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Comparative analysis of air sampling strategies for VOC monitoring

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Caroline Widdowson

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An Indian Case Study….

News > Science

India's pollution crisis linked to pre-term births and low birth weight, study warns

Just 10mg increase in PM 2.5 per cubic metre of air linked to 5 per cent rise in rate of low birth weight

Quarter of all deaths worldwide linked to environmental damage and pollution, UN says

'Do we continue on our current path, which will lead to a bleak future for humankind, or do we pivot to a more sustainable development pathway? That is the choice our political leaders must make, now'

Josh Gabbatiss Science Correspondent | @josh_gabbatiss |
Wednesday 13 March 2019 12:30 |

WORLD ECONOMIC FORUM

In India, air pollution is cutting lives short by up to 11 years

Source: University of Chicago's Air Quality Life Index (AQLI)

New Delhi air pollution: Schools closed and construction stopped as smog worsens to levels far above WHO safety limit

A thick, toxic smog has enveloped India's capital, home to more than 33 million people. One technology firm which monitors air pollution ranked New Delhi as the most polluted city in the world.

Air pollution responsible for more deaths than smoking, study says

'EU lagging a long way behind' in tackling toxic air, say researchers as study shows pollution deaths double previous estimates

Alex Matthews-King Health Correspondent |
Tuesday 12 March 2019 10:45 |

We Made Plastic. We Depend on It. Now We're Drowning in It.

The miracle material has made modern life possible. But more than 40 percent of it is used just once, and it's choking our waterways.

Tuesday, 9 April 2019

Air pollution: Low ozone layer found over Brahmaputra river valley

Tropospheric, or ground level ozone, is created by chemical reactions between oxides of nitrogen (NOx) and volatile organic compounds (VOC).

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Where should we be monitoring?

Where start?:

- **Establish baseline VOC levels** using advanced analytical tools
- **Deploy real-time ambient air quality system** near industrial clusters
- **Prioritize regulation enforcement** in pollution hotspots
- **Use data for policy advocacy** and public health protection

Ref: WHO, 2018

Case Study

New Bureau of Indian Standards

- BIS 5182-27
  - Air Pollution - Methods for Measurement Part 27 Vapour-Phase Organic Chemicals Vinyl Chloride to nC22 Hydrocarbons in Air and Gaseous Emissions by Diffusive (Passive) Sampling onto Sorbent Tubes or Cartridges Followed by Thermal Desorption (TD) and Capillary Gas Chromatography (GC) Analysis.
- BIS 5182-28
  - Air Pollution - Methods for Measurement Part 28 Vapour-Phase Organic Chemicals C3 to nC22 Hydrocarbons in Air and Gaseous Emissions by Pumped Sampling onto Sorbent Tubes or Cartridges Followed by Thermal Desorption (TD) and Capillary Gas Chromatography (GC) Analysis.

Analytical Instrumentation: TD-GC-MS system

How do we monitor VOCs in air?

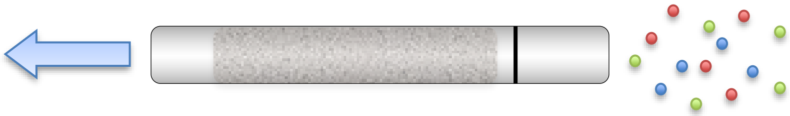
Markes – Thermal desorber (TD)

Agilent – GCMS

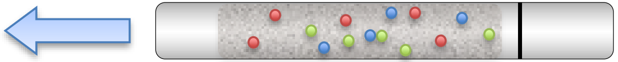
What is thermal desorption (TD)?

Sample collection on sorbent tube

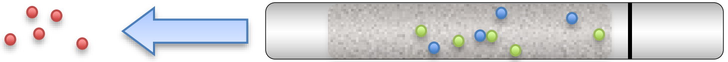
- Sample (*e.g.* air) is collected



- Compounds of interest are adsorbed on the sorbent surface



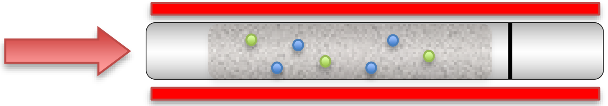
- Lighter gases such as nitrogen, argon and carbon dioxide pass through



What is thermal desorption (TD)?

Sample desorption

- Tube heated in a reversed flow of clean carrier gas (‘backflushed’)



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What is thermal desorption (TD)?

Sample desorption

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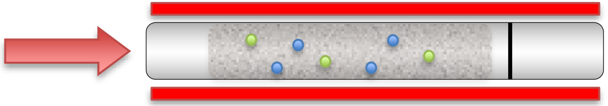
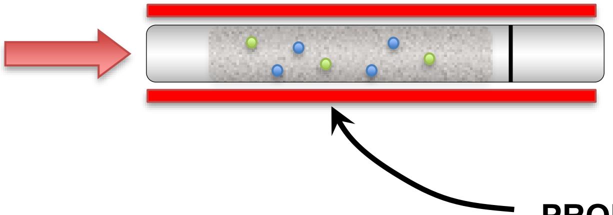
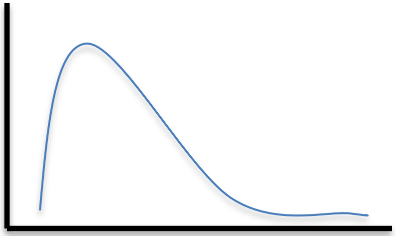


- Compounds are released from the sorbent into the flow of carrier gas





PROBLEM:

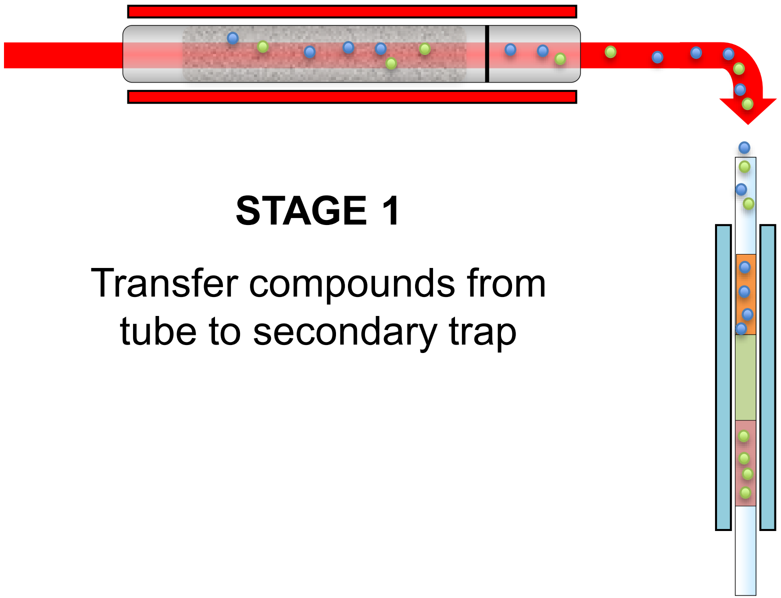
Compounds are released SLOWLY from the sorbent tube

Would lead to very wide chromatographic peaks and low sensitivity

Two stage thermal desorption

Stage 1: Sample desorption

SOLUTION: Use a narrow secondary trap



STAGE 1

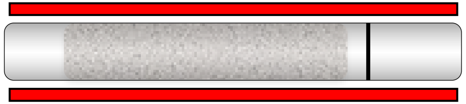
Transfer compounds from tube to secondary trap

Electrically cooled narrow bore cold trap

Two stage thermal desorption

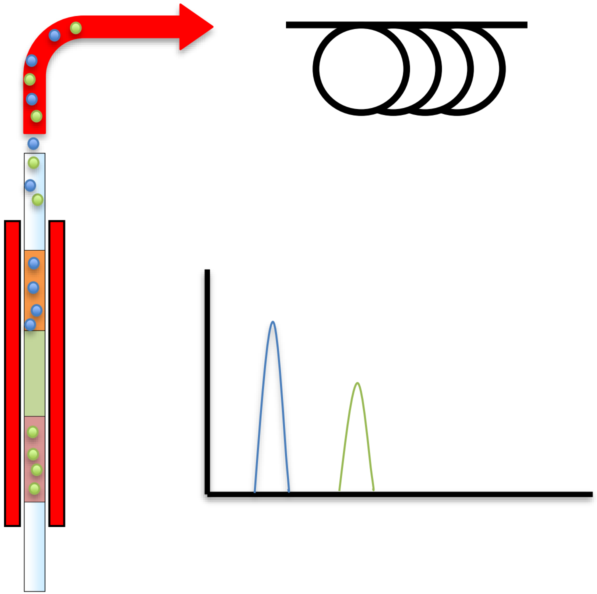
Stage 2: Trap desorption

- Cold trap heated rapidly (100°C/sec) for sharp chromatographic peaks
- **Backflush** of cold trap for greater volatility range

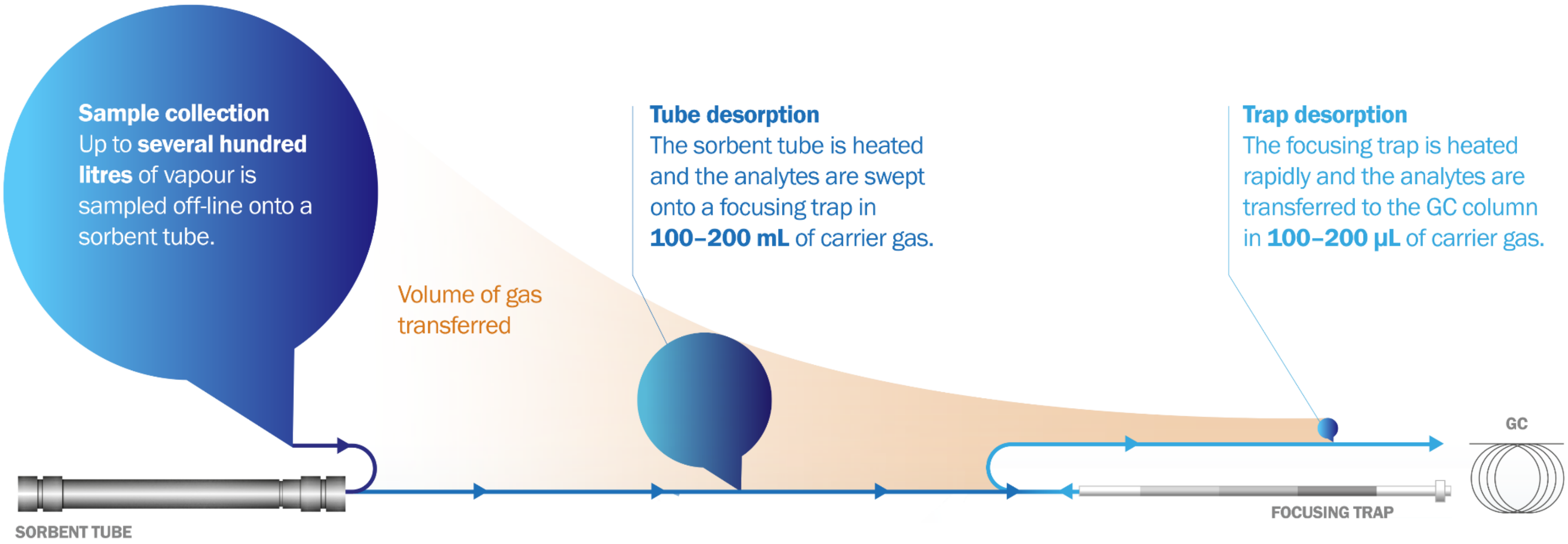


STAGE 2

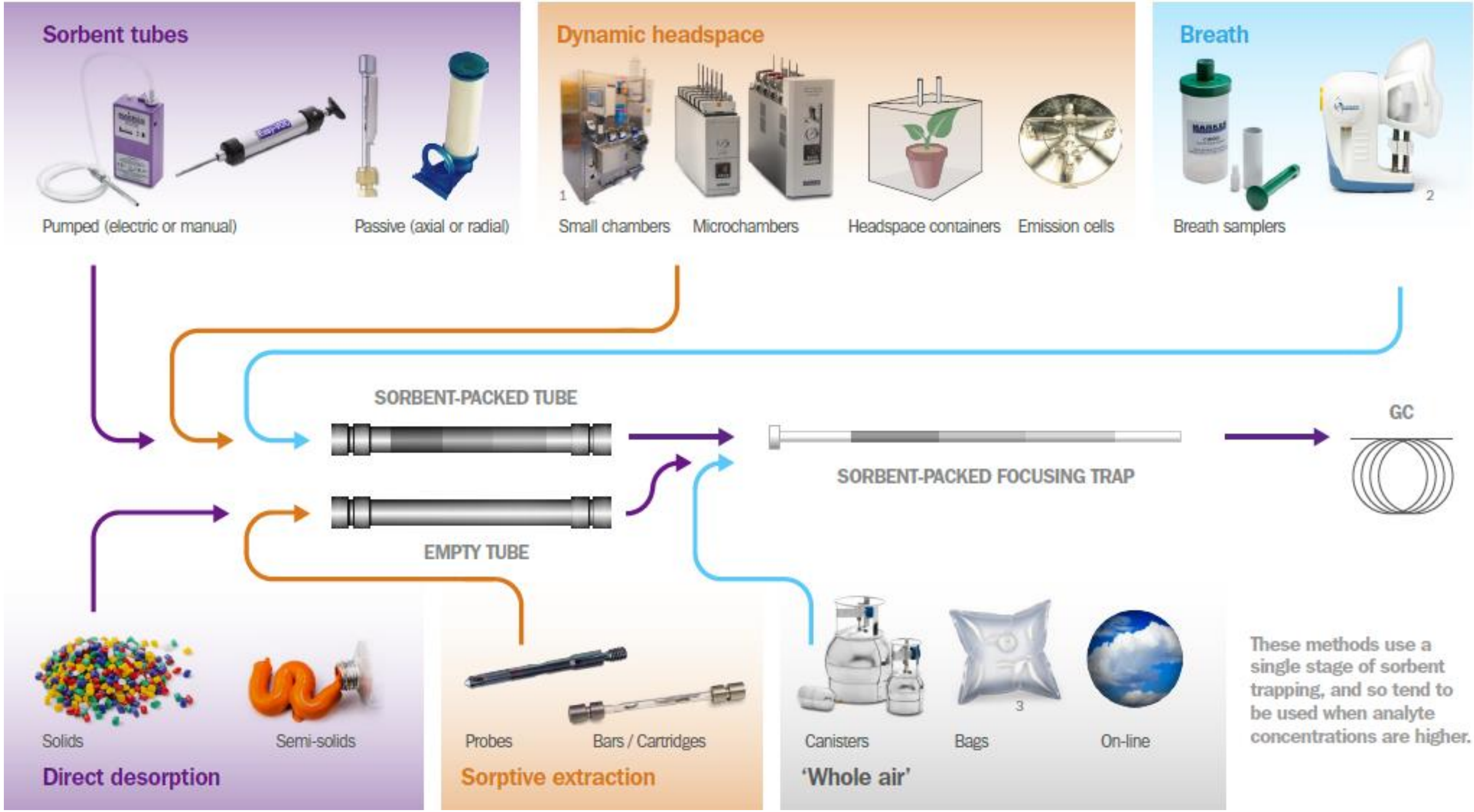
Rapid transfer of compounds from cold trap to GC



What is thermal desorption (TD)?



TD sampling options



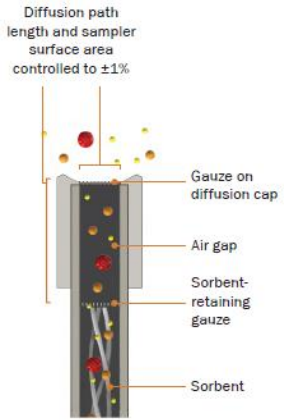
Sampling methods

Passive (Diffusive) sampling

- Simple and low-cost for large scale air monitoring studies
- Unobtrusive for personal monitoring
- Single bed sorbent
- Tube inlet must have 15 mm air gap with 5 mm I.D.

Key methods:

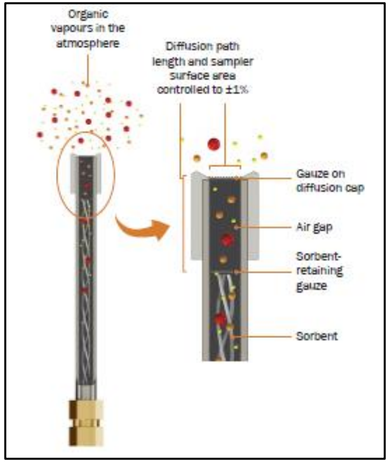
- Fenceline monitoring (US EPA Method 325)
- Ambient air quality / Industrial air (EN 14662-4)
- Indoor, ambient and workplace air (ISO 16017-2, BIS 5182-27)

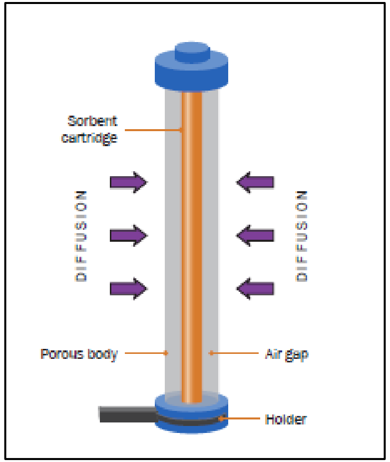


Passive sampling

Axial and Radial

- **Axial (tube based) sampling**
  - Sorbent bed exposed through diffusion cap fitted to an industry standard sorbent tube
  - The industry standard sampling route
  - Allows for short and long-term sampling (8 hours to 4 weeks)
- **Radial sampling**
  - Sorbent cartridge exposed through cylindrical (coaxial) outer surface of a diffusive body
  - Allows for a much larger exposed surface area, and a shorter diffusive path length
  - Allows faster uptake rates (typically 1 hour to 3 days)





Passive sampling

Axial

- Simple and low-cost for large scale air monitoring studies
- Unobtrusive for personal monitoring (doesn't impact human behavior)
- The mass of each VOC collected is proportional to the ambient concentration

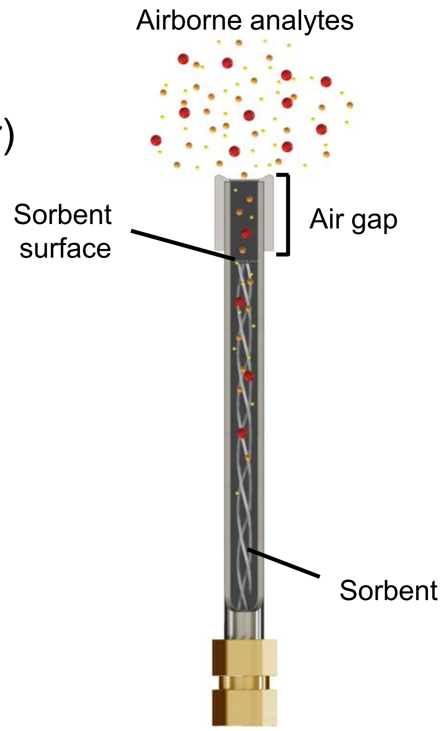
To calculate ambient concentration we need to know:

Constant

- **U: Uptake rate** → Verified, pre-published data. Dependant on air gap and surface area.

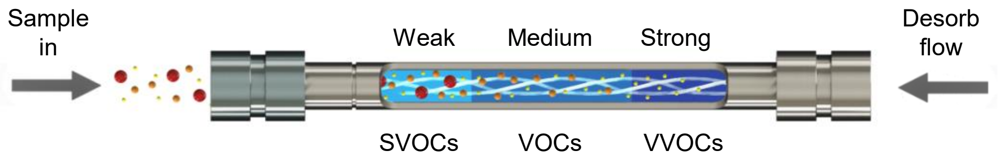
Experimentally determined

- t: Time
- M: Mass on sorbent tube



Sampling methods

Pumped (Active) sampling



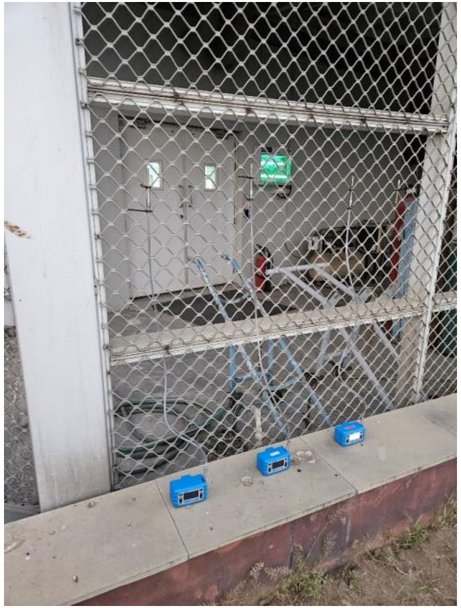
- Pump air through sorbent tube (typically 10-200 mL/min)
- Multiple sorbents ⇒ wide volatility range
- Targeted and untargeted compounds can be sampled and analysed in a single experiment

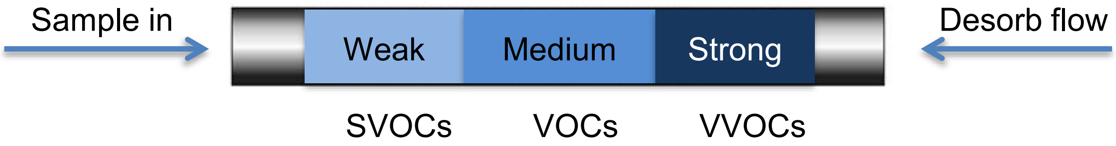
Key methods:

- PFAS (ASTM D8591-24)
- Ambient air (US EPA TO-17 / Chinese EPA HJ 644 / EN 14662-1)
- Stack emissions (CEN/TS 13649 / Chinese HJ 734)
- Indoor, ambient and workplace air (ISO 16017-1, BIS 5182-28)
- Polycyclic Aromatic Hydrocarbons (PAHs)
- Breath – Active sampling

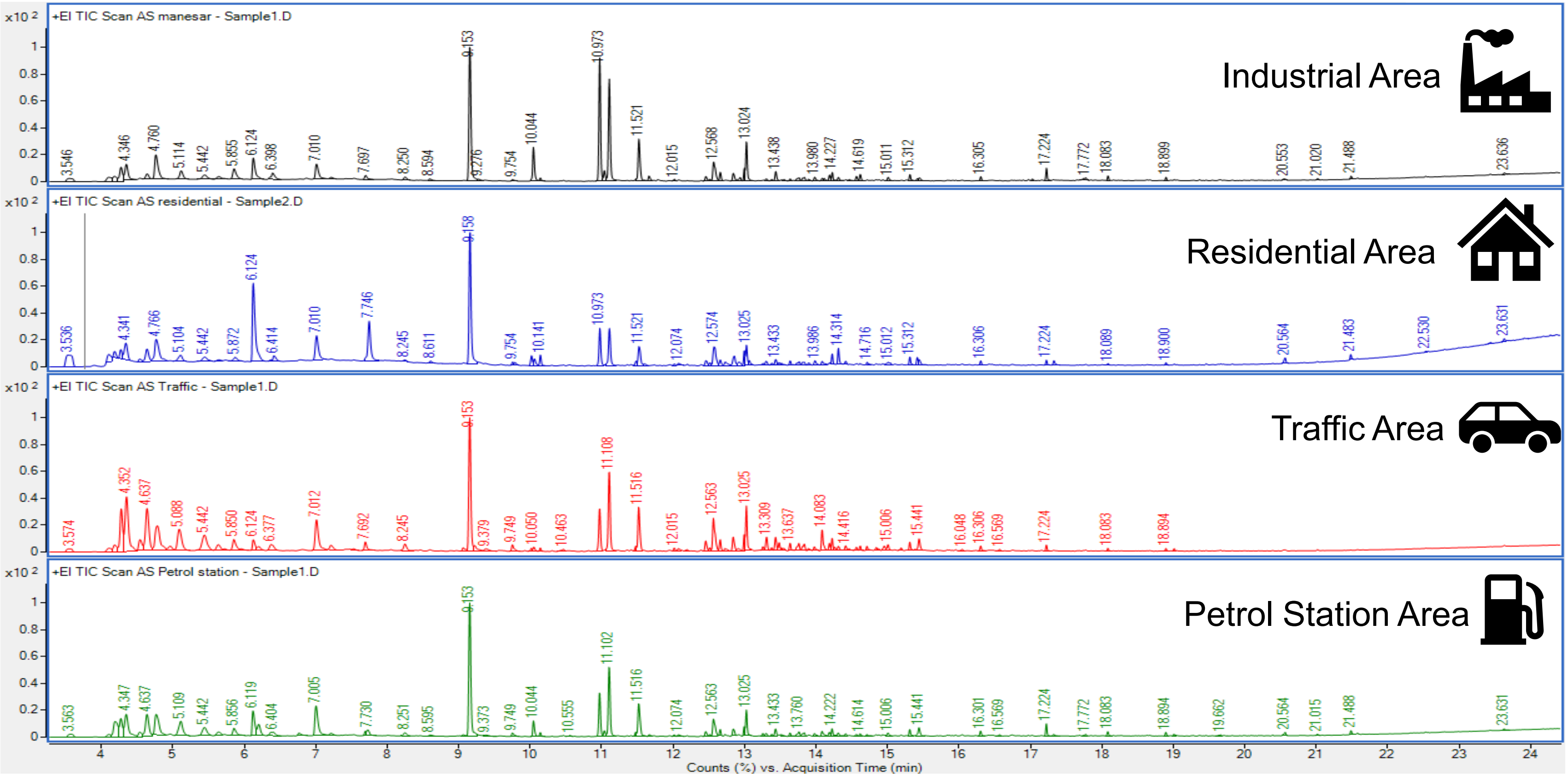
Active Sampling Experiment

- Pump air through sorbent tube
  - Flow rate: **20 mL/min**
  - Time: 1 hr
  - Volume: 1.2 L
  - 4x locations:
    - Industrial Area
    - Residential Area
    - Traffic Area
    - Petrol station





Active Sampling – Chromatogram overlays



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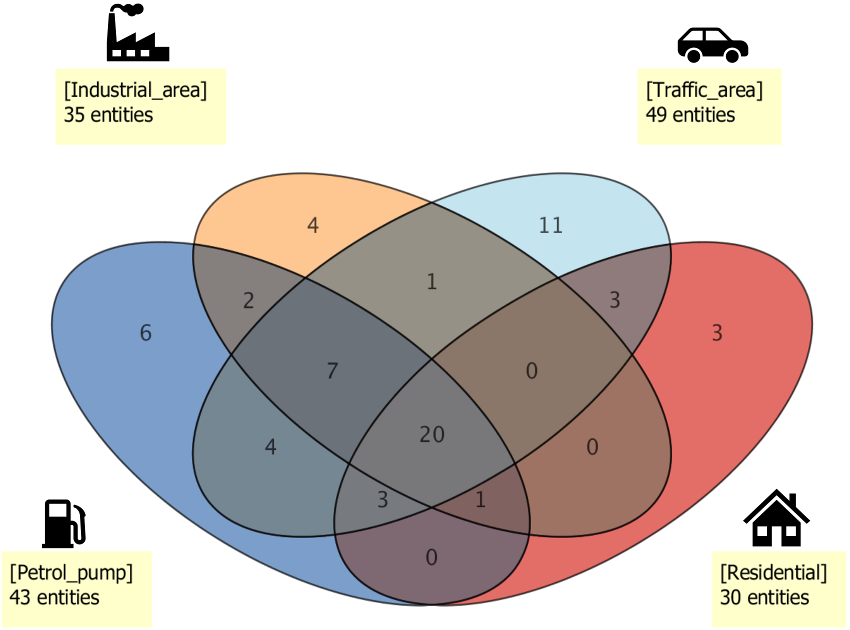
Common compounds found in all locations

Compound	RT	Mass	Formula
Isobutane	4.27	43.08	C4H10
Butane	4.35	43.07	C4H10
Butane, 2-methyl-	4.64	43.07	C5H12
Pentane, 2-methyl-	5.44	43.07	C6H14
Ethyl Acetate	6.12	43.04	C4H8O2
Benzene	7.01	78.04	C6H6
Cyclohexane, methyl-	8.25	83.07	C7H14
Toluene	9.15	91.07	C7H8
Octane	9.75	43.07	C8H18
Acetic acid, butyl ester	10.05	43.04	C6H12O2
Ethylbenzene	10.97	91.06	C8H10
Benzene, 1,3-dimethyl-	11.11	91.05	C8H10
m,p-Xylene	11.52	91.05	C8H10
Benzene, propyl-	12.46	91.04	C9H12
Benzene, 1,2,3-trimethyl-	13.24	105.05	C9H12
Indane	13.64	117.06	C9H10
Undecane	14.23	57.08	C11H24
Dodecane	15.31	57.07	C12H26
Tridecane	16.30	57.06	C13H28
Tetradecane	17.22	57.07	C14H30



Unique compounds for each location

Active sampling

- **Industrial area**
  - Heptane, 2,2,4,6,6-pentamethyl-
  - Hexadecane, 2,6,10,14-tetramethyl-
  - 2-Ethoxyethyl acetate
  - Tridecane, 6-methyl-

- **Petrol station area**
  - Cyclohexane, 1,4-dimethyl-
  - 2-Naphthalenol, decahydro-
  - 2,4-Dimethyl-1-heptene
  - Propane, 1,2-dichloro-
  - Ethanol, 2-butoxy-
  - Ethane, 1,2-dichloro-

- **Residential area**
  - Trichloroethylene
  - Cyclotetrasiloxane, octamethyl-
  - Octanal

- **Traffic area**
  - Tricyclo[5.2.1.0(2,6)]dec-4-ene, 4-methyl-
  - 2-Heptene, (E)-
  - Heptane, 3-methyl-
  - 3a,4,5,6,7,7a-Hexahydro-4,7-methanoindene
  - Linalool
  - Furan, 3-methyl-
  - Butane, 2,2-dimethyl-
  - Cyclohexane, 1,3-dimethyl-, cis-
  - Cyclohexanol, 5-methyl-2-(1-methylethyl)-
  - Cyclohexane, ethyl-
  - 1H-Indene, 2,3-dihydro-1,6-dimethyl-

Quantification of BTEX

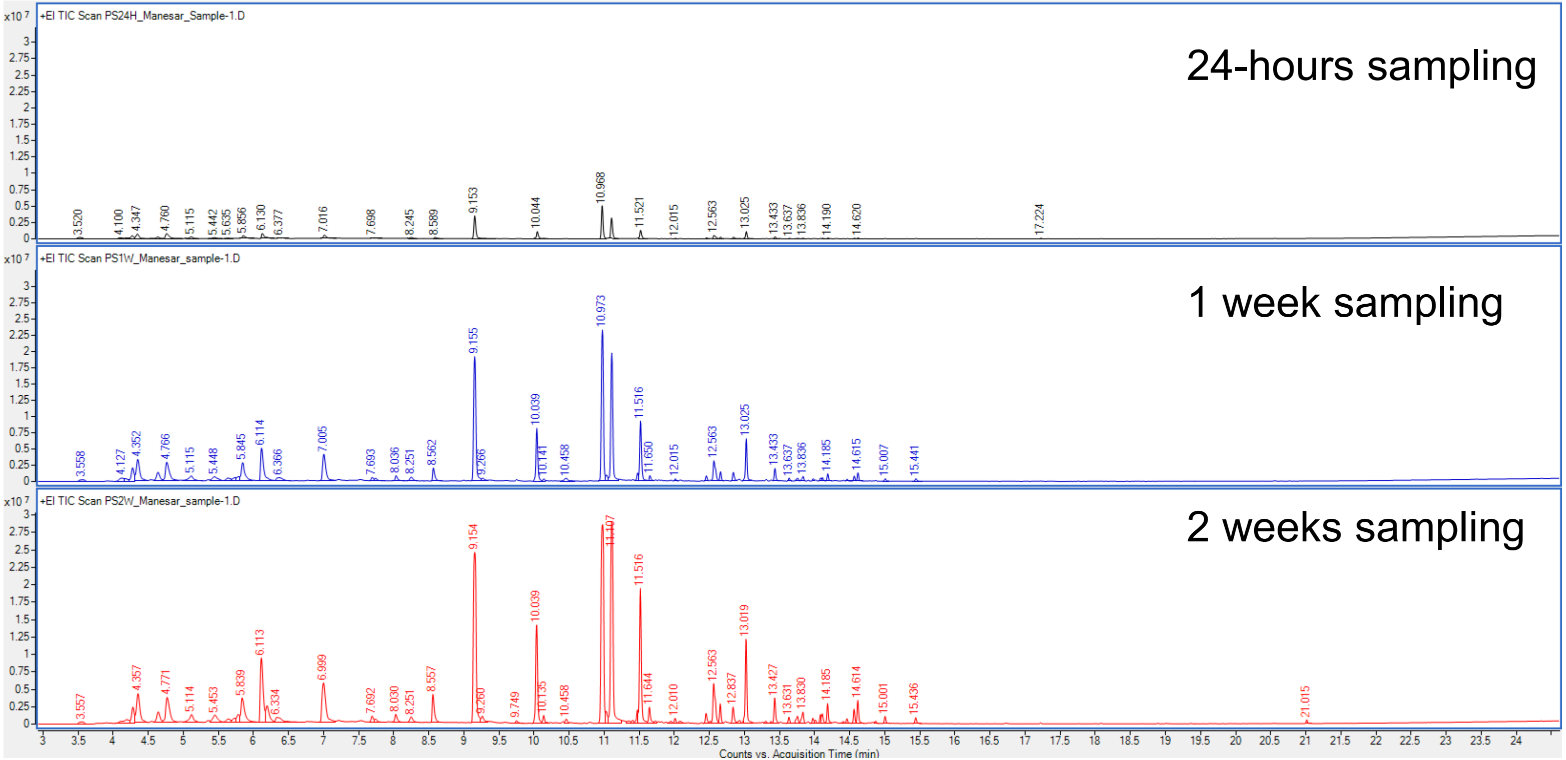
Active – 1hr sampling (20ml/min; 1.2L sample)

Compound (ppb)	Industrial	Residential	Traffic	Petrol station
Benzene	4.94	4.20	18.60	10.37
Toluene	48.04	12.62	52.84	37.79
Ethylbenzene	45.29	3.82	18.36	13.55
m,p-Xylene	119.64	14.26	142.70	75.08

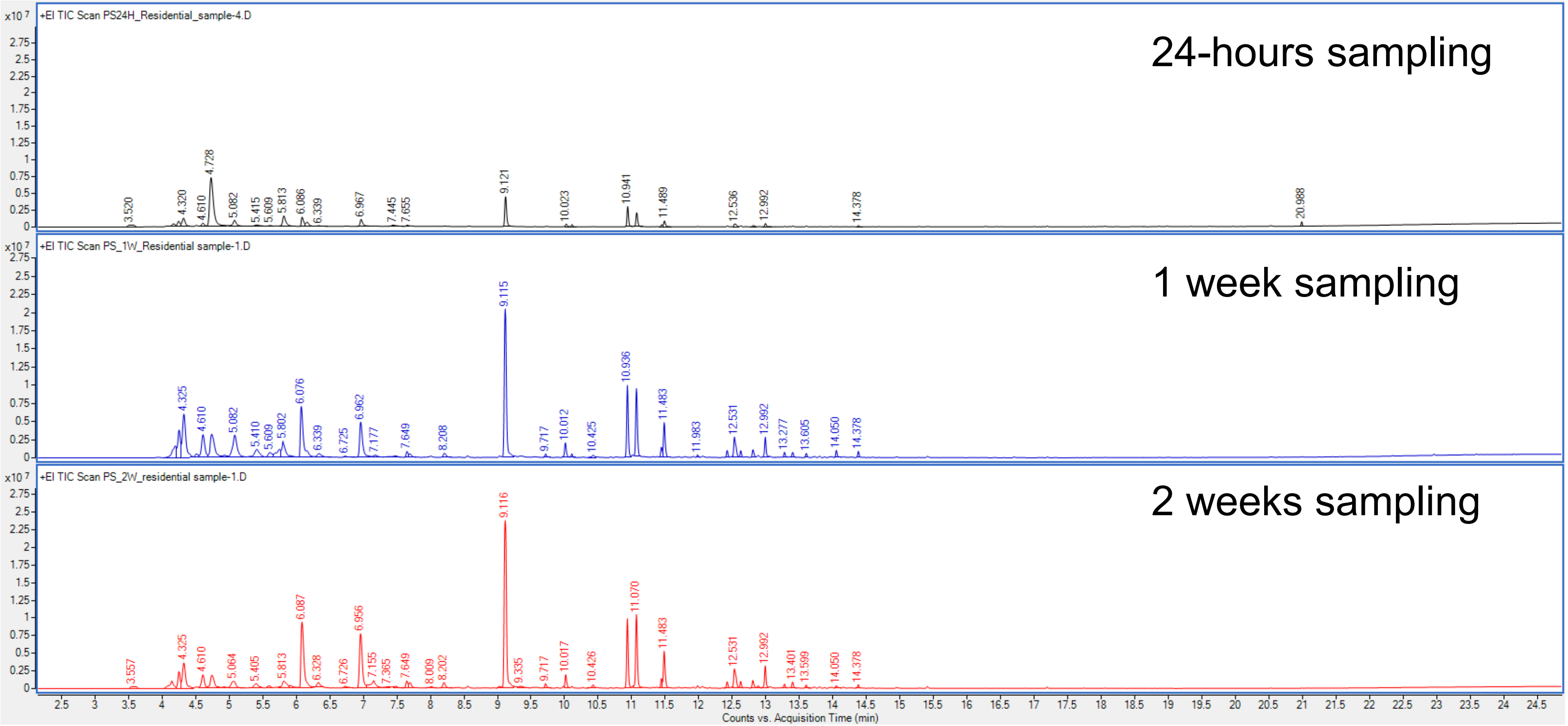
Passive Sampling Experiment

- Sorbent tubes exposed for 24-hours, 1 week and 2 weeks respectively to the air at:
  - Industrial Area
  - Residential Area

Passive Sampling – Industrial area

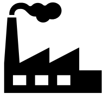


Passive Sampling – Residential area



Quantification of BTEX – Comparison

Passive (1-wk) v Active sampling



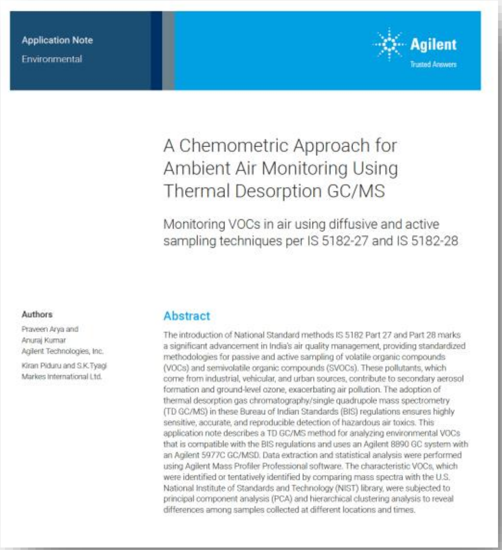
Compound (ppb)	Industrial		Residential	
	Passive	Active	Passive	Active
Benzene	4.03	4.94	6.17	4.20
Toluene	20.97	48.04	19.13	12.62
Ethylbenzene	29.73	45.29	8.57	3.82
m,p-Xylene	34.53	55.27	12.33	5.61

Summary

- Excellent linearity for calibrations R^2 >0.997
- Great correlation between passive and active sampling
  - Some variability with passive sampling, but still giving comparable results to active
- Passive and active sampling complimentary
  - Passive sampling appropriate technique when sampling over a long period of time
    - Weight time average reduces the impact of a one-off pollution event (Average conc over 1-week period)
  - Pumped sample accurate for sampling time
    - Would need to take multiple pumped samples to generate true picture

Thank you

- Praveen Arya - Agilent India
- Dr. SK Tyagi (retd) - **Former Director & Divisional Head** (Air Toxics Lab,CAAQM,Quality Assurance, Environmental Training) & Quality Manager at **Central Pollution Control Board**
- Kiran Piduru & Hannah Calder - Markes International



Application Note
Environmental

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A Chemometric Approach for Ambient Air Monitoring Using Thermal Desorption GC/MS

Monitoring VOCs in air using diffusive and active sampling techniques per IS 5182-27 and IS 5182-28

Authors

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Abstract

The introduction of National Standard methods IS 5182 Part 27 and Part 28 marks a significant advancement in India's air quality management, providing standardized methodologies for passive and active sampling of volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs). These pollutants, which come from industrial, vehicular, and urban sources, contribute to secondary aerosol formation and ground-level ozone, exacerbating air pollution. The adoption of thermal desorption gas chromatography/single quadrupole mass spectrometry (TD GC/MS) in these Bureau of Indian Standards (BIS) regulations ensures highly sensitive, accurate, and reproducible detection of hazardous air toxics. This application note describes a TD GC/MS method for analyzing environmental VOCs that is compatible with the BIS regulations and uses an Agilent 8890 GC system with an Agilent 5977C GC/MSD. Data extraction and statistical analysis were performed using Agilent Mass Profiler Professional software. The characteristic VOCs, which were identified or tentatively identified by comparing mass spectra with the U.S. National Institute of Standards and Technology (NIST) library, were subjected to principal component analysis (PCA) and hierarchical clustering analysis to reveal differences among samples collected at different locations and times.

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