Neue Möglichkeiten zur Überwachung der Umgebungsluft mit Thermodesorption und GC/MS
What is Thermal Desorption?

Sorbent Material

Sample Matrix

e.g. Chamber or micro-chamber air
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

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

Demonstrating quantitative recovery of high boilers

- 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

*NB: ASTM Method D6196 references quantitative re-collection for validation*
ULTRA 2 DiffLok™ caps

Inert or Stainless steel outer body (shown transparent)

Sample tube pushes into cap here

O-ring for sealing tube into cap

Coned end for Auto-alignment with tube nozzle on ULTRA (the TD autosampler)

Threaded diffusion-locking insert in plain, cylindrical body.

• 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

* Patent Numbers: GB 2337513, US 6,564656 B1
The TubeTAG™ advantage for air monitoring

“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:
• $< n-\text{C}_{40}$, 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$_2$O, 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

Online air monitoring applications

Acetylene – up to 2L of sample taken without breakthrough

Green house gas analysis

Diurnal profiling of ozone precursors

Key:
- Blue (3 am)
- Red (12 noon)
- Green (5.30 pm)
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 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?

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<th>Perception</th>
<th>Tubes</th>
<th>Canisters</th>
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<td>World-wide acceptance</td>
<td>Gold standard for US ambient air market</td>
<td></td>
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<tr>
<td>Applications</td>
<td>Ambient air, indoor air, vapor intrusion, industrial hygiene</td>
<td>Ambient air, indoor air, vapor intrusion, emergency response</td>
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<td>Material emissions</td>
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<td>Food &amp; flavor</td>
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<tr>
<td>Chemical weapons</td>
<td></td>
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<tr>
<td>Handling</td>
<td>Light weight for personal monitoring and general ease of use</td>
<td>Larger and heavier; more costly to ship</td>
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<tr>
<td>Sampling</td>
<td>$C_3$-$C_{40}$ Concentration range ppt to %</td>
<td>$C_2$-$C_{10}$ Concentration range ppt to low ppm</td>
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<tr>
<td>Cleaning</td>
<td>Analytical process automatically cleans tube for re-use</td>
<td>Canister cleaning requires separate equipment as additional step prior to background certification and sampling.</td>
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<tr>
<td>Cost</td>
<td>$50 – $130 each</td>
<td>$200 - $700 each</td>
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Profiles of soil gas contaminated with kerosene obtained using:

- **canister sampling** with TO-15 analysis (blue)
- **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

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

Industrial perimeter monitoring

Workplace air monitoring
(Occupational hygiene)

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

Stack and ‘fugitive’ emissions
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

In situ monitoring of underground contamination

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
- Soil Gas samples
- MTS-32
- no need for calibrated pumps
- Breath Samples
- Canisters and Bags
- Sorbent Tubes

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

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

Data analysis
- 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???

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