VOC Sampling and Analysis

David Shelow
US EPA – OAR – OAQPS
Ambient Air Monitoring Group

National Air Monitoring Meeting
May 2012
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 desorption)

• 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 $4 \times 10^{-9}$, 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 ($C_d$) from 0.11 to 0.28.
- Precision-formed metal bellows and nonrotating stem tip for reliable, repetitive shut-off.
- Variety of end connections - Swagelok® tube fittings, female and male NPT, integral male and welded female VCPR® fittings, tube socket and tube butt weld ends, and tube extensions.
- Panel and bottom mounting.
- Pneumatic actuator for HK series available.

Technical Data

<table>
<thead>
<tr>
<th>Body-to-Bolts Seal</th>
<th>Valve Body Material</th>
<th>Stem Tip</th>
<th>$C_d$</th>
<th>Internal Volume $V_i$ (in3/cm$^3$)</th>
<th>Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weld</td>
<td>316 SS</td>
<td>Stainless steel</td>
<td>0.11</td>
<td>0.03 (1.3)</td>
<td>2H</td>
</tr>
<tr>
<td>Weld</td>
<td>316 SS</td>
<td>304 SS</td>
<td>0.20</td>
<td>0.09 (1.2)</td>
<td>2H2</td>
</tr>
<tr>
<td>Gasket</td>
<td>Brass</td>
<td>FEP</td>
<td>0.28</td>
<td>0.10 (1.6)</td>
<td>H</td>
</tr>
</tbody>
</table>

Pressure-Temperature Ratings

<table>
<thead>
<tr>
<th>Material</th>
<th>316 SS</th>
<th>Brass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HK</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature, °F</td>
<td>Working Pressure, psig (kPag)</td>
<td></td>
</tr>
<tr>
<td>100 (-12) to 120 (-11)</td>
<td>1000 (68.9)</td>
<td></td>
</tr>
<tr>
<td>200 (93) to 300 (143)</td>
<td>1000 (68.9)</td>
<td></td>
</tr>
<tr>
<td>400 (210) to 500 (283)</td>
<td>1000 (68.9)</td>
<td></td>
</tr>
<tr>
<td>600 (321)</td>
<td>1000 (68.9)</td>
<td>1000 (68.9)</td>
</tr>
</tbody>
</table>

Materials of Construction

<table>
<thead>
<tr>
<th>Component</th>
<th>H Series</th>
<th>HK Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Handle</td>
<td>Green-anodized aluminum 3021</td>
<td></td>
</tr>
<tr>
<td>2 Panel mount nut</td>
<td>316 SS/3479</td>
<td>Brass 366/316</td>
</tr>
<tr>
<td>3 Retaining ring</td>
<td>31700</td>
<td>Stellite copper</td>
</tr>
<tr>
<td>4 Washer</td>
<td>316 SS/3479</td>
<td>Phosphor bronze C51000/B103</td>
</tr>
<tr>
<td>5 Spring</td>
<td>51780/5167</td>
<td>316 SS/3479</td>
</tr>
<tr>
<td>6 Stem</td>
<td>316 SS/3479</td>
<td>Phosphor bronze C51000/B130</td>
</tr>
<tr>
<td>7 Bonnet</td>
<td>321 SS/3479</td>
<td>Phosphor bronze C51000/B130</td>
</tr>
<tr>
<td>8 Bonnet adapter</td>
<td>316 SS/3479</td>
<td>Phosphor bronze C51000/B130</td>
</tr>
<tr>
<td>9 Stem tip</td>
<td>517400/4564</td>
<td>PTFE/600/EN30</td>
</tr>
<tr>
<td>10 Stem pin</td>
<td>430 SS</td>
<td>—</td>
</tr>
<tr>
<td>11 Gasket</td>
<td>—</td>
<td>PTFE-coated copper 110/112</td>
</tr>
<tr>
<td>12 Body</td>
<td>316 SS/3479</td>
<td>Brass 366/316</td>
</tr>
<tr>
<td>Nonwetted lubricant</td>
<td>Molybdenum disulfide-based paste</td>
<td></td>
</tr>
<tr>
<td>Wetted lubricant</td>
<td>—</td>
<td>Fluorinated-based</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Orifice Diameter (in.)</th>
<th>Flow Rate Range (mL/min.)</th>
<th>1L</th>
<th>3L</th>
<th>6L</th>
<th>15L</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0008</td>
<td>0.5–2</td>
<td>24 hr.</td>
<td>48 hr.</td>
<td>125 hr.</td>
<td>—</td>
</tr>
<tr>
<td>0.0012</td>
<td>2–4</td>
<td>4 hr.</td>
<td>12 hr.</td>
<td>24 hr.</td>
<td>60 hr.</td>
</tr>
<tr>
<td>0.0016</td>
<td>4–8</td>
<td>2 hr.</td>
<td>6 hr.</td>
<td>12 hr.</td>
<td>30 hr.</td>
</tr>
<tr>
<td>0.0020</td>
<td>8–15</td>
<td>1 hr.</td>
<td>4 hr.</td>
<td>8 hr.</td>
<td>20 hr.</td>
</tr>
<tr>
<td>0.0030</td>
<td>15–30</td>
<td>—</td>
<td>2 hr.</td>
<td>3 hr.</td>
<td>8 hr.</td>
</tr>
<tr>
<td>0.0060</td>
<td>30–80</td>
<td>—</td>
<td>—</td>
<td>1.5 hr.</td>
<td>4 hr.</td>
</tr>
<tr>
<td>0.0090</td>
<td>80–340</td>
<td>—</td>
<td>—</td>
<td>0.5 hr.</td>
<td>1 hr.</td>
</tr>
</tbody>
</table>

- 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
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

MSD

GC

Autosampler
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
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 humidified 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 known concentration of TO-15 into the canister and test over time to measure stability.
• The results tell a story.
• Log the results.
Thermal Desorption 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

- 2-Butoxyethanol
- Benzene
- Naphthalene
- Phenanthrene
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
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

• Contact me:
  – Dave Shelow
  – 919-541-3776
  – Shelow.david@epa.gov