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Determination of Volatile Organic Compounds (VOCs)

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- Definitions
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- Hazards
- Sampling and Analytical Methods
- Accreditation

Definitions

Selected definitions from Hong Kong and Overseas

- Hong Kong - Air Pollution Control (VOCs) regulation (CAP 311W):
- VOC means any volatile compound of carbon excluding methane, carbon monoxide, carbon dioxide, carbonic acid, metallic carbides, metallic carbonates, ammonium carbonate and exempt compounds

Definitions (Cont'd)

Selected definitions from Hong Kong and Overseas (Cont'd)

- World Health Organisation - WHO (1989):
- "any organic compounds"
- Very volatile organic compound (VVOC) <0 up to 50^{o}C
- volatile organic compound (VOC) 50 - 100 up to 240 - 260^{o}C
- semivolatile organic compound (SVOC) 240 - 260 up to 380 - 400^{o}C

Definitions (Cont'd)

Selected definitions from Hong Kong and Overseas (Cont'd)

- United Nations Economic Commission for Europe - UN-ECE protocol (nov. 1991):
- "..any organic compounds of anthropogenic nature, other than methane, that are capable of producing photochemical oxidants by reacting with nitrogen oxides in the presence of sunlight."
- This definition relates to ozone formation

Definitions (Cont'd)

Selected definitions from Hong Kong and Overseas (Cont'd)

- US Environmental Protection Agency - US EPA :
- "any volatile compound of carbon excluding methane, carbon monoxide, carbon dioxide, carbonic acid, metallic carbides, metallic carbonates, ammonium carbonate and other compounds"
- This definition relates to ozone formation

Definitions (Cont'd)

Selected definitions from Hong Kong and Overseas (Cont'd)

- European Unit - EU – 2001/81/EC (National Ceiling Directive):
- "..VOC means all organic compounds arising from human activity, other than methane, which are capable of producing photochemical oxidants by reactions with nitrogenic oxides in the presence of sunlight."
- This definition relates to ozone formation

Sources

Potential Sources of VOC Emissions

- Ambient mobile and stationary sources (e.g. benzene from automotive exhaust and vapor release from gasoline service stations);
- *Off-gassing of chemicals from furniture (e.g., formaldehyde from desks made of particleboard);*
- *Construction, demolition and building renovation activities (e.g., painting the walls);*
- *Personal hygiene products (e.g., perfumes and hairsprays);*
- *Pesticides and insecticides;*
- *Commercial activities (e.g., automotive painting and dry cleaning exhausts)*

Hazards

Health Effects of VOC

- Carcinogenic Effects
  - The ability of a substance to cause cancer in humans and animals
  - Carcinogenicity of VOCs varies between species
  - According to US EPA, VOCs typically account for 35 to 55% of outdoor air cancer risk in the United States

Hazards (Cont'd)

Health Effects of VOC

- Non-Carcinogenic Effects
  - A number of VOCs if above certain endpoints tend to affect the respiratory, digestive and certain nervous systems
  - These endpoints vary widely between compounds and exposure pathways

Hazards (Cont'd)

Health Effects of VOC

- Odour and Annoyance
  - The malodorous properties of certain VOCs may lead to irritation or annoyance in humans
  - Odour threshold is used to describe the theoretical minimum concentration of odourant necessary to be detected
  - Odour threshold concentrations for many VOCs may be below those considered toxic to humans

Hazards (Cont'd)

Environmental Effects of VOC

- Ozone Formation Capacity
  - The formation of ground-level ozone (O_3) through photochemical oxidation of certain VOCs
  - Negative impacts on human health, including lung damage, chest pains, coughing, nausea, throat irritation and congestion
  - Negative vegetative effects, such as the reduced ability of plants to produce and store food, making them more susceptible to disease, insects, other pollutants and harsh weather
  - Ozone is the primary component of smog, the brownish haze commonly seen over urban areas during the summer

Hazards (Cont'd)

Environmental Effects of VOC

- Particular Matter
  - Particulate matter (PM) includes solid particles as well as liquid droplets that are suspended in air
  - The most common size categories are: $PM_{2.5}$ and PM_{10}
  - Elevated concentrations of PM_{10} most commonly a result of direct natural emissions, primarily of materials derived from the earth's crust, such as soil and minerals
  - Elevated concentrations of $PM_{2.5}$ caused partly by direct emissions and partly by indirectly formation from pollutants such SO_2, NO_x, VOCs and NH_3, therefore usually the result of anthropogenic activities

Hazards (Cont'd)

Examples

- Benzene
  - Boiling point: 80.1 ˚C
  - Second-hand tobacco smoking, solvents, paints, fax machines
  - Known to cause cancer
- Tetrachloroethylene
  - Boiling point: 121.1 ˚C
  - Dry-cleaned fabrics, furniture coverings, spot/textile cleaners
  - Suspected carcinogen

Hazards (Cont'd)

Examples

- Toluene
  - Boiling point: 111 ˚C
  - Solvent, perfumes, detergents, dyes, water-based adhesives
  - Insufficient data on cancer (animals)
- Trichlorofluoromethane
  - Boiling point: 23.8 ˚C
  - Refrigerants, fire extinguishers
  - Ozone depleting chemicals (banned)

Sampling and Analytical Methods

Sample Matrices for VOCs Analysis

- Air
  - Indoor and Outdoor Air, Mobile and Stationary Sources
- Water
  - Wastewater, Drinking Water
- Soil/Sediment
- Products
  - Wooden Board, Hairspray

Sampling and Analytical Methods (Cont'd)

Types of Sampling Methods - Air

- Active sampling
  - The process of connecting sample collection media to a sampling train consisting of inert tubing and a sample pump operating at a know flow rate
  - The sampling pump draws air through the sample media, resulting in a know sample volume

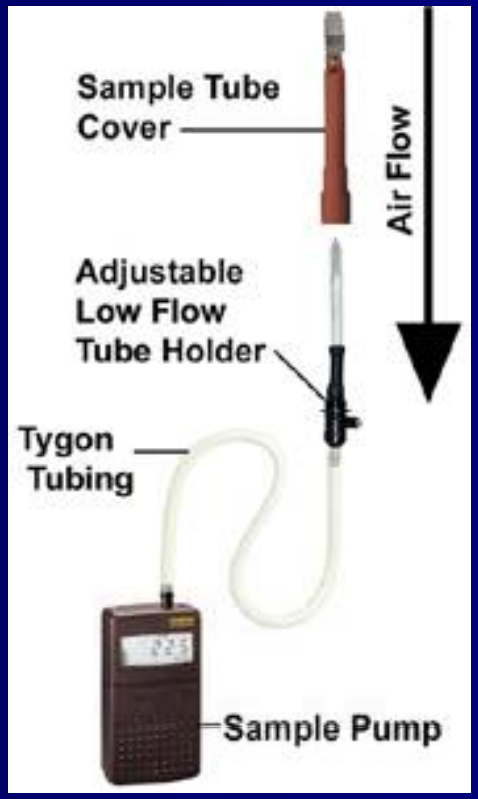
Sampling and Analytical Methods (Cont'd)

Types of Sampling Methods

- Active sampling
  - Inlet
  - Sampling Media (Tubes or Bags)
  - Tubing
  - Pump

Sampling and Analytical Methods (Cont'd)

- Active sampling



- *Courtesy of SKC Corporation

Sampling and Analytical Methods (Cont'd)

- Active sampling – Pumps

*Courtesy of SKC Corporation

Sampling and Analytical Methods (Cont'd)

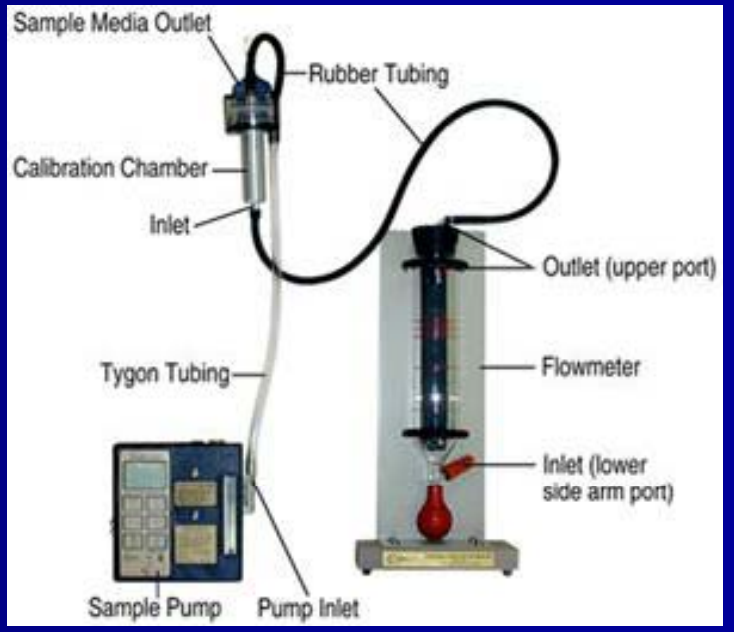
- Active sampling – Pumps (Cont'd)

Sampling and Analytical Methods (Cont'd)

- Active sampling – Sampling Tubes and Bags

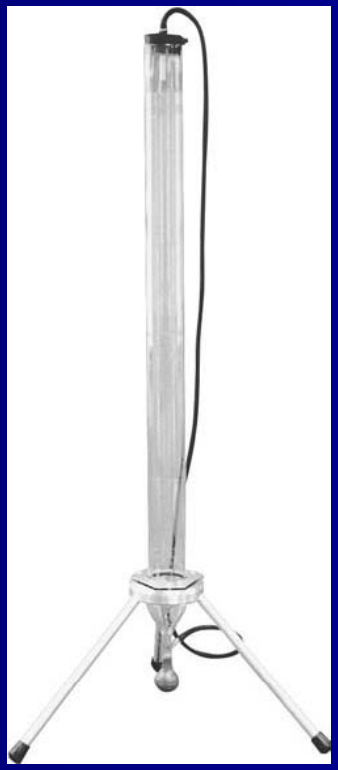
Sampling and Analytical Methods (Cont'd)

- Active sampling – Calibration of Flow Rate



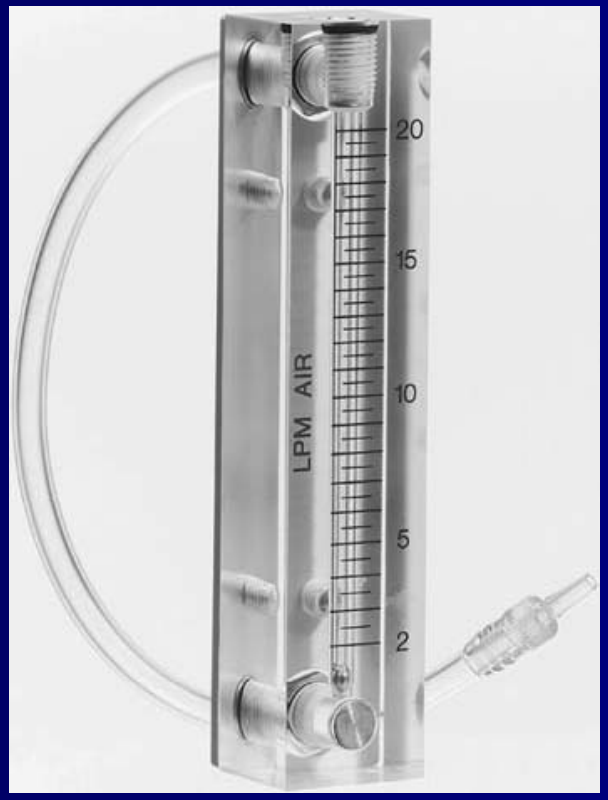
Sampling and Analytical Methods (Cont'd)

- Active sampling – Calibration of Flow Rate (Cont'd)



Sampling and Analytical Methods (Cont'd)

- Active sampling – Flow Rate Measurements



Sampling and Analytical Methods (Cont'd)

Types of Sampling Methods

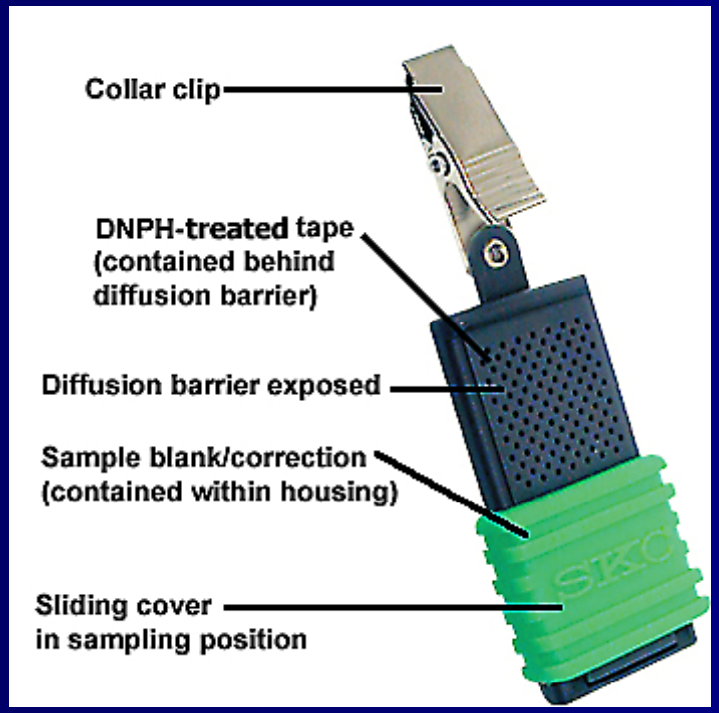
- Passive sampling
  - allowing sample collection media (e.g., solvent or thermal desorption tube) to passively diffuse air through the sample media without benefit of 'forced air'.
  - This allows for longer potential sampling periods without concern for overloading the sampling media.

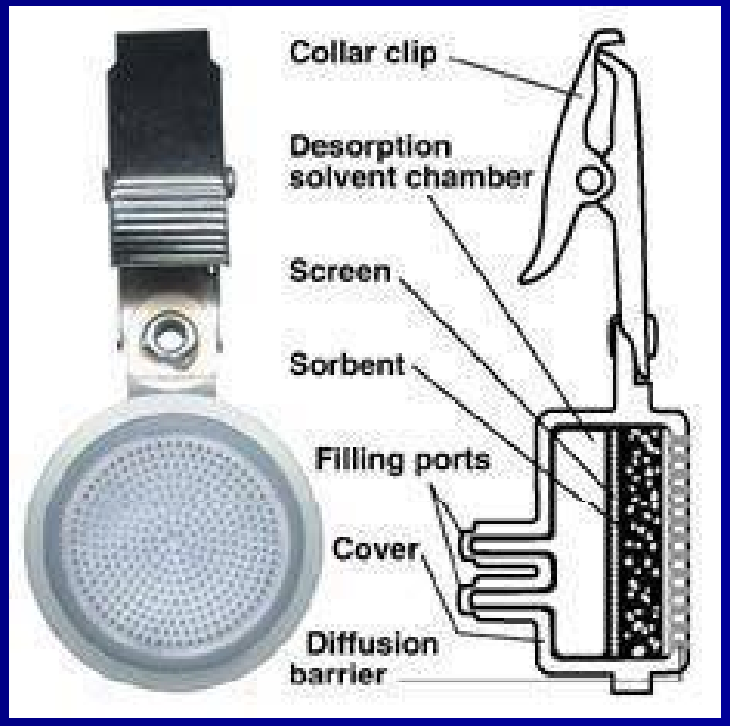
Sampling and Analytical Methods (Cont'd)

- Passive samplers

Sampling and Analytical Methods (Cont'd)

- Passive samplers (Cont'd)





Sampling and Analytical Methods (Cont'd)

- Passive/Active samplers - Canisters

Sampling and Analytical Methods (Cont'd)

- Canister Sampling – Two basic modes
  - Grab sampling
    - Sample is taken over a short interval, i.e. 1 to 5 minutes
  - Integrated sampling
    - Sample is taken over an extended period, e.g. 0.5 to 2 hours or 0.5 to 24 hours

Sampling and Analytical Methods (Cont'd)

- Direct-reading Devices
- Two major types:
  - Colorimetric Devices
    - Concentration of VOCs indicated by color change
    - Examples: Dräger/indicator tube by active or passive sampling
  - Electronic Direct Reading Instruments
    - Comprised of detector, signal processing unit, data display and pump (no pump for passive instrument)
    - Examples: PID, FID, IR

Sampling and Analytical Methods (Cont'd)

- Colorimetric Devices – Indicator Tube (Active)

Sampling and Analytical Methods (Cont'd)

- Indicator Tube Operations – Step 1
  - Break tube tips, push in pump handle, and insert tube

Sampling and Analytical Methods (Cont'd)

- Indicator Tube Operations – Step 2
  - Align guides, pull out handle until locked, and wait for flow finish indicator to pop out

Sampling and Analytical Methods (Cont'd)

- Indicator Tube Operations – Step 3
  - Read measurement at end of color changed layer. Mark on the tube with pen

Sampling and Analytical Methods (Cont'd)

- Colorimetric Devices – Indicator Tube (passive)

Sampling and Analytical Methods (Cont'd)

- Electronic Direct Reading Instruments
- Metal Oxide Semiconductor Sensor (MOS)
  - Change in resistance of a sensitive metal oxide layer induced by the surface interaction with ambient gases
  - Compact and low cost
  - Suffer from humidity sensitivity, non-linear response and long term drift
  - Response to inorganic gases, such as NO, NO2 or CO
  - Not suitable to measure low concentrations of VOCs where inorganic gases are present in higher concentrations

Sampling and Analytical Methods (Cont'd)

- Electronic Direct Reading Instruments (Cont'd)
- Metal Oxide Semiconductor Sensor (MOS) (Cont'd)

Sampling and Analytical Methods (Cont'd)

- Electronic Direct Reading Instruments (Cont'd)
- Photo-ionization Detector (PID)
  - Use an ultraviolet (UV) light source to ionize the VOCs
  - Detect or measure the charge of the ionized gas with the charge being a function of the concentration of VOCs
  - No change to the sample gas, that is non-destructive
  - Give a total value of VOCs, not individual VOCs
  - Sensitivity differ to different individual VOCs

Sampling and Analytical Methods (Cont'd)

- Electronic Direct Reading Instruments (Cont'd)
- Photo-ionization Detector (PID) (Cont'd)

Sampling and Analytical Methods (Cont'd)

- Electronic Direct Reading Instruments (Cont'd)
- Flame Ionization Detector (FID)
  - Use a flame as source to break down VOCs into ions
  - Detect or measure the charge of the ionized gas with the charge being a function of the concentration of VOCs
  - Change to the sample gas, that is destructive
  - Give a total value of VOCs, not individual VOCs
  - Sensitivity differ to different class VOCs
  - Require hydrogen as fuel therefore not portable and high running costs compare to other types of detector/sensor

Sampling and Analytical Methods (Cont'd)

- Electronic Direct Reading Instruments (Cont'd)
- Flame Ionization Detector (FID) (Cont'd)

Sampling and Analytical Methods (Cont'd)

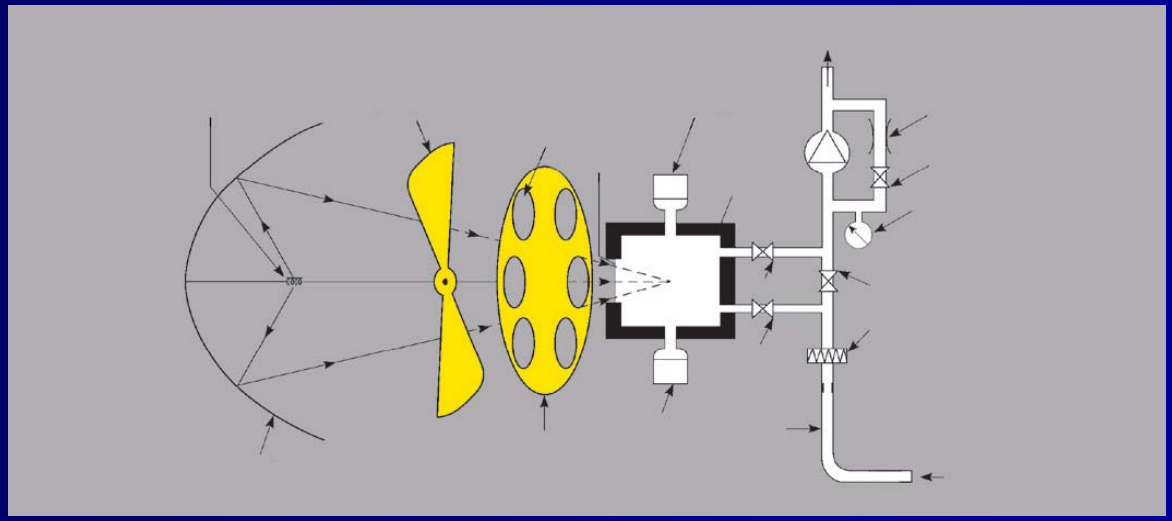
- Electronic Direct Reading Instruments (Cont'd)
- Photoacoustic Infrared Detector
  - Use Infrared (IR) (lamp) as source
  - Gas concentration is measured electro-optically by its absorption of specific wavelength in IR spectrum
  - Use optical filter to eliminate all light except the wavelength that the selected gas molecules can absorb
  - Gas molecules absorb some of the light energy and convert it into an acoustic signal which is detected by microphones
  - Can measure individual VOCs by selecting different filters
  - No change to the sample gas, that is non-destructive

Sampling and Analytical Methods (Cont'd)

- Electronic Direct Reading Instruments (Cont'd)
- Photoacoustic Infrared Detector (Cont'd)

Sampling and Analytical Methods (Cont'd)

- Electronic Direct Reading Instruments (Cont'd)
- Photoacoustic Infrared Detector (Cont'd)



Sampling and Analytical Methods (Cont'd)

Sample Analysis

- Extraction
  - Use known volume of solvent, e.g. carbon disulphide (CS_2) to extract the target analytes from the samplers (active or passive), except canister and thermal desorption tubes (direct instrumentation analysis)
- Instrumentation Analysis
  - Gas Chromatography coupled with flame ionization detector (GC-FID), Gas Chromatography coupled with mass selective detector (GC-MSD) and High performance liquid chromatography (HPLC)

Sampling and Analytical Methods (Cont'd)

- Analytical Procedure – Example
- NIOSH 1501
- Analyte: Benzene, Toluene, Ethyl Benzene, Xylenes
- Sampler: Solid Sorbent Tube (coconut shell charcoal)
- Flow rate: $\leq$ 0.20 L/min
- Volume: 5 to 30 L (benzene)
- Desorption: Carbon Disulphide (CS_2)
- Detection: GC-FID

Sampling and Analytical Methods (Cont'd)

- Analytical Procedure – Example (Cont'd)
- Sample Preparation Procedure
  - Place the front and back sorbent sections* of the sampler tube in separate vials
  - Add 1.0 mL CS_2 to each vial
  - Attach crimp cap to each vial immediately
  - Allow to stand at least 30 min with occasional agitation
  - Ready for GC-FID analysis

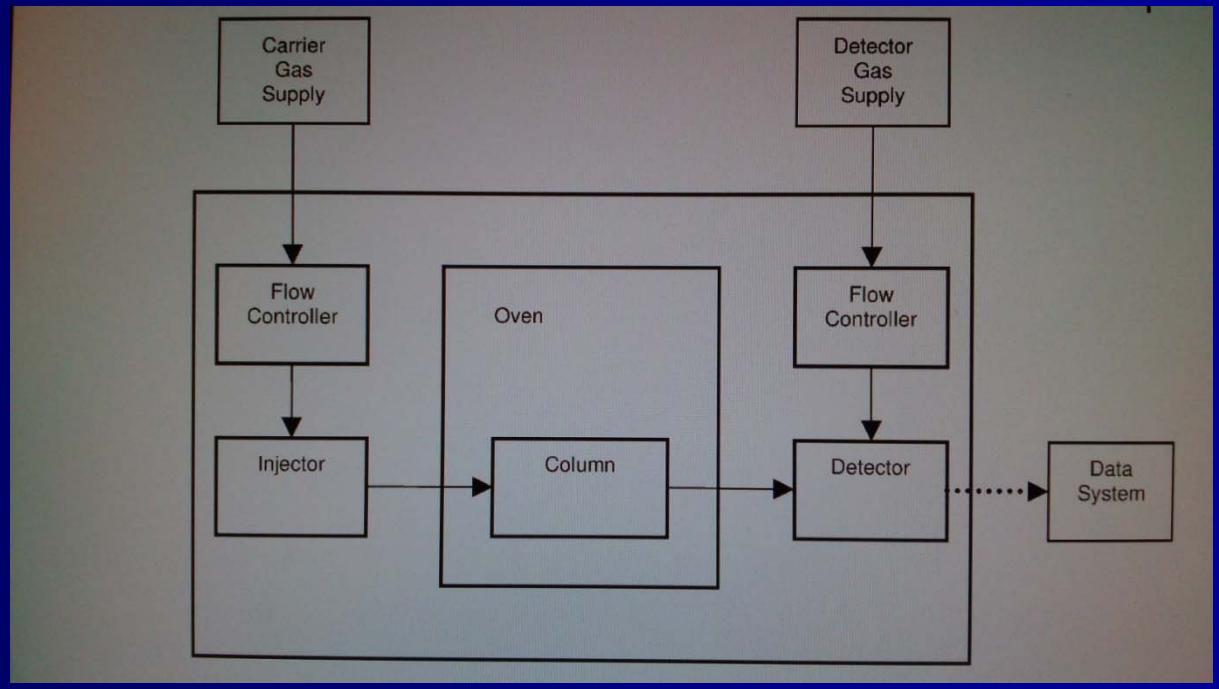
** Used for checking breakthrough*

Sampling and Analytical Methods (Cont'd)

- Instrumentation Analysis
- GC-FID or GC-MSD
  - Injection system
    - Hot or Cold
    - Split or Splitless
  - Oven
    - Isothermal or temperature programming
  - Column
    - Packed or capillary
  - Detector
    - FID, MSD or others

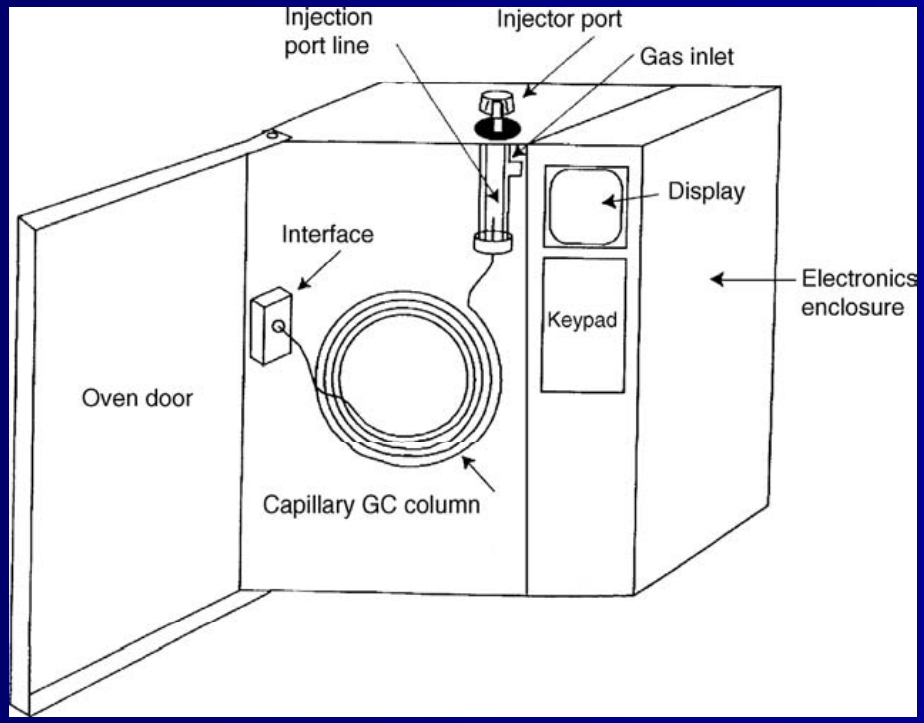
Sampling and Analytical Methods (Cont'd)

- Instrumentation Analysis (Cont'd)
- Block diagram of a typical gas chromatograph



Sampling and Analytical Methods (Cont'd)

- Instrumentation Analysis (Cont'd)
- Typical GC System

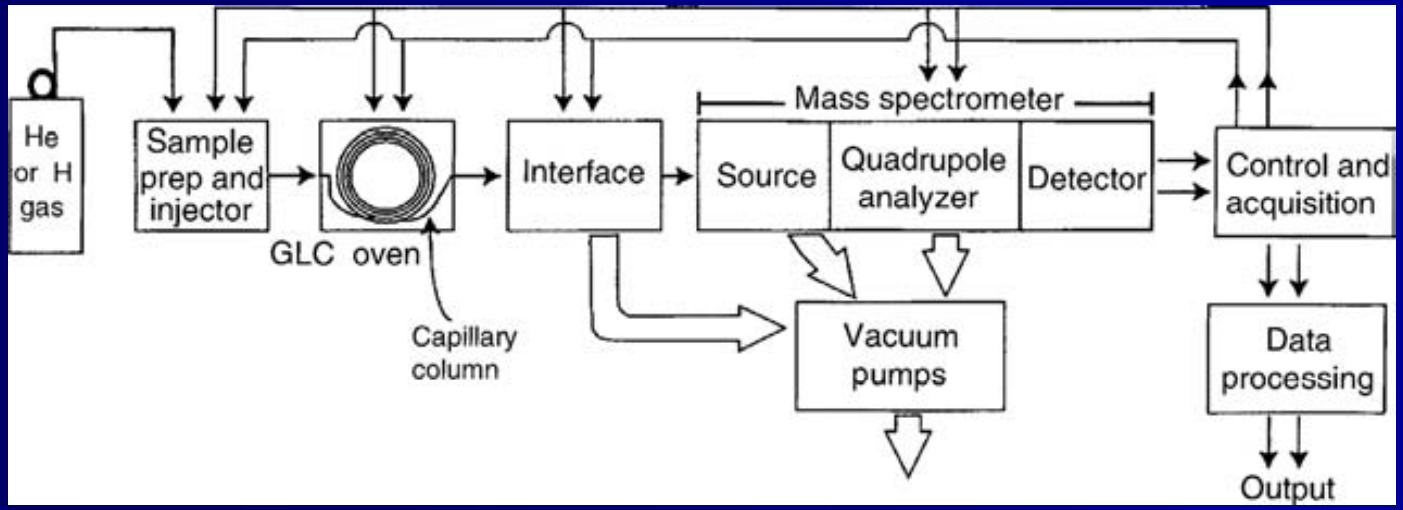


Sampling and Analytical Methods (Cont'd)

- Instrumentation Analysis (Cont'd)
- Typical GC-FID System

Sampling and Analytical Methods (Cont'd)

- Instrumentation Analysis (Cont'd)
- Typical GC-MSD System



Sampling and Analytical Methods (Cont'd)

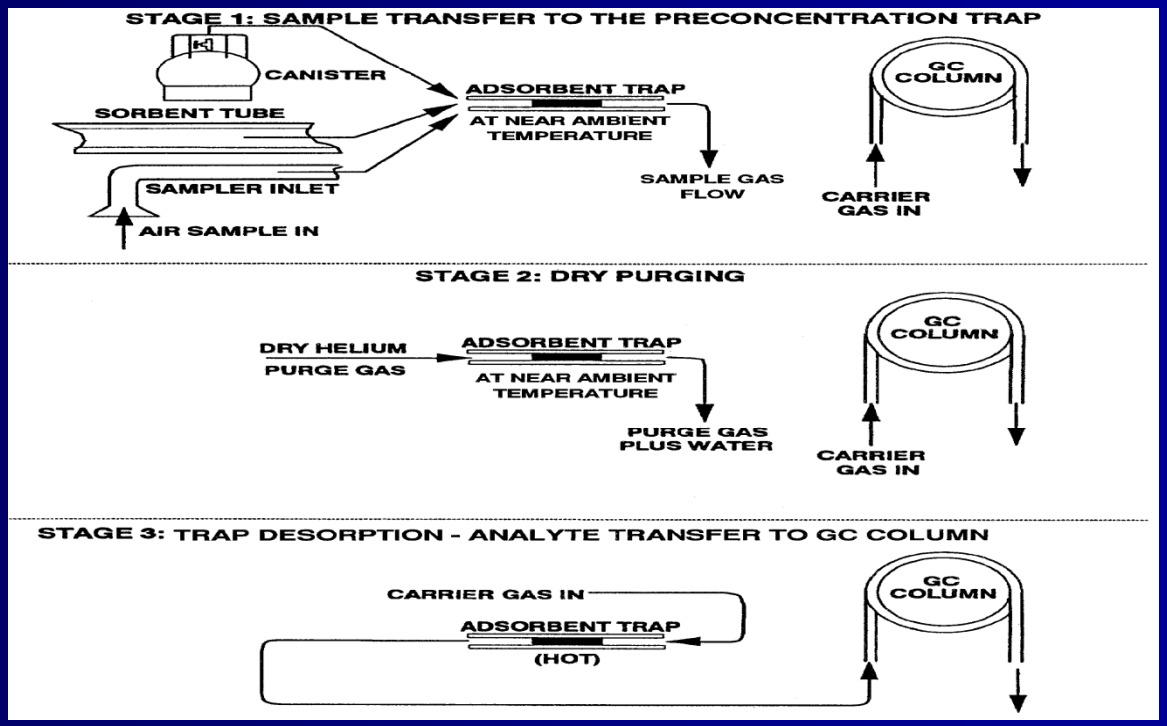
- Instrumentation Analysis (Cont'd)
- Typical GC-MSD System

Sampling and Analytical Methods (Cont'd)

- Instrumentation Analysis (Cont'd)
- Analytical System for Canister Sampling (Active/Passive)
- Preconcentrator
  - To remove water content and carbon dioxide
  - As an inlet to GC-MSD system
- GC-MSD System
  - To determine the VOCs concentration
  - Normally reported in ppbv level

Sampling and Analytical Methods (Cont'd)

- Instrumentation Analysis (Cont'd)
- Analytical System for Canister Sampling (Cont'd)



Sampling and Analytical Methods (Cont'd)

- Instrumentation Analysis (Cont'd)
- Analytical System for Canister Sampling (Cont'd)

Sampling and Analytical Methods (Cont'd)

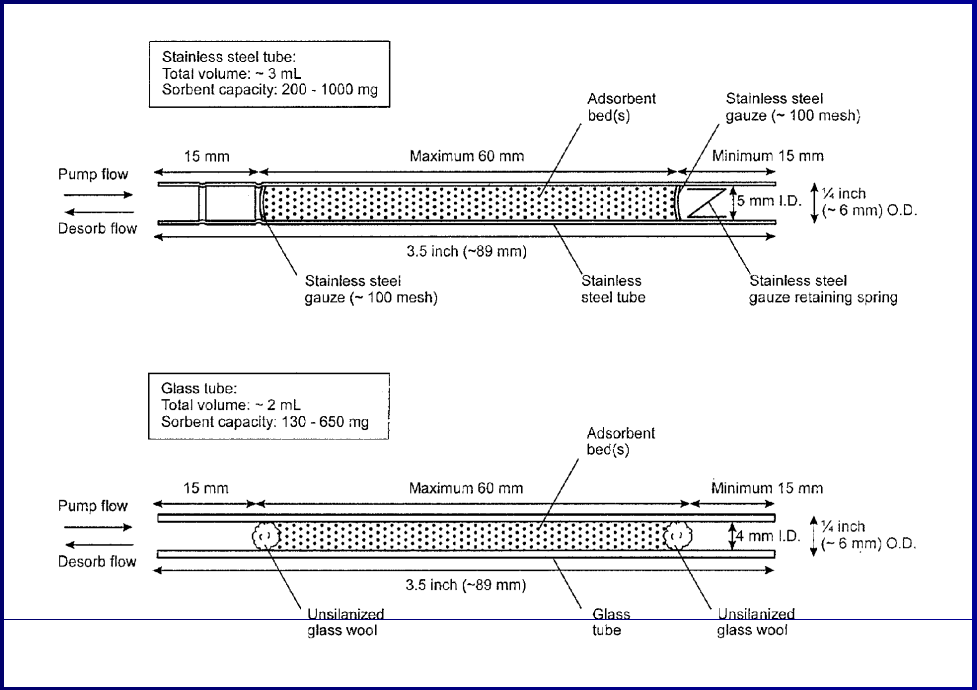
- Instrumentation Analysis (Cont'd)
- Analytical System for Canister Sampling (Cont'd)

Sampling and Analytical Methods (Cont'd)

- Instrumentation Analysis (Cont'd)
- Analytical System for Thermo-desorption Tube Sampling
- Thermo-desorber
  - To remove air and refocuses analytes on a secondary trap
  - As an inlet to GC-MSD system
- GC-MSD System
  - To determine the VOCs concentration
  - Reported in ppmv or ppbv level

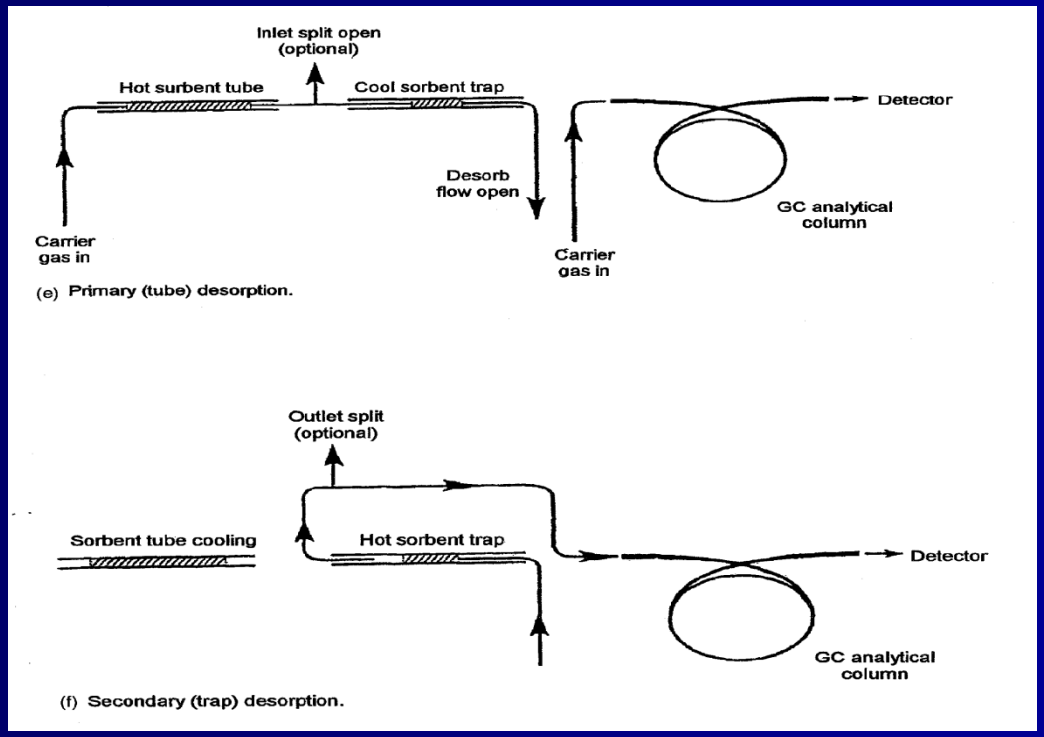
Sampling and Analytical Methods (Cont'd)

- Instrumentation Analysis (Cont'd)
- Analytical System for Tubes Sampling (Cont'd)



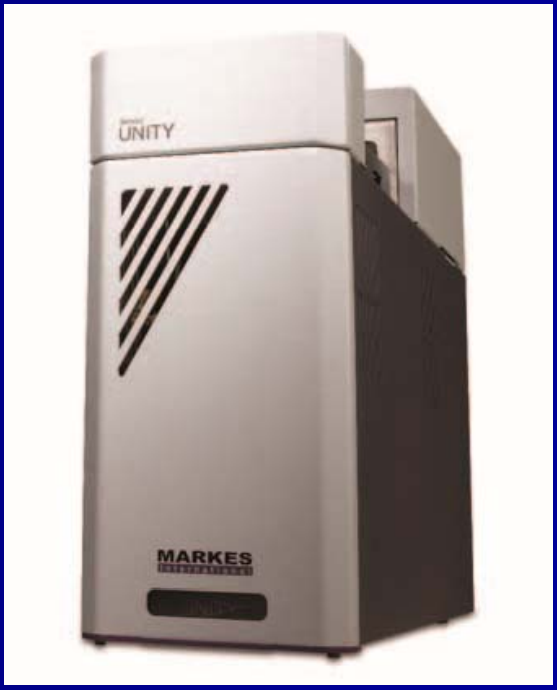
Sampling and Analytical Methods (Cont'd)

- Instrumentation Analysis (Cont'd)
- Analytical System for Tubes Sampling (Cont'd)



Sampling and Analytical Methods (Cont'd)

- Instrumentation Analysis (Cont'd)
- Analytical System for Tubes Sampling (Cont'd)



Accreditation

- What is accreditation?
- ISO/IEC 17000 definition
  - "***Third party attestation*** related to a conformity assessment body conveying a ***formal demonstration of its competence*** to carry out ***specific conformity assessment tasks***"
- What is the meaning?

Accreditation (Cont'd)

- "Accreditation Body" as "authoritative body that performs accreditation"
- Hong Kong Accreditation Service (HKAS) is the "Accreditation Body" in Hong Kong
- HKAS under Innovation and Technology Commission (ITC) of HKSAR

Accreditation (Cont'd)

- Conformity assessments activities are activities carried out to demonstrate that **specified requirements** relating to a product, process, system, person or body are fulfilled.
- Examples are testing, calibration, certification and inspection.

Accreditation (Cont'd)

- A third party is independent of both the conformity assessment body to be accredited and its customers
- Accreditation is granted to conformity assessment bodies, i.e., organisations performing testing, calibration, certification, inspection, etc. rather than individuals

Accreditation (Cont'd)

- "Competence" as "the ability to do something well or effectively"
- Most effort of accreditation is spent for assessing and monitoring competence.
- accreditation is applicable only to "specific conformity assessment tasks". In other words, accreditation is task specific.

Accreditation (Cont'd)

- the specific tasks an accredited organisation is accredited for performing are activities listed in its scope of accreditation.
- Any activities not listed in the scope are not covered under the accreditation.

Accreditation (Cont'd)

- Participation in HKAS accreditation schemes is voluntary
- In Hong Kong SAR, there is no statute to require laboratories, certification bodies or inspection bodies to obtain accreditation.

Accreditation (Cont'd)

- **Benefits of Accreditation**
  - Through gaining accreditation, organisations obtain formal and third party recognition of their competence
  - They can then demonstrate to their customers and to appropriate authorities that they are capable of working in accordance with currently accepted standards and practice

Accreditation (Cont'd)

- **Benefits of Accreditation (Cont'd)**
  - both accredited organisations and their customers, and through them community at large, benefit from accreditation

Thank you