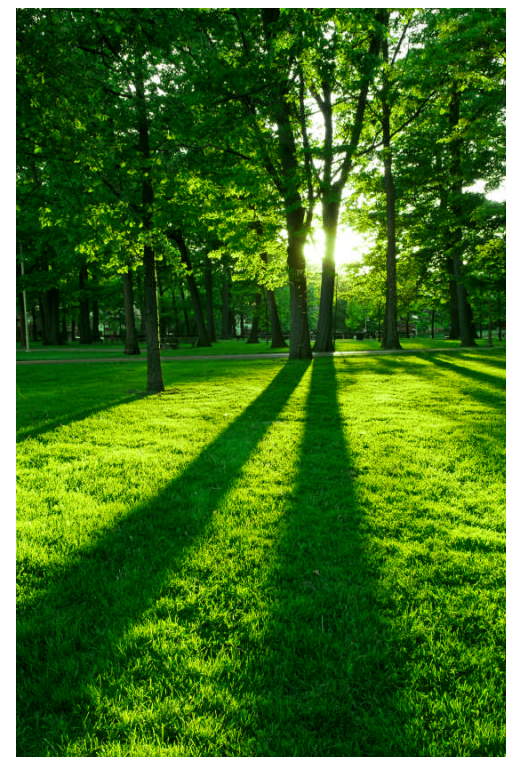
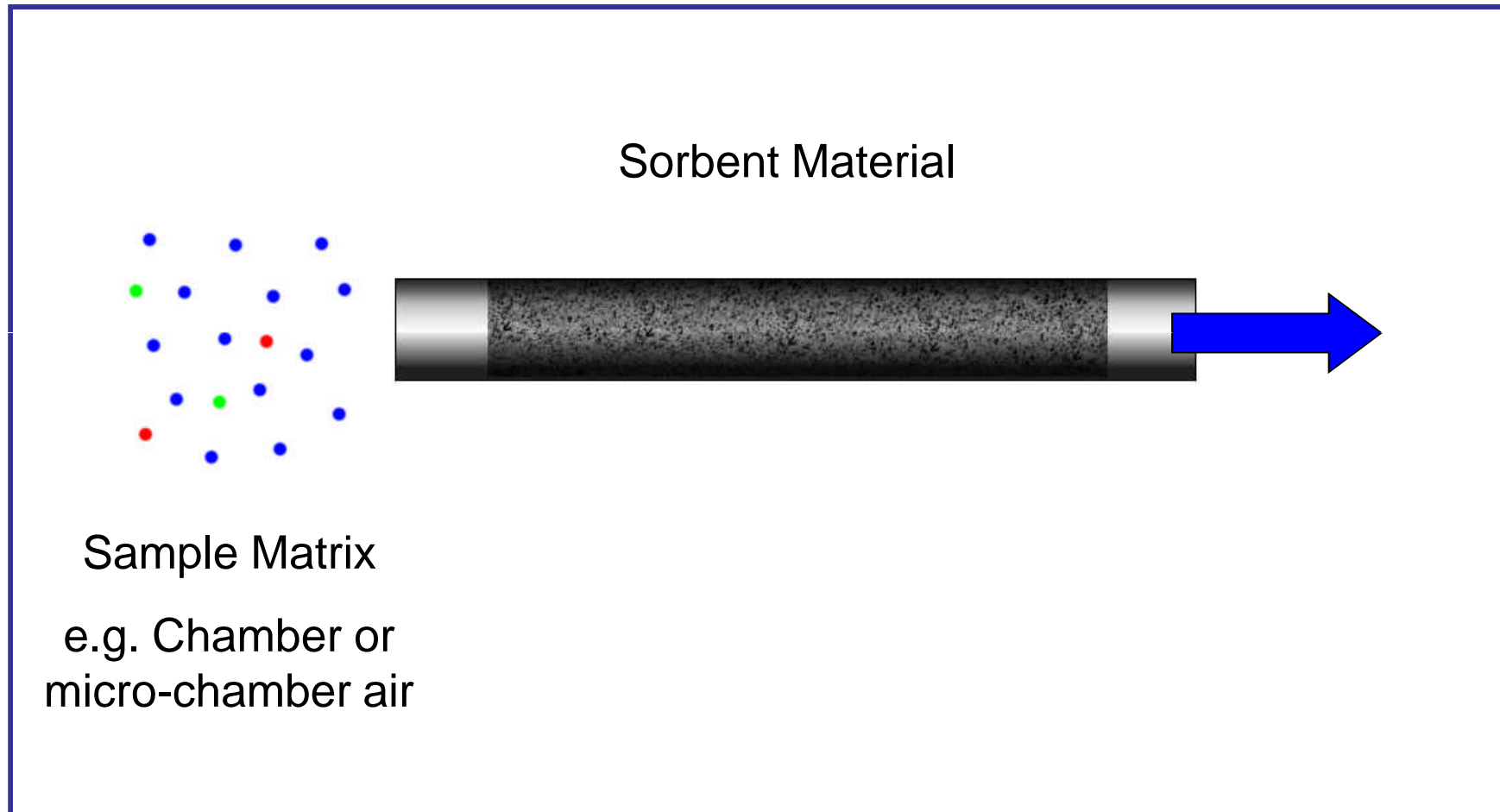


Neue Möglichkeiten zur Überwachung der Umgebungsluft mit Thermodesorption und GC/MS

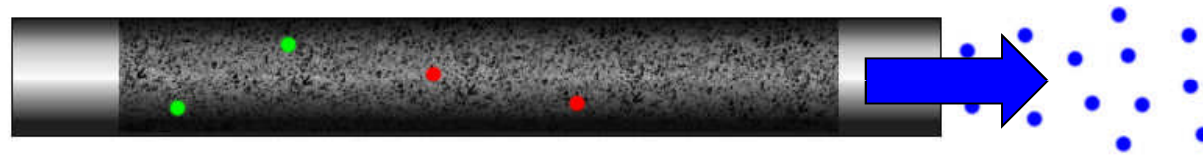


Bernhard Rothweiler
Senior Applications Chemist
Agilent Technologies
Europe, Middle East, Africa and India

What is Thermal Desorption?

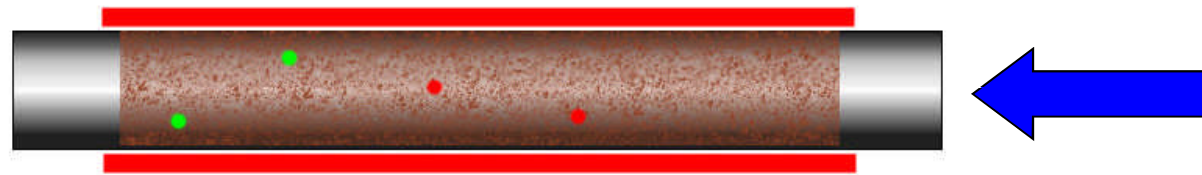


What is Thermal Desorption?



Lighter gases such as nitrogen pass through the sorbent

What is Thermal Desorption?



Sorbent is now heated in a reversed flow of clean carrier gas (back flushed)

What is Thermal Desorption?

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



It is a simple extension of the technique of Gas Chromatography and is a **sample introduction technology** for difficult or real-world samples

2 Stage Thermal Desorption

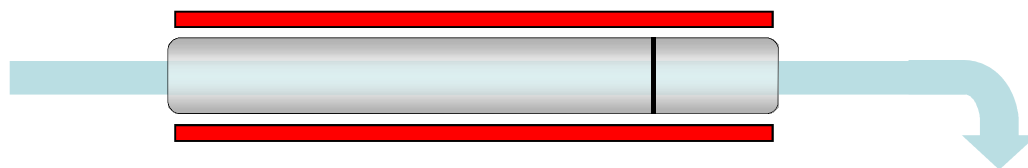
PROBLEM: Compounds are released SLOWLY from the sorbent tube



Would lead to **very wide** chromatographic peaks and low sensitivity

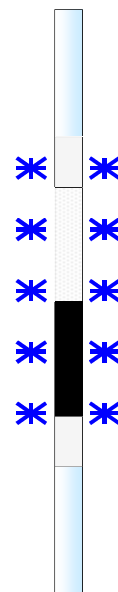
2 Stage Thermal Desorption

SOLUTION: Use a narrow secondary trap



STAGE 1

Transfer compounds from
tube to secondary trap



Electrically cooled
narrow bore cold trap

2 Stage Thermal Desorption

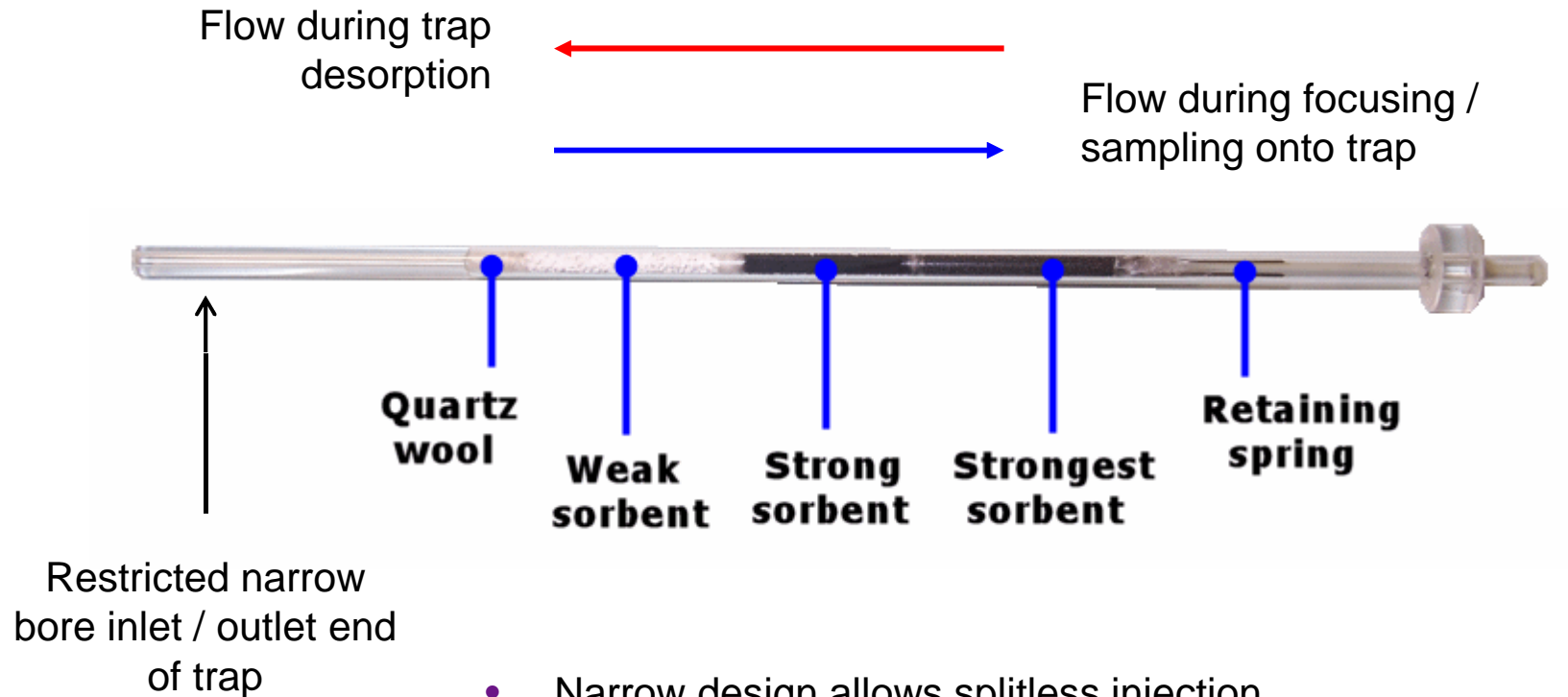
STAGE 2

Rapid transfer of
compounds from cold
trap to GC



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

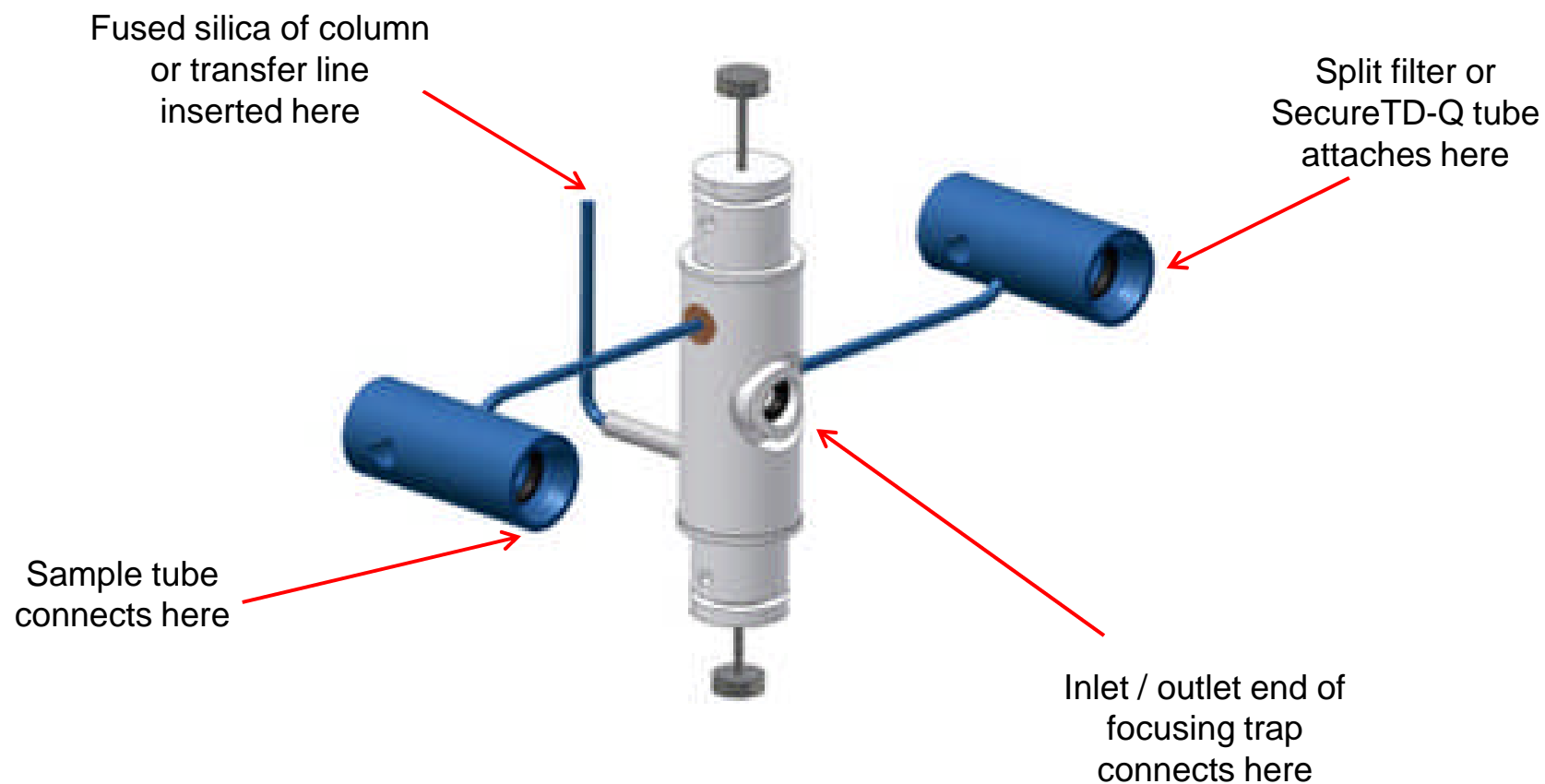
Cold Trap



- Narrow design allows splitless injection
- Use sorbent(s) to suit specific application
- 15 standard traps + custom packed traps available from Markes

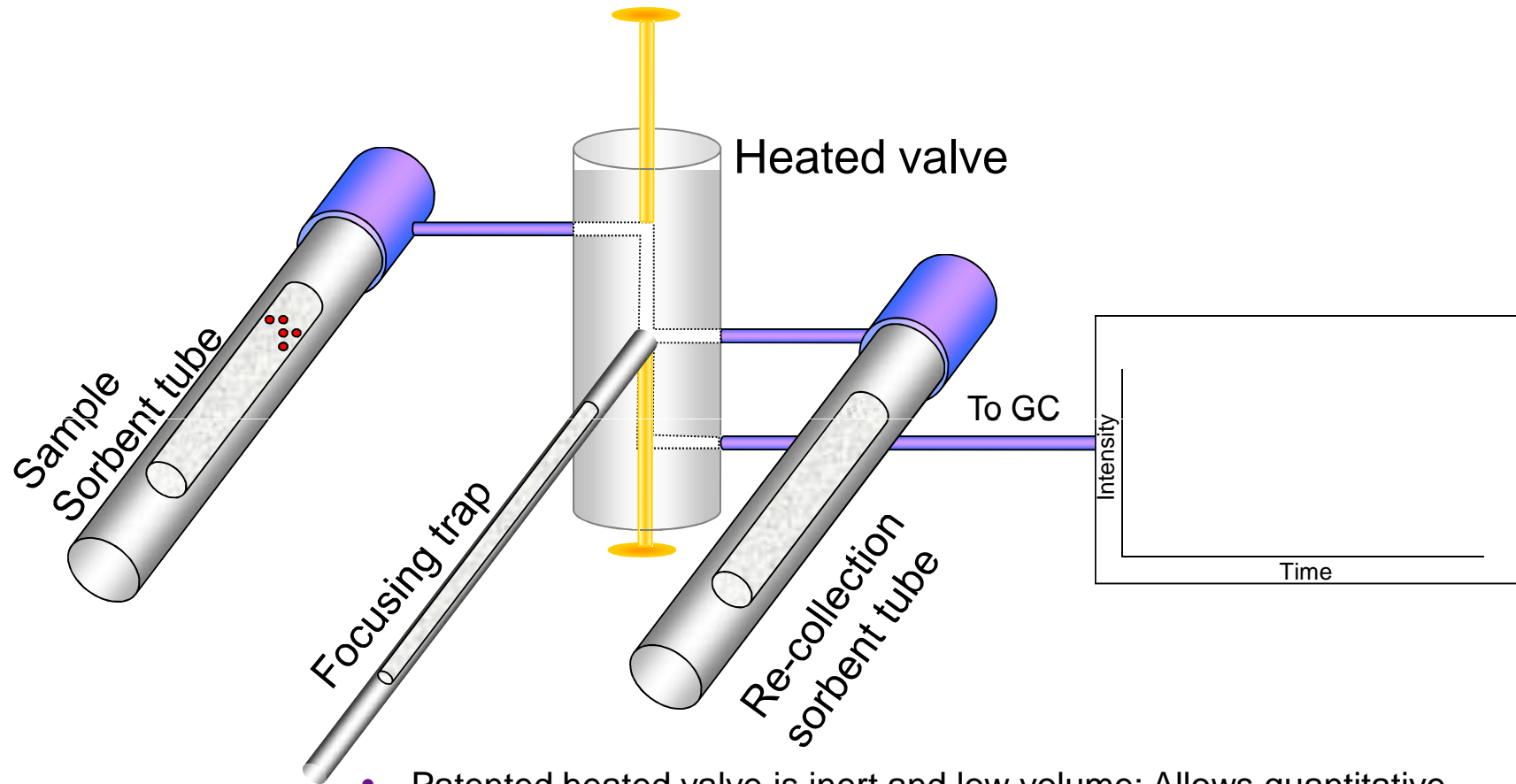
Key Component - Heated Valve

The sample flow path through the valve assembly is uniformly-heated, short (< 10 cm total) and narrow to eliminate condensation



Patented TD valve: All applications & sample re-collection

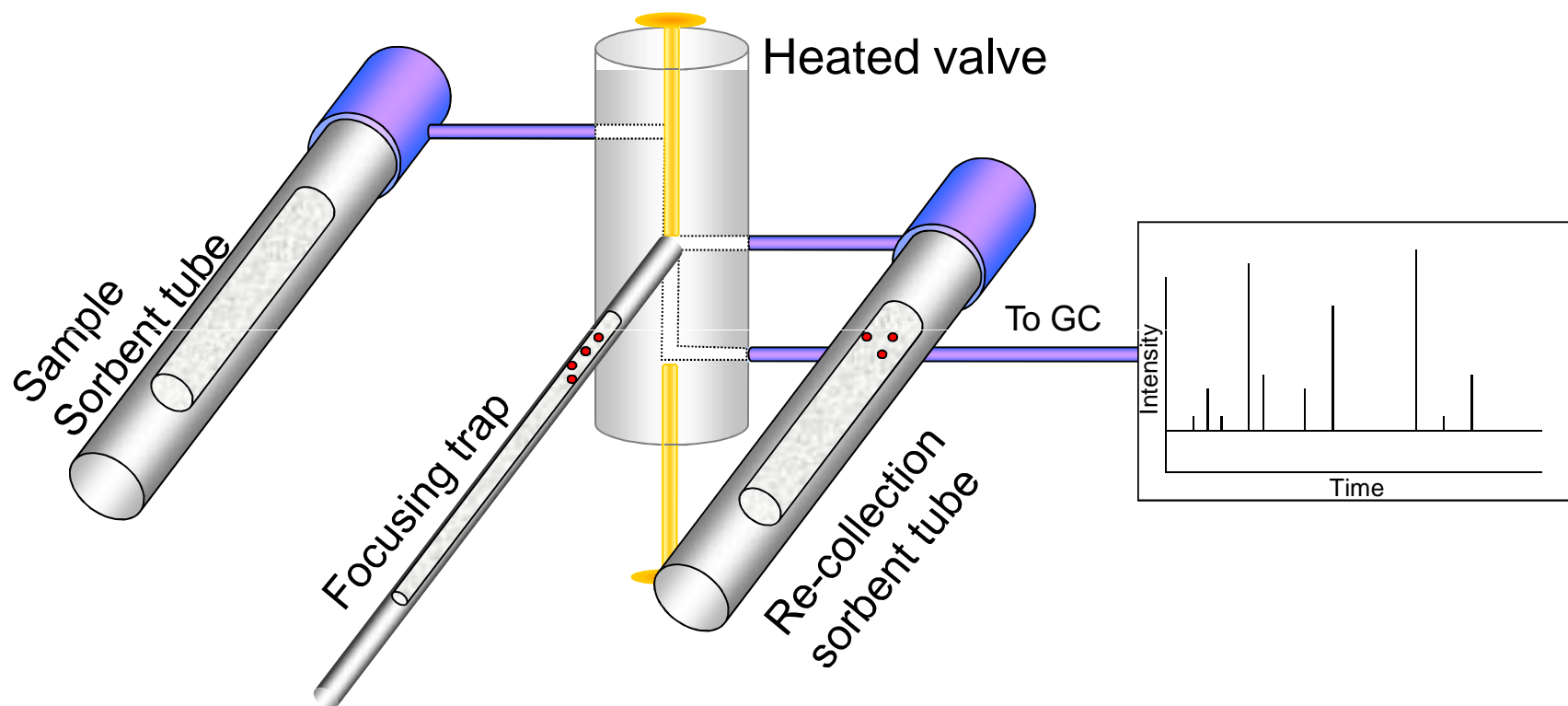
Stage 1: Primary (tube) desorption with optional (inlet) split



- Patented heated valve is inert and low volume: Allows quantitative recovery of high & low volatility and reactive compounds
- The heated valve isolates the TD system allowing method compliance: leak testing, backflush trap desorption, purge to vent, overlap mode, *etc.*

Patented TD valve: All applications & sample re-collection

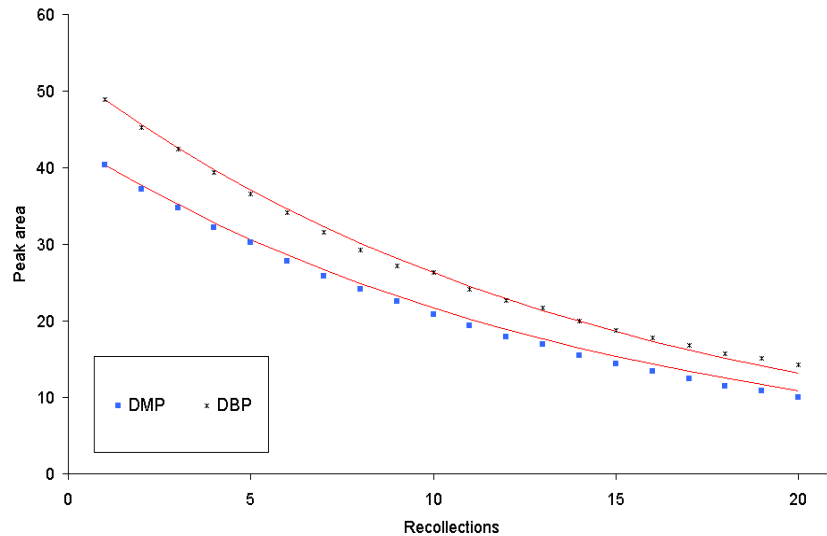
Stage 2: Secondary (trap) desorption with optional (outlet) split



- Repeat analysis of re-collected samples makes it easy to validate analyte recovery through the TD flow path
- A change to the overall VOC profile indicates any bias

Using Re-collection (SecureTD-Q™)

Validation of routine methods

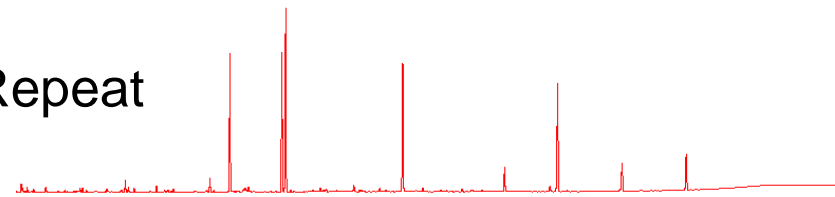


- 2 µL phthalate solution in methanol with 21:1 single split
- 20 re-collection, repeat analyses
- **Good match between expected decay (lines) and observed decay (points)**
- **Demonstrates quantitative recovery**

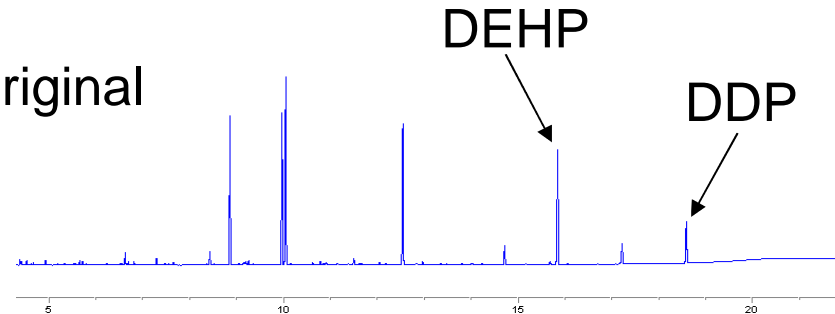
Demonstrating quantitative recovery of high boilers

- Repeat desorption of a mixed phthalate std – di-ethyl- to di-n-decylphthalate
- Repeat analysis shows quantitative recovery without bias, across the analyte range

Repeat

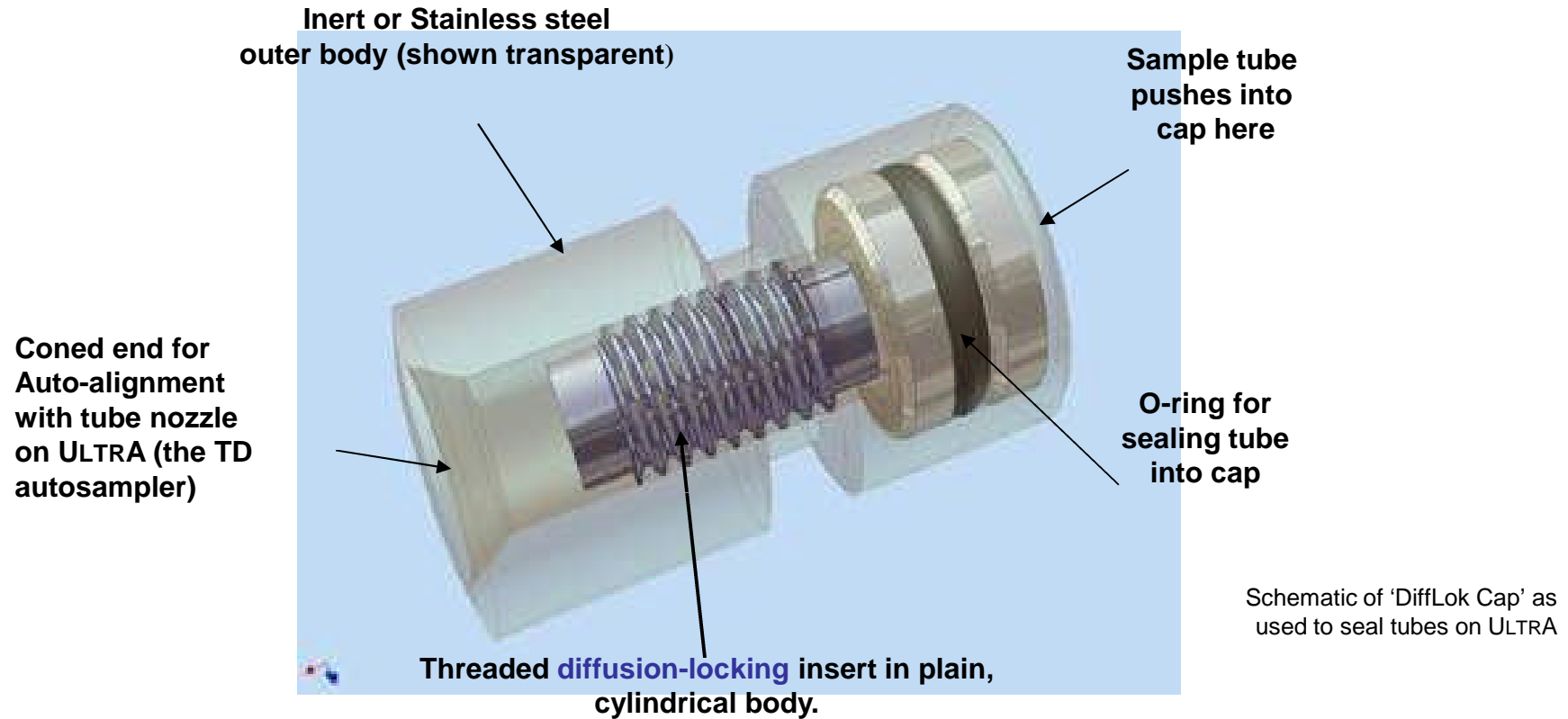


Original



NB: ASTM Method D6196 references quantitative re-collection for validation

ULTRA 2 DiffLok™ caps

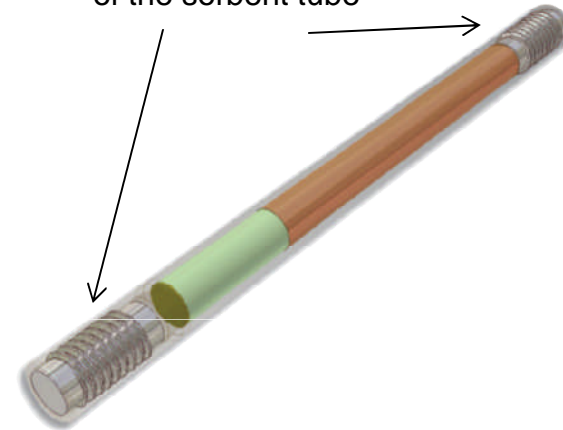


- Patented DiffLok caps provide a very effective seal for tubes on ULTRA 2 preventing artifact ingress and loss of analytes
- DiffLok caps allow gas to flow when pressure is applied & can stay on the tubes throughout TD operation – This makes automatic TD simple and mechanically robust

Unique SafeLok™ sorbent tubes

- SafeLok tubes reduce risk of artefact ingress and loss of sampled analytes
- They make it easier to handle tubes in the field (e.g. capping/uncapping) without risk of contamination
- They also facilitate collection and analysis of air samples from ultra-clean atmospheres.
- They allow pumped sampling at low flow rates over extended periods (< 1 mL/min)
- Same mass of sorbent and same external dimensions as standard tubes

Threaded DiffLok™ inserts protect both ends of the sorbent tube



* Patent Numbers: GB 2337513, US 6,564656 B1

The TubeTAG™ advantage for air monitoring

Tube Information

Tube Letter/Number	N	150781	Read Tube Info
TAG ID	20080721-0001		
Tube Type	Silcosteel 1/4"		
Adsorbent Packing	Sorbent packing		
Packing Date	15/07/2008		
Thermal Cycles	# thermal cycles		
TD Method	Single split Tenax desorption 50:30		
Pressure Ratio	Impedance		
Tube Status	Leak test info		
Tube re-collected from	0		

Select Instrument

Sampling Ultra

Collecting Ultra

Tube

Load 1

UnLoad

Sample Information

Sample Ref	SamPLe01	Clear Sample Info
Pump Ref	p01	
Sampling Mode	Pumped	
Sample Start Date	02/09/2008	Sample Start Time 08:52:36
Start Flow Rate	151	
Sample End Date	02/09/2008	Sample End Time 12:08:25
End Flow Rate	124	



"TubeTAG is a genuine breakthrough in TD technology. It allows the user to immediately identify the sorbent in each tube, when it needs repacking and whether or not it has a history of leak test failures, back-pressure anomalies, etc."

What can TD-GC/MS do?

Any volatile or semi-volatile organic compounds which meet the following criteria:

- $\leq n\text{-C}_{40}$, bpt $\leq 525^\circ\text{C}$
- Can be easily gas chromatographed
- The sorbent or matrix containing the compounds is compatible with the high temperatures required

Unsuitable compounds

- Inorganic compounds
- Most permanent gases – *exceptions include* N_2O , SF_6 & CS_2
- Compounds with volatility $> n\text{-C}_{40}$
- Compounds which don't work well with GC (including formaldehyde)
- Methane

Thermal Desorption systems

UNITY 2™

A universal platform for
single tube thermal
desorption



TD-100™

Automated TD system for
up to 100 RFID-tagged or
untagged tubes

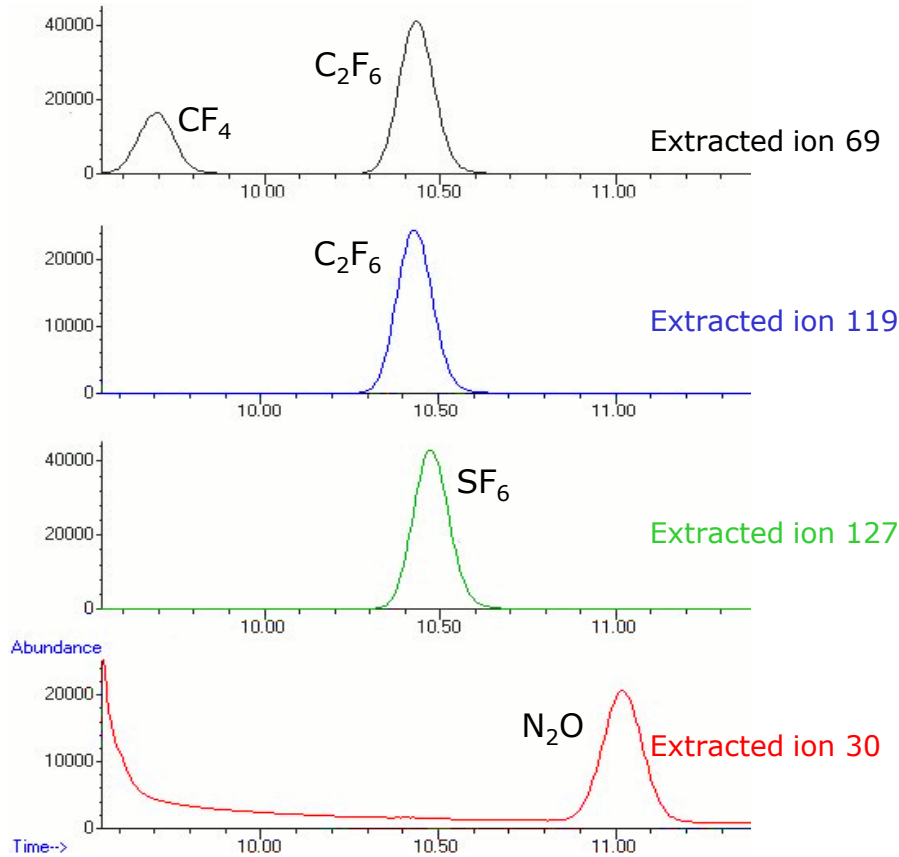


Standard methods

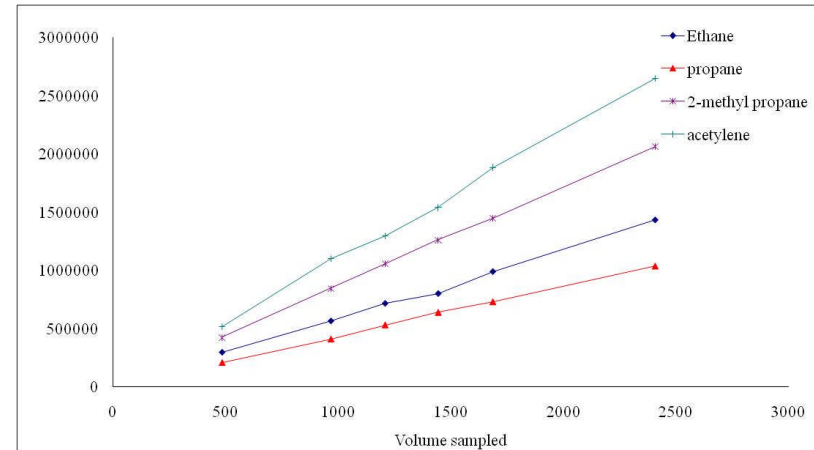


See TDTS 3: National and International Standard Methods Relating to Speciated Monitoring of Vapour-phase Organic Chemicals in Air

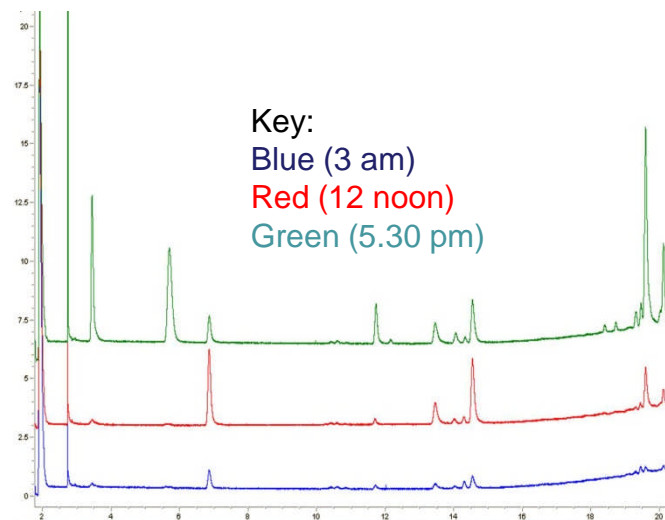
Online air monitoring applications



Green house gas analysis



Acetylene – up to 2L of sample taken without breakthrough

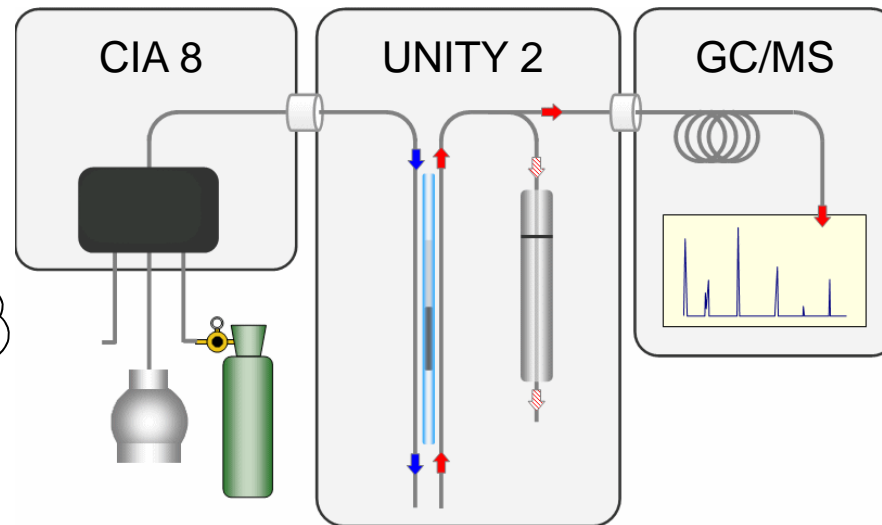
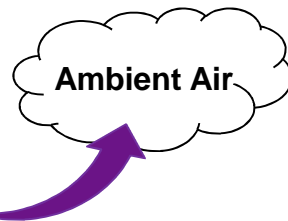


Diurnal profiling of ozone precursors

Canister analysis methods (e.g. US EPA TO-15)

Method summary

- Grab sampling using canisters is easy, TWA monitoring is not
- Samples may be stored for up to 30 days
- A small volume of air from the canister (typically ~500 mL) can be introduced straight to the focusing trap of the desorber
- Trapping conditions are set such that water is selectively eliminated during the trapping process.
- Analysis by GC/MS

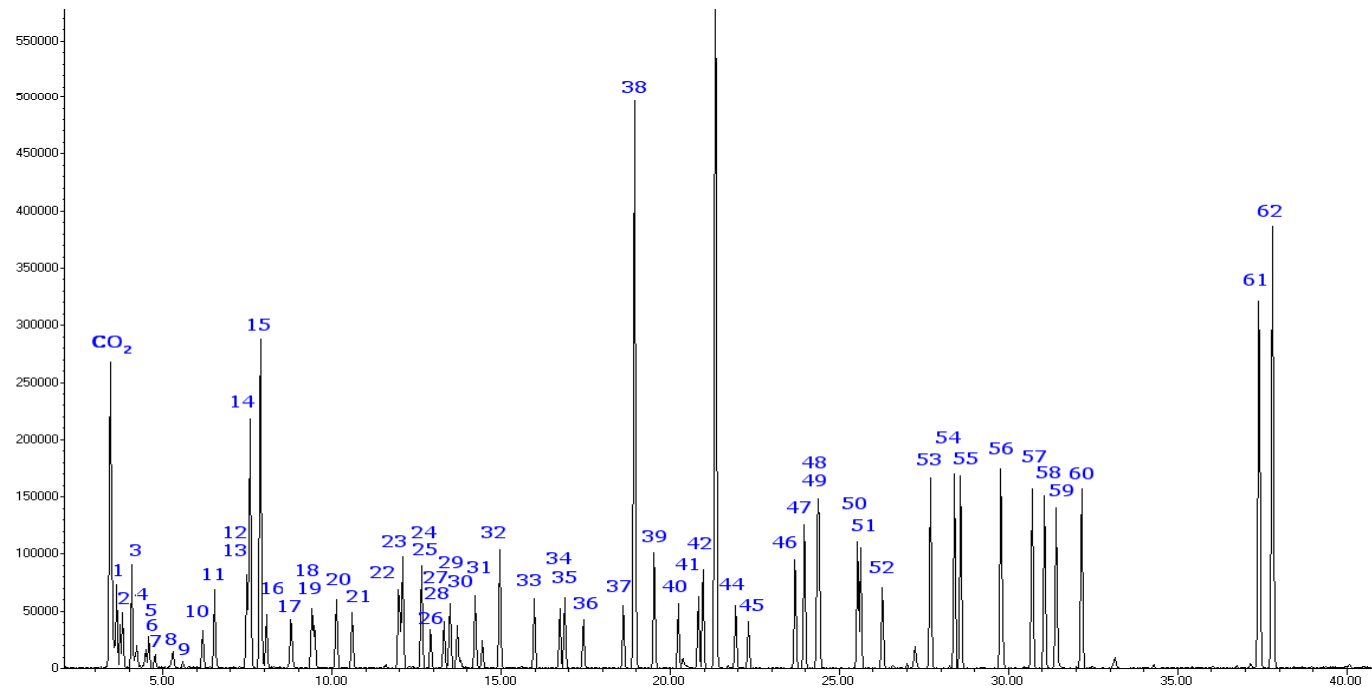


'Air toxics' in canisters: US EPA Method TO-15

- | | | |
|--|-------------------------------|----------------------------------|
| 1 Propylene | 22 Cis-1,2-Dichloroethylene | 43 Methyl <i>n</i> -butyl ketone |
| 2 Dichlorodifluoromethane | 23 Methyl ethyl ketone | 44 Dibromochloromethane |
| 3 1,2-Dichlorotetrafluoroethane | 24 Ethyl acetate | 45 1,2-Dibromoethane |
| 4 Methyl chloride | 25 Tetrahydrofuran | 46 Chlorobenzene |
| 5 1,2-Dichloroethane | 26 Chloroform | 47 Xylene |
| 6 1,3-Butadiene | 27 1,1,1-Trichloroethane | 48 Xylene |
| 7 Vinyl chloride | 28 Cyclohexane | 49 Xylene |
| 8 Methyl bromide (bromomethane) | 29 Carbon tetrachloride | 50 Styrene |
| 9 Chloroethane | 30 Benzene | 51 Tribromomethane |
| 10 Trichlorotrifluoroethane (Freon® 113) | 31 <i>n</i> -Heptane | 52 1,1,2,2-Tetrachloroethane |
| 11 Ethanol | 32 Trichloroethylene | 53 1,2,4-Trimethylbenzene |
| 12 1,2,-Dichloroethylene | 33 1,2-Dichloropropane | 54 1,3,5-Trimethylbenzene |
| 13 1,1,2-Trichlorotrifluoroethane | 34 1,4-Dioxane | 55 1-Ethyl-4-methyl benzene |
| 14 Acetone | 35 Bromodichloromethane | 56 Ethylbenzene |
| 15 Carbon disulfide | 36 Trans-1,3-dichloropropene | 57 1,2-Dichlorobenzene |
| 16 Isopropyl alcohol | 37 Methyl isobutyl ketone | 58 1,3-Dichlorobenzene |
| 17 Methylene chloride | 38 Toluene | 59 Chloromethylbenzene (alpha) |
| 18 Tert-butyl methyl ether | 39 Cis-1,3-Dichloropropene | 60 1,4-Dichlorobenzene |
| 19 <i>n</i> -Hexane | 40 Trans-1,2-Dichloroethylene | 61 1,2,4-Trichlorobenzene |
| 20 1,1-Dichloroethane | 41 1,1,2-Trichloroethane | 62 Hexachloro-1,3-butadiene |
| 21 Vinyl acetate | 42 Tetrachloroethylene | |

1 L of a 1 ppb air toxics mix analysed splitless and cryogen-free using UNITY-CIA 8

Source: TDTS 81



Air monitoring: Canisters or tubes?

Use canisters:

1. For non-polar compounds
2. Preferably at trace levels for ultra-volatiles
3. *When you have to*

Canister limitations

1. Expense (€500 -1000 each)
2. Poor recovery of anything higher boiling than Xylene
3. Cleaning needs expensive vacuum equipment, at least 3 cleaning cycles and verification with GC/MS

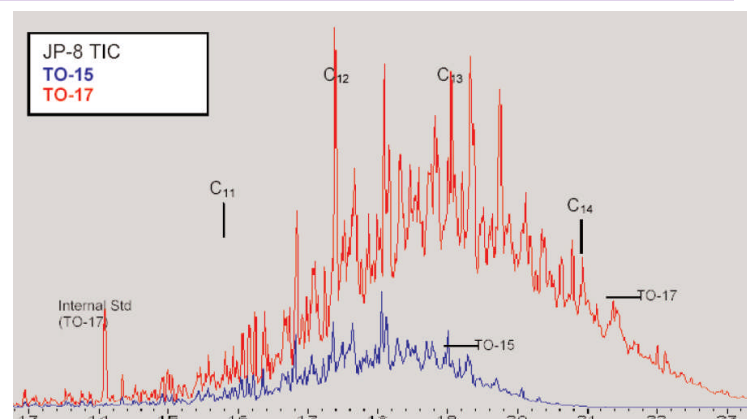


Canisters or tubes?

	Tubes	Canisters
Perception	World-wide acceptance	Gold standard for US ambient air market
Applications	Ambient air, indoor air, vapor intrusion, industrial hygiene Material emissions Food & flavor Chemical weapons	Ambient air, indoor air, vapor intrusion, emergency response
Handling	Light weight for personal monitoring and general ease of use	Larger and heavier; more costly to ship
Sampling	C ₃ - C ₄₀ Concentration range ppt to %	C ₂ -C ₁₀ Concentration range ppt to low ppm
Cleaning	Analytical process automatically cleans tube for re-use	Canister cleaning requires separate equipment as additional step prior to background certification and sampling.
Cost	\$50 – \$130 each	\$200 - \$700 each

Profiles of soil gas contaminated with kerosene obtained using:

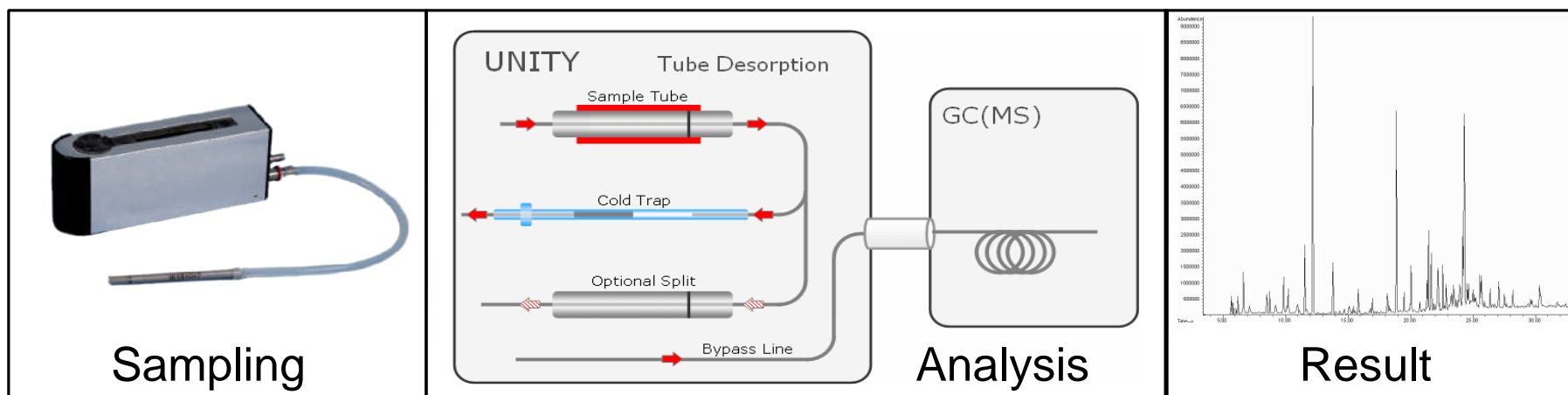
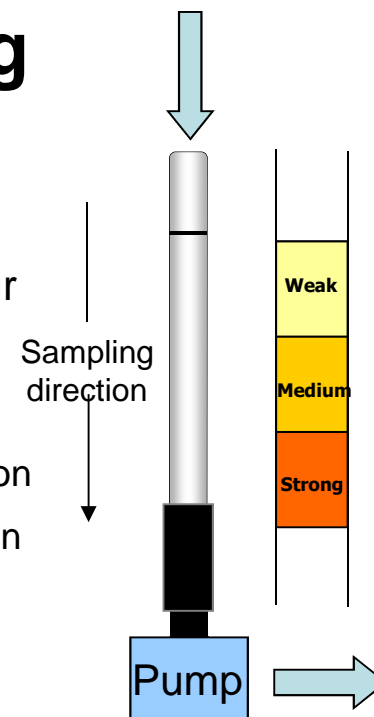
- a) **canister sampling** with TO-15 analysis (blue)
- b) **sorbent tube sampling** with TO-17 analysis (red)



Active (pumped) sampling

TO-17 summary:

- Pre-screen area using 2 tubes in parallel (50 mL/min, 1 & 4 L) to identify type/level of VOCs. Confirm sorbent selection. Sample air
- Store capped tubes up to 30 days (below 4°C if multi-sorbent)
- TD-GC/MS analysis steps:
 - Leak test then add gas phase IS and/or dry purge in sampling direction
 - Prepurge then desorb tube with carrier gas flowing in reverse direction
 - Refocus analytes in electrically-cooled trap and desorb rapidly in backflush direction
 - Analyse by GC/MS

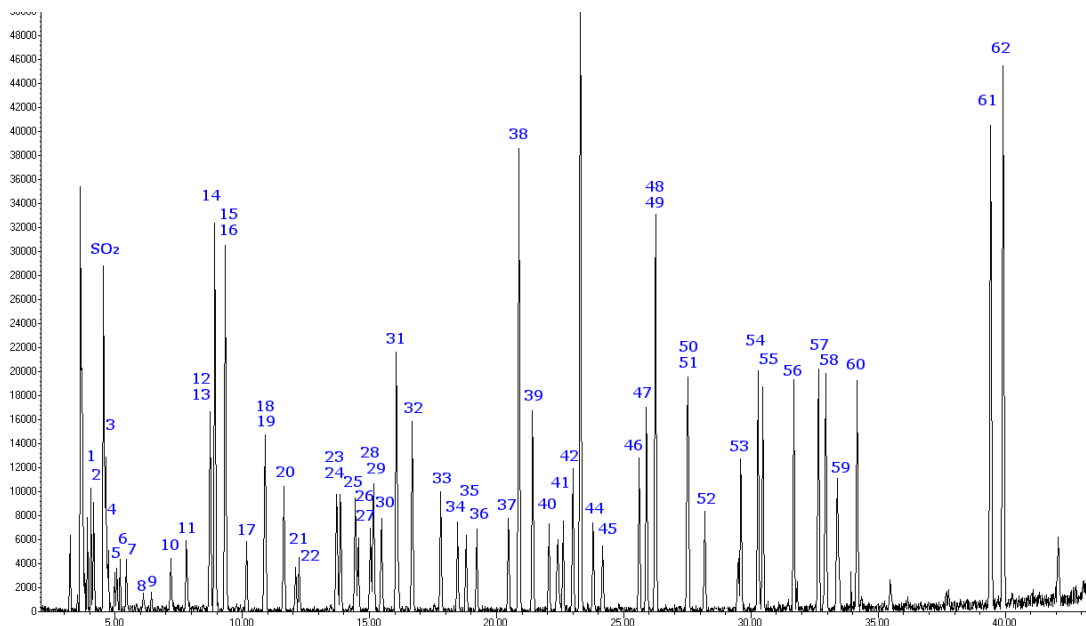


'Air toxics' on sorbent tubes: US EPA Method TO-17

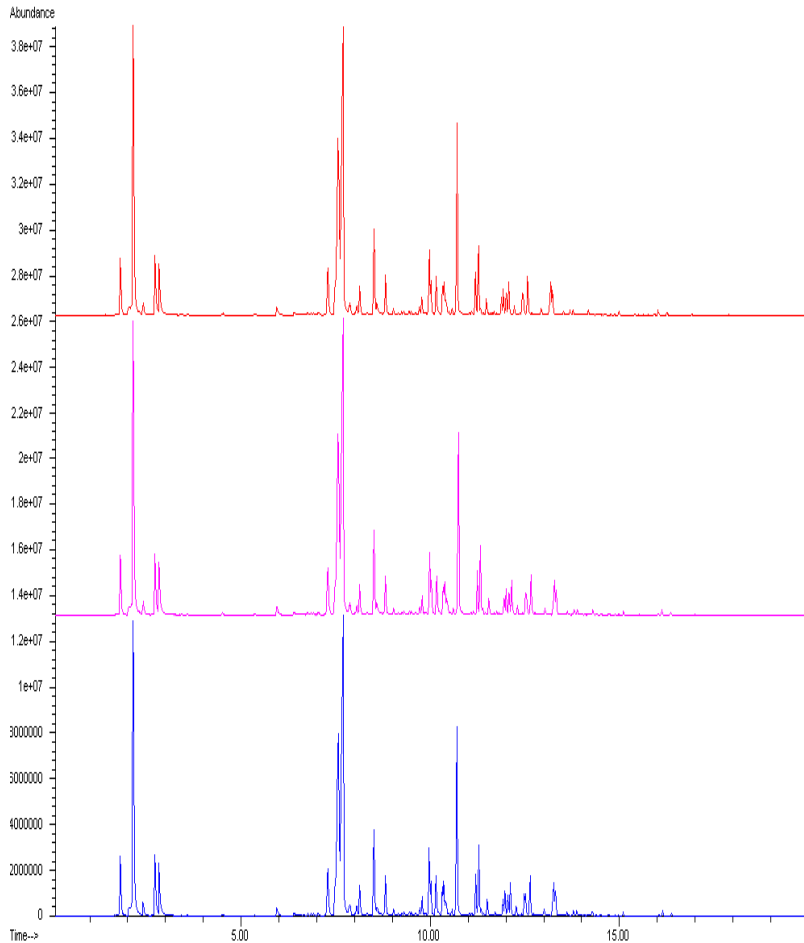
- | | | |
|--|-------------------------------|----------------------------------|
| 1 Propylene | 22 Cis-1,2-Dichloroethylene | 43 Methyl <i>n</i> -butyl ketone |
| 2 Dichlorodifluoromethane | 23 Methyl ethyl ketone | 44 Dibromochloromethane |
| 3 1,2-Dichlorotetrafluoroethane | 24 Ethyl acetate | 45 1,2-Dibromoethane |
| 4 Methyl chloride | 25 Tetrahydrofuran | 46 Chlorobenzene |
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| 10 Trichlorotrifluoroethane (Freon® 113) | 31 <i>n</i> -Heptane | 52 1,1,2,2-Tetrachloroethane |
| 11 Ethanol | 32 Trichloroethylene | 53 1,2,4-Trimethylbenzene |
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| 20 1,1-Dichloroethane | 41 1,1,2-Trichloroethane | 62 Hexachloro-1,3-butadiene |
| 21 Vinyl acetate | 42 Tetrachloroethylene | |

10:1 Split desorption of
'Air Toxics' tube loaded
with 1 L of 1 ppb std

Source: TDTS 86

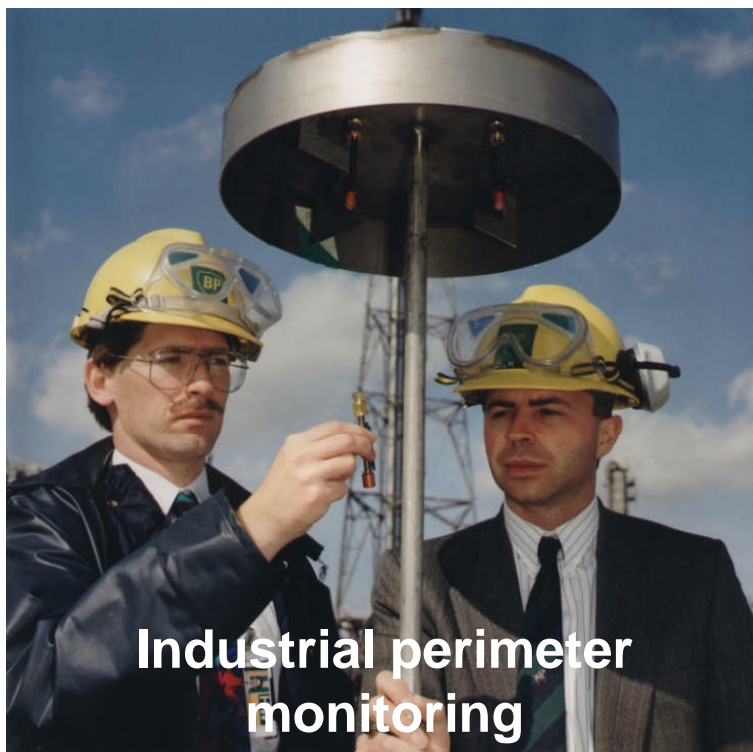


TD isn't just for trace levels: High-concentration industrial emission samples



- Pumped sampling of 1 L stack gas with TD-GC/MS analysis
- Sample splitting during both primary (tube) and secondary (trap) desorption. Total split ratio: **3000:1**
- **Quantitative re-collection of *both splits* allows repeat analysis for confirmation**

Typical applications for air monitoring in industry

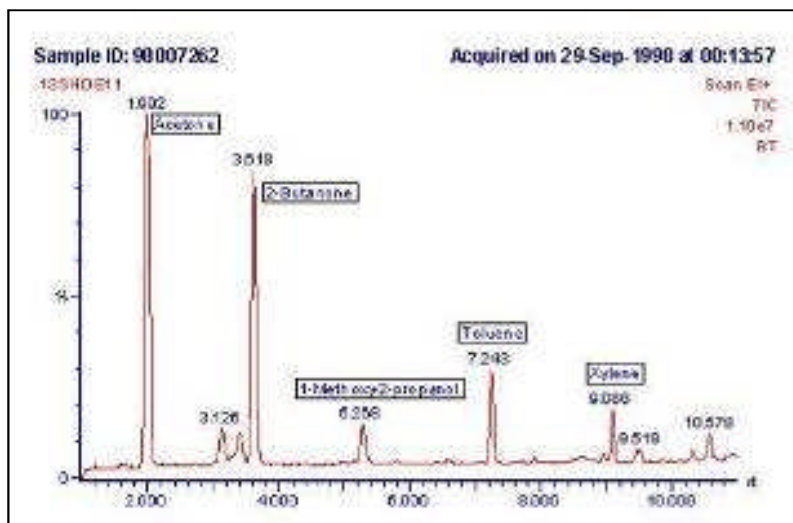


Monitoring guidelines (sorbents, uptake rates, sampling volumes, etc.) available from standard methods (and from Markes)



Breath sampling for occupational hygiene (Bio-VOC™)

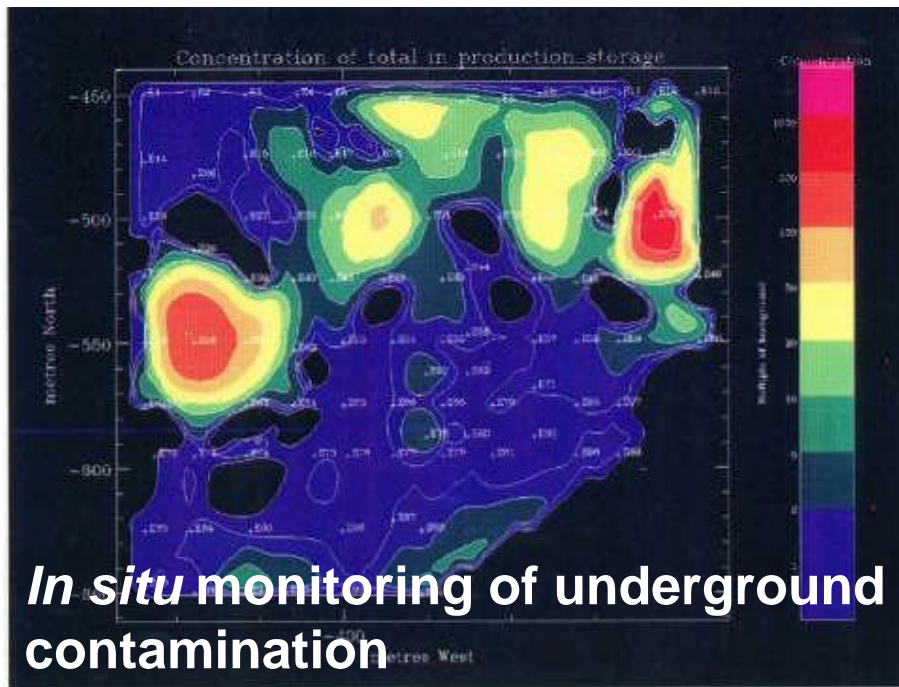
- Breath sampling is another application for TD-GC/MS
- It allows assessment of the total exposure – inhalation, skin absorption, ingestion
- Key applications include:
 - People working with chemicals absorbed by the skin
 - People wearing protective equipment (How effective is it)
 - Chronic exposure causing build up of chemicals in the body
 - Environmental exposure studies



Solvents in the breath of shoe workers

Specialist applications for air monitoring in industry

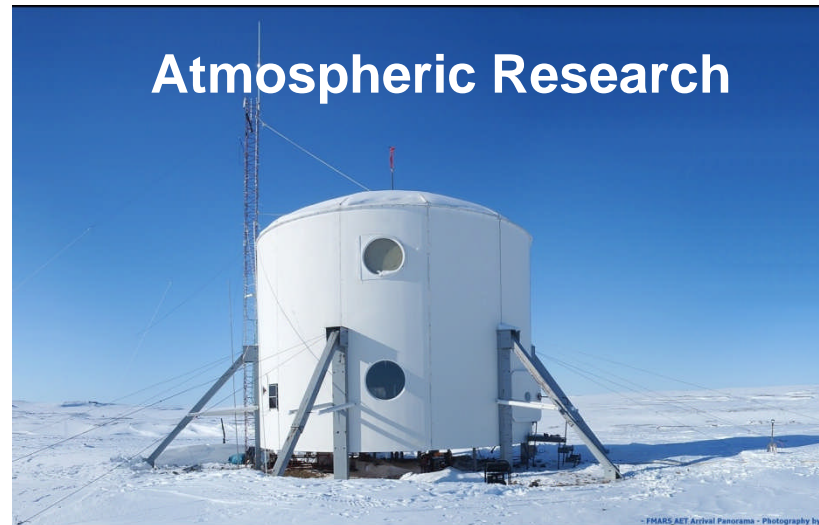
Soil gas and vapour intrusion assessments



Mapping criteria pollutants in ambient air, diurnal changes



Atmospheric Research



Specialist applications for air monitoring in industry

Landfill gas monitoring



Odorous industrial emissions



Indoor air quality and tracer gases used for ventilation studies



Biogenic emissions



Input from Agilent?

Sampling



Thermal desorption



GC/MS



Data analysis



Soil Gas samples



MTS-32



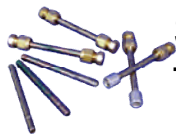
no need for calibrated pumps



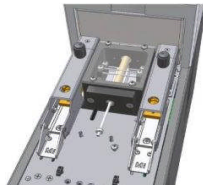
Breath Samples



Canisters and Bags



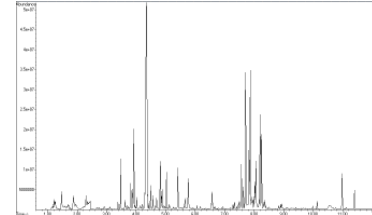
Sorbent Tubes



Cryogen-free
 Method compliant
 100 tubes
 Universal: C₂ to C₄₀ + reactive compounds
 Repeat analysis
 Water management
 TubeTAG



CFT (e.g. Backflush, Splitter, 2D-GC)
 Synchronous SIM/Scan
 5th generation of EPC
 EM Saver
 Normalized gain



ChemStation,
 MassHunter
 RTL + DRS
 Libraries

Summary

- Whichever vapour-phase organic chemicals are of interest
- Whatever your air monitoring application



Whether it's VOCs
in whale breath ...

... or the most
polluted air on the
planet

Photograph courtesy of: Dr. Rei Rasmussen,
Oregon Graduate Institute, USA

Thank you for your attention!

Questions???



moritz_hebestreit@agilent.com

MARKES
international

 Agilent Technologies

Food and Environmental
Solutions Seminars 2011