From Theory to Practice: Why Thermal Desorption Is the Perfect Solution for Air Analysis

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Lee Marotta, Principal Field Application Scientist, PerkinElmer

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Outline

- Introduction
- Thermal Desorption (TD): theory and operation
- Adsorbents and sampling
- Applications / solutions
- Troubleshooting / maintenance / method validation

Introduction

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GC Sample Introduction Techniques

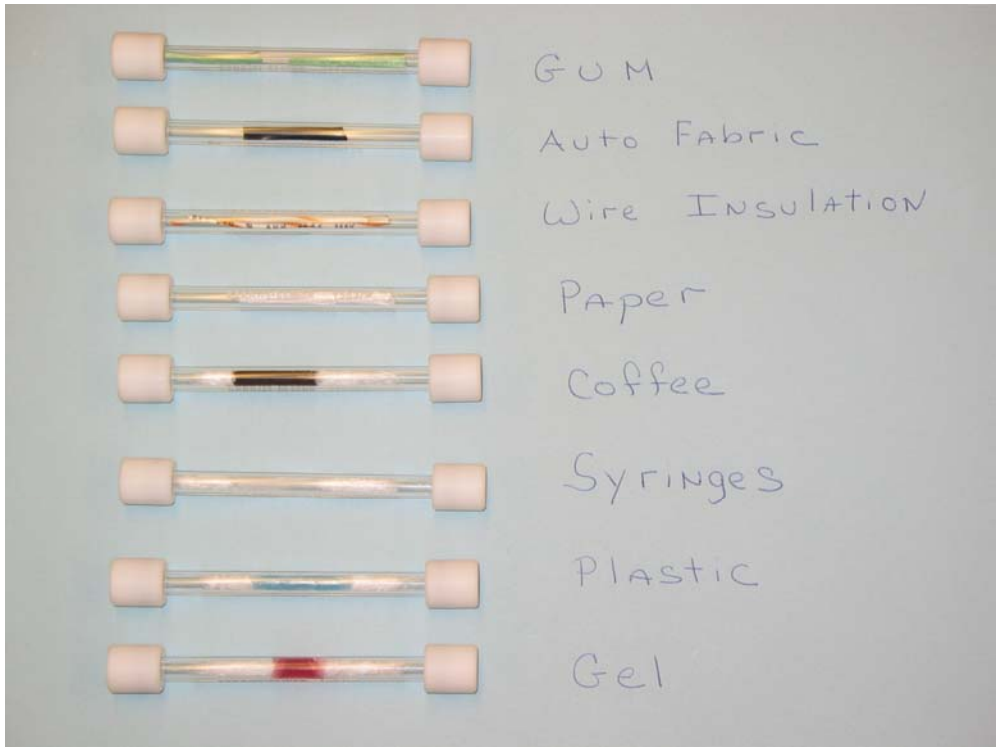
Injection Type	Concentrator	Conc compared to 1 µL	Maximum C #
Liquid Injection Techniques			
Packed	-	x	C44
Split Capillary	-	x	C44
Splitless Capillary (pressure pulsed)	-	x	C44
On-Column Capillary	-	x	C120
Large Volume Injection	yes	50x+	C60
Solvent Purge Injection	can be if LV	x	C60
Liquid Sampling Valve	-	x	C12
Gas Phase Injection Techniques			
Gas Sampling Valve	-	x	C7
Purge & Trap	yes	1000x+	C12
Headspace	yes	1000x+	C18
Thermal Desorption	yes	1000x+	C40
Other Injection Techniques			
Supercritical Fluid Extraction (SFE)/Inje	yes	1000x+	C44
Solid Phase Microextraction (SPME)	yes	1000x+	C18
Pyrolysis	-	x	C150+
Thermogravimetric Analysis (TGA)	-	x	C150+

History

- In 1980, introduced first Automated Thermal Desorber
- Model Automated Thermal Desorber 400
  - Portable
  - Ease of use
- Current: TurboMatrix five models to fit your requirements
  - TMX-1 dedicated system for online/and cannister sampling
  - TMX-650 with recollect and many more automated validation features. The standard for the analysis of toxic compounds in air
  - Minimizing plumbing. Optimize inertness. Ease of maintenance
- EPA Collaboration
  - 1992 – ozone precursors. Clean Air Act. Standardized on our Auto GC
  - Late 90's – developed TO-17 toxic compounds in air by ATD/GC/MS
  - Fenceline monitoring and EPA method 325 … 15 years of collaboration with others

Applications besides Environmental …

- Industrial hygiene
- Material or product testing
  - Aromas in air from flavors (i.e. percolated coffee) or in products such as coffee in a tube
  - Fragrances in air or in the material
  - Off – gassing from products in air or in materials
    - Resins
    - Car fabrics
    - Too many to name
- Medical human breath
  - To diagnose possibility of a disease
- Healthy building
- Forensics: Arson investigation
- Semiconductor
- Kinetic studies



... no laborious extractions and no solvent interferences. Saves time / optimizes profits

Environmental Applications

- Indoor/outdoor
- Stack monitoring
- Soil gas
- MGP sites (fenceline monitoring superfund)
- Fenceline monitoring (industrial sites
- Ozone Precursors

Benefits of Active and Passive Sampling

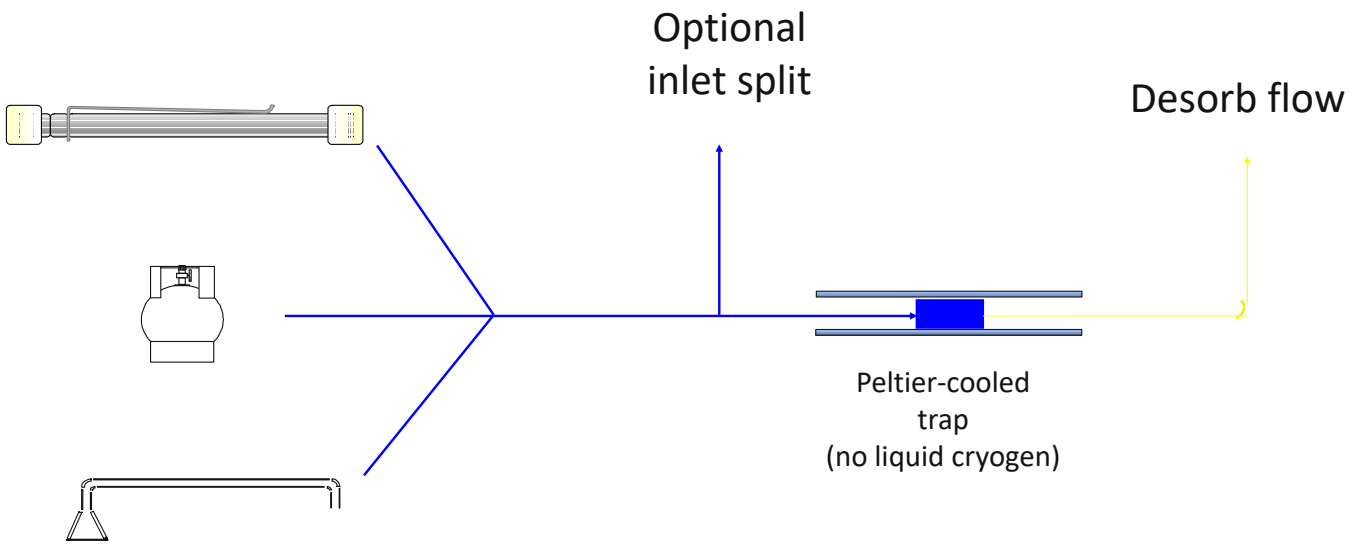
Benefits of VOC and SVOCs in one sample

Air Monitoring Solution

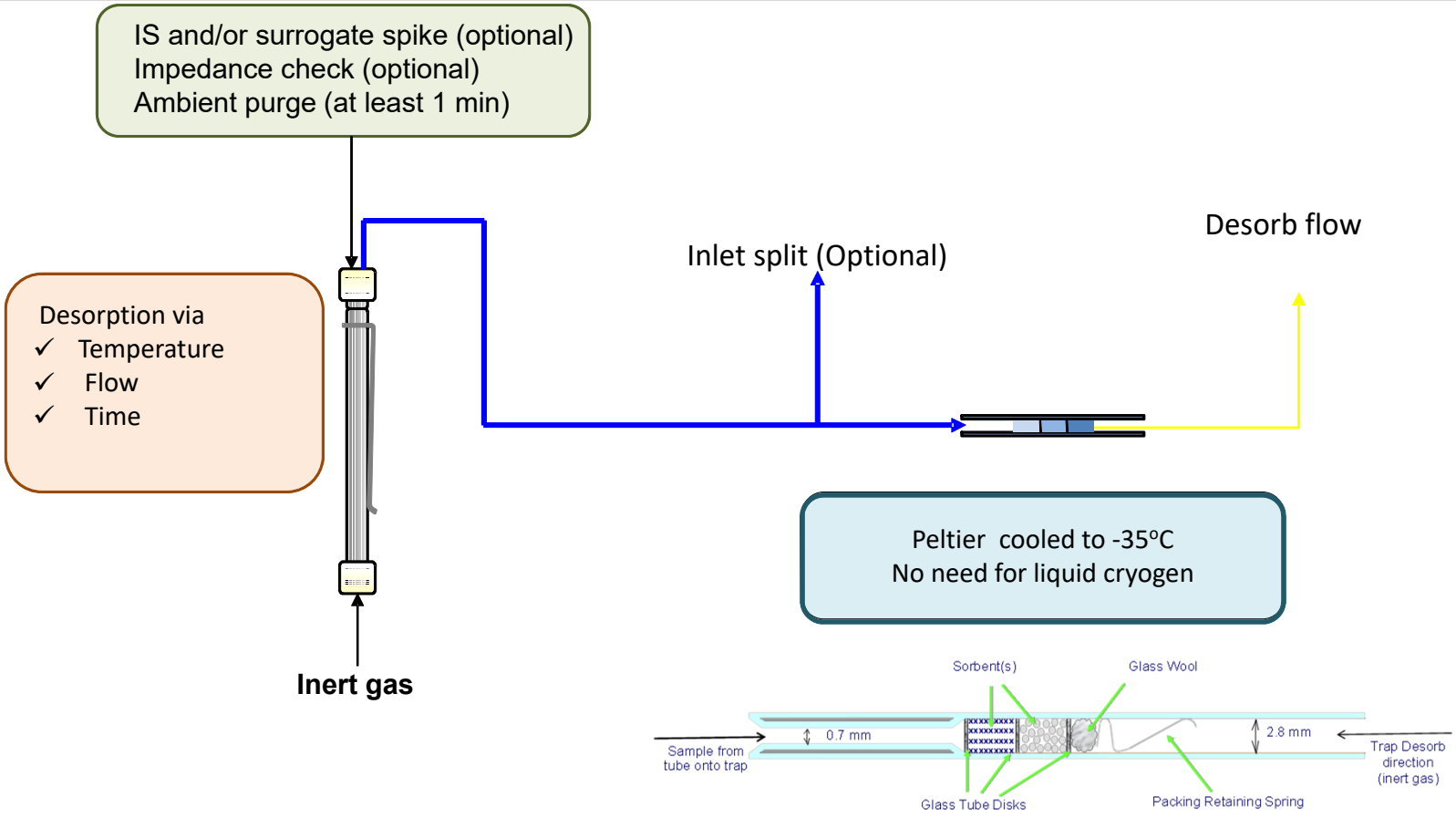
TurboMatrix 650 Automated Thermal Desorber
Clarus SQ8 GCMS

Thermal Desorption: Operation

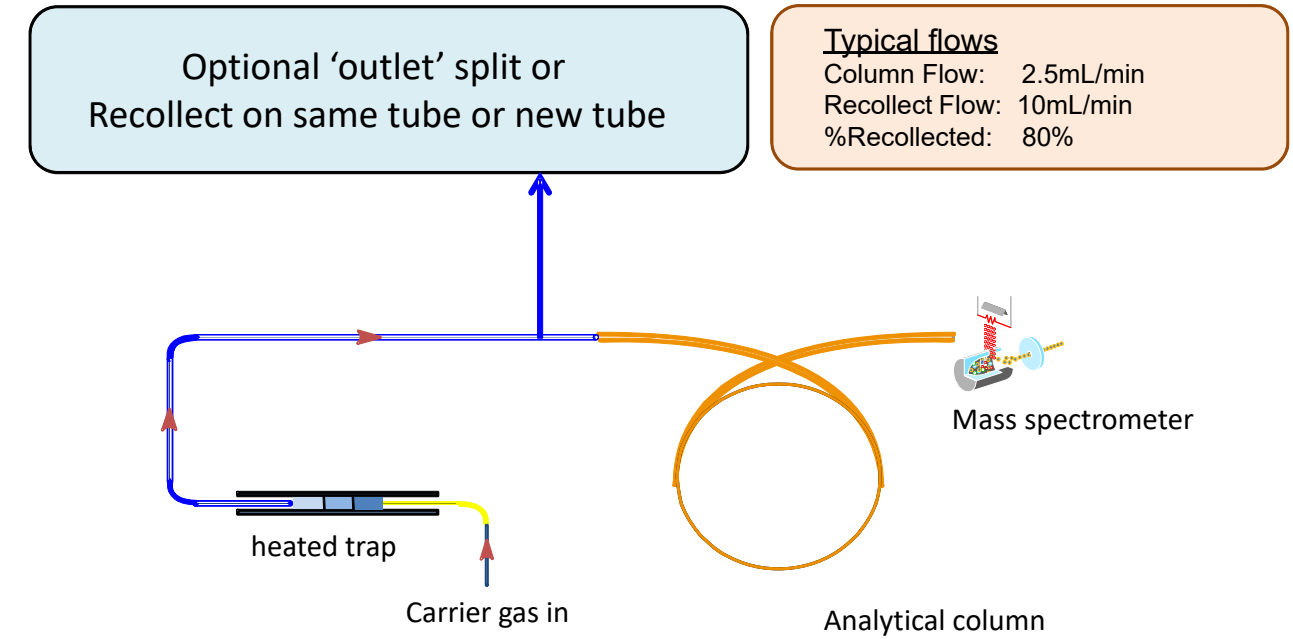
Many Ways to Sample



Sample Tube Desorption



Transfer of Sample to Instrument



The flow is reversed during desorption

sea sponge

Adsorbents

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Adsorbent Choice and How It Works

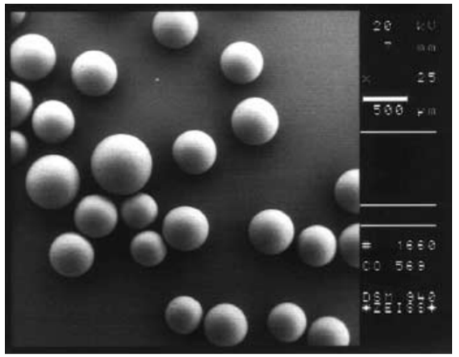
- Choose an adsorbent (s) that will retain and release (recover) the target components of interest in the sample. Active sampling allows for the broadest component range

- Moisture management
  - When possible, and in most environmental compounds it is, select adsorbent where moisture will not be retained while sampling. Hydrophobic adsorbents.

- How it works
  - Smaller surface areas are for greater boiling point components and larger surface areas are for more volatile components

Adsorbents: Most Retentive

- Carbon Molecular Sieves
  - Spherical
  - Surface area 400 to 1200 m^2/g
  - Retains and releases light components: typically, $C_2 – C_5$; However, 2016 has a range from $C_5 – C_{12}$
  - Upper temperature limit: 400 ^oC
  - Moderate to very hydrophilic. Requires dry purge if sampled in humid conditions environment

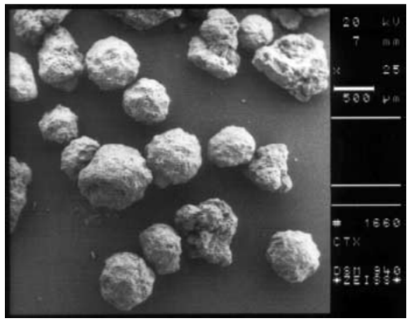


Carboxen-569, W. Engewald et al.,
Anal Bioanal Chem (2002) 373: 490–500

... information from Millipore Sigma's document Selecting the most suitable adsorbent for Air Monitoring

Adsorbents: Broad Range

- Graphitized Carbons
  - Granular
  - Surface area 2 to 240 m^2/g
  - Retains and releases from C_4 to C_{26}
  - Strongest to weakest X>B>F>C>F
  - For instance; B retains and releases components in the boiling point range from C_4 to C_{12}
  - Upper temperature limit: 400 ^oC
  - Hydrophobic



Carbotrap-X, W. Engewald et al., Anal Bioanal Chem (2002) 373: 490–500

... information from Millipore Sigma's document Selecting the most suitable adsorbent for Air Monitoring

Adsorbents: Legacy (old)

- Porous Polymers (legacy)
  - Tenax TA and GR; Porapak N; Chromosorb 106; HayeSep D
    - Surface area 24 to 795 m^2/g
    - Retains and releases mid to high boiling point components C_7 to C_{30}
    - Temperature limit: 260 to 350 ^oC
    - Hydrophobic
    - Tend to produce high backgrounds, adsorbents can pyrolyze and cause significant contamination. Carbon based adsorbents are preferred
    - Let's move away from legacy and move into new technology

Tube Sampling

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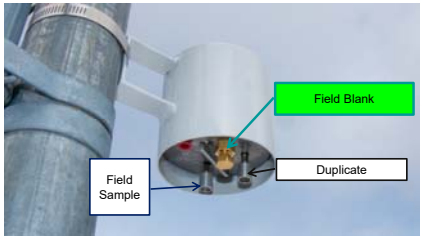
Tube Material Used for Thermal Desorption

- Glass – adsorbents held by glass wool or glass frits
- Metal – adsorbents held by screen
- Glass lined metal
- Deactivated metal

Active and Passive Sampling

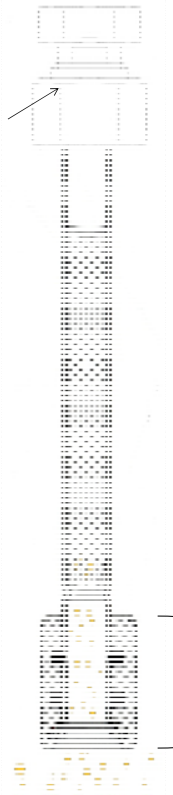
When used for passive sampling, the uptake of compounds of interest relies on the natural movement of the VOC molecules across the concentration gradient of the air gap in the inlet of the tube.



Passive

Long Term Storage Cap

Cap remains while during sampling



Diffusion Path

"Air Gap"

air sampling pump

Active

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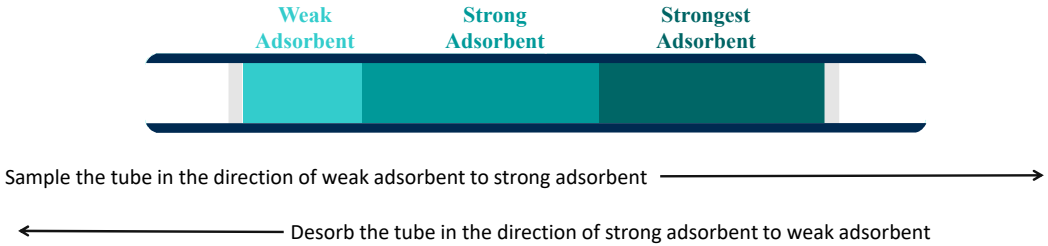
Tube Sampling

- Air Sampling
  - Adsorbent (s) in the tube, typically multi bed, which is selected to trap analytes of interest



Automated Sample Collection

- Automates sample collection of air matrix
- Unattended sampling of 25 tubes

Applications and Solutions

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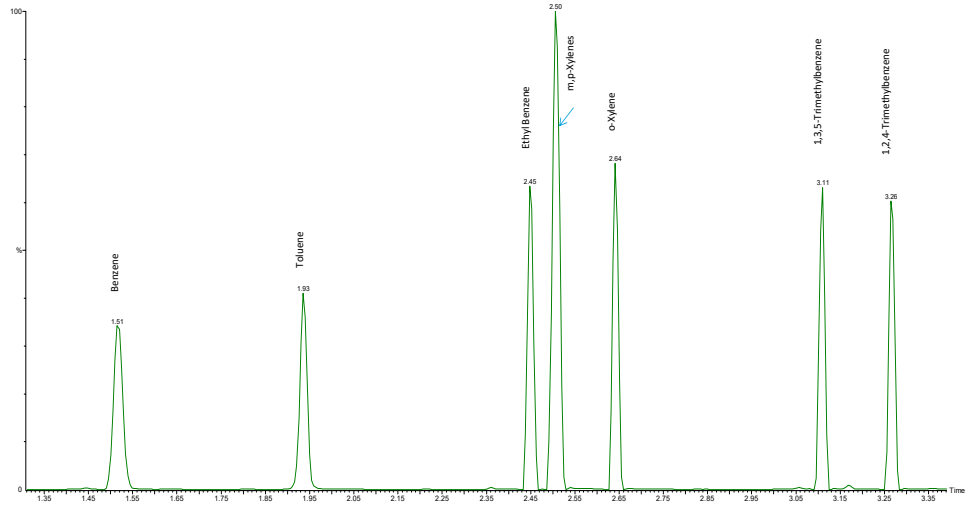
EPA Method 325 (passive)

Target	Retention Time (min)	Precision (n=7) % RSD	Linearity (range 0.2 to 200 ng)	S/N @ 0.2 ng
Benzene	1.51	1.80	0.9999	520 to 1
Toluene	1.93	2.13	0.9999	651 to 1
Ethyl Benzene	2.45	3.01	0.9995	877 to 1
m,p-Xylene	2.50	2.69	0.9993	1021 to 1
o-Xylene	2.64	2.84	1.0000	902 to 1
1,3,5-Trimethybenzene	3.11	3.69	0.9999	823 to 1
1,2,3-Trimethybenzene	3.26	4.01	0.9999	819 to 1

- Chromatography in under four minutes
- Outperformed method criteria
- Can perform TO-17 extended range and 325 on same configuration. When analyzing 325, can backflush unwanted targets through inlet to shorten run times

Optimized for high throughput

Inlet and outlet splits are enabled



Chromatogram courtesy of Pace Analytical Services, Minneapolis, MN

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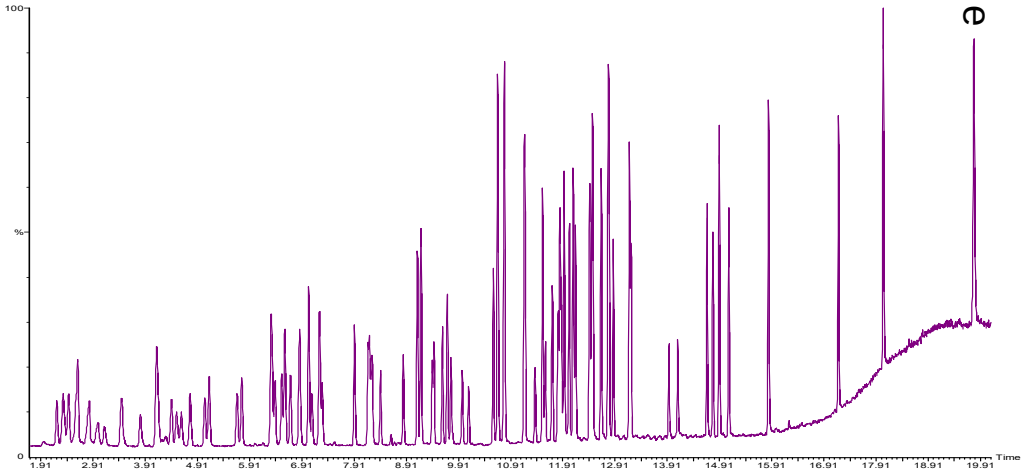
Soil Gas (extended range TO-17)

Class of Compound	# of analytes per group	Linear range 0.05 to 250 µg/m^3 r^2	Precision (n=10)	Signal to Noise at Reporting Limit 0.05 µg/m3
Gases	7	0.9994	7.39	530:1
Aliphatic Hydrocarbons (halogenated)	35	0.9996	4.80	560:1
Aromatics (halogenated)	9	0.9997	2.58	1350:1
Aromatics (non-halogenated)	14	0.9996	1.91	1220:1
Polynuclear Aromatic Hydrocarbons	7	0.9997	3.56	570:1
Others	13	0.9996	3.19	560:1

- Compounds were grouped into their classes to make the table easier to read
- The parameters for all compounds in the class had essentially the same results
- Target range: dichlorodifluoromethane to phenanthrene
- Compounds with boiling points nC3 through nC26



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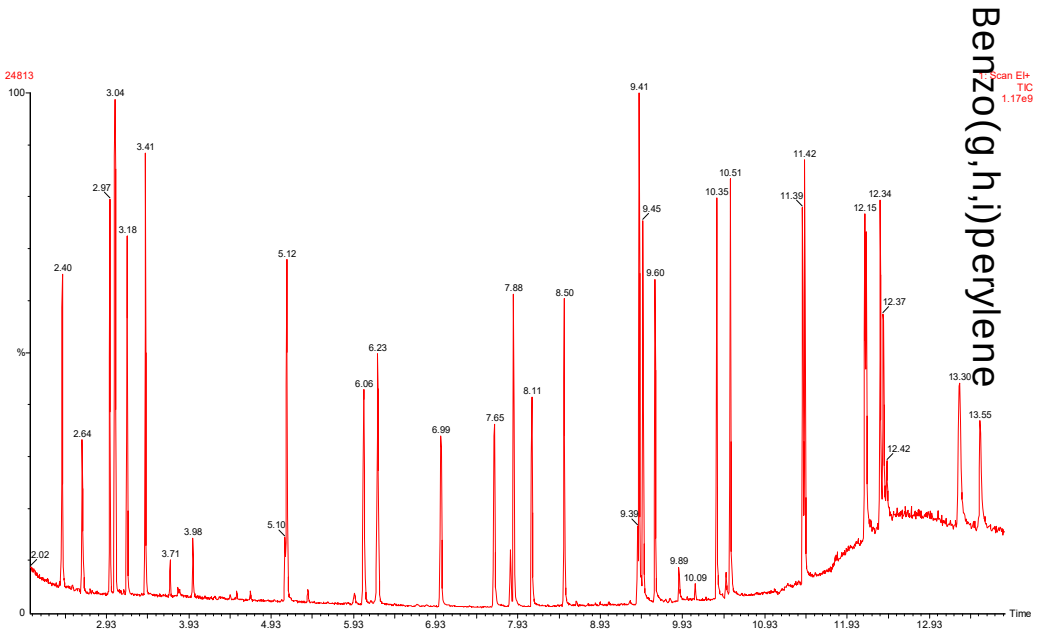
Extending to All PAH Concerns in Air

Compound	Calibration range 0.2 to 50 ng on tube	Reporting Limit µg/m^3 (sample)	Precision %RSD (n=6)
1,3-Butadiene	0.9981	0.0111	1.89
Benzene	0.9993	0.0044	0.9
Toluene	0.9994	0.0044	0.94
Ethyl Benzene	0.9991	0.0044	0.77
m,p-Xylenes	0.9994	0.0044	0.95
o-Xylene	0.9998	0.0044	1.57
Ave 19 PAHs	0.9990	0.0044	1.48

- The polynuclear aromatic hydrocarbons (PAHs) were grouped
- The parameters for all compounds in this class had essentially the same results
- Target range: 1,3 butadiene through benzo(g,h,i)perylene
- Compounds with boiling points nC4 through nC44



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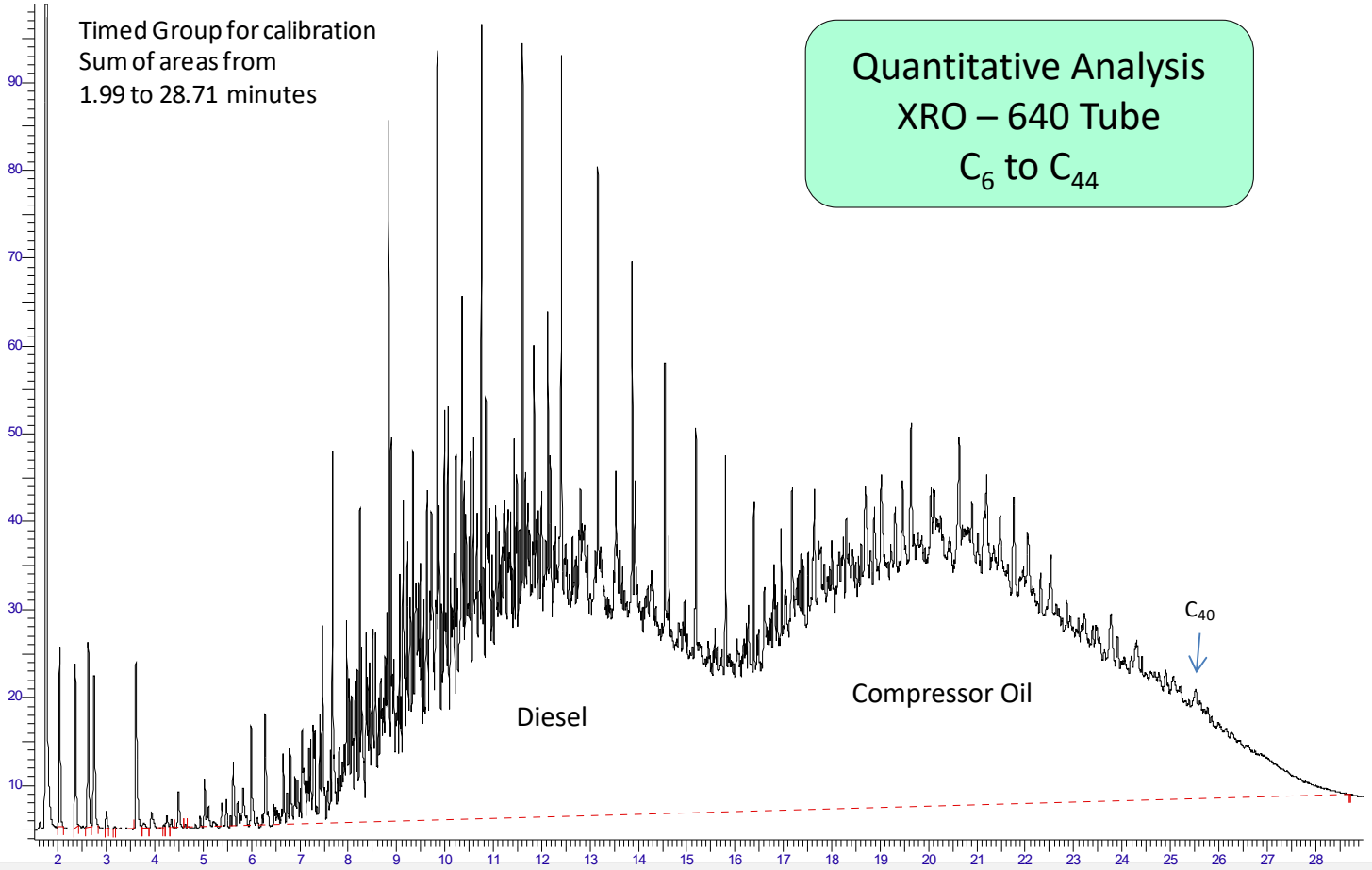
Residue in LPG by TD/FID: C_6 through C_{44}



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Troubleshooting / Maintenance / Validation … not in this order ☺

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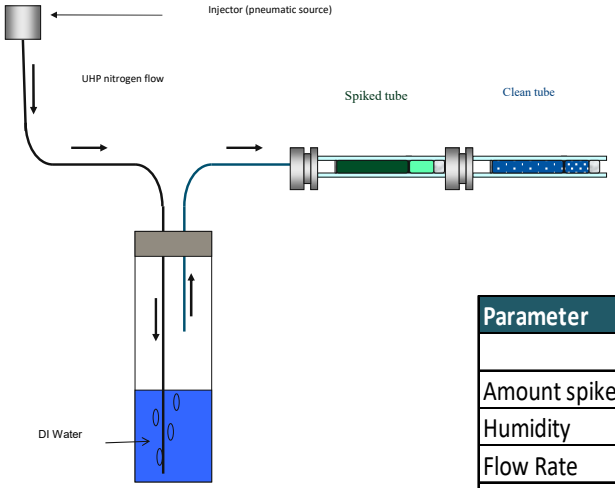
Retaining Components of Interest



Parameter	SVI Tube	XRO - 440 Tube
Amount spiked on Tube	34.6 ug*	8.0 ug**
Humidity	85%	85%
Flow Rate	100 mL/min	100 mL/min
Time	100 minutes	100 minutes
Total Volume	10 liters	10 liters

*Restek: 300ng 502.2 voa #1; 300ng 1,3-budiene; 300ng 8260 Mega mix; 250 ng 4 PAH; 10ug diesel: Total 34.6 ug components

**custom TO-15 mix and Custom stock mix BTEX and 16 regulated PAHs

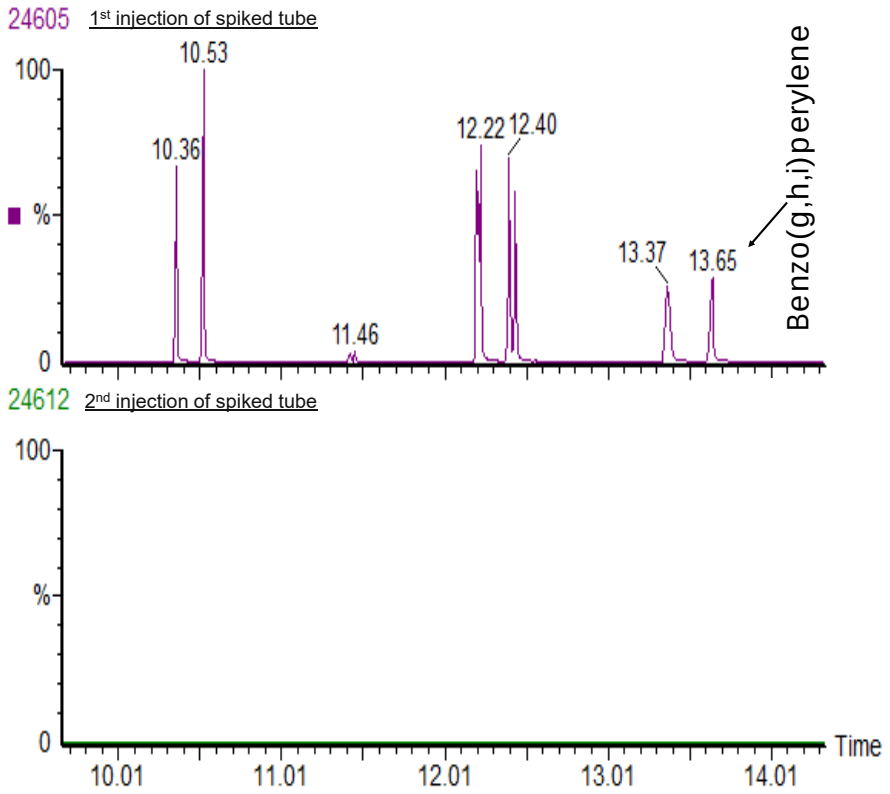
- Validation for the SVI and XRO tubes have been done for 10 liter sample volume
- Laboratories have validated on 50 L sample volumes with concentrated targets successfully
- If additional sample volume is required, this is an easy test to confirm safe sample volume

New Site

- A secondary tube connected to the primary tube
- Tube background should be confirmed prior to deployment in the field
- A field blank is SOP protocol for all environmental methods
- Fortunately, ATD has excellent recoveries (99.9%) so the tubes are clean with one sampling cycle unlike canisters

Recovery Validation

- Experiment
  - Analyze concentrated spiked tube
  - Run trap test
  - Blank tube (no adsorbent)
  - Re-analyzed spiked tube to ensure recovery was achieved from spiked tube



... work courtesy of Roberta Provost, Pace Analytical Services

Instrument Inherent Validation

- Automate spiking internal standard
- Automate surrogate spike
- Automate sample tube and cold trap impedance check to validate trap and tube
- Automate sample recollection on the same or new tube
- Automate leak check of tube and trap prior to each analysis
- Automate water management

Contamination in GC Land … Isolating Components is Crucial for Quick Results

- Schedule acquisition. Select start on GC (no injection from ATD). If clean, have isolated problem to ATD. If not clean, discussion (column may be source).
- Trap test: Setup acquisition. Perform a trap test. This isolates the trap to determine if this may be problem. If “clean”
- Run a blank tube (no adsorbent) to test entire system. If free from contaminants
- Run suspected tube

Cost Savings and Enhanced Performance with ATD

- In addition to better data compared to cans
  - Better recovery and polar recovery
  - In a box: 4 cans or more than 500 tubes.

    Optimize profits with shipping
  - Space … cannisters take a lot of space
  - Outstanding recoveries with TO-17 compared to TO-15
  - TO-15 – can't do SVOCs
  - Don't have to wait days for a clean can

Questions?

Lee Marotta
Principal Field Application Scientist
PerkinElmer
lee.marotta@perkinelmer.com

Reporting results with confidence

Thank you so much ☺

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