Measurement of Ambient Air Volatile Organic Compounds (VOCs)

CHEM/TOX 3360, Environmental Chemistry and Toxicology

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Outline

- What are VOCs?
- Typical VOC target compounds
- Measurement of VOC target compounds
- Assignments

What are VOCs?

Volatile organic compounds (VOCs) are usually defined as any organic compound with a boiling point between -35 and 220°C

VOC Target Compounds

- Non-methane organic compounds – non-polar examples:
  - ethylene, acetylene, ethane, propylene, propane, butane, hexane, heptane, propene, methylcyclohexane, isobutane, butene, toluene, isopentane, ethylbenzene, xylenes, styrene, isoprene, isopropylbenzene, cyclopentane, hexene, decane, methylcyclopentane, diethylbenzene, benzene, cyclohexane
- Polar examples:
  - formaldehyde, acetone, acetaldehyde

Sources of VOC Emissions

- Vehicle exhaust
- Industrial vapors
- Waste incinerators
- Thermal power plants
- Human activities
- Trees (isoprenes & terpenes)

Why VOC Analysis?

- To monitor the extent and degree of VOCs that impact human health and environment
- To monitor compliance with regulations
- To evaluate the effectiveness of abatement and environmental protection efforts
- To reduce ground level ozone, particulates and air toxics

Who Does VOC Analysis in Ontario ?

- Ontario Ministry of the Environment
- Environment Canada
- Contract and grant supported laboratories
- Local environmental interest group (e.g., Lambton Industrial Society)
- Universities (e.g., York University)

VOC Analytical Methods (pre-1990)

- TO-1, Tenax solid sorbent cartridge sampling and (GC/MS) analysis for non-polar VOCs with boiling points (b.p.) from 80 to 200°C
- TO-2, Carbon molecular sieve solid sorbent sampling and GC/MS analysis for non-polar VOCs with b.p. from -15 to 120°C
- TO-3, Cryogenic trapping and GC/FID or ECD analysis for non-polar VOCs with b.p. from -15 to 200°C
- TO-5, Dinitrophenyhydrazine liquid impinger sampling and HPLC/UV analysis for polar VOCs such as aldehydes and ketones

TO-1 to TO-13, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, R.M. Riggin and L.J. Purdue, EPA-600/4-84-041

CarboSieve/CarboTrap solid sorbent sampling and dual-column GC/dual-FID analysis for non-polar VOCs with b.p. from -35 to 220°C (LSB Method E3314, MOEE)

GC/MS: gas chromatography/mass spectrometry
FID: flame ionization detector
ECD: electron capture detector
HPLC/UV: high performance liquid chromatography/ultraviolet detector

VOC Analytical Methods (post-1990)

- TO-14, Summa canister sampling and GC/MS analysis for non-polar VOCs with b.p. from -35 to 220°C
- TO-15, Summa canister sampling and GC/MS analysis for VOCs with b.p. from -35 to 220°C
- TO-16, Open-path FT-IR measurement and classic least square determination for polar and non-polar VOCs with b.p. from -35 to 220°C
- TO-17, Solid sorbent sampling, dry purge, GC/AAD analysis (pending on final publication). TO-17 will replace TO-1 and TO-2 upon its publication

MOEE Method E3314B, CarboTrap300/CarboSieve/Carboxen solid sorbent sampling, dry purge, GC/MS analysis with deuteriated method surrogate

FT-IR: Fournier Transform-Infrared
GC/ADD: gas chromatography/atomic adsorption detector

Outline

- Photochemical Assessment Monitoring Stations (PAMS)
- Target compounds of PAMS
- Measurement of PAMS target compounds
- Assignments

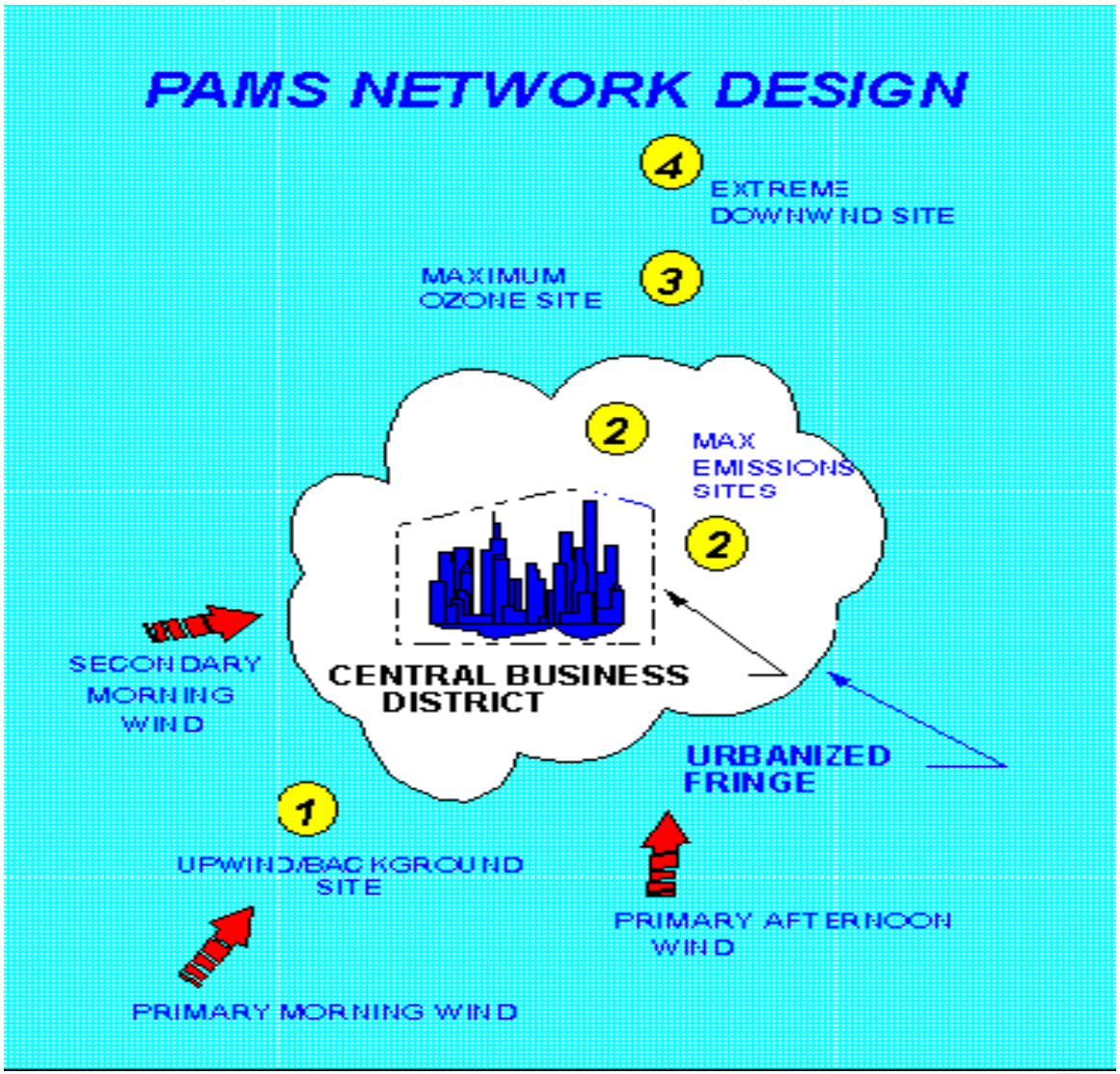
What is PAMS ?

- Enhanced real-time monitoring of ozone, oxides of nitrogen (NOx), and VOCs to obtain more comprehensive and representative data on ozone air pollution

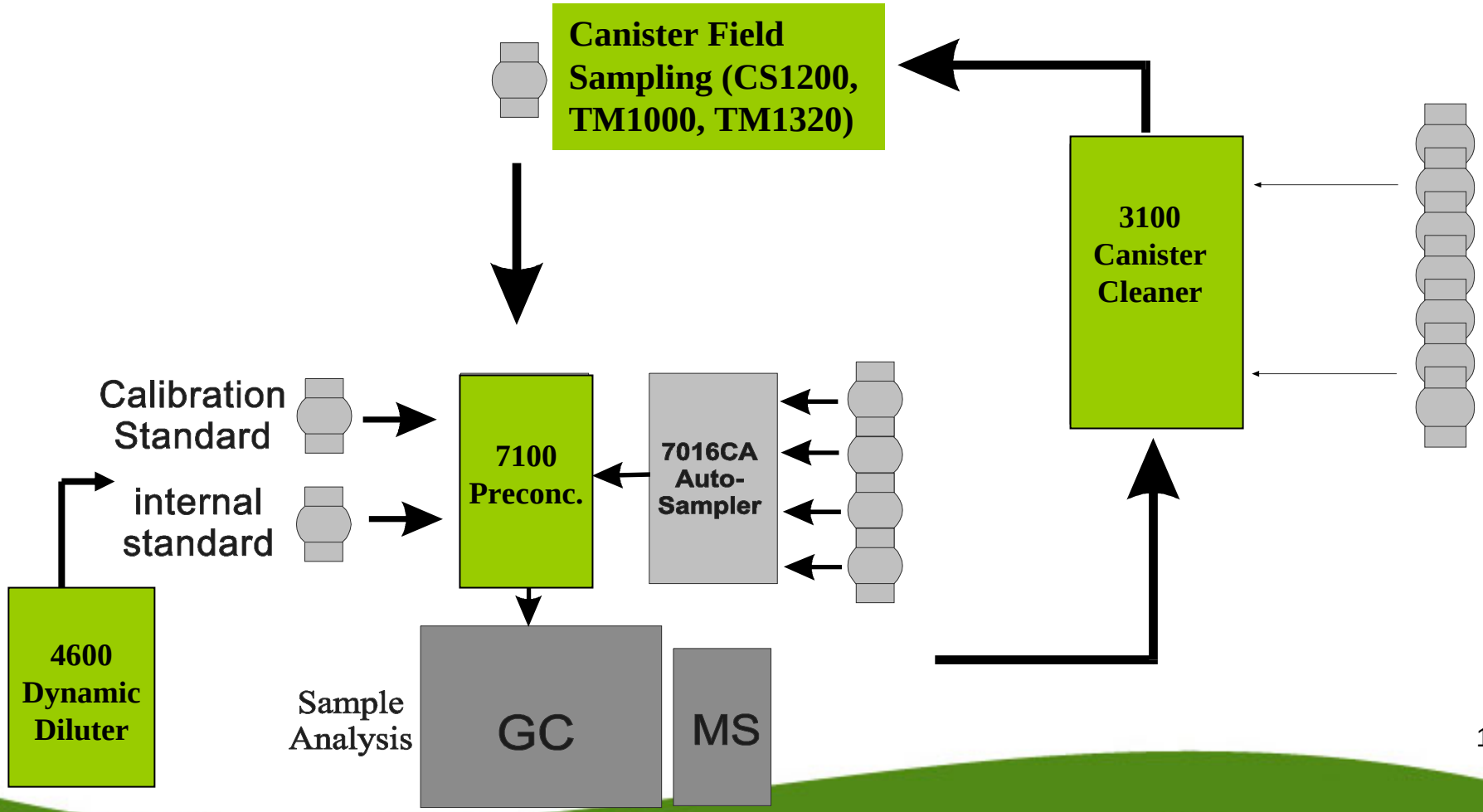
- Chief objective: provide air quality database to assist air pollution control agencies in evaluating, tracking and, if necessary, refining control strategies for attaining the ozone regulatory limits

- 38 1-hour ozone nonattainment areas in the US: 24 are classified as serious or severe or extreme and are subject to PAMS. Only 22 operating networks currently exist.

http://www.epa.gov/oar/oaqps/pams/general.html

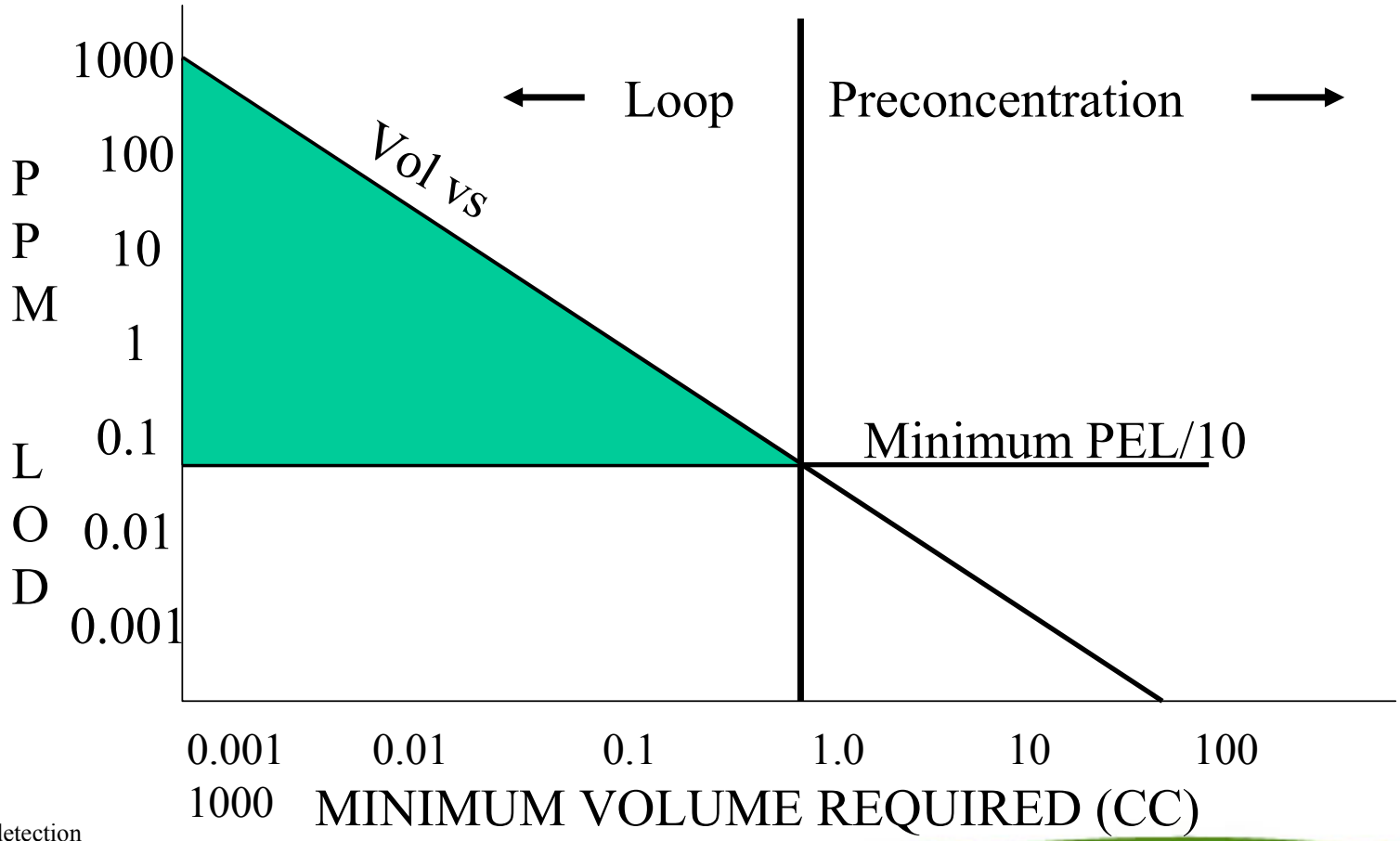


Canister Based VOC Analysis
US Environmental Protection Agency (US EPA) Method TO14/T015 Applications



From the Drawing Board to Laboratory Equipment

Minimum Volume vs Concentration Requirements for VOC Analysis

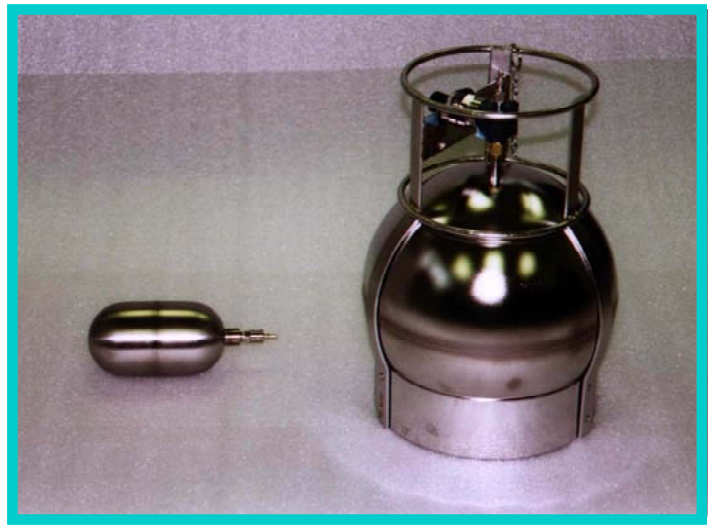


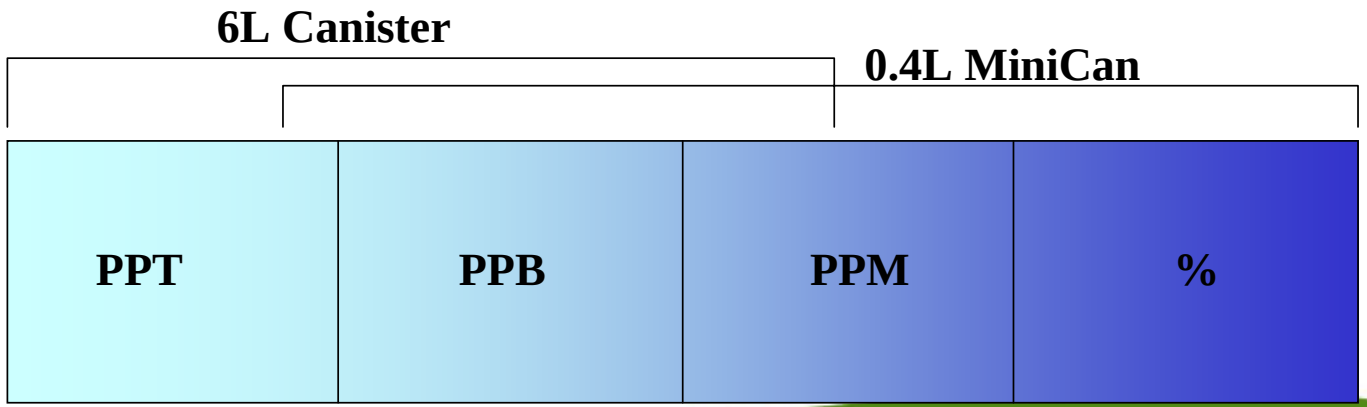
LOD: limit of detection
PEL performance evaluation level

MiniCan Technology
Complimentary to 6L Canisters

Sub-ppb ambient air analysis (TO14) requires large sample sizes (1L) and therefore large canisters.

ppb-ppm analysis requires small sample sizes (0.1 to 20 cc) and therefore smaller canisters can be used.





Passive Field Sampling Strategies

Grab Sample:

Canister fills in 5 – 10 seconds with no restriction.

Restricted Grab Sample:

Canister fills in 3 – 15 minutes with critical orifice

Regulator Integrated Sample:

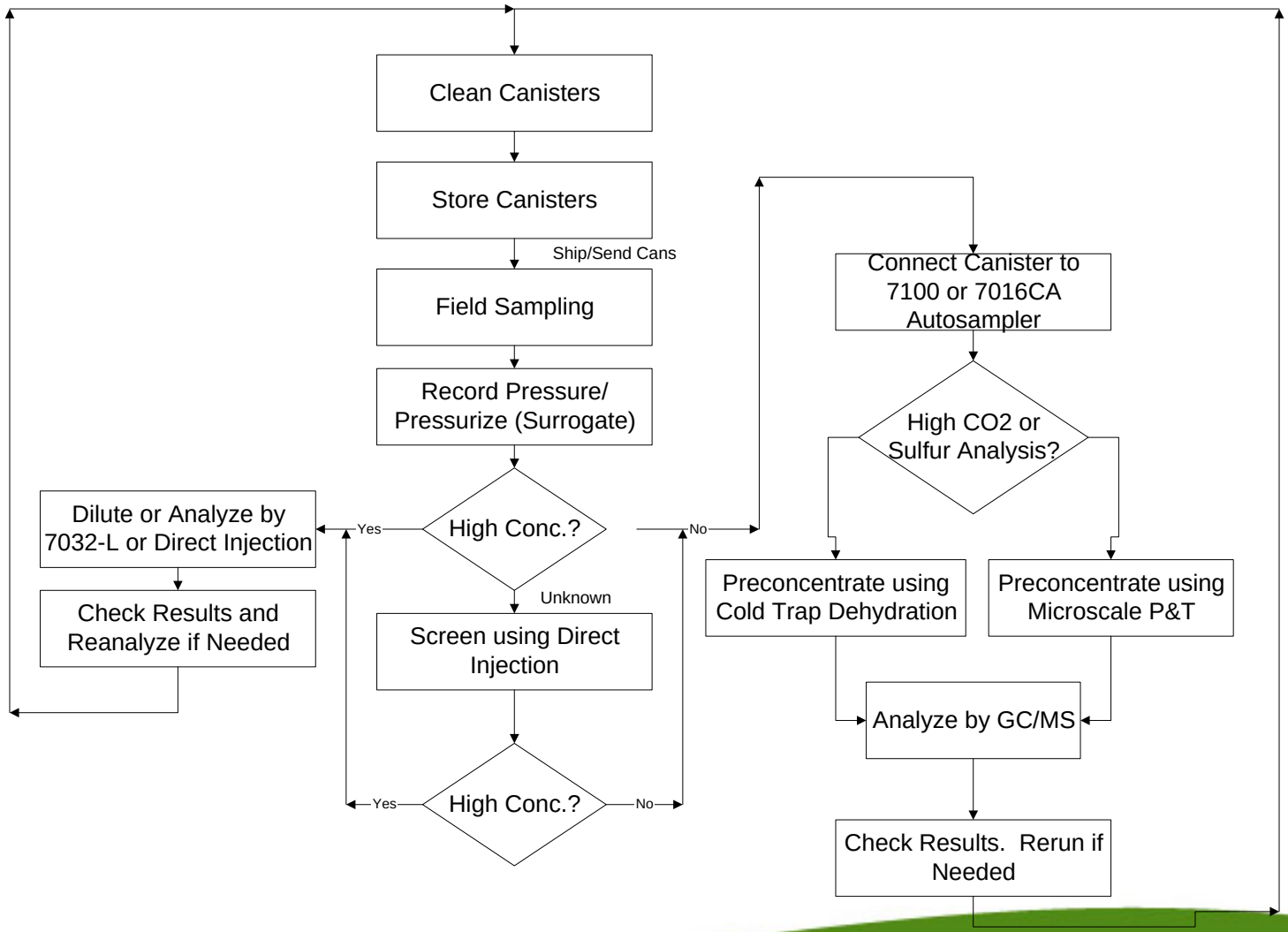
Canister fills at a constant rate usually over 0.5 hour to 1 week without using power to find average VOC concentration

Passive Sampling – The Most Popular Approach

- **Field sampling of ambient level VOCs (TO14 / TO15)**
- **Maintains constant fill rates over 1,3,8, or 24 hours, or 1 week.**
- **Combines pressure regulation with sapphire orifice technology to maintain a constant flow over a wide temperature range**
- **Ultra inert fused silica lined canister maintains VOC stability for weeks.**
- **Does not require power to operate**
- **Flow rate preset in the laboratory to eliminate the need for field adjustment.**
- **Simple, rugged approach. Very little to go wrong during sampling**

CS1200E & Silonite Canister

VOC Analysis Using Canisters



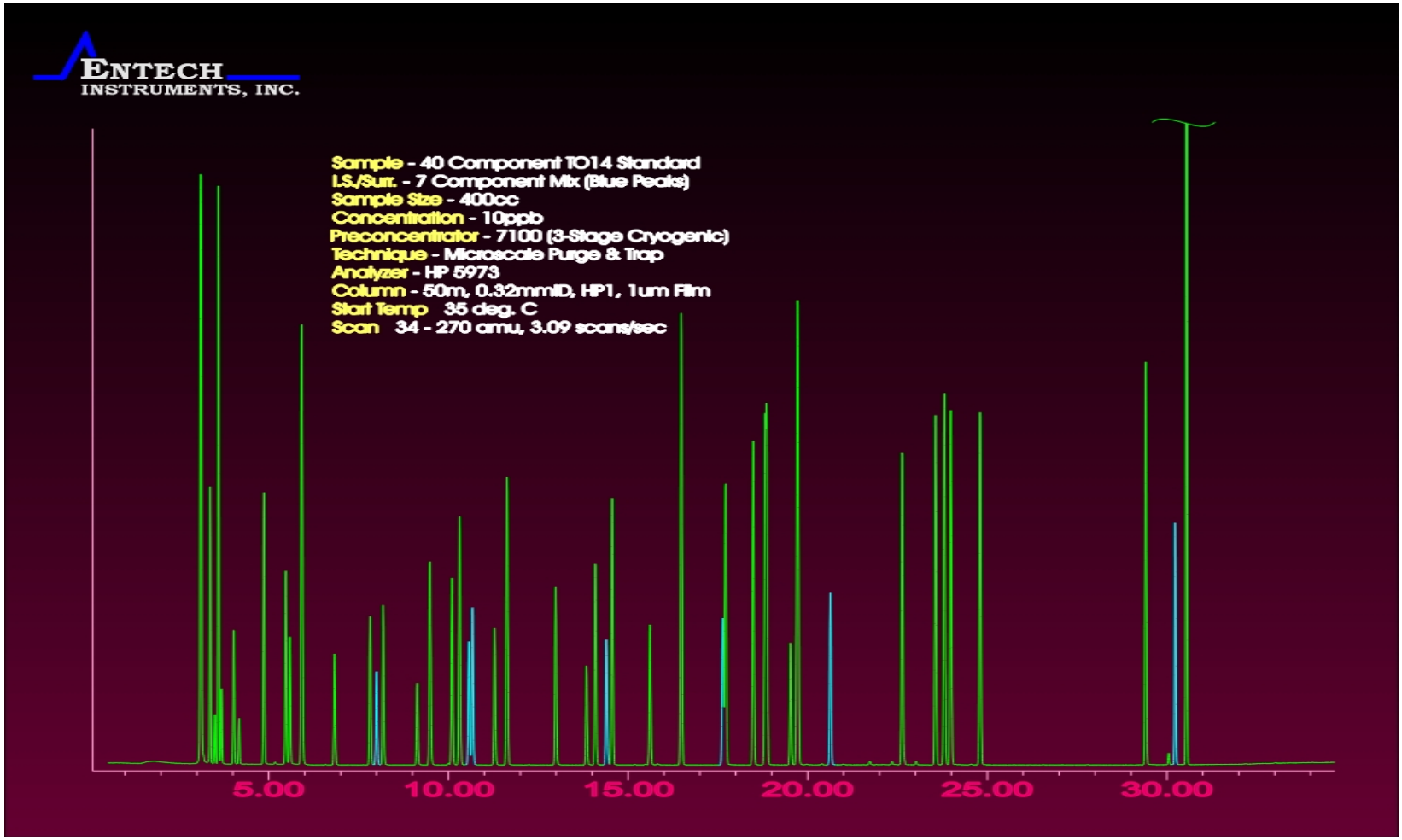
Laboratory Analysis

7100 **3-Stage Preconcentrator**

7032L **21-Position MiniCan Autosampler**

4600 **Multi-Channel Standards Diluter**

Typical Results



Analyzing Low ppb and Sub-ppb Level Samples

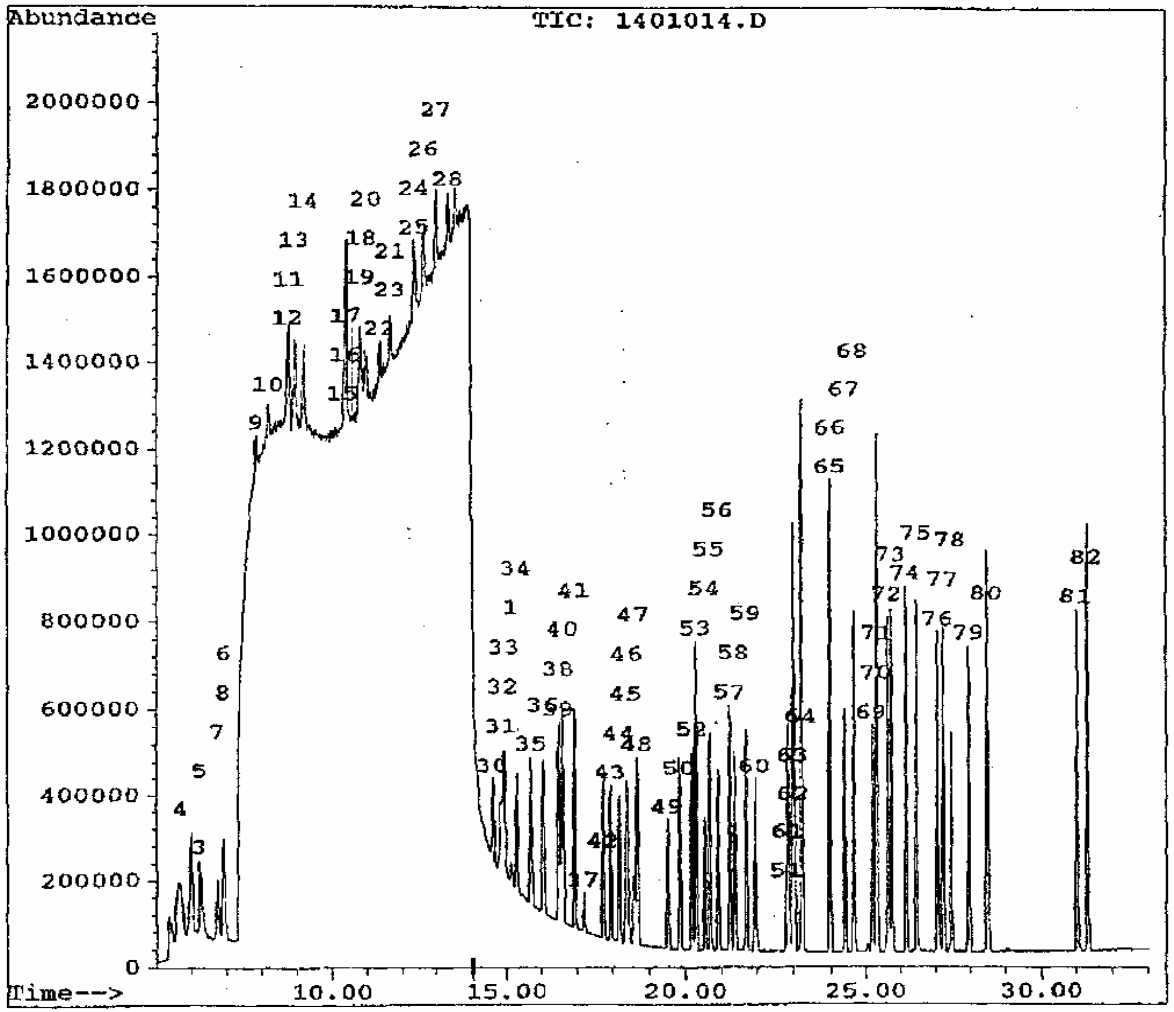
Requirement: Sample Volume 50 to 1000 mL
Canister: 6L can if LOD <1 ppb, otherwise MiniCan

For:

- Ambient / Urban Air
  - TO14, TO15
  - Freons
  - Ozone Precursors

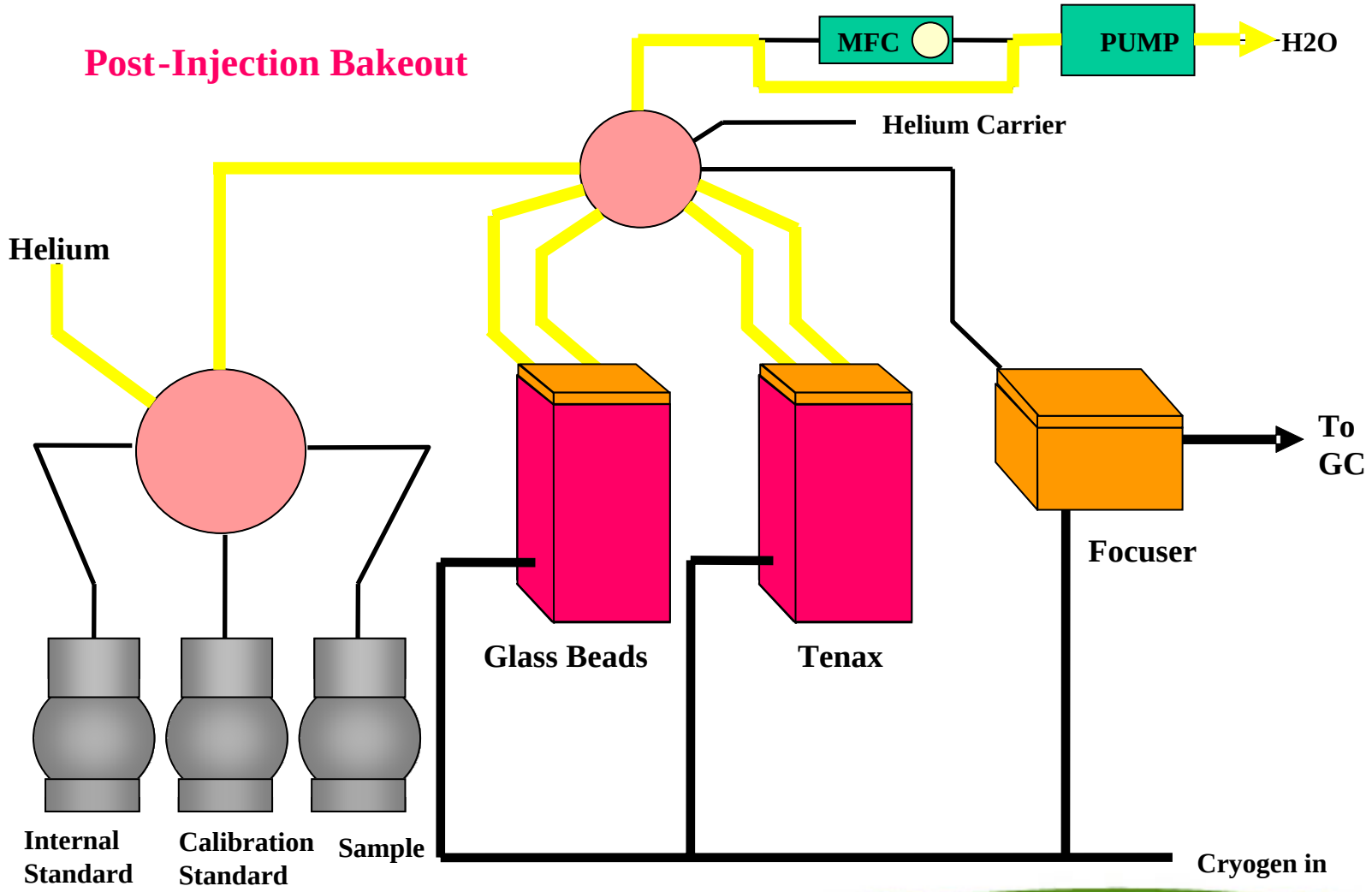
- Indoor Air Quality
  - Odors, Irritants
  - Solvents / Synthetics

Improper Water Management – Full Scan 15 – 270 amu



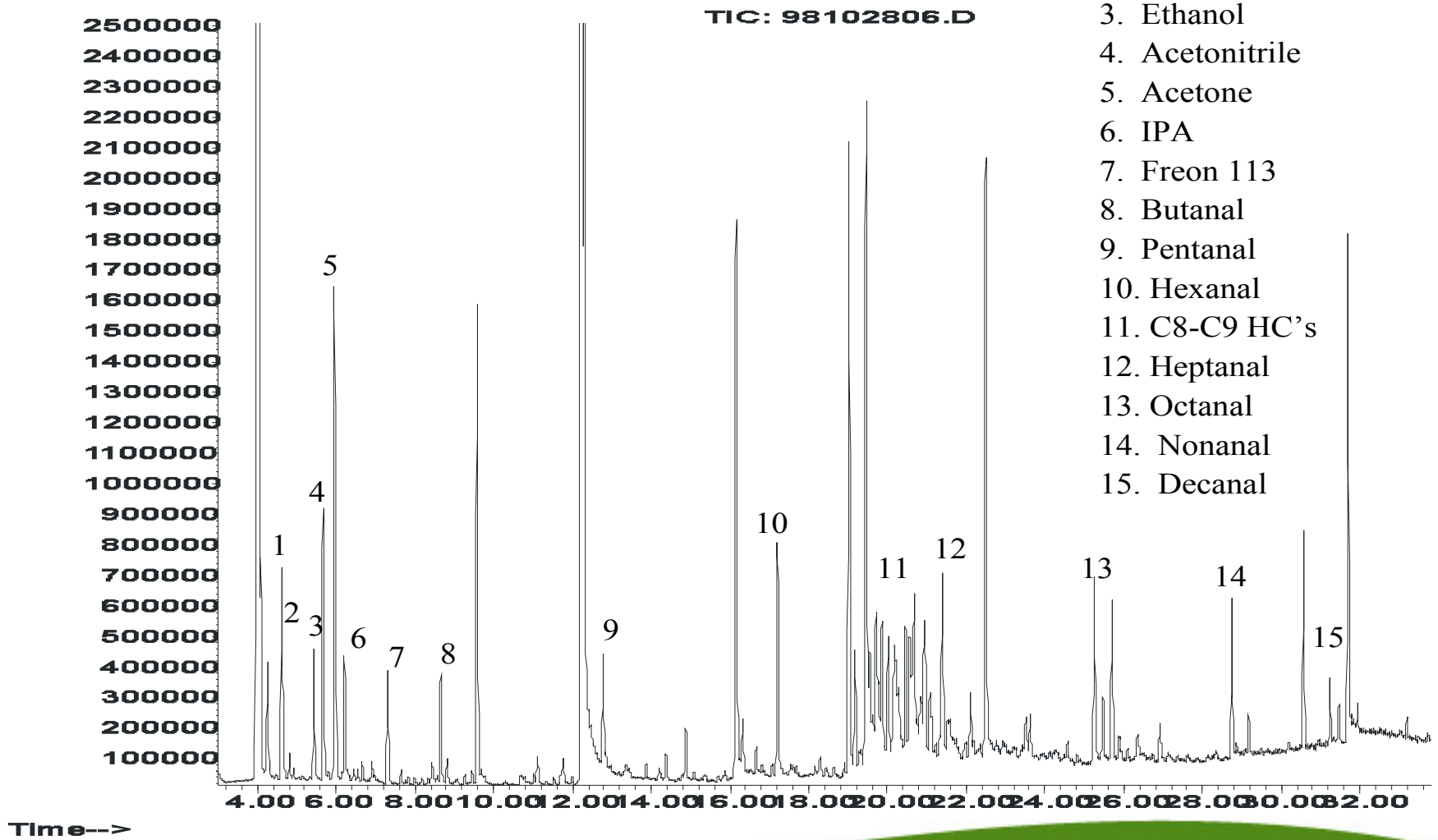
amu: atomic mass unit

7100 Water and CO_2 Management Techniques



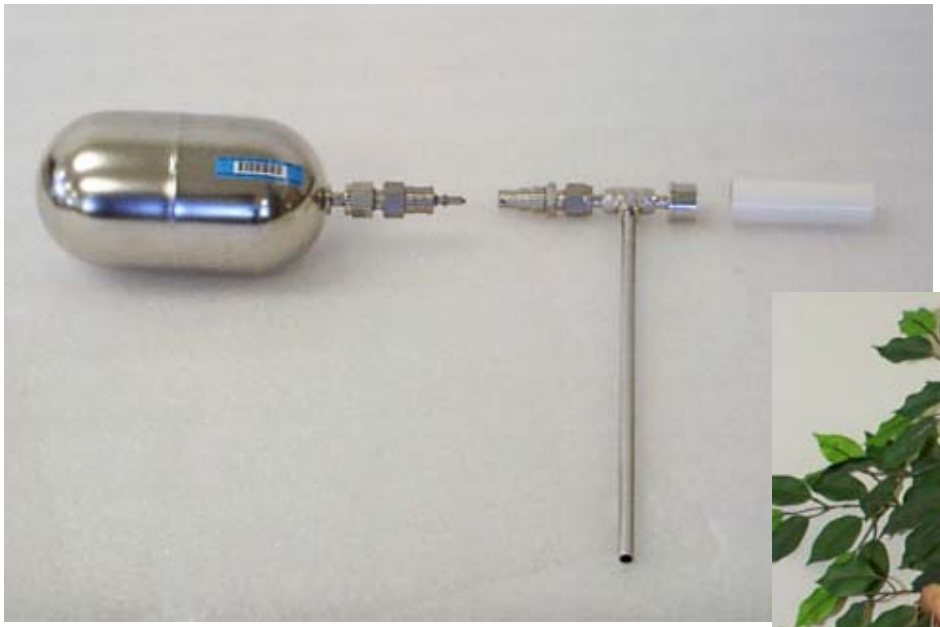
MFC: mass flow controller

Indoor Air Sampled into MC400L
50cc + Surr. Injection into 7100/5973 GCMS

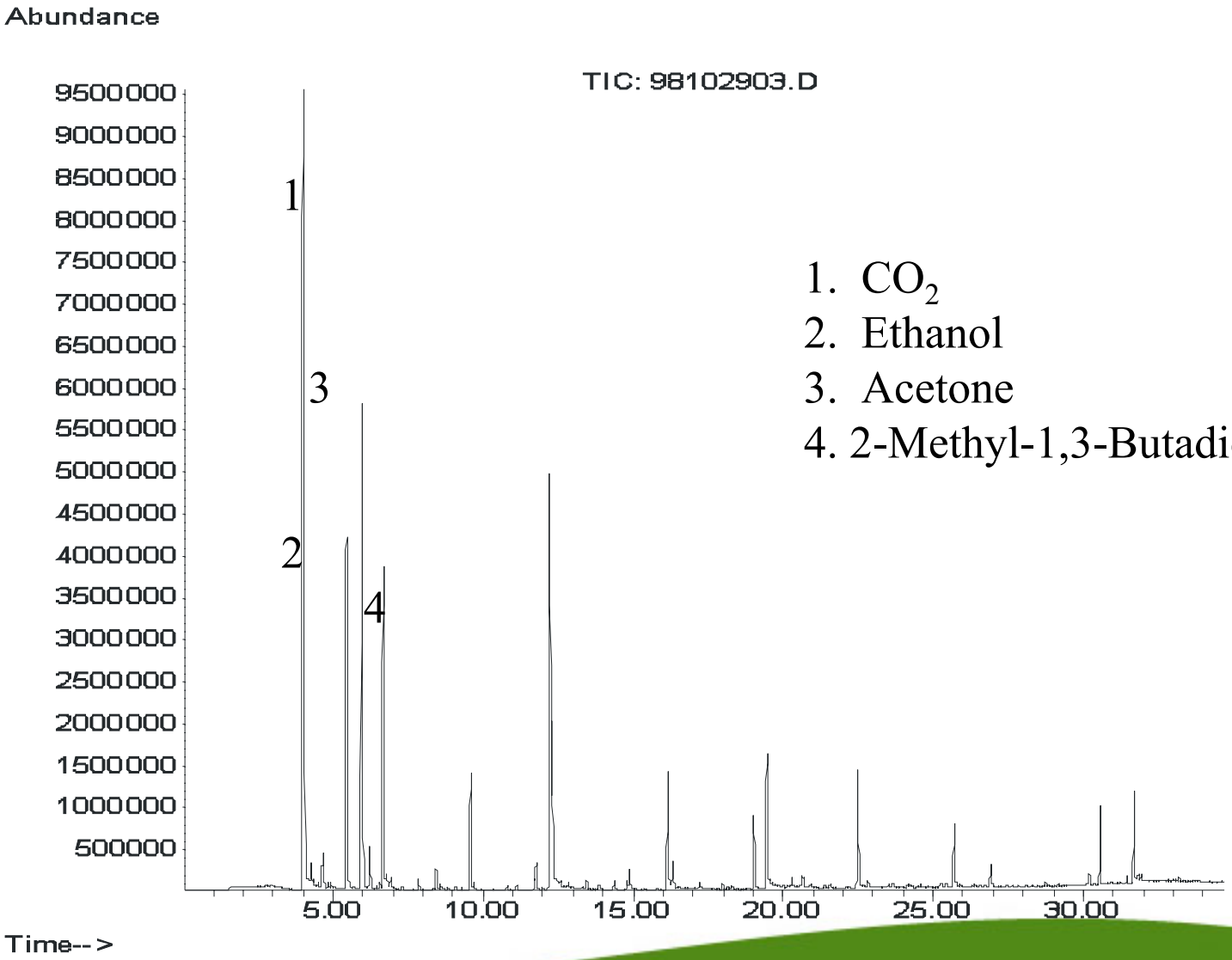


1. Norflurane
2. Acetonitrile
3. Ethanol
4. Acetonitrile
5. Acetone
6. IPA
7. Freon 113
8. Butanal
9. Pentanal
10. Hexanal
11. C8-C9 HC's
12. Heptanal
13. Octanal
14. Nonanal
15. Decanal

Low Volume Breath Sampler



VOCs in Human Breath



Homework assignments
Select one topic from the followings

- How are ozone and NO_x measured?
- Canister sampling vs cartridge sampling.
- An alternative method for VOC analysis.
- Why measurement of VOC is important?
- Pros & cons of US EPA methods TO-15 and TO-17