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

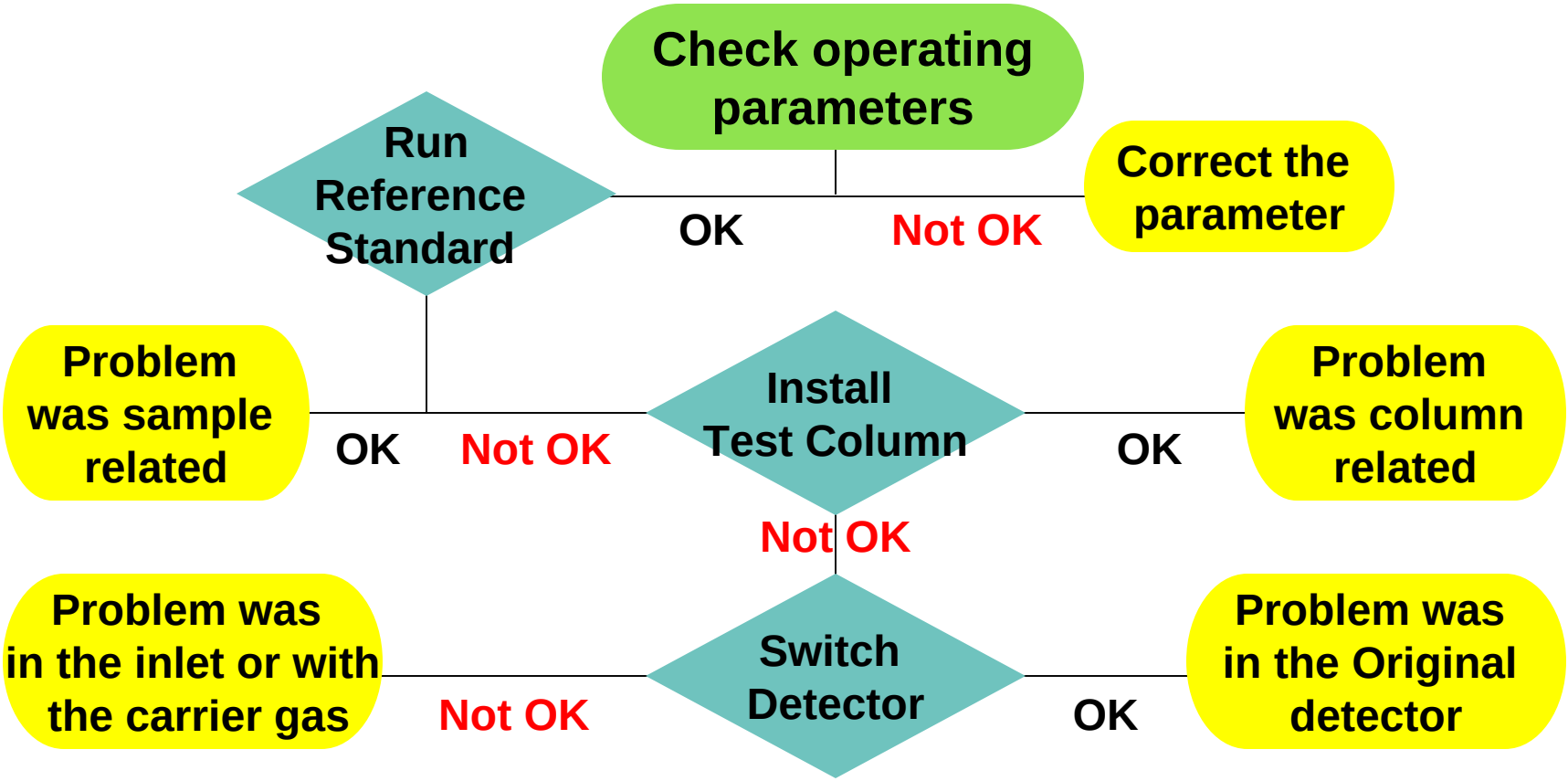
- Have appropriate equipment and supplies on hand.
- Establish a systematic approach.
- Know what to look for first.
- Record what you did to correct the problem.

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:**



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:**

Impurity / Maximum Concentration

Gas	O2	H2O	CO2	CO	Total Hydrocarbons
Helium	<1.0 ppm	<1.0 ppm	<1.0 ppm	<1.0 ppm	<1.0 ppm
Nitrogen	<1.0 ppm	<1.0 ppm	<1.0 ppm	<1.0 ppm	<1.0 ppm
Air	20-22%	<1.0 ppm	<1.0 ppm	<1.0 ppm	<1.0 ppm
Hydrogen	<1.0 ppm	<1.0 ppm	<1.0 ppm	<1.0 ppm	<1.0 ppm
Argon/ Methane	<1.0 ppm	<1.0 ppm	<1.0 ppm	<1.0 ppm	<1.0 ppm

Gas Purification

- **Suggested gas purifiers:**

	Hydrocarbons	Water	Oxygen
Carrier	Supelcarb™ HC Supelpure™ HC	Mol Sieve 5A	OMI™-2
H_2			
Air		Mol Sieve 5A	
N_2 makeup			
P-5	OMI™-2		OMI™-2

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

Liner Length	Liner ID	Liner Volume
78.5mm	4.0mm	986µL
78.5mm	2.0mm	246µL
78.5mm	1.0mm	62µL

Injection Technique

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

		200°C Inlet			300°C Inlet Temp.		
		Head pressure			Head pressure		
Solvent	**BP (°C)**	**10**	**20**	**30**	**10**	**20**	**30**
Ethyl acetate	77	236	168	131	286	204	58
Hexane	68.7	177	126	98	214	153	119
Isooctane	99.2	140	100	77	170	121	94
Methanol	64.5	570	406	315	691	492	382
chloride	40.1	360	257	200	437	311	241
MTBE	55	194	138	108	235	167	130
Water	100	1279	910	706	1548	1102	855

Injection Technique

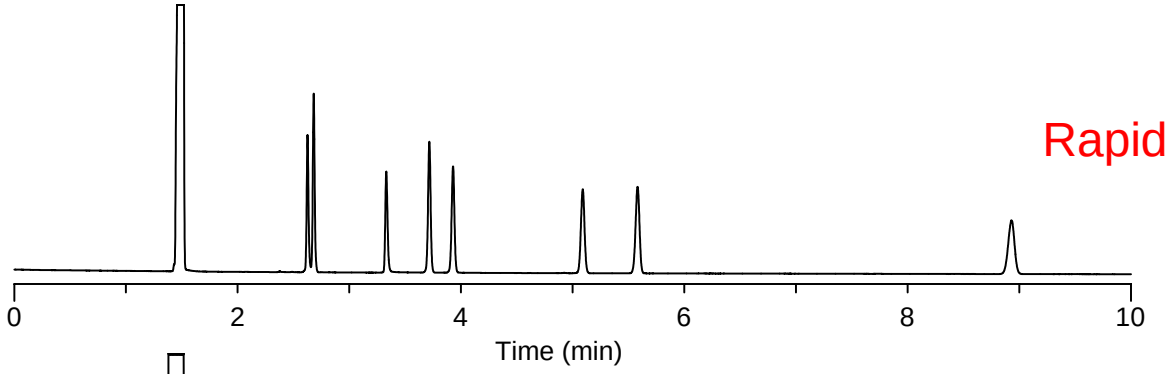
- **Direct Injection**
  - A vaporizing type injection typically used with wide bore capillary columns in a converted packed column GC.
  - Sample is injected into a heated injection sleeve, vaporized, and transported directly to the column in the carrier gas flow. Similar to a packed column flash vaporization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

Injection Technique

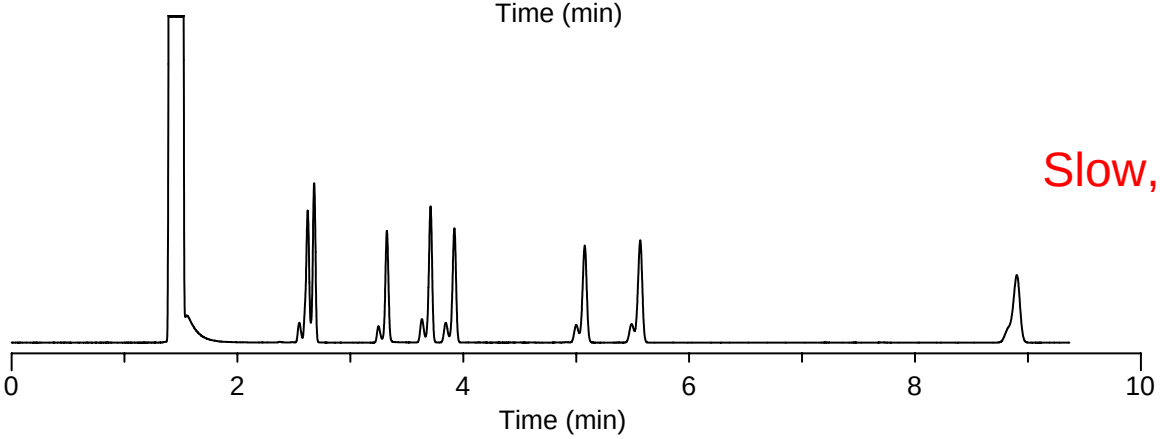
- **Cold On-Column Injection**
  - A non-vaporizing type injection in which the liquid sample is directly deposited at the inlet of the capillary columns.
  - All analyses are temperature programmed analyses since a liquid sample is deposited in the column.
  - No liners are typically required.
  - Special 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

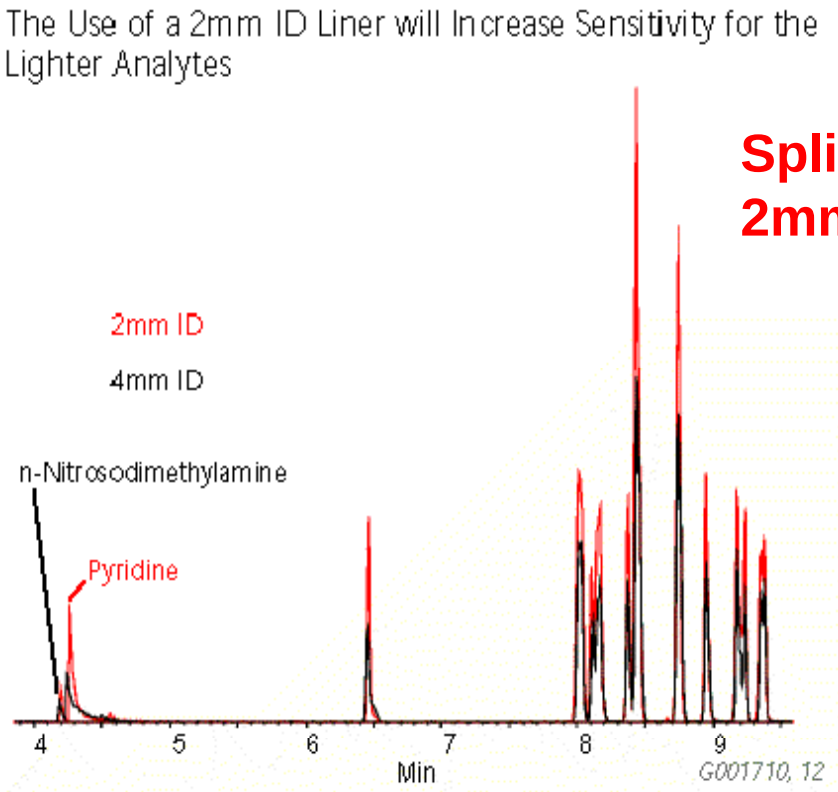
Single-tapered

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:**



Splitless injection, 2mm vs. 4mm ID liner

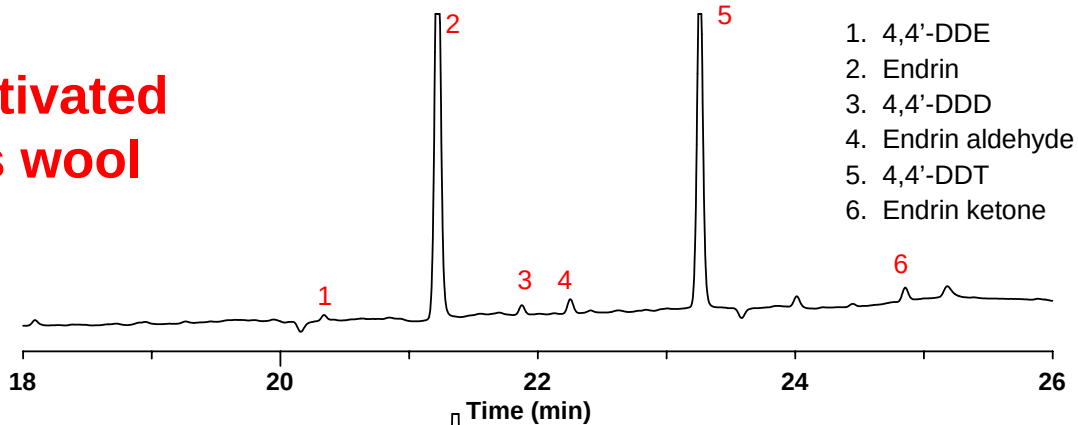
Liner Care

- **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.

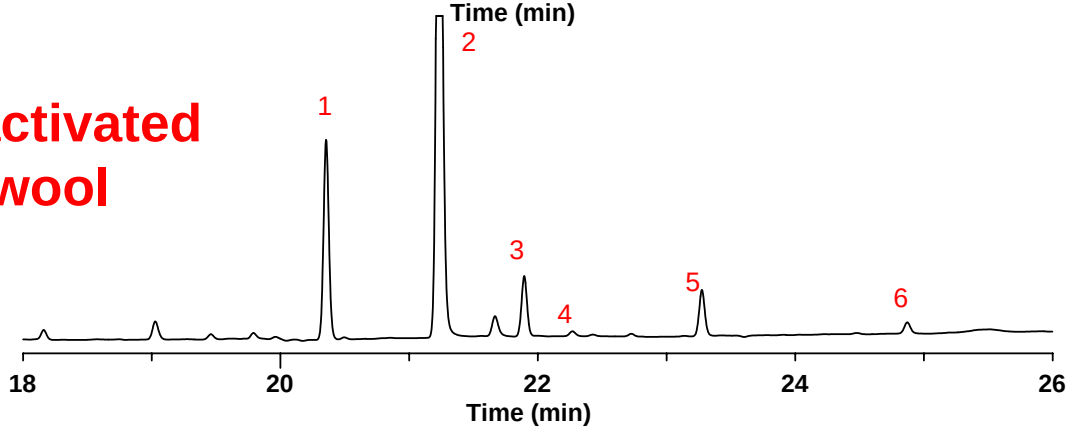
Liner Care

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

Deactivated glass wool

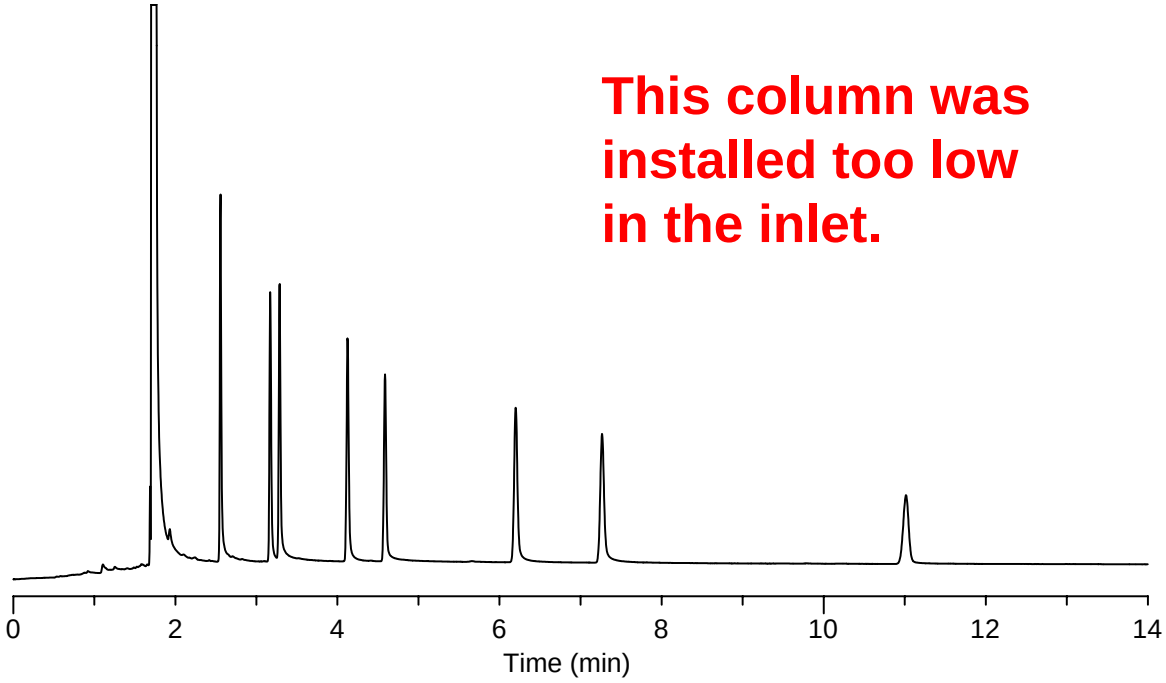


Undeactivated glass wool



Column Installation

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



Guard Columns

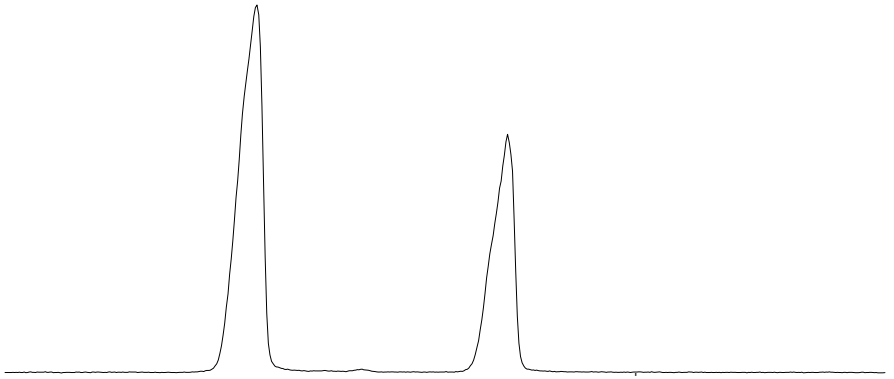
- Choose a guard column that has been deactivated.
- Usually, the ID of the guard matches the analytical column.
- A 5-10 meter length is normally used.
- Connect with either a GlasSeal™ or butt connector.

Common Problems

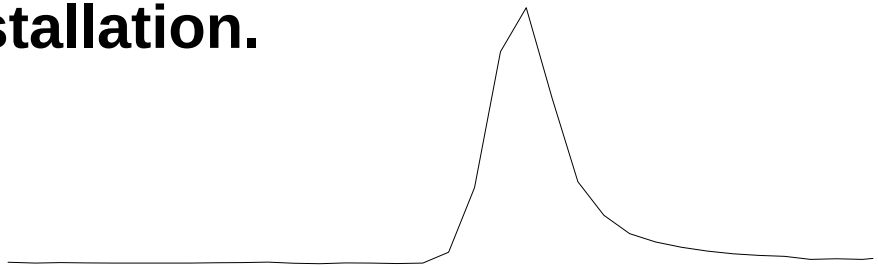
1. Poor Peak Shapes (either tailing, fronting, or just generally ugly.)
2. Nonlinearity
3. Baseline Noise and /or Drift
4. Ghost Peaks
5. Missing Peaks / Poor Response
6. Insufficient Resolution

Poor Peak Shape

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

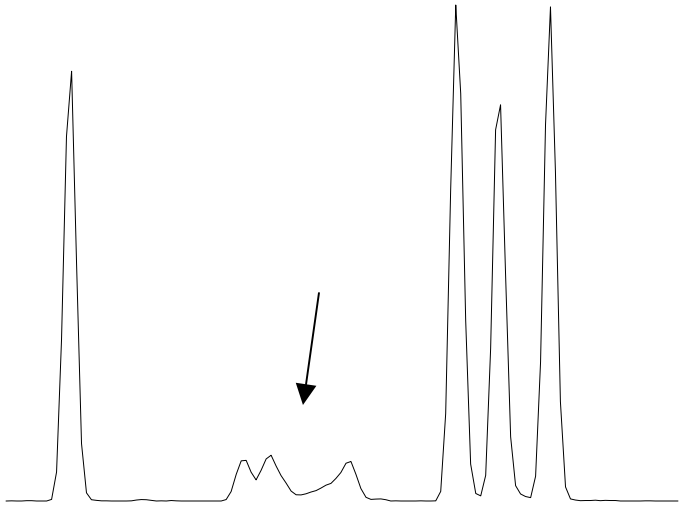


- **Tailing may indicate activity in the system or improper column installation.**



Poor Peak Shape

- **Generally ugly peaks, such as α,α-dimethylphen-ethylamine, can be caused by a variety of problems.**

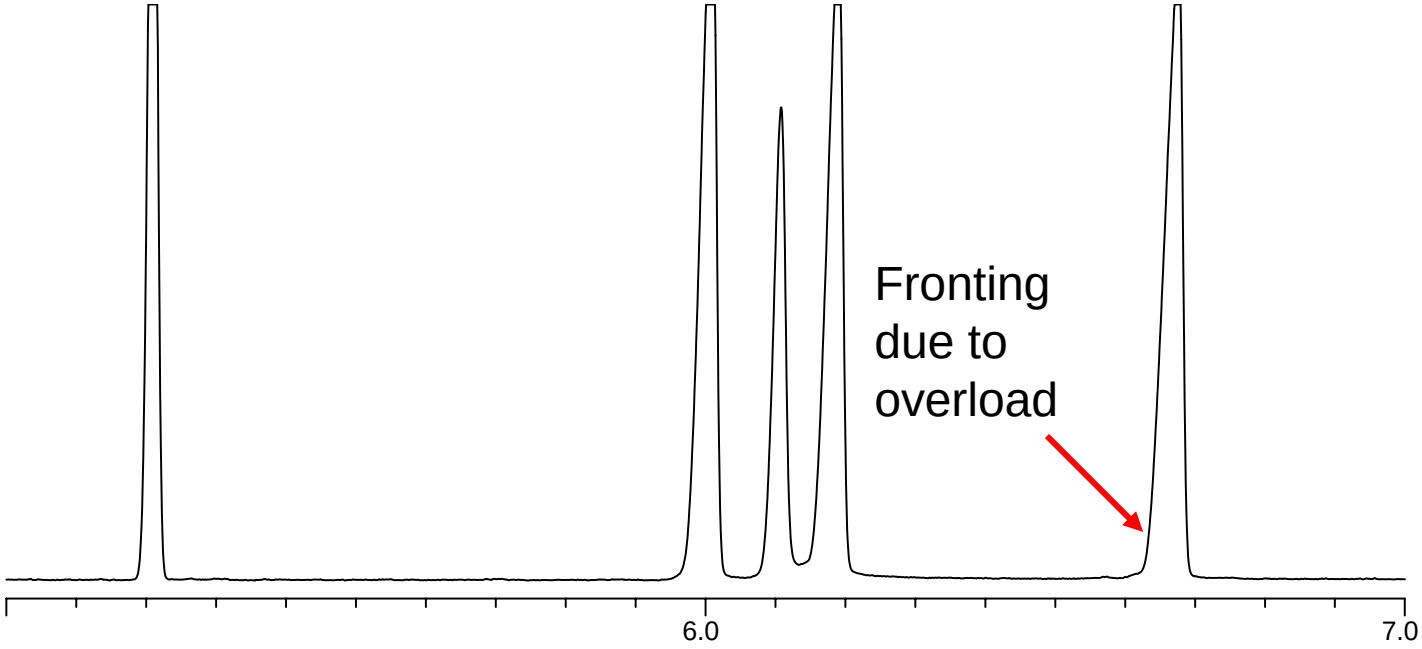


Nonlinearity

- **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:**

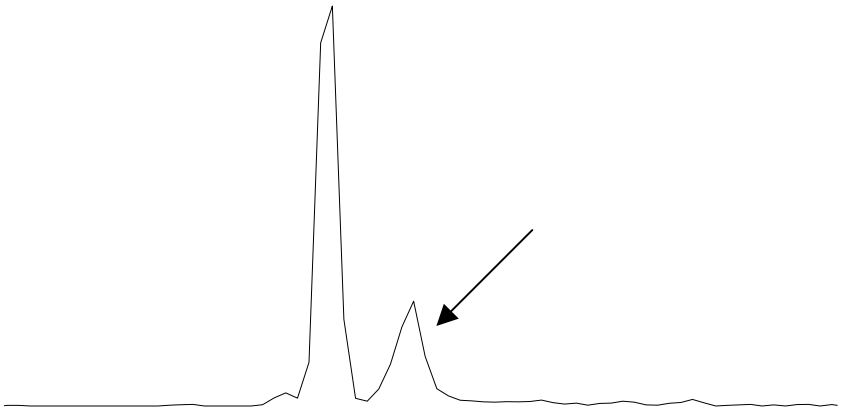


An Example of Column Overload:

- **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

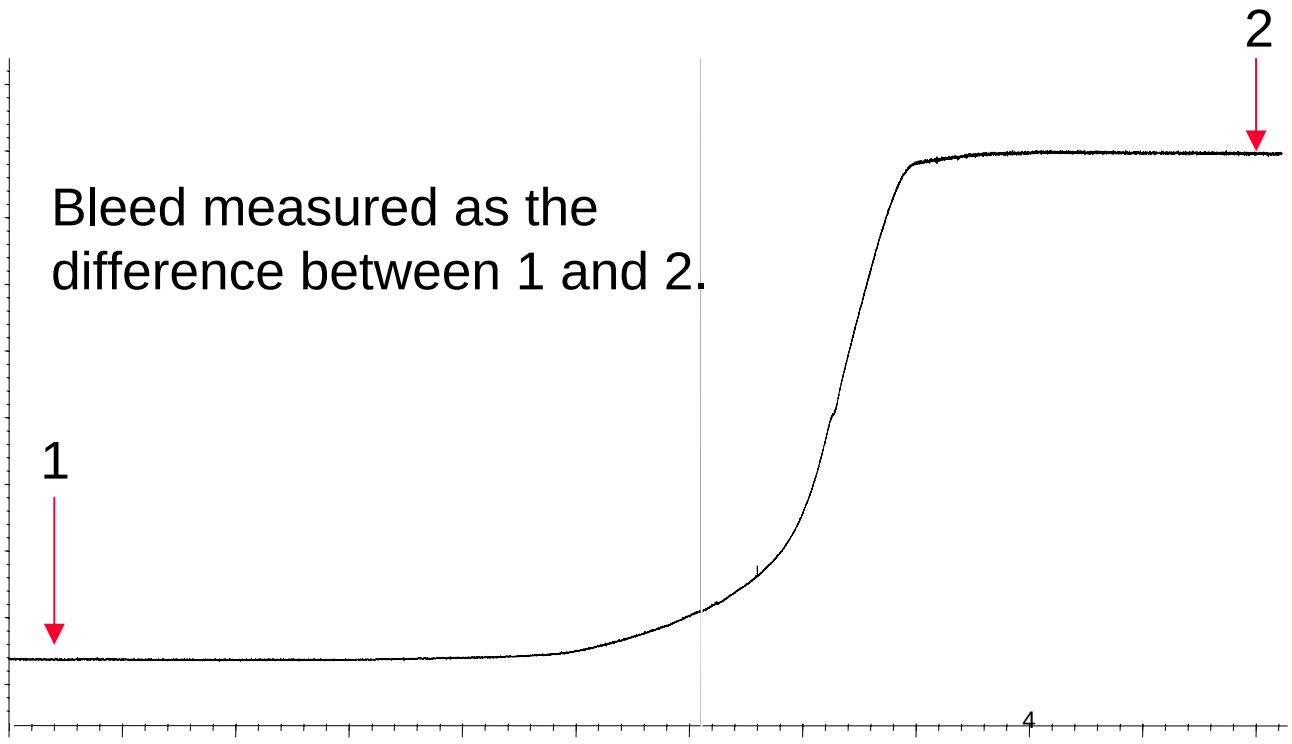
- **Common causes:**
  - Column bleed
  - Septa bleed
  - Dirty detector
  - Contaminants in carrier gas / carrier gas purity

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:**

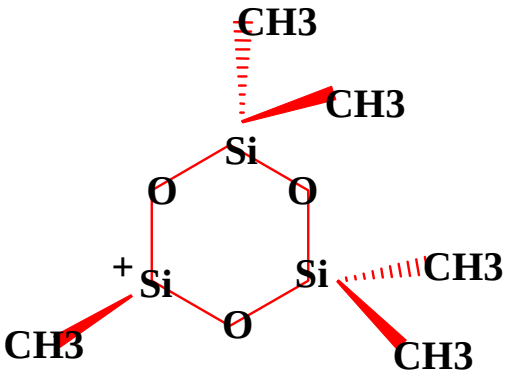


Column Bleed

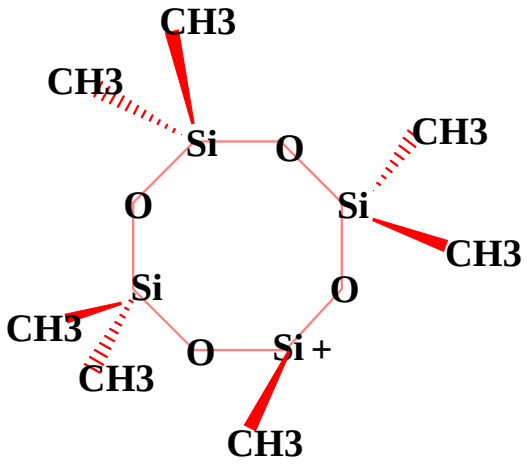
- **Column bleed and an MSD:**
  - Visible as baseline rise in the TIC.
  - Check spectra for key bleed ions:
    - Equity-1: 73, 207, 281
    - Equity-5: 207, 281
    - Equity-1701: 207, 269
    - SPB™-624: 207, 269
- **Make sure interface temp. is < column max. temp.**

Column Bleed

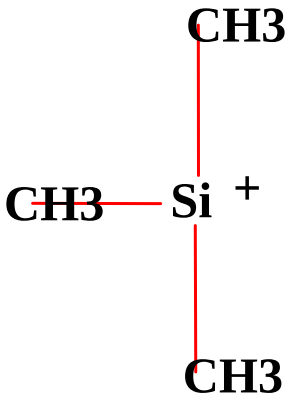
- **Common Bleed Ions**



207: D3



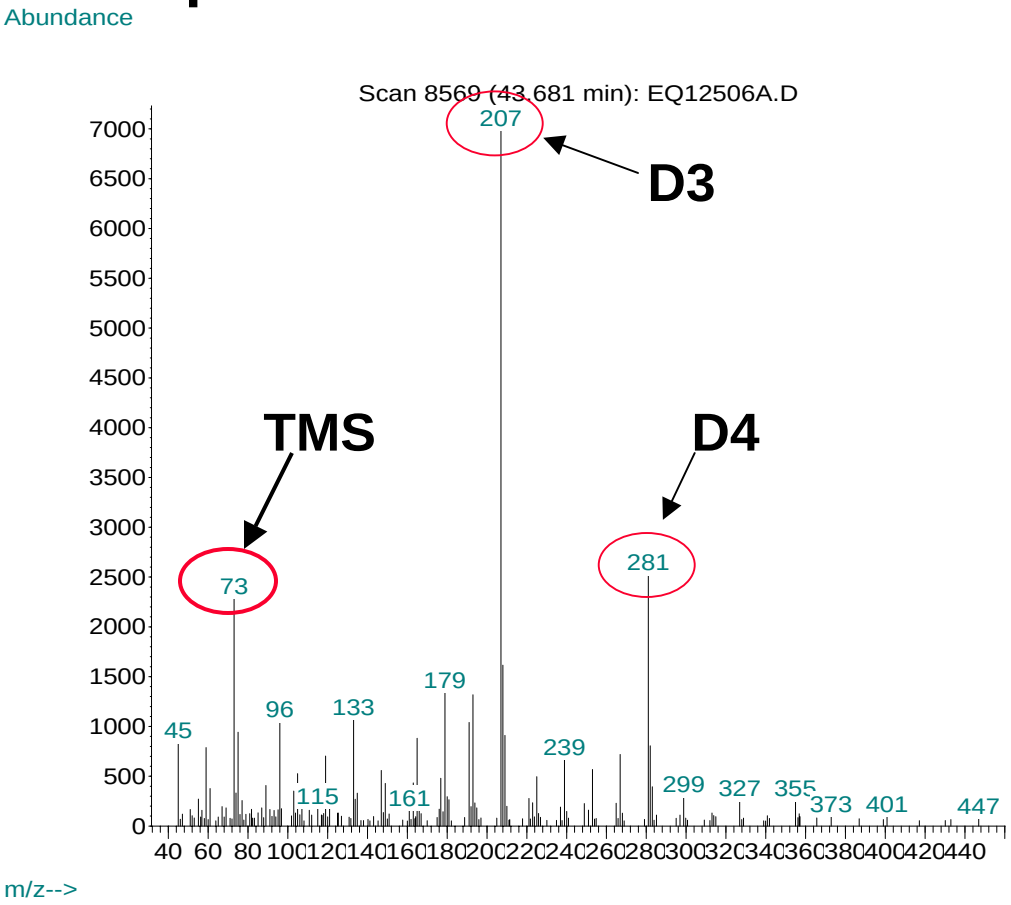
284: D4



73: TMS

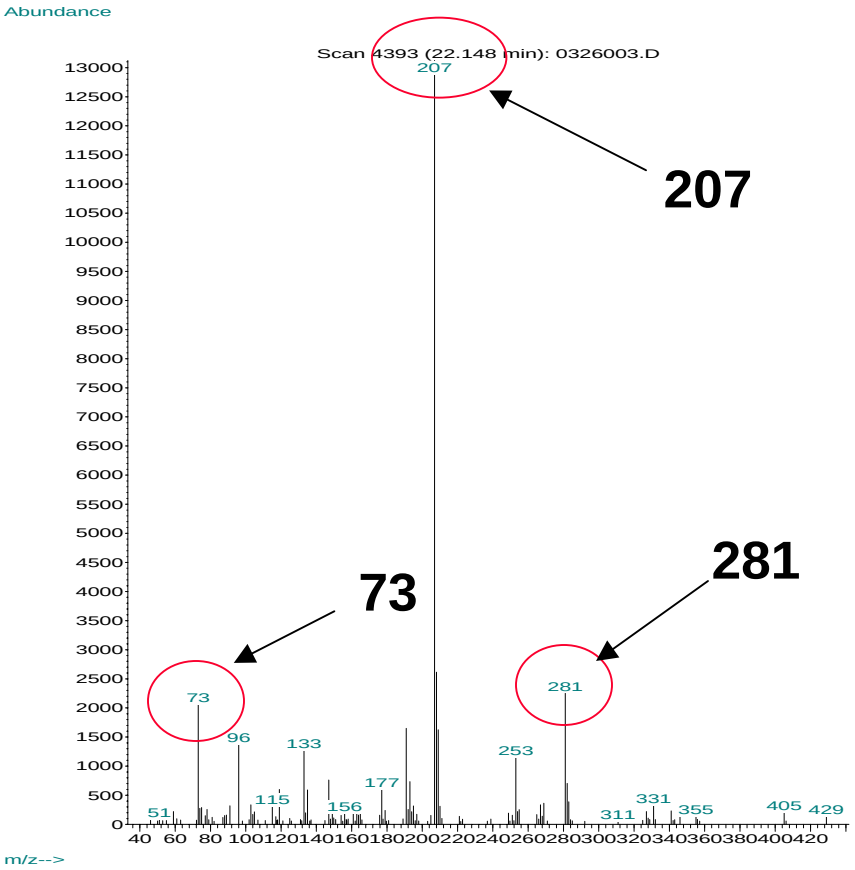
Column Bleed

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



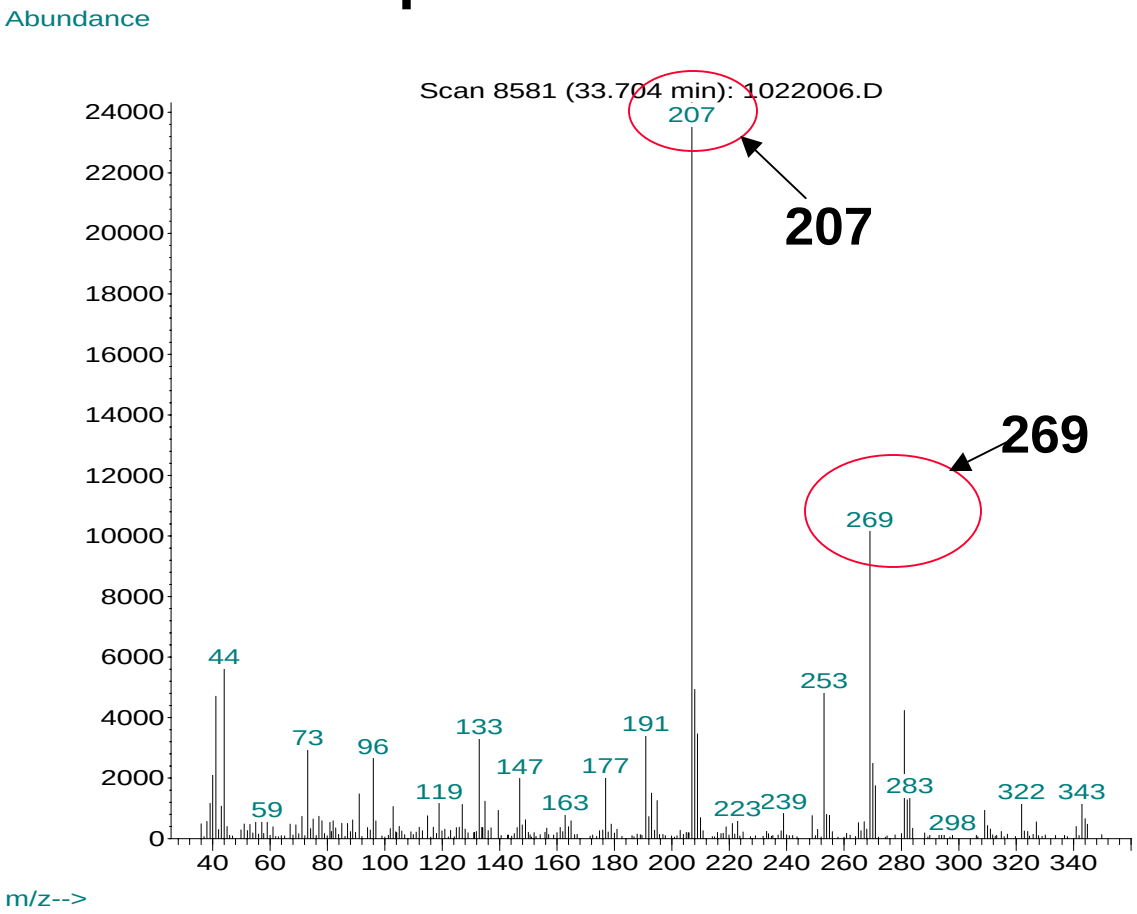
Column Bleed

- **Equity-5: MS Spectra of Bleed**



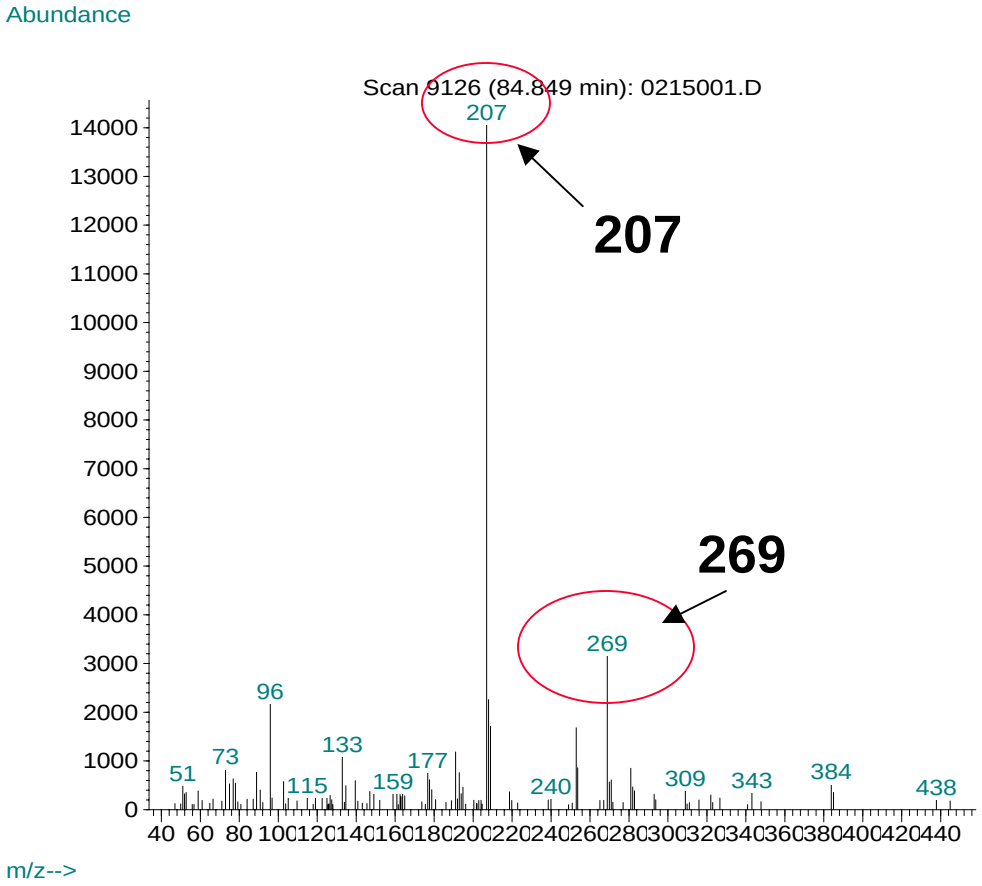
Column Bleed

- **SPB™-624: MS Spectra of Bleed**



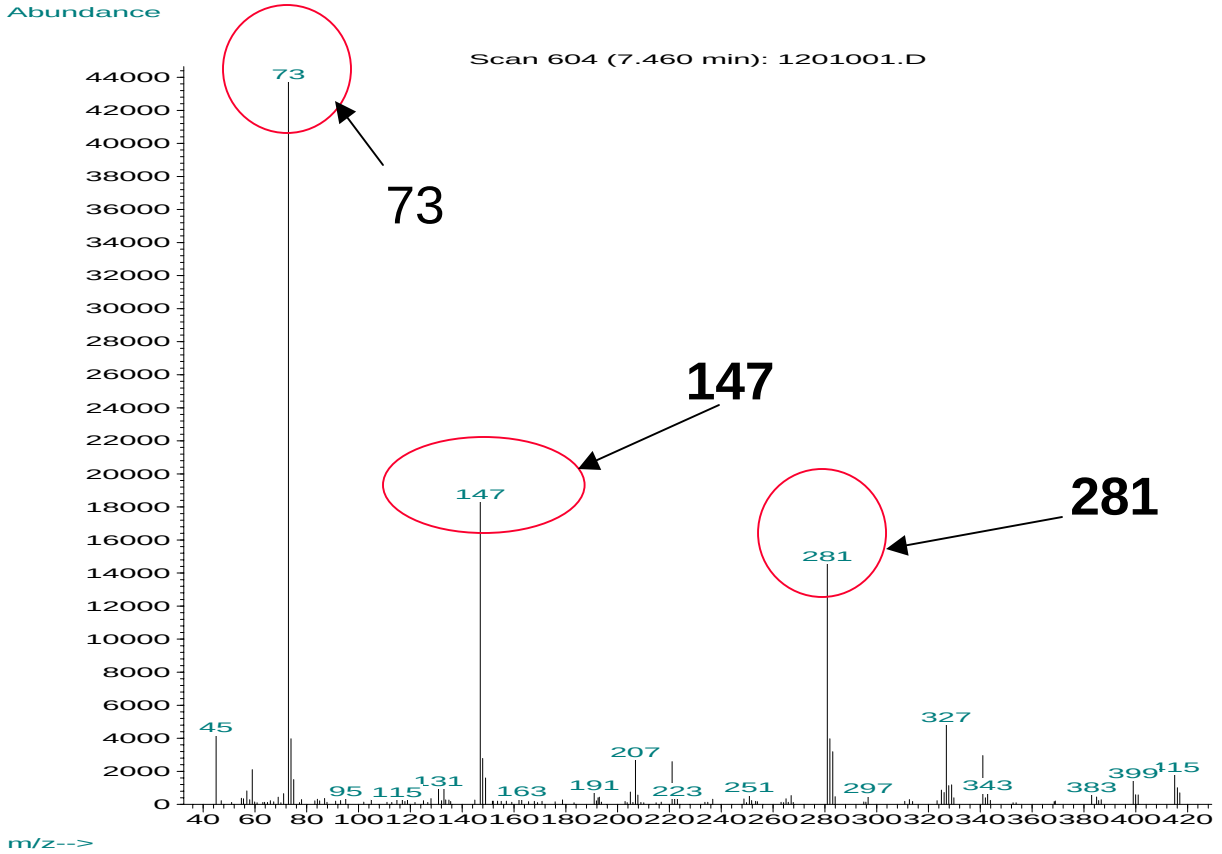
Column Bleed

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



Septa Bleed

- **Septa Bleed: MS Spectra**

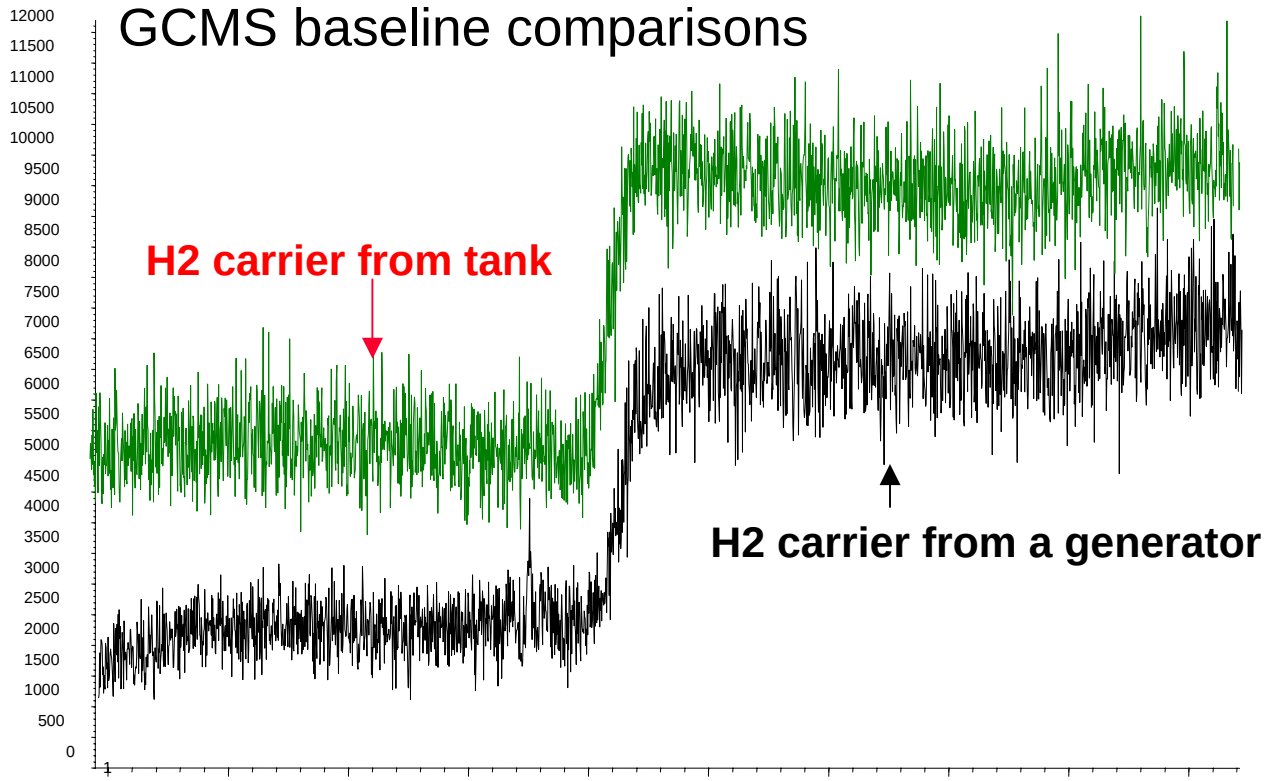


Column & Septa Bleed

- **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:**

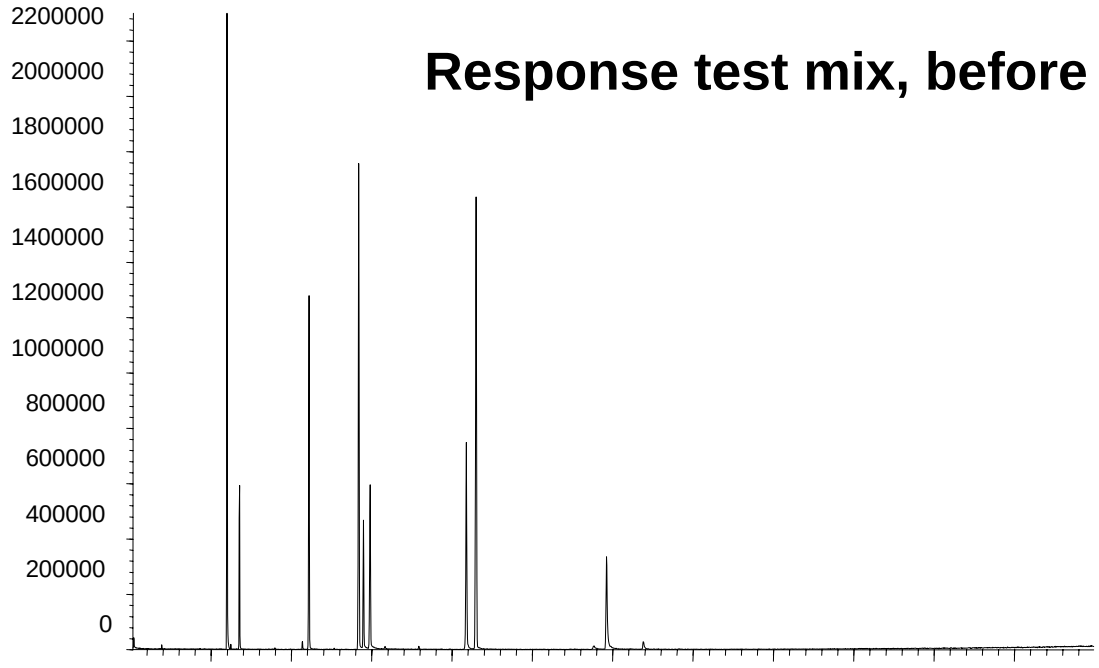


Ghost Peaks

- **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

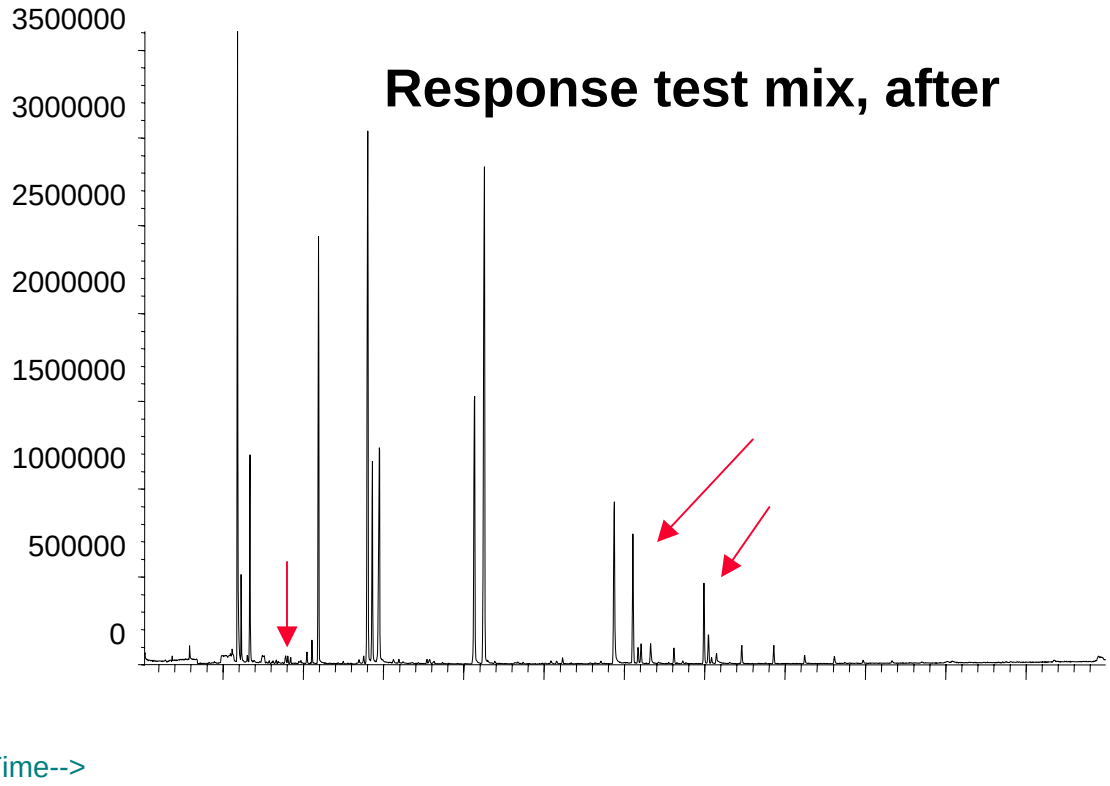
- **If pieces of septa get into an inlet liner...**



Response test mix, before

Ghost Peaks

…even a simple analysis can be ruined.



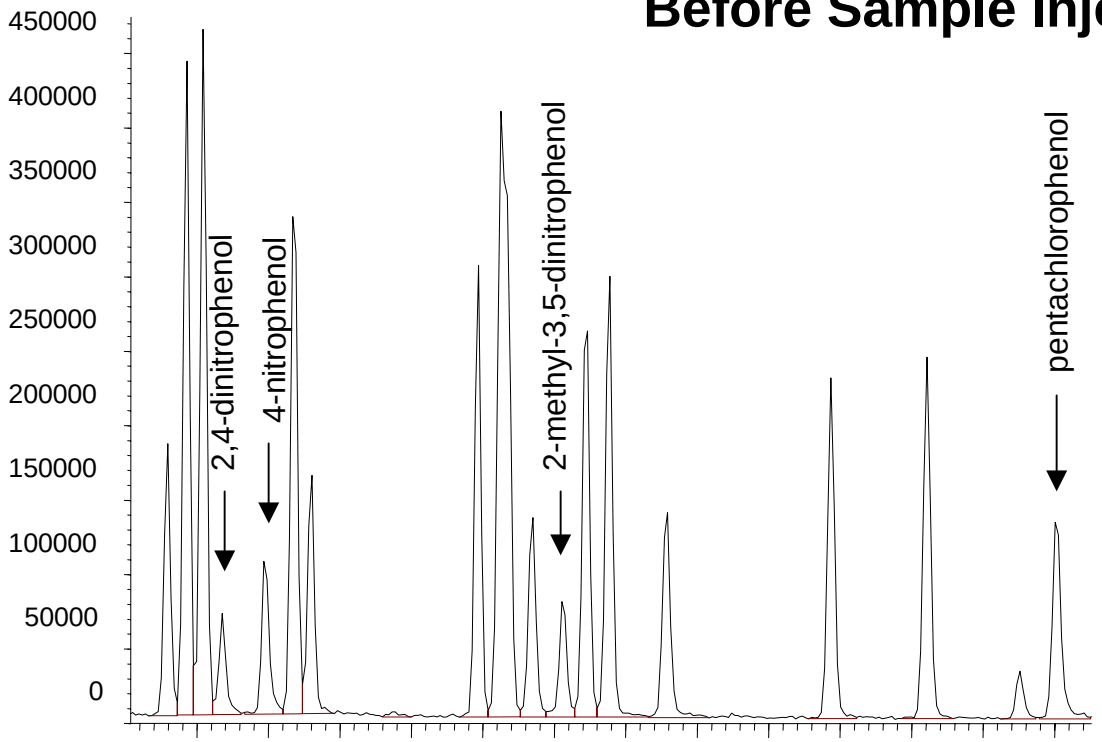
Missing Peaks / Poor Response

- **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

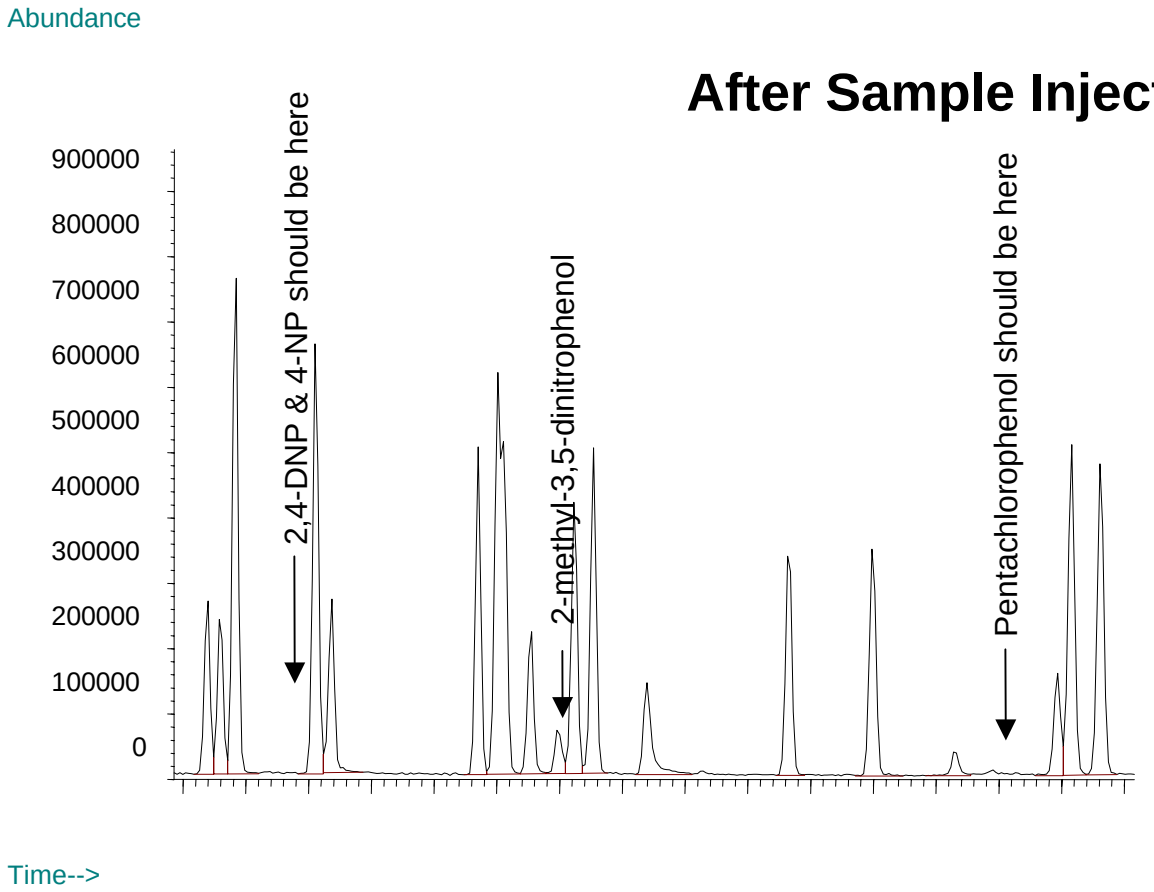
- **Nasty samples can damage a column by creating active sites.**

Before Sample Injection



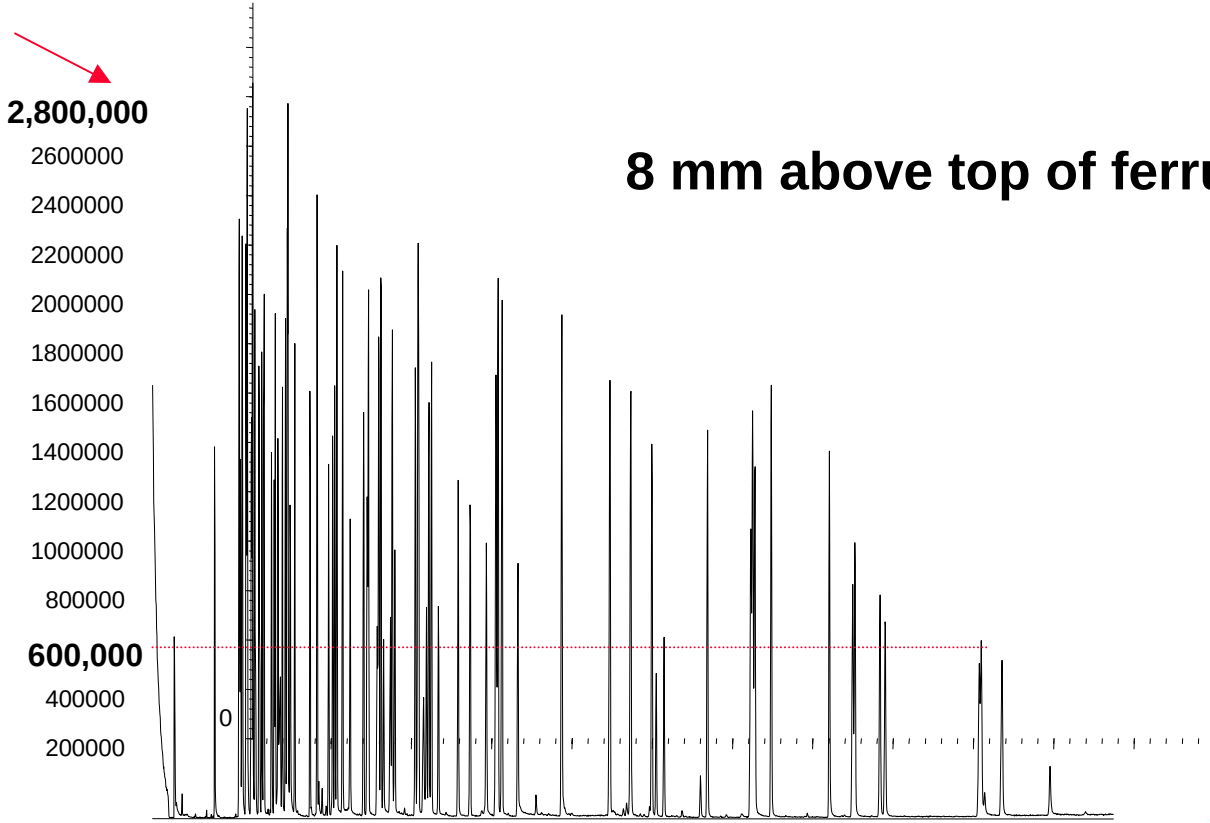
Missing Peaks / Poor Response

- **Responses of some acidic compounds were affected.**



Missing Peaks / Poor Response

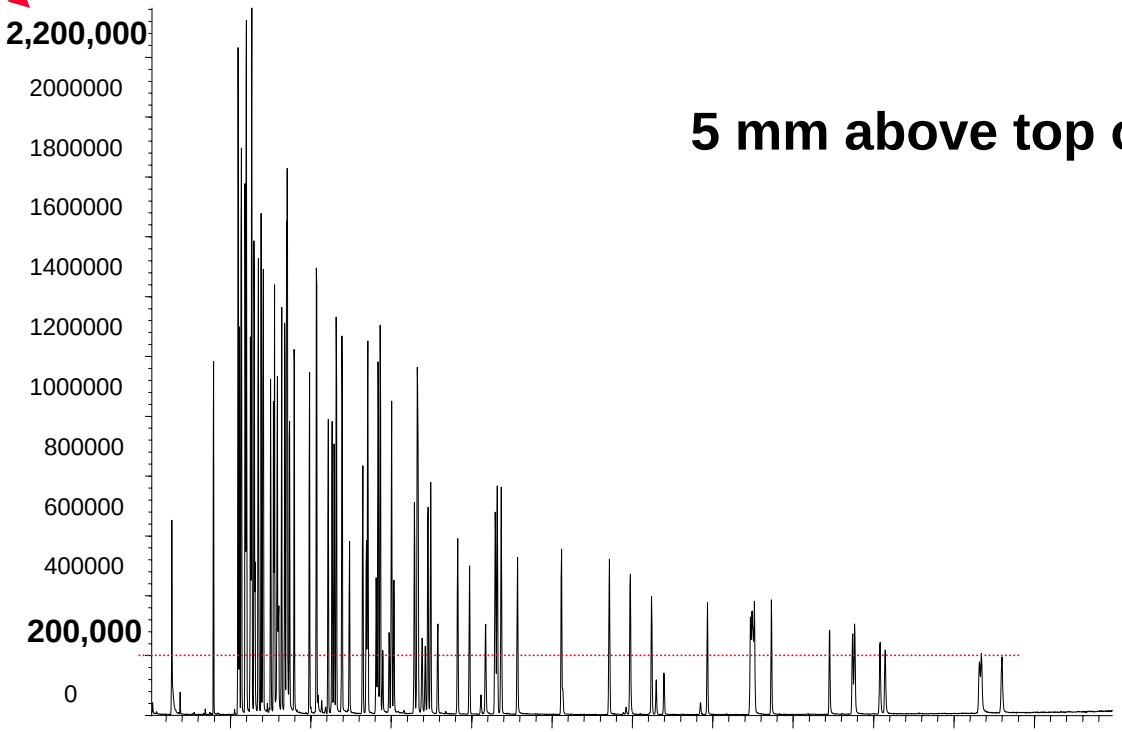
- **Response can also be affected by the position of the column in the inlet.**



8 mm above top of ferrule

Missing Peaks / Poor Response

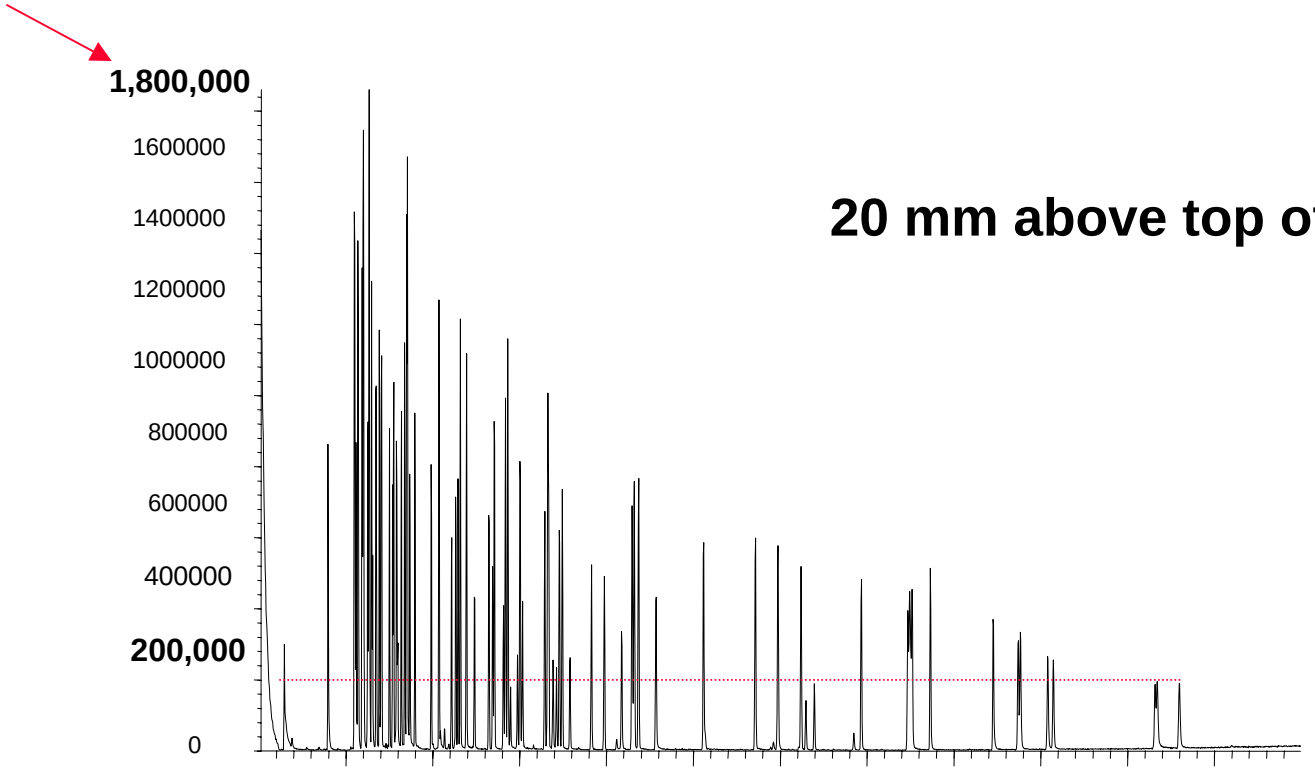
- **Here, the column was not inserted far enough.**



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**
  - phone: 1-800-359-3041 (US only), 814-359-3041
  - email: techservice@supelco.sial.com
- **Supelco Customer Service**
  - phone: 1-800-247-6628 (US only), 814-359-3441
  - email: supelco@sial.com
- **Sigma-Aldrich Website**
  - www.sigma-aldrich.com

Discussion