Tips and Tricks for Environmental GC Analysis

Dr. Frank Michel, Katherine K. Stenerson

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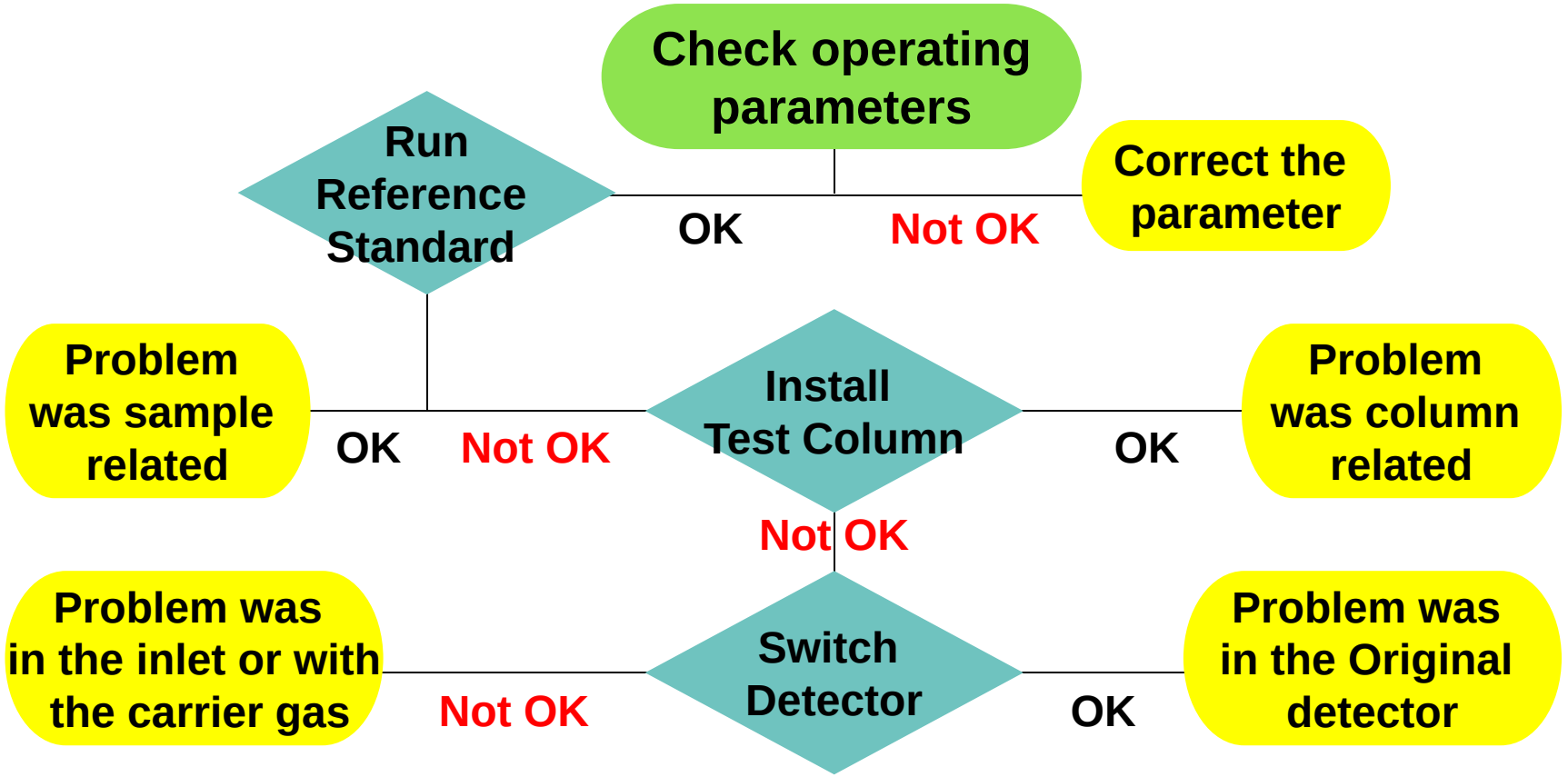
Troubleshooting Strategy

- Approaching the problem…

- Stop, take a breath and think!
  - When did the problem start?
  - Has something changed?
- Check first to see if a “fix” for the problem is already known.
  - Talk to others in your lab
  - Check instrument maintenance/service log

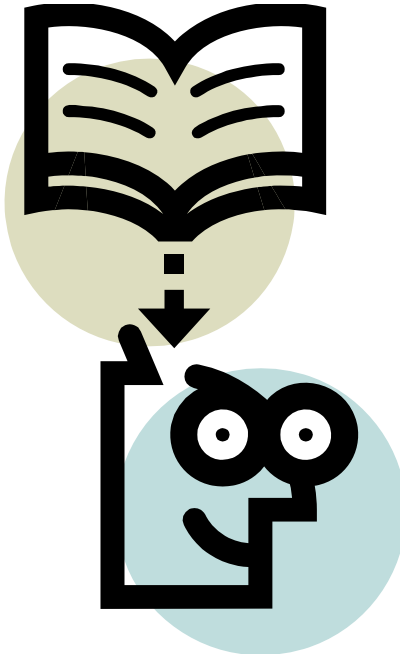
Troubleshooting Strategy

Isolate the source of the problem:



First thing, review your method parameters…

- Injection type?
  - Should it be splitless?
- Split vent time
  - Too long or too short?
- Column flow
  - Using EPC?
- Heated zones
  - Double check temp. settings
- Liner type
  - Is there something better out there?

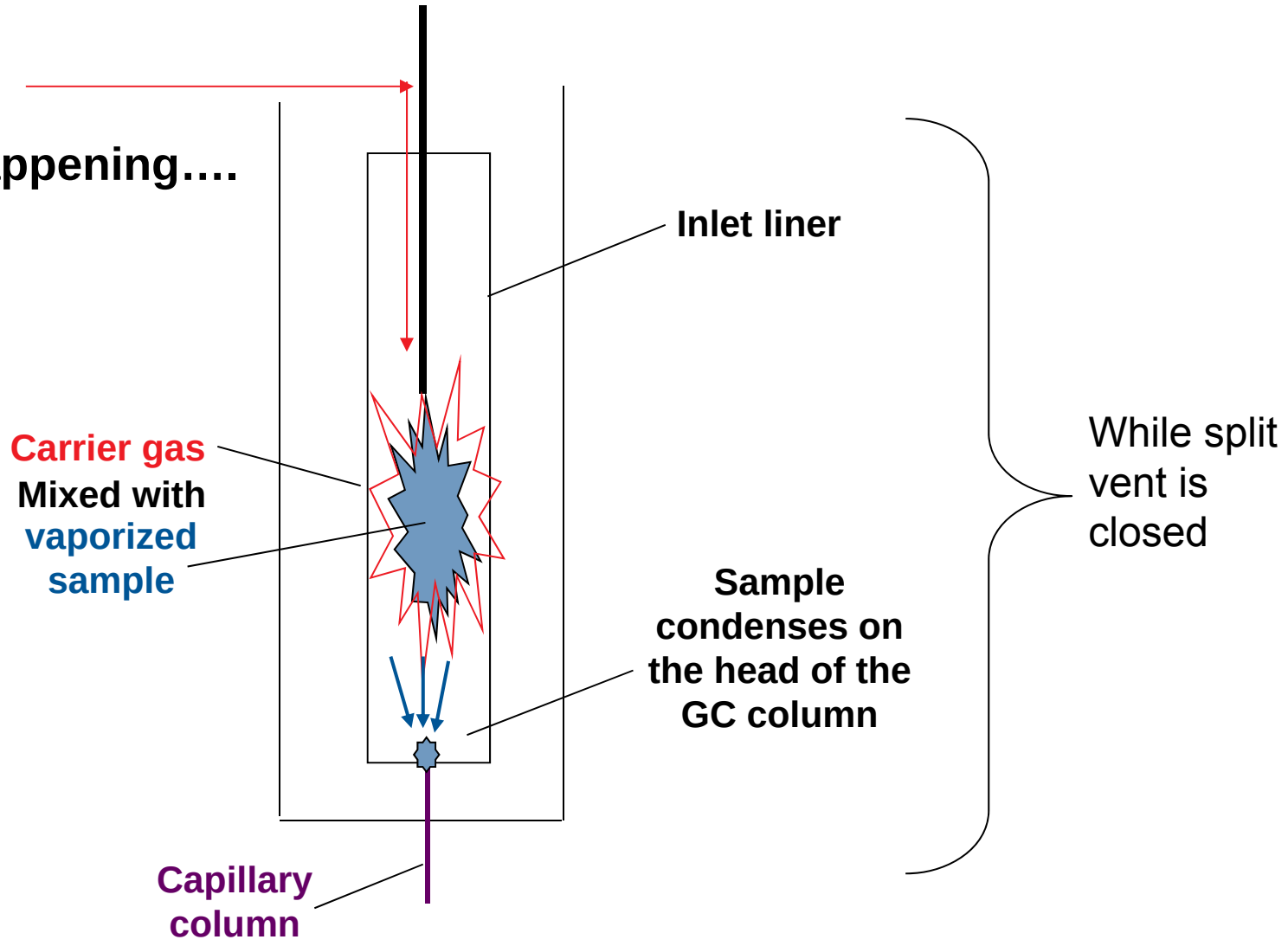


Splitless Injection & Liners

Splitless Injection & Liners

What you need to know about splitless Injection

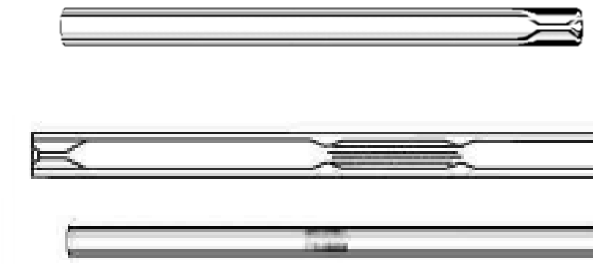
What is happening….



For splitless injections, consider:

1. The splitless time — Too short → Loss of response (esp. higher MW)
   Too long → Too much solvent on column

2. The volume of the liner:



Volume of liner

4 mm ID, Single taper: 850 µL

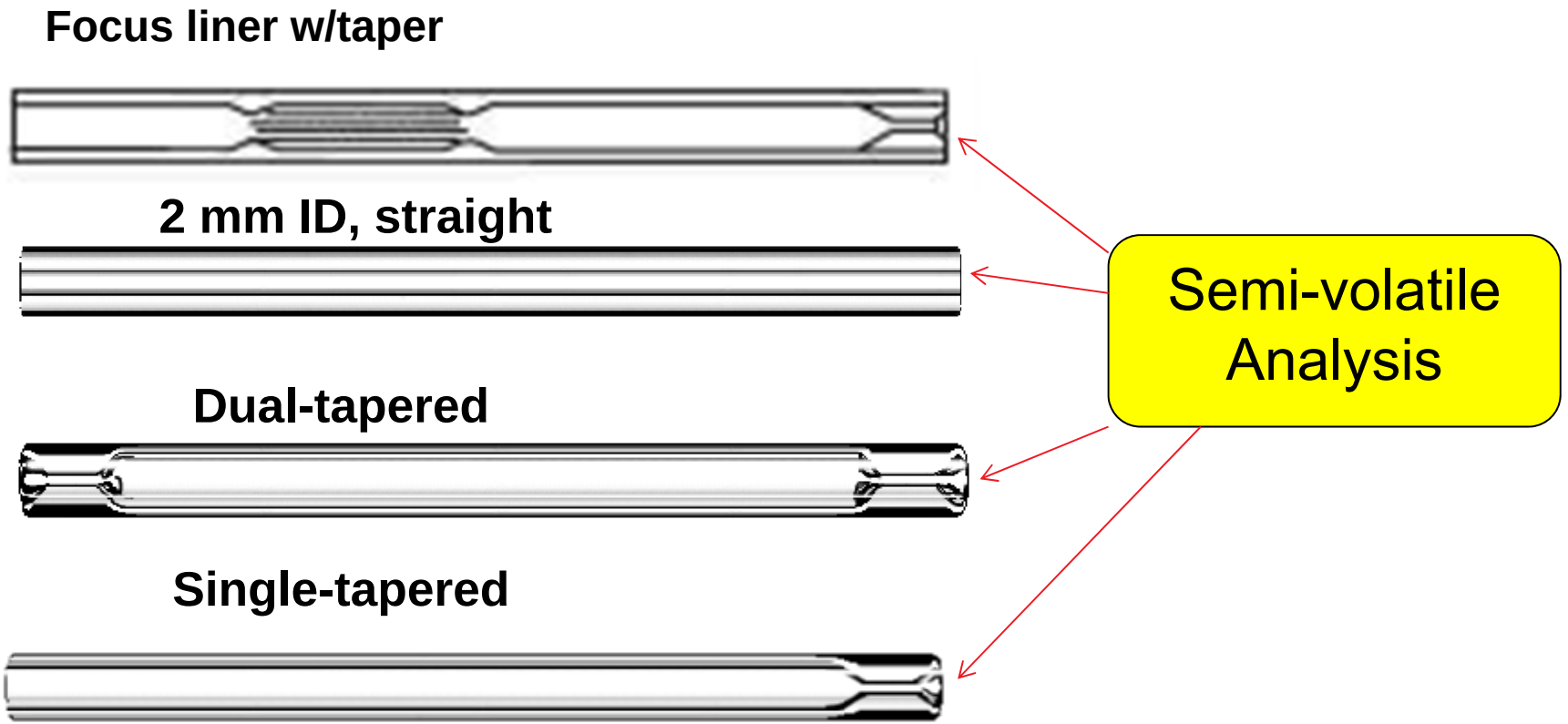
4 mm ID, focus liner w/taper 880 µL

4 mm ID, straight w/wool: 985 µL

		200° C Inlet Temp.		300° C Inlet Temp.	
	B.P. (° C)	10 psi	30 psi	10 psi	30 psi
Methylene chloride	40	360	200	437	241
Methanol	64.5	570	315	691	382
Water	100	1279	706	1548	855

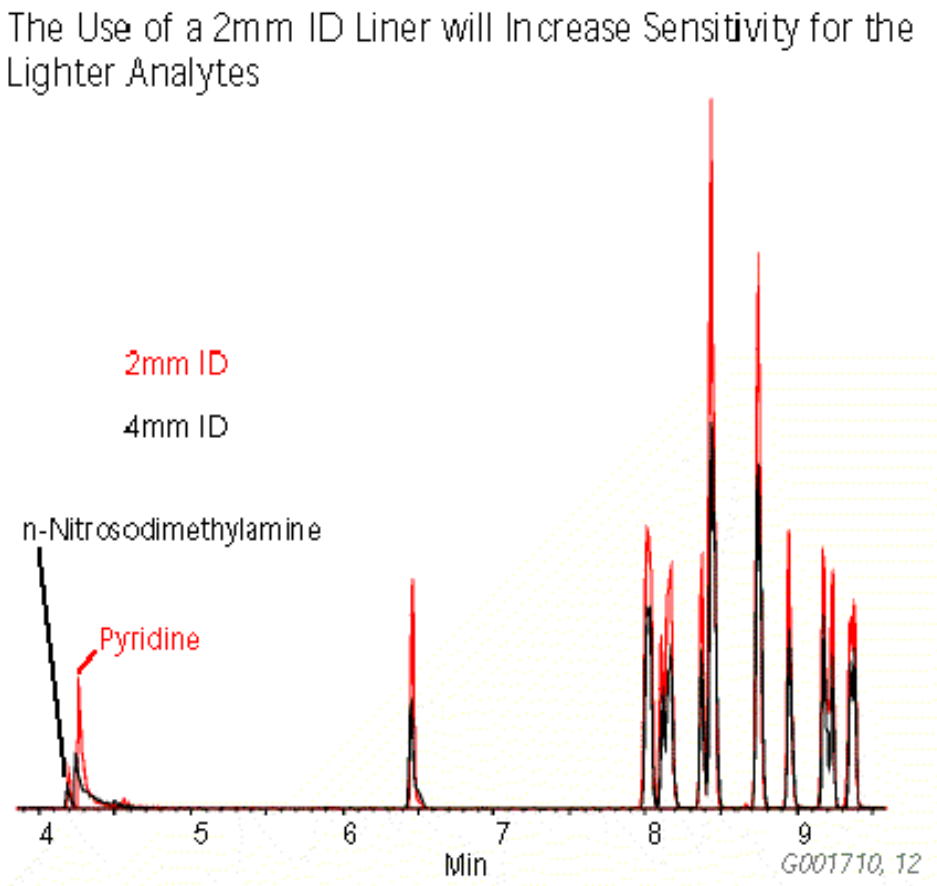
Resulting vapor volume of solvent

Some Popular Styles for Splitless Injection



Liner ID

The ID of the liner can affect sensitivity:



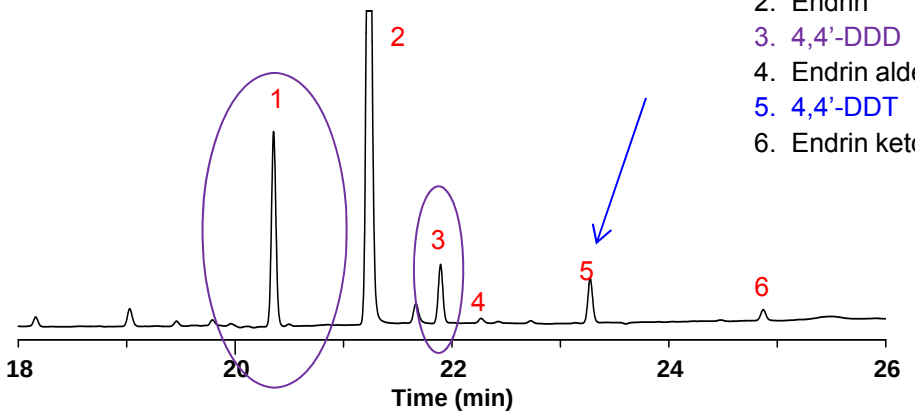
Splitless injection, 2mm vs. 4mm ID liner

Liner Care

If you *must* clean a liner….

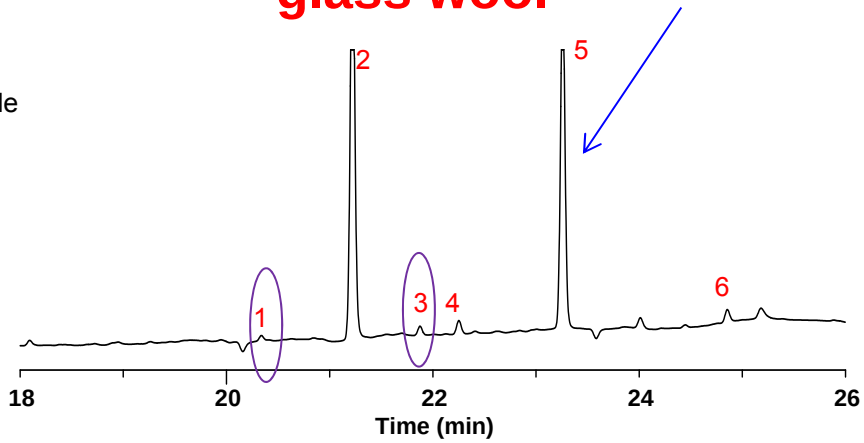
- Handle with gloves or forceps.
- Use clean compressed gas and/or a fine brush to remove particles.
- Rinse in an appropriate solvent and dry with clean compressed gas.
- Use mineral acid and/or detergent only if absolutely necessary. Be sure to deactivate the liner after this process.
- If repacking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

Undeactivated glass wool



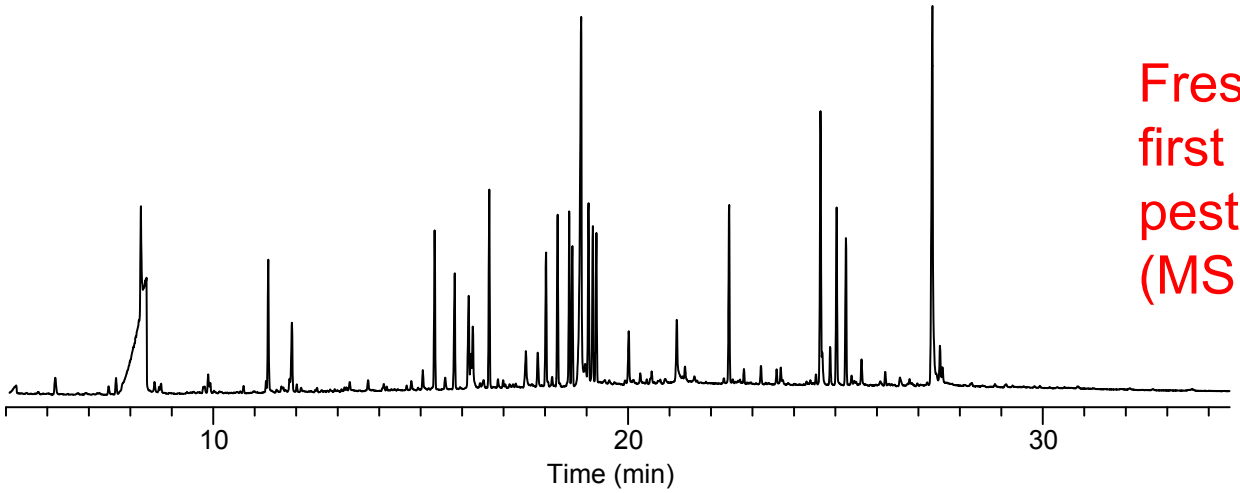
1. 4,4'-DDE
2. Endrin
3. 4,4'-DDD
4. Endrin aldehyde
5. 4,4'-DDT
6. Endrin ketone

Deactivated glass wool

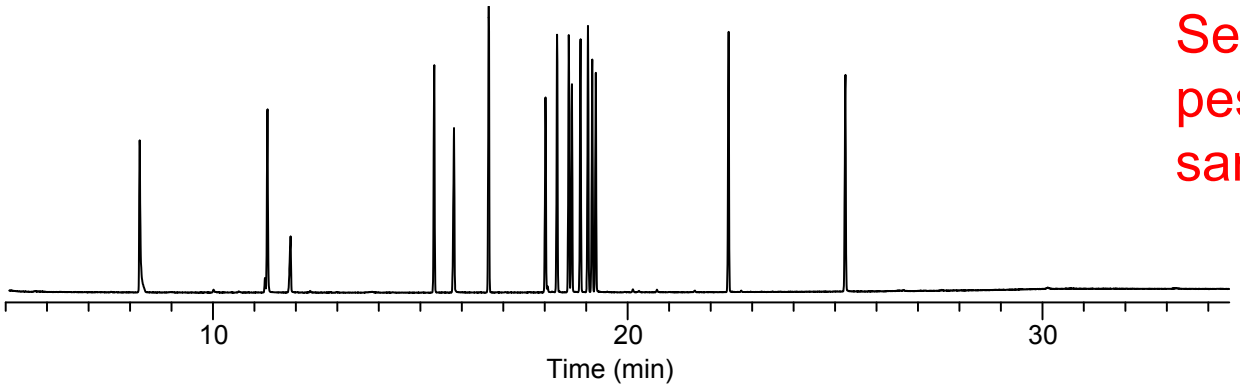


Give a new liner a chance!

Allow a “junk” injection after installing a new liner.



Freshly installed liner, first injection of pesticide standard (MSD)



Second injection of pesticide standard on same system

Common Chromatographic Problems

Common Chromatographic problems

1. Baseline Noise and Drift

Common causes:

- Column bleed
- Septa bleed
- Dirty detector
- Contaminants in carrier gas / carrier gas purity

2. Peak Shape & Response

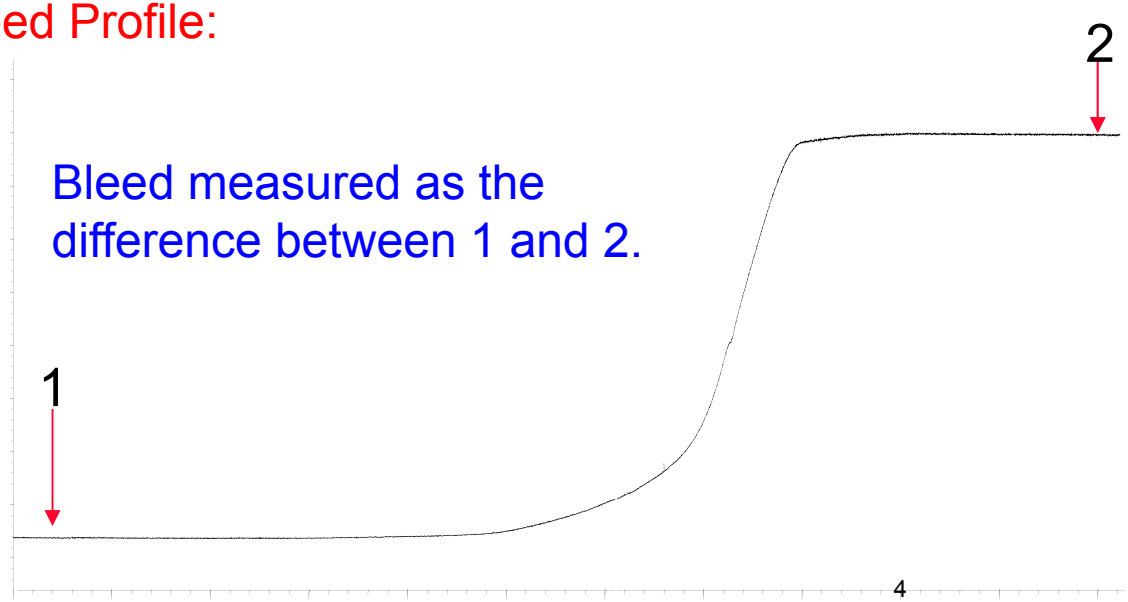
- No response or poor response
- Extraneous peaks
- Poor peak shape

Problem: Column Bleed

Did you know?

- 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.

A Typical Bleed Profile:

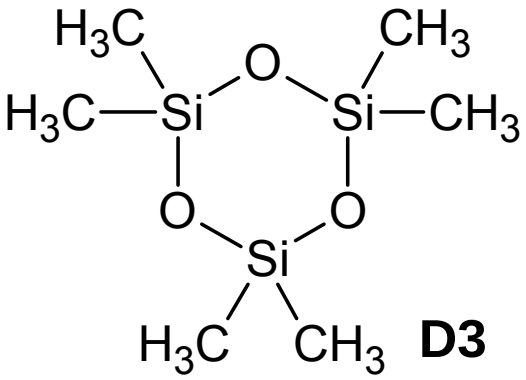


Column Bleed and an MSD

- Visible as baseline rise in the TIC.
- Check mass spectra for key bleed ions:
  - Stationary Phase -1: 73, 207, 281
  - Stationary Phase -5: 207, 281
  - Stationary Phase -1701: 207, 269
  - Stationary Phase -624: 207, 269

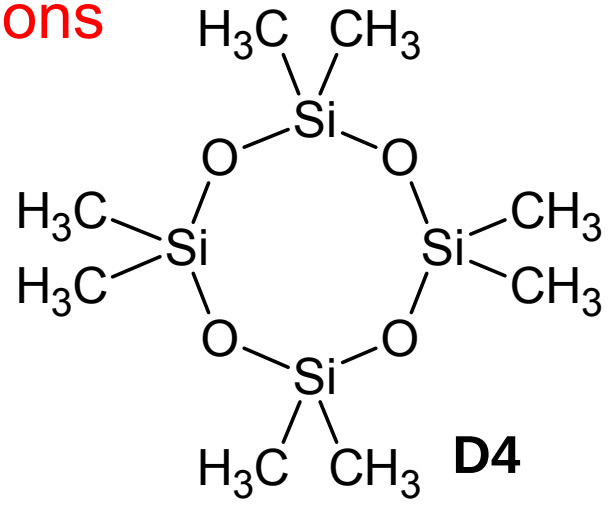
Make sure interface temp. < column max. temp.

Common bleed ions



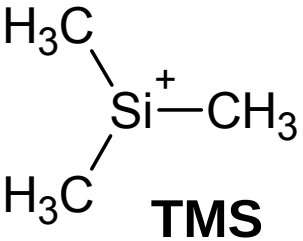
D3

D3 – CH_3: 207



D4

D4 – CH_3: 281



TMS

73

So, what can I do about 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.

To help prevent column bleed and other problems…remember gas purification

Minimum recommendations for removal

	Carrier	Hydrogen	Air	Nitrogen	P-5
Oxygen	X				X
Water	X		X		
Hydrocarbons	X	X	X	X	X
Halocarbons					X

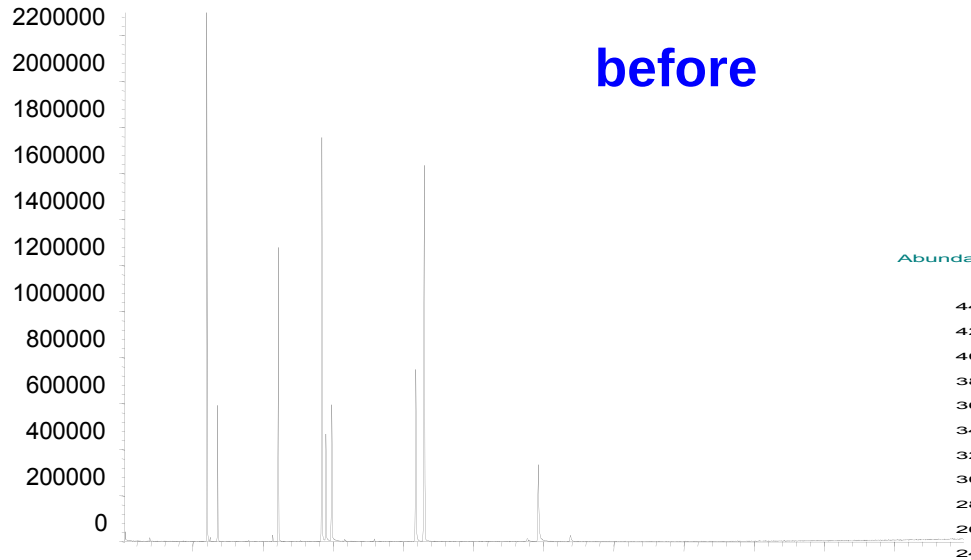
A wide variety of purifiers are available

Problem: Too many peaks or “Ghost” Peaks

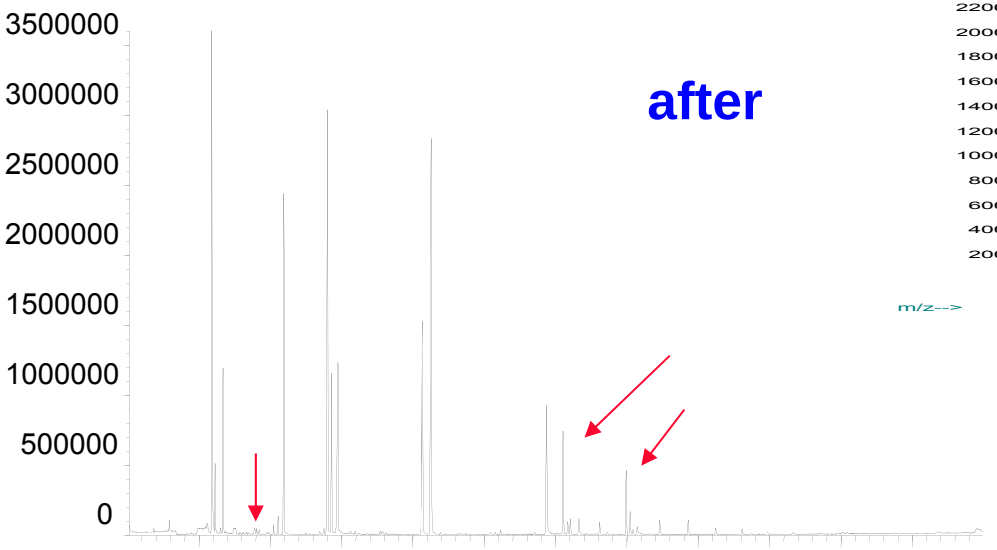
Possible causes:

- 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
- Septa pieces in liner

Ghost peaks caused by septa pieces in a liner:

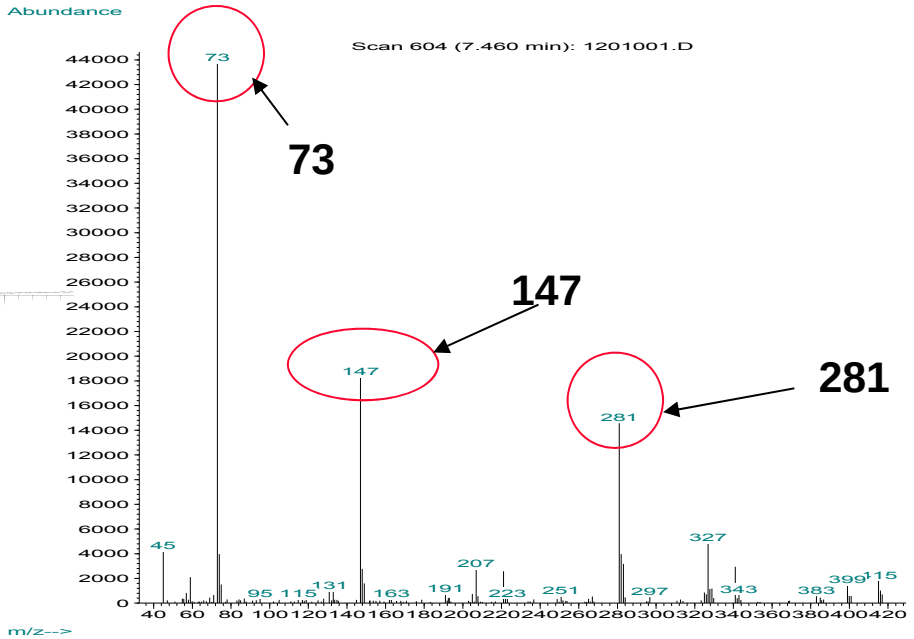


before



after

Septa Bleed: MS Spectra



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Problem: Missing Peaks and Poor Response

Possible causes:

Sample decomposition

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

Column Installation

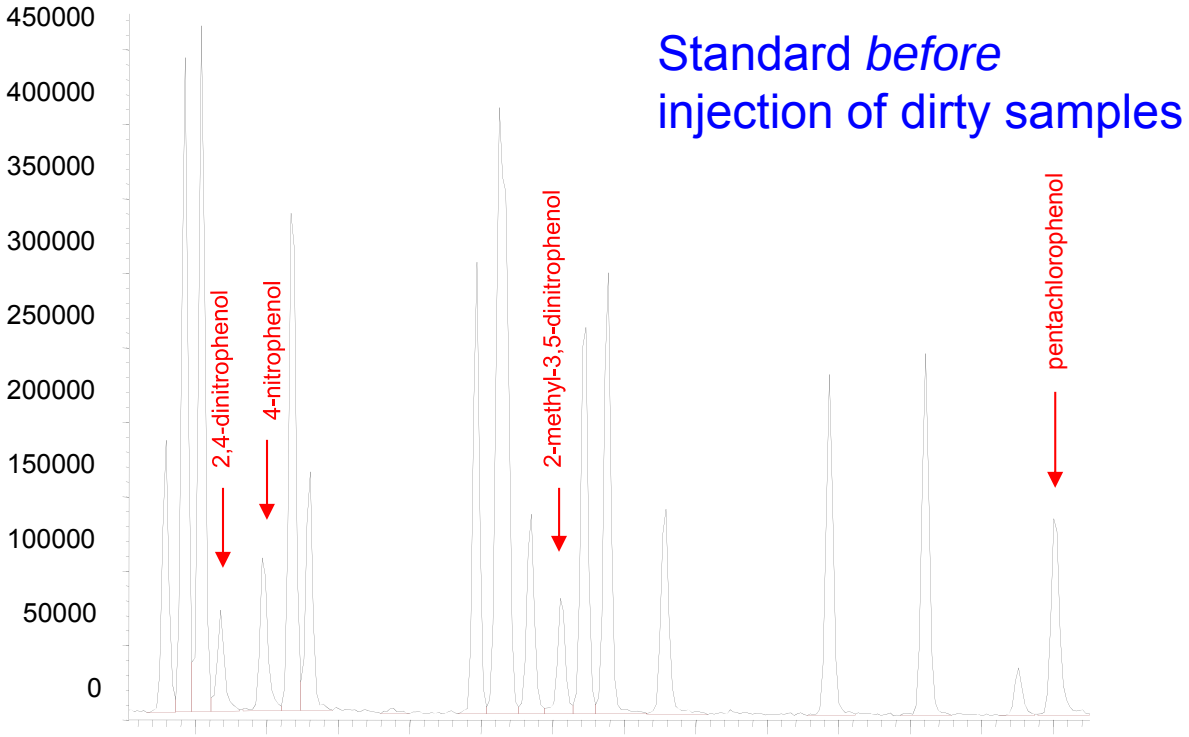
- Make sure your GC column is installed at the proper distance; both injector and detector

Coelution

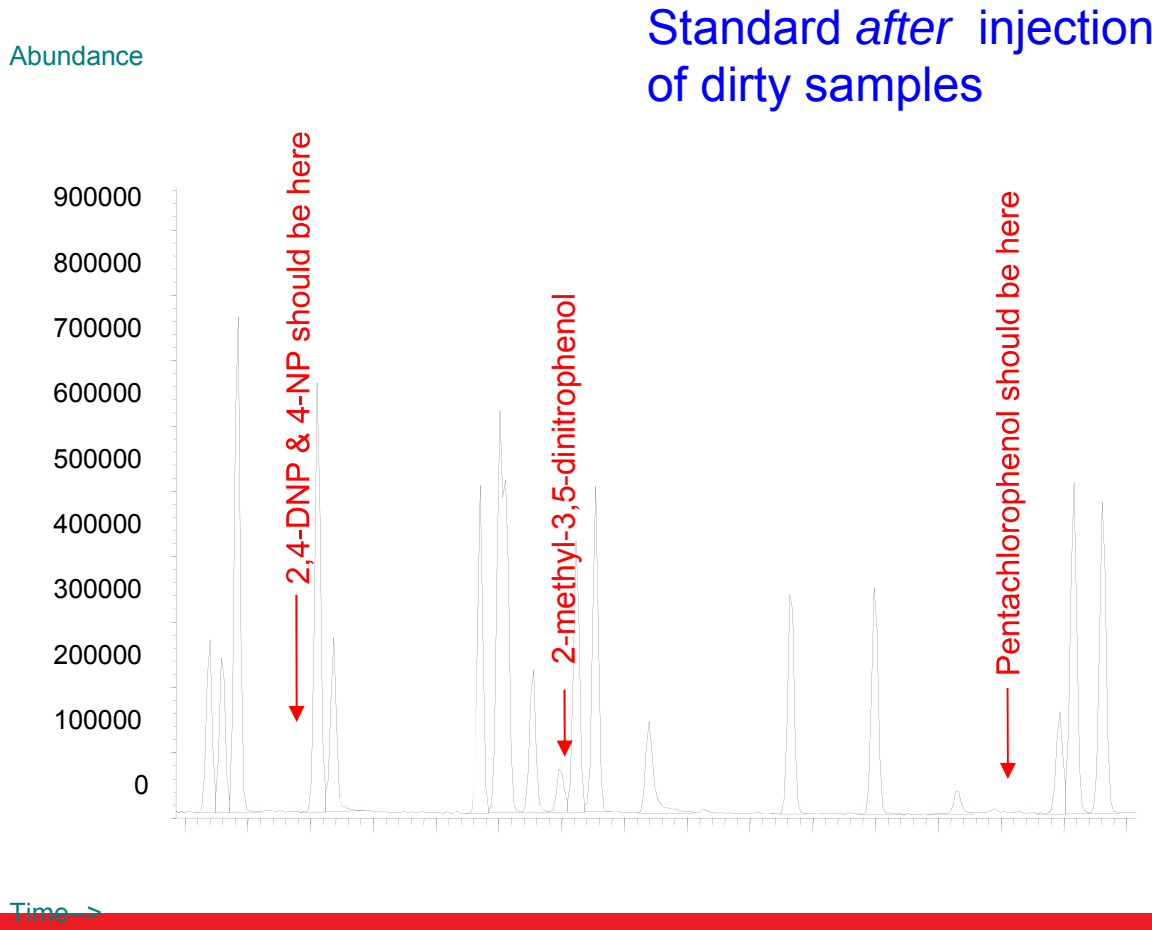
- Insufficient run time / final temperature
- Sample not volatile enough for GC
- Improper column installation

Loss in response caused by creation of active sites:

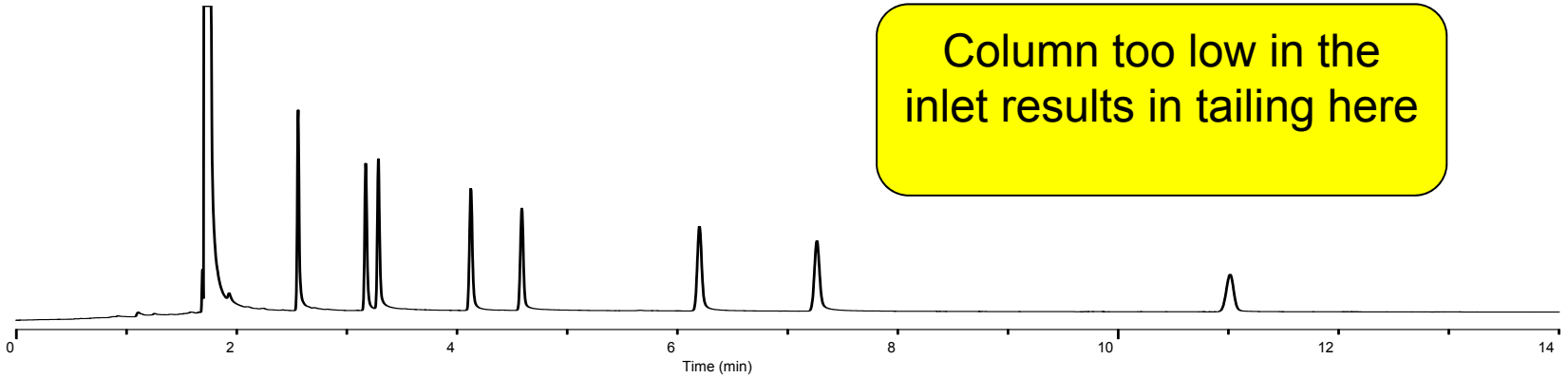
Nasty samples can damage a column by creating active sites.



Responses of some acidic compounds were affected.

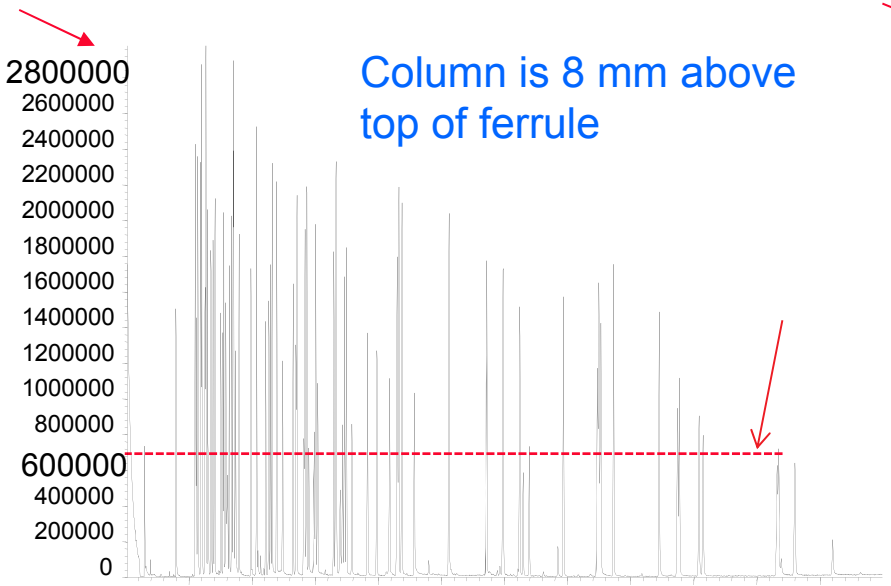


Improper column installation can affect response and peak shape

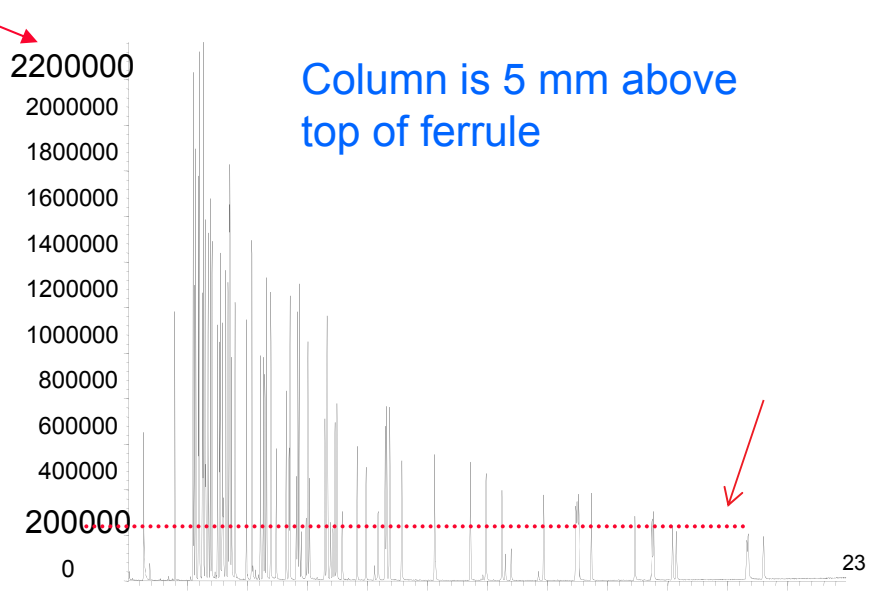


Column too low in the inlet results in tailing here

Installation distance can affect response!



Column is 8 mm above top of ferrule



Column is 5 mm above top of ferrule

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What if my problem is coelution?

Go back to the basics – consider the resolution equation

$$R_s = (k/1+k)\ (\alpha-1/\alpha)\ (N^{1/2}/4)$$

capacity selectivity efficiency

column

Longer column	→	capacity, efficiency
Thicker film column	→	capacity
Smaller ID column	→	efficiency
Diff. Stationary phase	→	selectivity

GC Parameters

Carrier gas flow	→	efficiency
Oven ramp rate	→	capacity
Starting or ending oven temp.	→	capacity

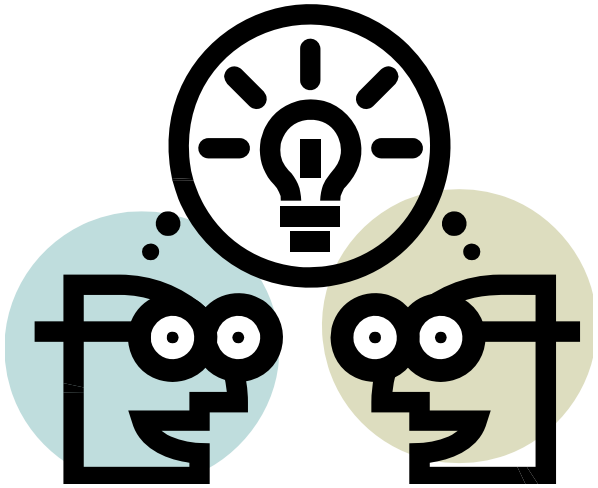
The best way to solve problems is to prevent them!

- Gas purification
  - Install and use appropriate filters/getters
- Injector maintenance
  - Liner, septa, seal
- Column installation
  - Check insertion distance
- Guard column
  - Use when necessary

Troubleshooting Best Practices

✓Documentation

- Use maintenance log books
- May save weeks of troubleshooting



✓Make one change at a time

- To uncover root cause
- Multiple changes may offset each other

✓Keep a ‘good’ trap

- Remove and store the trap as a reference for when issues occur at a later time
- Replace the caps, place in original shipping container, label properly, and protect from vibration

Suggested Literature from Supelco

1. GC Column Selection Guide – Achieve Optimal Performance, T407133
2. Fast GC – A Practical Guide for Increasing Sample Throughput without Sacrificing Quality, T407096.
3. Capillary GC Inlet Liner Selection Guide (Bulletin 899A), T100899A
4. **Capillary GC Troubleshooting Guide: How to Locate Problems and Solve Them** (Bulletin 853C), T112853.
5. Purge and Trap System Guide (Bulletin 916), T197916
6. Gas Chromatography Accessories and Gas Purification/Management Products, T407103

Bulletin 853B

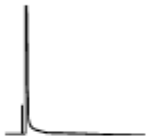
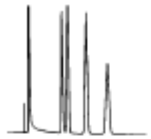
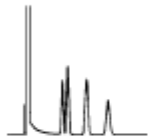
Capillary GC Troubleshooting Guide: How to Locate Problems and Solve Them

The real task in correcting a problem with your capillary GC system is identifying the cause of the problem without wasting time. The systematic approach to troubleshooting described in this guide will enable you to solve many problems yourself. The guide also contains suggestions for maintaining your system, including the column, at optimal performance levels. By following these recommendations, you can reduce repair costs and instrument down time.

Contents

SUPELCO

T112853C

Symptom	Possible Cause	Remedy
Symptom No. 2 — Missing peaks/solvent peak only (cont'd.)		
 Problem 796-0217	5. Incorrect linear velocity/column flow rate.	5. Measure column flow and adjust if necessary (see page 4).
	6. Sample components adsorbed by column or inlet liner.	6. Inject standard on column known to be performing well. If results are good, rinse original column (bonded phase only) or remove 1-2 coils from inlet end (see page 8). If column performance is not restored, replace column. To prolong column life, use guard columns (see page 8) and reverse column periodically. Remove inlet liner and check cleanliness. Replace glass wool and packing or use new, deactivated liner. If sample has never been analyzed and is chemically active, you may need a column with a different (or specialized) stationary phase.
	7. Column cannot separate components from solvent.	7. Change solvent or column.
Symptom No. 3 — Detector response low for all peaks (retention times correct)		
 Normal	1. Sample size too small or split ratio too large.	1. Increase sample size or reduce split ratio.
	2. Sensitivity setting wrong.	2. Check sensitivity setting, adjust if necessary. Inject standard for comparison.
	3. Makeup gas flow inadequate.	3. Adjust flow to detector manufacturer's specifications.
	4. Poor injection technique.	4. Use correct syringe size and appropriate injection technique for sample and analysis.
	5. Syringe defective.	5. Inject sample with a new syringe. If problem disappears, discard old syringe.
 Problem 796-0216	6. Carrier gas leak at septum or column connection.	6. Check for leaks (see page 3). Replace septum or tighten connections if necessary.
	7. Injection port temperature too low (sample not vaporized).	7. Verify temperature with accurate thermometer, adjust if necessary. If instrument setting and thermometer agree, increase temperature (do not exceed stationary phase limit).
	8. FID: hydrogen or air flow incorrect.	8. Adjust gas flows to detector manufacturer's specifications.
	9. FID: low oxygen level in compressed air.	9. Replace air tank.

Thank you!