VOC Sampling and Analysis

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Topics

- Sampling media – canisters, tubes, bags
- Making Standards
- Preconcentration & Analysis – GC/MS
- Canister cleaning
- Canister cleanliness testing
- AutoGCs

Sampling

- Canisters (WholeAir)
  - SUMMA, Silco/Silonite
  - Active sampling (aka non-passive)
  - Passive sampling
- Tubes
  - Active
  - Passive

- Bags
  - Chambers for filling

Methodology

- EPA Compendium Toxic Organic Methods
- VOCs (C2 to C12)
  - TO-14 (canister based non-polars)
  - TO-15 (canister based with addition of polars)
  - TO-17 (tube based, thermal desorbtion)
- VOCs not criteria pollutant so no FRMs, just "guideline" methods
- Performance based
- Old….ASTM is written more updated methods, EPA has no plans to update.

Canister Sampling

- Grab sampling
  - Emergency response
  - Capturing event
  - Qualitative
  - Fills in seconds up to minutes
- Integrated Sampling/Time weighted average (TWA)
  - 24 hr most common
  - 3hr and 8hr sampling for patterns

What is a Canister?

- Typically 304L grade stainless
- Whole Air sampling – representation of the ambient air
- Should be leak free to a leak rate of 4×10^{-9}, canister should hold vacuum 30 days.
- SUMMA[R] is an electropolished Stainless Steel
- Silco/Silonite – is amorphous silica coated

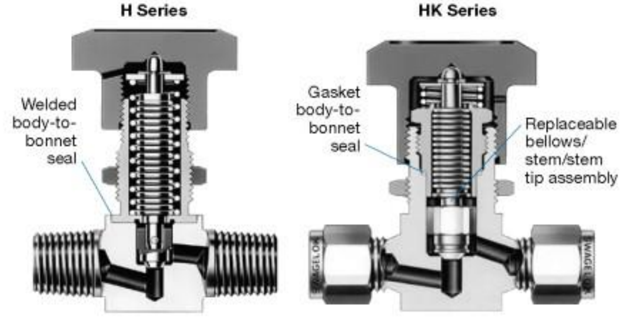
- Registered trademark of Molectrics Corp

Canister Valves

- Most critical part of canister
- No soft seat, Must have a metal seat, what does that mean?
- Very difficult for metal seats to seal repeatedly. Easily damaged.
- Expensive (b/c seat)
- SS wetted path
- Temperature limitation during cleaning

Features

- Flow coefficients (C_v) from 0.11 to 0.28
- Precision-formed metal bellows and nonrotating stem tip for reliable, repetitive shutoff
- Variety of end connections—Swagelok® tube fittings, female and male NPT, integral male and welded female VCR® fittings, tube socket and tube butt weld ends, and tube extensions
- Panel and bottom mounting
- Pneumatic actuator for HK series available



316 SS body material

Brass body material

Technical Data

Body-to-Bellows Seal	Valve Body Material	Stem Tip	C_v	Internal Volume① in.³ (cm³)	Series
Weld	316 SS	Stainless steel	0.11	0.08 (1.3)	2H
			0.20		2H2
			0.28		4H
Gasket	Brass	PCTFE	0.28	0.10 (1.6)	HK

① Determined using valves with Swagelok tube fitting end connections.

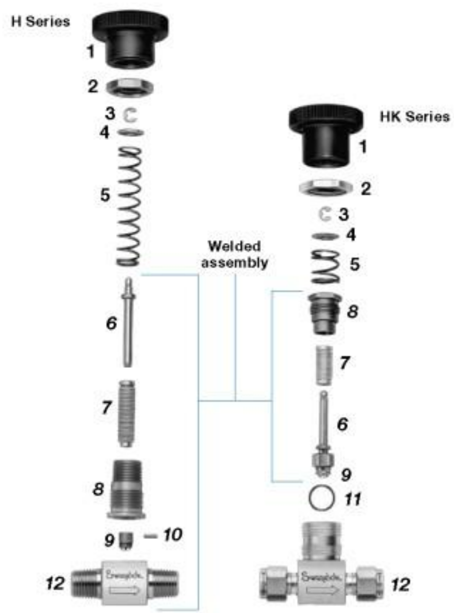
Pressure-Temperature Ratings

Material	316 SS	Brass
Series	H	HK
Temperature, °F (°C)	Working Pressure, psig (bar)	
−80 (−62) to −40 (−40)	1000 (68.9)	—
−20 (−28) to 100 (37)	1000 (68.9)	1000 (68.9)
200 (93)	1000 (68.9)	500 (34.4)
300 (148)	1000 (68.9)	—
400 (204)	1000 (68.9)	—
500 (260)	1000 (68.9)	—
600 (315)	1000 (68.9)	—

Materials of Construction

Component	H Series	HK Series
	Material Grade/ASTM Specification	
1 Handle	Green-anodized aluminum/B211	
2 Panel mount nut	316 SS/A479	Brass 360/B16
3 Retaining ring	S15700	Beryllium copper
4 Washer	316 SS/A240	Phosphor bronze C51000/B103
5 Spring	S17700/AMS 5678	
6 Stem	*316 SS/A479*	*Phosphor bronze C51000/B139*
7 Bellows	*321 SS/A269*	*Phosphor bronze C51900*
8 Bonnet adapter	*316 SS/A479*	*Phosphor bronze C51000/B139*
9 Stem tip	*S17400/A564*	*PCTFE 6060/ D1430*
10 Stem pin	*420 SS*	*—*
11 Gasket	*—*	*PTFE-coated copper 110/B152*
12 Body	*316 SS/A479*	*Brass 360/B16*
Nonwetted lubricant	Molybdenum disulfide-based paste	
Wetted lubricant	*—*	*Fluorinated-based*

Wetted components listed in *italics*.



Lubricate threads on bonnet and handle periodically for increased valve life.

Entech Canister valve

- Repairable
- Packless
- Low internal volume
- SS wetted pathway
- Can be silica lined

TWA Canister Sampling

- Passive or non-passive (active)
- Passive is commonly used when no power source is available.
- Use vacuum of canister to pull sample into canister.
- Must be stainless steel wetted pathway.
- Flow restriction kits commercially available

Passive Sampling kits

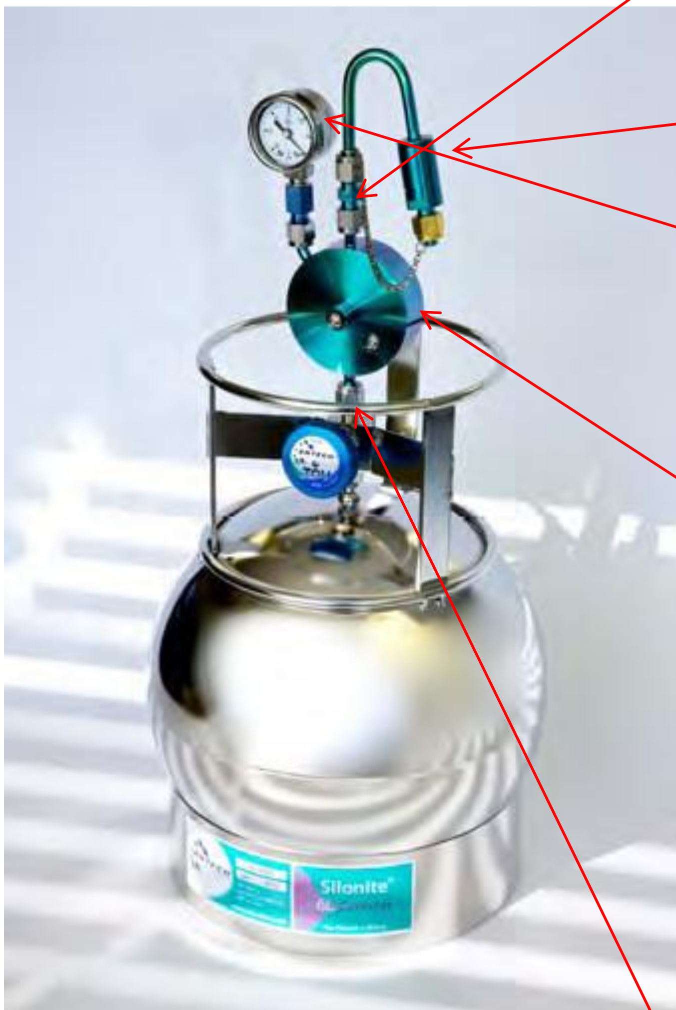
- Critical Elements:
  - Sapphire Orifice to restrict flow to flow range
  - SS Diaphragm to regulate flow (to a point)
  - Filter to remove particulates
  - “candy cane” to prevent rain entering
  - Vacuum gauge

Passive Sampling Kits

Critical Orifice (sapphire)

Particulate Filter

Vacuum Gauge



Internal SS diaphragm

Easy Connection to canister valve

Critical orifice flow ranges

Critical orifice diameter vs. flow rate.

Orifice Diameter (in.)	Flow Rate Range (mL/min.)	Canister Volume / Sampling Time 1L	3L	6L	15L
0.0008	0.5–2	24 hr.	48 hr.	125 hr.	—
0.0012	2–4	4 hr.	12 hr.	24 hr.	60 hr.
0.0016	4–8	2 hr.	6 hr.	12 hr.	30 hr.
0.0020	8–15	1 hr.	4 hr.	8 hr.	20 hr.
0.0030	15–30	—	2 hr.	3 hr.	8 hr.
0.0060	30–80	—	—	1.5 hr.	4 hr.
0.0090	80–340	—	—	0.5 hr.	1 hr.

- Select orifice size based on flow range/sampling time interval
- Dial the exact flow rate you want.

Setting flow rate on passive sampling kits

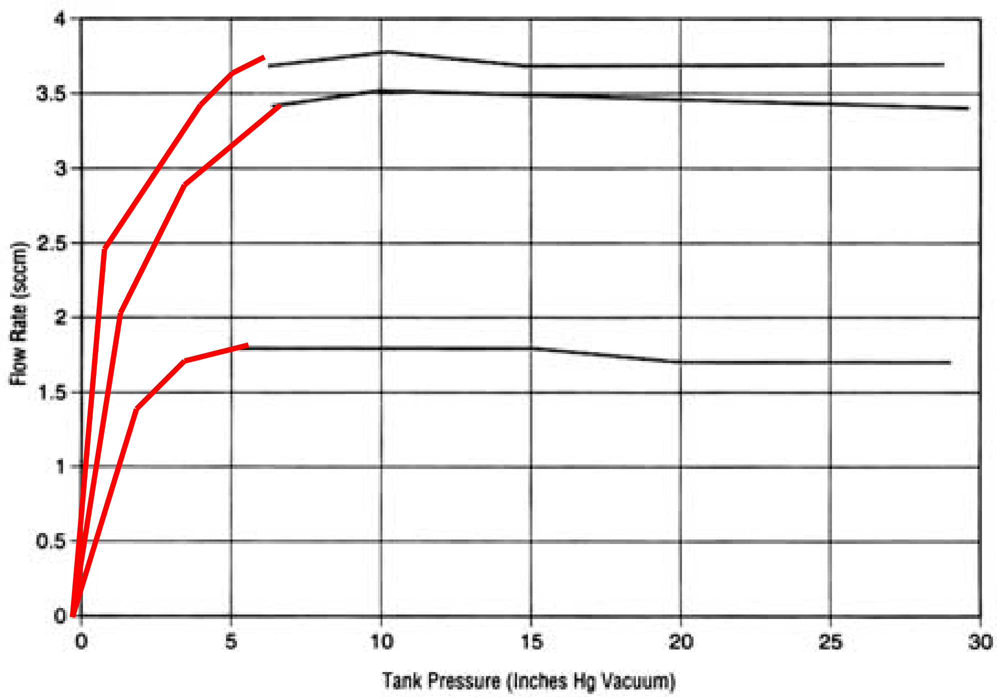
1. Pull air thru flow controller
2. Using a good flow meter, set flow by adjusting piston
3. Replace cap to protect piston

Passive Sampling kits

- No power needed.
- Uses vacuum of canister to pull sample
- However, flow controller maintains constant flow to a point.
- That point is around 7"Hg vacuum.
- Therefore, to have a valid sample the canister should not be allowed to come to ambient pressure (0 psig).
- Stop sampling prior to canister reaching 7"Hg vacuum. (**Subambient sampling**)

Passive Sampling Kit flow controllers

Flow Stability Curve- .0012 orifice



Subambient Sampling

Advantages

- Mechanical failure eliminated
- Contamination minimized.
- Less potential for leaks
- No power req.

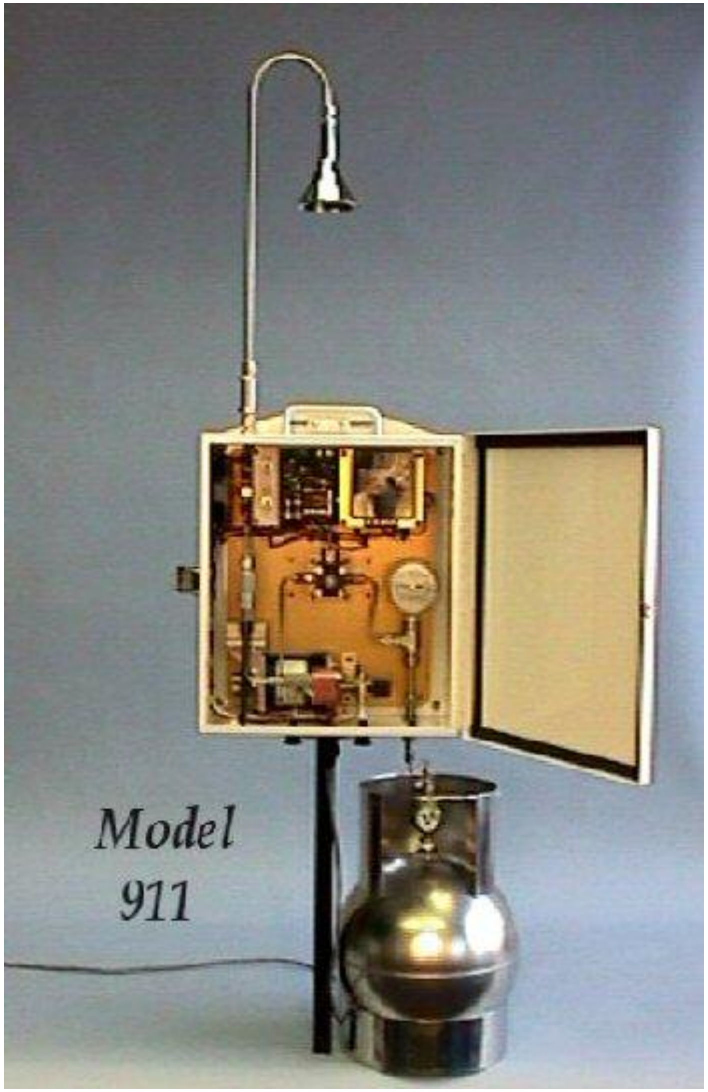
Disadvantages

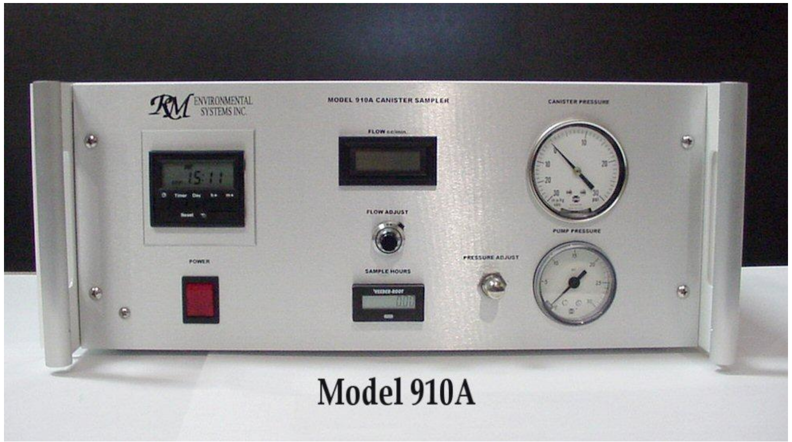
- Low flow rate
- Sample is under vacuum
- Preconcentrators struggle with this
- Pressurizing results in dilution of sample

Non-Passive or Active sampling

- Pressurized sampling.
- Canister sampler will “push” or “pump” air into the canister at a constant flow rate.
- You don’t have to stop at 7”Hg vacuum, can actually put positive pressure sample.
- Ensure constant flow rate
- Can collect more than 6 liters of air.
- Requires electricity
- Can do multiple canisters

Multi Canister Samplers - Active





Pressurized Sampling

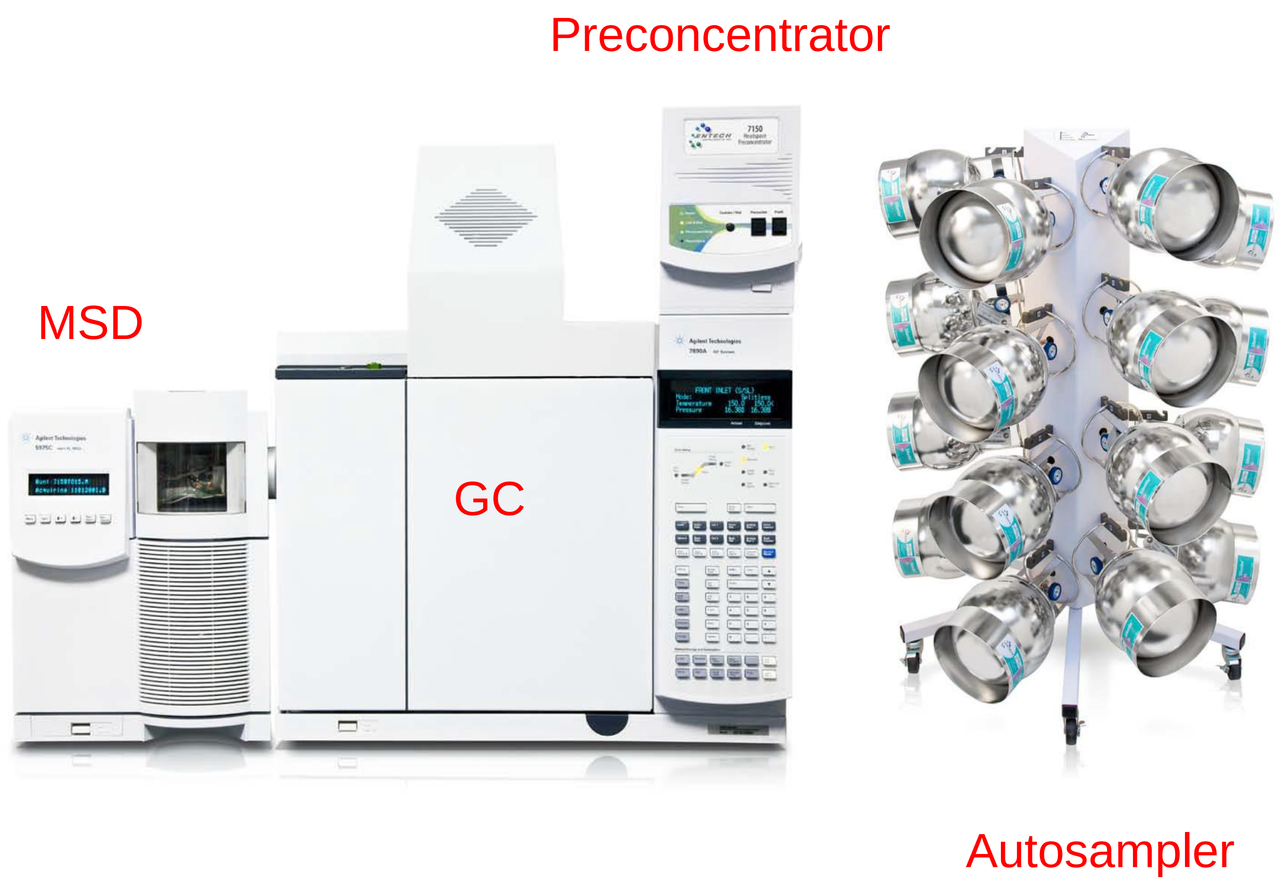
Advantages

- Sample transfer is easier to preconcentrator
- Multiple canister sampling (3hr)

Disadvantages

- Pump is a source of contamination
- Lots of leak potential, many connections.
- Mechanical failure
- Difficult to clean once contaminated.

The Analytical System



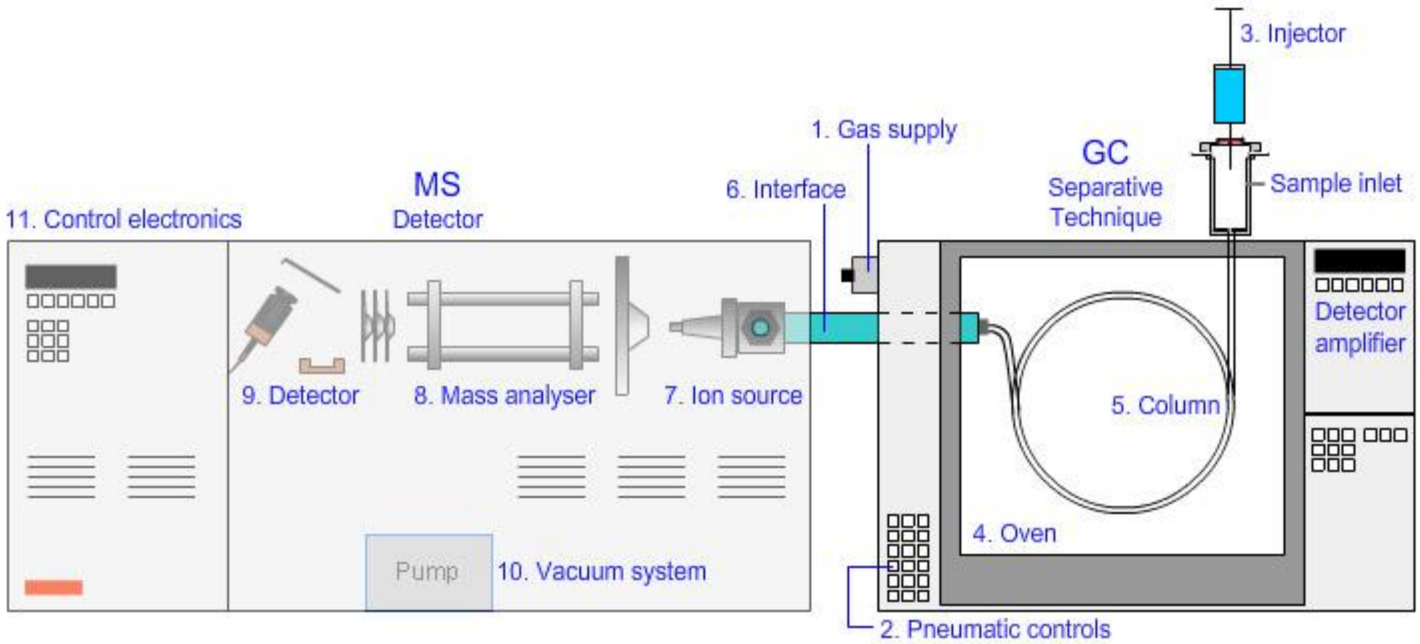
Preconcentrator

- Purpose - to concentrate the sample.
- Cryogenically cooled (liquid N2)
- Thermally desorbed
- Water and CO2 management is key
- Pumps capable of sampling in subambient canisters
- Only a few commercially available.
- Multiple traps.
- Autosamplers for 16 canisters is typical.

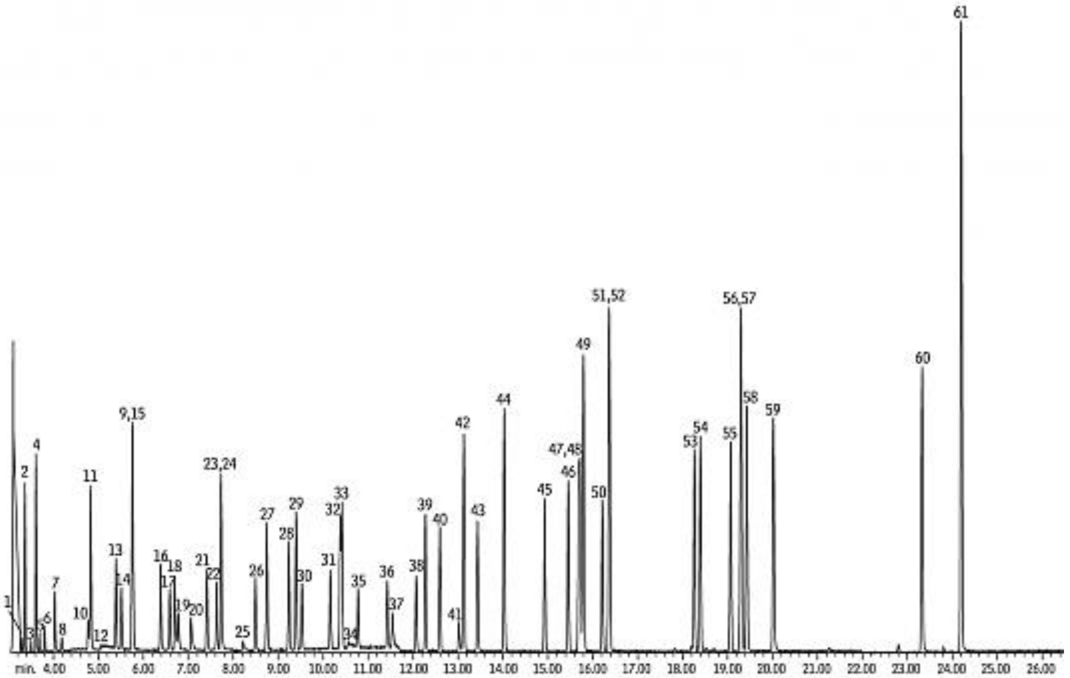
GC/MSD

- GC column should be a fused silica High resolution capillary column for VOCs (different column for semi-volatiles)
- Pumping capacity of Mass Spec determines ID of column
- Mass Spec is capable of indentifying compounds using spectral analysis
- Some labs split effluent of GC to two detectors (FID)

GC/MSD


3. Injector
1. Gas supply
GC
Separative
Technique
Sample inlet
MS
Detector
6. Interface
11. Control electronics
Detector
amplifier
9. Detector
8. Mass analyser
7. Ion source
5. Column
4. Oven
Pump
10. Vacuum system
2. Pneumatic controls

TO-15 Chromatogram



1. Propylene
2. Freon®-12 (dichlorodifluoromethane)
3. Chloromethane
4. Freon®-114 (dichlorotetrafluoroethane)
5. Vinyl chloride
6. 1,3-Butadiene
7. Bromomethane
8. Chloroethane
9. Carbon disulfide
10. Acetone
11. Freon®-11 (trichlorofluoromethane)
12. Isopropyl Alcohol
13. 1,1-Dichloroethene
14. Methylene Chloride
15. Freon®-113 (1,1,2-trichloro-1,2,2-trifluoroethane)
16. *trans*-1,2-Dichloroethene
17. 1,1-Dichloroethane
18. Methyl *tert*-butyl ether
19. Vinyl acetate
20. Methyl ethyl ketone
21. *cis*-1,2-Dichloroethene
22. Hexane
23. Chloroform
24. Ethyl Acetate
25. Tetrahydrofuran
26. 1,2-Dichloroethane
27. 1,1,1-Trichloroethane
28. Benzene
29. Carbon Tetrachloride
30. Cyclohexane
31. 1,2-Dichloropropane
32. Trichloroethylene
33. Bromodichloromethane
34. 1,4-Dioxane
35. Heptane
36. *cis*-1,3-Dichloropropene
37. Methyl Isobutyl Ketone
38. *trans*-1,3-Dichloropropene
39. 1,1,2-Trichloroethane
40. Toluene
41. Methyl butyl ketone
42. Dibromochloromethane
43. 1,2-Dibromoethane
44. Tetrachloroethylene
45. Chlorobenzene
46. Ethylbenzene
47. *p*-Xylene
48. *m*-Xylene
49. Bromoform
50. Styrene
51. *o*-Xylene
52. 1,1,2,2-Tetrachloroethane
53. 4-Ethyltoluene
54. 1,3,5-Trimethylbenzene
55. 1,2,4-Trimethylbenzene
56. 1,3-Dichlorobenzene
57. Benzyl chloride
58. 1,4-Dichlorobenzene
59. 1,2-Dichlorobenzene
60. 1,2,4-Trichlorobenzene
61. Hexachloro-1,3-Butadiene

Mass Spec

- Full Scan (TIC)
  - Scans multiple scan ranges every microsecond
  - Common VOC scan range 35 – 250amu
  - Reports area of primary quantitation ion
  - Use this mode for Emergency response!!
- Selected Ion Mode – SIM
  - Certain masses within a retention time window.
  - Much more sensitive

VOC Standards Prep

- Purchase commercially available standards at concentrations of 1ppm or higher.
- Dilute working levels using a dynamic dilutor.
- Humdification is extremely important. >35%RH.
- Measure humidity of diluent gas to ensure proper %RH

How to Humidify Canisters for Stds

- Inject H2O with syringe (gas tight)
- The dynamic dilutor have small vessels
- Make your own
  - Erlenmeyer flask
  - Solvent bottles
  - Dryrite vessels
- Measure %RH output

Canister Cleaning

- The most important aspect to VOCs.
- Everybody's definition of ambient air is different.
- Source level samples will contaminate the whole cleaning and analytical system.
- Keep a canister log of each canister.
- Batch test vs individual testing.

How to clean a canister

- Pressure and evacuation with <u>humidified</u> air or nitrogen. How long?
- Heat canisters but at what temperature?
- Valve's are the limiting factor.
- Above 100°C, creating steam. Is that good or bad?
- Steam is not a good thing for fused silica lined canisters.
- Most cleaning cycles run 4-8hrs.

How to Heat Canisters during Cleaning

- Ovens
- Heat bands
- Heating jackets

How to Humidify Canister Cleaning

- Make your own
  - – Erlenmeyer flask
  - – Solvent bottles
  - – Dryrite vessels

- Measure %RH output.
- Cold trap to collect contaminate and prevent oil vapors from pump.

Canister Cleanliness Testing

- Typically batch testing is done.
  - Eg. 2 out of 16
- Which canisters do you test?
  - Typically the canisters that had the highest values during analysis testing.
- TO-15 cleanliness spec is 0.2ppbv per component….this is not low enough (10^{-6} risk level)
- Can you test every canister?
- Recommend testing over time (2-3 weeks)

What about Canister stability?

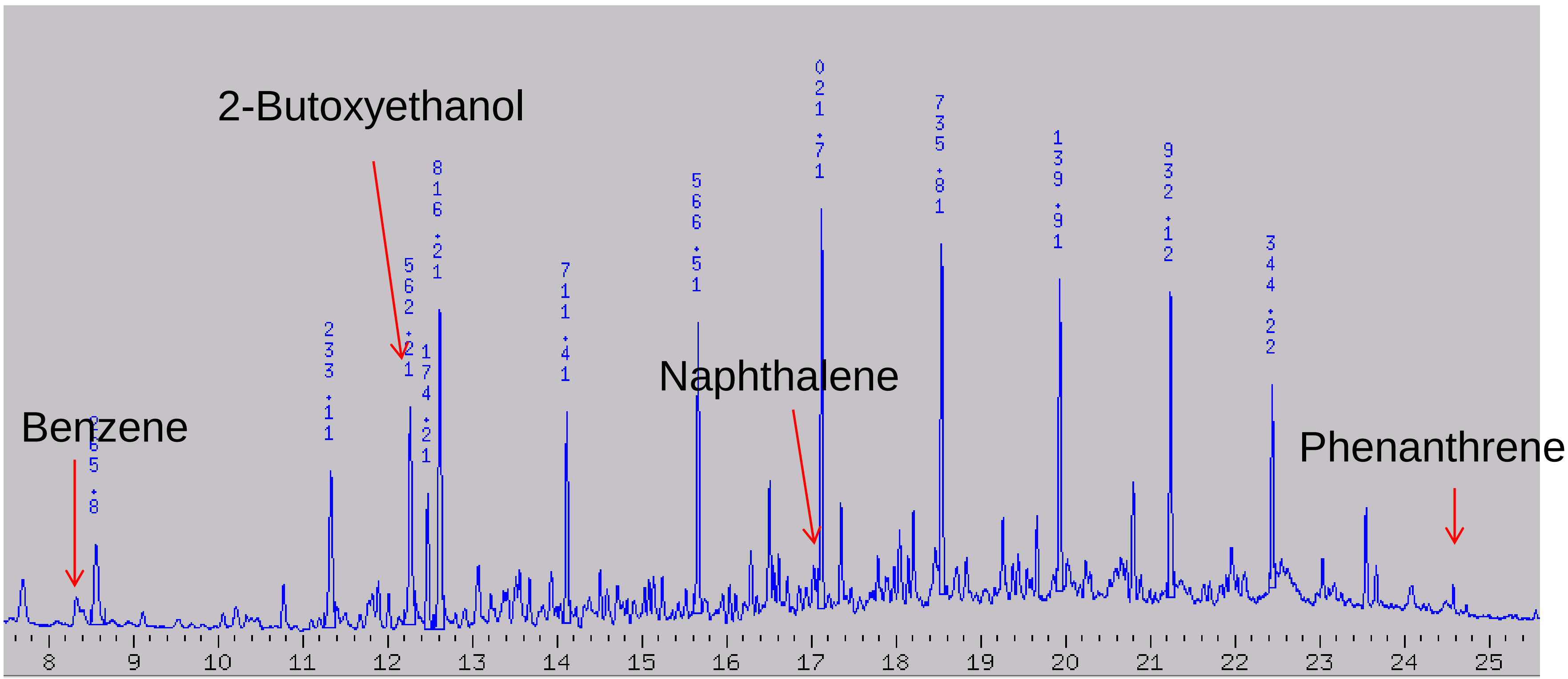
- It is good practice to test canisters for cleanliness over time periodically…
- It is also good to test canisters for stability as well.
- What does that mean? Place a know concentration of TO-15 into the canister and test over time to measure stability.
- The results tell a story.
- Log the results.

Thermal Desorbtion Tubes

- Active
  - Pumps pull air thru at a constant rate
- Passive
  - Diffusion over time eg. 2 weeks
- Advantages and disadvantages
- Thermally desorbed
- Can get higher MW range

TO-17 Chromatogram

C6 to C16 VOCs

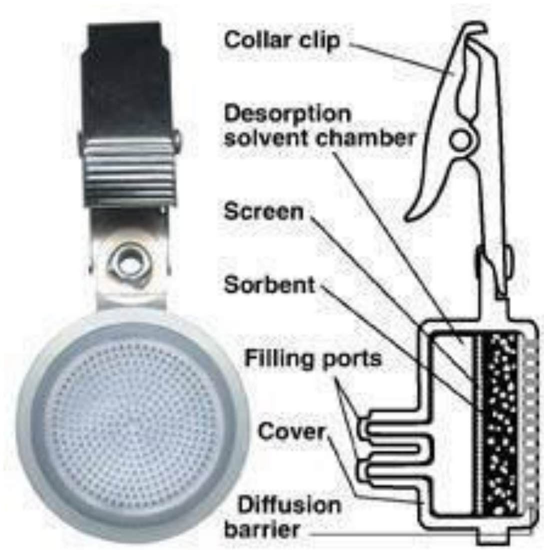


Active Tubes

- Pump required
- Multi bed tubes
  - Tenax
  - Carbotrap
  - Carboxen
- Thermally desorbed
- Can be reused
- Markes, Perkin Elmer, Dynatherm

Diffusive Badges

- Diffusive badges for certain VOCs
  - SKC, Radiello, Markes Int.
- CS2 Solvent extracted
- Thermally Desorbed



Tubes

Advantages

- Larger MW range
- $ - less exp
- Longer sampling times
- Match adsorbents with compounds

Disadvantages

- One shot
- Breakthrough
  - Effect Temp, %RH
- Background

AutoGCs

- Many advancements in last 10 years
- Metal columns (unbreakable)
- Smaller detectors
  - Photo Ionization Detectors (PID)
  - Flame Ionization Detectors (FID)
  - No MSD versions yet
- More efficient trapping (preconcentration)
- Single and dual column configurations
- Better software for data analysis, QA

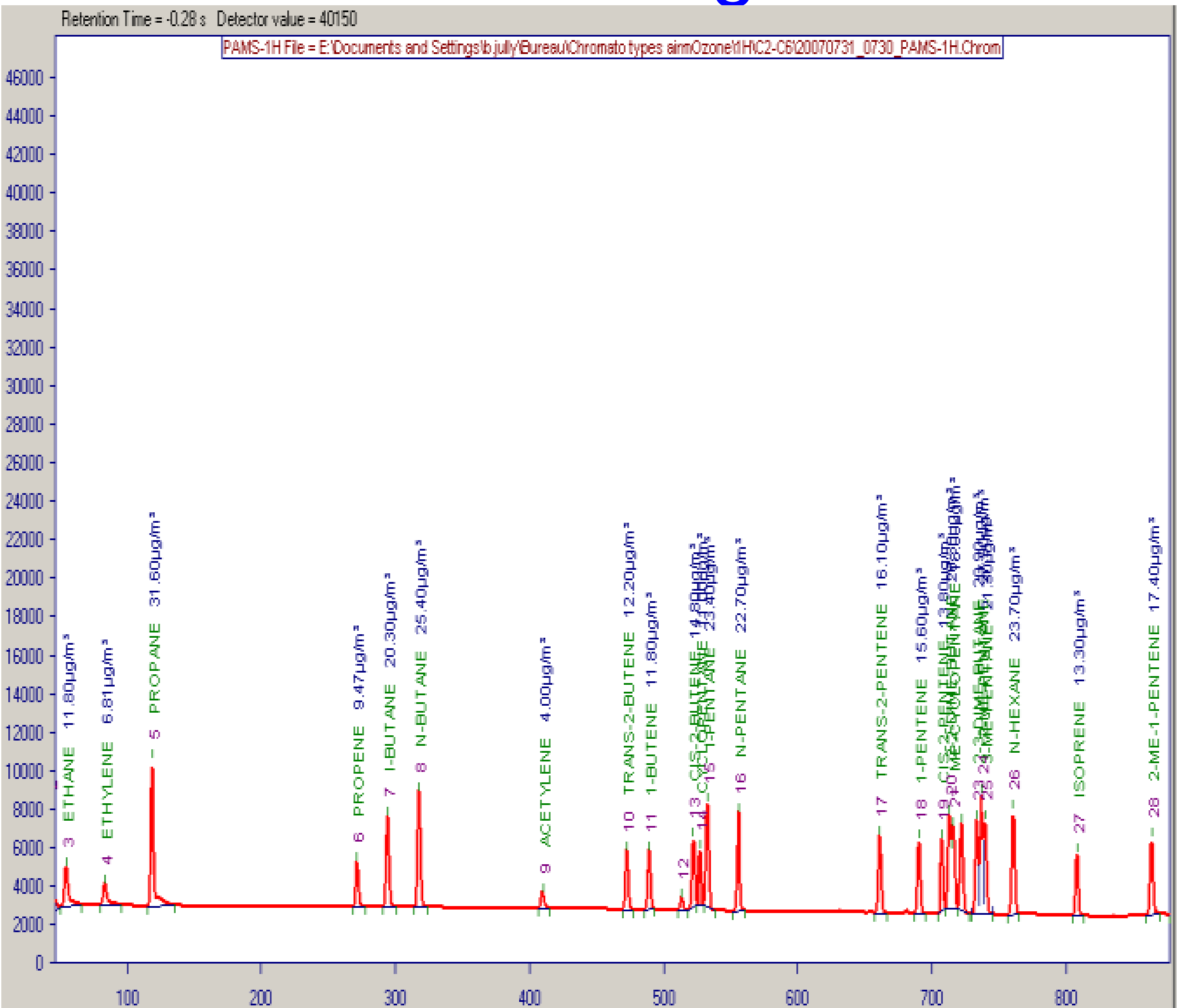
AutoGCs for VOCs

- No Cyrogenics
- Sorbent traps or sample loops
- Hydrocarbon range dependent
- One column for C2-C6 VOCs
- A different column for C6-C12 VOCs
- Identification by Retention time
- Backflushing capabilities

AutoGCs Manufacturers

- SynSpec
- American Ecotech
- Perkin Elmer ITD
- OI Corp

C2-C6 Cgram


Retention Time = -0.28 s Detector value = 40150
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3 ETHANE 11.80µg/m³
4 ETHYLENE 6.81µg/m³
5 PROPANE 31.60µg/m³
6 PROPENE 9.47µg/m³
7 I-BUTANE 20.30µg/m³
8 N-BUTANE 25.40µg/m³
9 ACETYLENE 4.00µg/m³
10 TRANS-2-BUTENE 12.20µg/m³
11 1-BUTENE 11.80µg/m³
16 N-PENTANE 22.70µg/m³
17 TRANS-2-PENTENE 16.10µg/m³
18 1-PENTENE 15.60µg/m³
26 N-HEXANE 23.70µg/m³
27 ISOPRENE 13.30µg/m³
28 2-ME-1-PENTENE 17.40µg/m³
46000
44000
42000
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
100
200
300
400
500
600
700
800

Summary

- Canisters are still most common media for VOCs sampling
- Canister cleanliness is crucial
  - Test canister over time
  - For cleanliness and stability
- GC/MSD – Full Scan mode vs SIM
- Tubes can collect in VOC/SVOC range

Contact Information

- Questions/Comments
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