Practical Steps in GC Troubleshooting

Techniques, Tips, and Tricks

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Application Engineer
GC Columns & Supplies

Agilent Technologies

What went wrong and how to fix it…

Common problems

Troubleshooting tools

Troubleshooting examples

"Everything was just fine and then this happened!

How do I go about TROUBLESHOOTING?"

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"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.

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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**

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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
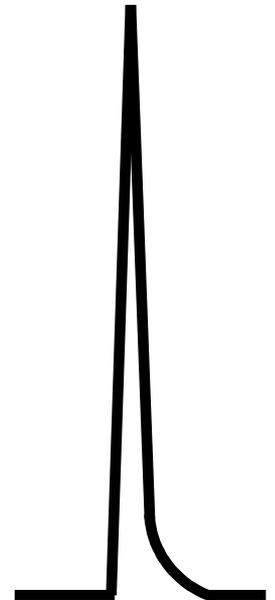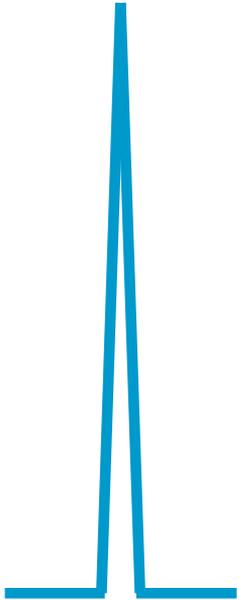
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Peak Tailing

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.

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Bonus Peaks

$W_h = 0.106$

$W_h = 0.029$

$W_h = 0.030$
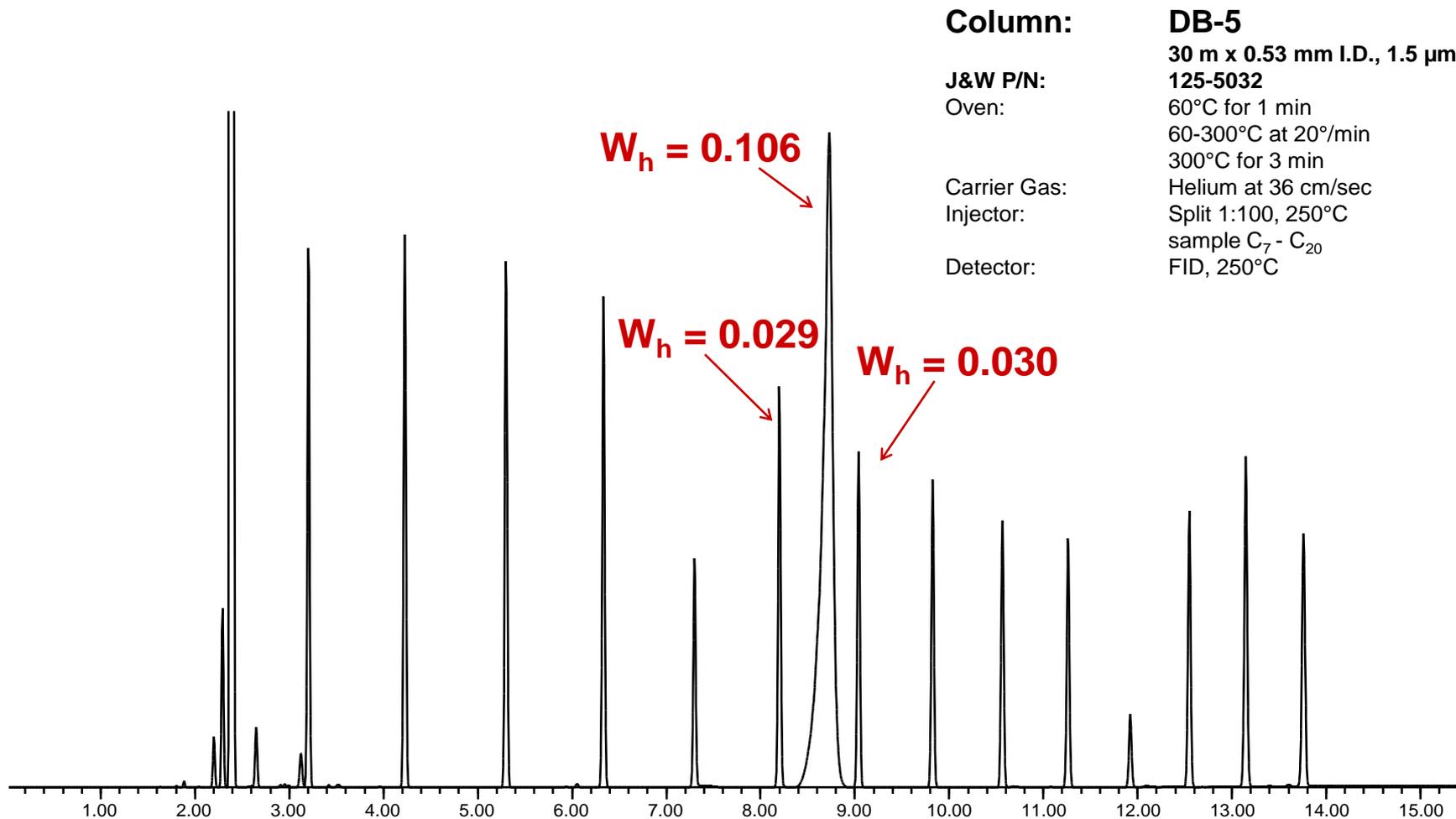
Column: **DB-5**
30 m x 0.53 mm I.D., 1.5 µm
J&W P/N: **125-5032**
Oven: 60°C for 1 min
60-300°C at 20°/min
300°C for 3 min
Carrier Gas: Helium at 36 cm/sec
Injector: Split 1:100, 250°C
sample C_7 - C_{20}
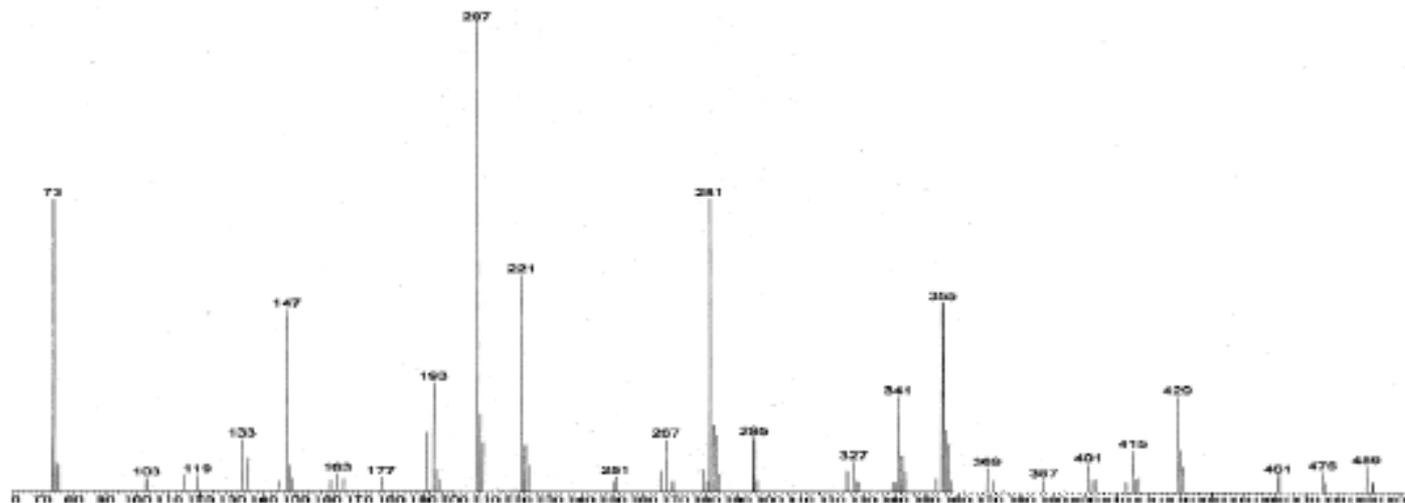Detector: FID, 250°C
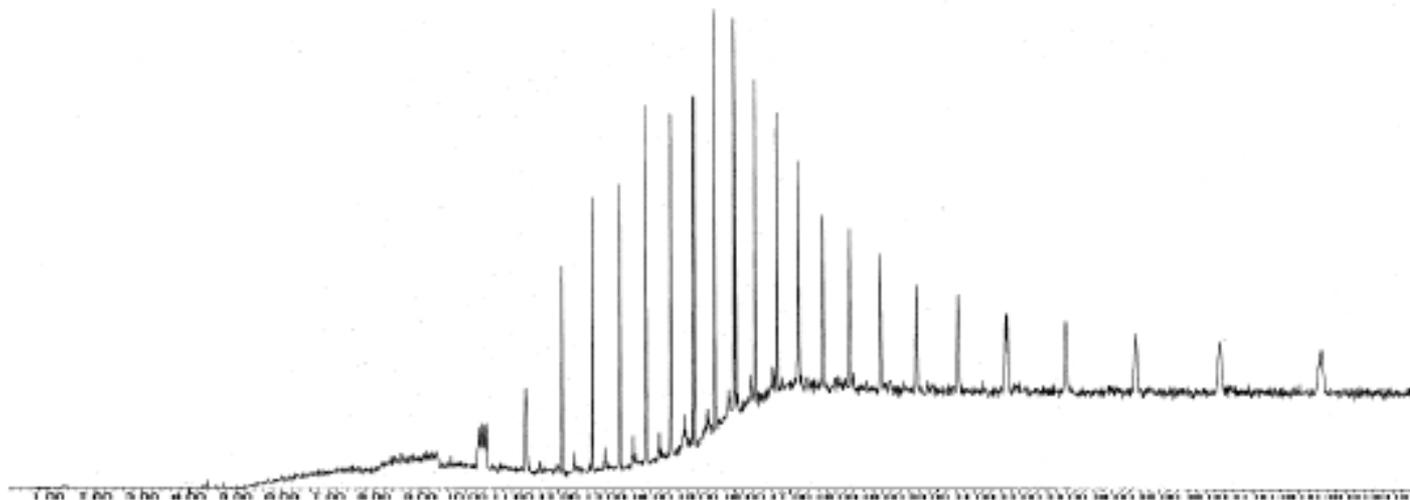
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Bonus Peaks or Ghost Peaks
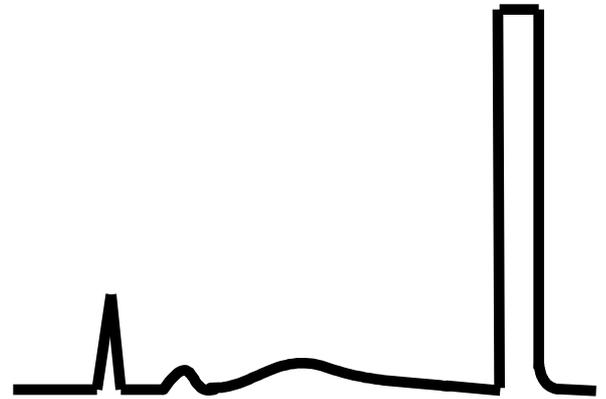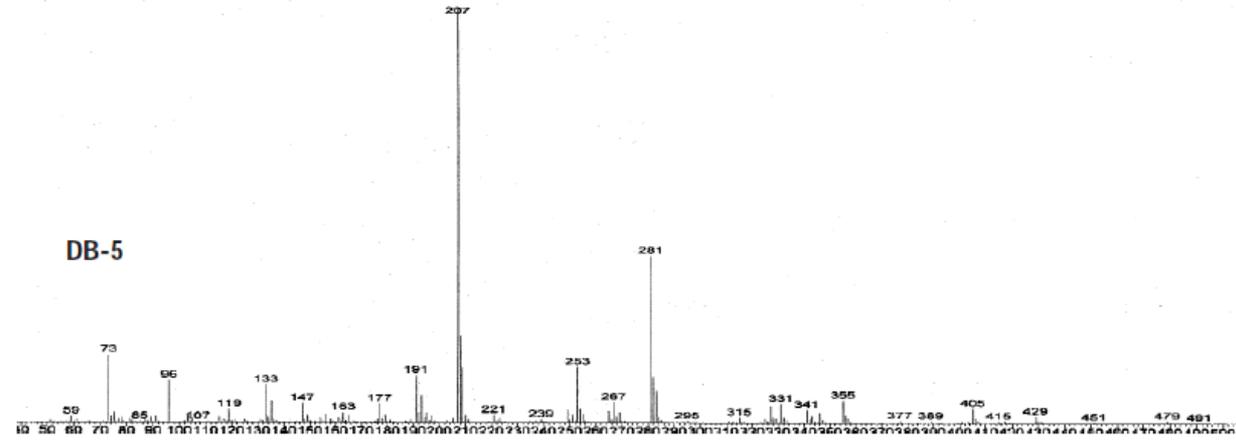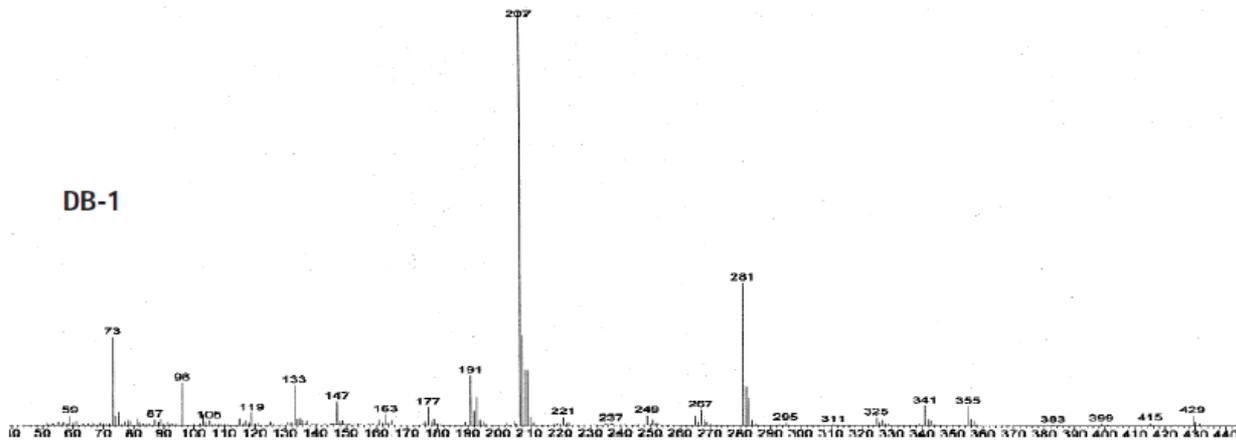
Contamination in INJECTOR, COLUMN or FLOW (carrier gas)

-Carry-over from a backflash or previous sample

-Bad tank of gas or traps have expired
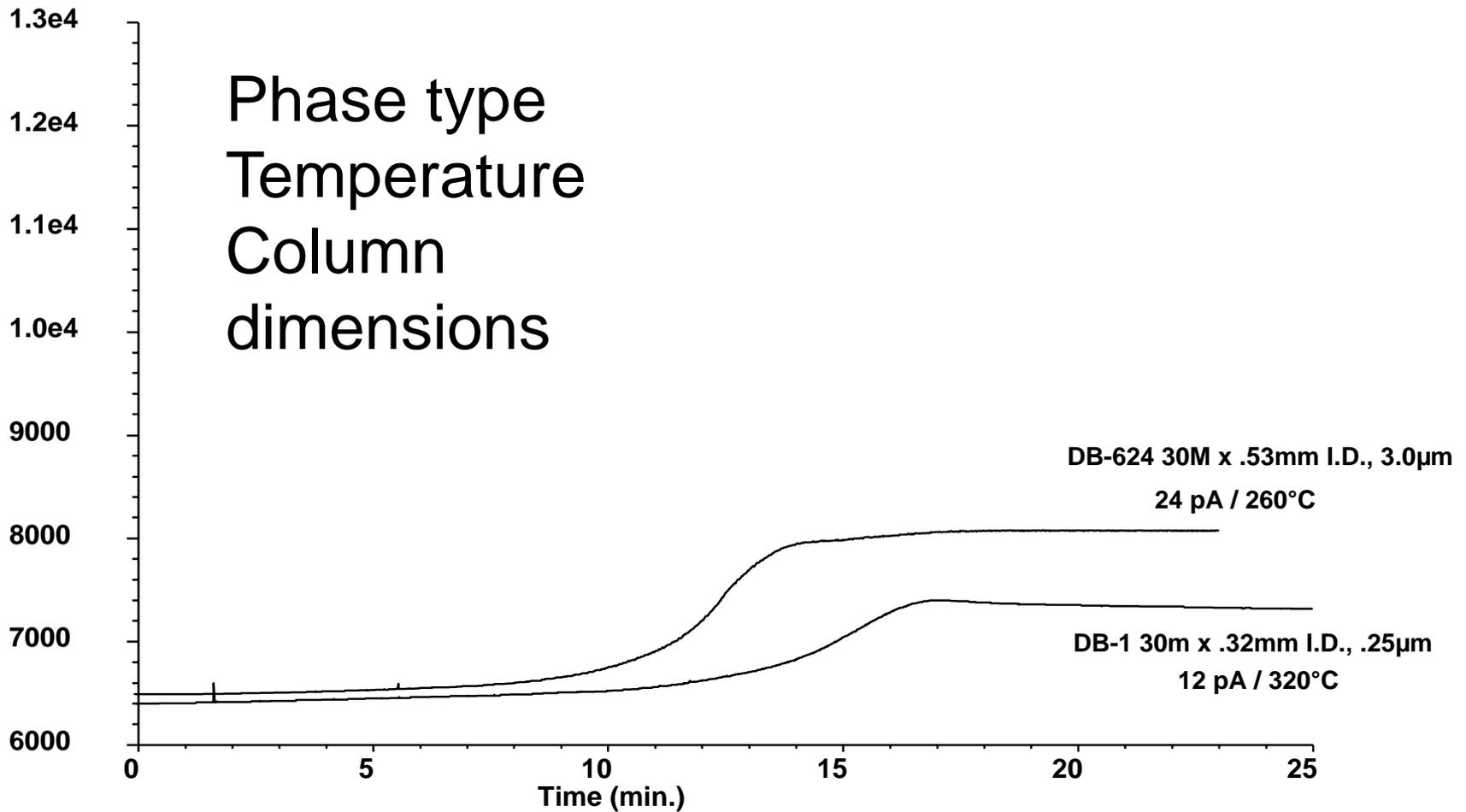
-Septum bleed

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

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Bonus 'Siloxane' Peaks

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GC Column Bleed Ions

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Column Bleed is Influenced by:

Phase type
Temperature
Column
dimensions

DB-624 30M x .53mm I.D., 3.0µm
24 pA / 260°C

DB-1 30m x .32mm I.D., .25µm
12 pA / 320°C

Time (min.)

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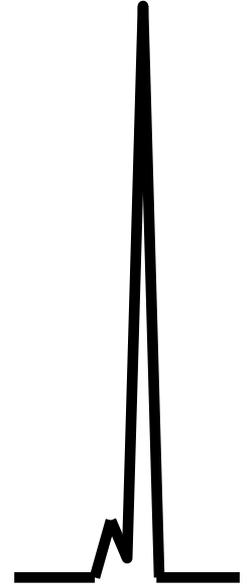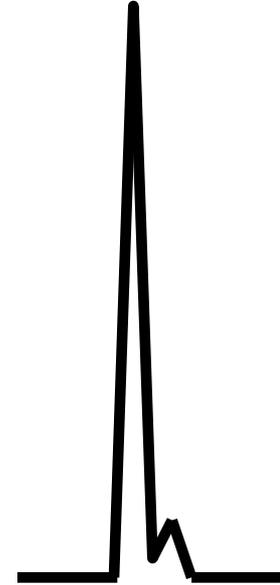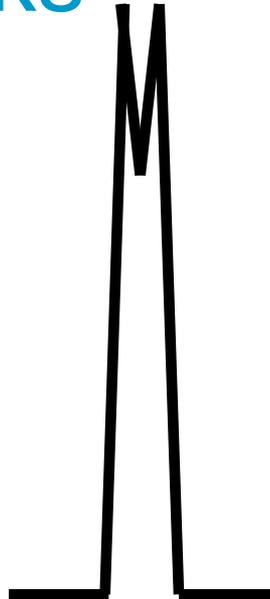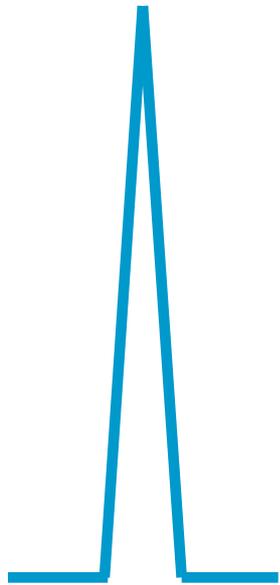
Split Peaks

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

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No Peaks
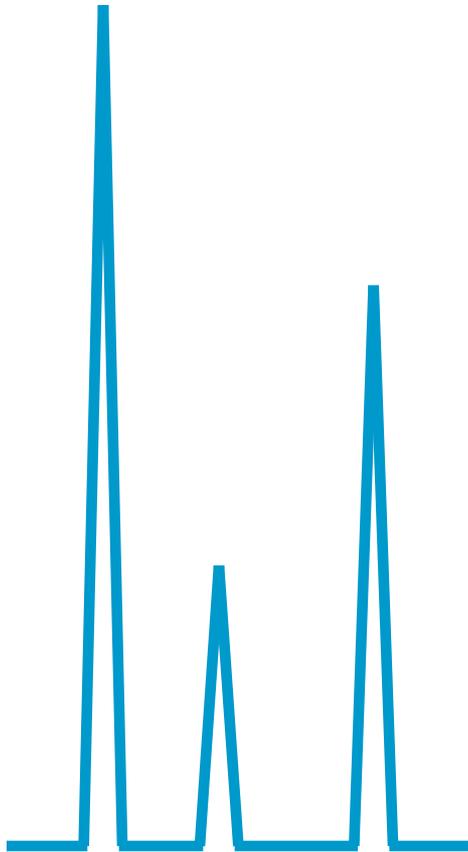
DETECTOR (not on or not operational)

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

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Peak Response
All Change in Size
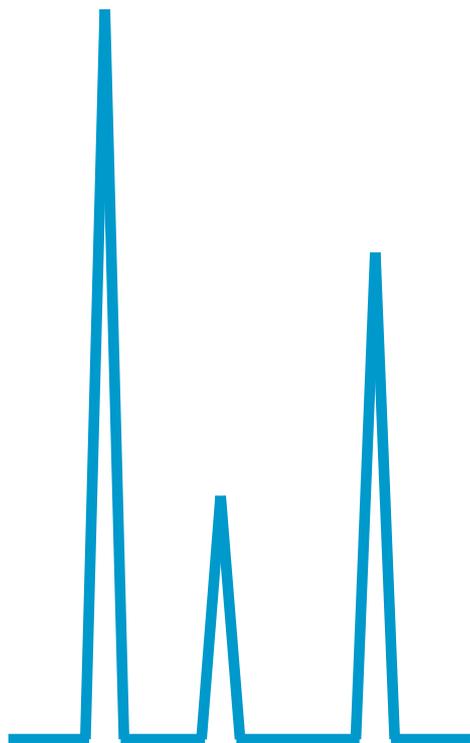
INJECTOR

-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

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Peak Response
Some Change in Size
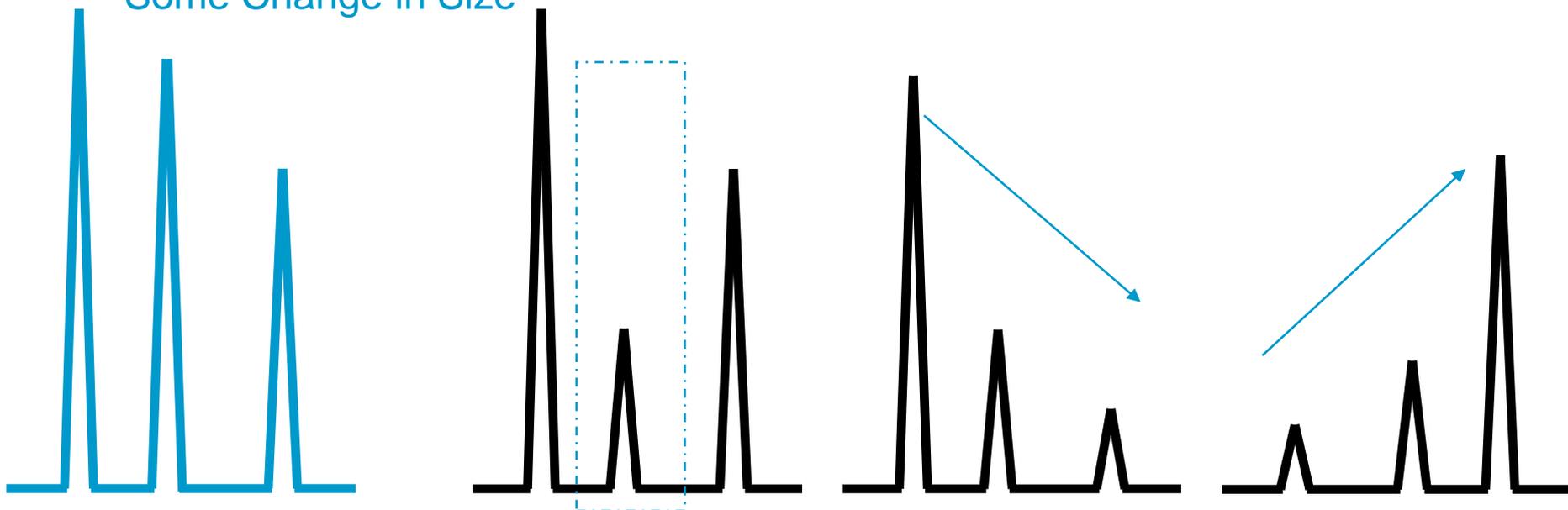
INJECTOR or COLUMN is active/contaminated

-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.

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Peak Fronting
Shark Fin Shaped or Just Slight

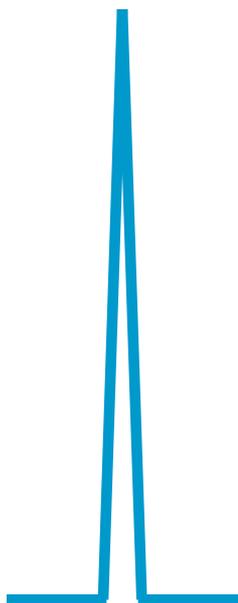**COLUMN** (contaminated)

-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

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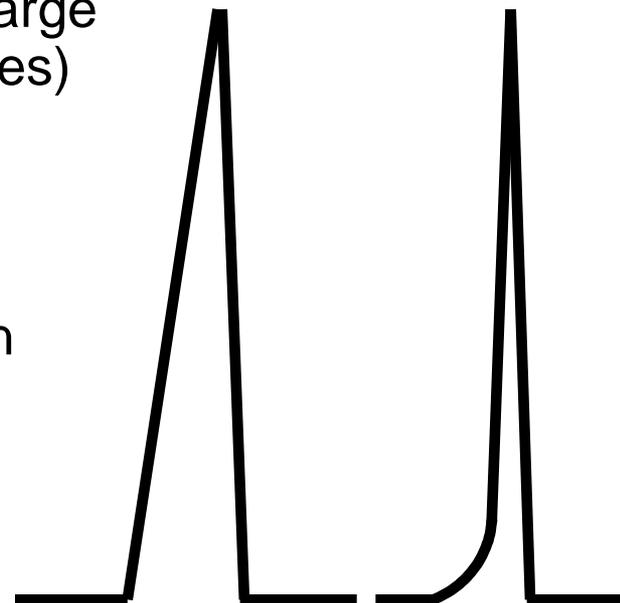
Retention Time Shift
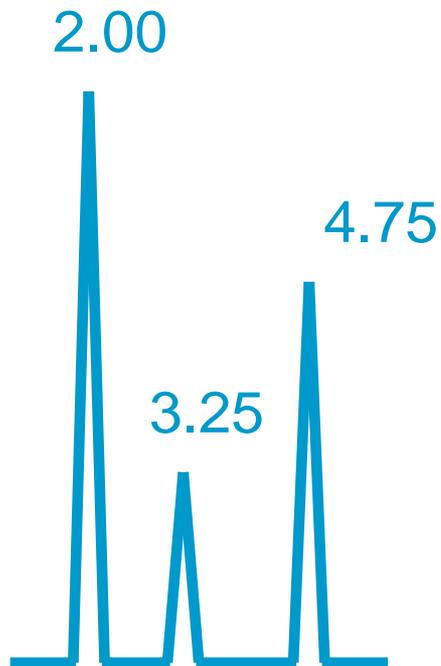
INJECTOR

-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

2.00

3.25

4.75

1.75

3.00

4.50

2.75

4.00

5.50

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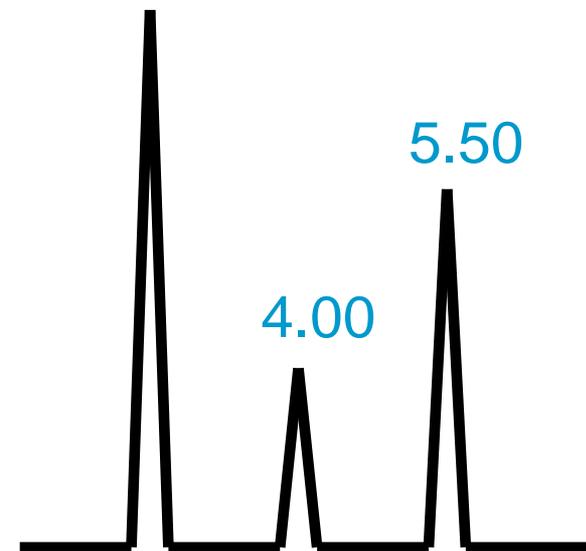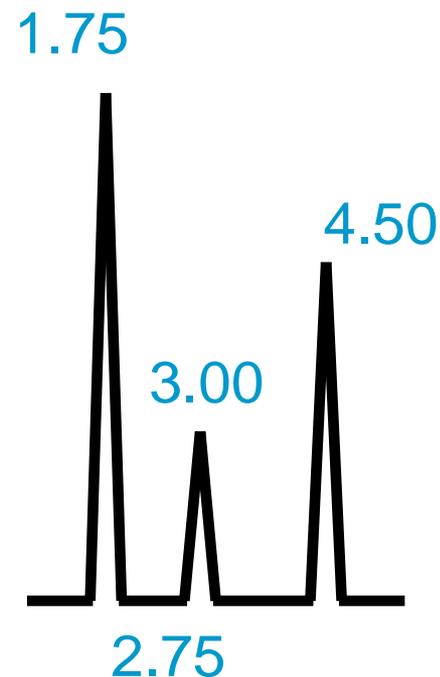
Effect of Sample Overload on Retention Time and Peak Shape

1400 ng

7 ng

8   9   10   11   min

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Loss of Resolution
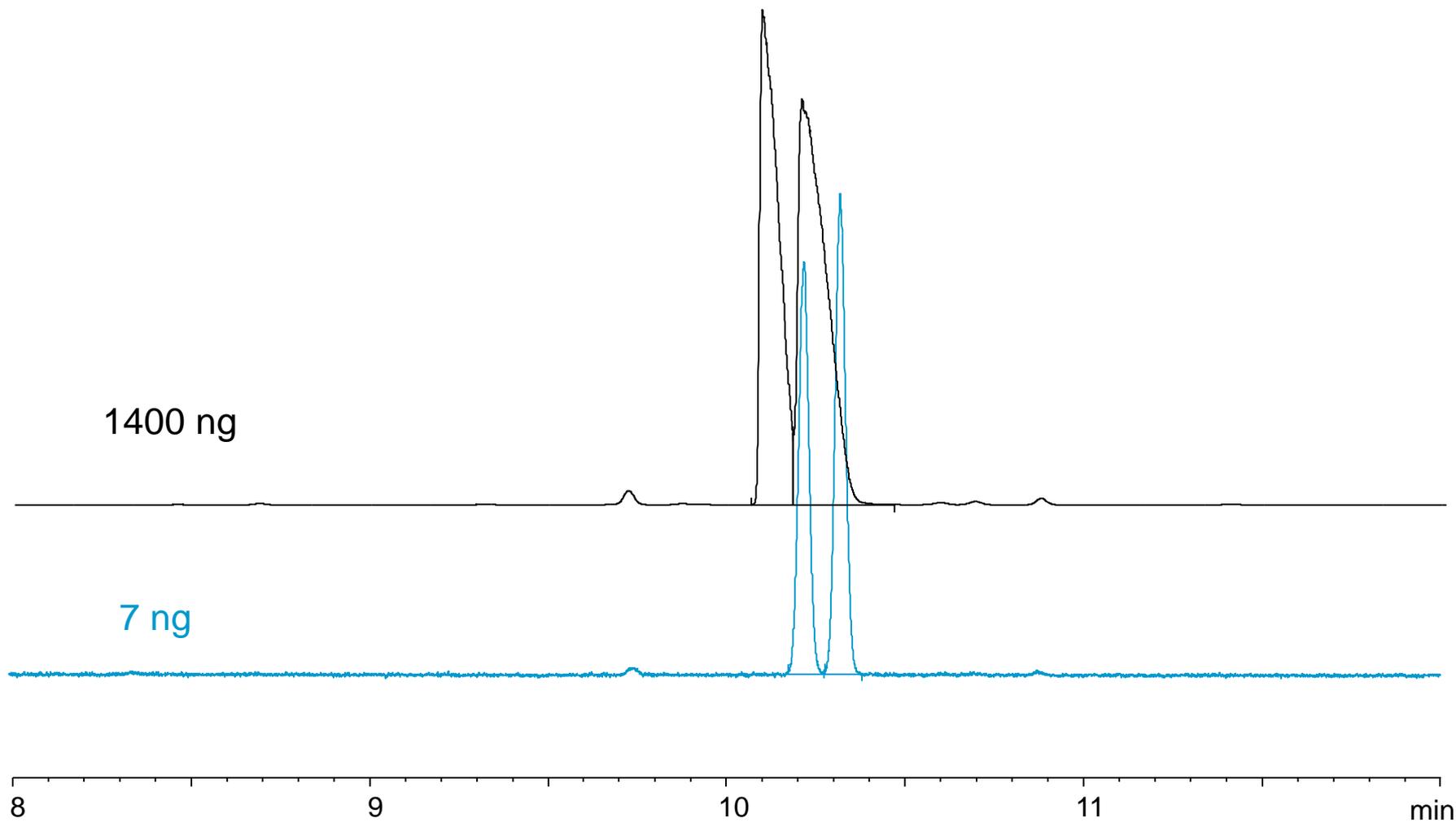
Separation
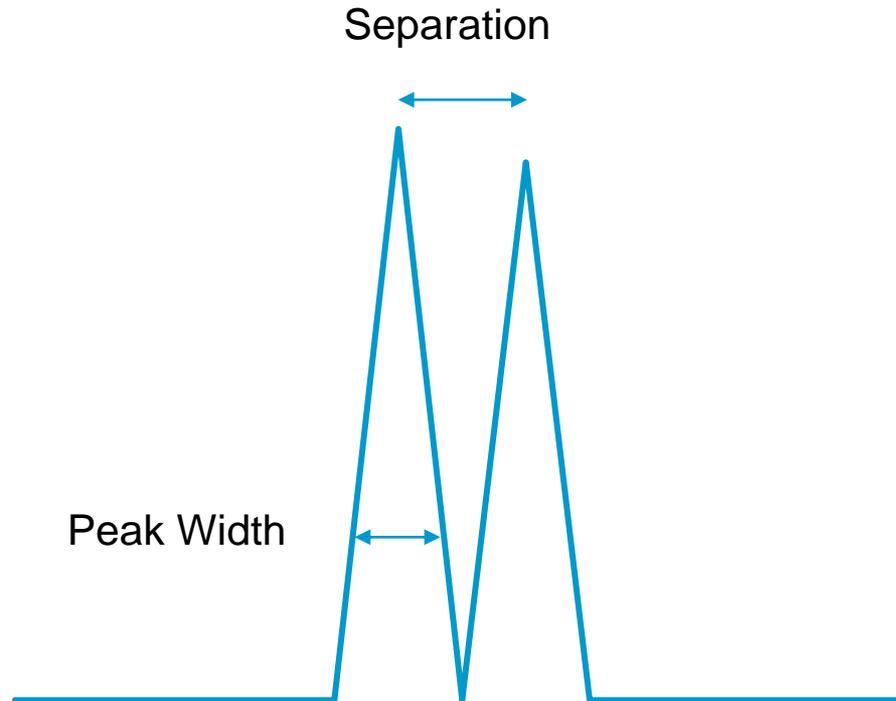
Peak Width

Resolution is a function of separation and peak width

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Loss of Resolution - Separation Decrease

COLUMN

-Different column temperature

-Contamination (more phase?)

-Matrix components co-eluting

-Different column phase?

Separation

Peak Width

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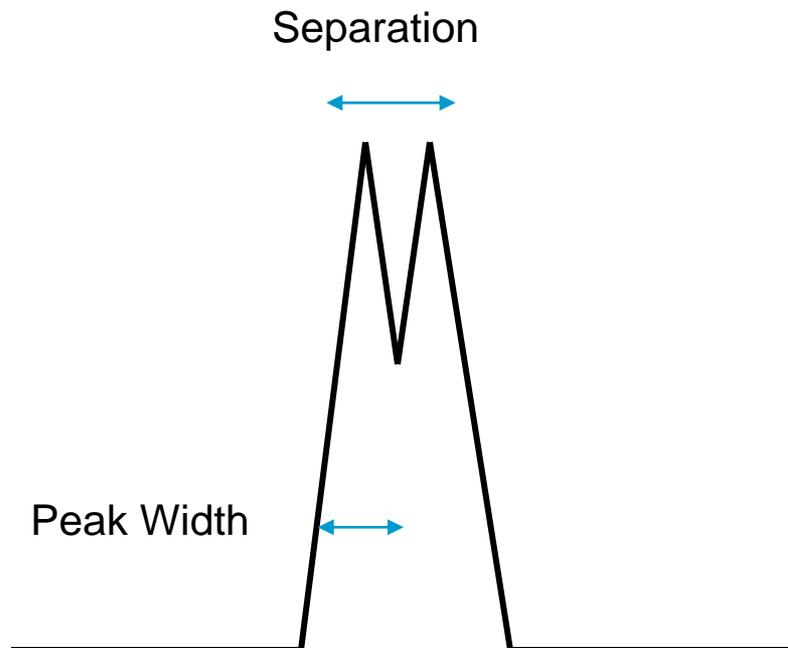
Loss of Resolution - Peak Broadening

FLOW

-Change in carrier gas velocity

-Make-up gas

COLUMN

-Contamination

-Phase degradation

INJECTOR (efficiency)

-Settings, Liner, Installation, etc.

Separation

Peak Width

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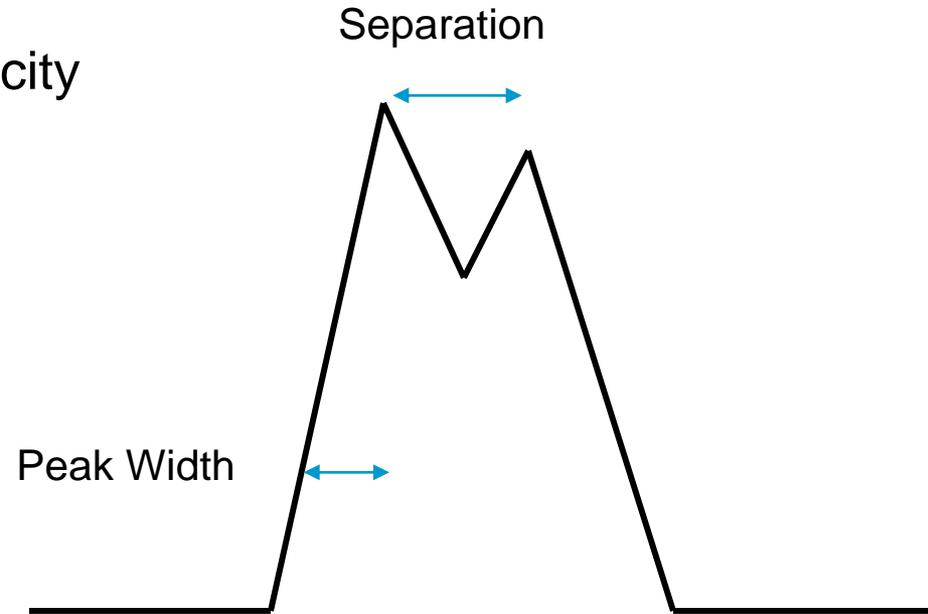
Baseline Disturbances

Sudden Changes, Wandering, or Drifting

WANDER
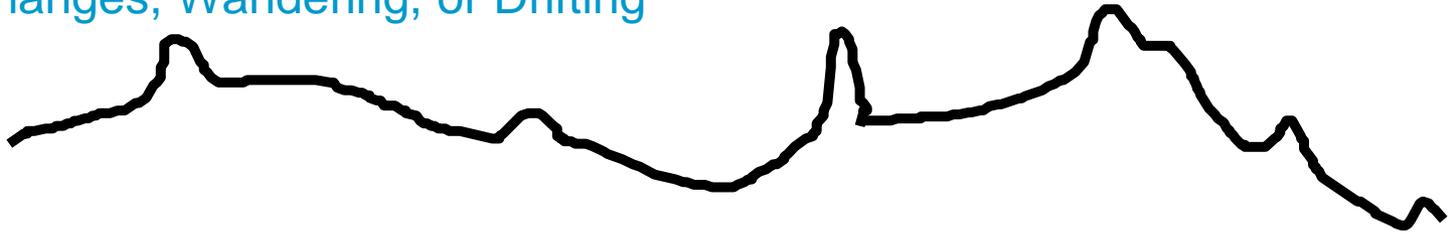
COLUMN or DETECTOR

-Not fully conditioned or stabilized (electronics)

-Contamination

FLOW

-Changes in carrier and/or detector gas flows

-Valves switching, leaks

DRIFT

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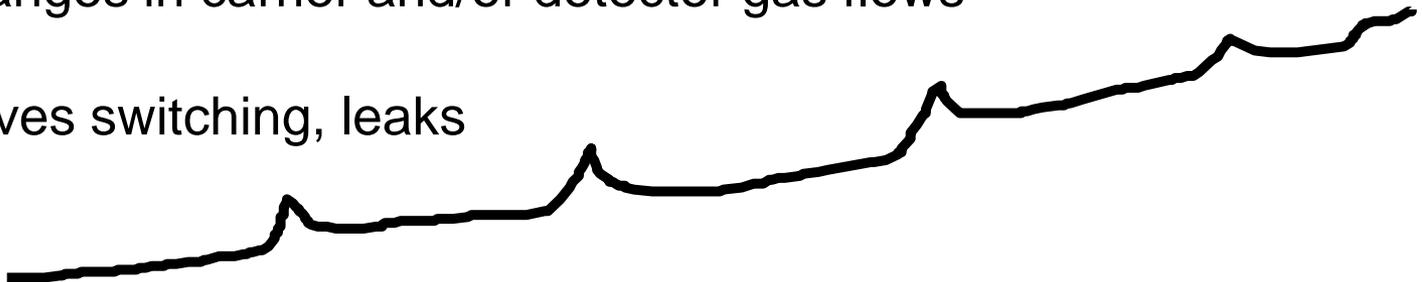
Noisy Baseline

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

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Spiking Baseline
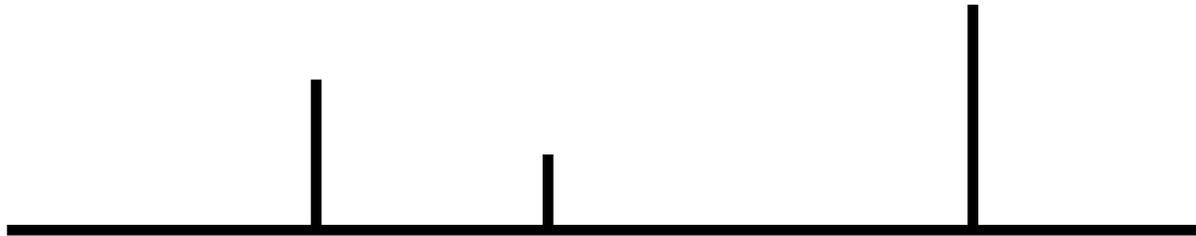
DETECTOR

-Particles entering the detector

-Random: poor connection

-Regular: nearby "cycling" equipment (electronics)

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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

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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*

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Generating a Bleed Profile

Produce when the column is new (for future reference) when there is a baseline problem
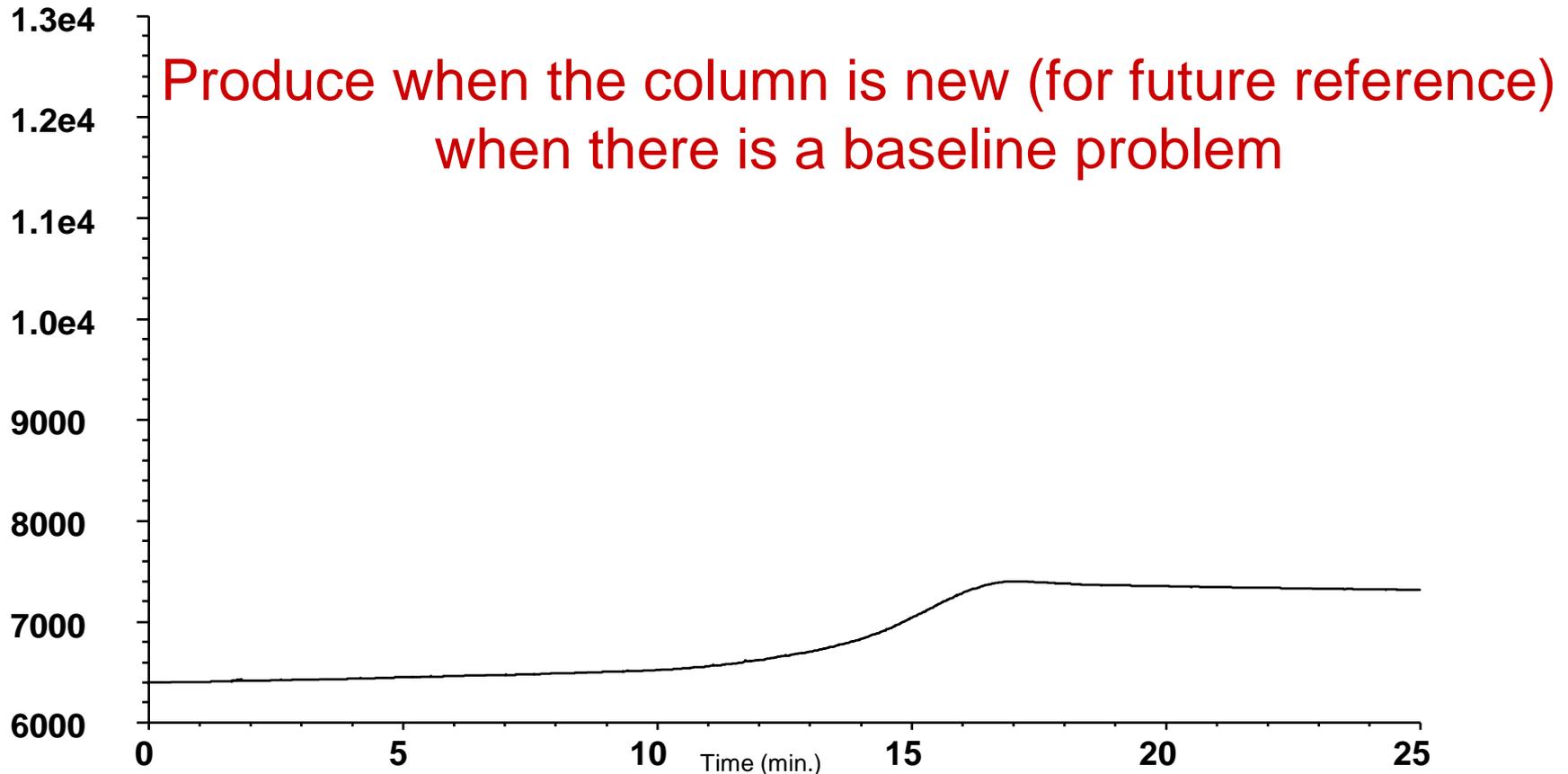
*DB-1 30m x .32mm I.D., .25µm
Temperature program // 40°C, hold 1 min // 20°/min to 320°C, hold 10 min.

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Non-Retained Peak Shapes

Used to Check Flowpath
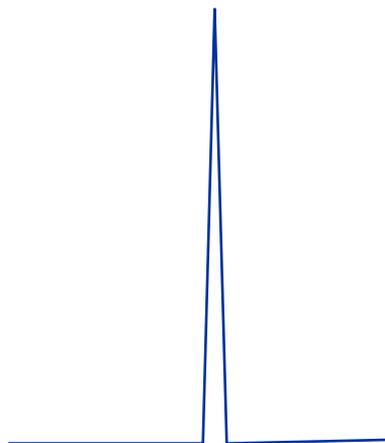
Good Installation
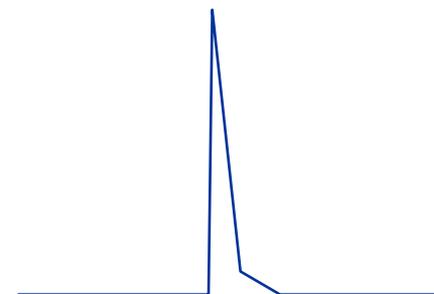
Improper Installation or Injector Leak

Potential problems:

Injector or septum leak

Too low of a split ratio

Liner problem
(broken, leaking, misplaced)

Column position in injector and detector

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Test Mix

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

Analyst: BAO\GC36B
Y-Scale Max: 75pA
Base Axis: 7.0pA

Test Conditions

Inlet: Split (250°C)   Detector: FID (320°C)

Carrier Gas: Hydrogen   Flow: 37.3 cm/sec (1.8 ml/min)

Holdup Compound: Methane   (0.671-min)

Temperature Program: Isothermal at 110°C

325°C
Spec: 4.0 pA
Meas: 1.0 pA

110°C

Retention Time (min)

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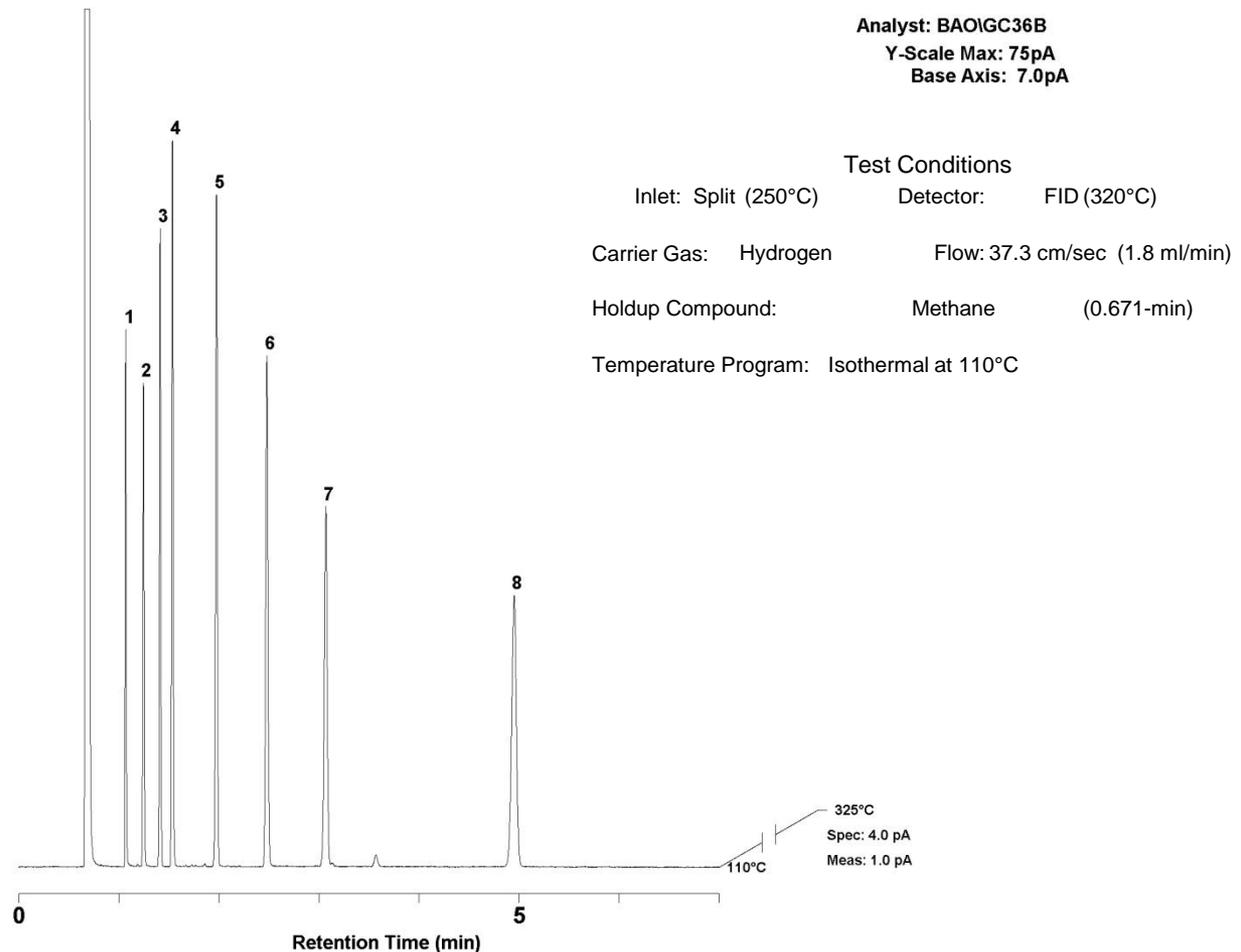
Test Mixture Components

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

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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

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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

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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

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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*

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Jumper Tube Test

Purpose

Helps to locate the source of contamination or noise

Isolates GC components

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Jumper Tube Test

Isolate the Detector

Remove column from the detector

Cap detector and turn on

Blank run

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Jumper Tube Test

Isolation of Detector - Results

Detector OK

Detector is the problem

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Jumper Tube Test

Isolate the Injector

Connect the injector and detector

-   1-2 meters deactivated fused silica tubing

Turn on carrier gas

Blank run

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Jumper Tube Test

Isolate the Injector - Results

Injector OK
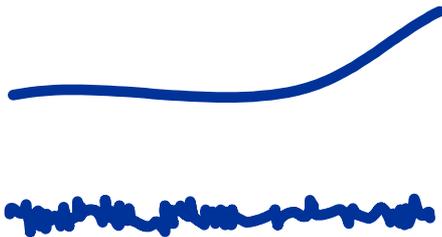
Injector, lines or carrier gas contaminated

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Jumper Tube Test

Isolate the Column

Reinstall the column

Setup as before

Blank Run

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Jumper Tube Test

Isolate the Column - Results

Problem returns: It's the column

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

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And Now Let's do Some

TROUBLESHOOTING

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Troubleshooting-Example #1

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A Real Troubleshooting Example

No Peaks

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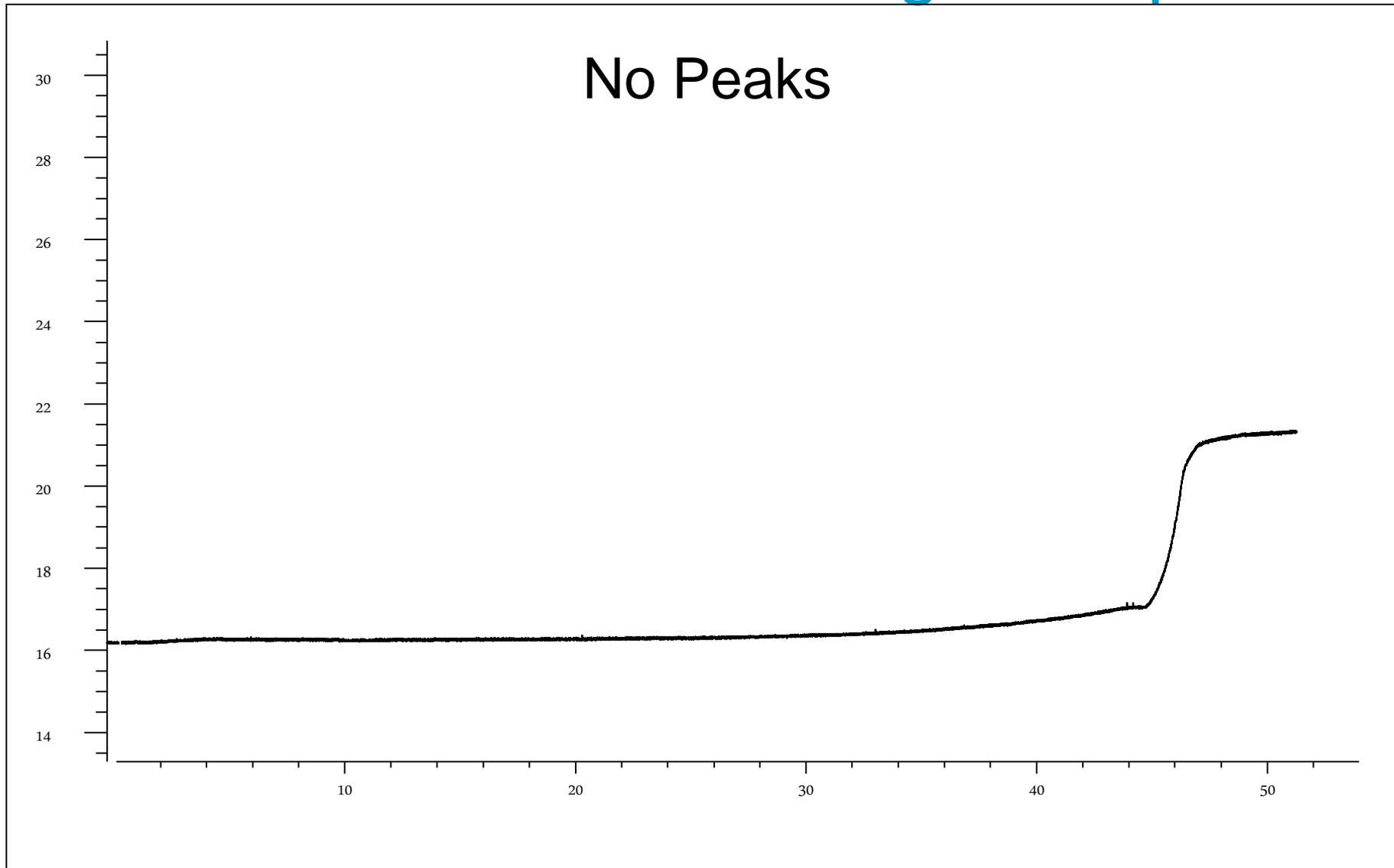
Logical Steps Taken to Find Peaks
(most of our problems are leaks and plugs)

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*

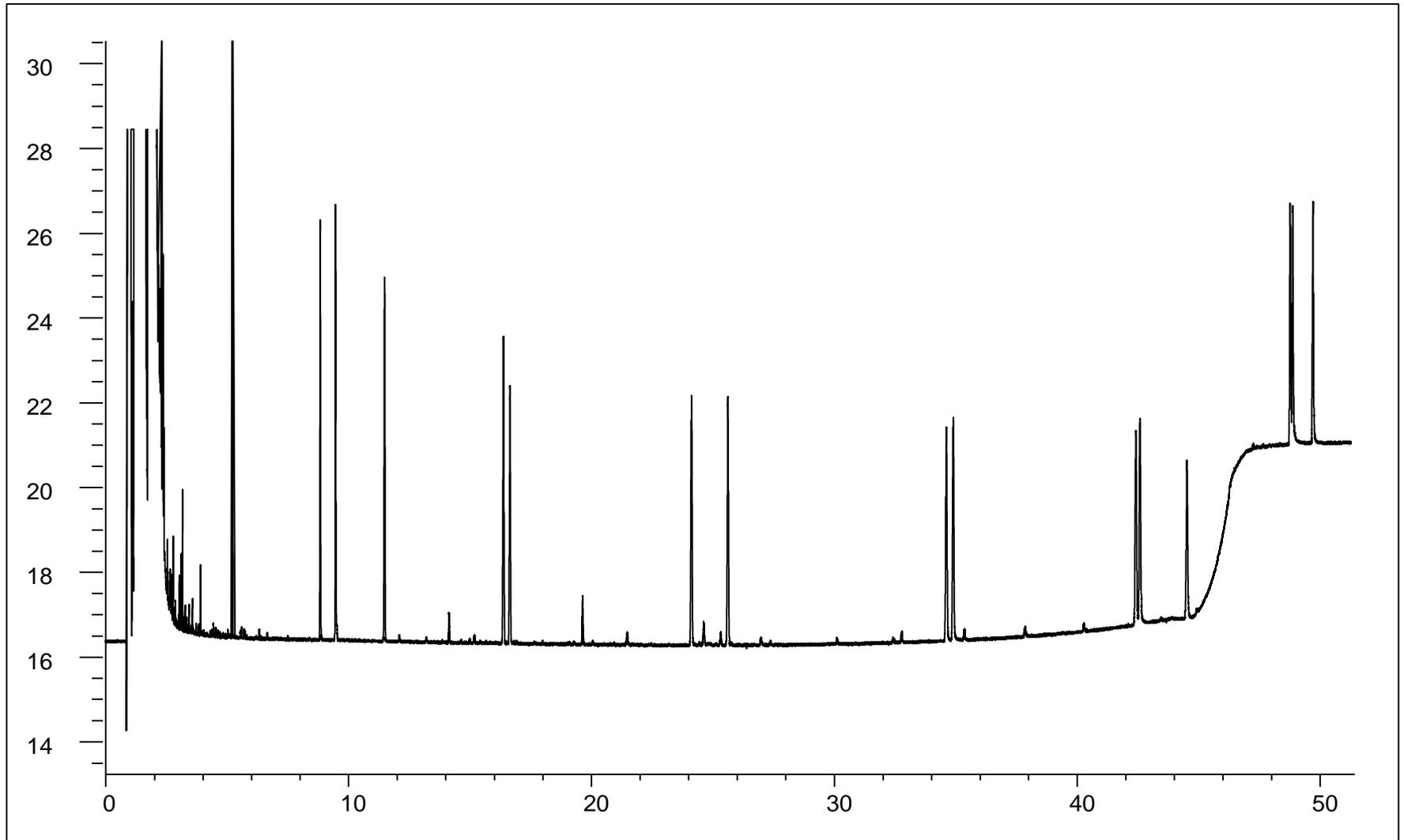▪ *Hypothesis: Sample not getting on column-syringe plugged?*

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
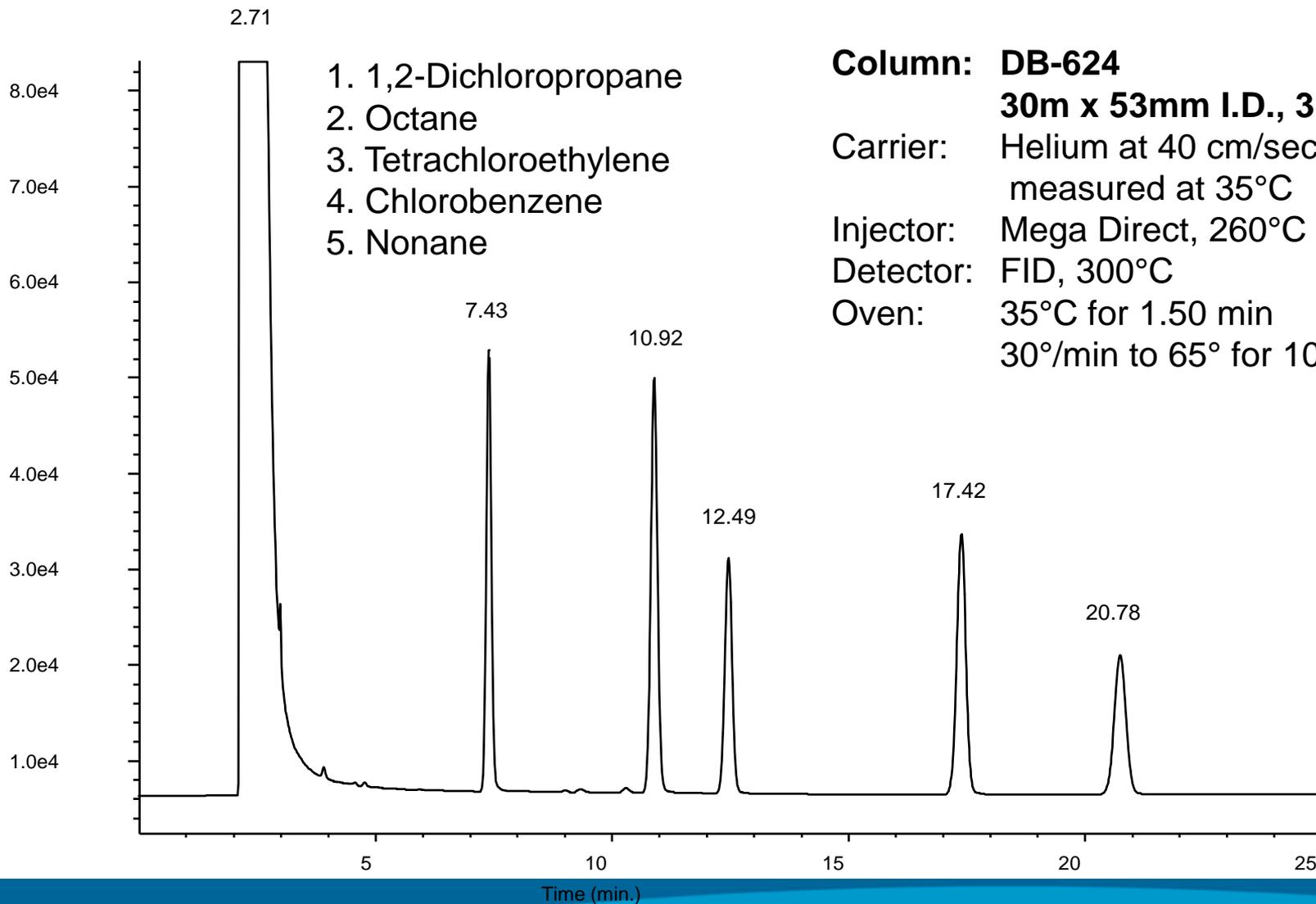
Reassemble the Injector & Re-inject

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Peaks !!

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Troubleshooting-Example #2

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DB-624 COLUMN

QC Test Mix

1. 1,2-Dichloropropane
2. Octane
3. Tetrachloroethylene
4. Chlorobenzene
5. Nonane
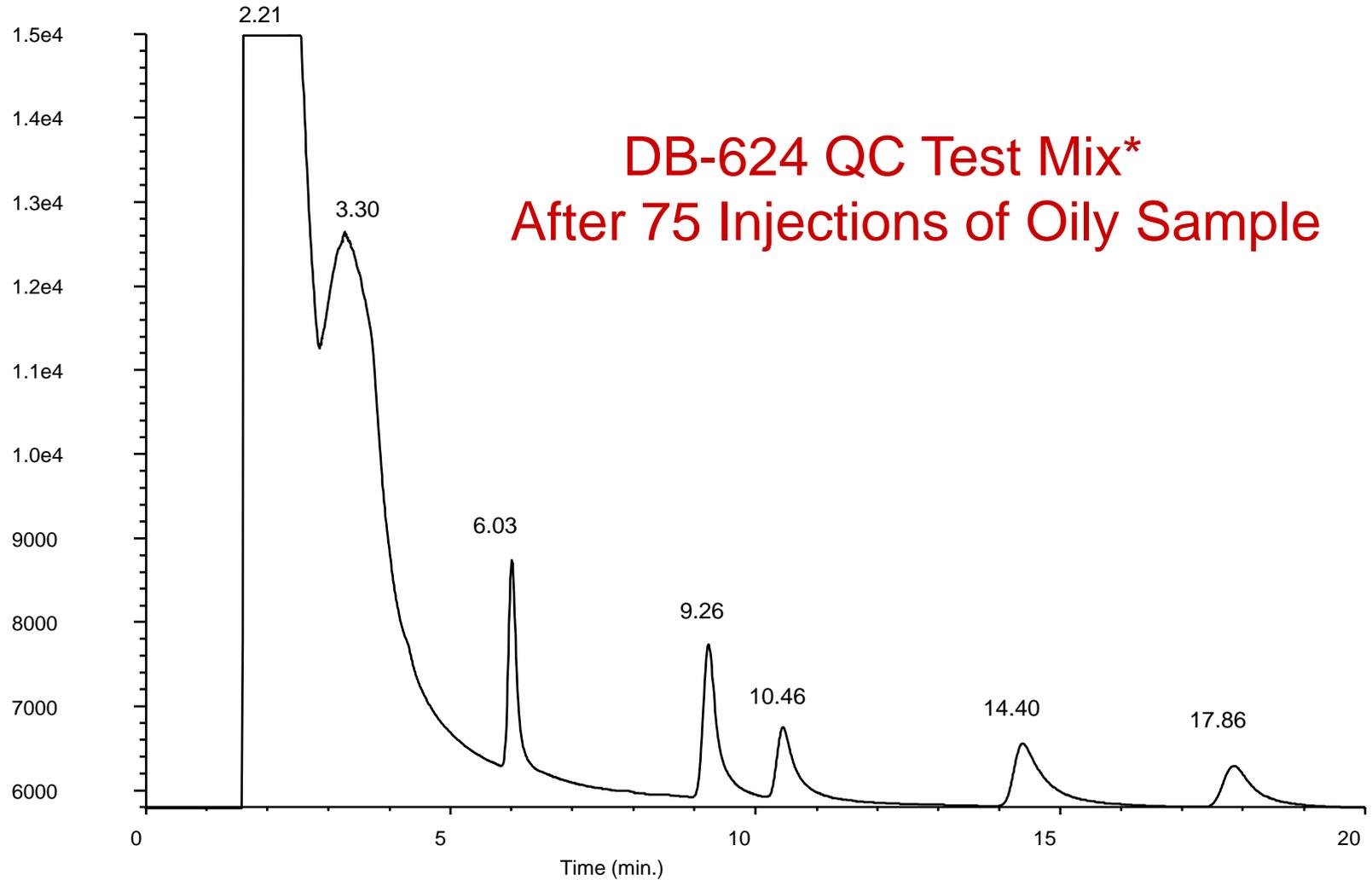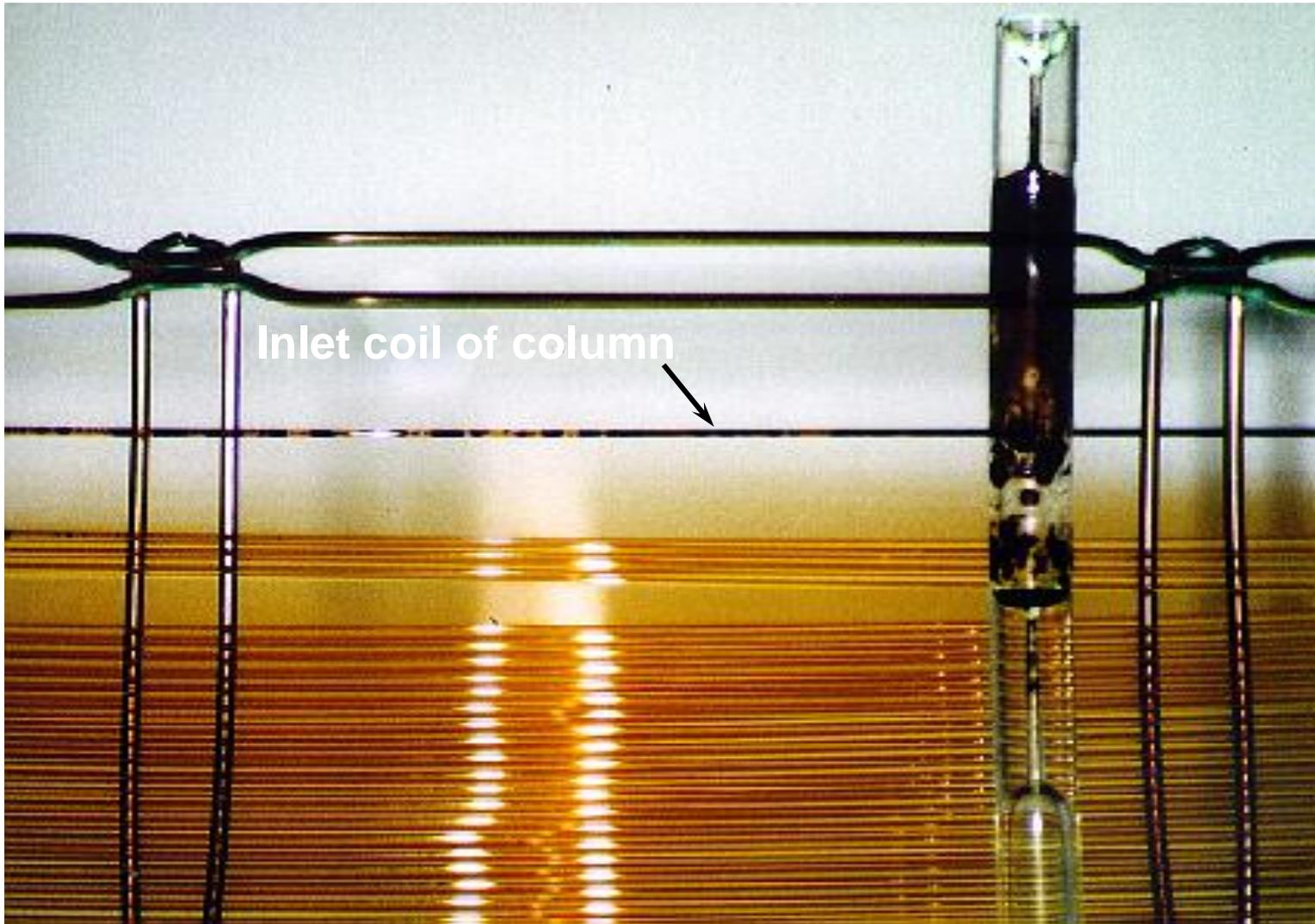
Column: **DB-624**
30m x 53mm I.D., 3.0μm
Carrier: Helium at 40 cm/sec
measured at 35°C
Injector: Mega Direct, 260°C
Detector: FID, 300°C
Oven: 35°C for 1.50 min
30°/min to 65° for 10 min

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Example of Column Contamination

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

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Column and Liner Contamination

Inlet coil of column

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Example of Column Contamination

Removed 1 1/2 m from injector end *
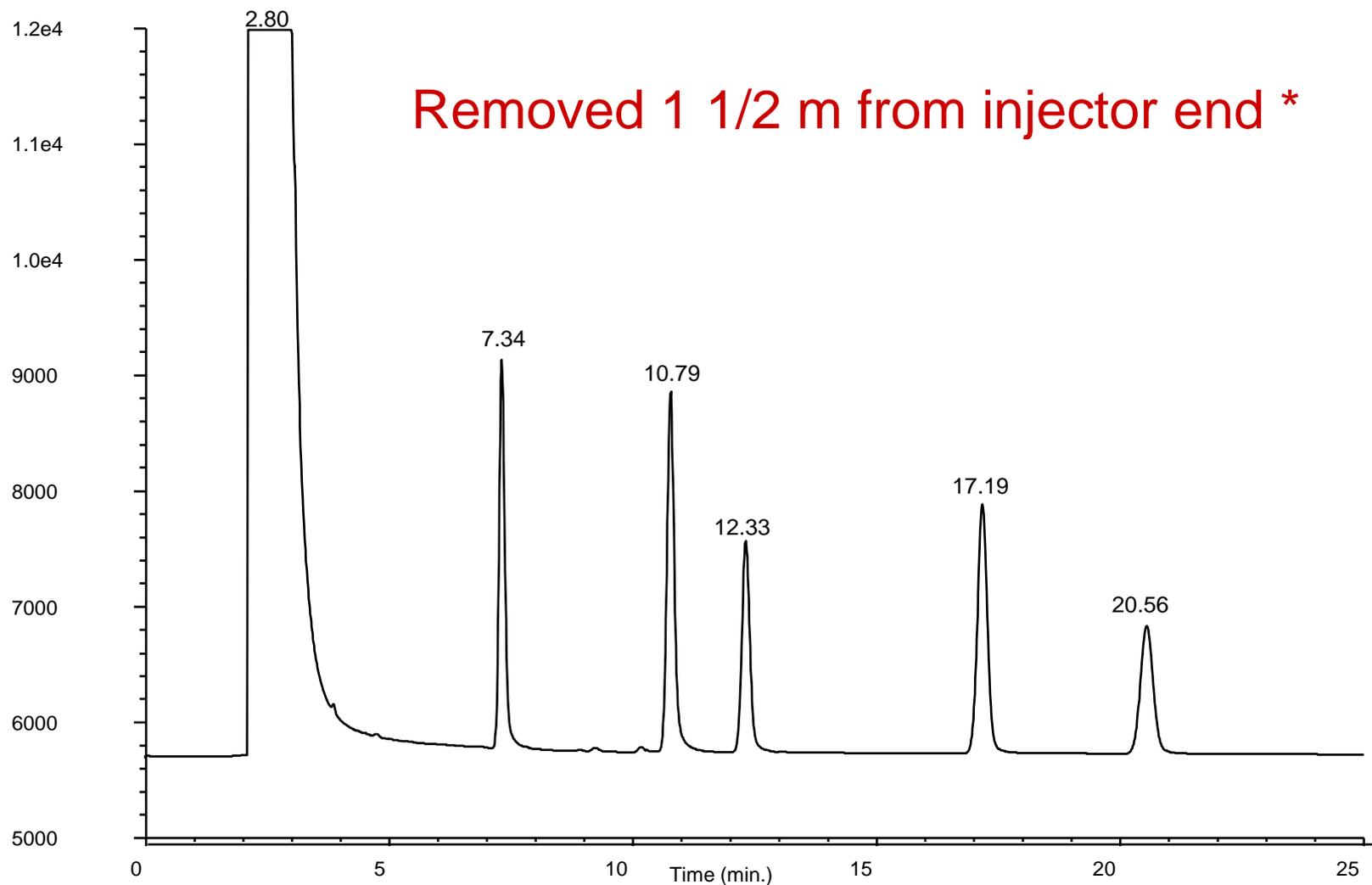
*Before Column rinse and bake
Temperature program // 35°C hold 1.50 min // 30°/min to 65°C, hold 10 min

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Looks Fixed Doesn't it?

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Example of Column Contamination

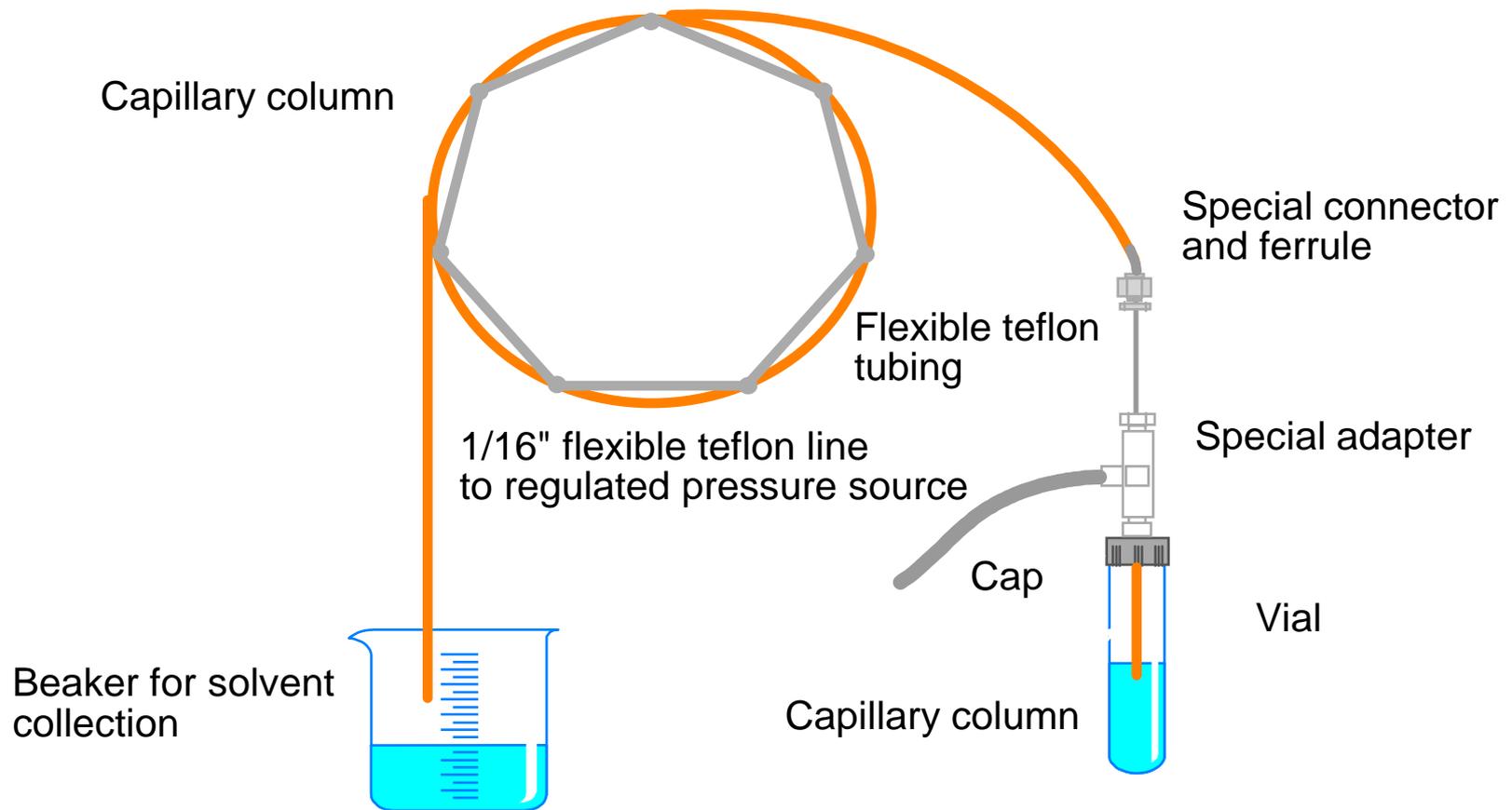**1 1/2 mtrs removed***
QC Test mix to Upper Temperature Limit
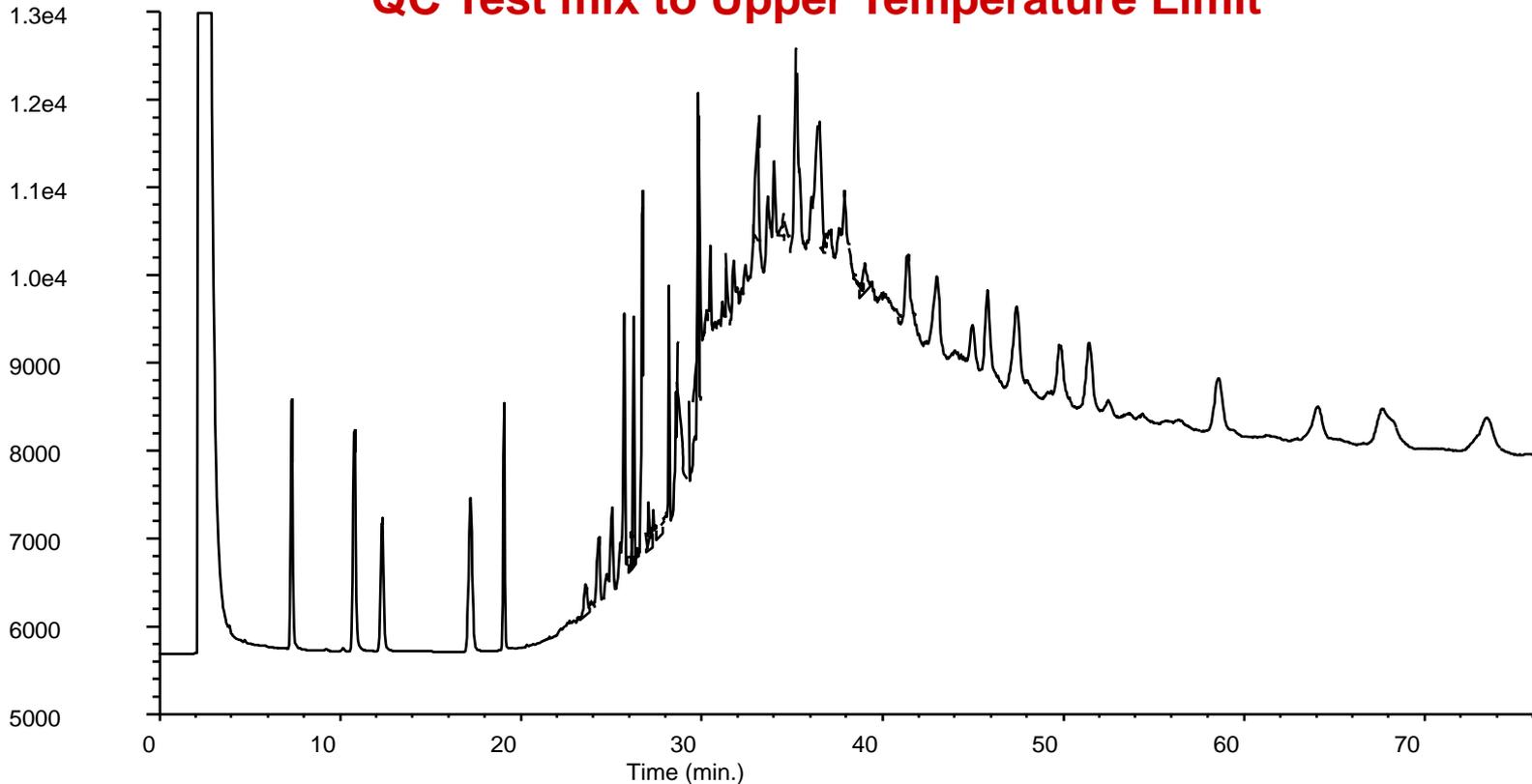
*Before Column rinse and bake.
Temperature program // 35°C, hold 1.50 min // 30°/min to 65°C,
hold 15 min // 20°/min to 260°, hold 50 min

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Backflush Column

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

Capillary column

Special connector and ferrule

Flexible teflon tubing

1/16" flexible teflon line to regulated pressure source

Special adapter

Cap

Vial

Beaker for solvent collection

Capillary column

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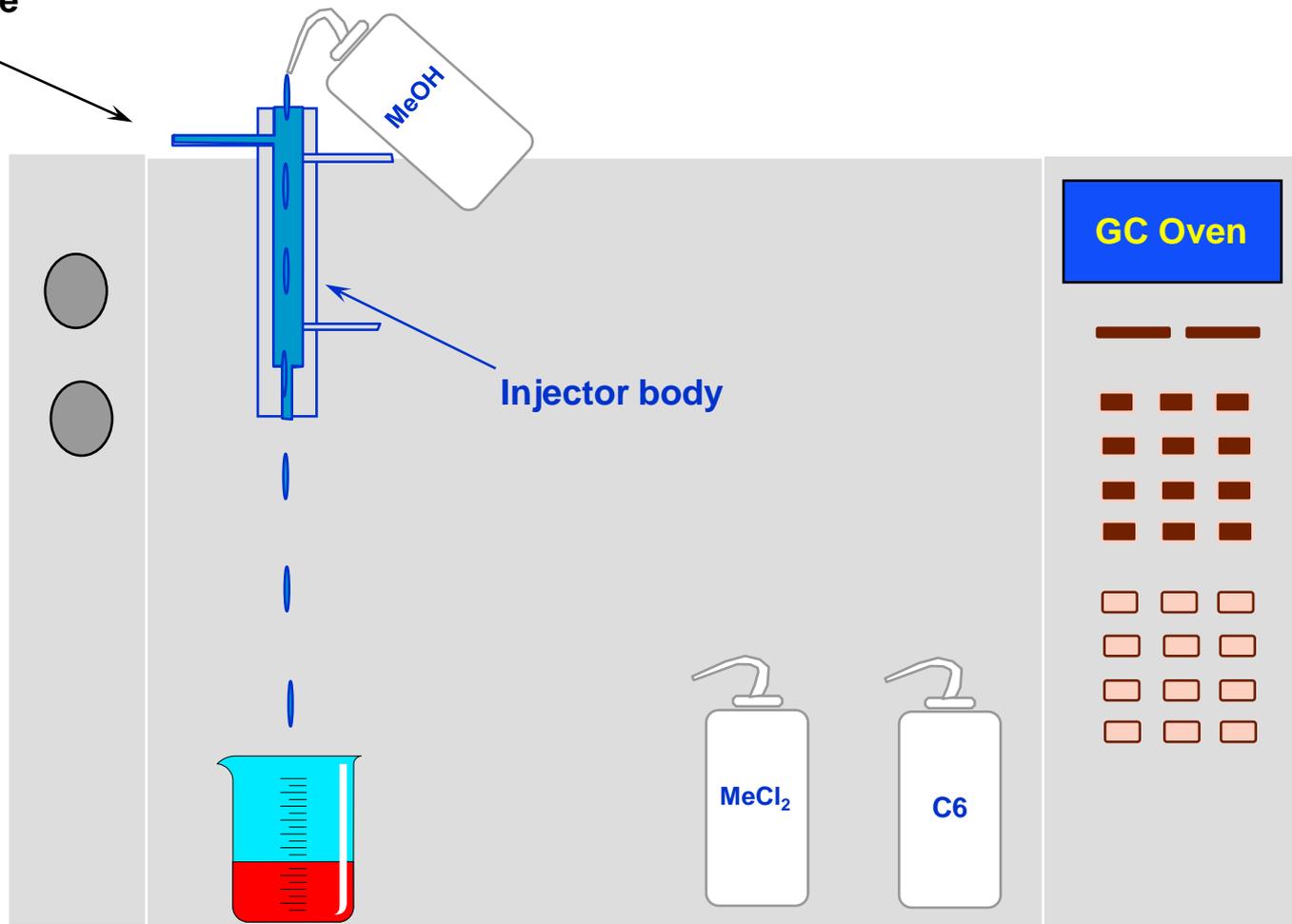# Jumper Tube Test

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.

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Contaminated Inlet

Jumper Tube Test*

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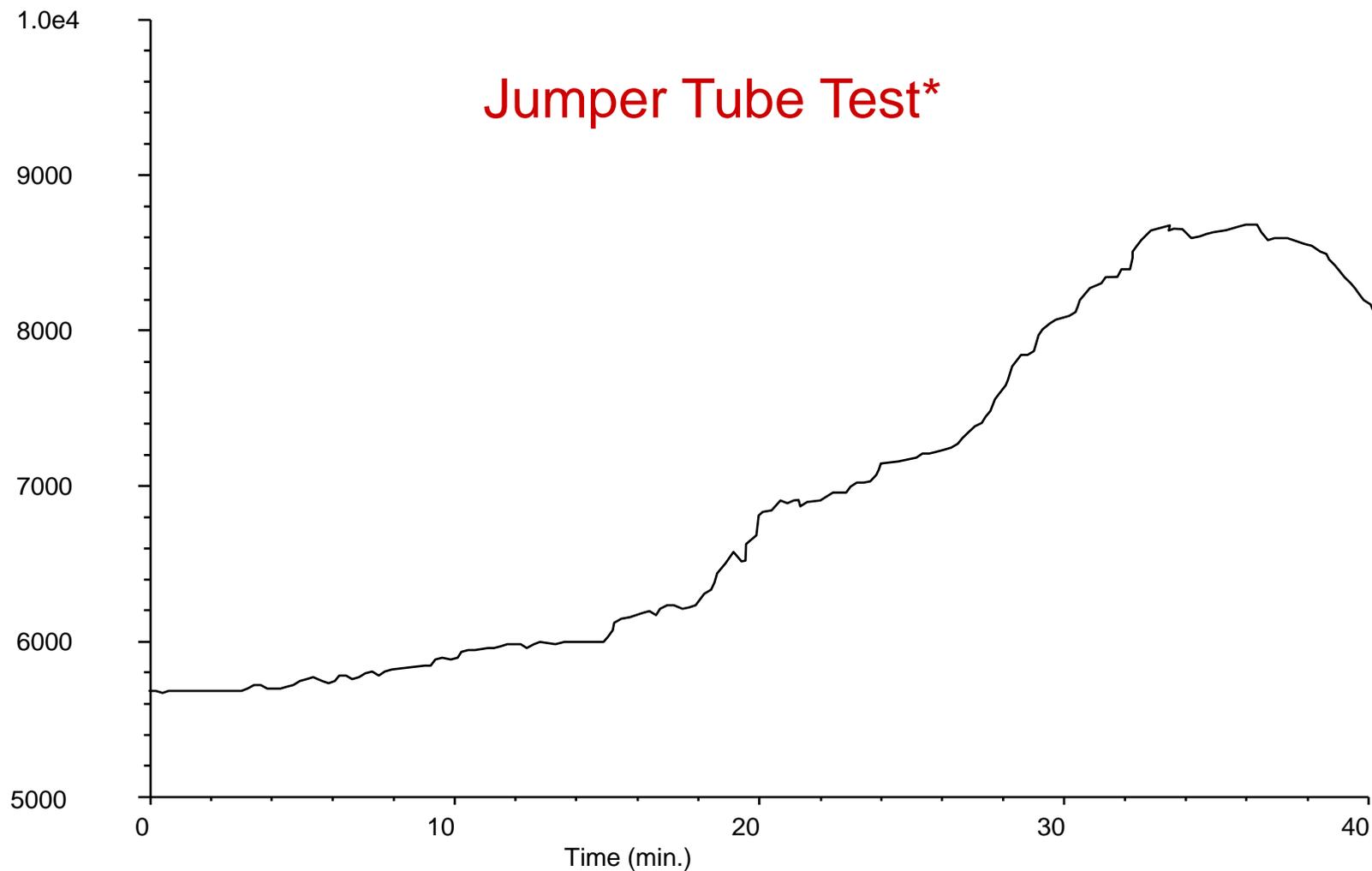
Rinsing Injector

Carrier gas line

MeOH

GC Oven

Injector body

MeCl$_2$

C6

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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.

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Remember

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

Multiple cause and effect

Do not change too many variables at once

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TECHNICAL SUPPORT

1-800-227-9770, #3, #3, #1

E-mail: gc-column-support@agilent.com

866-422-5571 (FAX)

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