Simple Heart Cutting with Deans Switch and Backflushing with Capillary Flow Technolgy

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Applications Engineer

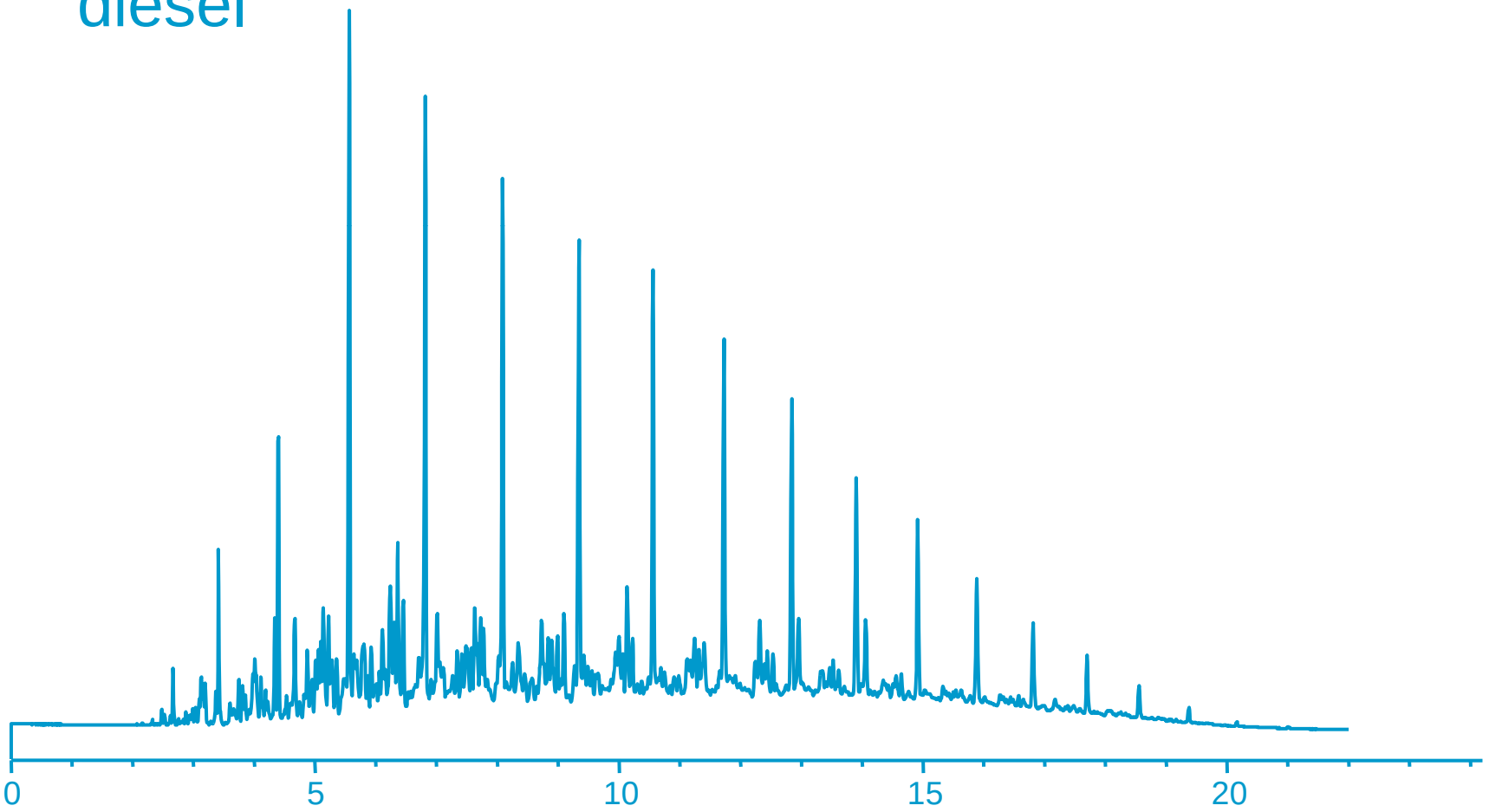
GC or GC/MS Analysis in Complex Matrices

- In complex sample matrices, there are often too many overlapping compounds to allow resolution of the compound(s) of interest, even with the highest resolution columns available.
- Must use some approach which gives *selectivity*

- Selective sample prep like SPE
- Selective stationary phase like Carbowax
- Selective element detector like FPD, AED, NPD etc.
- Spectral detector like GC-MS or GC-IR
- Multidimensional (2-D) GC

Example: Diesel Fuel

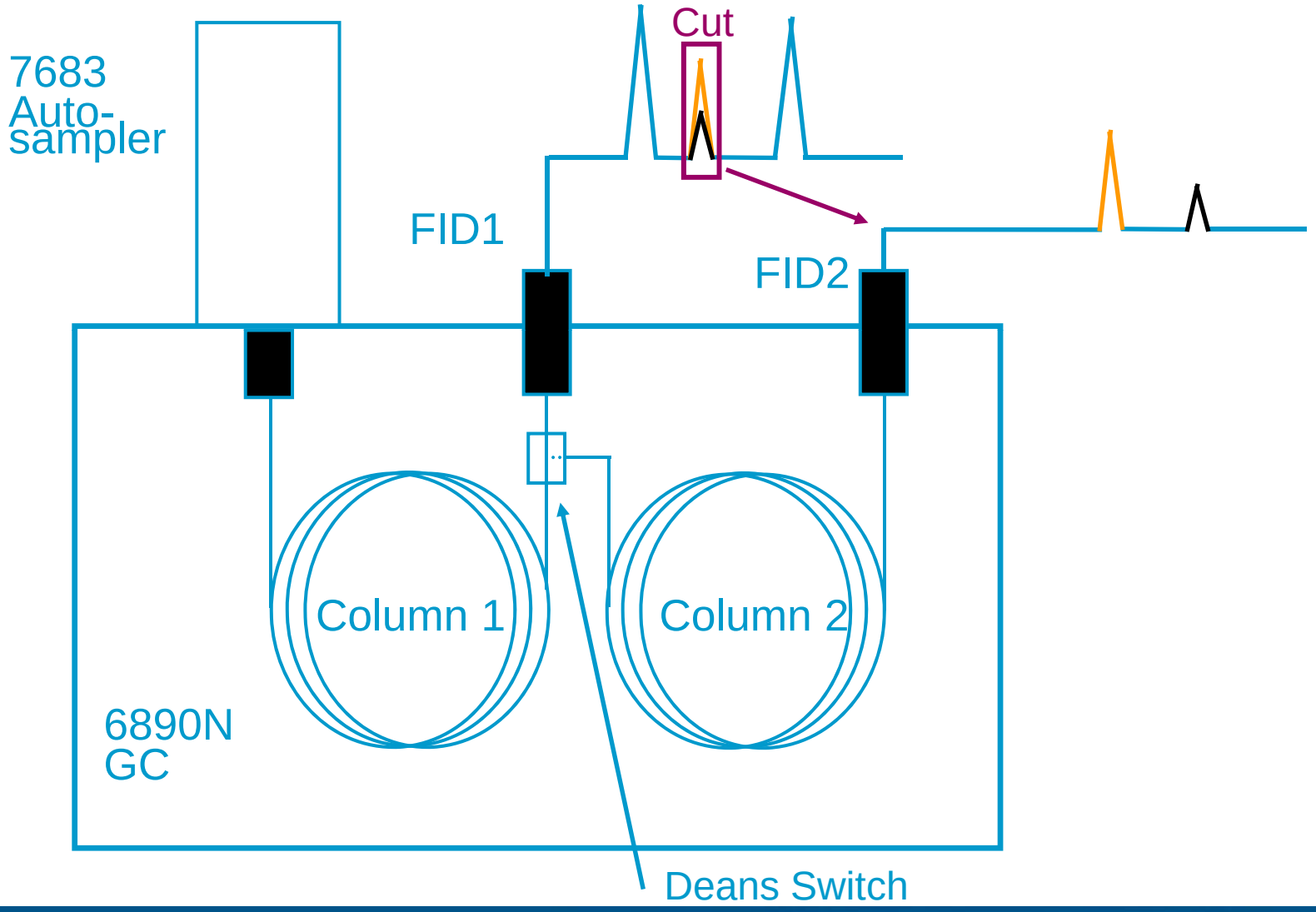
There are *thousands* of compounds in diesel



Multidimensional (2-D) GC

- Very old (>25 yrs) but powerful separation technique
- Based on cutting peak(s) from one GC column onto another with stationary phase of different selectivity
- Compounds that co-elute with analyte on first column separate from analyte on second column
- Example pairs of complimentary phases:
- DB-1 (non-polar) with Innowax (polar)
- TCEP (very polar) with DB-1
- DB-5 (low polarity) with Cyclosil (chiral)

“Simplified” 2-Dimensional GC



Early 2-D GC Had Some Challenges

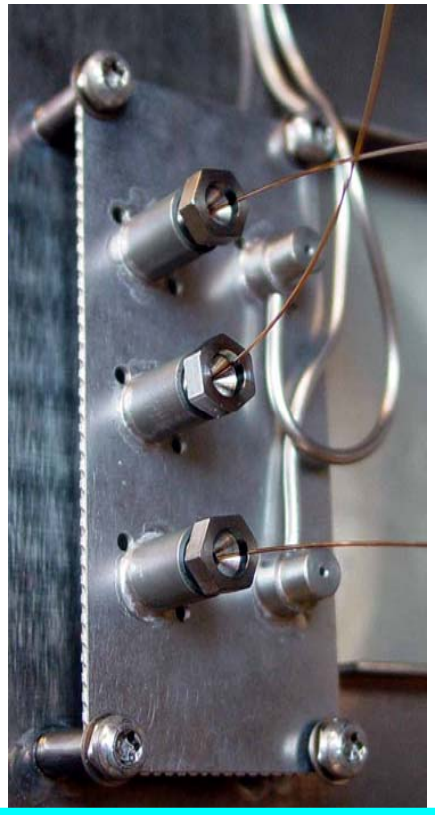
- Early systems were difficult to use. “2-D” often implied “2-difficult”
- Column connections: inertness, dead volume
- Balancing gas flows: complex flow system, needle valves
- Retention time drift: wide cut windows, lower resolution
- Inertness problems: loss of polar analytes
- High cost:
  - Multiple GC ovens
  - Cryogenic focusing devices

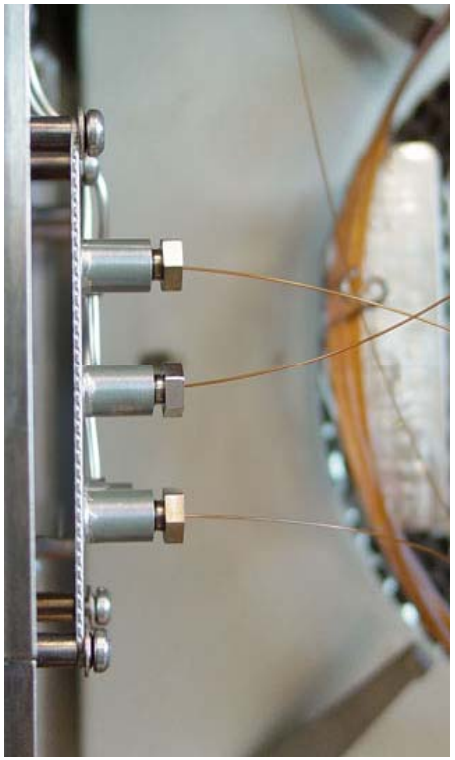
Why 2-D GC? What's Changed?

- 7890 Simplified 2-D GC systems are *much* easier to use
- Column connections are easier, zero dead volume, inert, and reliable
- Balancing gas flows done with EPC and Flow Calculator
- Retention time drift greatly reduced with modern oven and EPC
- Inertness problems with switch hardware eliminated with surface coatings
- Because RT control is so tight and the switch is so quick, multiple ovens and cryo focusing devices can often be avoided

New Deans Switch Design

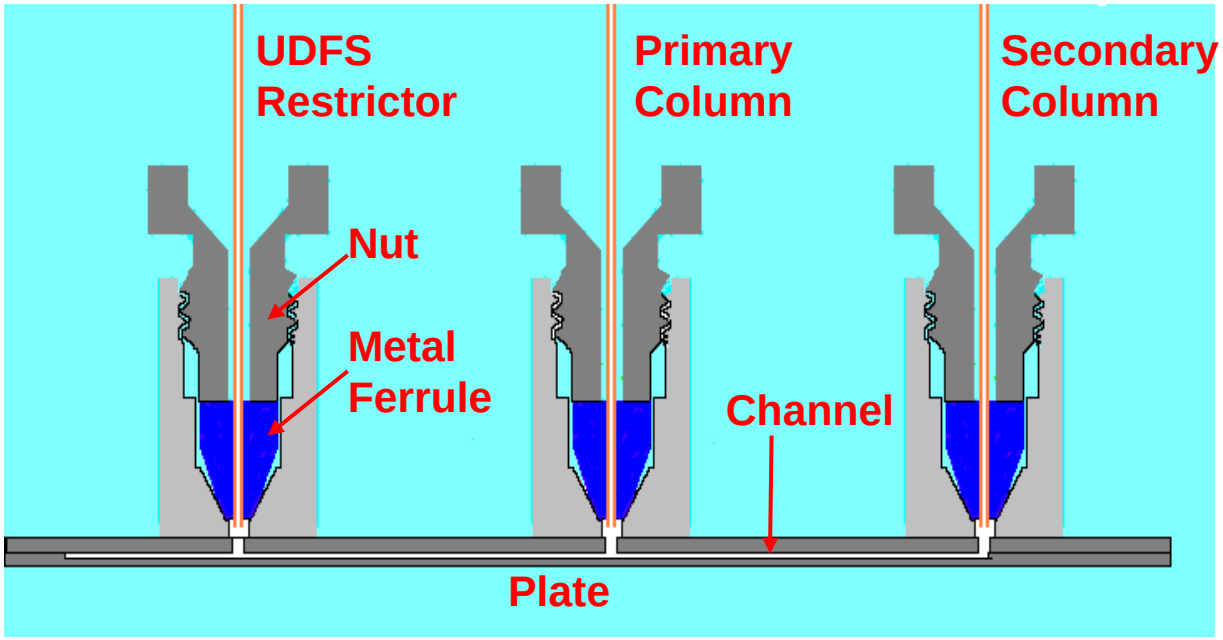
Photolithography and chem-milling technologies used to produce a New Gas Phase Deans Switch





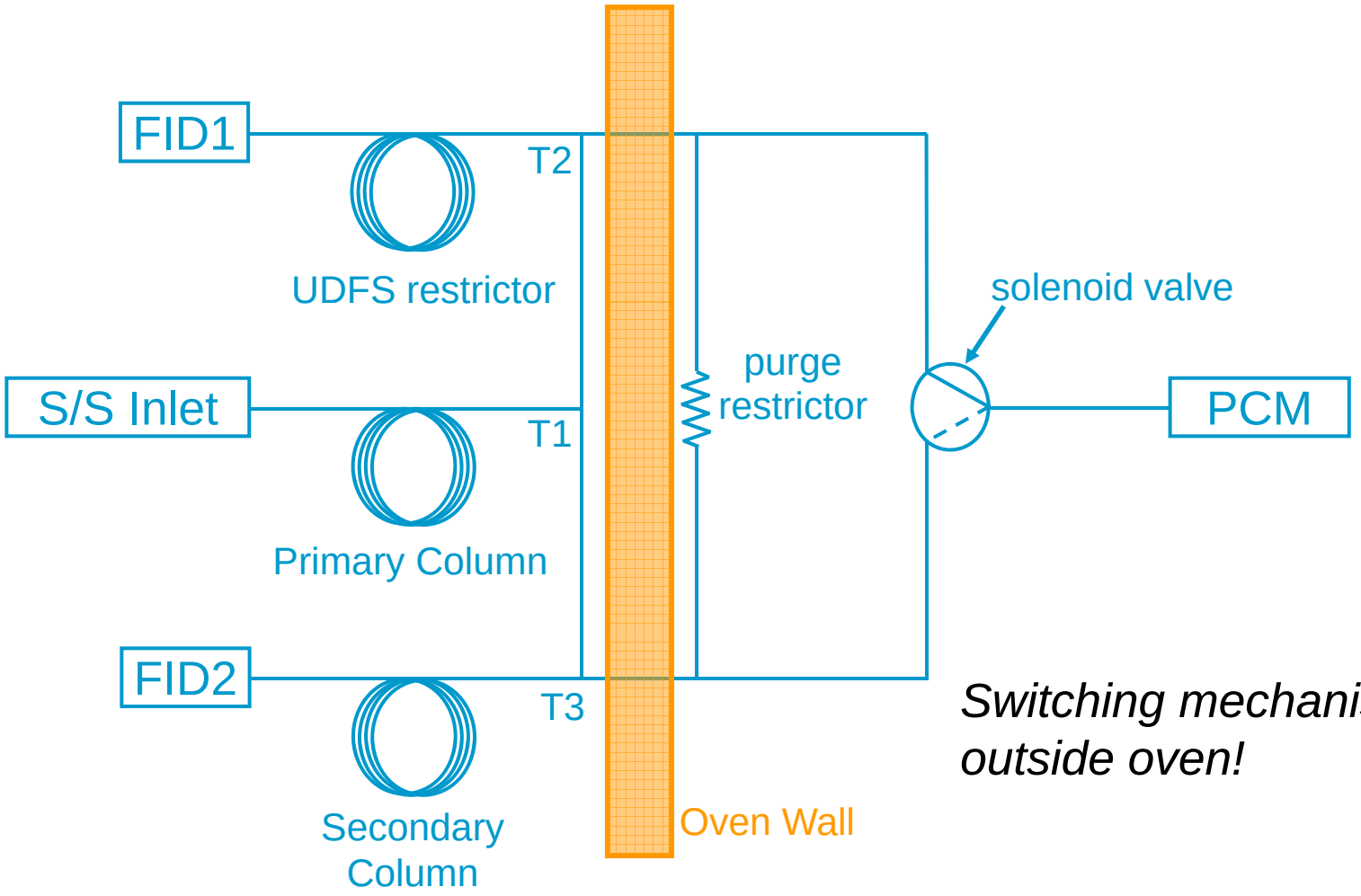
4x less thermal mass than traditional hardware

Connections for Deans Switch



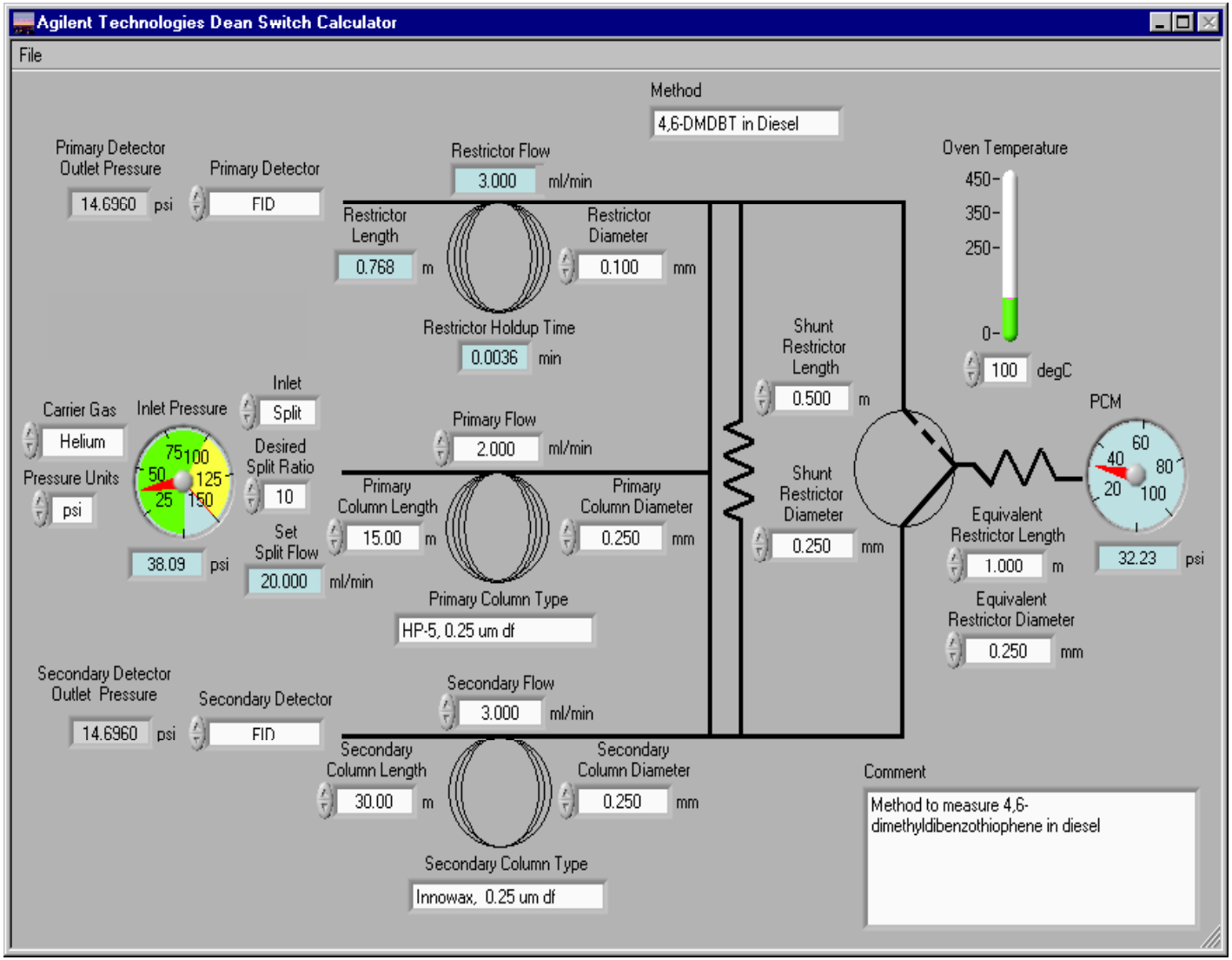
- Simple, easy to make connectors
- A single, special design metal ferrule
  - More inert that graphite/vespel
  - Does not leak at high oven temperature (>400 ^{o}C)

Deans Switch System



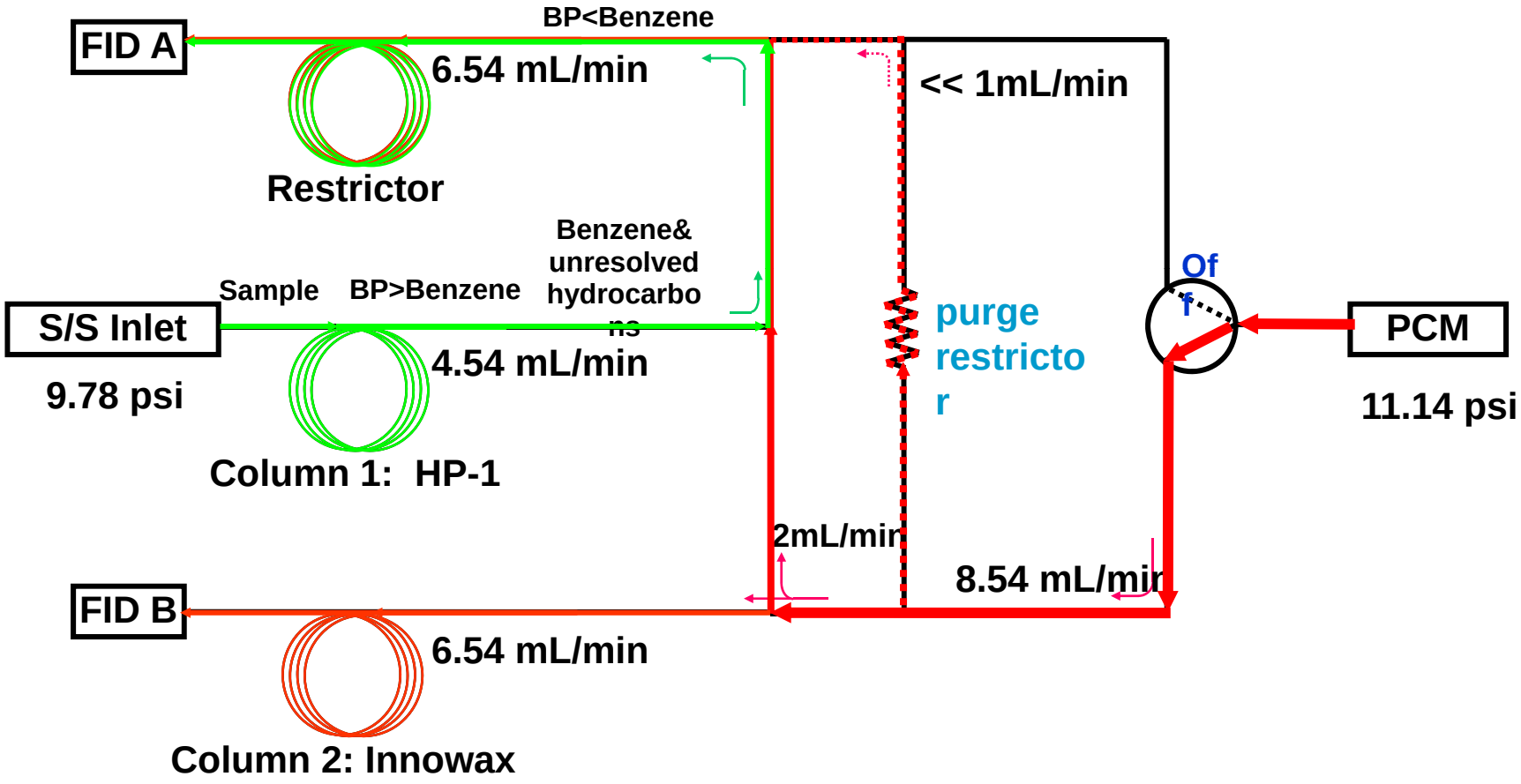
Switching mechanism outside oven!

Calculator to correctly set flows and restrictor size



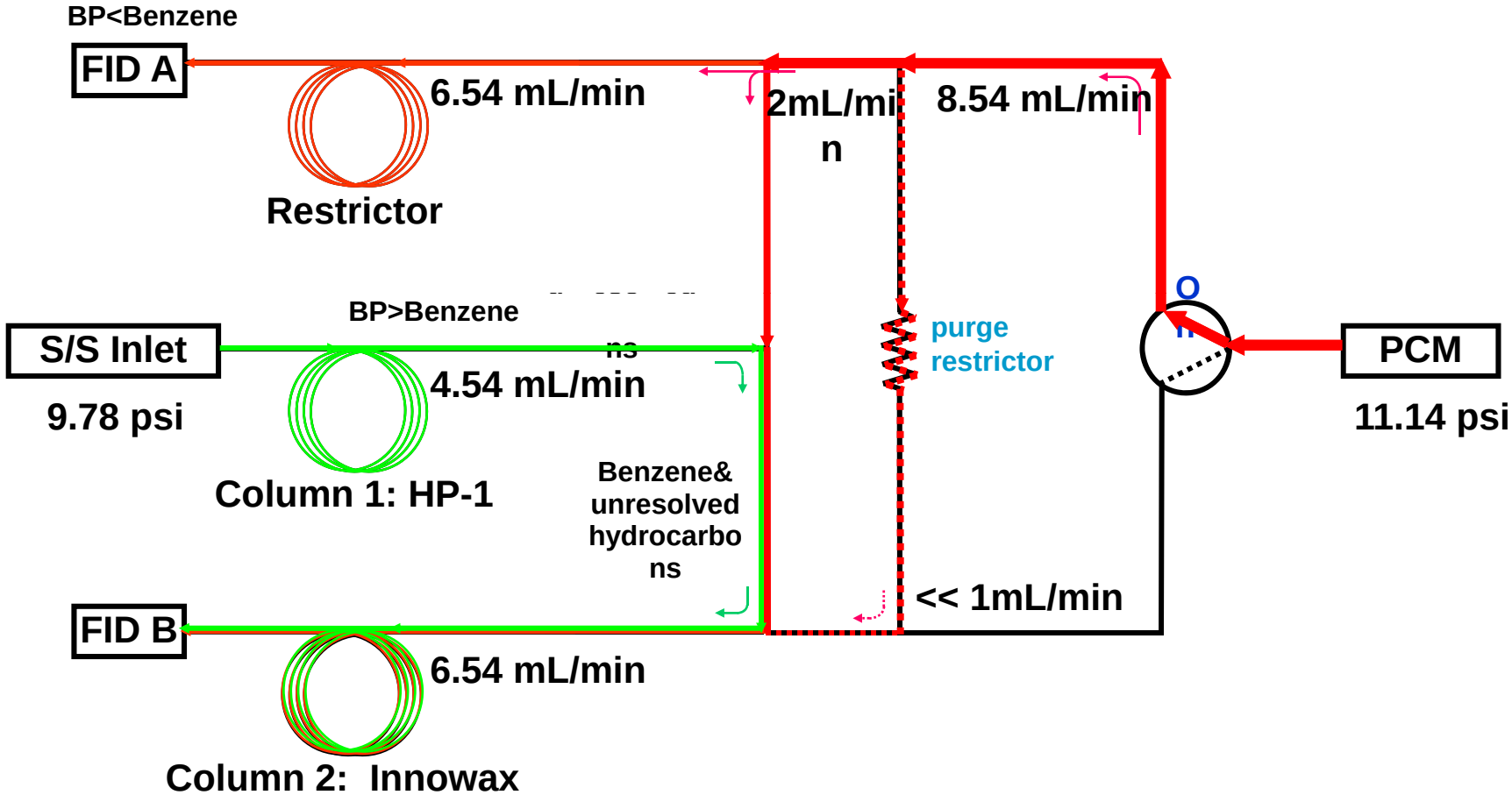
Heart Cutting 2-D GC – How It Works

Valve off, no heart cutting– inject sample, initial separation on column 1



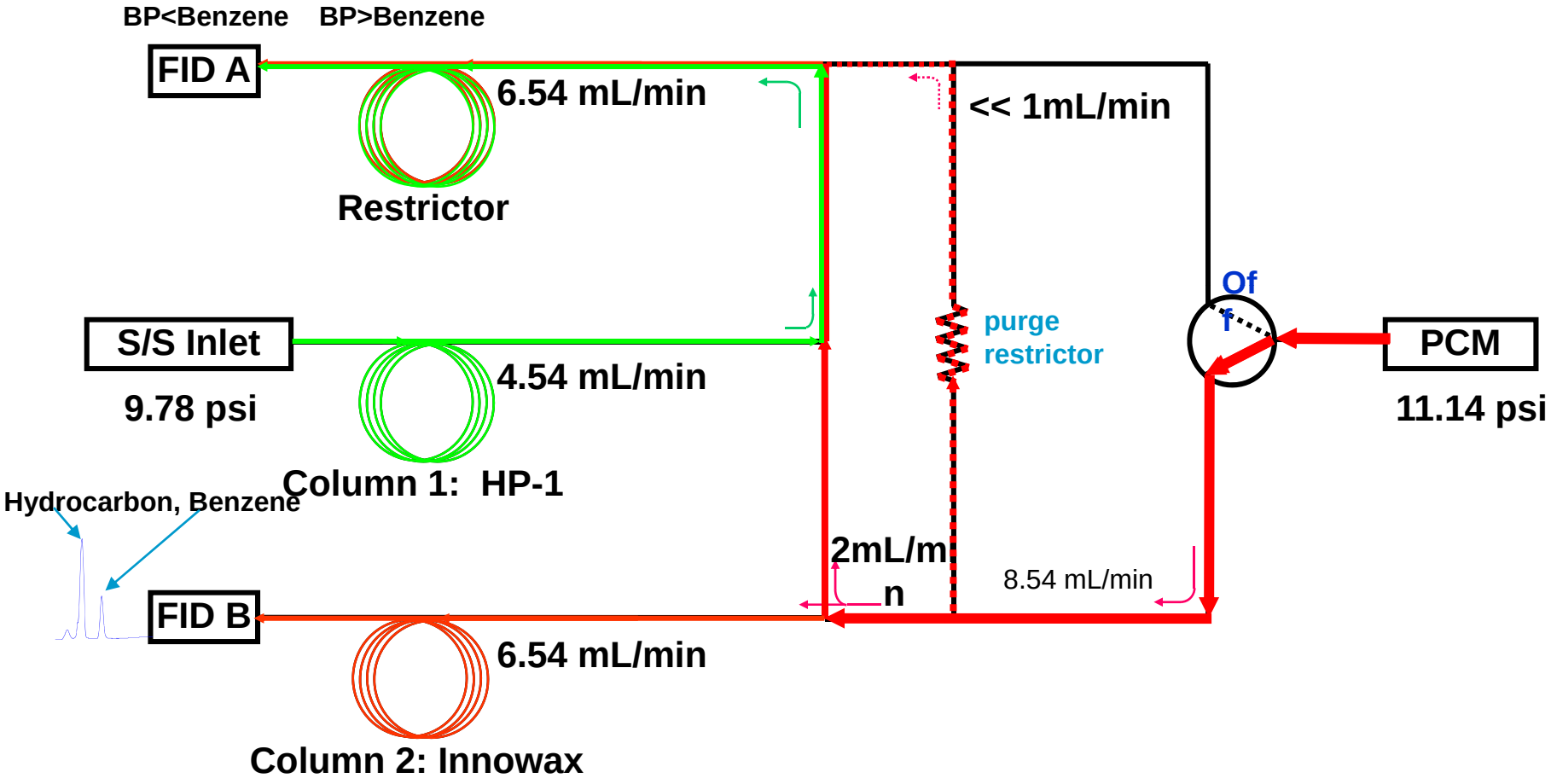
Heart Cutting 2-D GC – How It Works

Valve on – start heart cut from column 1 to column 2



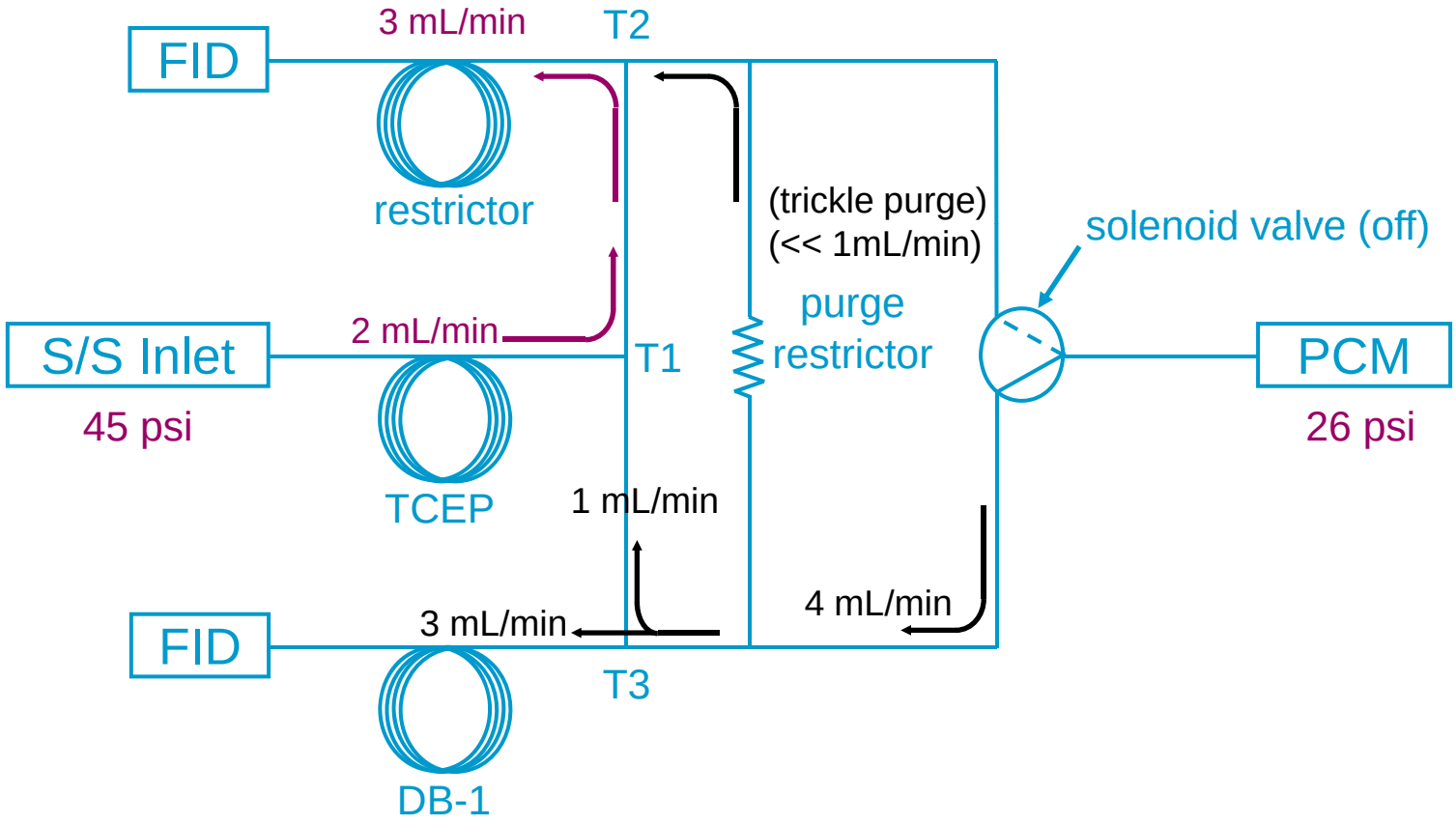
Heart Cutting 2-D GC – How It Works

Valve off – end heart cut, perform 2nd separation on column 2



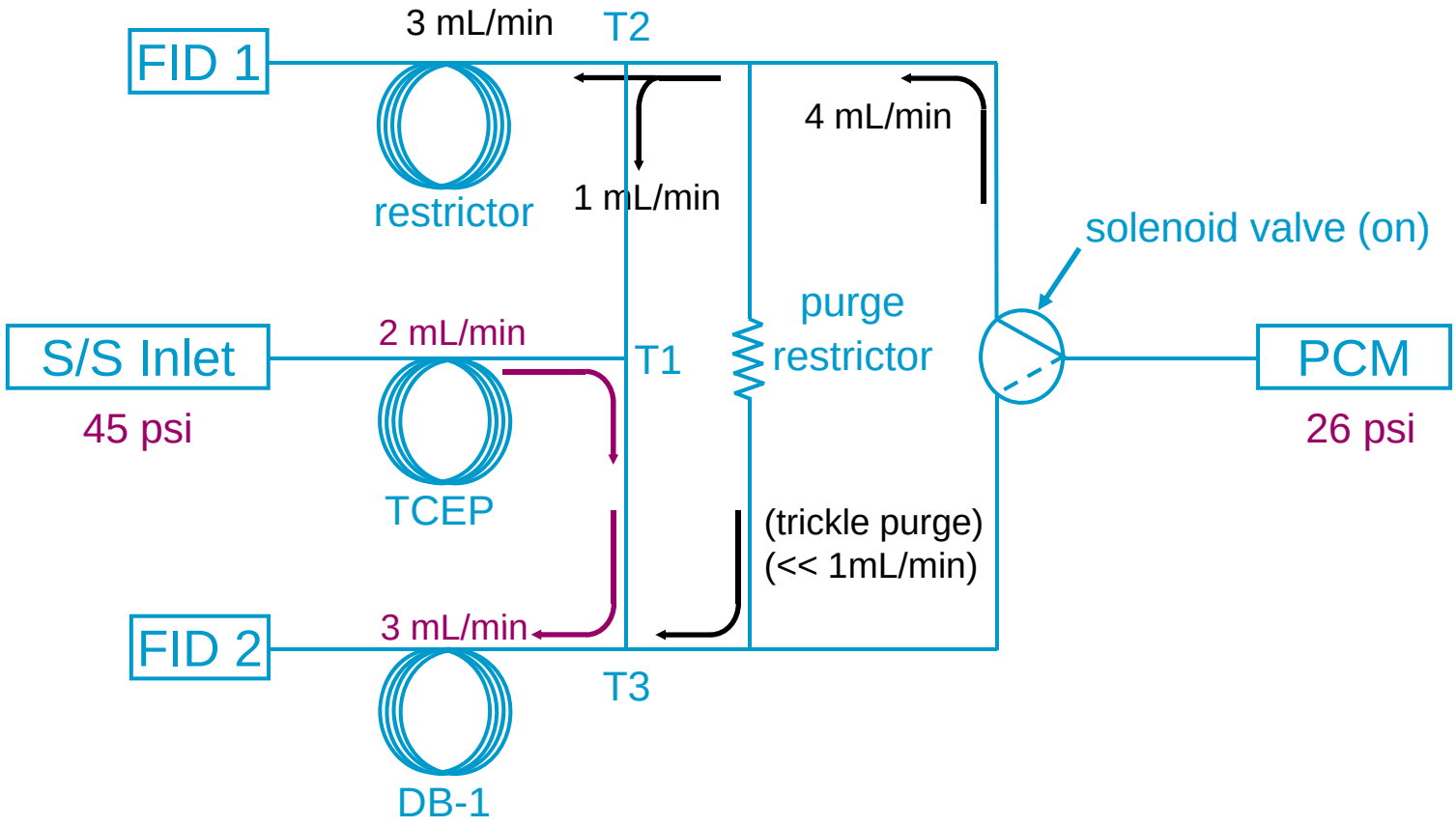
Oxygenates in Gasoline

Switch off, TCEP effluent goes to monitor FID (no cut)



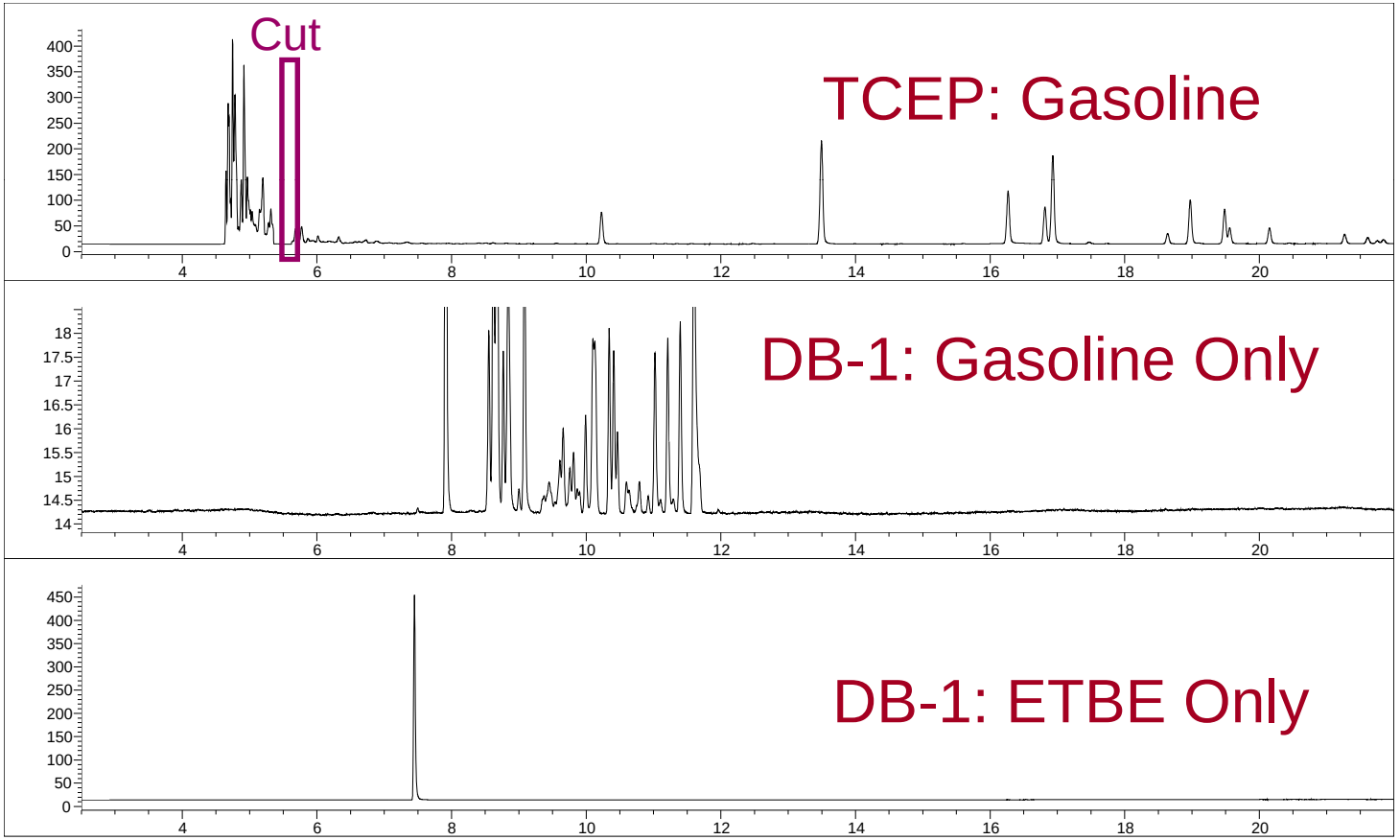
Oxygenates in Gasoline

Switch on, TCEP effluent is cut to DB-1 column



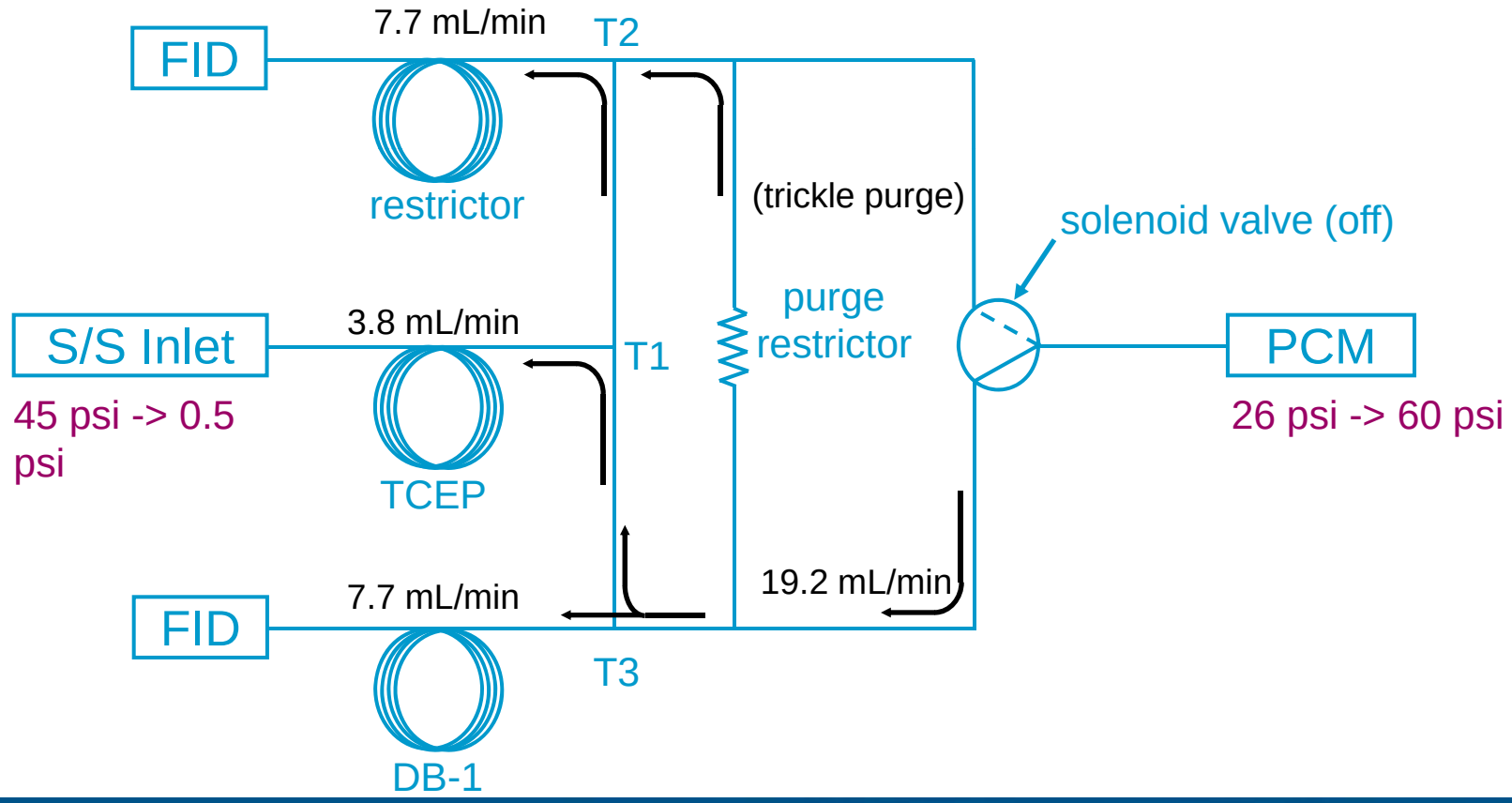
ETBE in Gasoline

These chromatograms show the hydrocarbons that come over during the ETBE cut. Note no interference with ETBE measurement



EPC Backflush to Save Time!

Program S/S to 0.5 psi, PCM to 60 psi at 20 min (or earlier). Heavies on TCEP are backflushed out split vent. Cuts run time from 70 min to < 25 min

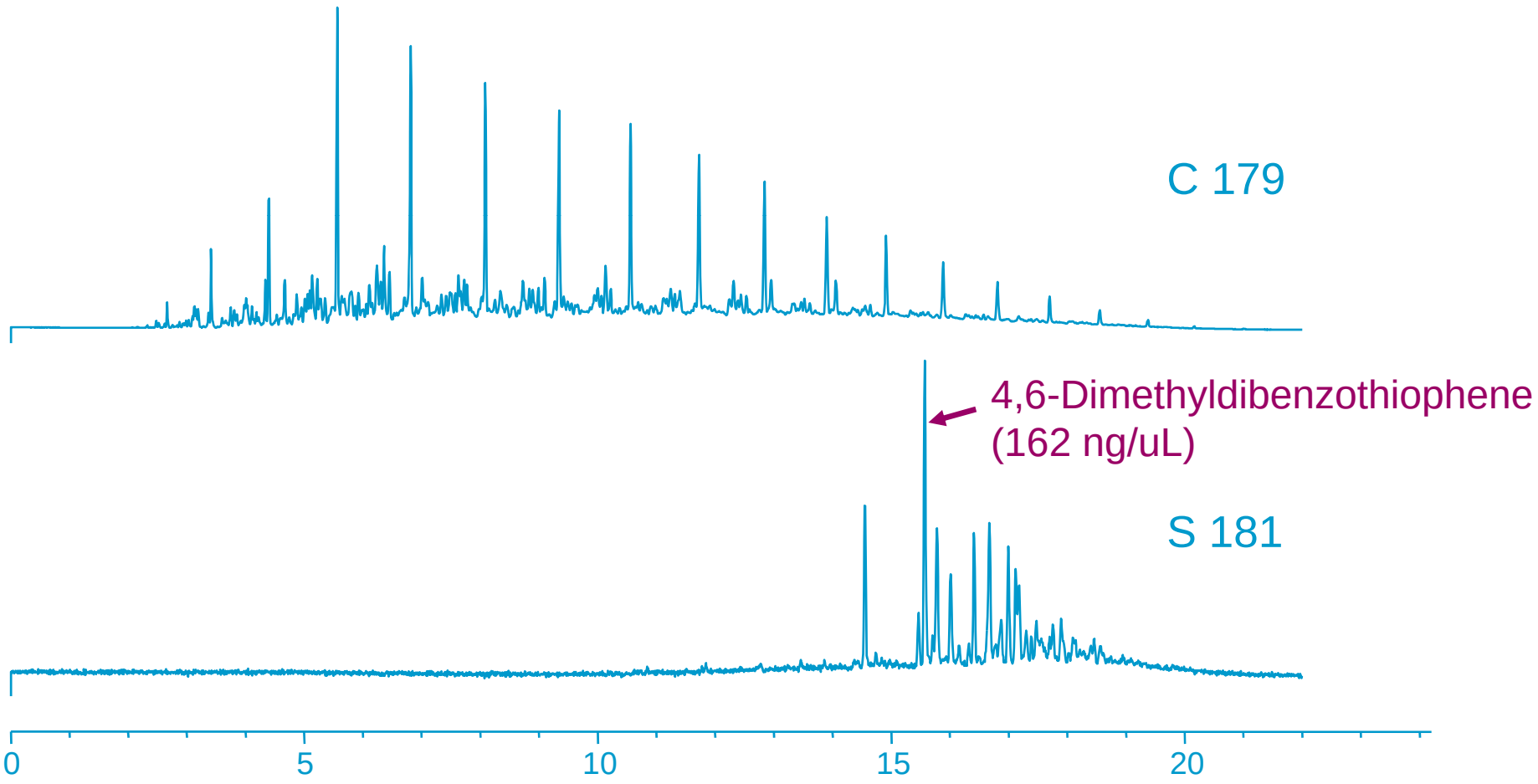


2-D GC Applications

- 4,6-Dimethyldibenzothiophene (low ppm) in diesel with FID
- most difficult sulfur compound to hydro-treat
- used to monitor overall trace sulfur in diesel
- does not require SCD or AED
- Trace (ppb) thiophene in benzene with FID
- method meets new specification for benzene
- does not require SCD or AED
- suitable for on-line
- Purity of denatured fuel ethanol (blending stock for RFG)
- fuel ethanol denatured with 4% natural gasoline
- must know the ethanol purity and methanol content
- ASTM method uses DHA-type column to separate alcohol from C4 and C5 hydrocarbons (60 minute run with cryo)
- 2D GC solution 10x faster and more reliable

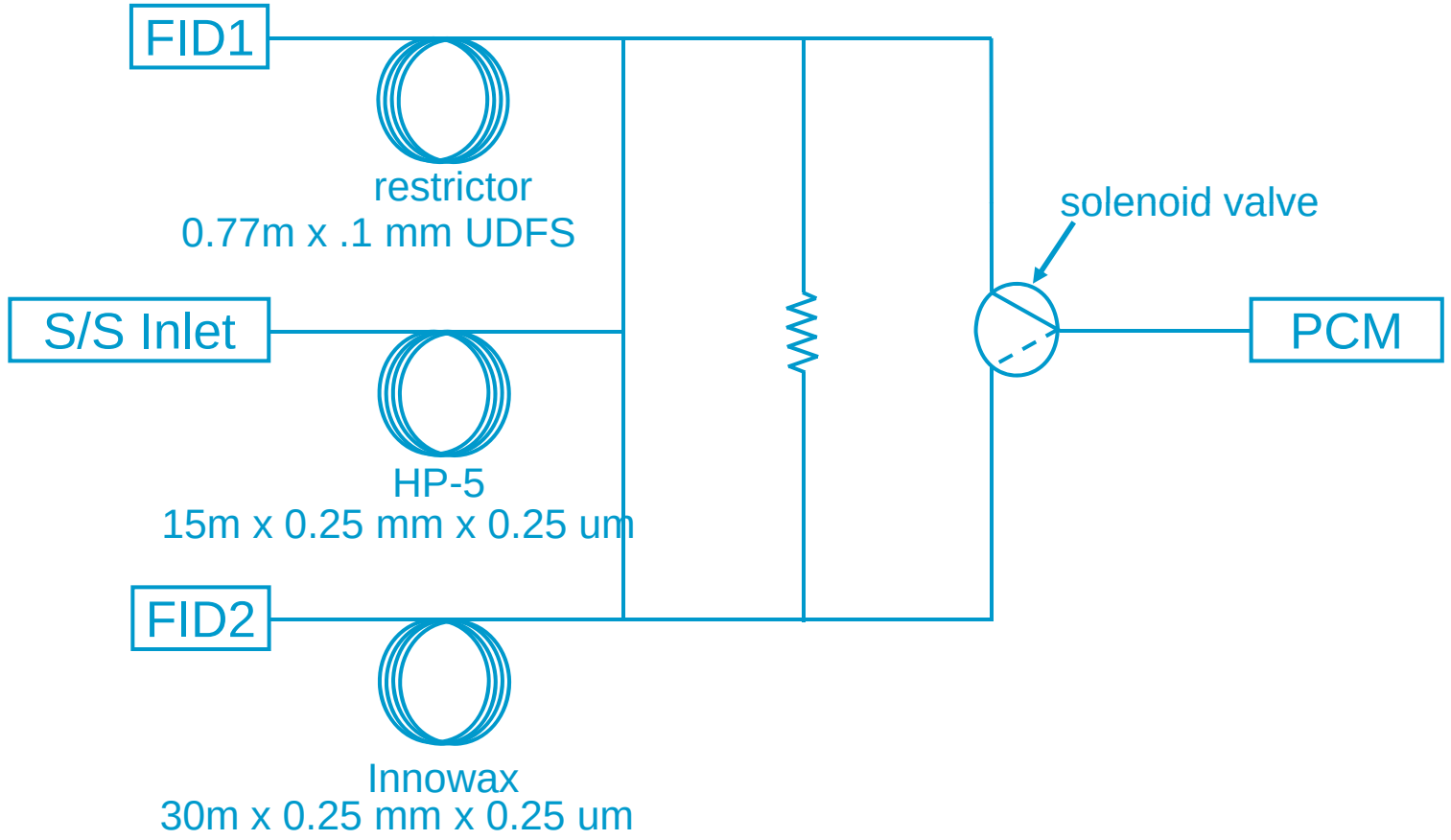
4,6-DMDBT in Diesel Fuel

426 ppm wt/wt total sulfur, run on GC-AED



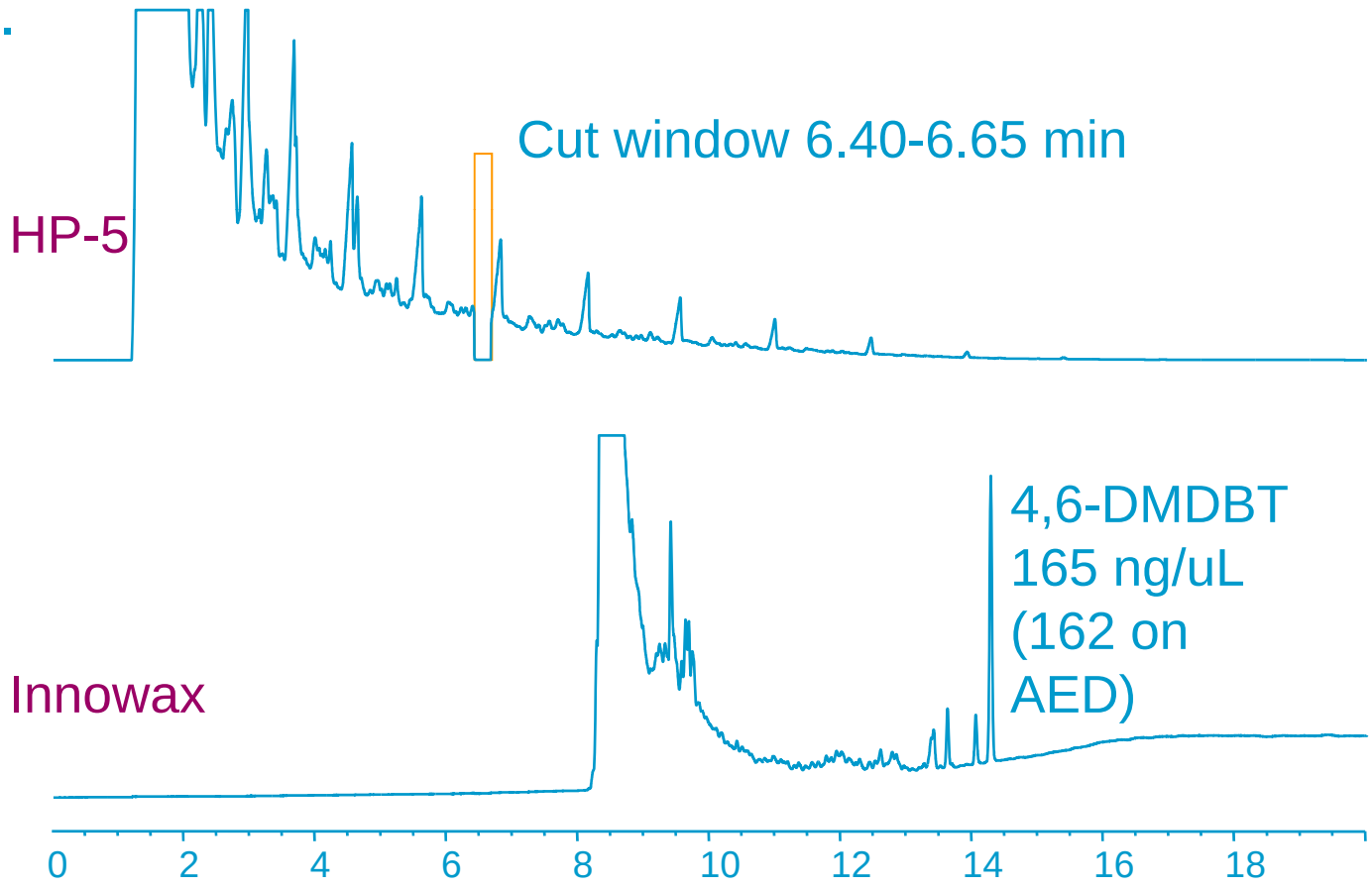
Diesel Fuel Deans Setup

Used to “heart cut” 4,6-DMDBT from HP-5 to Innowax column



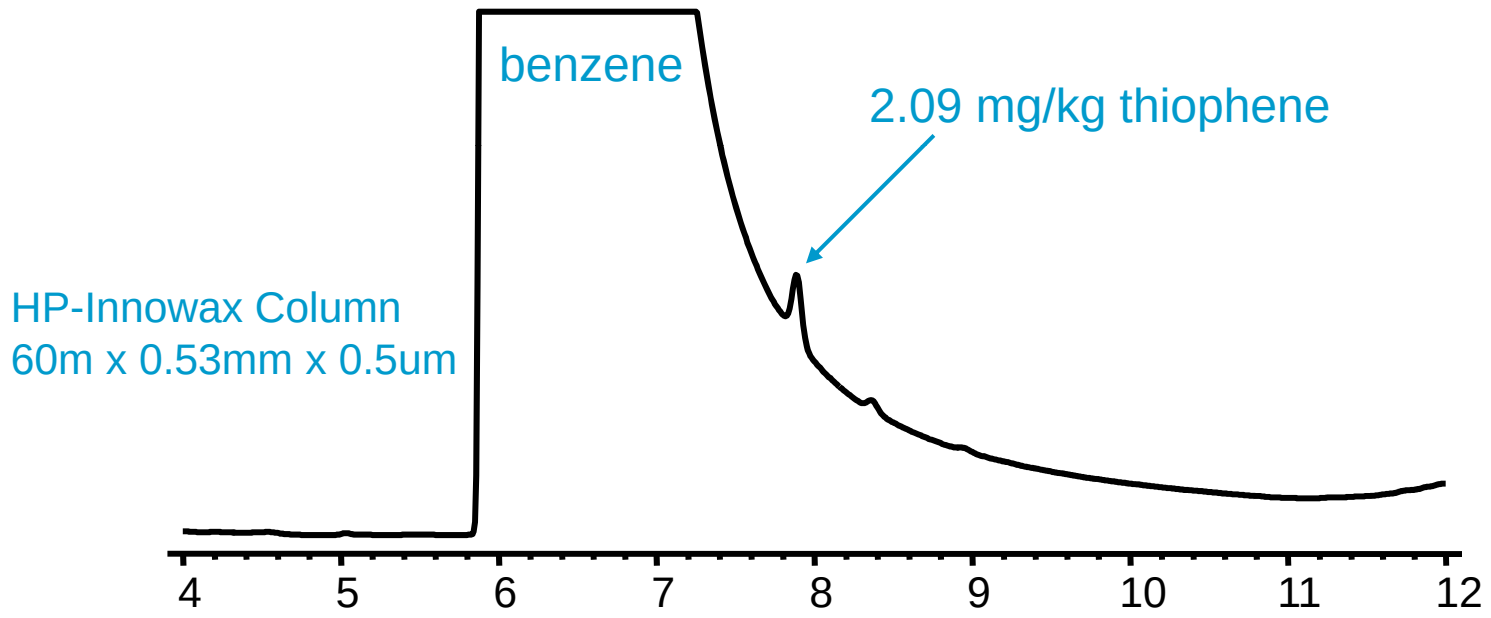
4,6-DMDBT in Diesel Fuel

4,6-DMDBT is completely resolved using FIDs. Method good to low ppm level and comparable to AED.



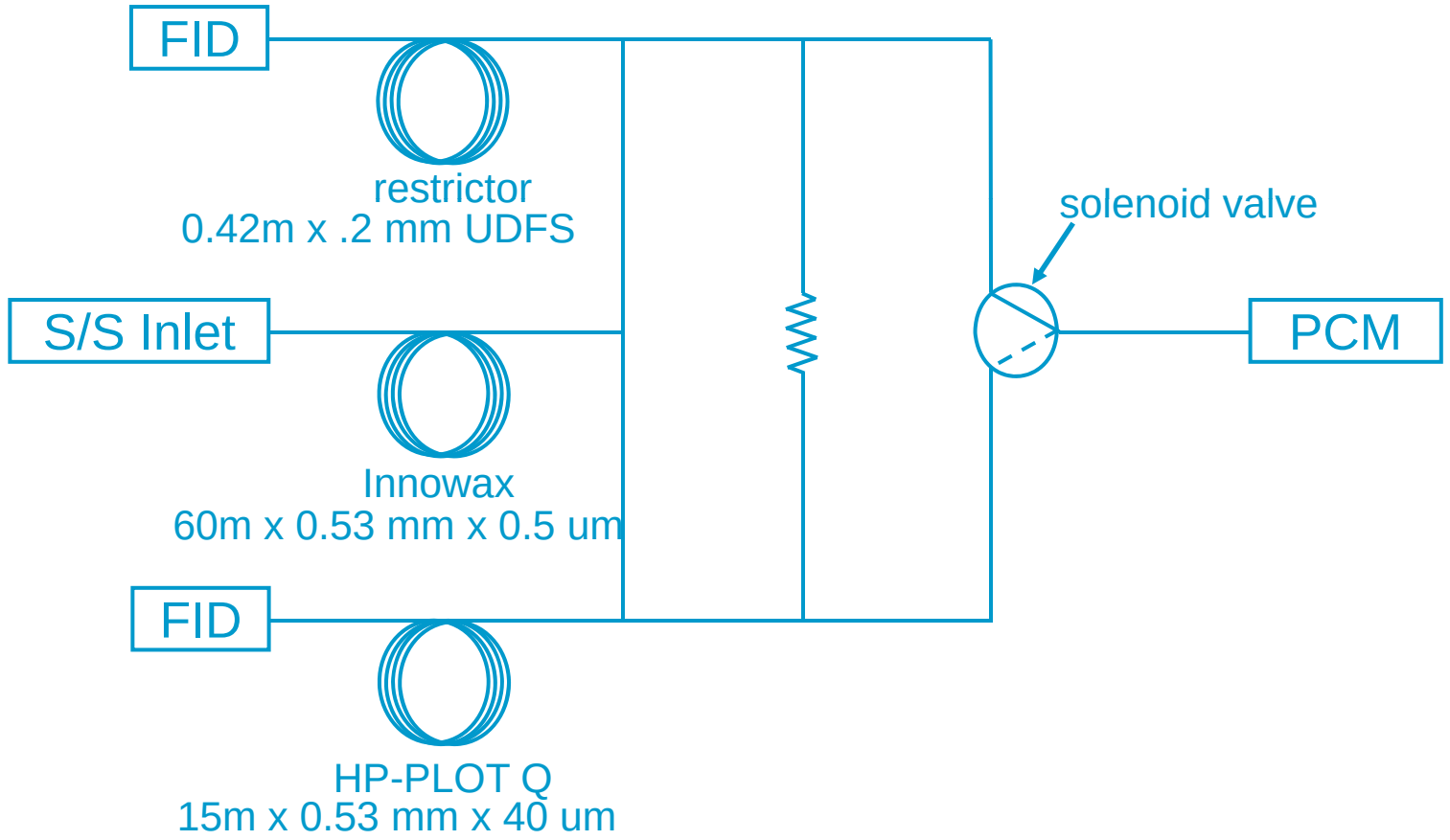
Trace Thiophene in Benzene

Need to measure 0.02 to 2.00 mg/kg thiophene in pure benzene



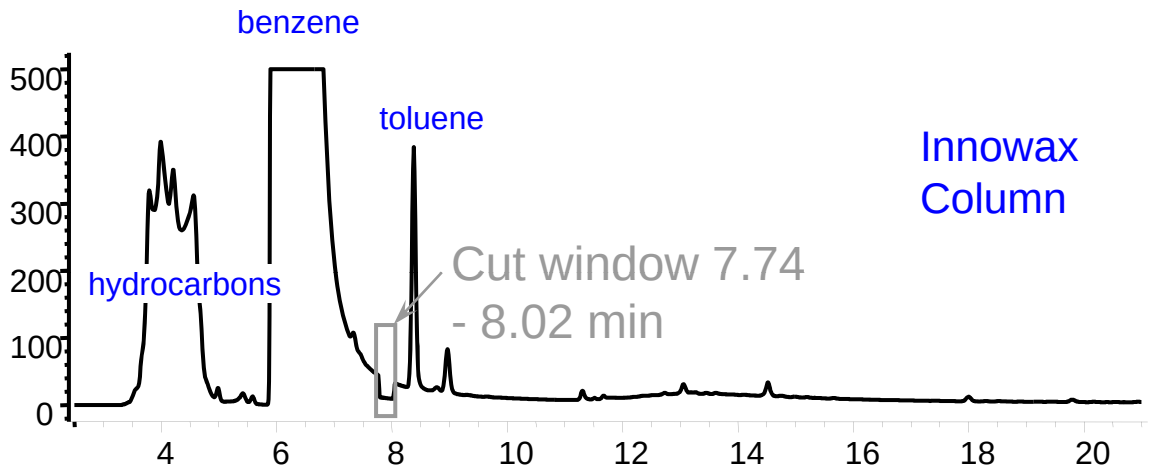
Trace Thiophene in Benzene Setup

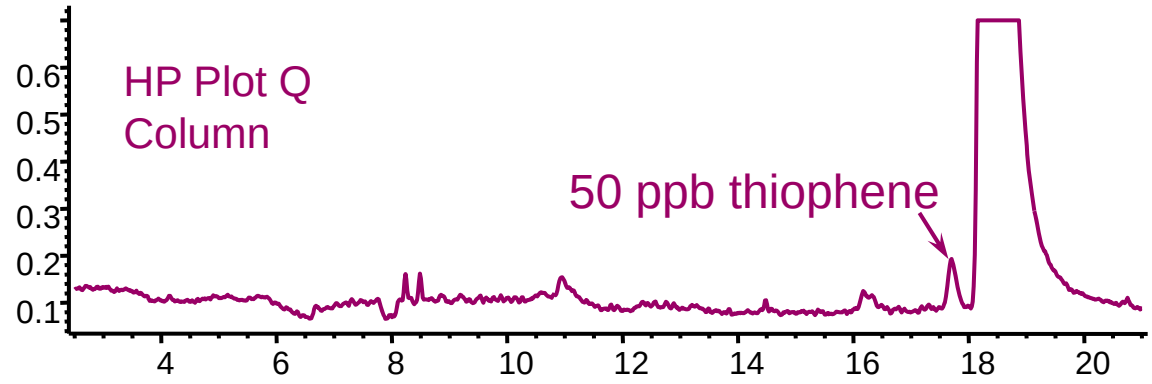
Used to “heart cut” thiophene from Innowax column to PLOT Q



Trace Thiophene in Benzene

Analysis of 20 ppb to 2 ppm using FID





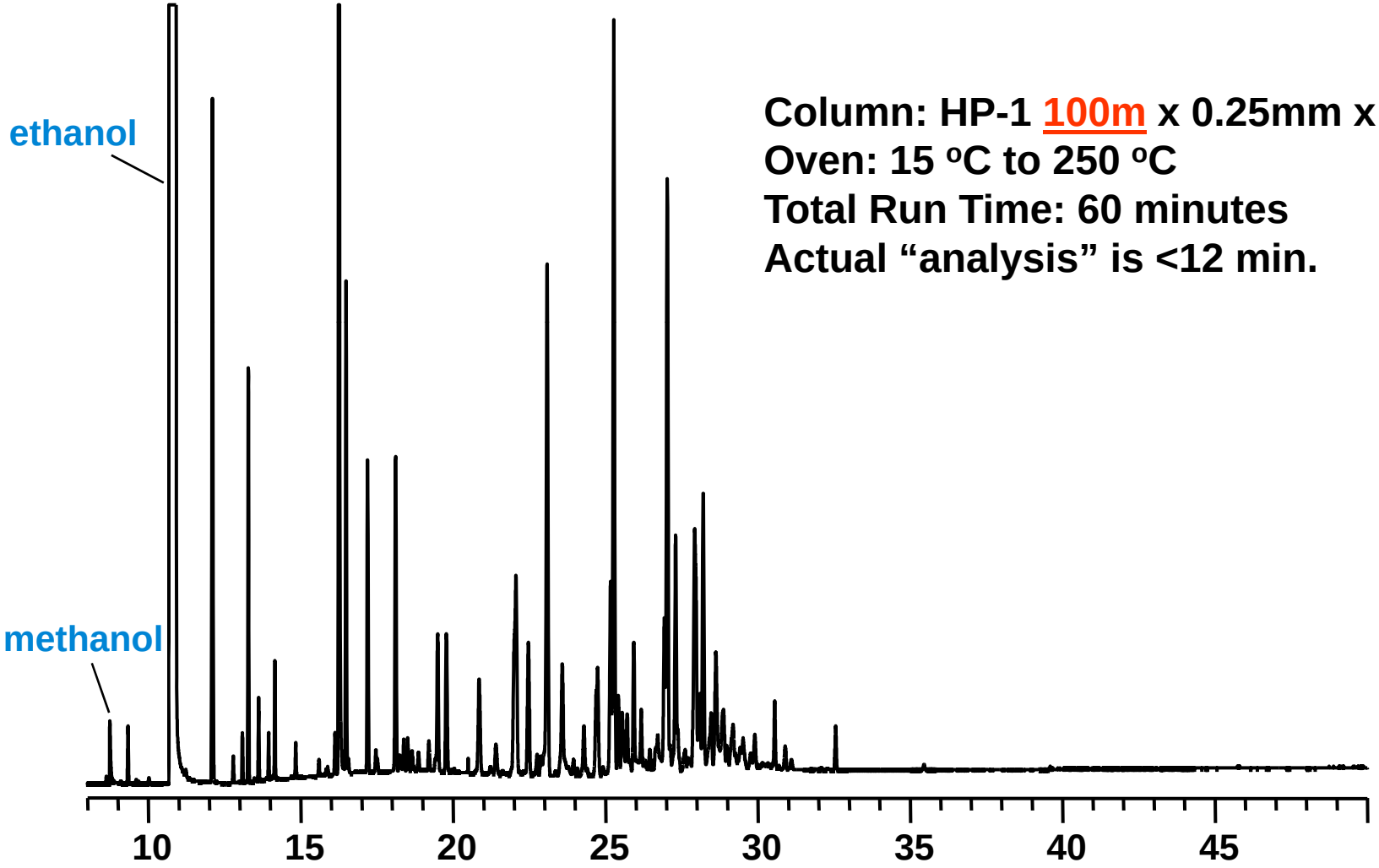
Analytical Precision (15 runs over 5 days)

Avg Amt: 50 ppb

Std Dev: 0.003 ppb

RSD: 1.9%

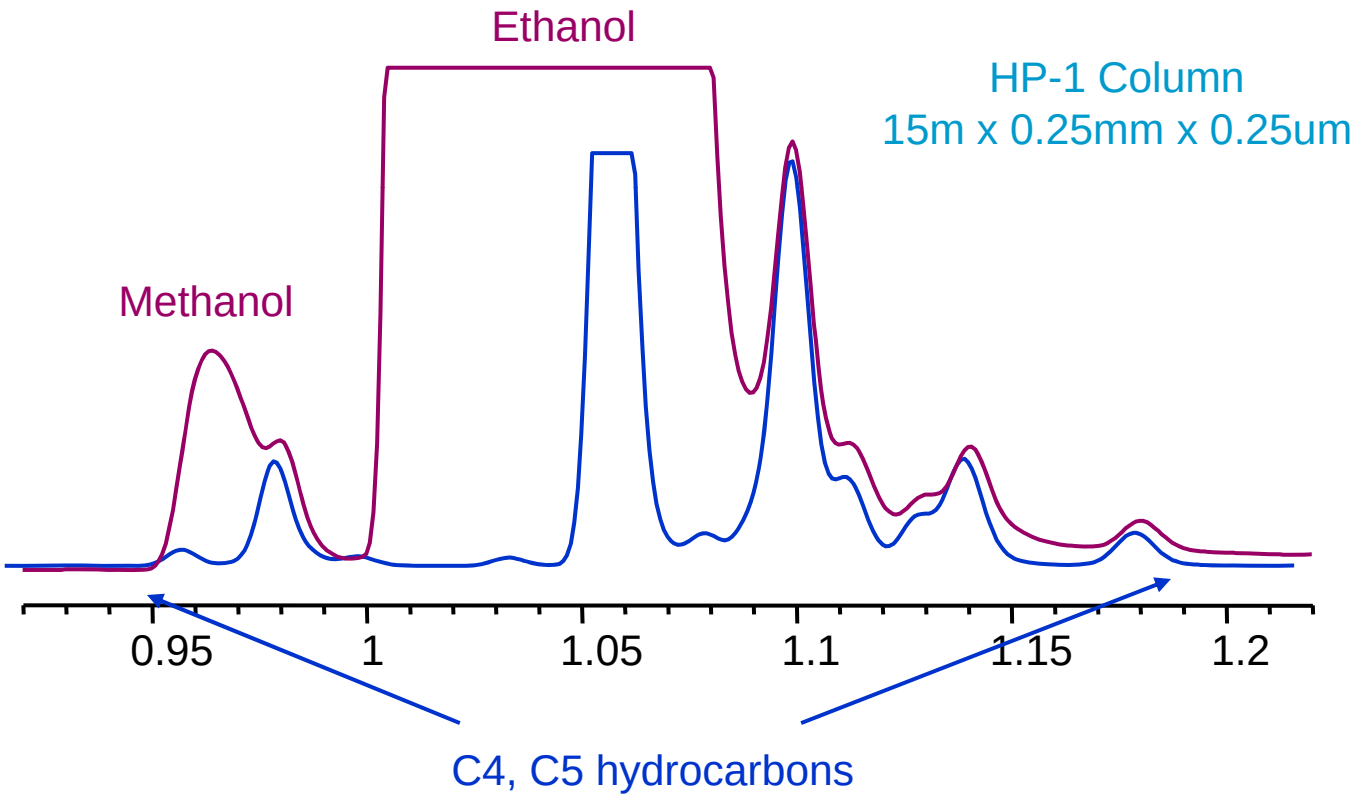
ASTM Method D5501
- Denatured Fuel Ethanol Purity



Column: HP-1 100m x 0.25mm x 0.5um
Oven: 15 °C to 250 °C
Total Run Time: 60 minutes
Actual “analysis” is <12 min.

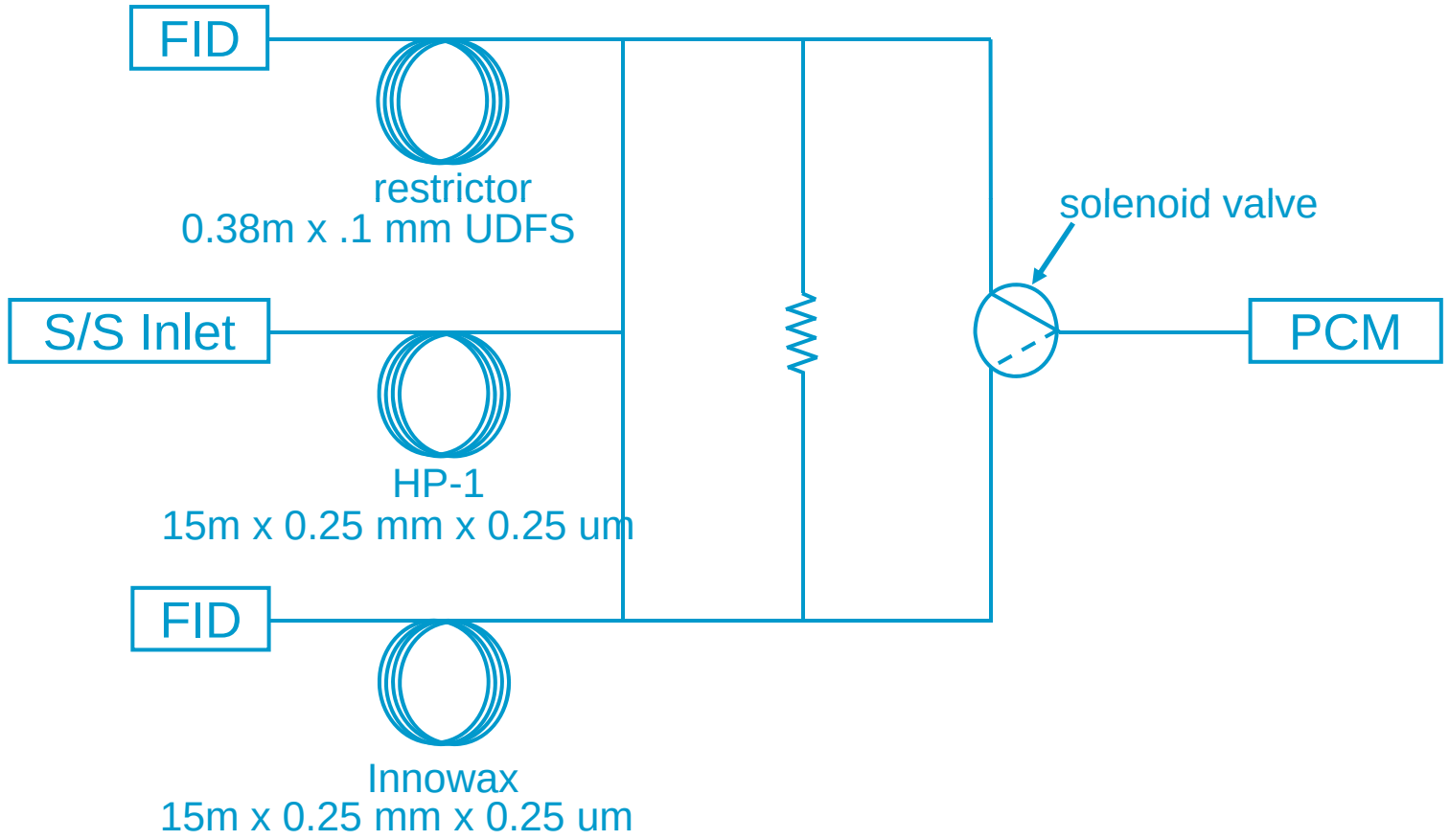
Denatured Fuel Ethanol Purity

C4 hydrocarbons co-elute with methanol and ethanol



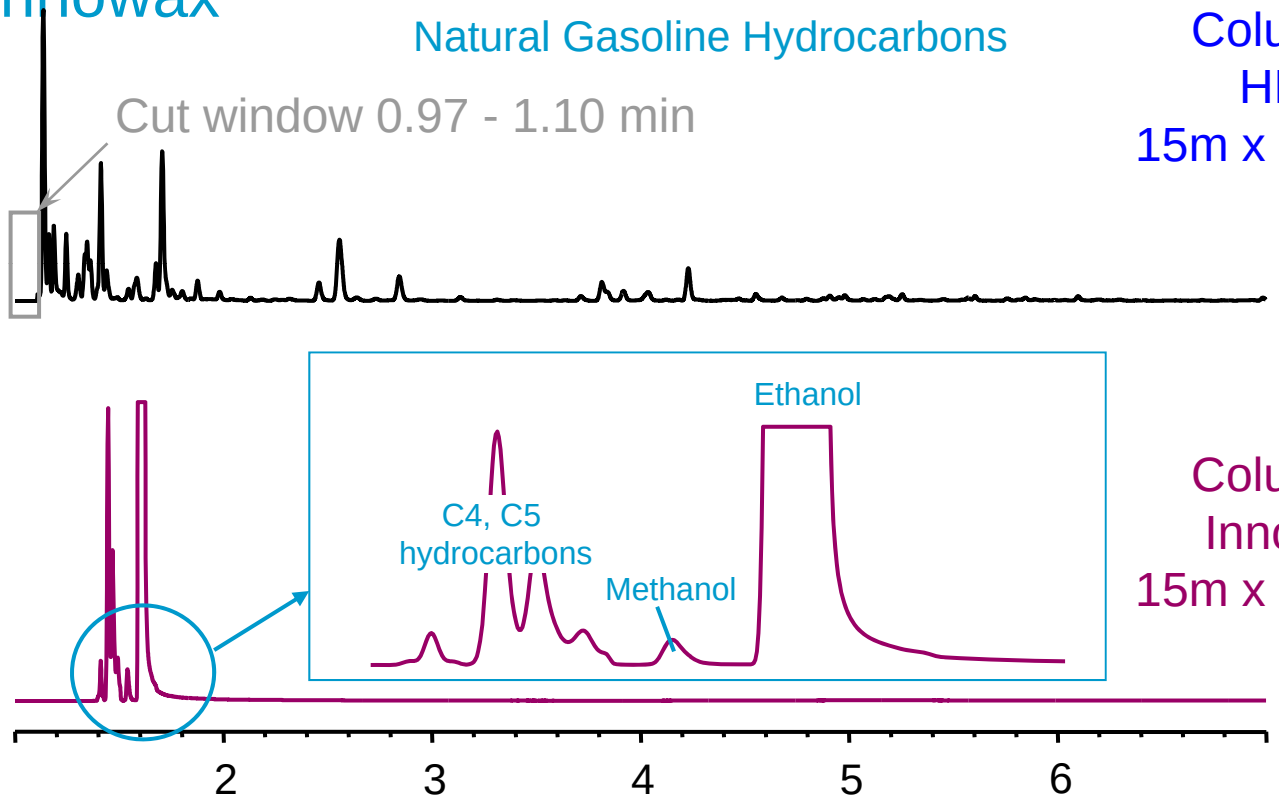
Denatured Fuel Ethanol Purity

Used to “heart cut” alcohols from HP-1 column to Innowax



Denatured Fuel Ethanol Purity

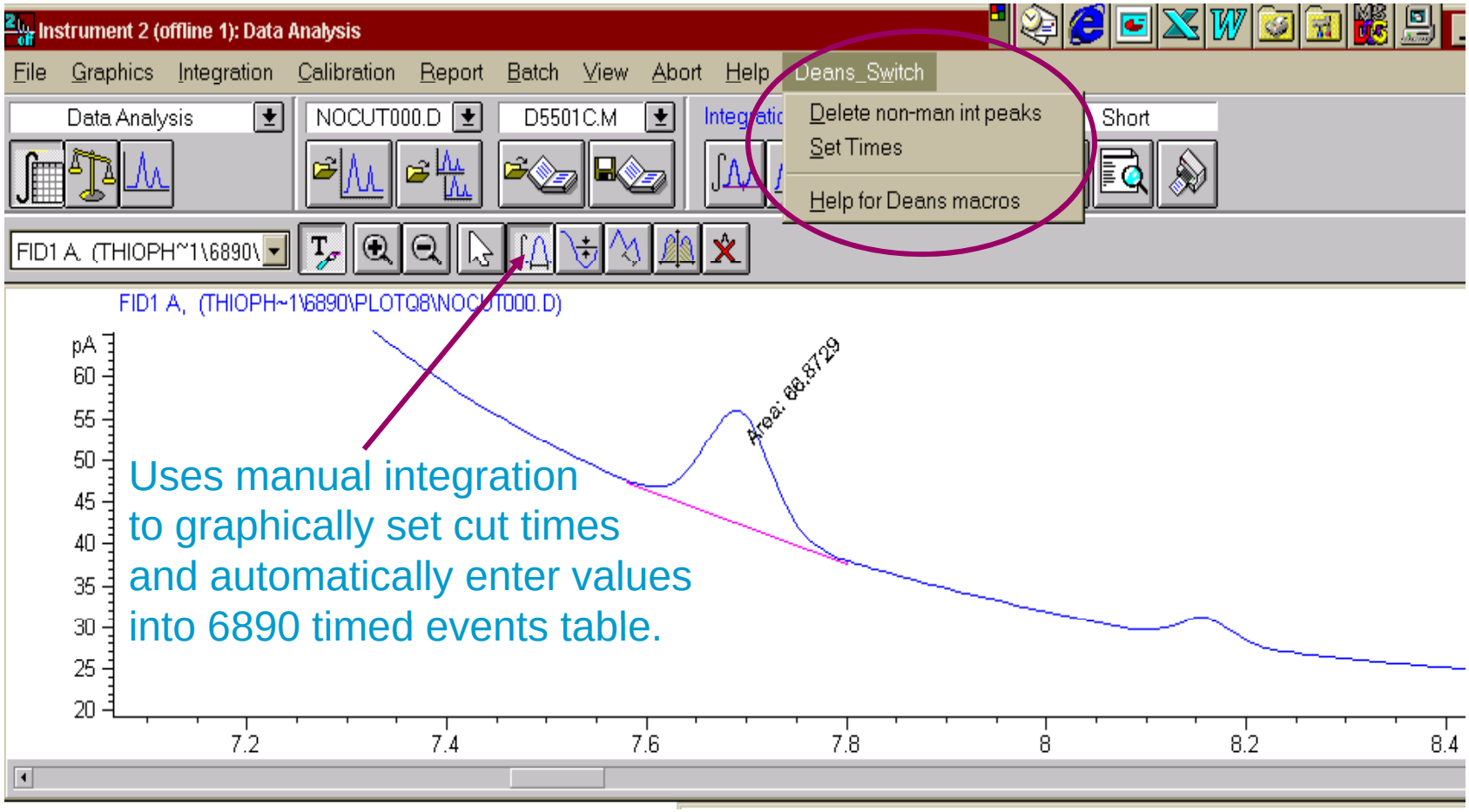
Used to “heart cut” alcohols from HP-1 column to Innowax



Run time is less than 7 minutes

Method Developers Tools

Macros to graphically set precise cut windows



Heart Cutting or 2-D GC Summary

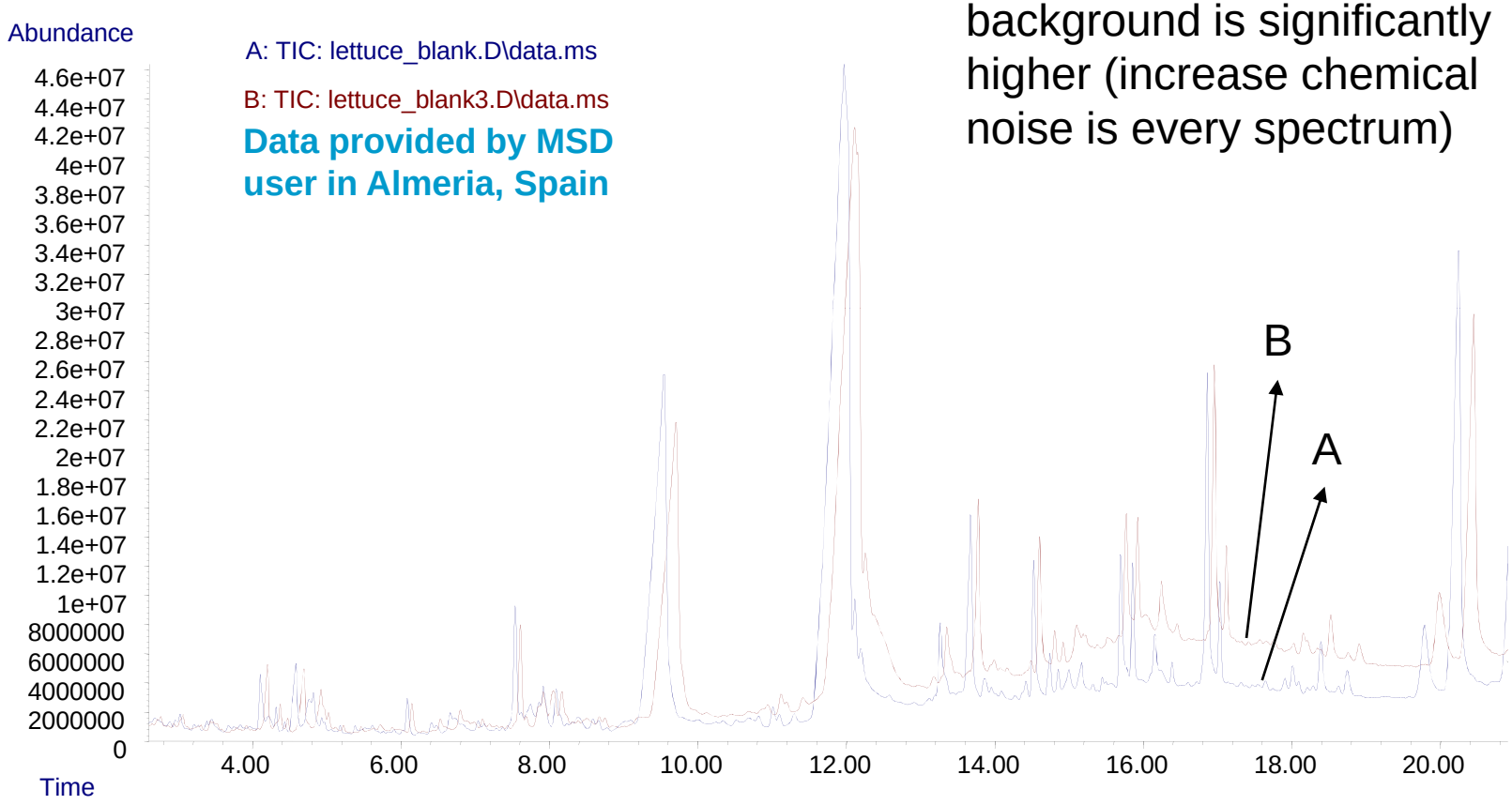
- Developments in GC hardware in recent years have made Deans switch systems easier to construct, use, and maintain.
- Single oven, non-cryo systems can often solve the problem
- 2-D GC is a powerful tool that can be used by itself or combined with other selective techniques to solve difficult separation problems.

Backflushing the Easy Way with CFT

- Many late eluting peaks are not “chromatographically ideal” and leave a residue throughout the column
  - This residue **increases with each subsequent injection**
  - Matrix carryover increases as more samples are injected
- Heavy matrix contaminates the source faster and **sensitivity is LOST**!

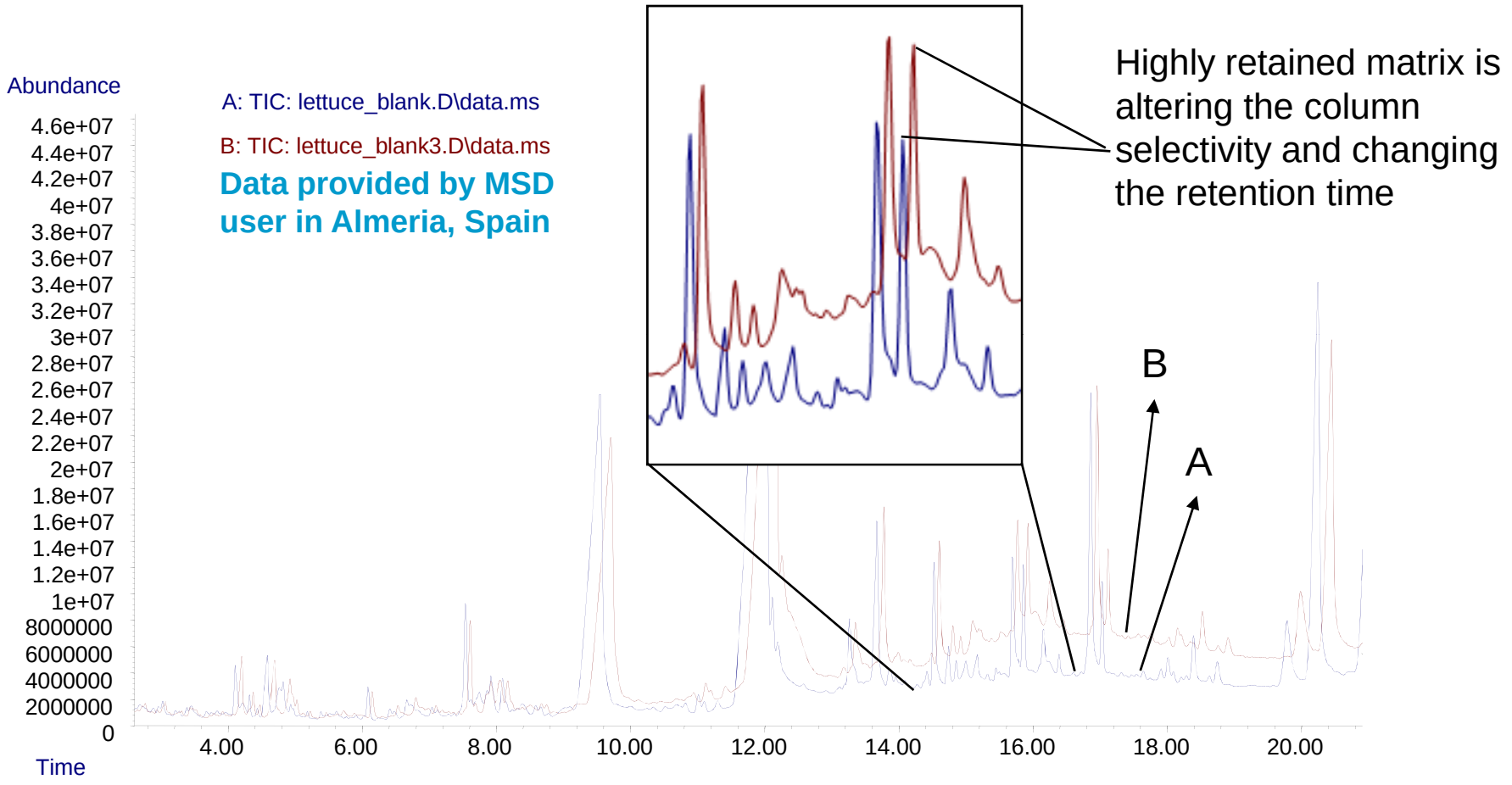
GC/MS Complex Matrix Without Backflush

After **only 3 samples**, the background is significantly higher (increase chemical noise is every spectrum)



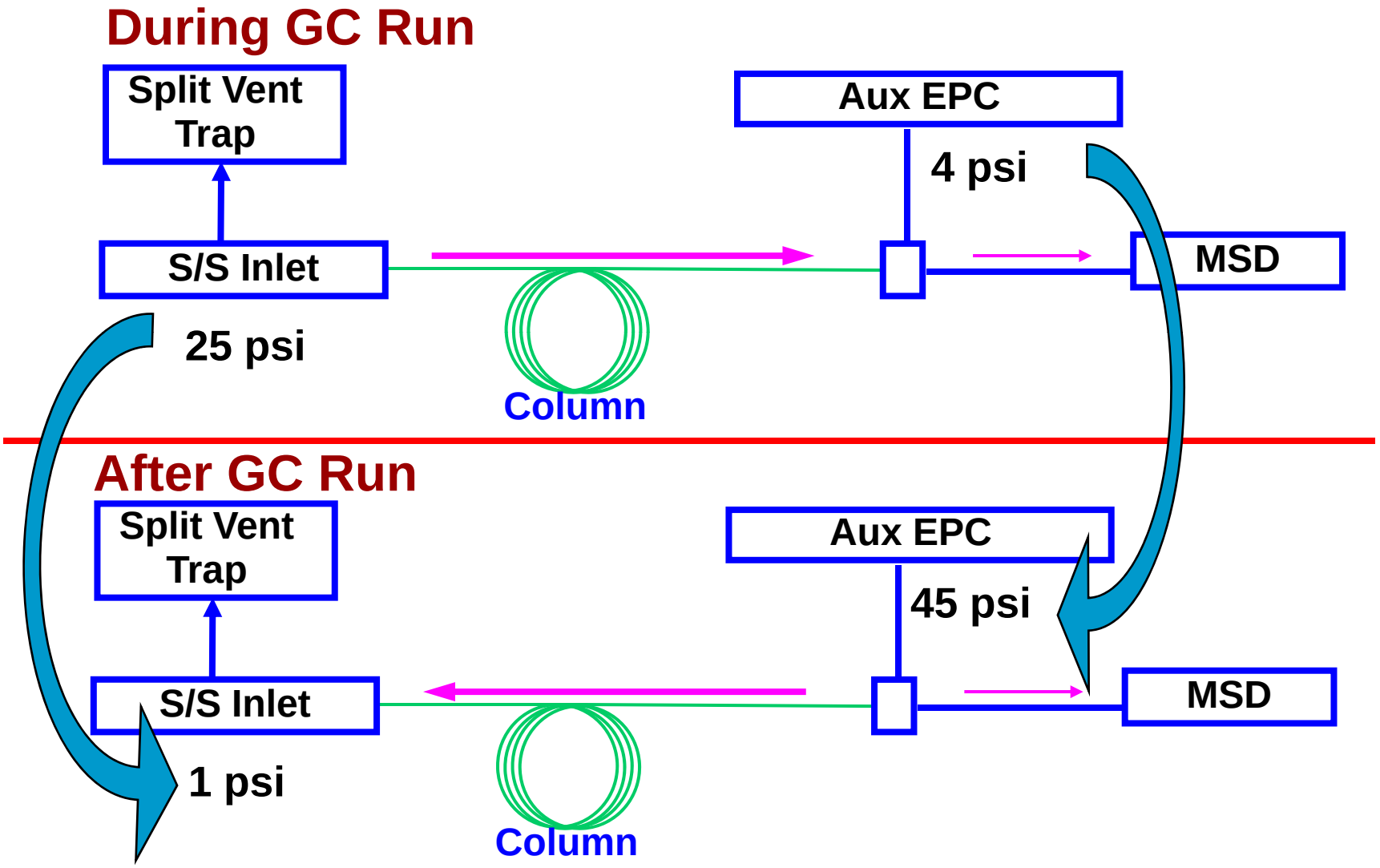
Overlay of two chromatograms of a blank extract injected BEFORE (A) and AFTER (B) three injections without backflush

MS Without Backflush: Changes in Retention Time

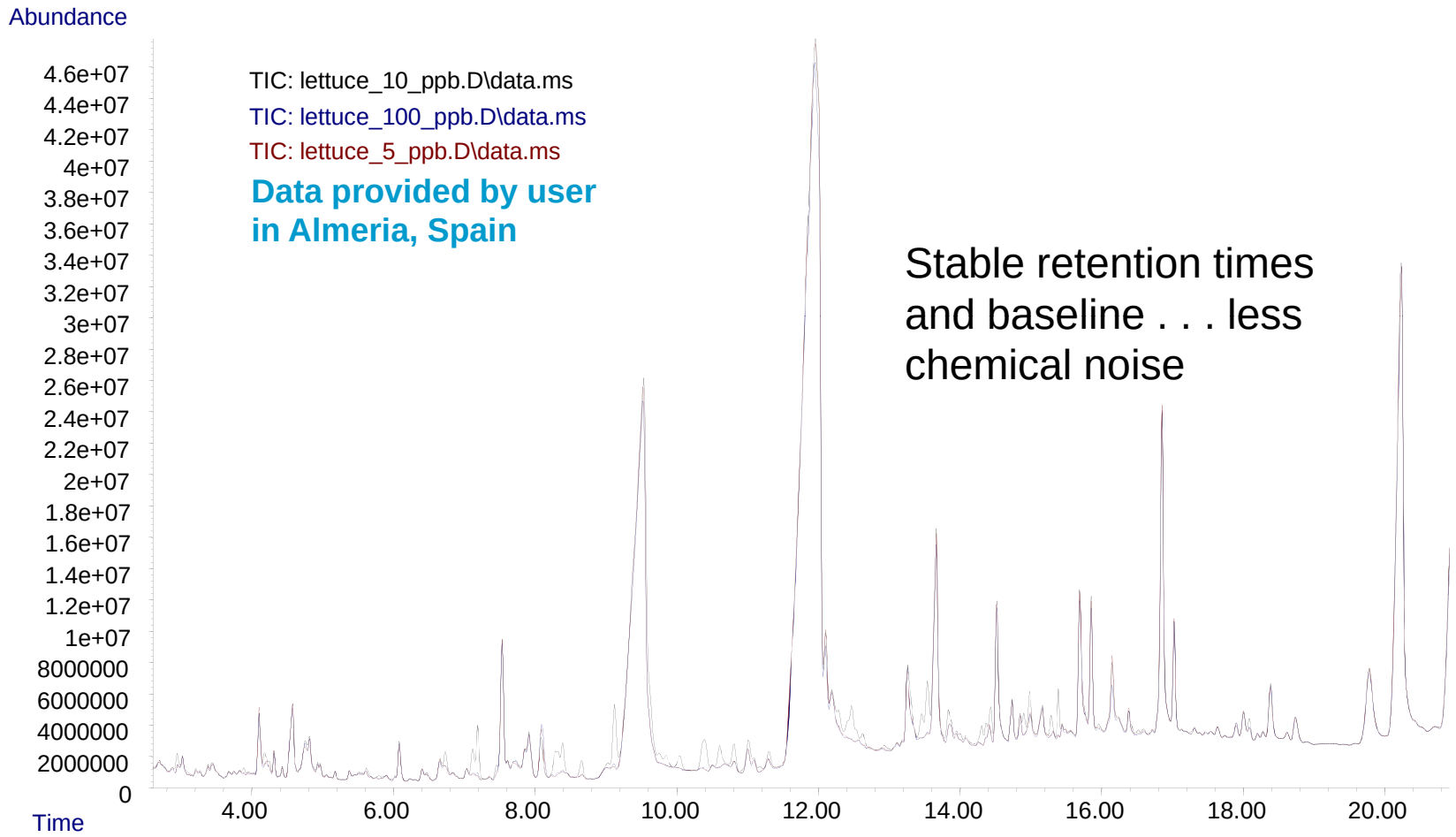


Overlay of two chromatograms of a blank extract injected BEFORE (A) and AFTER (B) three injections without backflush

Post-column Backflush

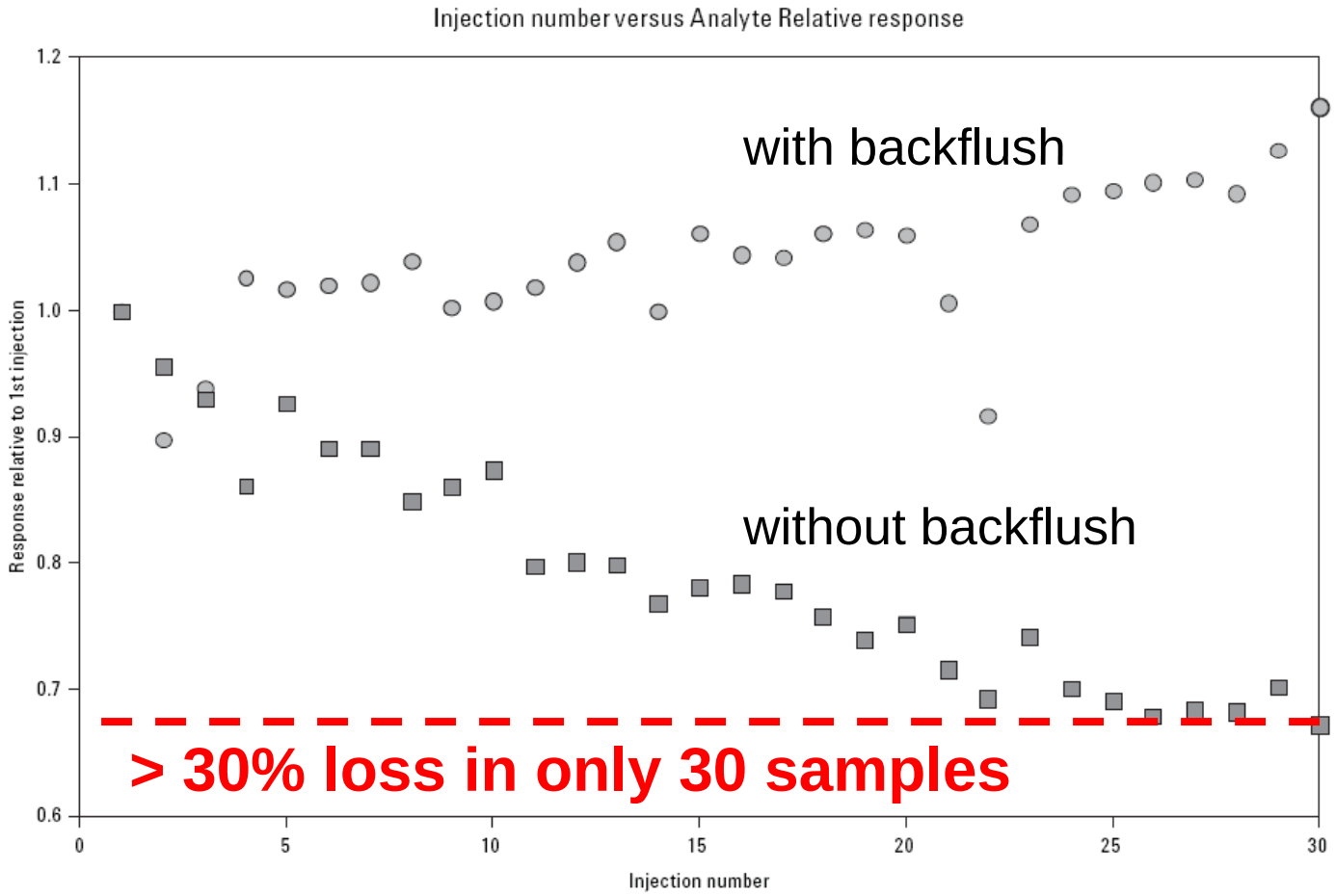


MS With Backflush: No Increased Background (Less Spectral Noise) and Consistent Retention Times

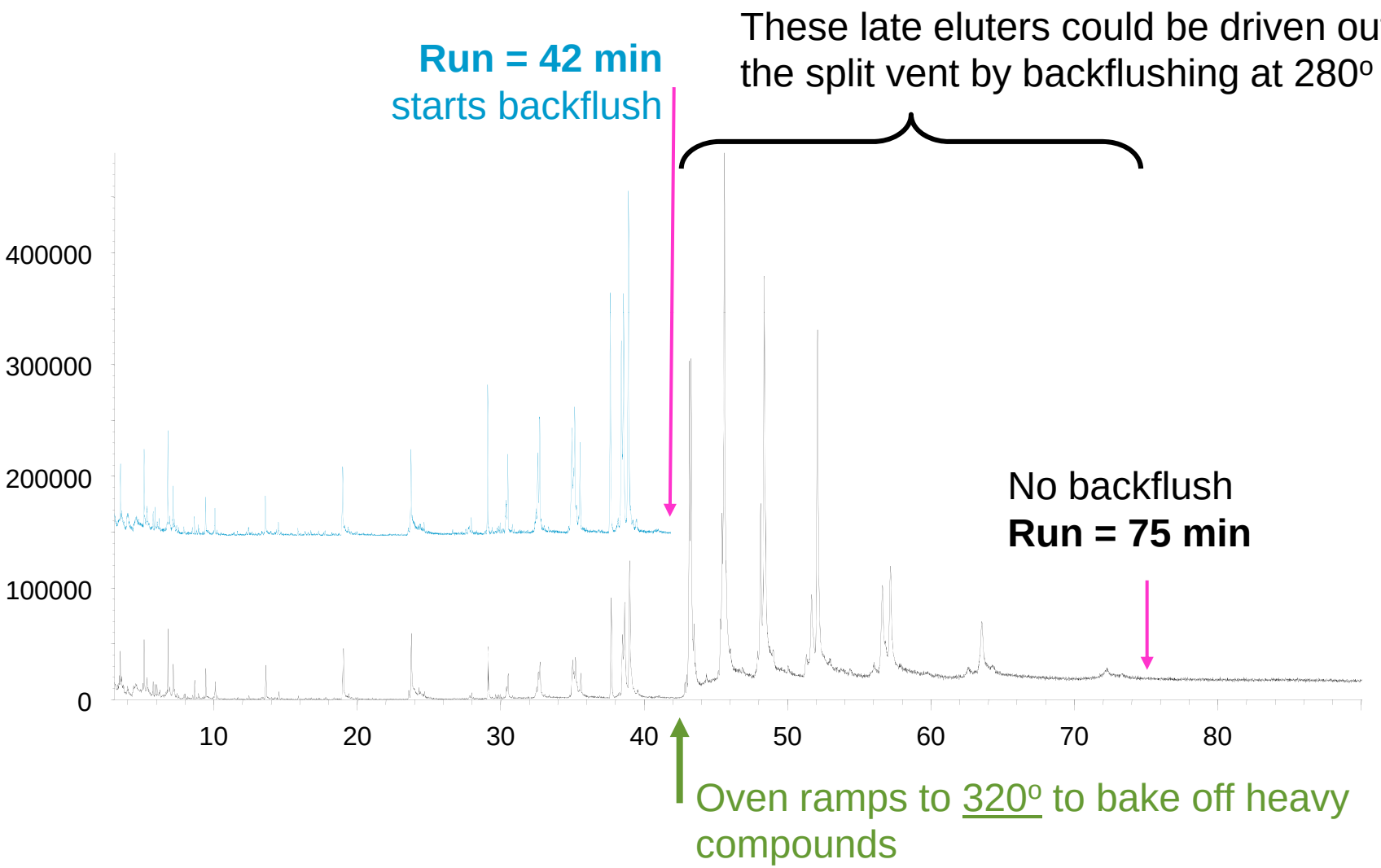


Overlay of three chromatograms of lettuce extract run with 2 min of back flush

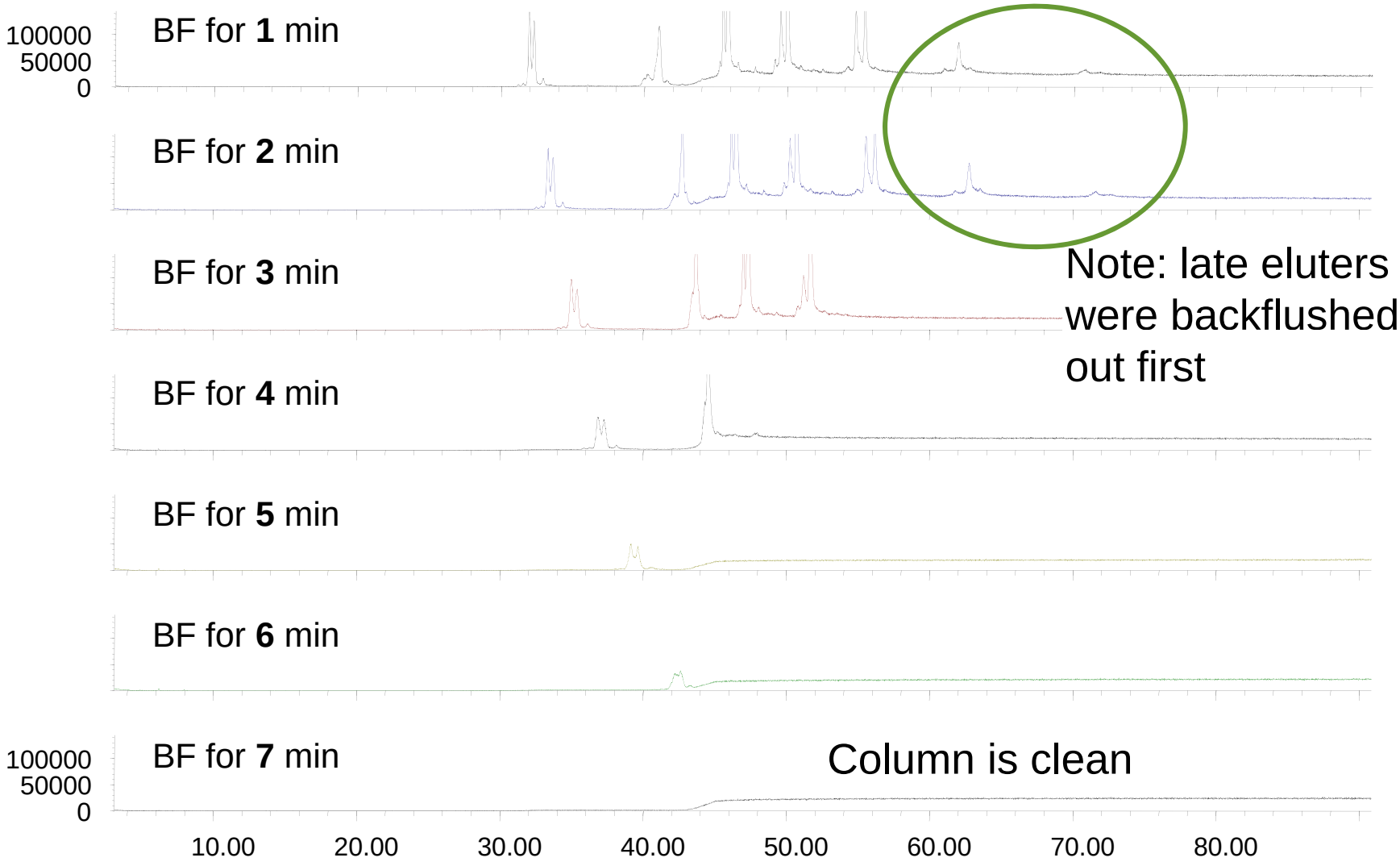
Loss of Response without Backflush Lipid Peroxidation Products in Blood



Milk Extract (MSD TIC)



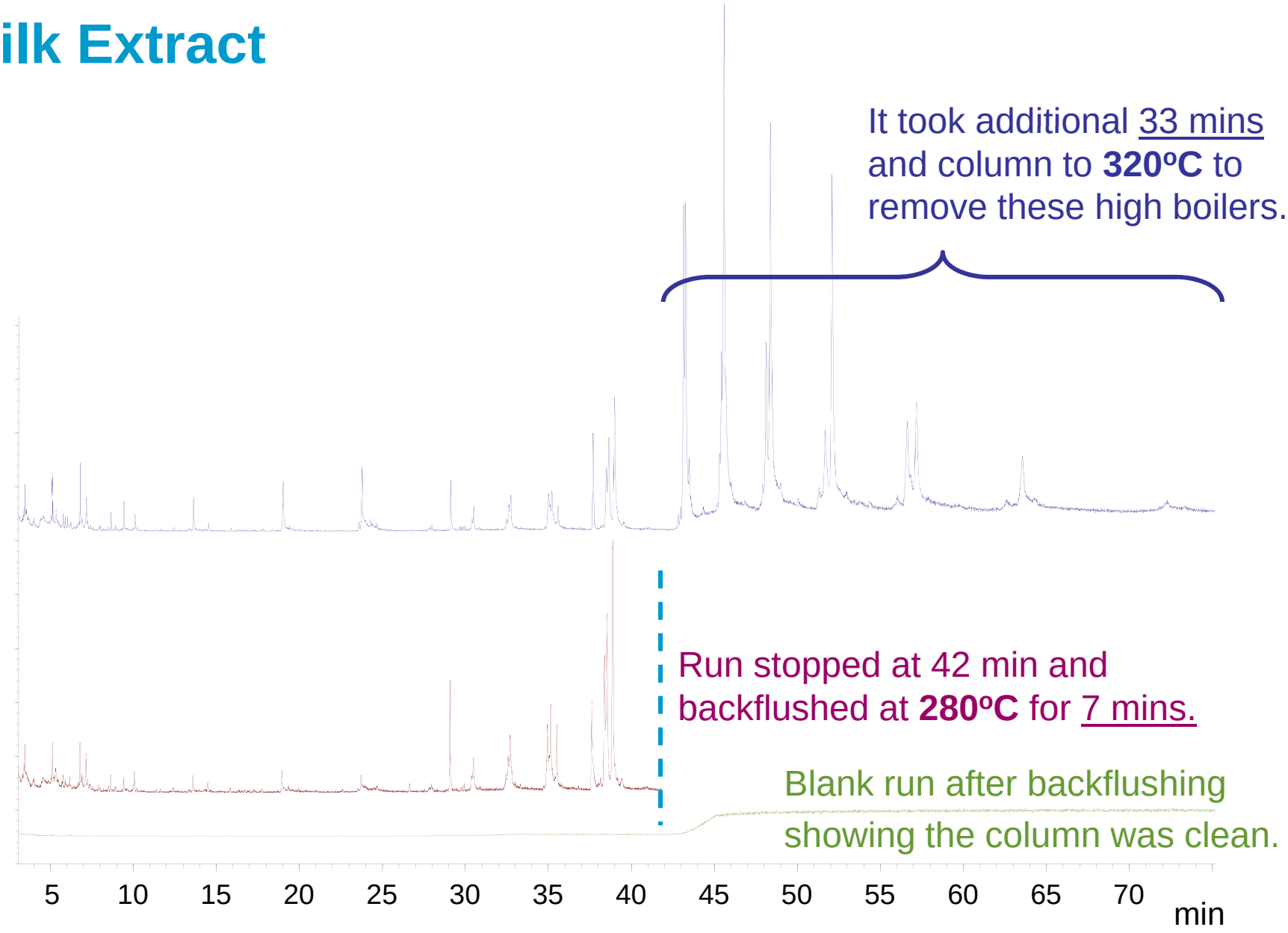
Blank Runs After Backflushing @ 60 psi



Note: late eluters were backflushed out first

Column is clean

Milk Extract

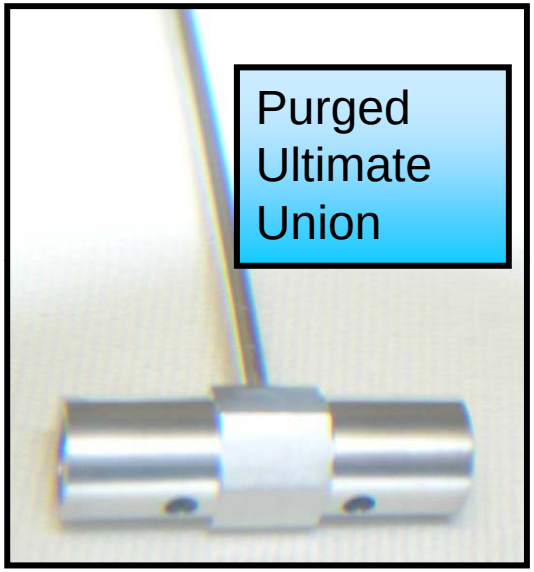


Technical Advantages of Column Backflush

- Provides more consistent GC retention times
- Provides better, more consistent MS spectra through a sample sequence
  - Reduces chemical noise that may increase during a sequence of samples due to small carryover of matrix from sample to sample
  - Higher quality quantitation (no increase in interfering ions during analysis sequence)
- Consistent ion source sensitivity

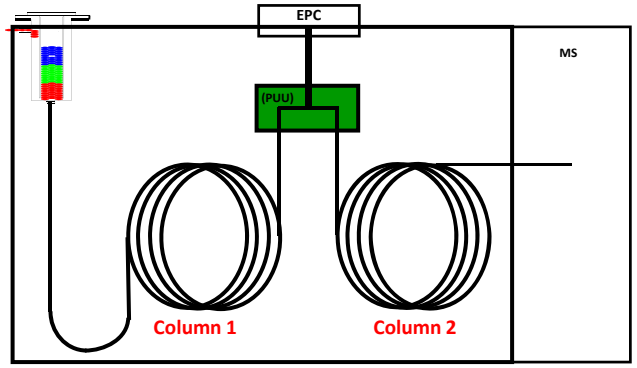
If Backflush Is So Great . . .
Why Is Backflush Not More Common?

- Faulty hardware implementation
  - Flow control
  - Leaks in connections
  - Inertness of connections
  - Cold spots (too much mass)
  - Confusion about configurations



The Purged Ultimate Union (PUU) configurations

MANY, MANY POSSIBLE CONFIGS !!
=> Many possible uses / applications



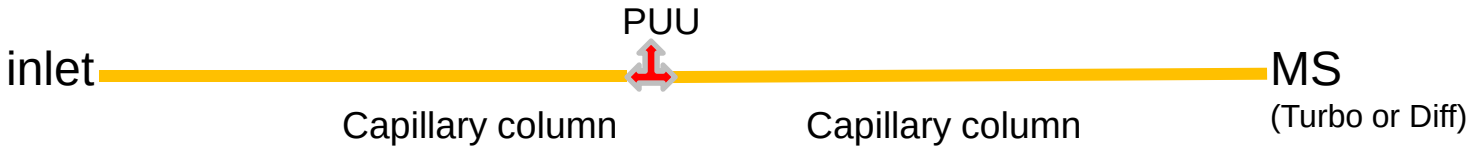
How to decide?

Vocabulary

Post-column

Uncoated Pre-column

Intra-column:
Pressure Controlled Tee (PCT)

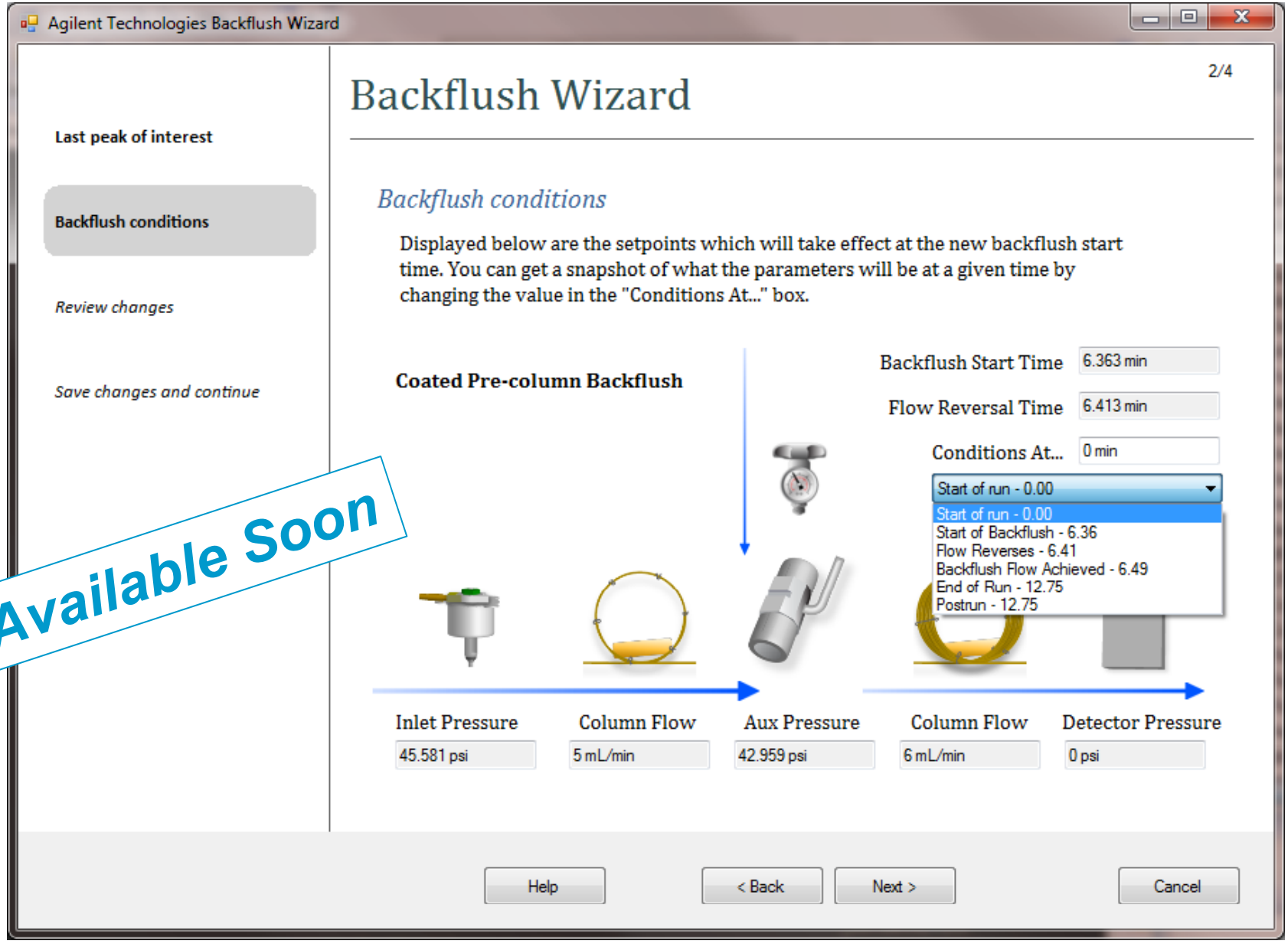


Comparison of PUU Backflush Configurations

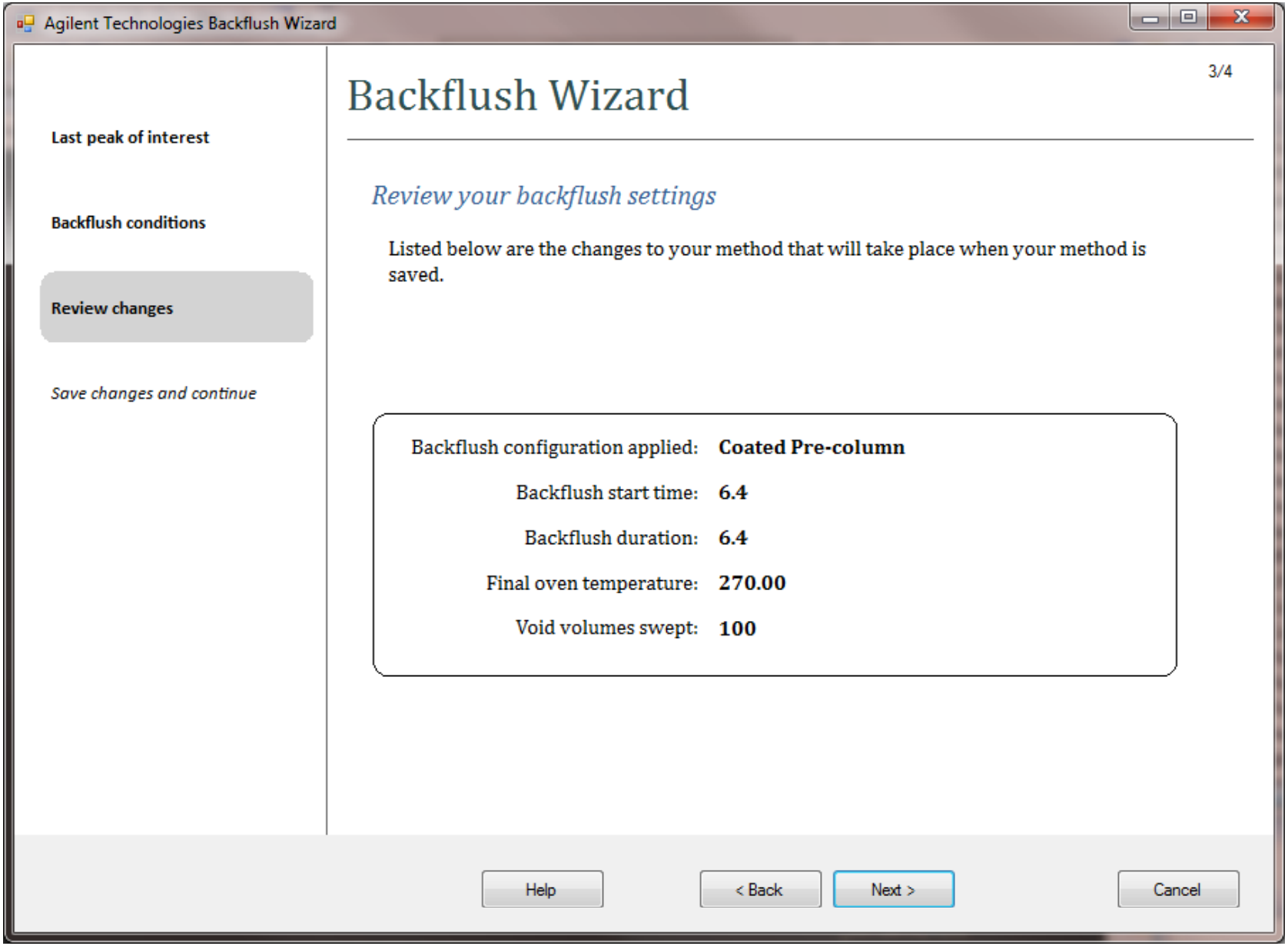
CONFIGURATION	*POST COLUMN*	*UNCOATED PRE-COLUMN*	*PCT: INTRA-COLUMN*
Application requirements			
Trace Analysis	Greatest dilution	Moderate	Least dilution
Active compounds	Moderate	Moderate	Best
Column Phase swapping	Frequent changes	One-phase	One-phase
RTL (Constant P or Flow)	AUTO CP & CF	Manual CF & CP	Manual CF Best
MS systems	Turbo ONLY	Turbo & Diff	Turbo & Diff
BACKFLUSHING Features			
Post-Run or Concurrent	Post-Run ONLY	Concurrent required	Post-Run or Concurrent
Ease of Use	Easy Use	Difficult Use	Post-Run easy/CCBF harder
BF speed (e.g., turbopump)	Slowest (~4.7min)	Fastest (<0.03min)	Moderate (~1.7 to 0.8min)
Gas use in Backflush	Highest	Lowest	Moderate
Selectivity (Cut out matrix)	Highest	Lowest	Moderate
Robustness in use	Moderate	Lowest	Highest
HW SETUP	Restrictor cutting	EPCs close together!!	Buy columns
Target Market (examples)	Flavor & Fragrances		Pesticides, SVOAs, etc.

If Backflush Is So Great . . .
Why Is Backflush Not More Common?

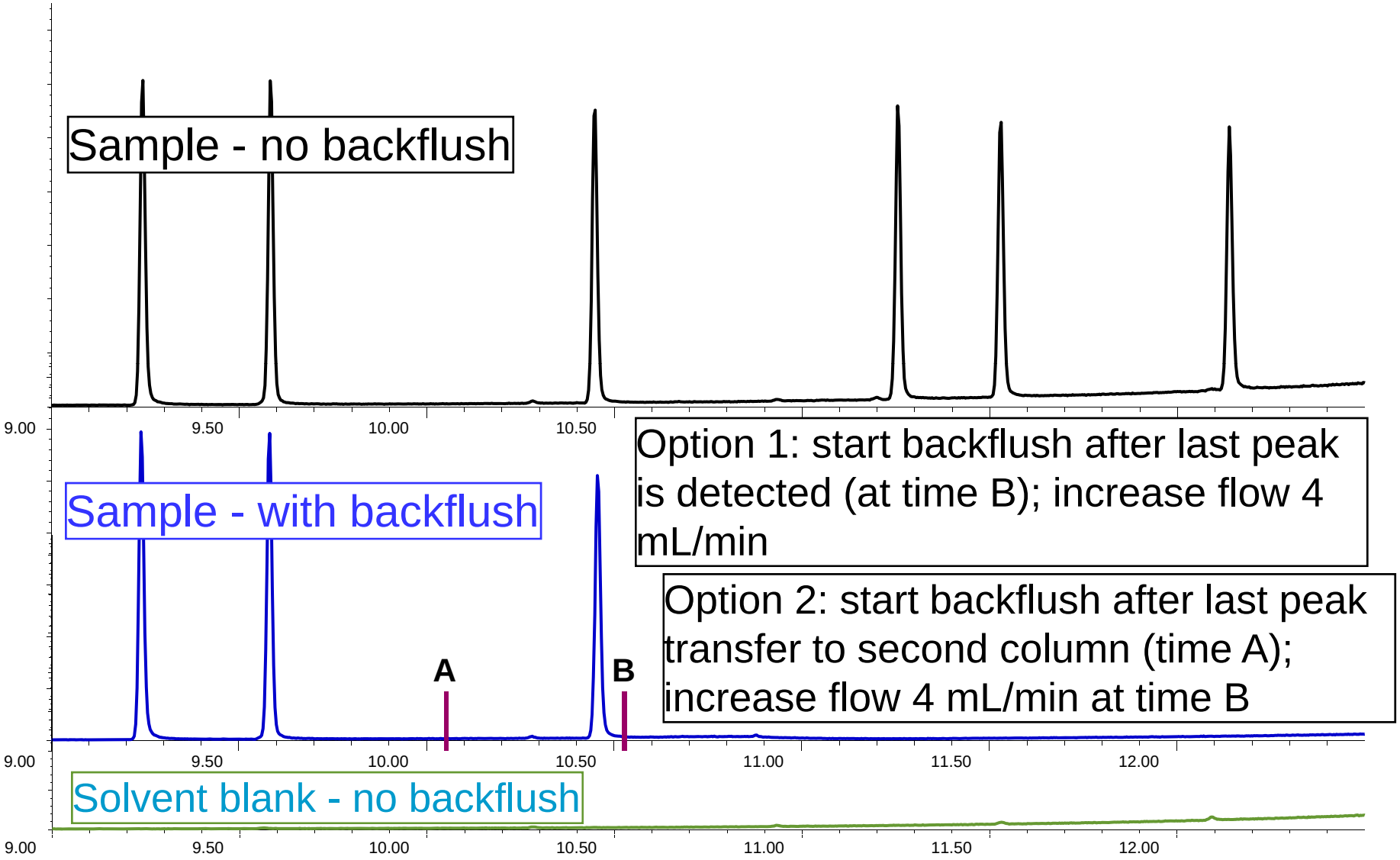
- Faulty hardware implementation
  - Flow control
  - Leaks in connections
  - Inertness of connections
  - Cold spots (too much mass)
- Confusion about configurations
- Uncertain about pressure settings, time, etc.



Available Soon


Agilent Technologies Backflush Wizard
3/4
Backflush Wizard
Last peak of interest
Backflush conditions
Review changes
Save changes and continue
Review your backflush settings
Listed below are the changes to your method that will take place when your method is saved.
Backflush configuration applied: Coated Pre-column
Backflush start time: 6.4
Backflush duration: 6.4
Final oven temperature: 270.00
Void volumes swept: 100
Help
< Back
Next >
Cancel

Backflush (BF) with the Purged Ultimate Union



Productivity Added Benefit
Rima Juskelis, NCFST

- Backflush flow to protect the MS and column during maintenance
  - No-vent maintenance when replacing the inlet liner
  - No-vent maintenance when trimming the column

- Less ‘down time’ during maintenance, back running samples sooner

Conclusions

- Good technical justifications for backflush
  - Retention precision, limiting matrix carryover
- Good tools to simplify transition to backflush
  - Purged Ultimate Union, EPC, Backflush Assistant Wizard
- Good economic justifications for backflush
  - Saving personnel time
  - Reducing cost for supplies
  - Increasing the number analysis per unit time

Any purged cft device can be used to Backflush

Acknowledgements

- Thank you for your kind attention!

- Bruce Quimby, Agilent Wilmington, DE
- Terry Sheehan, Agilent Santa Clara, CA
- Ken Lynam and Doris Smith, Agilent Wilmington, DE
- Rima Juskelis, NCFST

Agilent/J&W Technical Support

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*** Select option 3..3..1**

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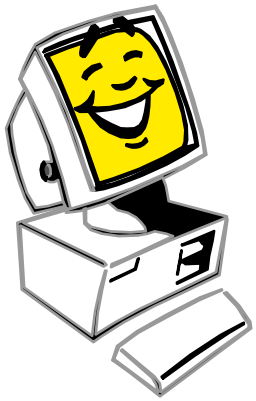

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