# Material Emission Testing by TD-GC/MS

PRESENTED BY

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# Topic

- What is Thermal Desorption (TD)?
- Thermal desorption Sampling.
- Target analytes range.
- Example: Material emission applications.

# What is Thermal desorption (TD) ?

Thermal desorption is also

- An alternative to solvent extraction for measuring VOC and SVOC compounds in many different sample matrices – solids, liquids or gases








# What is Thermal desorption (TD) ?

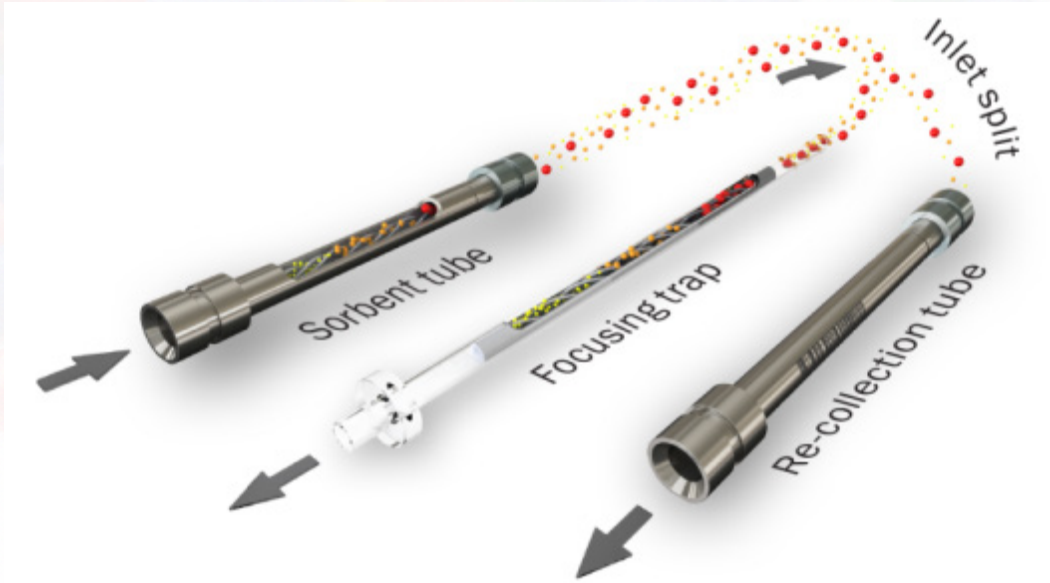
- Thermal desorption is arguably the world's most versatile, readily-automated injector mechanism for gas chromatography.

- It is powerful in its own right and is also used as the basis for several other GC front-end technologies:
  - Head space
  - Purge-and-trap,
  - SPME,

# The analytical thermal desorption process

## Stage 1

- Tubes containing the sample materials or sampled sorbents are heated in a reverse flow of inert (carrier) gas, releasing the trapped compounds and sweeping them into an electrically-cooled, low thermal mass sorbent focusing trap, typically held at -30 to +30°C.

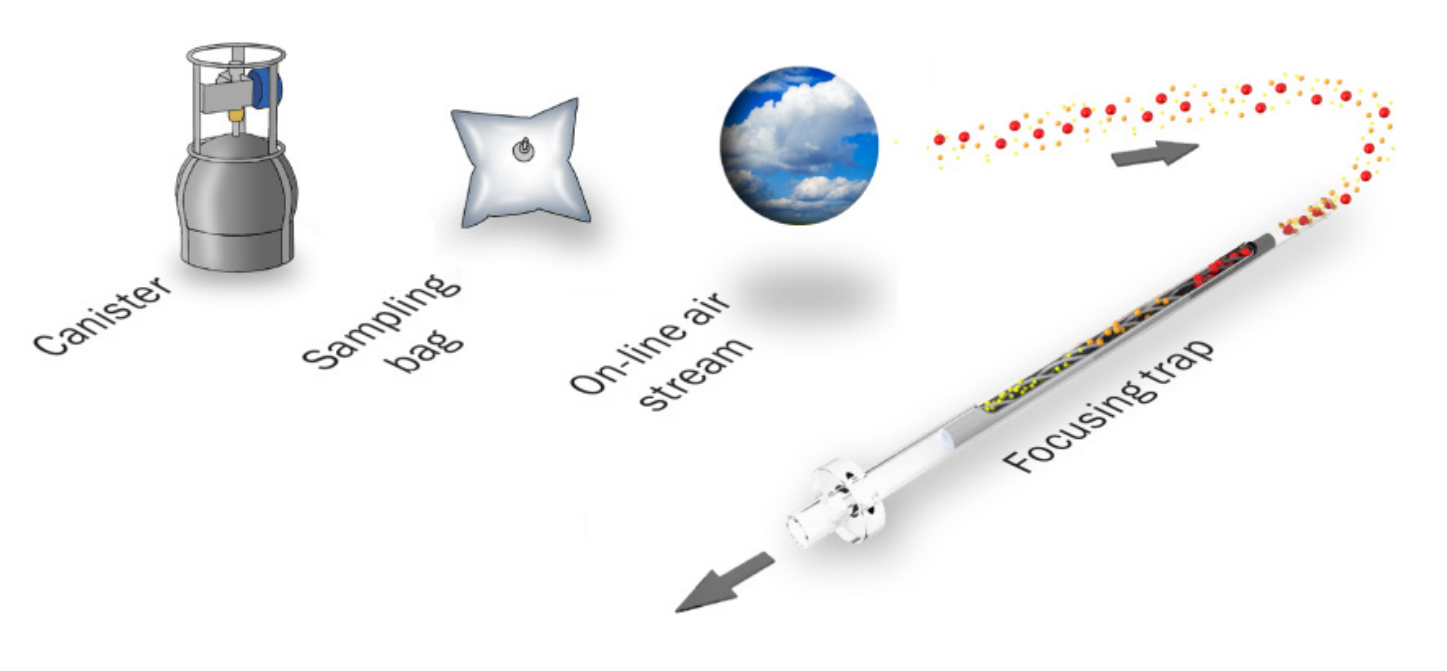



*Optional 'inlet' split with re-collection*

# The analytical thermal desorption process

## Stage 1

- Alternatively, whole air/gas samples, from canisters, bags or manifolds, are introduced directly to the focusing trap at controlled flows.

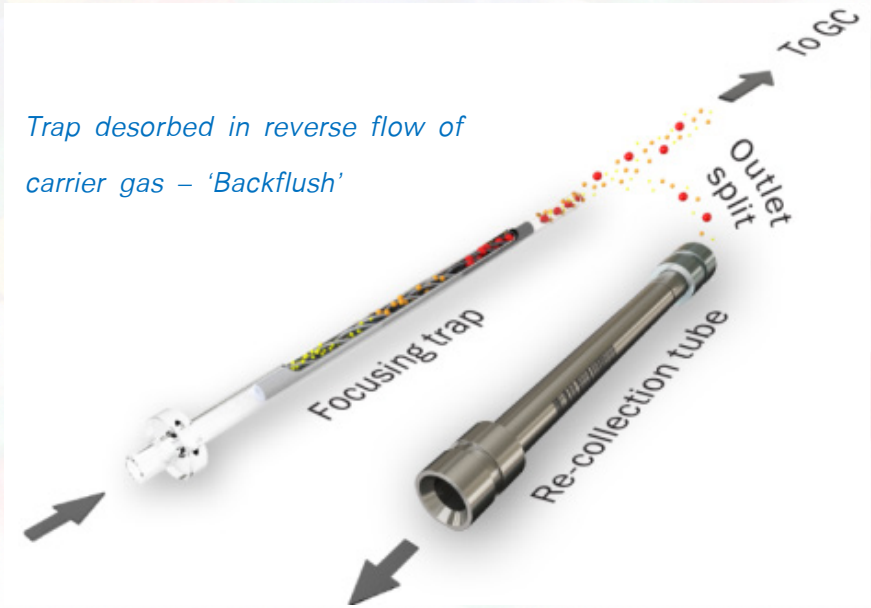


# The analytical thermal desorption process

## Stage 2

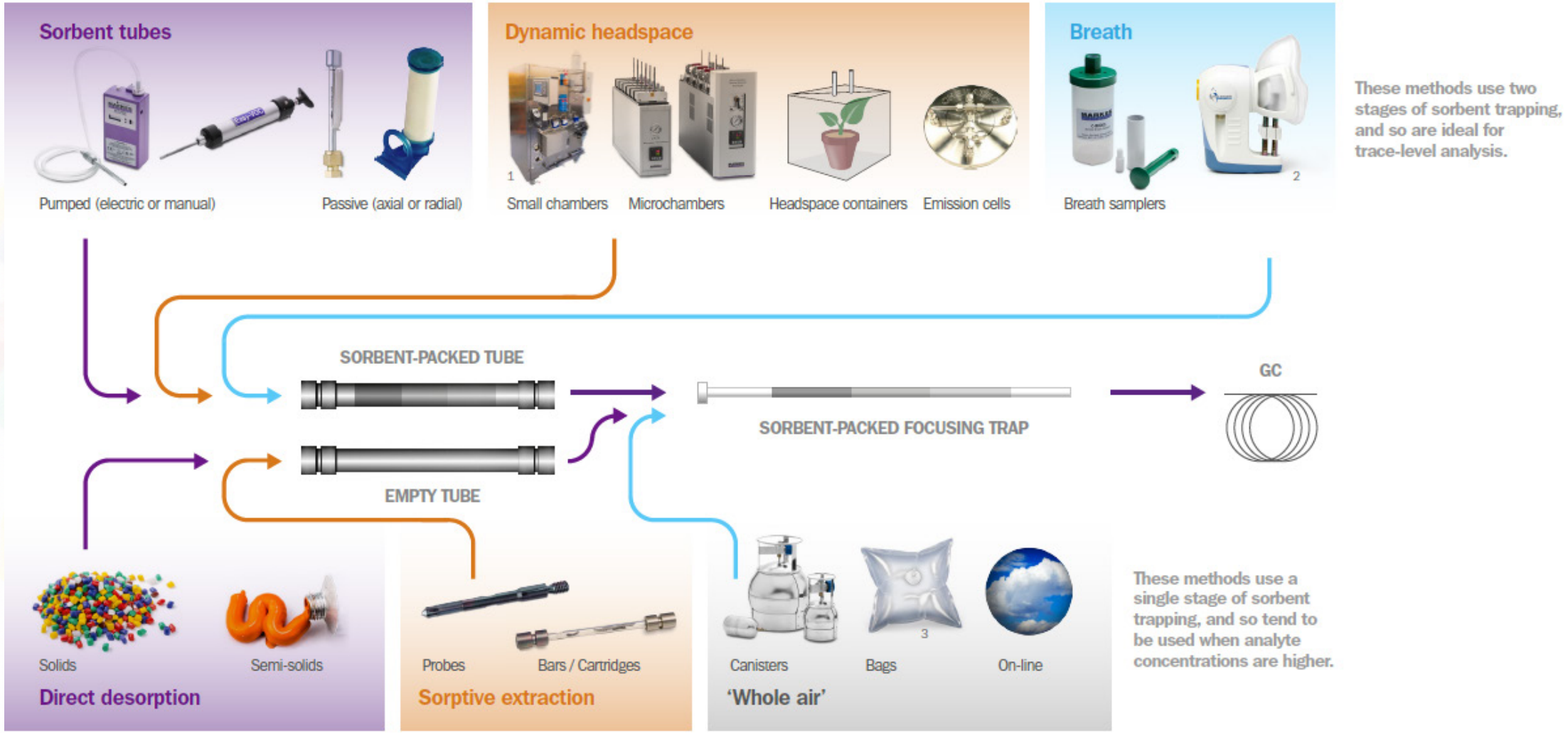
- Once the sample has been focussed onto the trap it is rapidly heated, at rates up to 100°C s-1, in a reverse flow of carrier gas.
- Retained compounds are released and injected into the GC in a narrow band of vapour - delivering high sensitivity capillary GC performance.

*Trap desorbed in reverse flow of carrier gas – 'Backflush'*




*Optional 'outlet' split with re-collection*

# Thermal desorption Sampling

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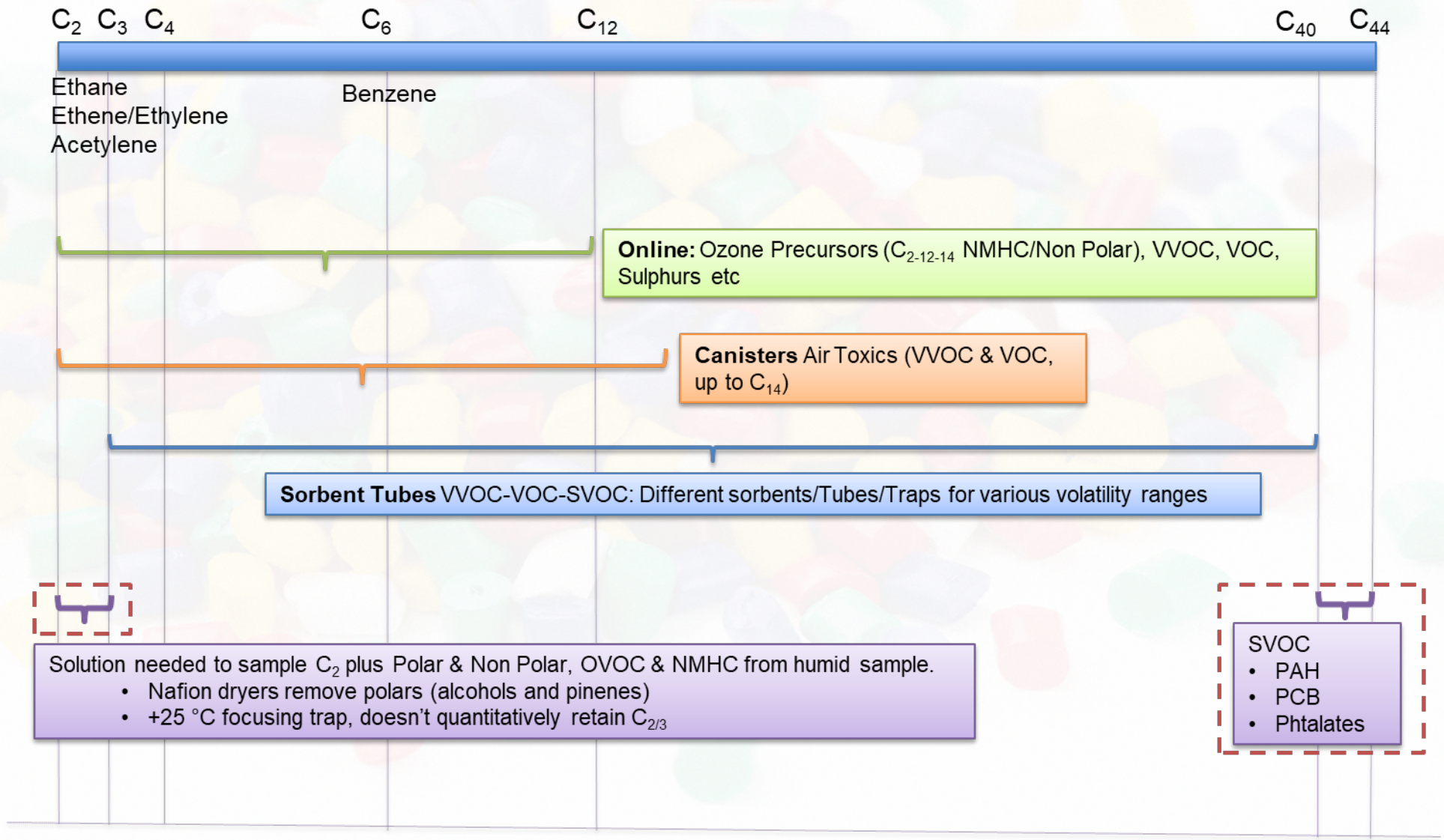
# Extending TD Target Analytes range



# Thermal desorption application

Air monitoring

Research applications

Material emission testing

Flavour and fragrance profiling

Chemical warfare and forensic

# Air monitoring

- Ambient air:
  - ‘Air toxics’ – US: TO-15/17 and CN: HJ 644,
  - Ozone precursors – PAMS,
  - VOC / OVOC,
  - SVOCs.
- Industrial fence line and stack emissions:
  - US Method 325, CN: HJ,
  - CEN TS 13649.
- Indoor and in-vehicle air quality:
  - ISO 16000 and 12219-series methods,
  - Ventilation tests.
- Soil gas and vapor intrusion into buildings.
- Workplace air.
- Odour monitoring – round landfill, waste water treatment and other industrial/urban centres.
- Atmospheric research.

# Flavour and fragrance profiling – Food and Drink

- Product aroma profiling:
  - Shelf-life and ripeness studies,
  - Quality assurance,
  - Brand comparison,
  - Identifying taint or adulteration,
  - Confirmation of authenticity,
  - Detecting migration from packaging.
- Allergens in personal care products.
- Cigarettes and e-cigarettes.
- Essential oils in creams/ointments.
- Fragrances in soaps, shampoo and other consumer products.






# Chemical warfare and forensic - Defence and homeland security

- Chemical agent destruction.
- Monitoring the safety of agent stockpiles.
- Battlefield protection equipment.
- First responder / mobile labs.
- Counter terrorism / civil defence.
- Decontamination.
- Accelerants in arson debris.
- Forensicating of inks and trace contaminants.
- Detection of traces of proscribed drugs.
- Explosives and propellants.


# Material emission testing

- Car trim:
  - ISO 12219, HJ 400 & VDA 278.
- Construction products:
  - ISO 16000 series & EN 16516,
  - Flooring, wall coverings, insulation (etc).
- Decorative products:
  - Adhesives, paints, sealants, etc.
- Spray applied polyurethane foam (SPF) and other PUF products:
  - ASTM D8142.
- Medical devices in contact with patient breathing space:
  - ISO 18562-3 & ISO 18562-4.
- Cleaning products.
- Semi-conductor fabrication & electronics.
- Furniture:
  - BIFMA M7.1.
- Air fresheners & scented candles:
  - EN 16738.







Example:

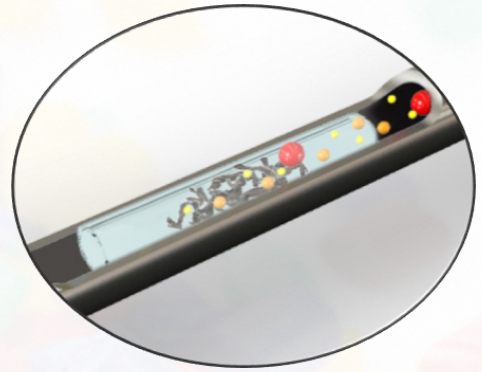
Material emission applications

Quick screening of small samples with direct desorption

# Direct desorption

## Simplified sampling of solids and liquids

- Sample measured directly into empty TD tube or disposable tube liner and desorbed.
  - Typically at moderate temperatures.
  - Glass tubes with a central restriction hold the sample in the correct position
- Direct thermal desorption of materials can be used:
  - To completion for measuring (S)VOC content
  - Or to get a representative (S)VOC profile
- Provides a 'gas extraction' or 'dynamic headspace' alternative to conventional solvent extraction
- Minimizes sample preparation and injector contamination



High (%) concentrations of analytes accommodated using double splitting.

# Automotive interior VOC and FOG emissions

## Stipulations of VDA 278 regarding sample size and preparation

| Material type | Sample size |
|---|---|
| Foam | 15 ± 2 mg |
| Fiber-based materials* | 60 ± 20 mg |
| Films | 30 ± 5 mg |
| Leather | 10 ± 2 mg |
| Paint | 50 ± 5 µm film thickness |
| Adhesives or similar | 30 ± 5 mg |

* For example, fiberglass or carbon-fiber-reinforced polymer.

## Sample preparation

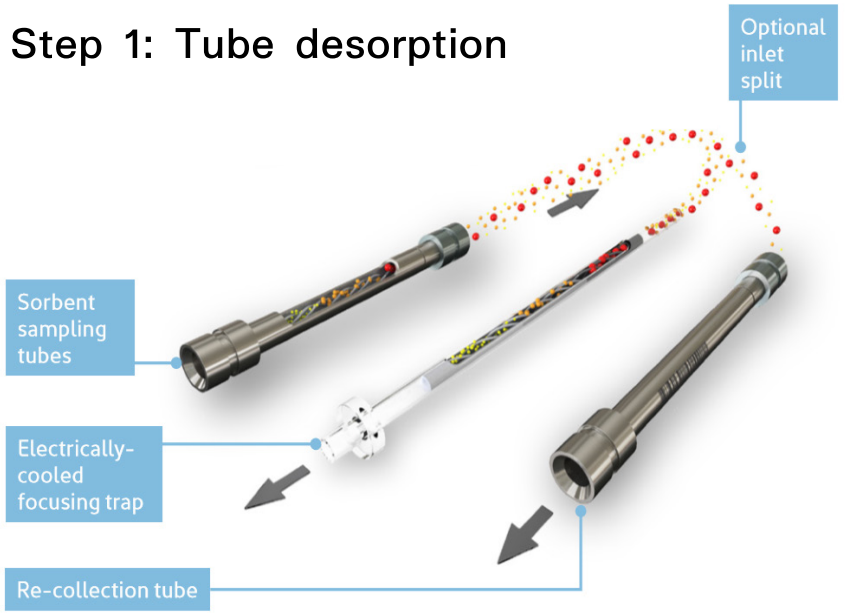
- Cutting the sample to a width of 3 mm.
- Weigh a sample
- Load sample to sample tube.

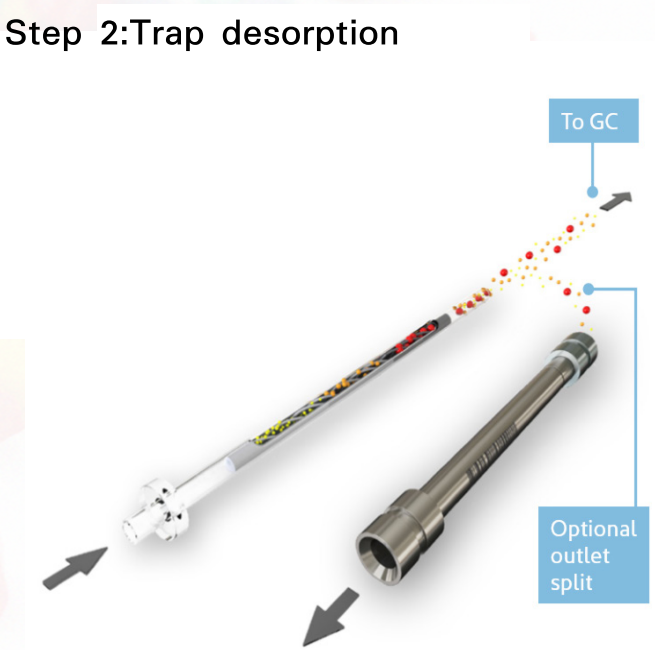
Sample of rubber flooring material placed into a glass TD tube, ready for direct desorption.

# Automotive interior VOC and FOG emissions

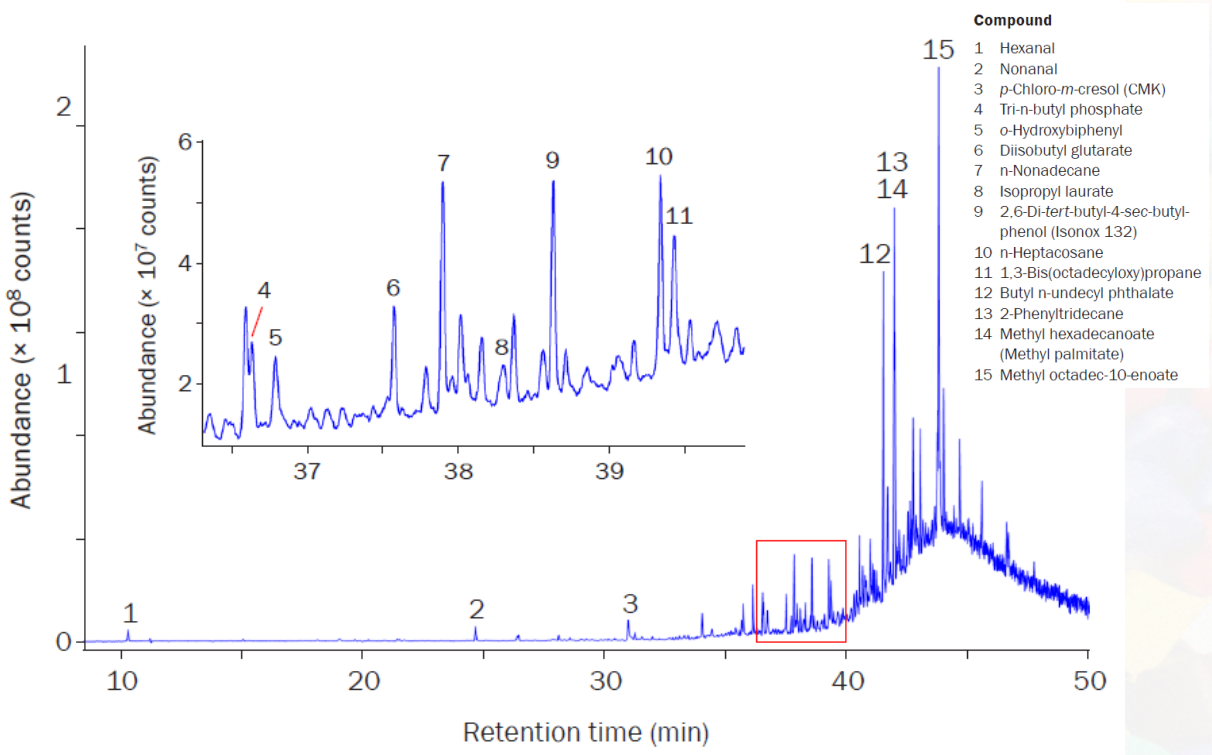
- VOC analysis: this involves desorbing the sample at 90 °C for 30 minutes to quantify volatile compounds up to *n*-C25.

- FOG analysis: FOG compounds (those with volatility range from *n*-C14 to *n*-C32) are then determined by leaving the sample in the desorption tube and raising the temperature to 120 °C for 60 minutes.

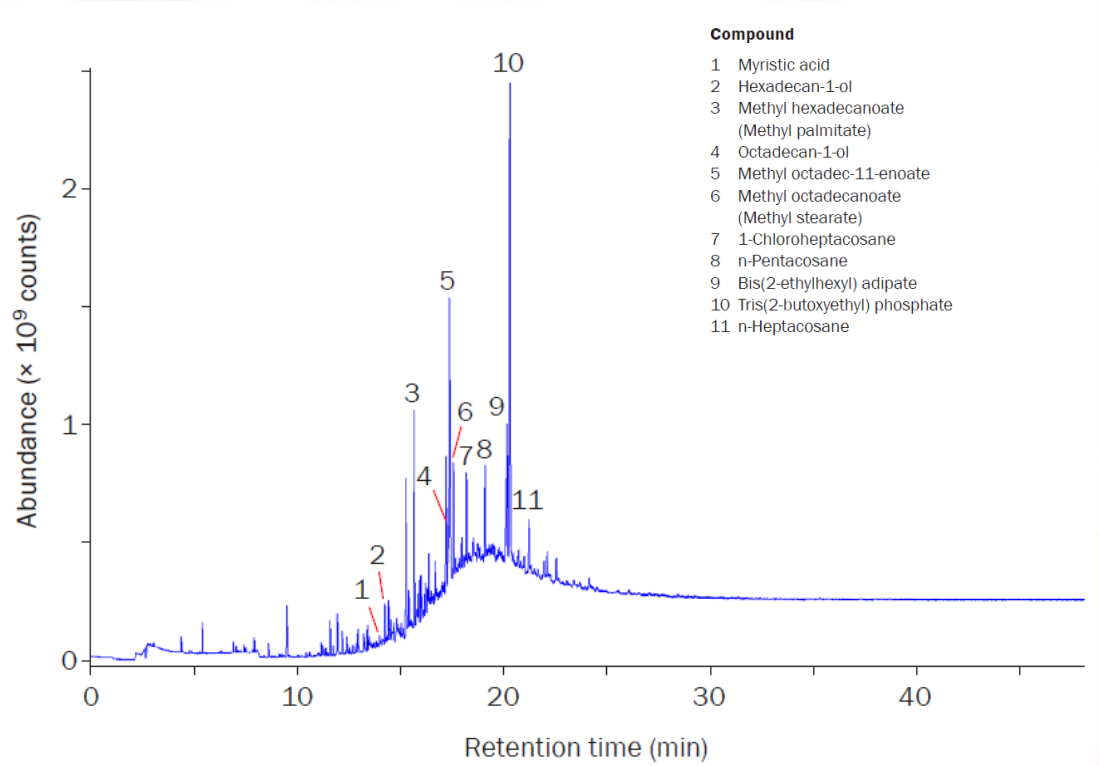


# Automotive interior VOC and FOG emissions



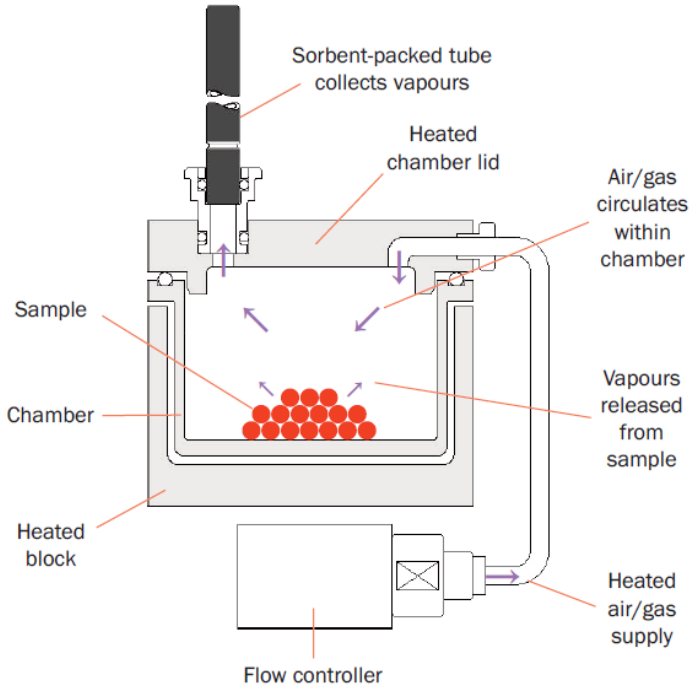

VOC analysis chromatogram of the leather car trim.

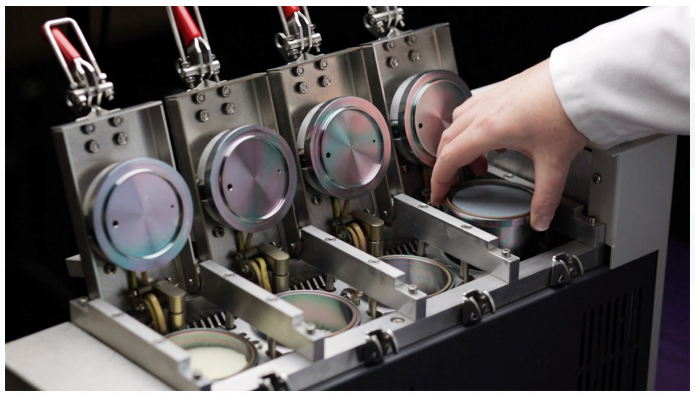


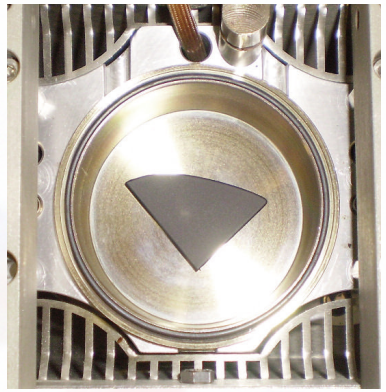

FOG analysis chromatogram of the leather car trim.

Long-term reference tests with small chamber/microchamber

# Rapid microchamber tests for screening chemical emissions from car trim.





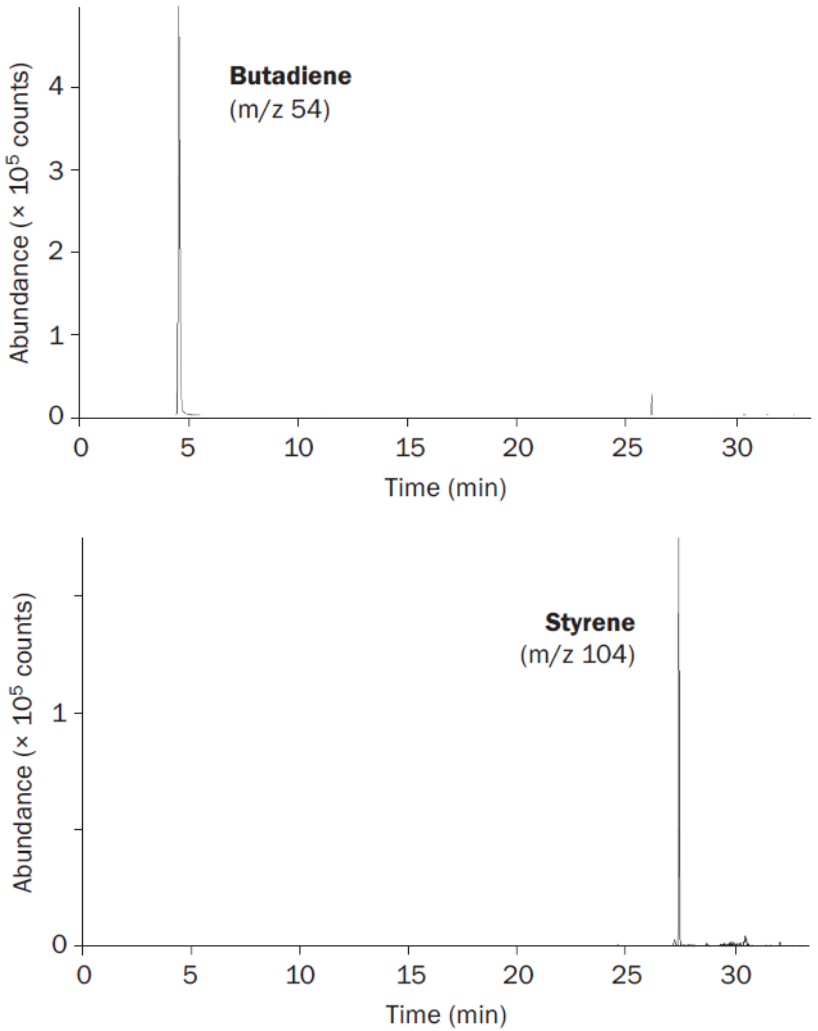
**Sample preparation**

- Cutting the sample to a width of 2 $cm^2$
- Load sample to chamber cup

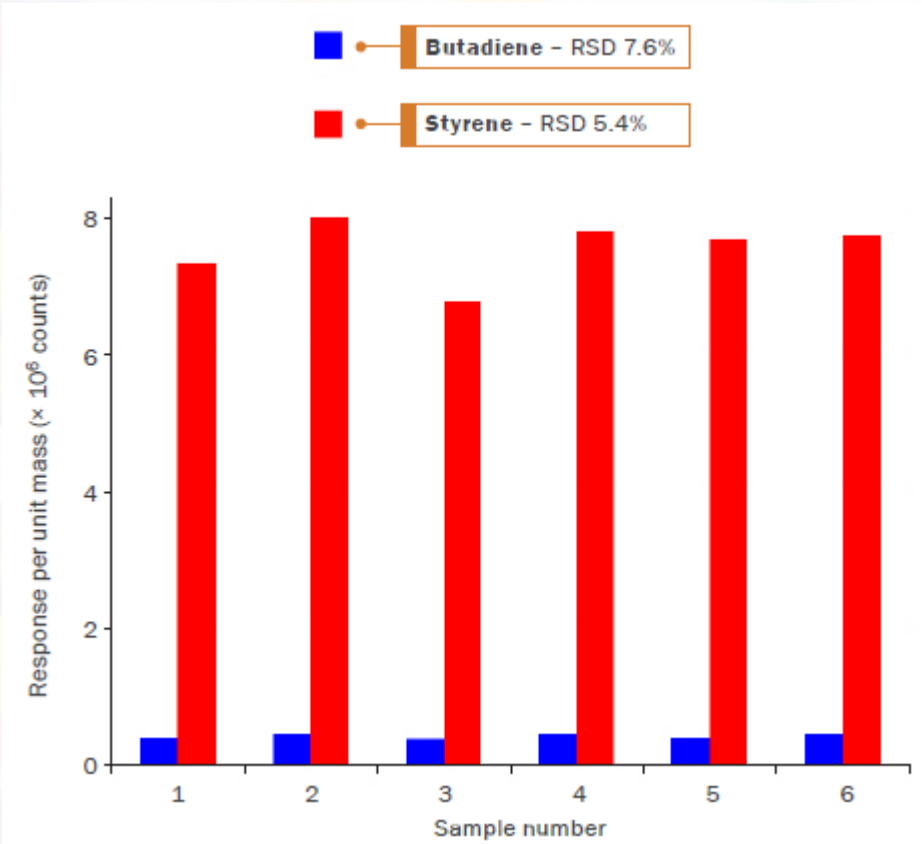
**Extraction**

- Temperature of 65°C and a flow of helium at 50 mL/min
- Equilibration time 20 min.
- A two-bed sorbent tube containing Tenax TA and Carbograph 5TD was then attached and emissions collected for 15 min.

# Rapid microchamber tests for screening chemical emissions from car trim.




Extracted-ion chromatograms for butadiene and styrene from Sample



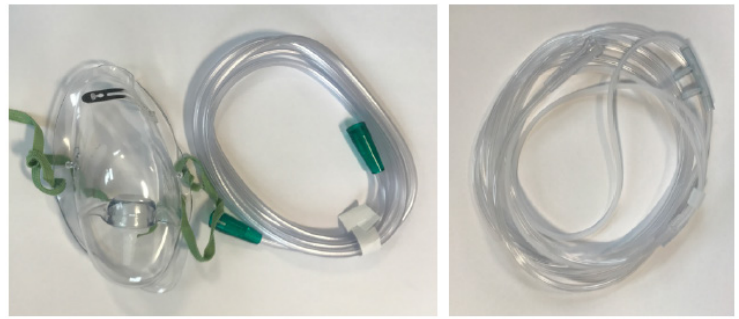

Reproducibilities of just 5–8% RSD were obtained when Markes' µ-CTE was used to test six identical samples of plastic material.

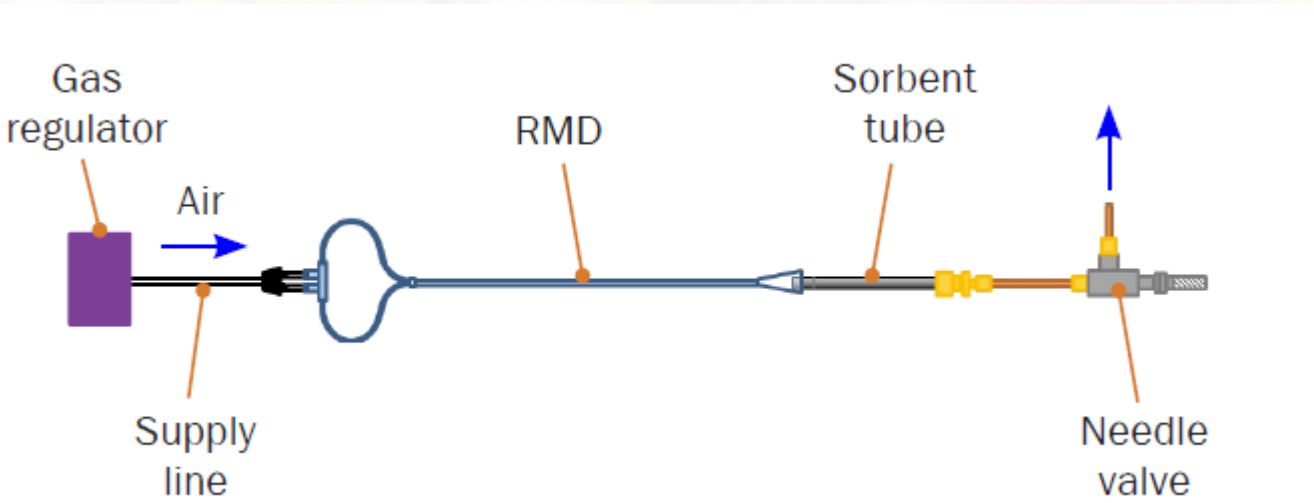
Monitoring VOC emissions from respiratory medical devices

# Monitoring VOC emissions from respiratory medical devices

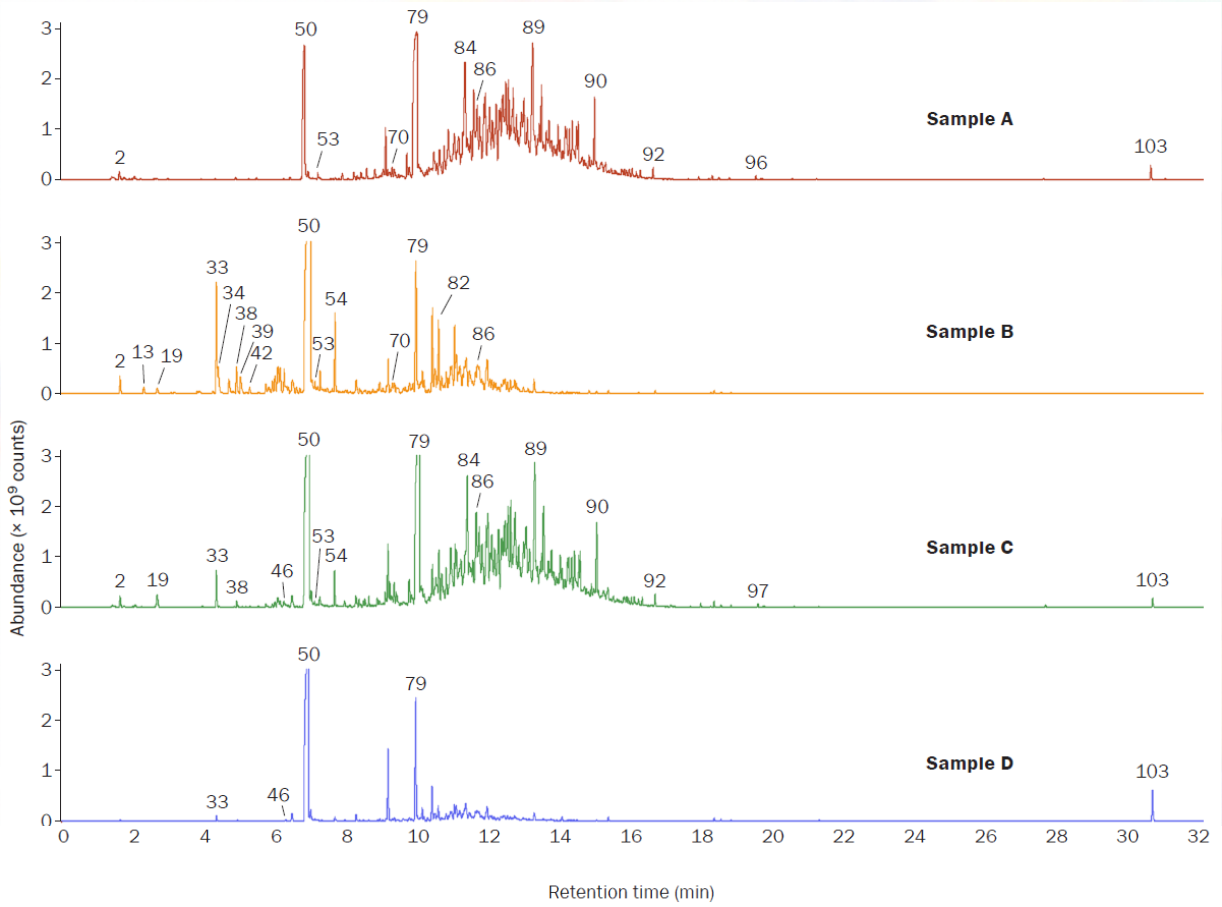
**Sample preparation and extraction**

- Cutting the sample tubing (which in each case was ~2 m long)
- Connect sample to sorbent tube and supply gas.
- Supply gas setup at 100 mL/min for 1 h at room temperature (~21°C), to transfer released VOCs onto the sorbent tube.



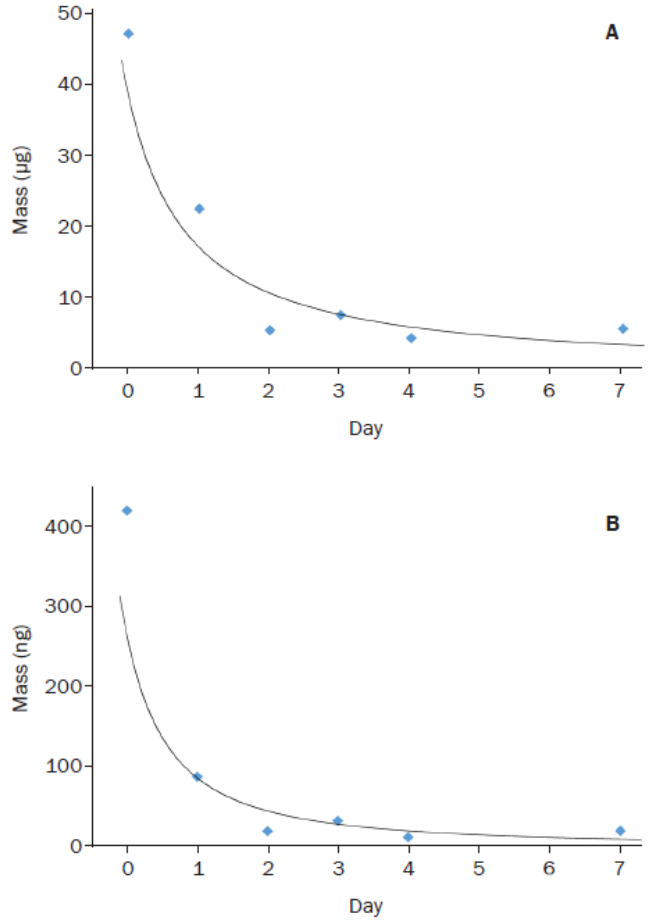


# Monitoring VOC emissions from respiratory medical devices




| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 2 | Acetone | 38 | Hexanal | 53 | 2-Butoxyethanol | 82 | Acetophenone | 92 | n-Tetradecane |
| 13 | 2-Methylpropan-1-ol | 39 | n-Octane | 54 | Cumene | 84 | n-Undecane | 96 | Diethyl phthalate |
| 19 | Cyclohexane | 42 | n-Butyl acetate | 70 | n-Decane | 86 | 1,2,4,5-Tetramethylbenzene | 103 | Bis(2-ethylhexyl) phthalate |
| 33 | Toluene | 46 | Ethylbenzene | 77 | o-Cymene | 89 | n-Dodecane | | |
| 34 | Pentan-1-ol | 50 | Cyclohexanone | 79 | 2-Ethylhexan-1-ol | 90 | n-Tridecane | | |

**Time-course study**

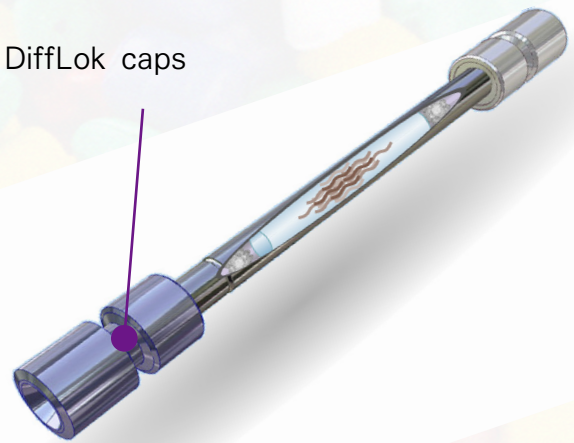



Decay profiles for (A) cyclohexanone and (B) toluene over a period of 7 days (samples were not taken on days 5 and 6). Power-law trendlines have been added

# Microplastics by TD-GC-MS

# Workflow: Sample Preparation

- Simplified using TD-GC-MS




Filtering
0.2µm quartz filter

Washing
with reagents

Drying
30min at 100˚C

Quick Preparation
filter into TD-tube

1 h
Sample
preparation
time

Direct Desorption at
320˚C

30 mins
analytical cycle

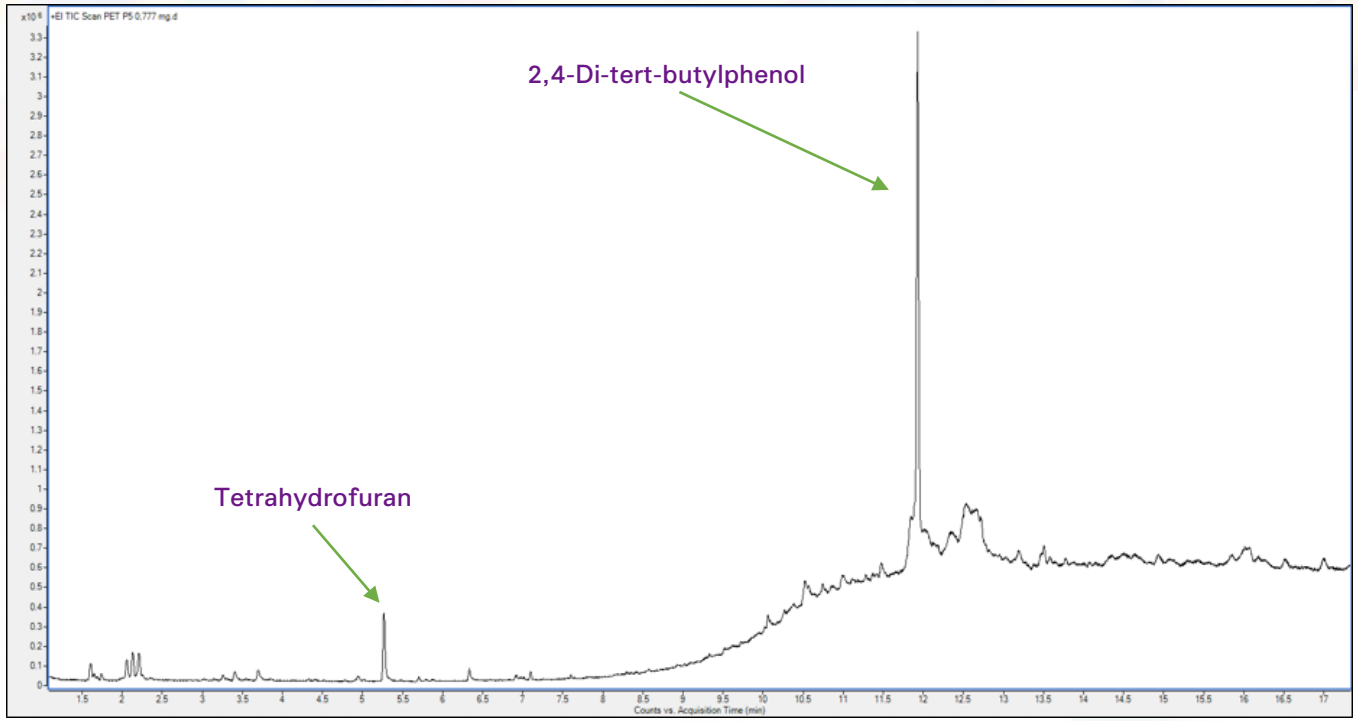
- Hundreds of mL to liters of water are filtered
- The filter is then washed with multiple reagents to remove organic matter
- Dried filter is then placed directly into an empty thermal desorption tube for analysis

# Microplastics in beverages: Case study

## Polyethylene terephthalate (PET) in beverages

Identify marker compounds for PET by TD–GC–MS analysis of standard pellets.

- 2,4-di-tert-butylphenol used as quantitation marker
- Tetrahydrofuran is used to confirm presence of PET

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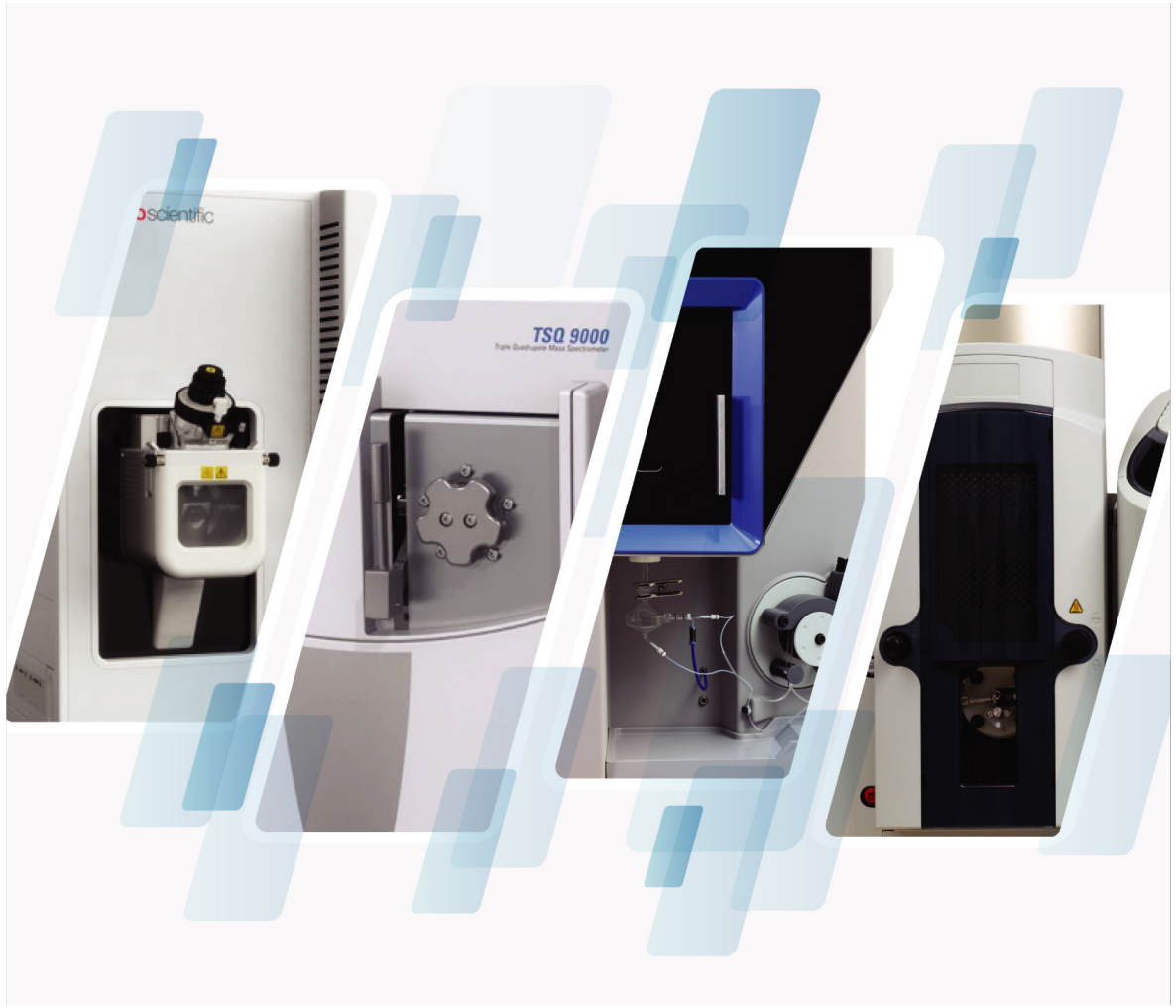


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