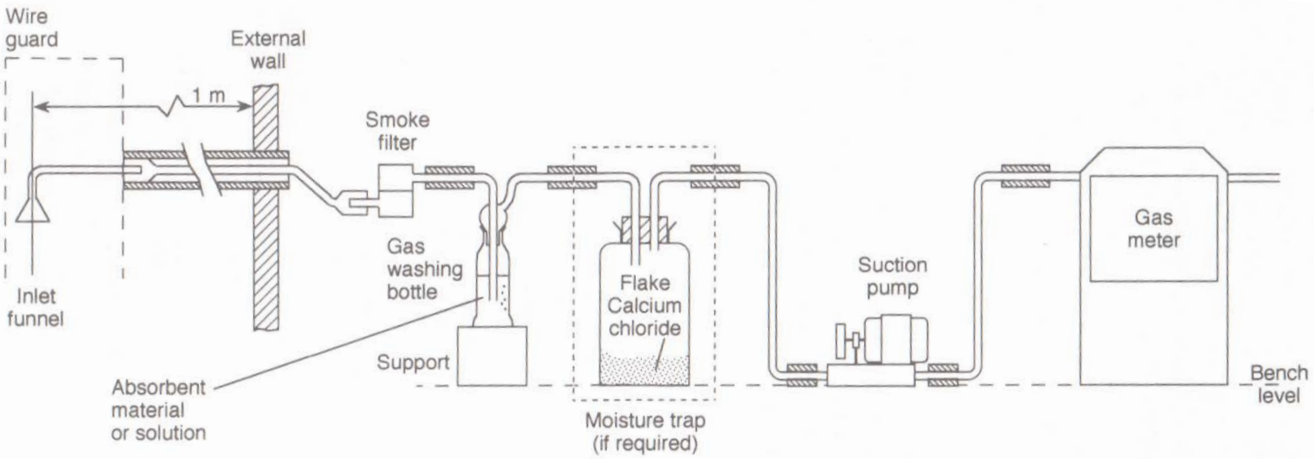


Fig. 6.2b. *Components of a gas absorption train*

- Sample volume ; gas meter or air-flow regulator

- Reagent ; highly specific to the analyte gas

  Resistant to oxidation and to being stripped from solution

- Absorption of the analyte has to be quantitative (ppb).

<High volume air sampler
; can sample more than 1500m3>

<low volume air sampler
; only 24 m3 or less>

- Active sampling

-Draw air through the sample tube by means of a pump (sampling rate, some tubes contain two sections of adsorbent (analysis + back up))

- lower concentration can be monitored for a given sampling time

- Desorption of sample

- Thermal desorption or solvent extraction

- Problem of these sampling methods

-absorption and desorption efficiencies of the sampling

-possibility of overloading the adsorbent (breakthrough volume ; theoretical capacity of the adsorbent)

• Solid Adsorbents

- Commonly used for low-conc organic components

-Passive sampler (diffusion sampler) ;
Adsorbent contained in a small tube sealed at one end, the other exposed to air

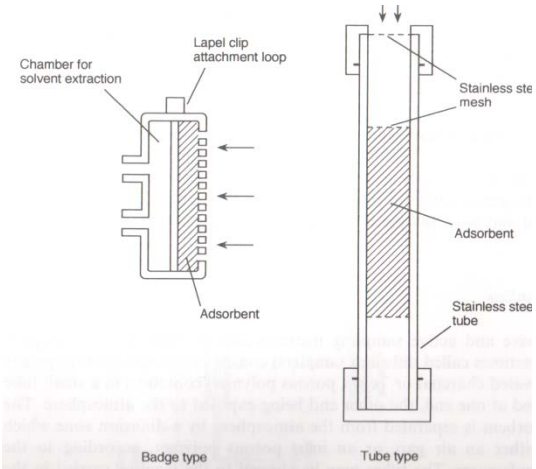


Fig. 6.2c. *Examples of passive (diffusion) samplers*

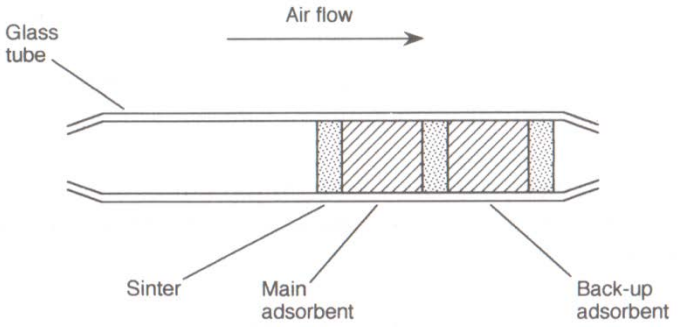
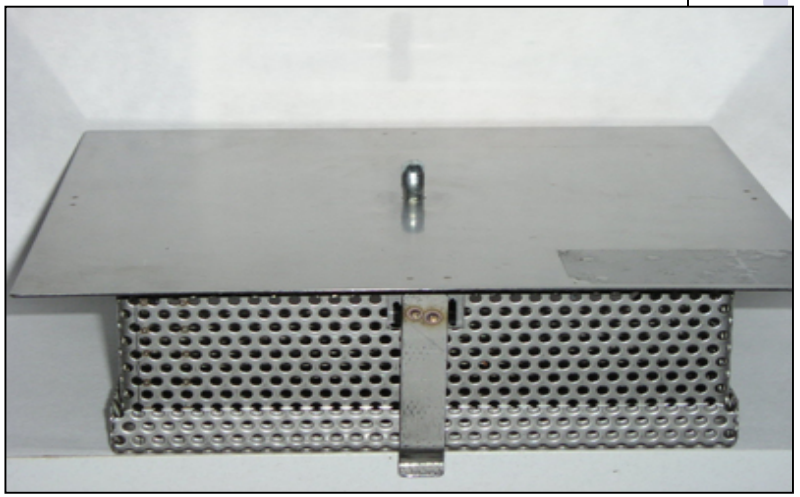
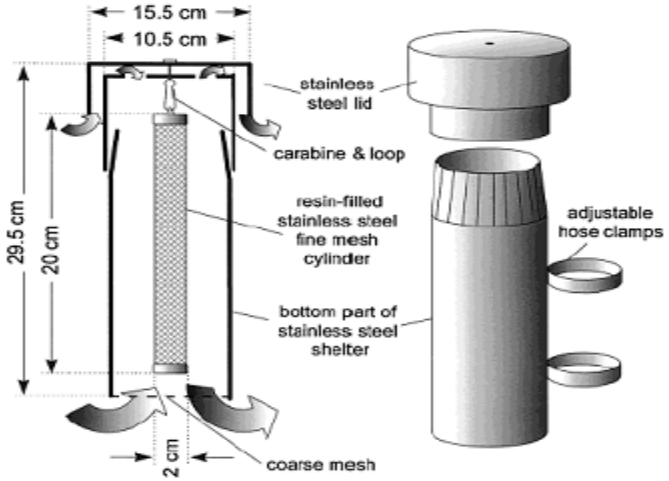


Fig. 6.2d. *A typical adsorption tube used for active sampling*

Passive Air Sampler (PAS)



Resin-based PAS
University of Toronto



SPMD

- **tp://www.passamtec.com**

Installation of the PAS

These researches are conducting centering around the Canadian and American regions.

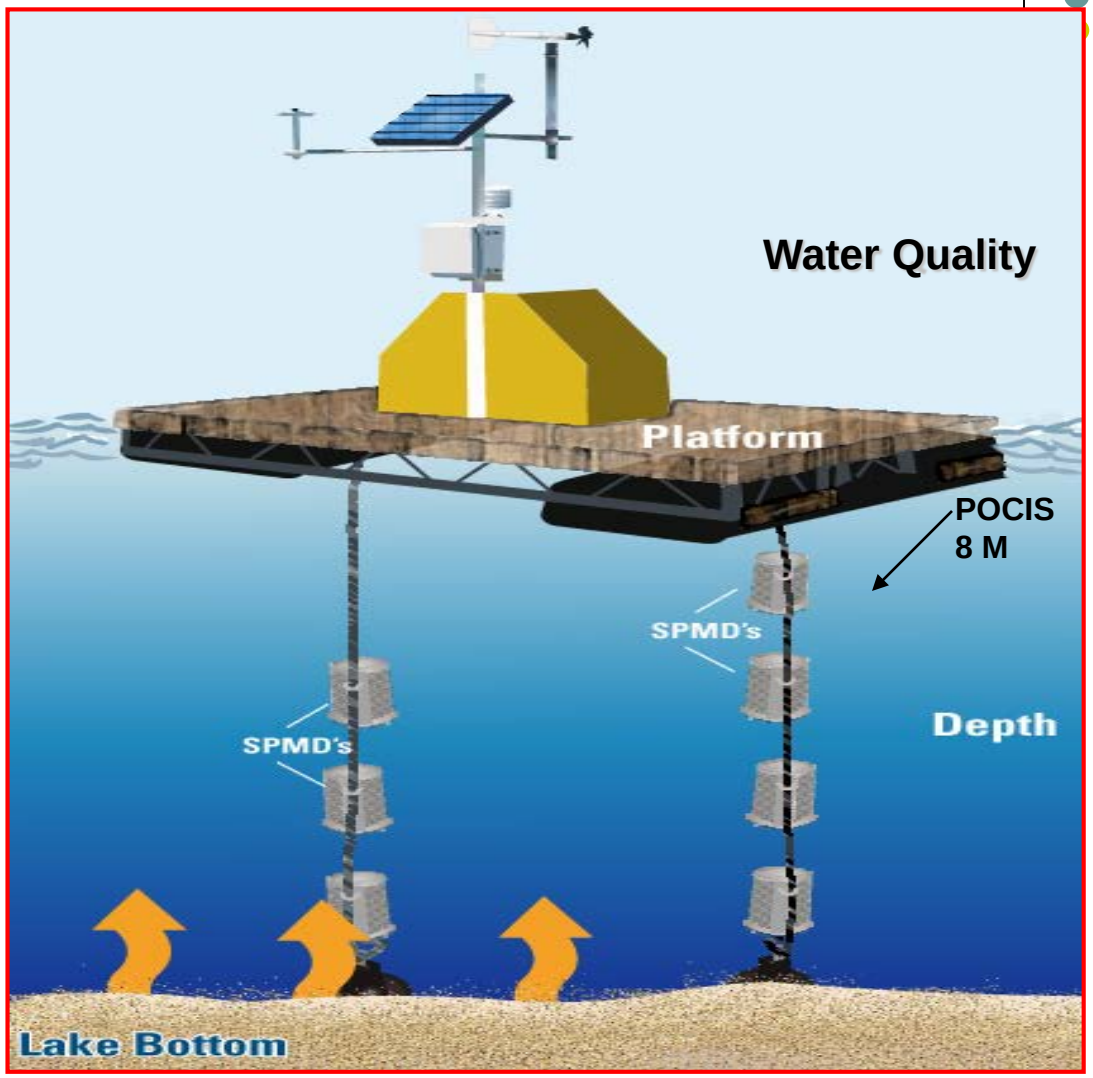
SPMD

(Semipermeable membrane device)

POCIS

(Polar Organic Chemical Integrative Samplers)

Passive Sampling Setup



Deployment and Retrieval of Samplers

• Diffusion tubes

- Large number of sites are being simultaneously monitored

- Simple and easy to construct, no electricity

-A short tube which is open at one and and has a liquid adsorbed on stainless-steel mesh at the closed end.

-Rely on the natural diffusion of the gas into the liquid
the rate of adsorption is determined by the rate of diffusion of the gas

-Commonly used for NO_2
(Ex ; adsorbent liquid is triethanolamine, spectrometric analysis (550nm))

-Precision of the technique is not large
hard to obtain exact sampling volume, only collect gas phase of chemicals

- Low cost of the apparatus

• Determination of instantaneous concentrations

- Often based on spectrometric techniques

-Light emission (chemiluminescence and fluorescence) ; most sensitive
Nitrogen oxides, sulphur dioxide and ozone etc

• Chemiluminescence and Fluorescence

1) $NO + O_3 \rightarrow NO_2^* + O_2$
$NO_2^* \rightarrow NO_2 + h\nu$ λ=600~875nm (DL ; 10 ppb (18 ug/m3))

2) O_3 react with ethlylene and monitor light emission at 430nm (DL ;1ppb, 2ug/m^3)

3) SO_2 ; without chemical pretreatment. Fluorescence spectrometry (DL;2ppb,5ug/m^3)

UV photometric ambient O3 analyzer

• Infrared Spectrometry

–used for monitoring various inorganic gases and organic vapours

–complex spectra and each molecule gives a unique absorption pattern

– Dispersive infrared spectrometer ; absorption of radiation after separating IR and measure the different wavelength

–non–dispersive spectrometer ; no spectral spectral separation

ex; CO, CO_2,SO_2, acetylene, methane and water etc

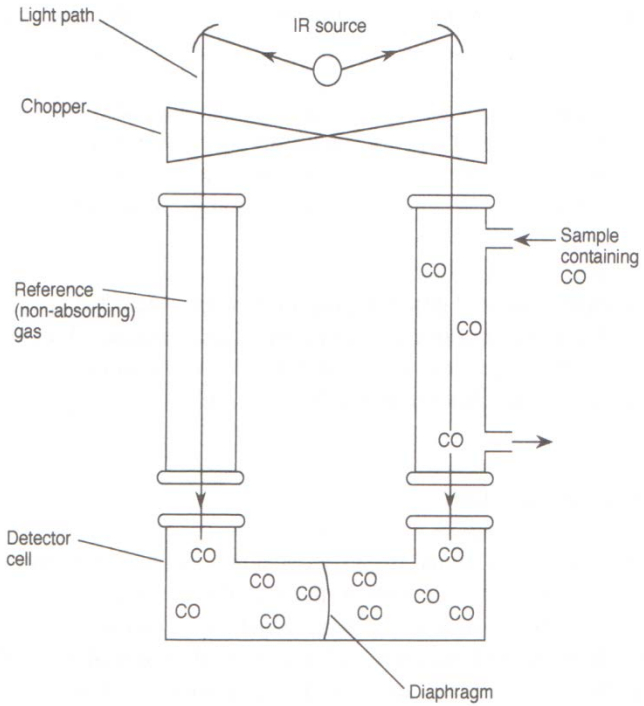


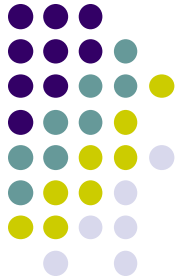
Fig. 6.3b. *Non-dispersive infrared carbon monoxide analyser*

Measure the oscillation of the detector cell

Each gas needs a separate instrument

–Difficult to measure many species because of possibility of overlap of absorptions in multi–component mixtures

• Electrochemical sensors



–Use different sensing head being required for each gas
(ex ; CO_2, Cl_2, HCN, HCl, H_2S, SO_2)

–The reaction of the analyte gas at an electrode produce a current ; proportional to its gas phase concentration

• Gas Detector tubes

–Hand held and easy to use instrument ; often measure internal atmosphere where high concentrations of hazardous can quickly accumulate

–Packed with an analyte specific reagent adsorbed on inert solid
ex) Pb^{2+} + H_2S → PbS + $2H^+$ (black lead sulphide)
CO_2 + N_2H_4 → $H_2N-NH-CO_2H$ (change to purple)

– Precision ; varied with compound types

–Interference ; separate zone of reactive solid is needed to remove potential common interferences


GASTEC
TIP BREAKER

• Gas Chromatography

-Can be used as portable instrument ;
onsite monitoring or permanently positioned at the sampling point

- Portable GC ; decreases in size, mass and # of gases
use column to separate components at ambient (near) T.
(don't need oven and additional gas supplies)

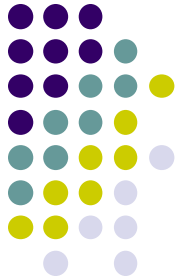
-Sampling

・container ; sampling bulb, evacuated sample container sampling bag
gas-tight syringe. Sampling loop.

・problem of on-site sampling
; need large sample vessels, difficult to check for leakage or contamination
loss by rxn on the walls of the vessel, injection of large volume disturbs the carrier gas flow

- Chromatographic analysis

• gas-solid chromatography ; inorganic gases and low molecular mass organics
molecular sieves ; separate gases in order of molecular size
silicagel column ; suitable for carbon dioxide
conventional gas-liquid column ; may be used for VOCs



- Detector for inorganics

  -Thermal conductivity ; for all gases

  low sensitivity (DL ; a few hundred ppm)

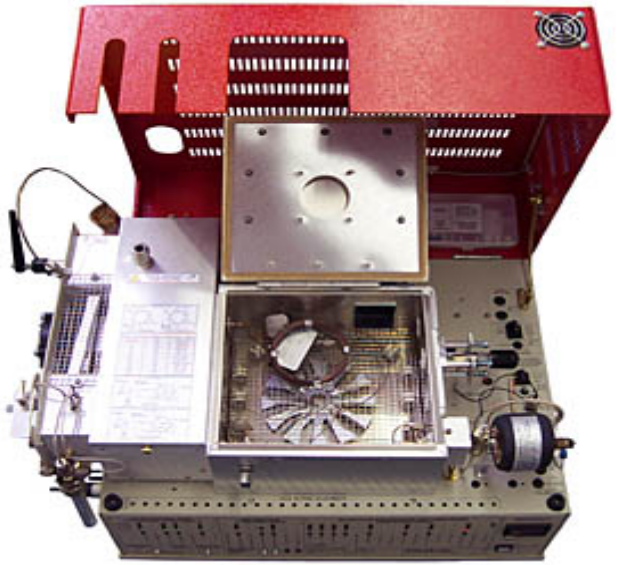
  low mass carrier gas increase sensitivity (ex ; H2 but not safe, He)

  -Flame ionisation detector ; not easily detect most inorganic gases,

  can detect organic components, easy to portable and maintain of flame

- Method for determining total VOCs without separation

  - Inject a sample directly into FID without column



- **Remote sensing**

(the acquisition of information about an object or phenomenon without making physical contact with the object)

- Spectrometric methods ; long path length can measure low conc compounds.

- UV region ; SO_2, NO_2. O_3

-IR region; compounds which do not absorbe in the UV region
(CO_2 and water hinder)

- Light source ; pulsed laser

<Configuration of UV-DOAS (dedicated outdoor air system) > √