Practical Steps in GC Troubleshooting

Techniques, Tips, and Tricks

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“Everything was just fine and then this happened!

How do I go about TROUBLESHOOTING?”

“Everything was just fine and then this happened!”

Logic = Something changed (slowly or sudden) = Something is different

Track Events – log book

-Changed column, liner, septum, syringe, etc.

-Injected samples, other method, etc.

-Did maintenance, cut column, inlet flush, etc.

Logical Troubleshooting

- **Troubleshooting Starts with Isolating the problem**
  - There are 5 basic areas from where the problem arises

  - INJECTOR
  - FLOW
  - COLUMN
  - DETECTOR
  - ELECTRONICS

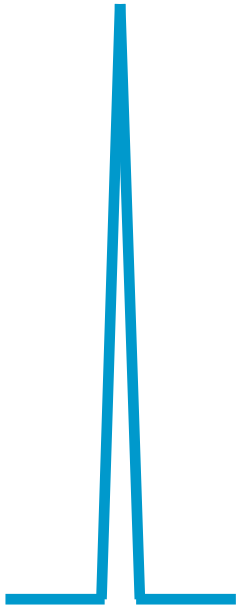
  - But of course it can always be some COMBINATION

- *Knowing what can & <u>can't</u> cause the symptom is the key*

Typical Problems of Optimized Methods becoming Unoptimized…and the Reason Why.

- Peak Tailing – Flow Path or Activity
- Bonus Peaks – In Sample or Back Flash (Carry Over)
- Split Peaks – Injector Problems, Mixed Solvent
- No Peaks – Wasn't Introduced, Wasn't Detected
- Response Changes – Activity, Injector Discrimination, Detector Problem
- Peak Fronting – Overload or Solubility Mismatch, Injector Problems
- Shifting Retention – Leaks, Column Aging, Contamination or Damage
- Loss of Resolution – Separation Decreasing, Peak Broadening
- Baseline Disturbances – Column Bleed, Contamination, Electronics
- Noisy or Spiking Baseline – Electronics or Contaminated Detector
- Quantitation Problems – Activity, Injector or Detector Problems

Peak Tailing

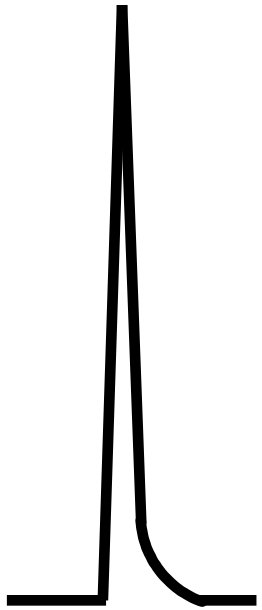


INJECTOR or COLUMN is Active

-Reversible adsorption of active compounds

(-OH, -NH, -SH)

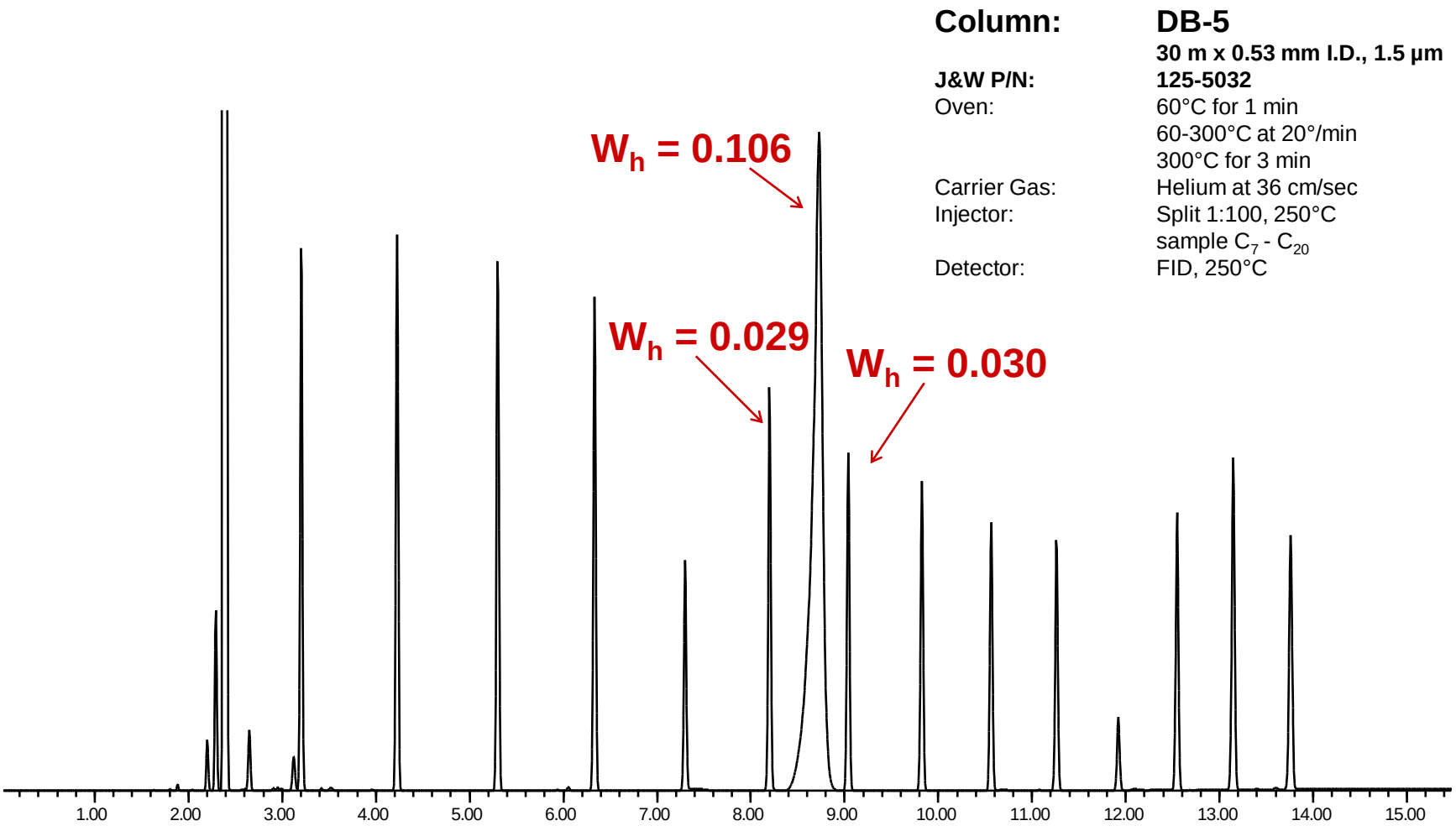
FLOW problem
- dead volume, obstruction, poor installation, or severe column contamination



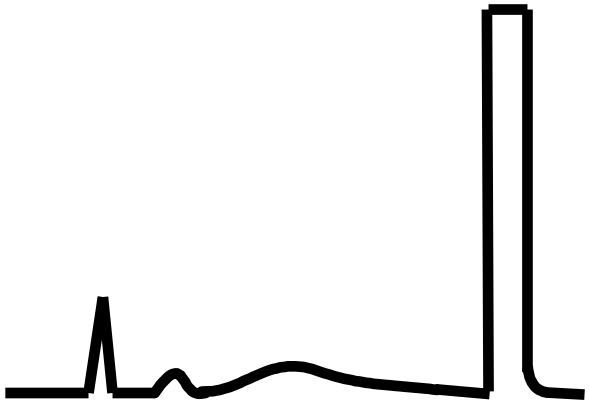
Miscellaneous - overloading of PLOT columns, co-elution, polarity mismatch between phase, solute or solvent, and some compounds always tail

*Tip = Inject a light hydrocarbon, should not tail unless flow path problem.

Bonus Peaks


Column: DB-5
30 m x 0.53 mm I.D., 1.5 µm
J&W P/N: 125-5032
Oven: 60°C for 1 min
60-300°C at 20°/min
300°C for 3 min
Carrier Gas: Helium at 36 cm/sec
Injector: Split 1:100, 250°C
sample C7 - C20
Detector: FID, 250°C
Wh = 0.106
Wh = 0.029
Wh = 0.030
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
15.00

Bonus Peaks or Ghost Peaks



Contamination in INJECTOR, COLUMN or FLOW (carrier gas)

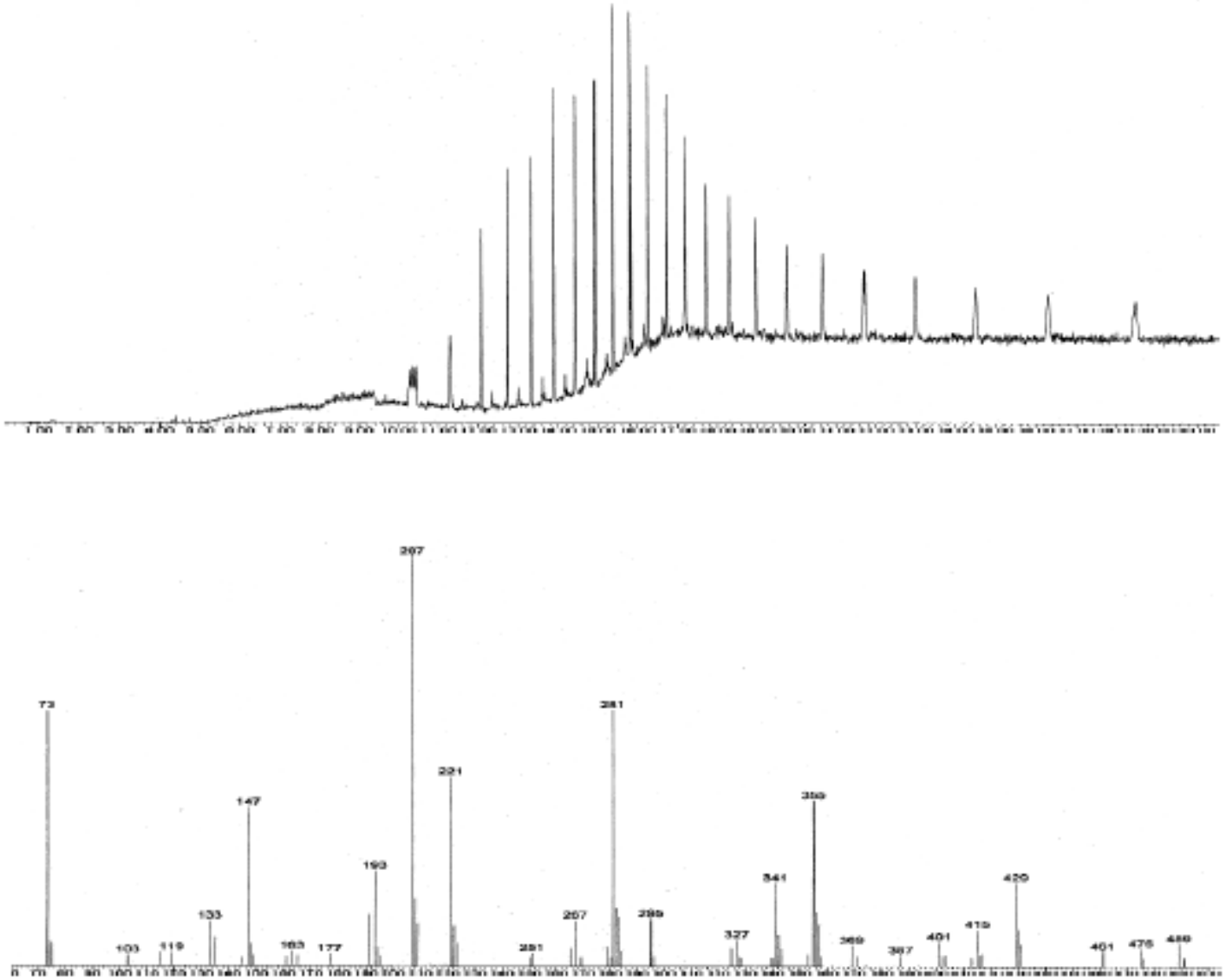
-Carry-over from a backflash or previous sample

-Bad tank of gas or traps have expired

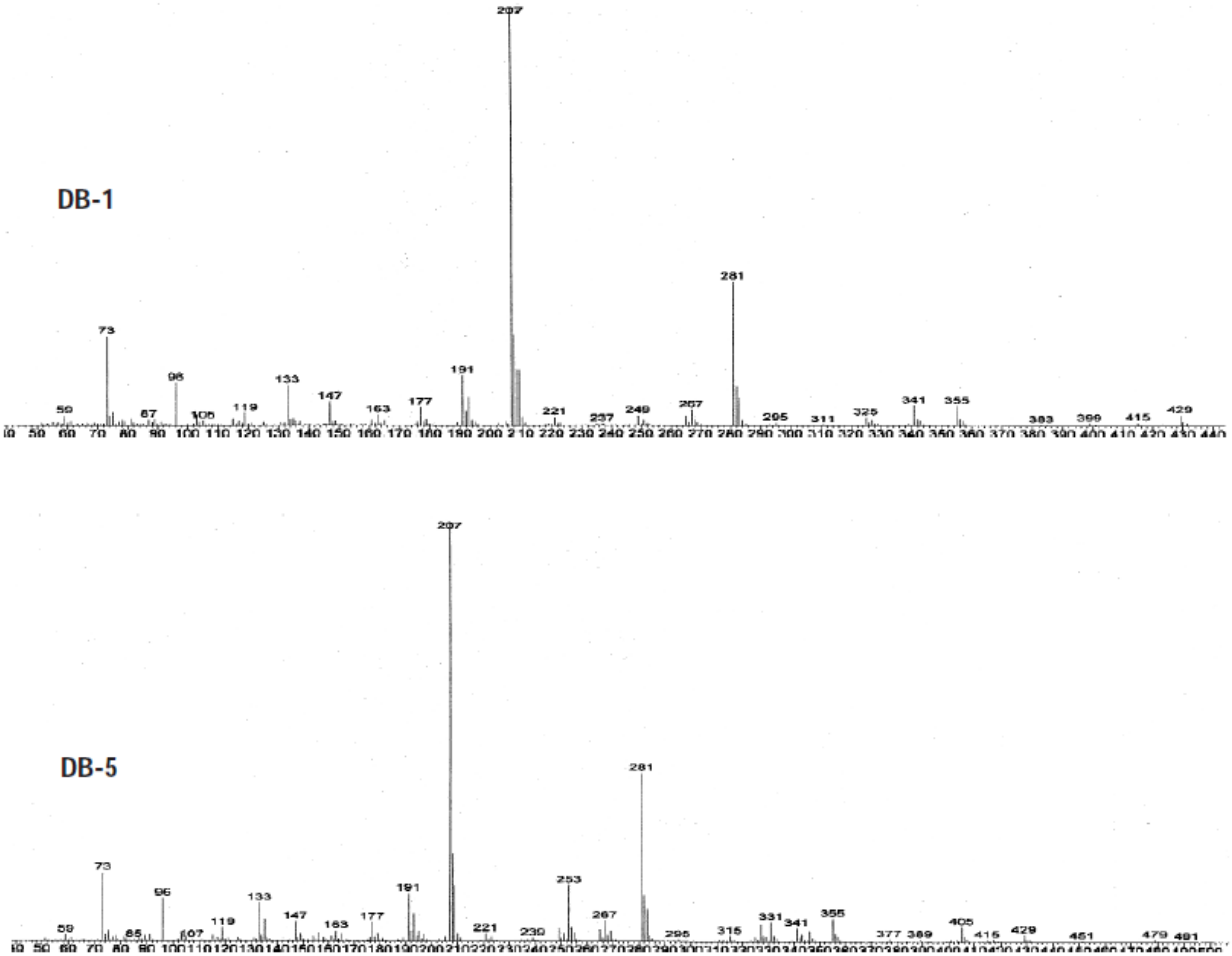
-Septum bleed

*TIP = Run a blank run…it should be blank!

Bonus ‘Siloxane’ Peaks

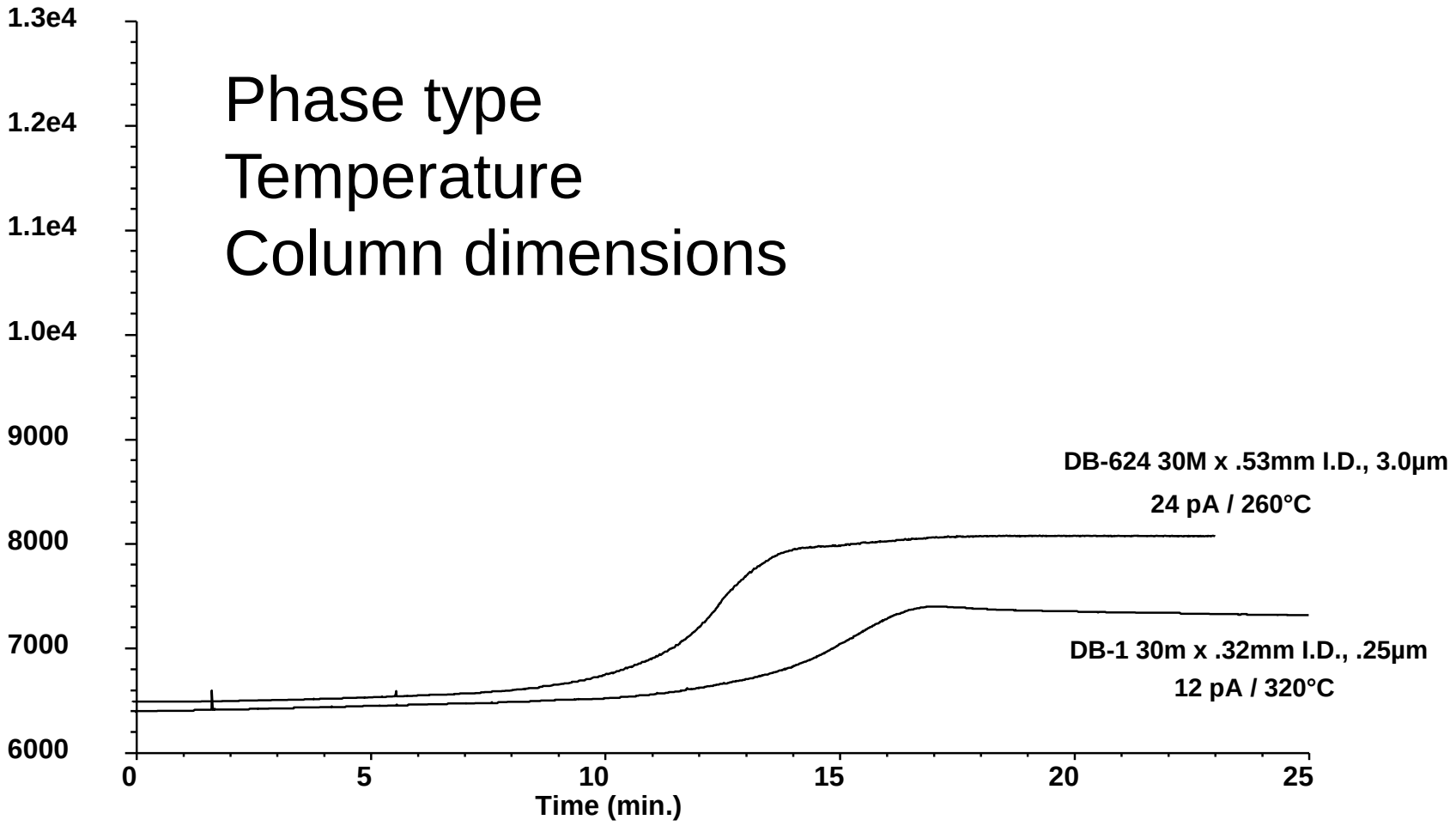


GC Column Bleed Ions

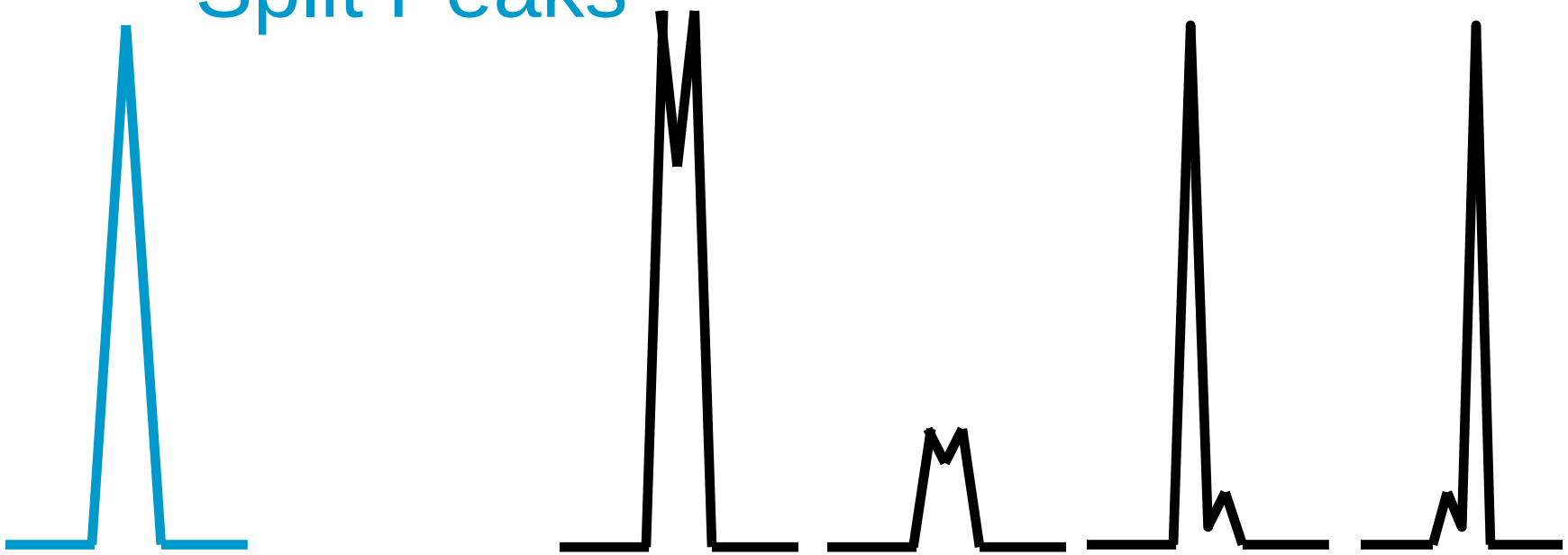


Agilent Technologies

Column Bleed is Influenced by:



Split Peaks



INJECTOR (poor sample introduction)

-Injecting the sample twice (some how?)

-Mixed sample solvent (polarity difference)

-Sample in syringe needle (manual inject)

INJECTOR (activity)

-Breakdown (not really a split peak, 2 peaks)

-Sample degradation in injector

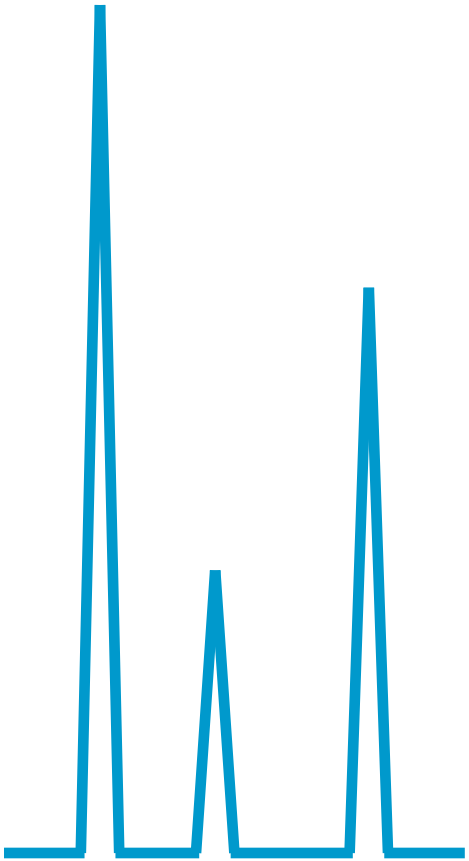
VOLATILITY

High boilers dropping out on Cold Spots

-Transfer line temps

-Unions or fittings not tracking column temp

No Peaks



DETECTOR (not on or not operational)

INJECTOR (not working)

-Plugged syringe/plunger not moving

-Wrong injector (or detector)

-Huge leak (older systems)

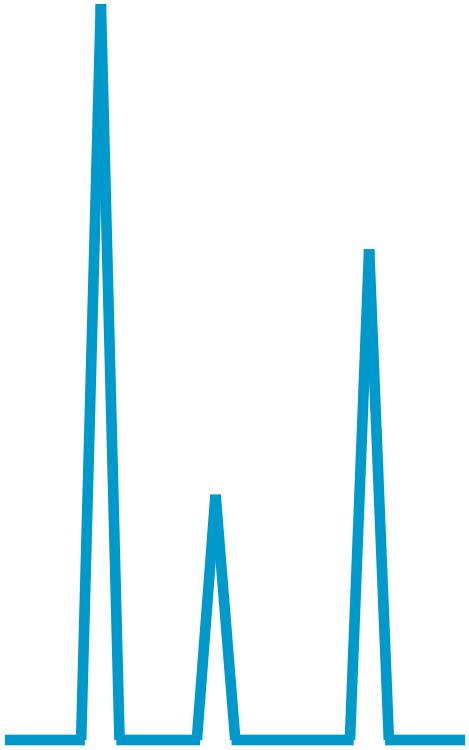
-No carrier gas flow

NOT the COLUMN Unless…

-Broken column or No column

Peak Response

All Change in Size



INJECTOR

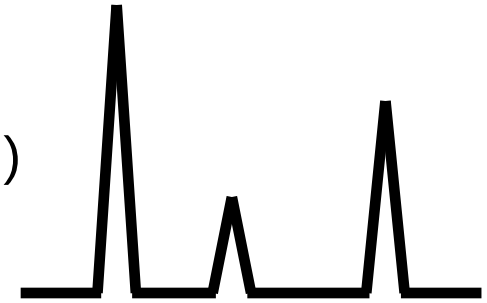
-Leaky syringe

-Split ratio set incorrectly

-Wrong purge activation time

-Septum purge flow too high

-Injector temperature too low*



DETECTOR (response problem)

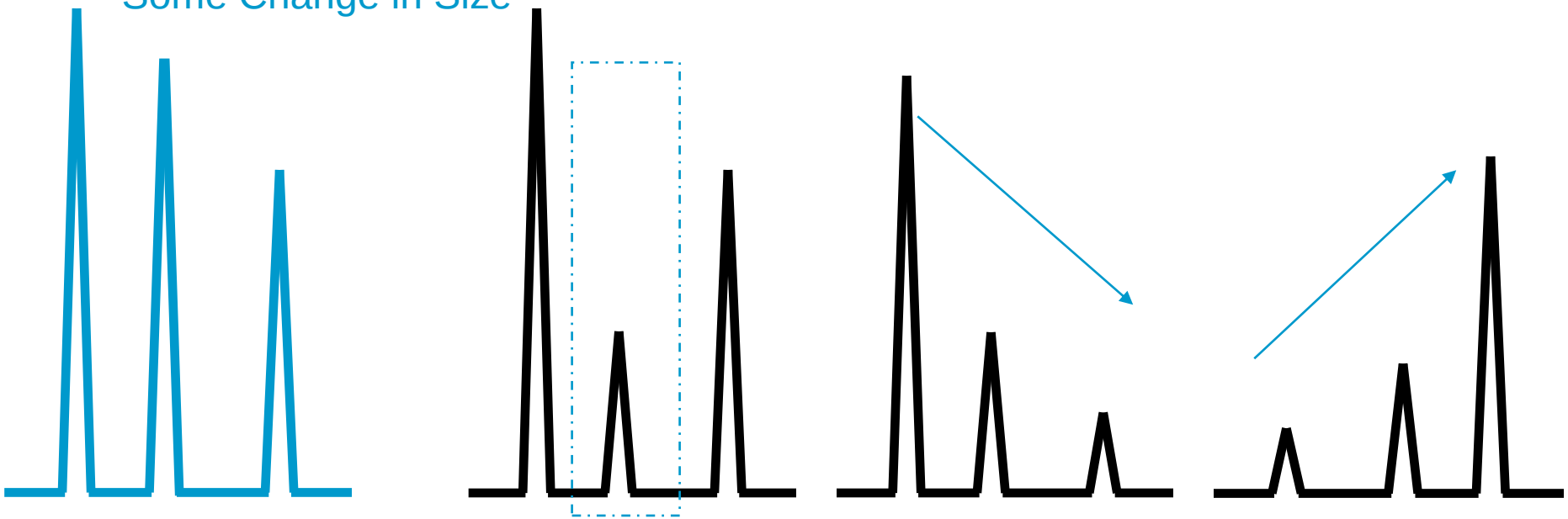
-Settings or flows changed

-Electronics failing

*Tip = Ask is it all of them or some of them, if all then injector or detector

Peak Response

Some Change in Size



INJECTOR or COLUMN is active/contaminated

-Irreversible adsorption of active compounds (-OH, -NH, -SH)

-Decomposition of sample

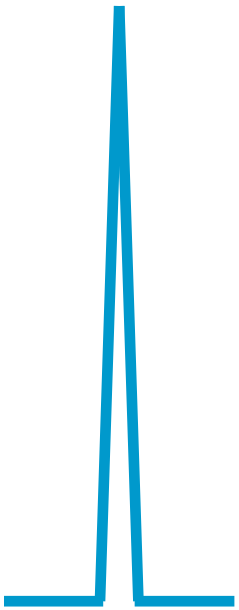
-Temperature Change – Discrimination

-Evaporation from sample

*Tip = If only some change, then ask which ones? If active compounds then activity. If tracks volatility then cold spots or inlet discrimination.

Peak Fronting

Shark Fin Shaped or Just Slight



COLUMN (contaminated)

-Overload (More pronounced with large solute and phase polarity differences)

INJECTOR

-Column installation

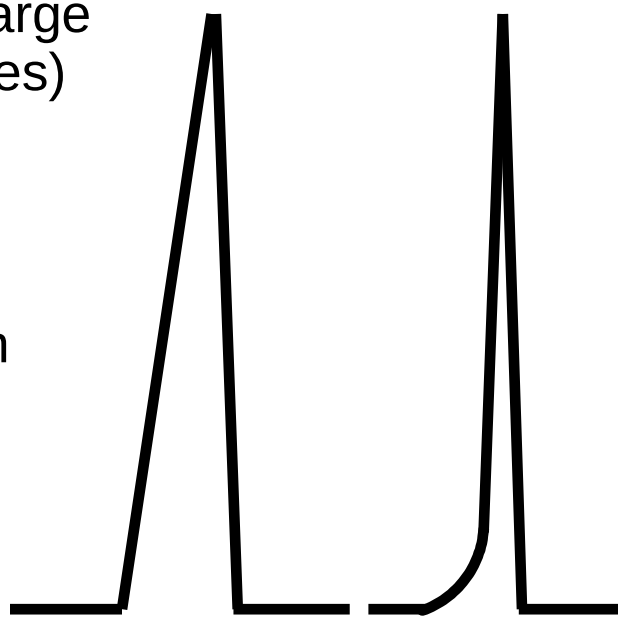
-Compound very soluble in injection solvent (need retention gap)

-Mixed sample solvent

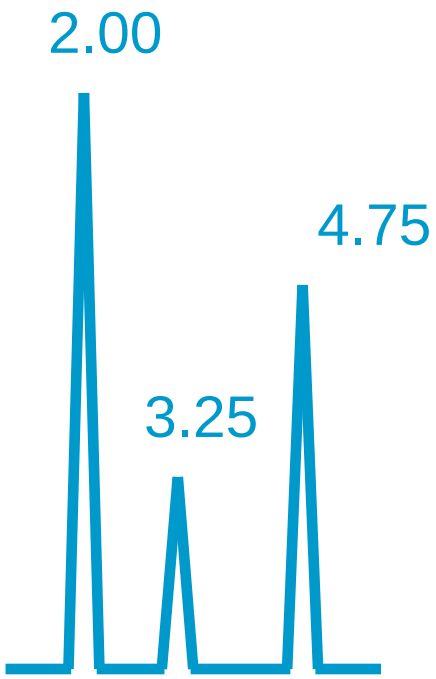
OTHER

-Co-elution

-Breakdown



Retention Time Shift



INJECTOR

-Leak in the septum

-Change in injection solvent

-Large change in sample concentration

FLOW

-Change in gas velocity

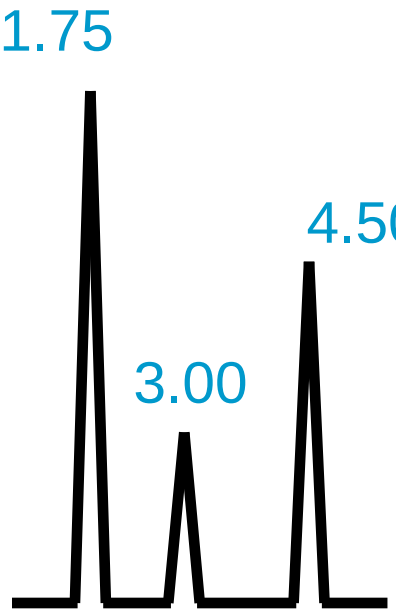
COLUMN

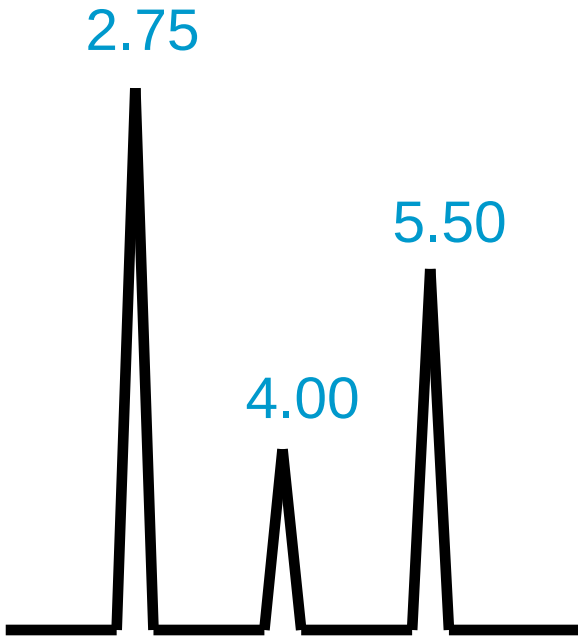
-Contamination

-Damaged stationary phase

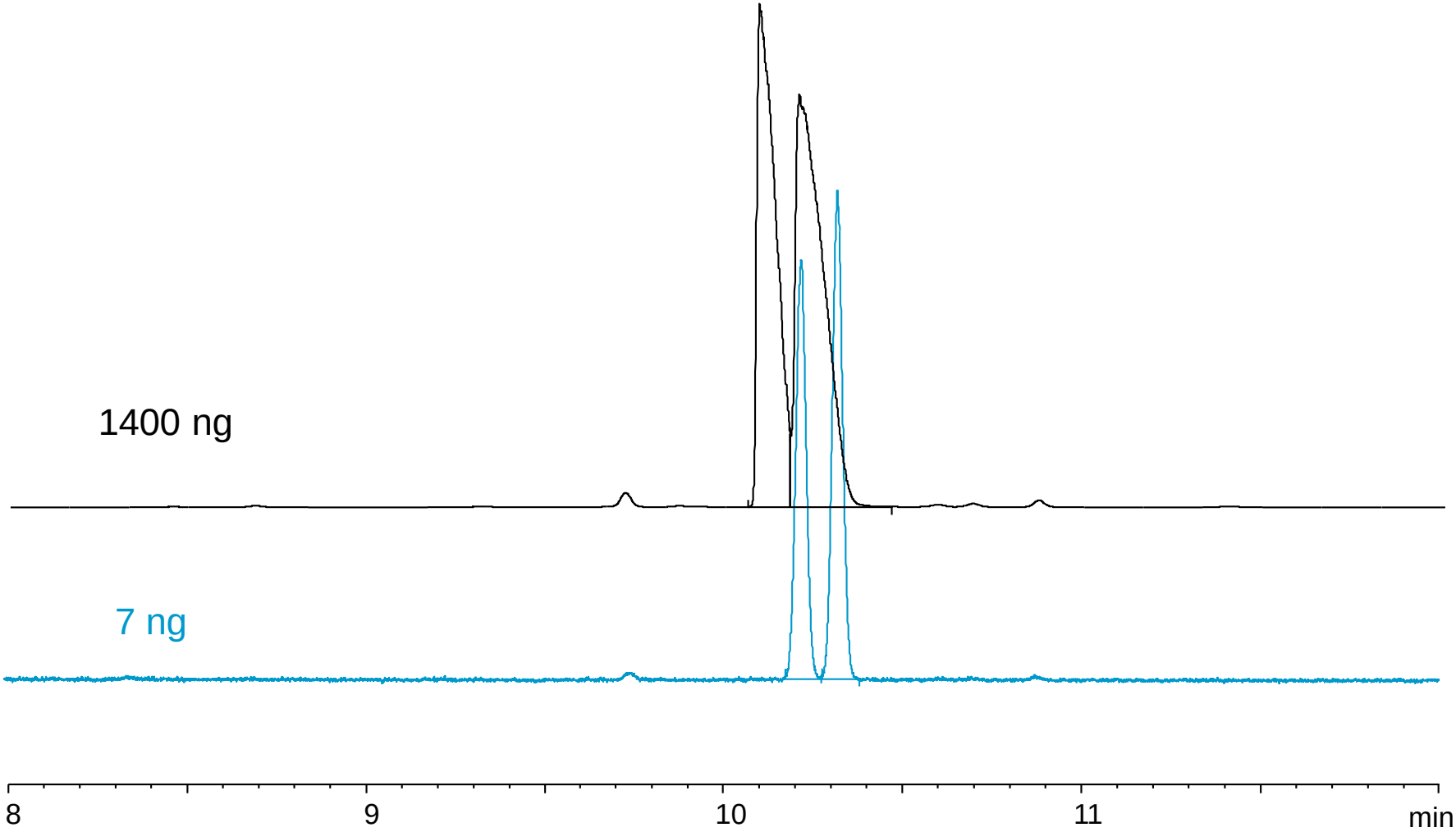
-Loss of stationary phase

-Change in temperature

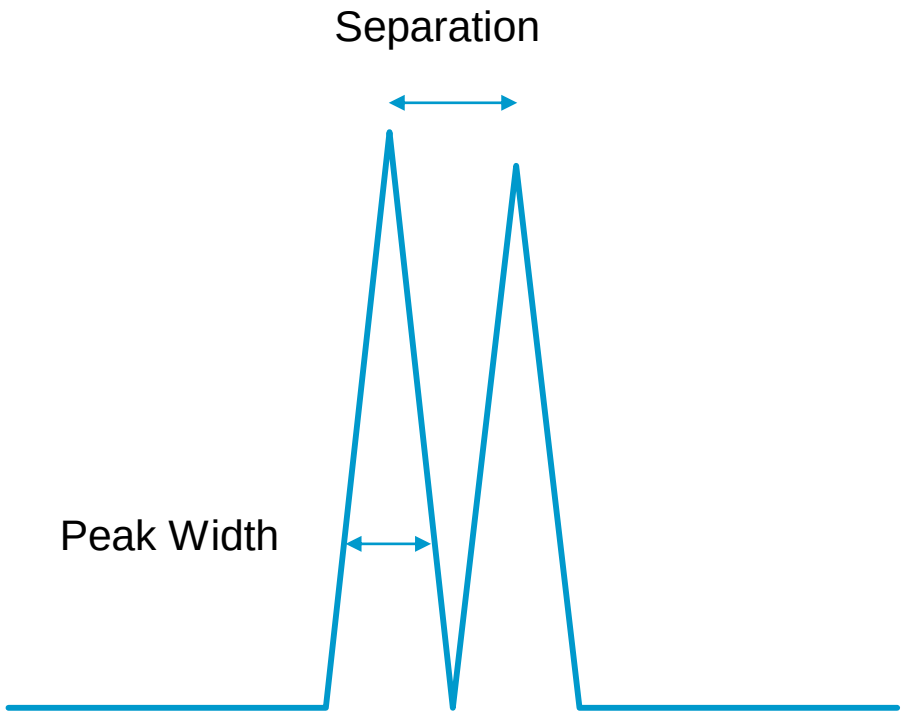




Effect of Sample Overload on Retention Time and Peak Shape



Loss of Resolution



Resolution is a function of separation and peak width

Loss of Resolution - Separation Decrease

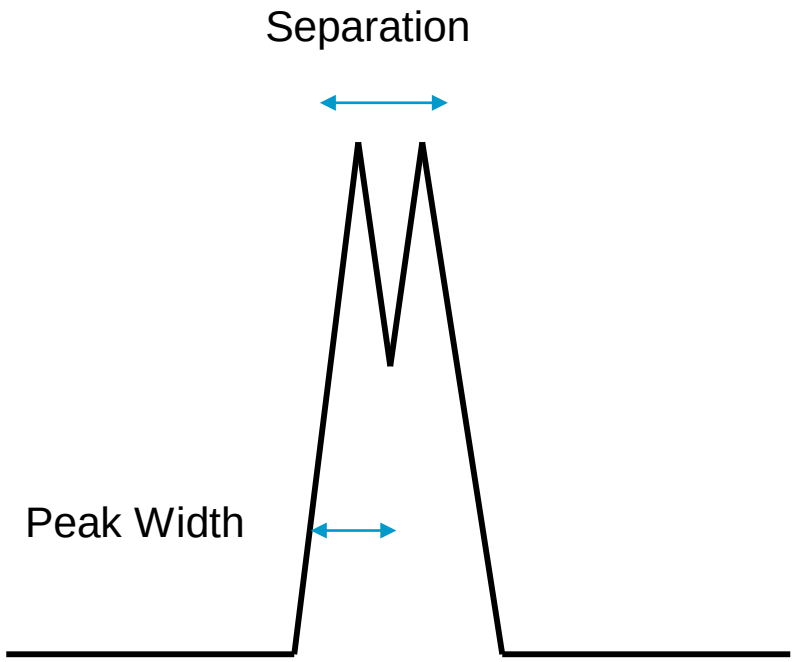
COLUMN

-Different column temperature

-Contamination (more phase?)

-Matrix components co-eluting

-Different column phase?



Loss of Resolution - Peak Broadening

FLOW

-Change in carrier gas velocity

-Make-up gas

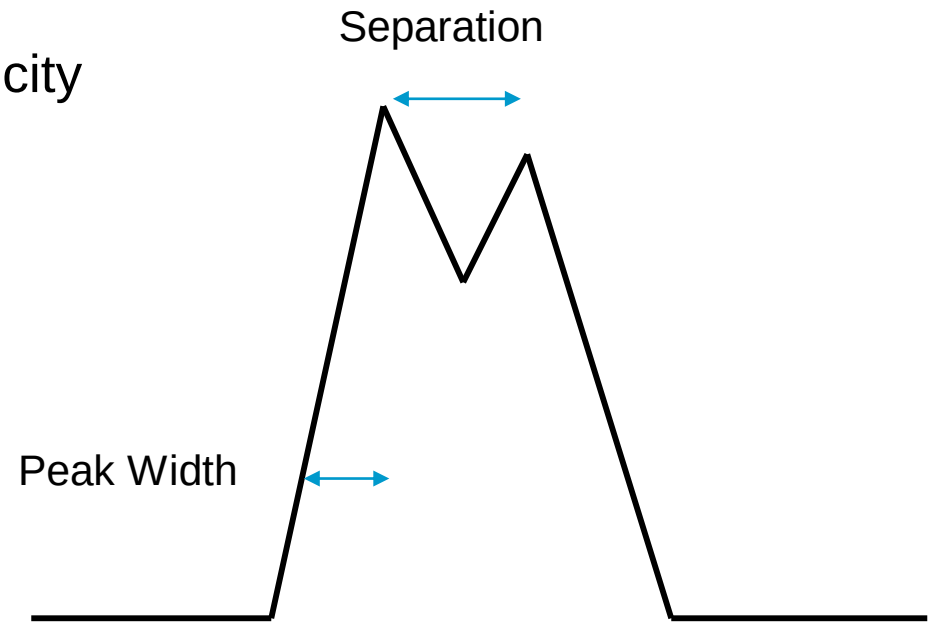
COLUMN

-Contamination

-Phase degradation

INJECTOR (efficiency)

-Settings, Liner, Installation, etc.



Baseline Disturbances

Sudden Changes, Wandering, or Drifting

WANDER

COLUMN or DETECTOR

-Not fully conditioned or stabilized (electronics)

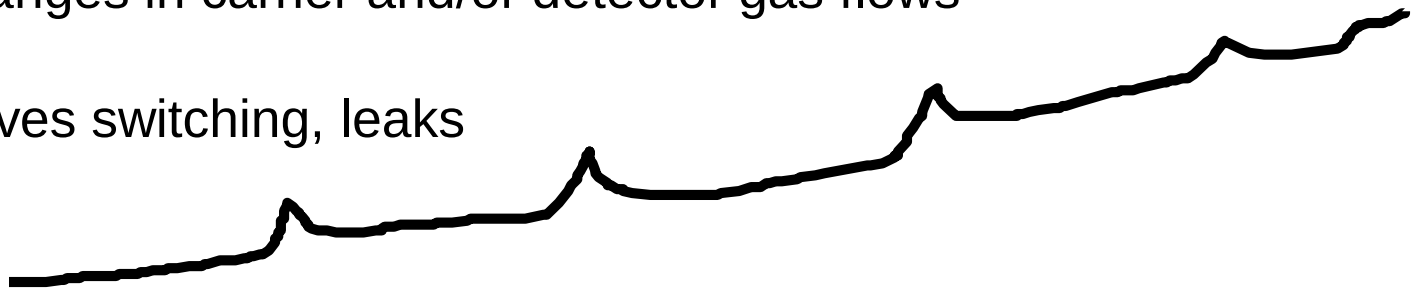
-Contamination

FLOW

-Changes in carrier and/or detector gas flows

-Valves switching, leaks

DRIFT



Noisy Baseline

MILD

SEVERE

FLOW

-Contaminated gas

-Incorrect detector settings

COLUMN

-Bleed if at high temperature

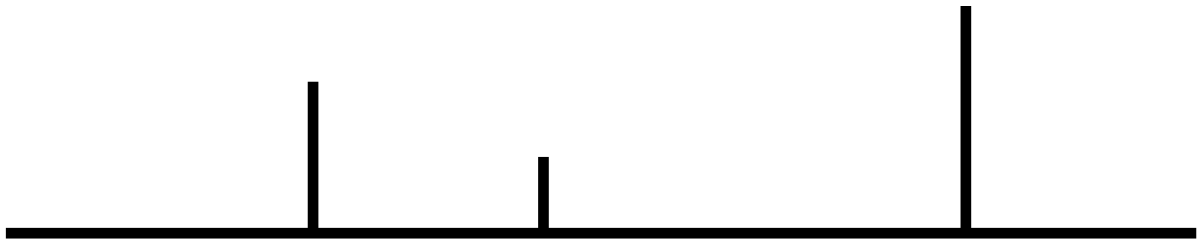
-In detector flame (poor installation)

DETECTOR

-Air leak - ECD, TCD

-Electronics malfunction

Spiking Baseline



DETECTOR

-Particles entering the detector

-Random: poor connection

-Regular: nearby "cycling" equipment (electronics)

Quantitation Problems

DETECTOR

-Poor stability (electronics) or Baseline disturbances (contamination)

-Outside detector's linear range or wrong settings

Activity (adsorption) in INJECTOR or COLUMN

INJECTOR

-Technique, settings, conditions

-Syringe worn

OTHER

-Co-elution

-Matrix effects

-Sample evaporation – leaky vials

-Sample decomposition

What is NOT caused by a Column???

Peaks!!

- Any reproducible, sharp ‘chromatographed’ peak!
- Siloxanes
- Degradation product peaks: Endrin Aldehyde, Endrin Ketone, DDE, DDD….

Carryover of sample compounds

Splitting of peaks

Troubleshooting “Tools”

Bleed Profile: *baseline problems*

Inject a non-retained peak: *peak shape problems*

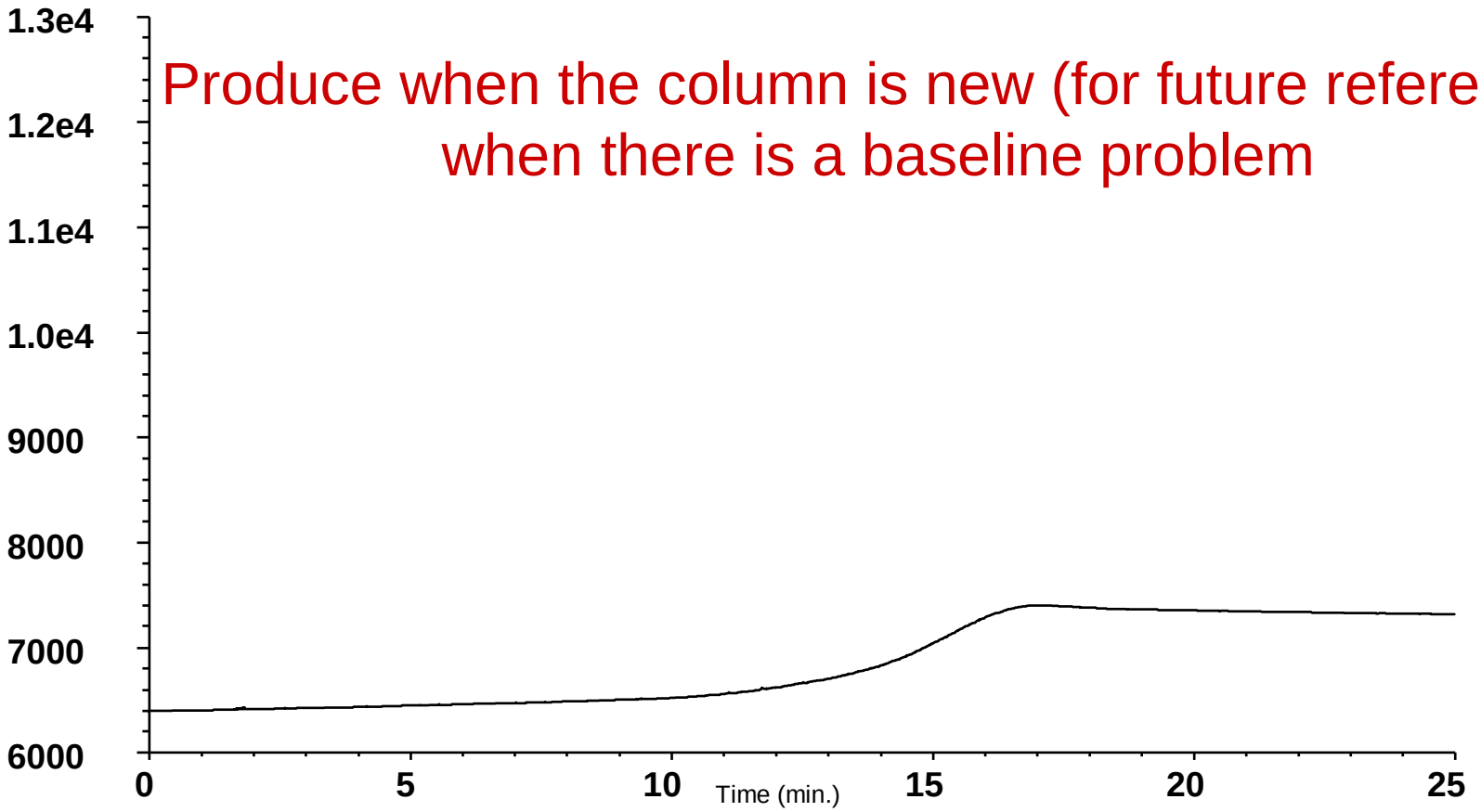
Test mix: *all problems*

Isolate the components: *all problems*

Condensation Test: *baseline problems*

Jumper Tube Test: *baseline problems*

Generating a Bleed Profile

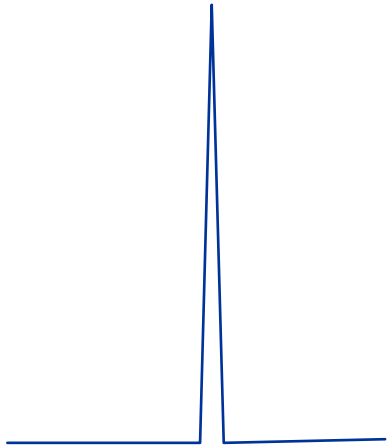


Produce when the column is new (for future reference)
when there is a baseline problem

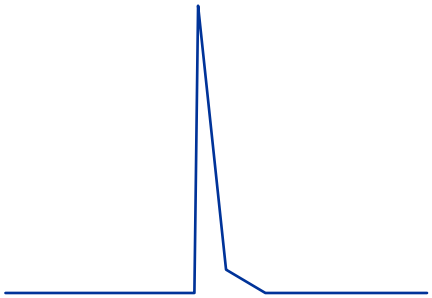
***DB-1 30m x .32mm I.D., .25µm**
Temperature program // 40°C, hold 1 min // 20°/min to 320°C, hold 10 min.

Non-Retained Peak Shapes

Used to Check Flowpath



Good Installation



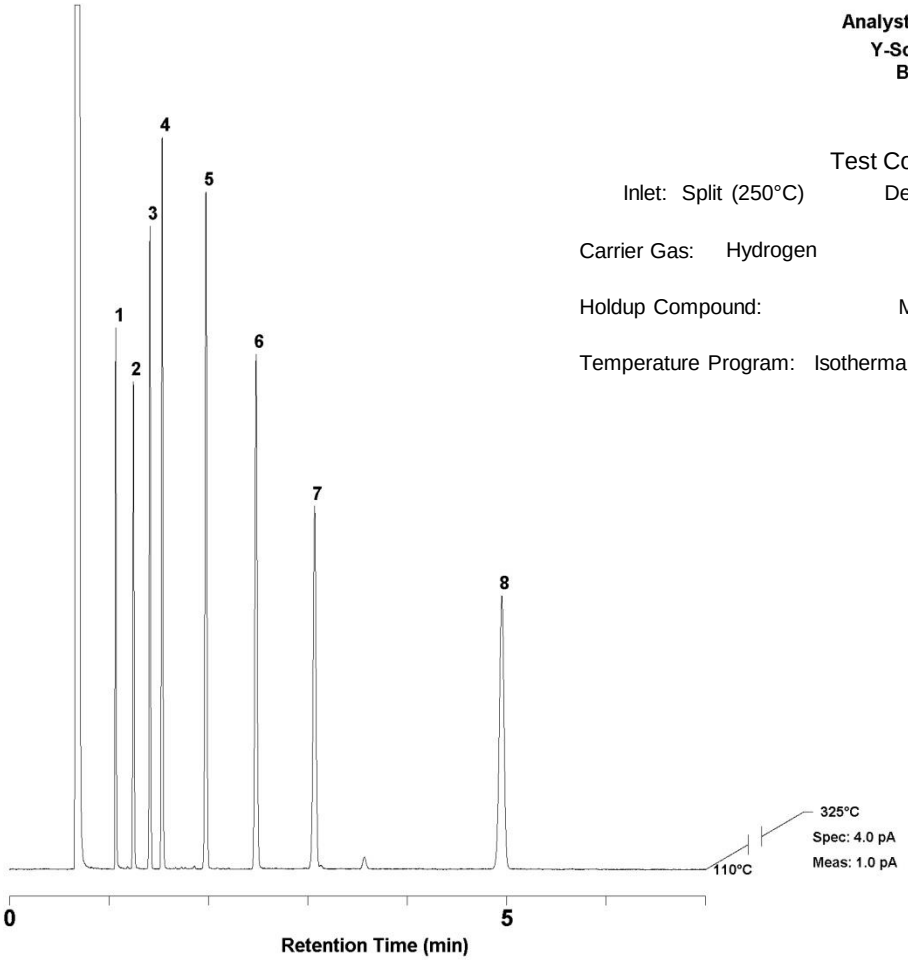
Improper Installation or Injector Leak

Potential problems:

- Injector or septum leak
- Too low of a split ratio
- Liner problem (broken, leaking, misplaced)
- Column position in injector and detector

Test Mix

Used to determine how “good” the column is or if the problem is related to the chemical properties of the analytes.



Test Mixture Components

Compounds	Purpose
Hydrocarbons	Efficiency
	Retention
Alcohols	Activity
FAME’s, PAH’s	Retention
Acids	Acidic Character
Bases	Basic Character

Own Test Mixture

- More specific to your application
- Selective detectors
- Concentrations specific to your application
- Use same instrument conditions
- Easiest to simply inject a calibration standard
- Store for future measure of column performance

Isolate the Components

Simplify the system:

- example - Direct injection instead of P&T sample introduction

Put in a known good column

Move column to a different GC, inlet or detector

Condensation Test

Used* to isolate the cause of:

- Erratic baselines
- Ghost peaks or carryover

***Use when problems are worse after periods of GC non-use**

Condensation Test

Procedure

Leave GC at 40-50°C for > 8 hours

Blank run

Repeat a blank run immediately after the first blank run is complete

Compare the two blank runs

Condensation Test

Results

First blank run is worse:

- Contaminants (from injector, lines, traps or carrier gas) carried into the column

Blank runs the same: *contaminants are not strongly focused on the front of the column*

Jumper Tube Test

Purpose

Helps to locate the source of contamination or noise

Isolates GC components

Jumper Tube Test

Isolate the Detector

Remove column from the detector

Cap detector and turn on

Blank run

Jumper Tube Test

Isolation of Detector - Results

Detector OK

Detector is the problem

Jumper Tube Test

Isolate the Injector

Connect the injector and detector

- 1-2 meters deactivated fused silica tubing

Turn on carrier gas

Blank run

Jumper Tube Test

Isolate the Injector - Results

Injector OK

Injector, lines or carrier gas contaminated

Jumper Tube Test

Isolate the Column

Reinstall the column

Setup as before

Blank Run

Jumper Tube Test

Isolate the Column - Results

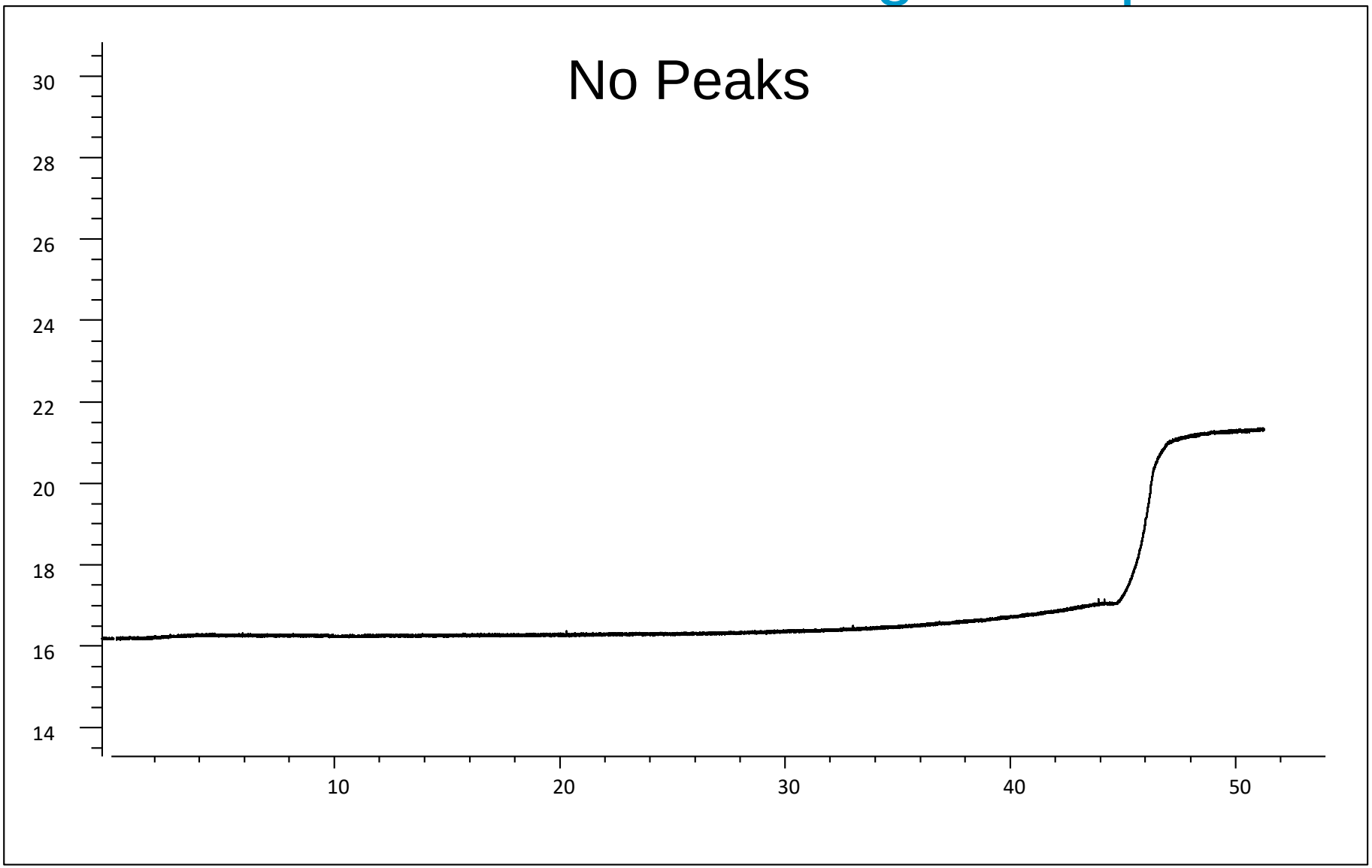
Problem returns: It's the column

Problem gone: Previous leak, solid debris, or installation problem

And Now Let's do Some

Troubleshooting-Example #1

A Real Troubleshooting Example



Logical Steps Taken to Find Peaks
(most of our problems are leaks and plugs)

Is the flame Lit?

- put glass piece over FID outlet----*Answer in this case, Water condenses*
- look at output in instrument guage-- is the digital value greater than 0.0?

Answer in this case is approximately 16.2 pico amps

Is there flow through the column?

- disconnect column from detector and measure flow with bubble solution or meter

Answer in this case was YES THERE IS FLOW

Assess the observations

- *Flame is lit and we have flow from end of column*
- *Hypothesis: Sample not getting on column-syringe plugged?*

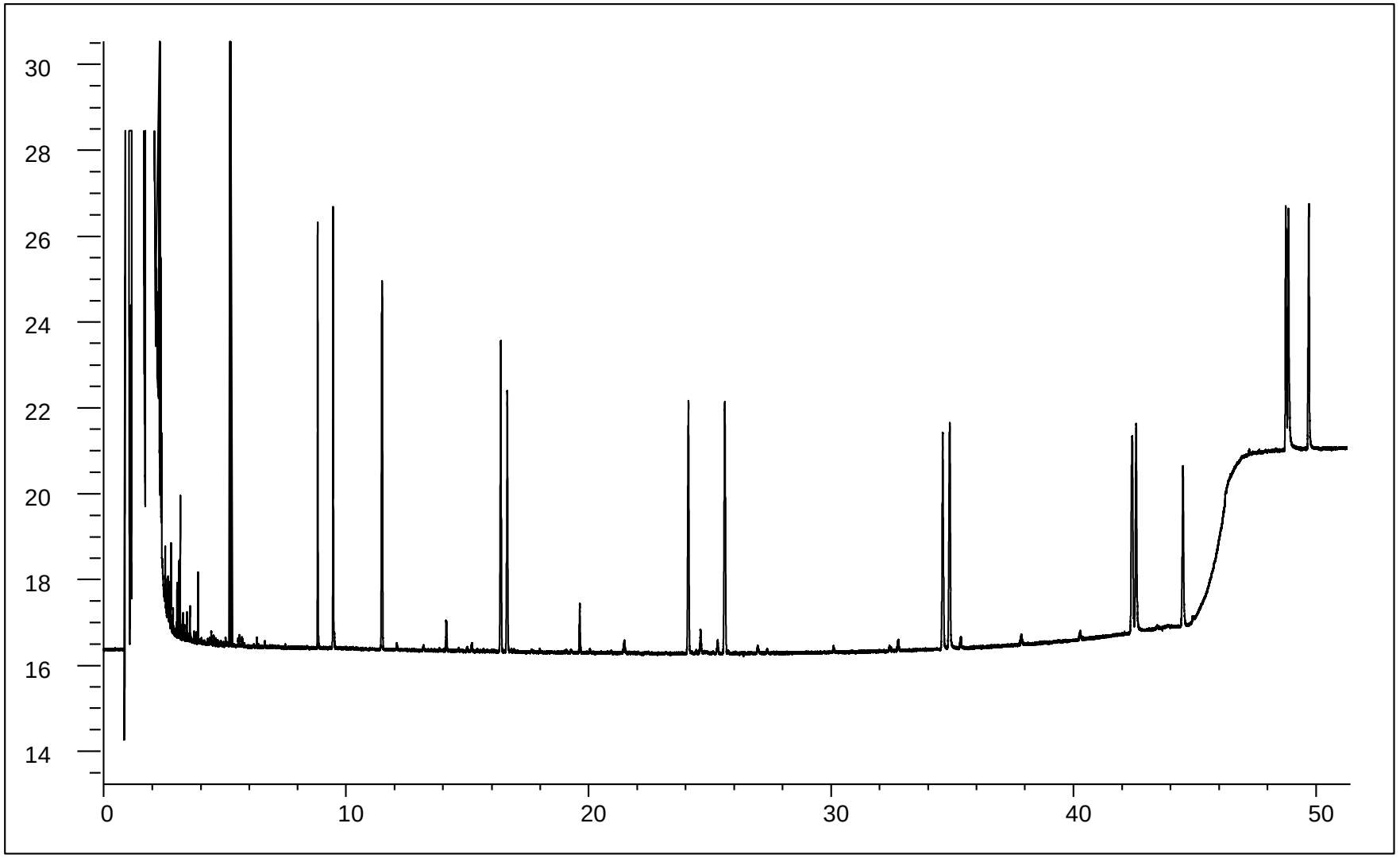
Take syringe out and make injection manually on a dry paper towel

Answer – towel stayes dry (Syringe was clogged with septum)

Pull plunger out top, add solvent and replace plunger will usually dislodge septum particle (should hear a little pop) If you can't dislodge plug, Replace syringe

Reassemble the Injector & Re-inject

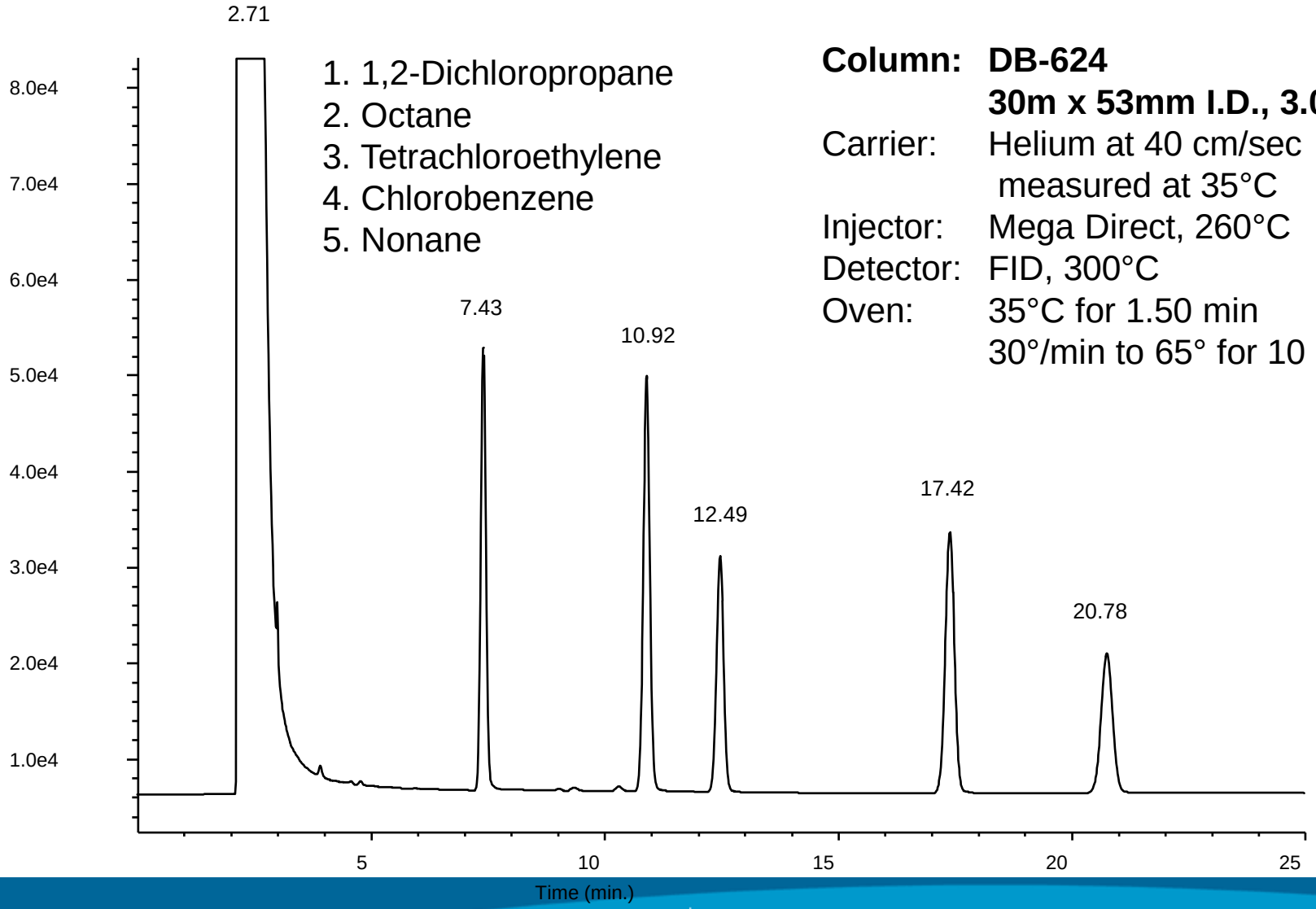
Peaks !!



Troubleshooting-Example #2

DB-624 COLUMN

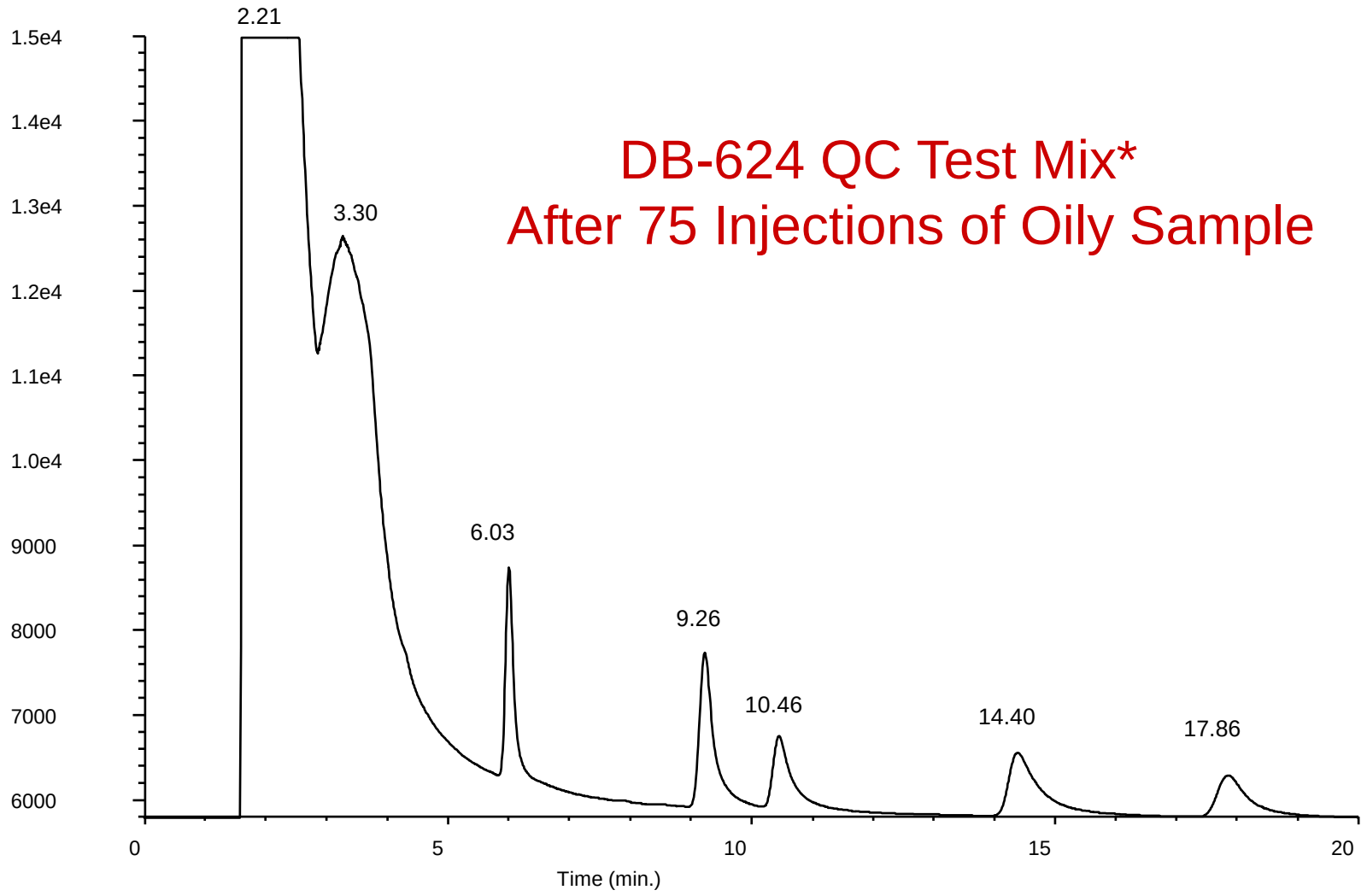
QC Test Mix



1. 1,2-Dichloropropane
2. Octane
3. Tetrachloroethylene
4. Chlorobenzene
5. Nonane

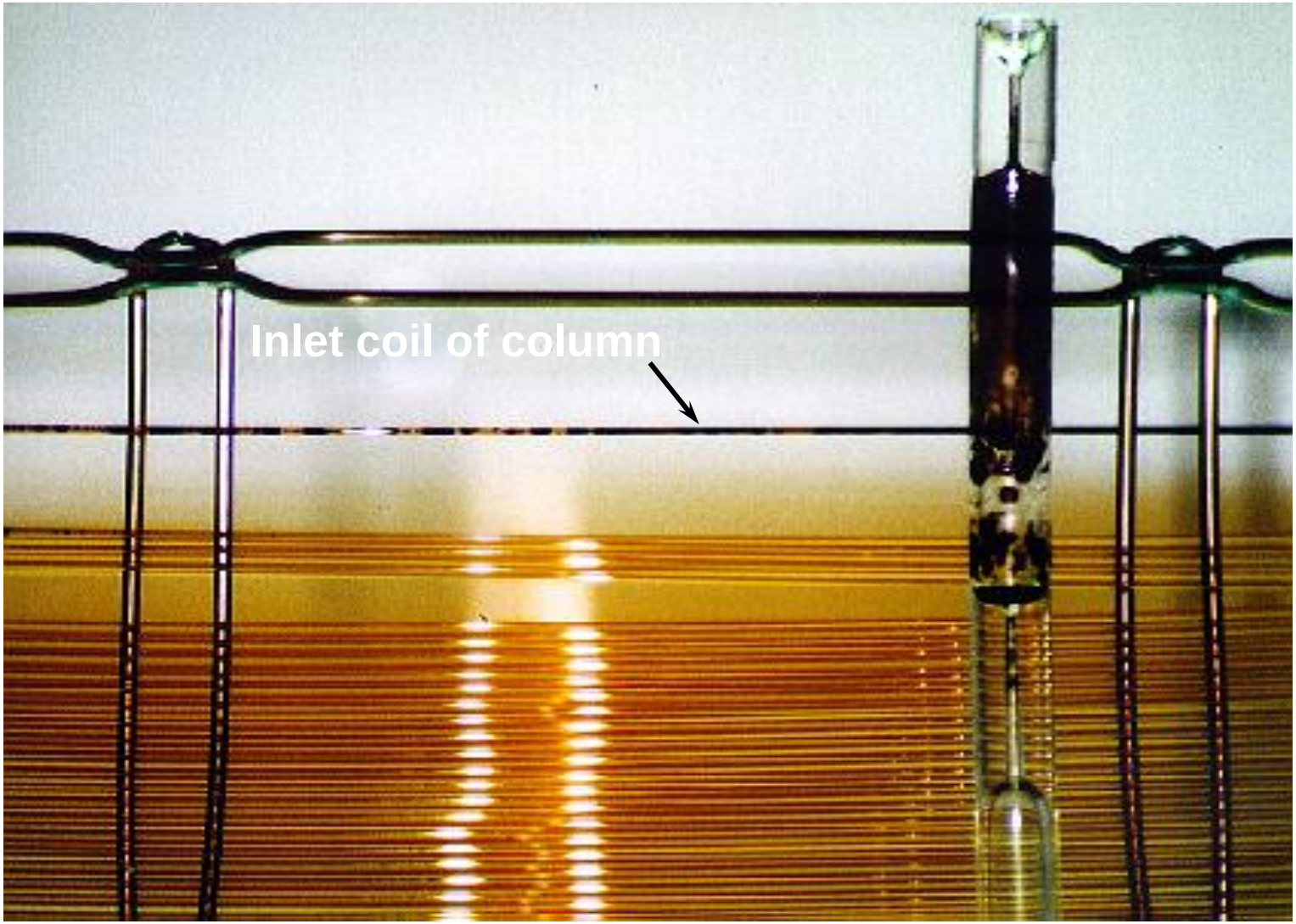
Column: **DB-624**
30m x 53mm I.D., 3.0µm
Carrier: Helium at 40 cm/sec measured at 35°C
Injector: Mega Direct, 260°C
Detector: FID, 300°C
Oven: 35°C for 1.50 min
30°/min to 65° for 10 min

Example of Column Contamination

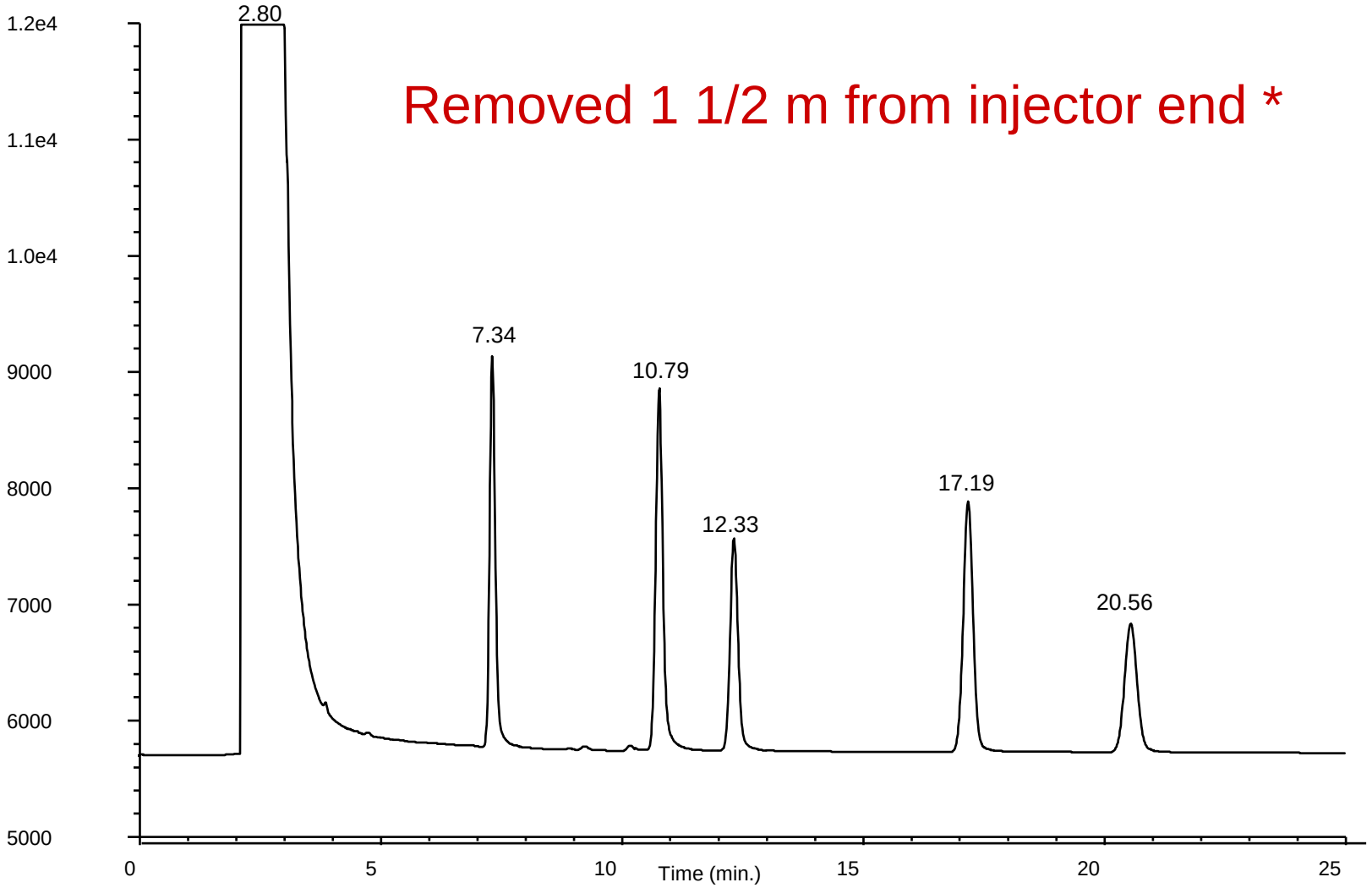


DB-624 QC Test Mix*
After 75 Injections of Oily Sample

Column and Liner Contamination



Example of Column Contamination



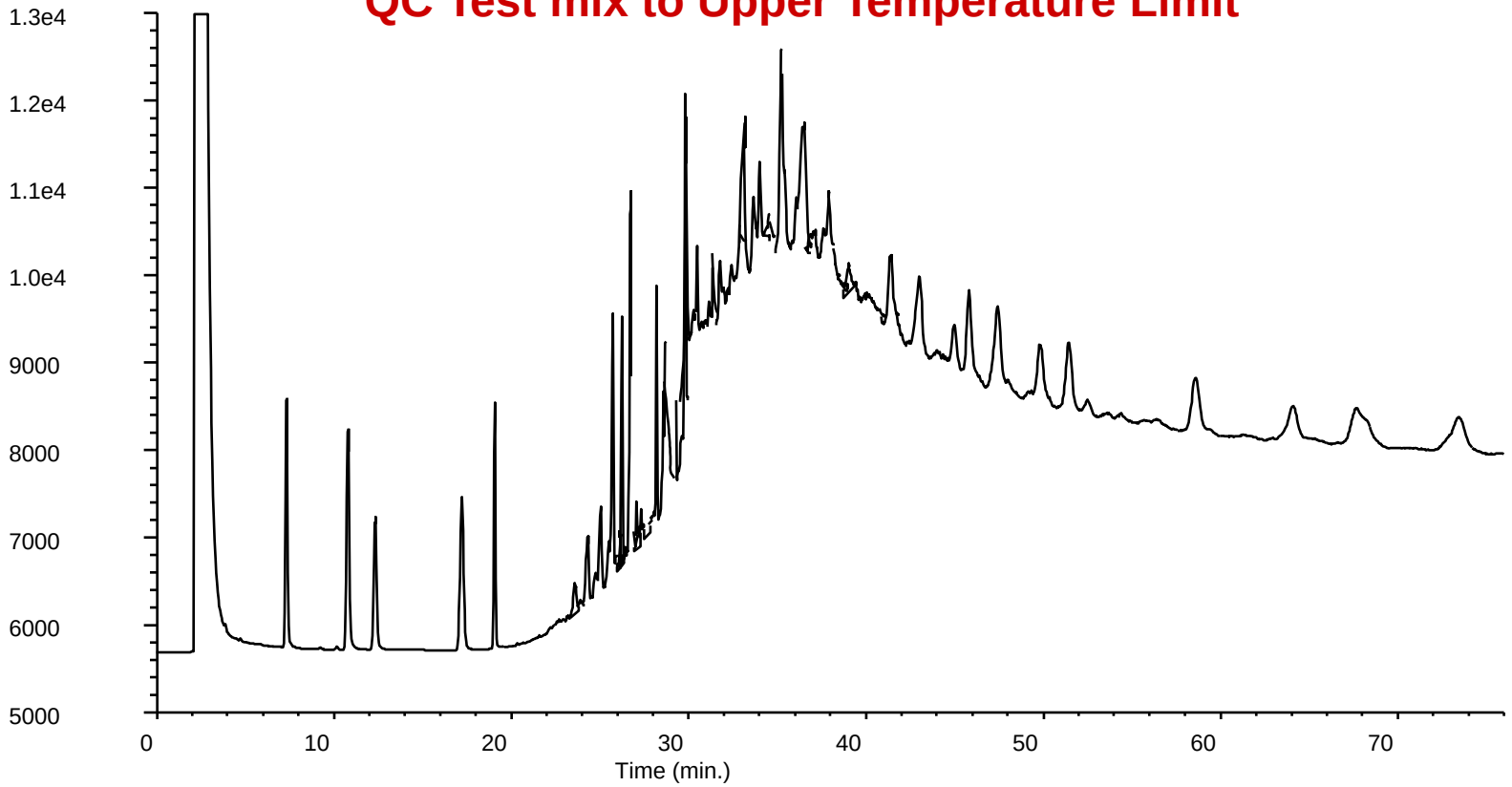
***Before Column rinse and bake**

Temperature program // 35°C hold 1.50 min // 30°/min to 65°C, hold 10 min

Looks Fixed Doesn't it?

Example of Column Contamination

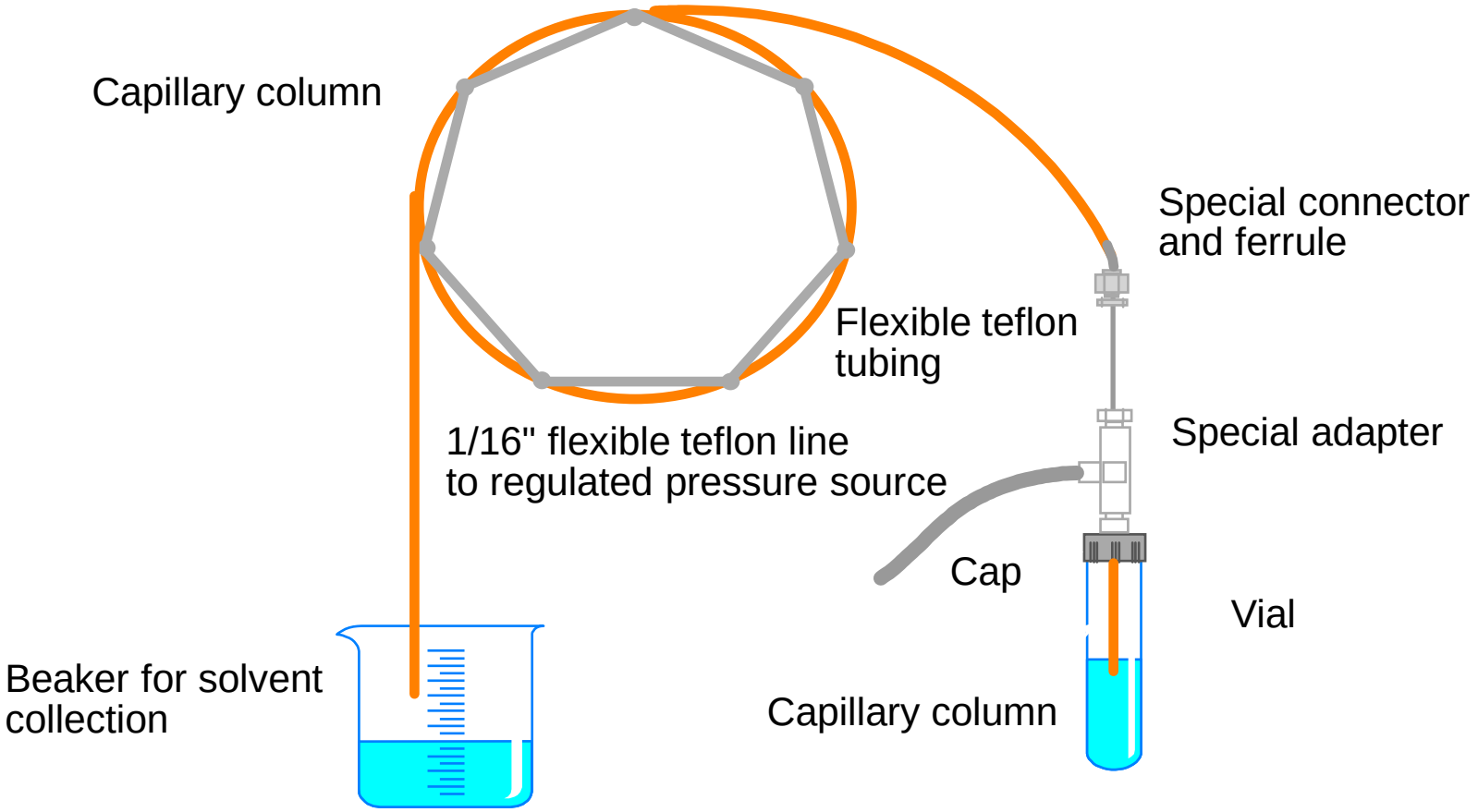
1 1/2 mtrs removed*
QC Test mix to Upper Temperature Limit



*Before Column rinse and bake.
Temperature program // 35°C, hold 1.50 min // 30°/min to 65°C, hold 15 min // 20°/min to 260°, hold 50 min

Backflush Column

Rinse with 10ml each:
Methanol, Methylene Chloride, Hexane



Jumper Tube Test

Used to Isolate Source of Contamination

. Cap off the detector and establish normal gas flows and temperature.

. Plot the baseline using a temperature program. If flat.....

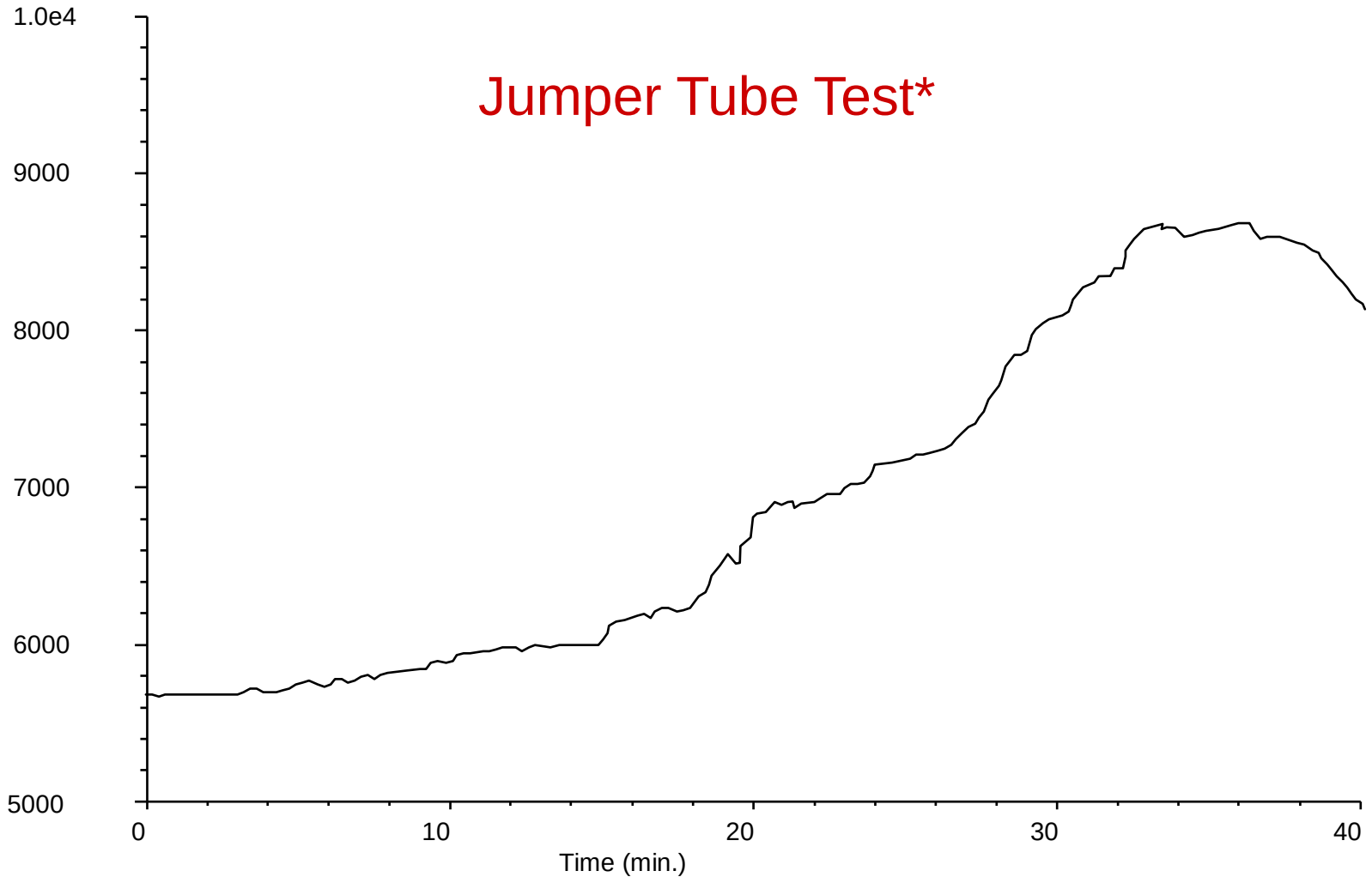
. Connect 1 meter of deactivated tubing between the injector and detector

. Plot the baseline using a temperature program. If flat.....

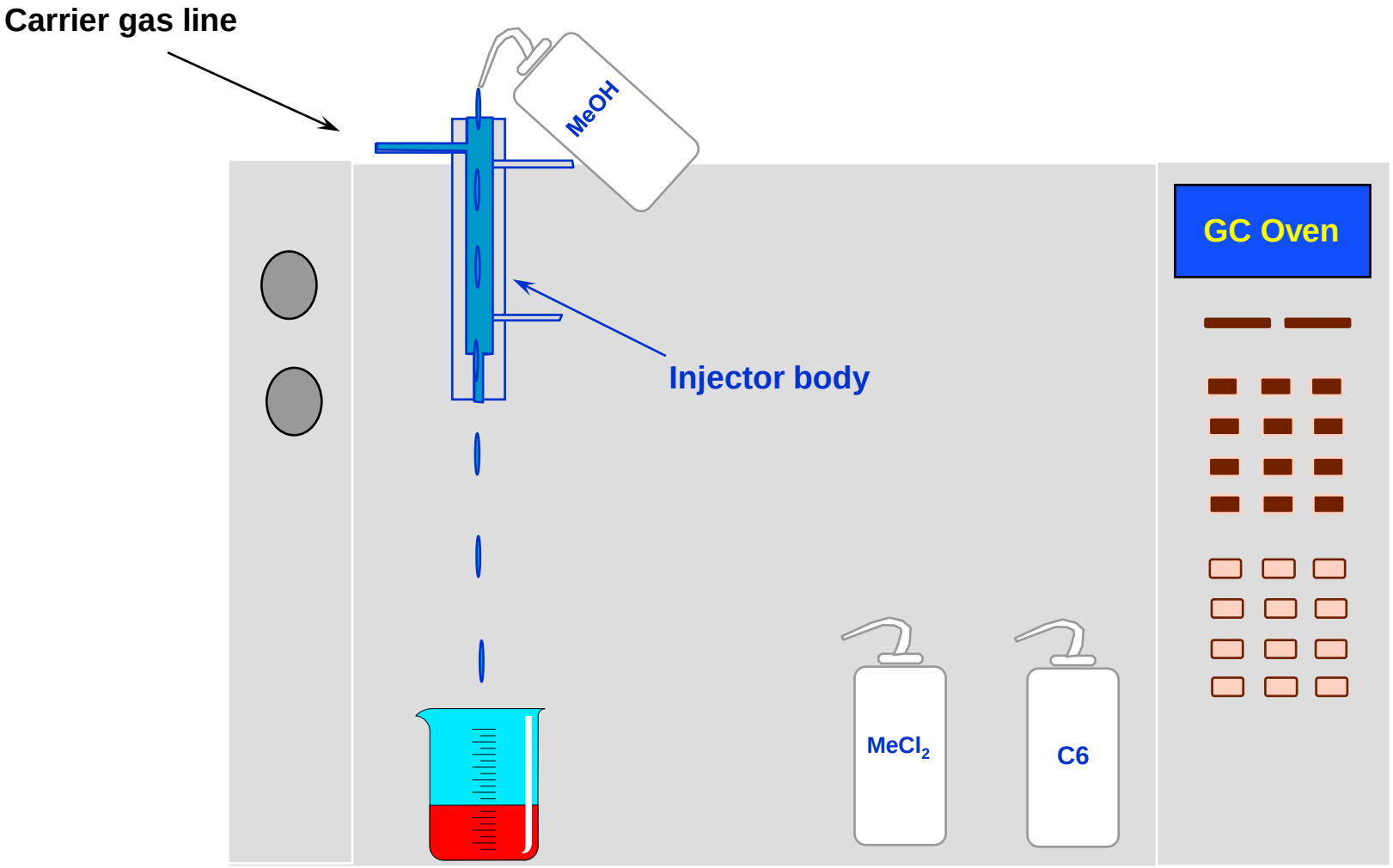
. Install the column.

. Plot the baseline using a temperature program.

Contaminated Inlet



Rinsing Injector



Troubleshooting Tips

1. Isolate the problem.

(Blank Run, Inject Un-retained Compound, Jumper Tube Test)

2. Change only one variable at a time.

3. Compare before/after chromatograms.

(Peak shape, response, retention, baseline rise, background, look for trends, etc.)

4. Utilize Technical Support.

Remember

Complete system = Carrier Gas + Injector + Column + Detector + Data System

Multiple cause and effect

Do not change too many variables at once

Contact Agilent Chemistries and Supplies Technical Support

1-800-227-9770 Option 3, Option 3:

Option 1 for GC/GCMS Columns and Supplies

Option 2 for LC/LCMS Columns and Supplies

Option 3 for Sample Preparation, Filtration and QuEChERS

Option 4 for Spectroscopy Supplies

Available in the USA 8-5 all time zones

gc-column-support@Agilent.com

lc-column-support@agilent.com

spp-support@agilent.com

spectro-supplies-support@agilent.com