THERMAL DESORPTION

Introduction and Principles
Thermal Desorption

- Thermal desorption is a simple extension of the technique of gas chromatography (GC).
- It involves the use of heat and a flow of inert gas to extract volatile and semivolatile organics from a solid sorbent or other sample matrix.
- The analytes are extracted into the stream of inert gas and are transferred to the GC in a small, discreet and concentrated volume of vapor.
Benefits of Thermal Desorption Versus Solvent Extraction

Versatility

• Detection limits enhanced by a factor of $10^3 - 10^4$. This makes thermal desorption compatible with both indoor and outdoor air monitoring as well as industrial hygiene.

• Reliable, 95% or better desorption efficiencies for all VOCs, including polar compounds, versus 30-80% for most solvent extraction methods.
Benefits of Thermal Desorption Versus Solvent Extraction - Continued

Cost saving

• No manual sample preparation thus reducing time and cost per analysis
• Reusable tubes - Thermal desorption tubes are reusable 100-200 times. At £30 per tube this equates to < 30p per analysis.
• Reduced consumable costs
• No solvent disposal costs and associated overhead expense
• No expensive air extraction equipment required
Benefits of Thermal Desorption Versus Solvent Extraction - Continued

No solvent required

- No masking of peaks of interest by the solvent (especially important with MS)
- No introduction of artifacts/impurities from the solvent
- No solvent selection issues with respect to materials analysis
- Improved laboratory working environment
- Eliminates a health hazard. - $\text{CS}_2$ is the most commonly used extraction solvent. This is a very hazardous chemical and exposes the analyst to unacceptable air pollution
Thermal Desorption - Applicability

Used for the analysis of volatile or semivolatile organics in sample matrices that cannot be directly introduced to the analyser/detector e.g......

- dilute vapor-phase samples such as polluted air or breath
- solids - powders, film, fibres, granules
- resins - adhesives,
- pastes tooth paste, ointment
- emulsions - paint, blood
- salt or sugar solutions
What Will Thermal Desorption Handle?

Any organic compound, volatility $\geq n$-C$_{40}$, which is easily gas chromatographed . . . .

. . . . PROVIDED the sorbent or matrix containing the analytes is compatible with the high temperatures required
What Won’t It Do?

- Compounds which are not compatible with gas chromatography
- Compounds with volatility < n-C$_{40}$
- Compounds which require special care during GC analysis, e.g., on-column injection
- Most inorganic (permanent) gases
  - exceptions include N$_2$O, SF$_6$ and CS$_2$
Sample \hspace{1cm} \rightarrow \hspace{1cm} GC

- Direct transfer of analytes from the sample to the GC is called single stage thermal desorption. It invariably takes at least a minute, often several minutes, to complete the analyte transfer. This long ‘injection’ time produces very broad peaks.
2-Stage Desorption Using a ‘Large’ Sorbent Trap at Ambient Temperature

Split on Inlet to Cold Trap

Hot Sample Tube

Ambient Trap

Primary (Tube) Desorption

Split on Outlet to Trap

Cooling Sample Tube

Hot Trap

Secondary (Trap) Desorption

Broad Peaks

Focusing on Volatiles
Single Stage Desorption or Focusing on Ambient Traps Produces Broad Peaks

4 mm ID Tube to 2 mm ID Tube to Column

Ethylene

Ethane

Acetylene

4 mm ID Tube to Column

0 2 4 Min.

0 2 4 Min.
2-Stage Desorption Using Capillary Cryofocusing

- **Split on Inlet to Cold Trap**
- **Primary (Tube) Desorption**
- **Secondary (Trap) Desorption**

- **Hot Sample Tube**
- **Capillary cryofocusing**
- **Cooling Sample Tube**
- **Hot Capillary**

**Focusing on Volatiles**
Disadvantages of Capillary Cryofocusing

- High consumption of liquid cryogen (sometimes over 2 L per hour)
- Capillary systems easily plug with ice
- Permanent gases such as CO$_2$, nitrogen and OXYGEN may also be retained and cause analytical instability
2-Stage Desorption Using a Small, Packed, Electrically-Cooled Trap
Advantages of Small, Packed, Electrically-Cooled Traps

- No liquid cryogen required
- Quantitative retention, even of very volatile components such as ethane
- Desorption in backflush mode gives quantitative recovery of analytes over a wide boiling range
- Rapid (60 deg/sec) desorption gives narrow capillary peaks with no additional focusing required \(\rightarrow\) High sensitivity and short analysis times
- No risk of ice plug formation blocking the sample flow path
Peak Shape from UNITY with no On-Column Focusing

1.6 seconds wide at half height
Speciated VOC Monitoring: An Overview of the Analytical Process

Sampling - Selective concentration - Desorption - Transfer - Measurement

On-line

Cryogen free cold trap

Canisters/bags

Tubes

~200 uL injection of vapour

GC / GC-MS

Focus on Volatiles
2-Stage Thermal Desorption: Electrically-cooled, Sorbent-packed Focusing Trap

Narrow bore end - Sample in and out
Concentration Enhancement Potential Using Pumped Sorbent Tubes and 2-stage TD

- Pumped sample volume: typically 5-100 L of air
- Desorb tube in 100-200 ml of carrier gas and transfer effluent to focusing trap
- Desorb focusing trap in 200-300 uL of carrier gas and transfer the effluent to the analytical system without band dispersion

*Overall concentration enhancement potential ~ \(10^5\) - even \(10^6\) if 100-200 L sample volumes are collected*
**Off-line Sampling: Sorbent Tubes**

**Summary information:**
- ¼” external diameter x 3 ½” long
- Accurate positioning of sorbent retaining gauzes in metal tubes allow these to be used for diffusive and pumped sampling. Also ensures all of bed in heated zone essential for passive sampling
- Glass tubes have same external dimensions but narrower I.D. Sorbent retained by glass wool. They are not suitable for diffusive sampling
Concentration Enhancement Potential: Whole-Air/Gas - Canisters, Bags, On-line

- Typically 200-2000 ml of air passed through focusing trap
- Focusing trap desorbed in as little as 200 uL of carrier gas and the effluent transferred to the analytical system without band dispersion

Single stage only - Overall concentration enhancement potential $10^3$ - $10^4$
Off-line Sampling: Passivated Stainless Steel Canisters

- Protective Shield
- Valve
- Summa® Passivated Interior
- 6L Volume typically used for samples

Focusing on Volatiles
Thermal Desorption - Key Parameters

Being an extension of gas chromatography, thermal desorption methods are optimised by adjusting the following key parameters:

- Temperature
- Gas flow
- Time
- (Sorbent / packing)
Optimising TD Methods for Sorbent Tubes - Primary (Tube) Desorption

- Temperature: As hot as possible within the constraints of sorbent or sample matrix stability
- Gas flow: As fast as possible through the tube
- Time: Just sufficient for complete (or representative) desorption of target analytes from the tube or for selective elimination of interfering compounds from the cold trap (if applicable), whichever is longer.
- Tube packing (where applicable): Strong enough for quantitative retention during sampling; weak enough for quantitative desorption during analysis
Optimising TD Methods for Sorbent Tubes
- Cold Trapping during Primary Desorption

- Sorbent(s): Strong enough to retain analytes during primary desorption; weak enough for quantitative desorption of target analytes during secondary desorption; weak enough also for selective elimination of interfering volatiles
- Temperature: Cold enough for quantitative retention of target analytes while allowing volatile interferents to pass through unretained to vent
- Gas flow: Sufficiently slow to prevent premature breakthrough of target analytes
- Time: Long enough to allow selective elimination of interfering compounds but otherwise as short as possible to minimise risk of analyte losses

Focusing on Volatiles
Optimising TD Methods for Sorbent Tubes - Secondary (Trap) Desorption

- Temperature: Hot enough for rapid, quantitative desorption of target analytes
- Gas flow: As fast as possible within the constraints of method detection limits
Selection of the Correct Sorbent(s) for the Sample Tube Ensures …….

- No breakthrough during sampling and
- Quantitative recovery during thermal desorption

……..with less than 1 g of adsorbent.

Standard, small - 1/4-inch O.D. - sorbent tubes are easy to condition, easy to desorb, quick to purge with carrier gas and inherently less subject to artifact formation than larger 5/8-inch O.D. tubes.
Two-Stage Thermal Desorption - A Complete Analytical Sequence

- Standby (split or splitless)
- Tube load
- Leak test (no flow / no heat / high pressure)
- (dry purge - in sampling direction)
- pre-purge - ambient temperature to remove air (to split and/or trap)
- (pre-purge - elevated temperature - invariably to split)
- primary (tube) desorption (split or splitless)
- Secondary trap desorption (split or splitless) and initiation of the GC(-MS) analysis
Why Backflush the Cold Trap?

- To allow use of multi-sorbents in series and thus extend the analyte volatility range
- To minimise desorption times / volumes
- Because it says so in std methods like TO-17
Why Do You Need a Heated Inert Valve in the TD Sample Flowpath?

- To isolate the cold trap from the carrier gas flow during standby and thus prevent its contamination with carrier gas artifacts
- To carry out a no-flow, low temp, high-pressure, pre-desorption leak test as required by standard methods
- To allow dry-purging of tubes in the sampling direction (per std methods)
Why Do You Need a Heated Inert Valve in the TD Sample Flowpath?

- To allow purging of air from the tube before desorption without any of that air being allowed to reach the analytical column and detector
- To allow selective elimination of volatiles (e.g. water, solvent) from the cold trap during primary desorption without the purged compounds reaching the GC column and detector
- To prevent quantitation errors due to premature migration of the solvent from the trap to the GC
Why Do You Need a Heated Inert Valve in the TD Sample Flowpath?

- To allow leak-testing, purging, primary desorption, etc of a subsequent sample while GC analysis of a previous sample is ongoing (optimises throughput)
- To prevent high boiling components still eluting from the sample tube from migrating slowly onto the hot trap and causing peak ghosting
- To allow backflush desorption of the cold trap
- To isolate the sample tube from the cold trap during secondary desorption
Why Do Injector Liners Not Make Suitable Sample Tubes?

- Non-standard tubes - i.e do not comply with standard methods
- Single stage desorption - broad peaks
- Desorption of the outside walls of the tube as well as its contents which introduces artifacts from sample handling
- Single split only
- The only possibility for focusing involves liquid cryogen cooling of the capillary analytical column
- All the limitations just described in connection with flow-through thermal desorption - No leak test, air reaching system, no selective purging of solvent (without some of the purged compounds reaching the GC column and detector), no dry purge option, etc, etc