New Developments in Thermal Desorption (TD) Tube & Canister Technologies for Collection & Analysis of Soil Gas

Presented by Roy Smith, M.Sc., MBA, C.Chem.
Why Use TD Tube or Canister Sampling For Collection of VOCs in Air?

• NIOSH & OSHA charcoal & other sorbent tube methods for VOCs require extraction of the sorbent with a solvent resulting in interfering peaks, poor recoveries & typically high (ppm) detection limits
• Sampling using TD tubes or canisters provides a universal approach for collecting VOCs (non-polar to polar; gases to semi-volatiles) in air
• One sample replaces the need for many NIOSH & OSHA methods providing greater ease & flexibility in sampling ambient, indoor & soil gas air
International Standard Methods for the Determination of Volatile Organic Compounds (VOCs) in Air (Partial List)

**TD Sorbent Tube**
1. EPA TO-17: Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes.

**Canister**
1. EPA TO-14A: The Determination Of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters With Subsequent Analysis By Gas Chromatography.
2. EPA TO-15: The Determination Of Volatile Organic Compounds (VOCs) in Air Using Collected In Specially-Prepared Canisters and Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS).
4. OSHA PV2120: Volatile Organics in Air
ALS Thermal Desorption GC-MS System
What’s New in TD Instrumentation?

- Electronic control of all flow paths for consistency of sample retention times
- Automated spiking of internal standard/surrogate as a gas onto TD tube
- Leak check of tube & trap prior to each analysis to confirm performance
- Automated recollection of sample on the same or different tube
- Excellent water management for accuracy of analysis

PerkinElmer 650 ATD showing capped TD tubes loaded in robotic autosampler (Courtesy of PerkinElmer)
Key Factors in Selection of a Universal TD Tube For Air Sampling

- Broad VOC molecular range for collection of gases to semi-volatiles on one tube
- Large Safe Sampling Volumes (SSV) for low DLs
- Optimal water management for collection of all types of air samples
- 100% recovery of VOCs from multi-adsorbents
- Clean to background levels after one desorption cycle

3½ inch Stainless Steel PerkinElmer Soil Vapour Intrusion (SVI) TD tubes
Multi-sorbent TD Tubes Investigated by ALS Environmental to Meet Key Factors

- Markes Universal (3 adsorbents)
- Supelco Carbotrap 349 (3 adsorbents)
- PerkinElmer Air Toxics (2 adsorbents)
- PerkinElmer Soil Vapour Intrusion (SVI) (3 adsorbents)
  ✓ SVI tube selected as meeting all key factors
What Is & Why Are Large Safe Sampling Volumes Important?

- Breakthrough volume (BV) for a given sorbent combination is the air sample volume at which there is 5% breakthrough of that analyte onto a back-up tube.
- Safe sampling volume is taken as 2/3 of BV.
- Large SSVs give low air reporting limits: e.g. indoor air 6-10L.
- SSVs for different VOCs on SVI tube (ALS results):
  - Chloromethane: 6L
  - Vinyl chloride: 10L
  - 1,3-Butadiene: >50L
  - Bromomethane: 10L
  - Dichlorodifluromethane (CFC 12): 10L
  - Dichloromethane: 40L
  - Benzene: >50L
  - N-Hexane: >50L
  - Trichloroethene: >50L
  - Naphthalene: >50L
Excellent Recovery of VOCs Off SVI Tube With Insignificant Carryover

20,000ng Gasoline & 200ng Volatiles Mix

2nd Desorption of Above Tube
< 1% VOCs Remaining on Tube
Active TD Tube Sampling for VOCs

CapLok Tool, Swagelok capped TD tube & uncapped TD tube

Low flow personal sampling pump with TD tube attached
What’s New in Canister Instrumentation?

- Robotic auto-sampler with single flow path heated silica coated line gives quantitative transfer of VOCs from canister to preconcentrator system
- Auto-sampler canister heater for analysis of semi-volatiles
- Improved sample analysis with volume measurement from canister by pressure
- Three stage, active SPME based preconcentrator system for accurate recovery of VOCs over a wider molecular range (gases to semi-volatiles)

7500A Robotic Headspace Autosampler
(Courtesy of Entech Instruments)
Improvements in Canister Sampling

• Micro-QT™ quick connect valves are easy to use & give superior performance
• Silica coated canisters, valves, & flow controllers provide more quantitative collection of VOCs
• Bottle-Vac™ glass samplers reduce the potential of sample contamination providing more accurate VOCs results
• Helium diffusion samplers offer simplified field sampling with increased VOCs MW range
• Large vacuum extraction headspace vials for analysis of finished products & bulk materials

(Courtesy of Entech Instruments)
Grab & TWA Canister Sampling For VOCs
Complimentary Techniques – Why Would You Use TD Tubes?

- Quantitative recovery high MW VOCs
- Quantitative recovery of polar VOCs even at high RH (>70%)
- Constant pump flows rates (<5%) for accurate TWA monitoring
- Volume of air collected is not dependent on canister size
- Volume of air sampled is easily adjusted to meet different regulatory requirements (ng/m³ to mg/m³)
- Sampling time easily changed in field by re-calibration of pump flow rate
- Sampler size favors use for personal exposure monitoring
- Easy & less expensive to ship
- Sample re-analysis is possible in recollect mode
- Easier cleaning of sampling media - 1 to 2 cleanings adequate to bring tube back down to background levels
Complimentary Techniques – Why Would You Use Canisters?

- Ideal for grab or short-term sampling
- Quantitative collection of low MW VOCs (C1-C4 range)
- Silica coated canisters suitable for collection of all VOCs including sulfur & other reactive compounds
- Different analyses are possible from the same canister if sufficient volume is collected (e.g. VOCs & methane)
- Dilution & multiple analyses of sample is possible
- Good in remote locations where charging of sampling pump is a problem
- 24hr & longer TWA sampling
- Prior knowledge of VOCs air concentration is not a controlling factor during sampling (no SSV issue)
- Helium diffusion may offer: 1) easier TWA sampling with increased VOCs MW range; 2) better collection of water reactive compounds such as H₂S, formaldehyde, etc.
Approaches to Soil Gas Sampling in the Vadose Zone

  – Collection of soil gas by a **whole-air or sorbent method** in an active or passive approach
  – Collection of a bulk soil or water sample for subsequent sampling of a **contained headspace atmosphere**

• As per ASTM, **contained headspace atmosphere** methods are not recommended since they “do not yield samples representative of in situ vadose zone atmospheres”:
  – The headspace atmosphere is not a true soil gas, but is an artificial atmosphere formed above a potential contaminant source, that is, the soil sample
  – Headspace atmospheres differ from in situ vadose zone atmospheres in that large percentages of vapour phase & moderate percentages of solute & sorbed phase contaminants can be lost in the act of soil sampling
Conceptual Model of Vapor Intrusion
(Courtesy of ITRC, Vapour Intrusion Pathway: Practical Guide VI-1, Jan. 2007)
Improved Sub-Slab & Soil Gas Sampling Train

- Combined filter & critical orifice element provides a 200 cc/min flow rate found in many sampling guidelines
- Micro-QT™ valve allows shipping under pressure (ensures clean sampling path from lab to field)
- Integrated vacuum gage
- Silonite® coated filter & lines to minimize VOCs surface interactions
- Low internal volume in train minimizes losses & makes easy to clean

(Courtesy of Entech Instruments)
Soil Probe Monitoring for VOCs in Soil Around Contaminated Sites

- VOCs soil probes & TD diffusion samplers allow in-situ screening of known & unknown underground leaks of chemical waste & petroleum fuels
- Typically, soil probes are placed in a grid pattern to monitor for 24hrs enabling concentration contour maps of total or speciated VOCs
- Soil probes placed along pipelines or around the perimeter of landfills can provide early warning of chemical leaks

Contour map from VOC-Mole soil probes at an industrial site (Courtesy of Markes International)
Soil Gas Monitoring & Risk Assessment

- Studies have shown that canisters can be prone to selective loss of petroleum hydrocarbons greater than the $C_{10} - C_{12}$ range.
- Selective loss will affect the risk assessment accuracy for human health since the F2 hydrocarbon fraction ($C_{10}-C_{16}$) range is of concern.
- Losses of heavy hydrocarbons contaminate canisters making them extremely difficult to clean to background levels.
- Active sampling with TD tubes is not subject to the same losses resulting in better recovery of heavier volatile petroleum hydrocarbons (VPHs).
Gasoline Spiked Sand Soil Gas Study
TO-15: Canisters versus TO-17: TD tubes
(Hayes et al., Proceedings A&WMA Conference, Vapour Intrusion, Sept 2007)
Diesel Spiked Sand Soil Gas Study
TO-15: Canisters versus TO-17: TD tubes
(Hayes et al., Proceedings A&WMA Conference, Vapour Intrusion, Sept 2007)
Jet Fuel Spiked Sand Soil Gas Study
TO-15: Canisters versus TO-17: TD tubes
(Hayes et al., Proceedings A&WMA Conference, Vapour Intrusion, Sept 2007)
Thank You
&
Your Questions?

Right Solutions…
… Right Partner