Environmental

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

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Minerals Coal Environmental Tribology Food & Pharmaceutical Industrial

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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.
2. ISO 16017: Air Quality - Sampling and Analysis of Volatile Organic Compounds in Ambient, Indoor and Workplace Air by Sorbent. Tube/Thermal Desorption/Capillary Gas Chromatography. Part 1: Pumped Sampling; Part 2: Diffusive Sampling
3. ASTM D6196-03: Standard Practice for Selection of Sorbents, Sampling & Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air. *(Pumped & Diffusive Sampling)*
4. NIOSH 2549: Volatile Organic Compounds - Screening Using Multi-bed Sorbent Tubes, Thermal Desorption, Gas Chromatography & Mass Spectrometry.

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).
3. ASTM D5466-01: Standard Test Method for Determination of Volatile Organic Chemicals in Atmospheres (Canister Sampling Methodology)
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

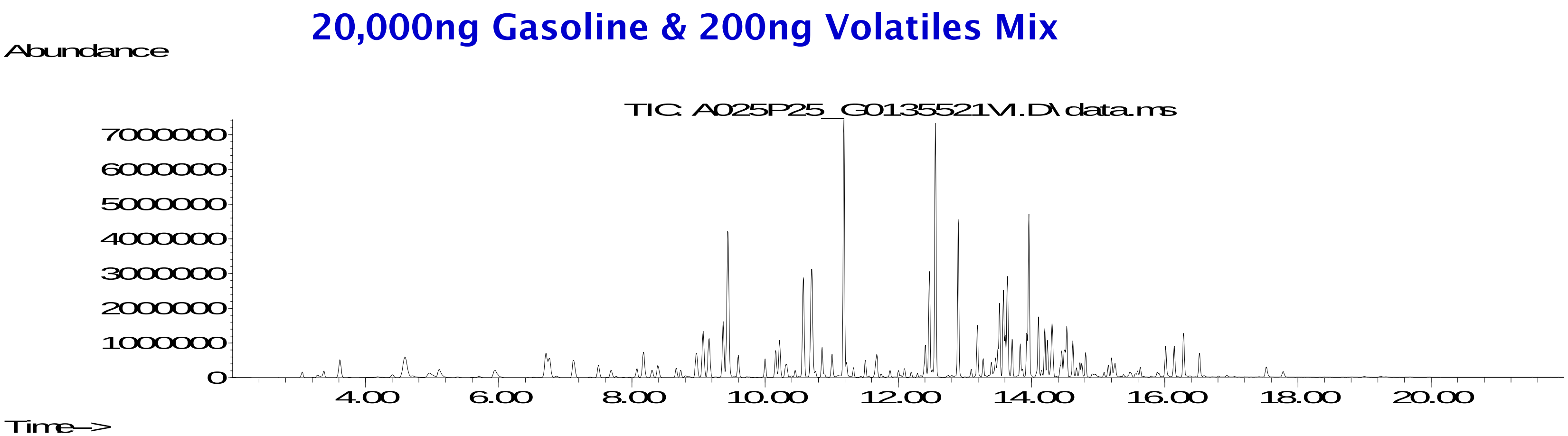
- **Markes Universal (3 adsorbents)**
- **Supelco Carbotrap 349 (3 adsorbents)**
- **PerkinElmer Air Toxics (2 adsorbents)**
- **PerkinElmer Soil Vapour Intrusion (SVI) (3 adsorbents)**
  - ✓ SVI tube selected as meeting all key factors

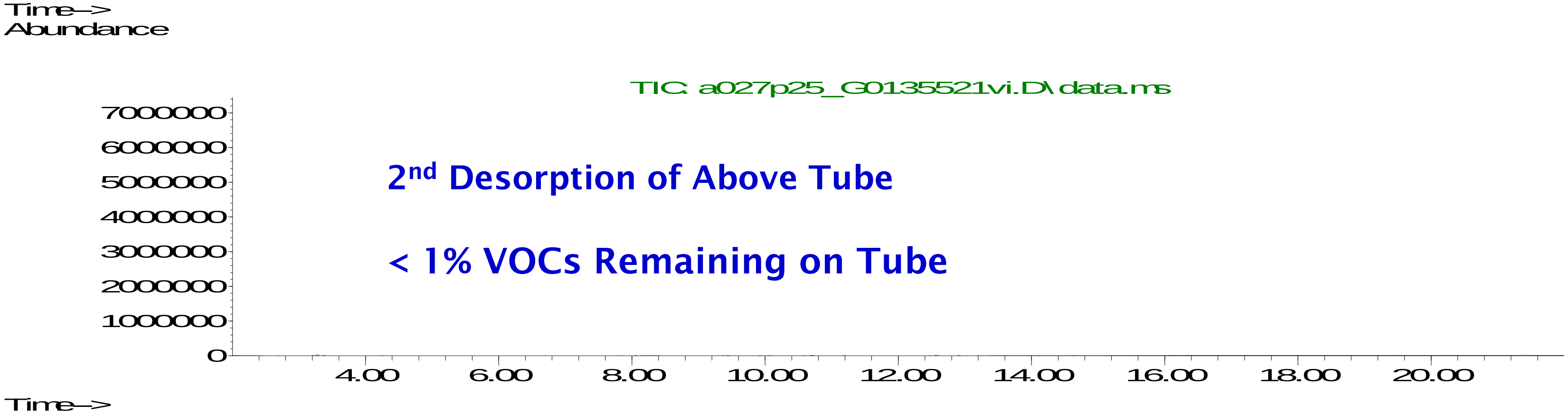
What Is & Why Are Large Safe Sampling Volumes Important?

- **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

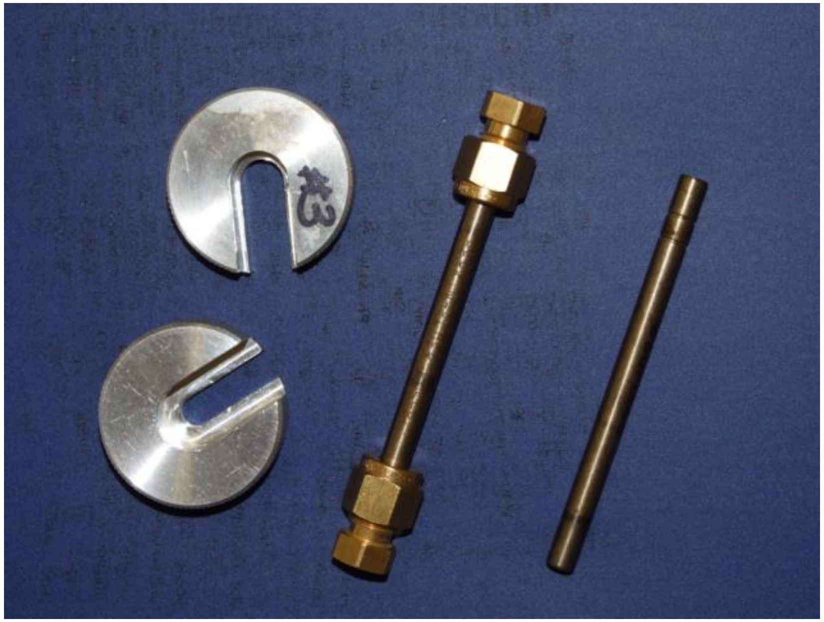
GASES → PAHs

Excellent Recovery of VOCs Off SVI Tube With Insignificant Carryover





Active TD Tube Sampling for VOCs



CapLok Tool, Swagelok capped TD tube
& uncapped TD tube

Low flow personal sampling pump
with TD tube attached

ALS Canister GC-MS System

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

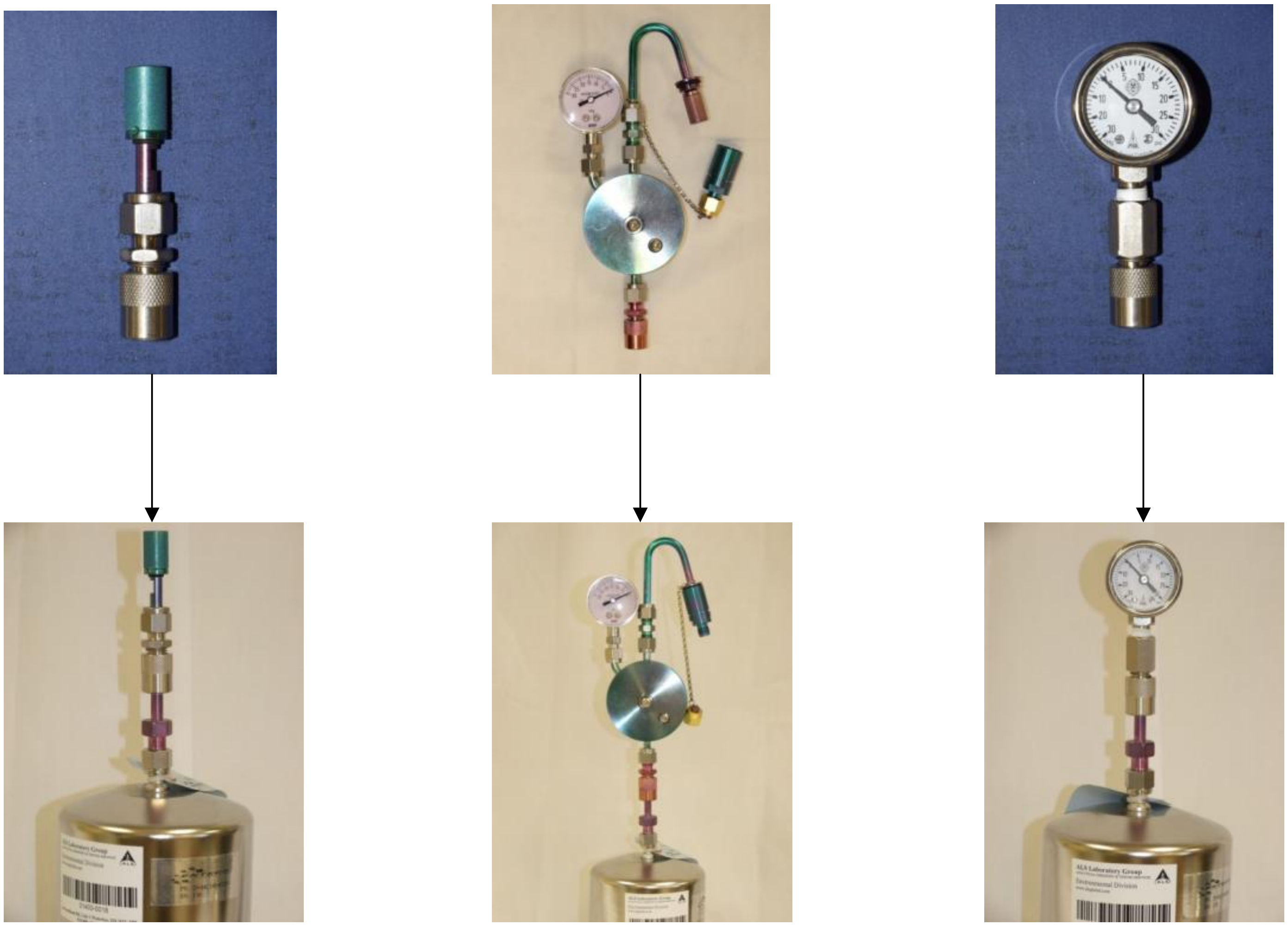






(Courtesy of Entech Instruments)

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/m^3 to mg/m^3)
- 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?

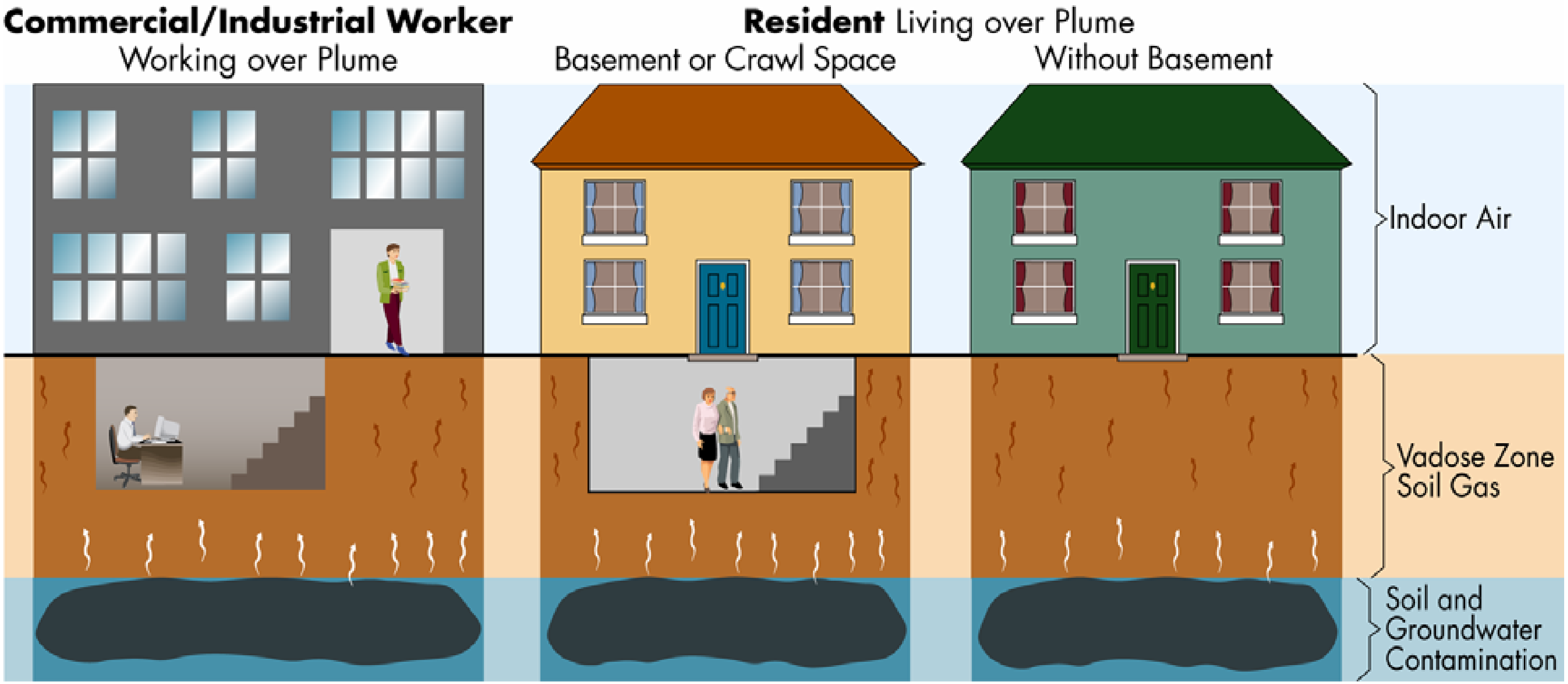
- Ideal for grab or short-term sampling
- Quantitative collection of low MW VOCs (C1-C4 range)
- Silica coated canisters suitable for collection of all VOCs including sulfur & other reactive compounds
- Different analyses are possible from the same canister if sufficient volume is collected (e.g. VOCs & 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 H_2S, formaldehyde, etc.

Approaches to Soil Gas Sampling in the Vadose Zone

- **ASTM D5314-92 (2006): "Standard Guide for Soil Gas Monitoring in the Vadose Zone" gives 6 sampling systems based on 2 main approaches for soil gas sampling:**
  - 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)



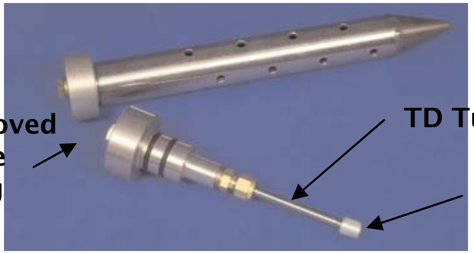
Improved Sub-Slab & Soil Gas Sampling Train

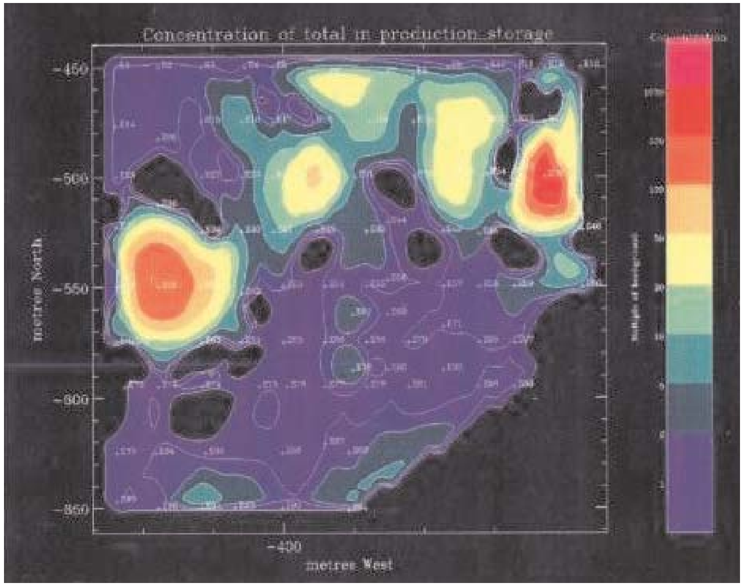
- Combined filter & critical orifice element provides a 200 cc/min flow rate found in many sampling guidelines
- Micro-QT™ valve allows shipping under pressure (ensures clean sampling path from lab to field)
- Integrated vacuum gage
- Silonite® coated filter & lines to minimize VOCs surface interactions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

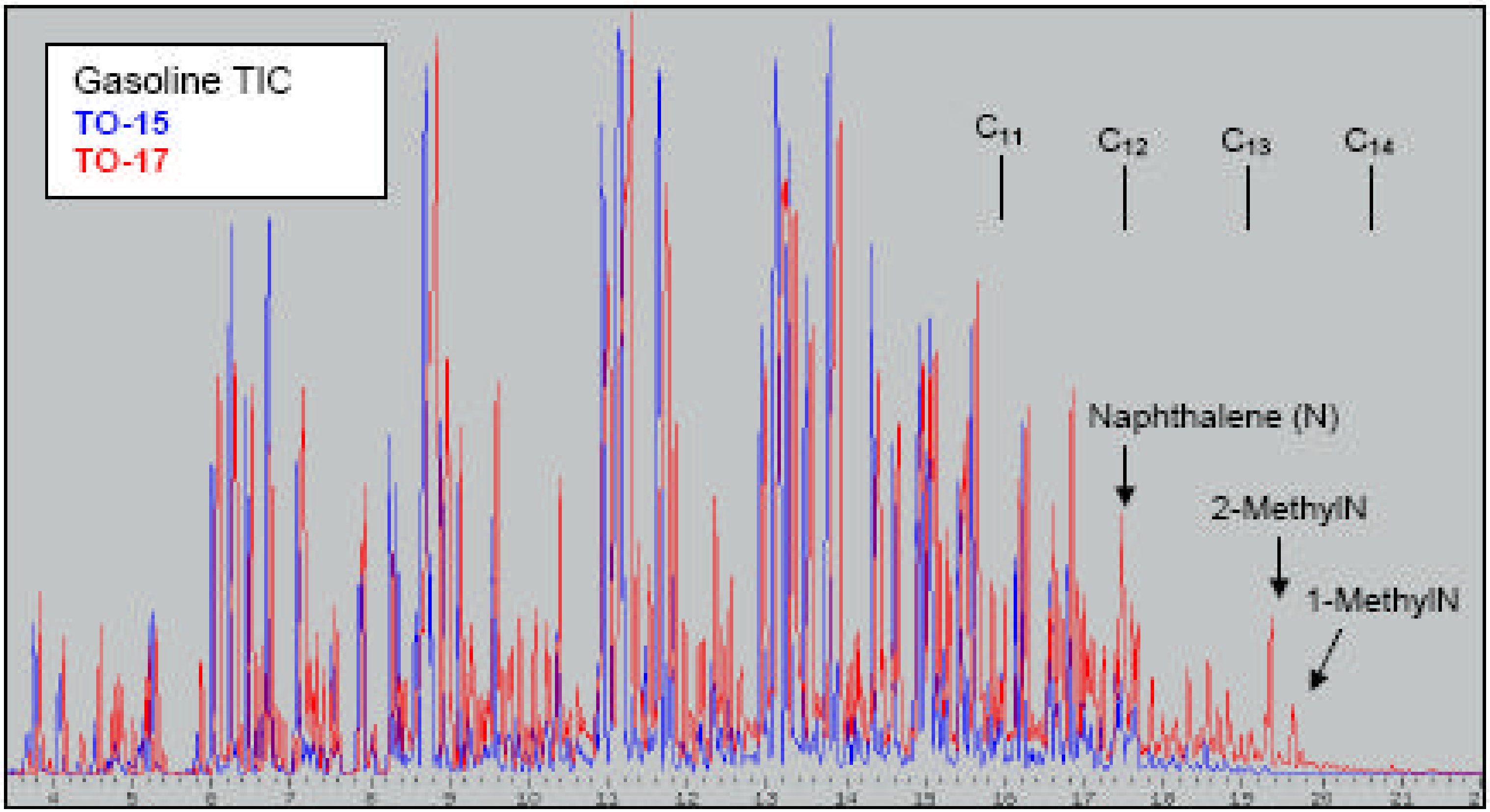
Soil Gas Monitoring & Risk Assessment

- 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

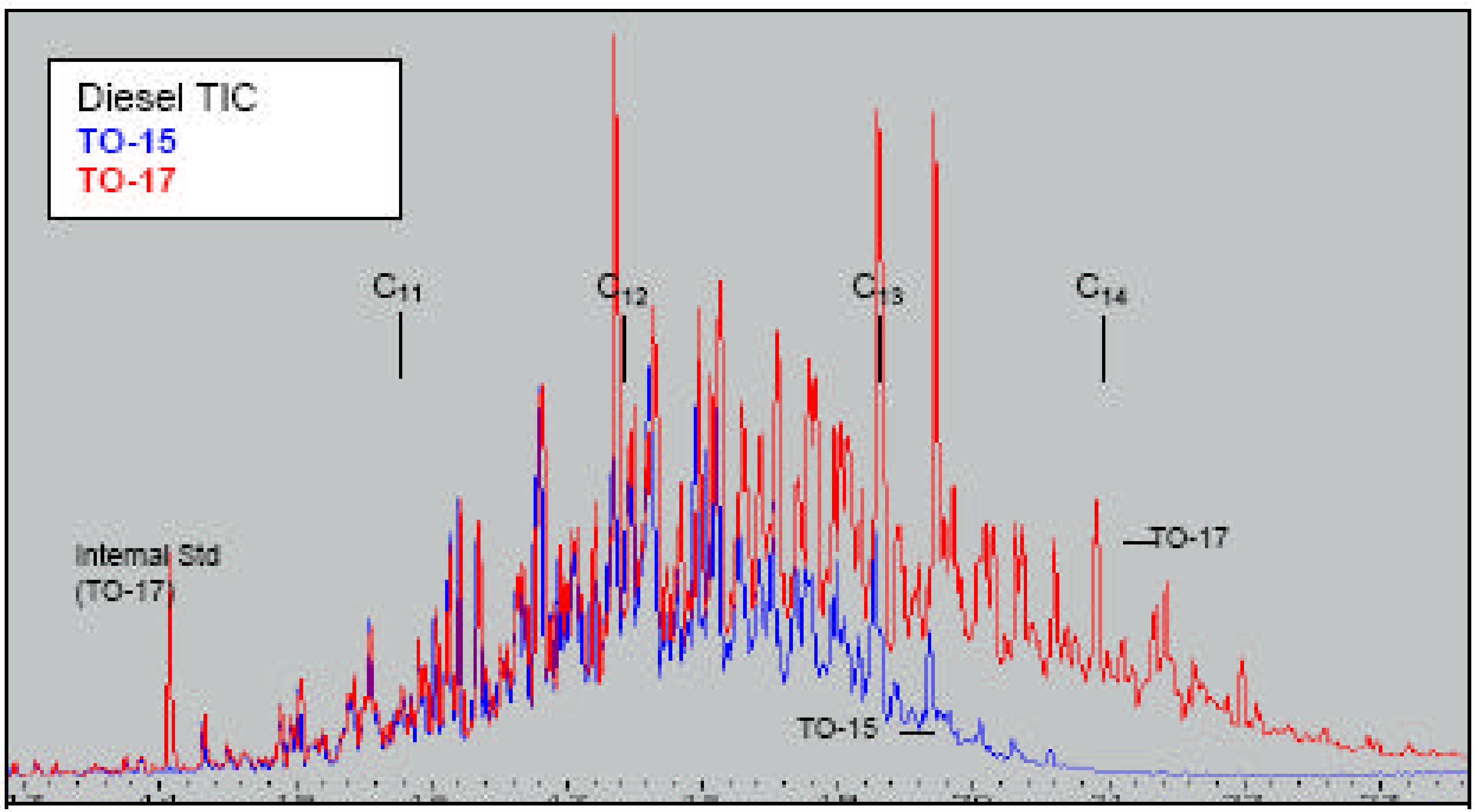
(Hayes et al., Proceedings A&WMA Conference, Vapour Intrusion, Sept 2007)



Diesel Spiked Sand Soil Gas Study

TO-15: Canisters versus TO-17: TD tubes

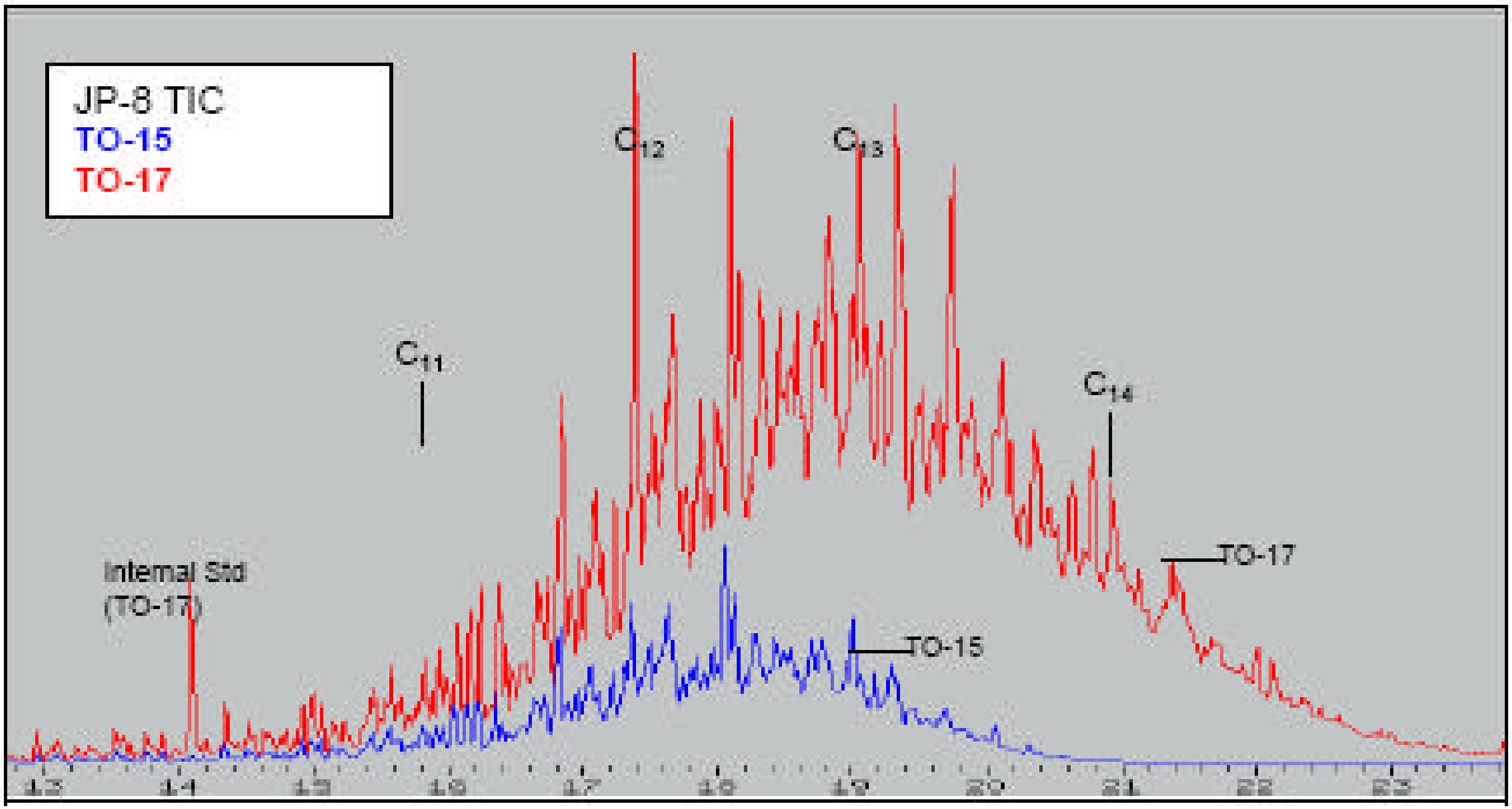
(Hayes et al., Proceedings A&WMA Conference, Vapour Intrusion, Sept 2007)



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