Basic Capillary GC Theory and Practical Troubleshooting

Part 4, Troubleshooting

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GC Troubleshooting: Topics

- Basic Troubleshooting Strategy
- Preventing Problems
  - Gas Purification
  - Injection Technique
  - Liner Selection and Care
  - Column Installation
  - Guard Columns
- Identifying Common Problems
- Recommended Reading
- Discussion
Troubleshooting Strategy

• Have appropriate equipment and supplies on hand.
• Establish a systematic approach.
• Know what to look for first.
• Record what you did to correct the problem.
Troubleshooting Strategy

• Suggested equipment to have on hand for troubleshooting:
  - Electronic Leak Detector
  - Flow Meter
  - “Test” Column
  - Replacement Accessories (Syringes, Ferrules, Septa, Liners)
  - Replacement Purifiers
Troubleshooting Strategy

- Isolate the source of the problem:

  - Run Reference Standard
  - Check operating parameters
    - Correct the parameter
    - OK
    - Not OK
  - Install Test Column
    - Problem was sample related
    - OK
    - Not OK
    - Problem was in the inlet or with the carrier gas
    - Not OK
  - Switch Detector
    - Not OK
    - OK
  - Problem was column related
    - OK
    - Problem was in the Original detector
    - OK
Troubleshooting Strategy

• Approaching the problem…
  - Check first to see if a “fix” for the problem is already known.
  - Check the Supelco Capillary GC Troubleshooting Guide (Bulletin 853.)
  - Check the instrument maintenance record.
  - Talk to others in your lab.
Troubleshooting Strategy

- **Five major sources of chromatographic problems:**
  - Operator Error
  - The Sample
  - The Column
  - The Gas Flow System (both internal and external to the GC)
  - The GC Electrical System
Troubleshooting Strategy

• When reviewing method parameters, consider these questions:
  - Should I be doing split or splitless injection?
  - Is my starting temperature low enough to allow sufficient sample focusing?
  - For splitless injections, is my splitter opening at the appropriate time?
  - Is my column flow set to give me maximum efficiency at the most critical point?
  - Are heated zones (injectors, detectors, interfaces) set appropriately?
  - Am I using the appropriate liner type?
Preventing Problems

- **The best way to solve problems is to prevent them!**
  - Install and maintain proper purification for all gases in the GC system.
  - Maintain the injector by periodically inspecting and changing the liner, septa, and seal.
  - Use the proper injection technique - this includes using the right liner for the job.
  - Install the column at the recommended insertion distances.
  - When necessary, use a guard column to protect the analytical column.
Gas Purification

- **Carrier Gas**
  - At minimum, remove hydrocarbons, water, and oxygen.

- **Hydrogen (FID)**
  - At minimum, remove hydrocarbons.

- **Air (FID)**
  - At minimum, remove water and hydrocarbons.

- **Nitrogen make-up (FID, ECD)**
  - At minimum, remove hydrocarbons.

- **P-5 make-up (ECD)**
  - At minimum remove hydrocarbons, halocarbons, and oxygen.
**Gas Purification**

- Acceptable purity levels for chromatography grade gases:

<table>
<thead>
<tr>
<th>Gas</th>
<th>O2</th>
<th>H2O</th>
<th>CO2</th>
<th>CO</th>
<th>Total Hydrocarbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
</tr>
<tr>
<td>Air</td>
<td>20-22%</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
</tr>
<tr>
<td>Argon/Methane</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
<td>&lt;1.0 ppm</td>
</tr>
</tbody>
</table>
## Gas Purification

- **Suggested gas purifiers:**

<table>
<thead>
<tr>
<th></th>
<th>Hydrocarbons</th>
<th>Water</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier</td>
<td>Supelcarb™ HC</td>
<td>Mol Sieve 5A</td>
<td>OMI™-2</td>
</tr>
<tr>
<td></td>
<td>Supelpure™ HC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td></td>
<td>Mol Sieve 5A</td>
<td></td>
</tr>
<tr>
<td>N₂ makeup</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-5</td>
<td>OMI™-2</td>
<td>OMI™-2</td>
<td></td>
</tr>
</tbody>
</table>
Gas Purification

• What are some signs that my purifiers need to be changed?

• Hydrocarbon Traps
  - Noise in the baseline (FID)
  - Increase in background peaks on tune (MSD)
  - Higher than normal baseline reading on FID
  - Extra peaks visible in run

• Molecular Sieve 5A
  - Increase in column bleed
  - Water visible in MS background
  - Poor peak shapes for gaseous VOCs (purge and trap)
  - Extra peaks visible in run
  - OMI™-2 color change
Injector Maintenance

• **Change (as needed):**
  - Septa
  - Liner and O-ring
  - Seal and washer

• **Inspect the Inlet Periodically**
  - Look for contamination in the liner
  - Look for residue on the seal
Injection Technique

• It is important to choose the injection technique that is appropriate for your analysis. In Capillary GC, the techniques used are:
  - Split
  - Splitless
  - Direct
  - On-column
Injection Technique

• Split Injection
  - A vaporizing type injection designed to limit the amount of sample reaching the capillary column.
  - Sample is split and a small portion flows to the column while the bulk is typically vented through the split vent port.
  - Split injection can be used in an isothermal or temperature programmed analysis.
Injection Technique

• Splitless Injection
  - Sample is introduced into a heated injection port operating in a nonsplitting mode.
  - Sample vaporizes and sample cloud is mixed with carrier gas and transferred into the column.
  - Sample condenses on head of the capillary column due to the oven temperature being 10-20ºC below matrix solvent boiling point.
  - After 1.5 to 2 injector volumes have entered the column, split vent is opened and inlet purged.
Injection Technique

• The volume of a splitless liner is important:

Typical Splitless Injection Liner Volumes

<table>
<thead>
<tr>
<th>Liner Length</th>
<th>Liner ID</th>
<th>Liner Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>78.5mm</td>
<td>4.0mm</td>
<td>986µL</td>
</tr>
<tr>
<td>78.5mm</td>
<td>2.0mm</td>
<td>246µL</td>
</tr>
<tr>
<td>78.5mm</td>
<td>1.0mm</td>
<td>62µL</td>
</tr>
</tbody>
</table>
## Injection Technique

- Solvent expansion volumes of 1µL injection at specified temperatures and pressures:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>BP (°C)</th>
<th>200°C Inlet Head pressure</th>
<th>300°C Inlet Temp. Head pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>77</td>
<td>236</td>
<td>168</td>
</tr>
<tr>
<td>Hexane</td>
<td>68.7</td>
<td>177</td>
<td>126</td>
</tr>
<tr>
<td>Isooctane</td>
<td>99.2</td>
<td>140</td>
<td>100</td>
</tr>
<tr>
<td>Methanol</td>
<td>64.5</td>
<td>570</td>
<td>406</td>
</tr>
<tr>
<td>Chloride</td>
<td>40.1</td>
<td>360</td>
<td>257</td>
</tr>
<tr>
<td>MTBE</td>
<td>55</td>
<td>194</td>
<td>138</td>
</tr>
<tr>
<td>Water</td>
<td>100</td>
<td>1279</td>
<td>910</td>
</tr>
</tbody>
</table>
Injection Technique

- **Direct Injection**
  - A vaporizing type injection typically used with wide bore capillary columns in a converted packed column GC.
  - Sample is injected into a heated injection sleeve, vaporized, and transported directly to the column in the carrier gas flow. Similar to a packed column flash vaporization injector.
  - Analyses can be isothermal or temperature programmed.
Injection Technique

• **Cold On-Column Injection**
  - A non-vaporizing type injection in which the liquid sample is directly deposited at the inlet of the capillary columns.
  - All analyses are temperature programmed analyses since a liquid sample is deposited in the column.
  - No liners are typically required.
  - Special syringes are required.
  - 0.53mm ID fused silica created to allow insertion of 26 gauge needle into column.
Injection Technique

- Injection speed can have an effect.

Rapid, smooth injection

Slow, “choppy” injection
Liner Selection

• Some liners used for split injection:

  - Cup
  - Baffle (Varian)
  - Split/splitless, wool packed
Liner Selection

- Some liners used for splitless injection:

  - 2 mm ID, straight
  - Dual-tapered
  - Single-tapered
Liner Selection

• Packed liners, PROs and CONs:

  • PROs
    - Packing liners helps aid in the vaporization process
    - Packing liners can help improve reproducibility of area counts by minimizing droplets reaching the head of the column
    - Packing can act as a particle trap

  • CONs
    - The packing does act as a short packed column and can influence results
    - Can cause discrimination of higher molecular weight compounds
    - Can cause adsorption & sample degradation
Liner Selection

• The ID of the liner can affect sensitivity:

The Use of a 2mm ID Liner will Increase Sensitivity for the Lighter Analytes

Splitless injection, 2mm vs. 4mm ID liner
Liner Care

• **If you must clean a liner...**
  - Handle liners with gloves or forceps.
  - Use clean compressed gas and/or a fine brush to remove particles.
  - Rinse liner in an appropriate solvent and dry with clean compressed gas.
  - Use mineral acid and/or detergent only if absolutely necessary. Be sure to deactivate the liner after after this process.
  - If repacking with glass wool, make sure it has been deactivated.
Liner Care

• The results of using undeactivated glass wool in 4mm ID liner used for pesticide analysis:

Deactivated glass wool

Undeactivated glass wool

1. 4,4'-DDE
2. Endrin
3. 4,4'-DDD
4. Endrin aldehyde
5. 4,4'-DDT
6. Endrin ketone
Column Installation

- Installing the column too low in the inlet can result in peak tailing.

This column was installed too low in the inlet.
Guard Columns

- Choose a guard column that has been deactivated.
- Usually, the ID of the guard matches the analytical column.
- A 5-10 meter length is normally used.
- Connect with either a GlasSeal™ or butt connector.
Common Problems

1. Poor Peak Shapes (either tailing, fronting, or just generally ugly.)
2. Nonlinearity
3. Baseline Noise and/or Drift
4. Ghost Peaks
5. Missing Peaks / Poor Response
6. Insufficient Resolution
Poor Peak Shape

- In Gas-liquid chromatography, fronting may indicate column overload.

- Tailing may indicate activity in the system or improper column installation.
Poor Peak Shape

- Generally ugly peaks, such as $\alpha,\alpha$-dimethylphen-ethylamine, can be caused by a variety of problems.
Nonlinearity

- The most common causes are:
  - Column overload
  - Detector overload
  - Standards preparation
  - Poor peak shape resulting in improper integration
Nonlinearity and Column Overload

• An Example of Column Overload:

[Diagram showing peaks with note: Fronting due to overload]
An Example of Column Overload:

• Preventing column overload:
  - Inject a smaller amount and/or increase split ratio.
  - Use a thicker film column.
  - Use a column with a wider ID.
  - Decrease upper limit of calibration range.
  - Use a column of slightly different polarity.
Nonlinearity and Poor Peak Shape

- An example of poor peak shape affecting linearity:
  - The poor peak shape of benzoic acid here is caused by solubility problems with the 5% phenyl methylpolysiloxane phase.
Baseline Noise and Drift

• **Common causes:**
  - Column bleed
  - Septa bleed
  - Dirty detector
  - Contaminants in carrier gas / carrier gas purity
Column Bleed

- Results from the normal degradation of the stationary phase.
- All columns bleed to some extent.
- Bleed increases with temperature.
- The amount of bleed will increase in the presence of oxygen.
Column Bleed

- A Typical Bleed Profile:

Bleed measured as the difference between 1 and 2.
Column Bleed

- **Column bleed and an MSD:**
  - Visible as baseline rise in the TIC.
  - Check spectra for key bleed ions:
    - Equity-1: 73, 207, 281
    - Equity-5: 207, 281
    - Equity-1701: 207, 269
    - SPB™-624: 207, 269
- **Make sure interface temp. is < column max. temp.**
Column Bleed

- Common Bleed Ions

207: D3  

284: D4  

73: TMS
**Column Bleed**

- **Equity-1: MS Spectra of Bleed**

Scan 8569 (43.681 min): EQ12506A.D

- TMS
- D3
- D4

m/z -->

Sigma-Aldrich.com
Column Bleed

- Equity-5: MS Spectra of Bleed
Column Bleed

• **SPB™-624: MS Spectra of Bleed**
Column Bleed

• **Equity-1701: MS Spectra of Bleed**

Abundance

Scan 9126 (84.849 min): 0215001.D

- 207
- 269
Septa Bleed

- Septa Bleed: MS Spectra
Column & Septa Bleed

• Minimize bleed!
  - Sufficiently purge column with carrier gas before ramping it up in temperature.
  - Make sure carrier gas is scrubbed for water and oxygen.
  - Check integrity of all fittings leading to the column.
  - Do not heat the column above its maximum temp.
  - Precondition the column prior to use.
  - Use a high quality, high temperature septa and ferrules.
Baseline Noise and Drift

• **Effect of carrier gas purity on baseline noise:**

GCMS baseline comparisons

- H2 carrier from tank
- H2 carrier from a generator
Ghost Peaks

- **Possible causes:**
  - Residue in the inlet liner and at the head of the column
  - Contaminated syringe / and or wash solutions on an autosampler
  - Sample carryover
  - Contaminated carrier gas
Ghost Peaks

- If pieces of septa get into an inlet liner...

Response test mix, before
Ghost Peaks

...even a simple analysis can be ruined.

Response test mix, after
Missing Peaks / Poor Response

• **Sample decomposition**
  - Activity in the inlet or column
  - Injection port temperature too high
  - Sample not stable enough for GC
  - Standards not stable

• **Coelution**

• **Insufficient run time / final temperature**

• **Sample not volatile enough for GC**

• **Improper column installation**
Missing Peaks / Poor Response

- Nasty samples can damage a column by creating active sites.

Before Sample Injection

- 2,4-dinitrophenol
- 4-nitrophenol
- 2-methyl-3,5-dinitrophenol
- pentachlorophenol
Missing Peaks / Poor Response

- Responses of some acidic compounds were affected.

After Sample Injection

- 2,4-DNP & 4-NP should be here
- 2-methyl-3,5-dinitrophenol
- Pentachlorophenol should be here
Missing Peaks / Poor Response

• Response can also be affected by the position of the column in the inlet.

8 mm above top of ferrule
Missing Peaks / Poor Response

- Here, the column was not inserted far enough.

5 mm above top of ferrule
Missing Peaks / Poor Response

- Here, the column was inserted too far:

20 mm above top of ferrule
Insufficient Resolution

**Column**
- Longer columns increase resolution
- Smaller ID columns increase resolution
- A different phase altogether may be needed

**Conditions**
- Carrier gas flow too fast or slow
- Oven ramp rate too fast
- Wrong starting or ending temperature
Supelco Bulletins

741: The Supelco Guide to Leak-Free Connections
783: Cleaning Flame Ionization Detectors
853: Capillary Troubleshooting Guide
875: Supelco Capillary GC Selection Guide
895: Installation and Maintenance Instructions for 0.25 mm and 0.32 mm ID Fused Silica Capillary Columns
897: Installation and Maintenance Instructions for 0.53 mm ID Fused Silica Capillary Columns
898: Gas Management Systems for GC
899: Capillary GC Inlet Sleeve Selection Guide
916: Purge and Trap System Guide
918: Selecting Purifiers for Gas Chromatography
Supelco Service

• Supelco Technical Service
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• Supelco Customer Service
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• Sigma-Aldrich Website
  - www.sigma-aldrich.com
Discussion