



Capillary Flow Technology – Productivity Enhancement Tools for Hydrocarbon Processing GC Analysis

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IF We Only Had A Technology That Provided Easy, Reliable Flow Structures In The GC Oven...



It would open up many new (and old) capabilities for GC

- **Column connections** (connect pre-column)
- **Change MSD columns** (without venting)
- **Backflush** (Reverse flow through column)
- **Detector splitter** (effluent split to two or more detectors)
- **Merge flows** (2 columns to 1 MSD)
- **Deans switch** (heart cut select peaks to 2nd column)
- **Comprehensive 2-D GC** (cut all peaks to 2nd column)
- **etc.**





Types of Connectors Used In The GC Oven



Advantages

Limitations

Metal Fittings



Packed columns, reliable

Not inert, no ferrule for capillary columns

Press Fit Glass



Low dead volume, inert, low cost

Difficult to assemble, comes apart

Graphite



High temperature

Sheds active graphite particles into sample path

Polyimide



Low initial leakage

Loosens and leaks with oven cycling, solvent tailing





Challenges For Inside the Oven Devices



- **Inertness** (it is in the sample path)
- **Low dead volume** (it is in the separation path)
- **Leak free** (especially with repeated temp cycling)
- **Fast thermal response** (follow rapid oven ramping)
- **High temp tolerance** (GC oven can go over 350C)
- **Reliable and easy to use**



5 Key Developments in Capillary Flow Technology



Metal Ferrules



Easy to use, do not loosen or leak with oven cycling to 400°C

Manifold Plates



Complex flow structures with low thermal mass

Deactivation of Metal



Makes metal surfaces as inert as column

EPC



Backflushing now possible, change MSD columns without venting, known column outlet pressure

Calculators



Accurately predict flows and pressures **BEFORE** installing devices

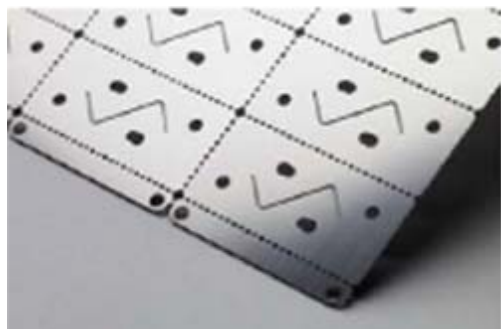
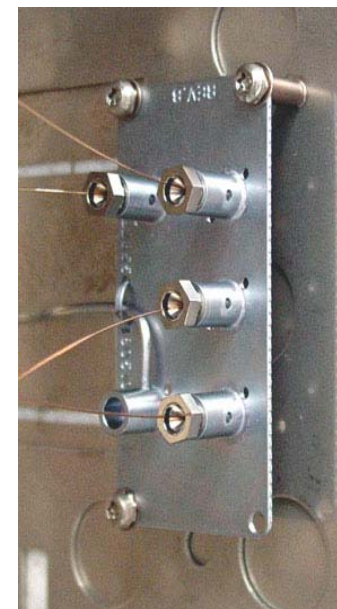


Capillary Flow Technology- Design



... a proprietary Agilent Technology

- Photolithographic chemical milling for low dead volume
- Diffusion bond two halves to form a single flow plate
- Small, thin profile provides fast thermal response
- Projection welded connections for leak tight fittings
- Deactivation of all internal surfaces for inertness





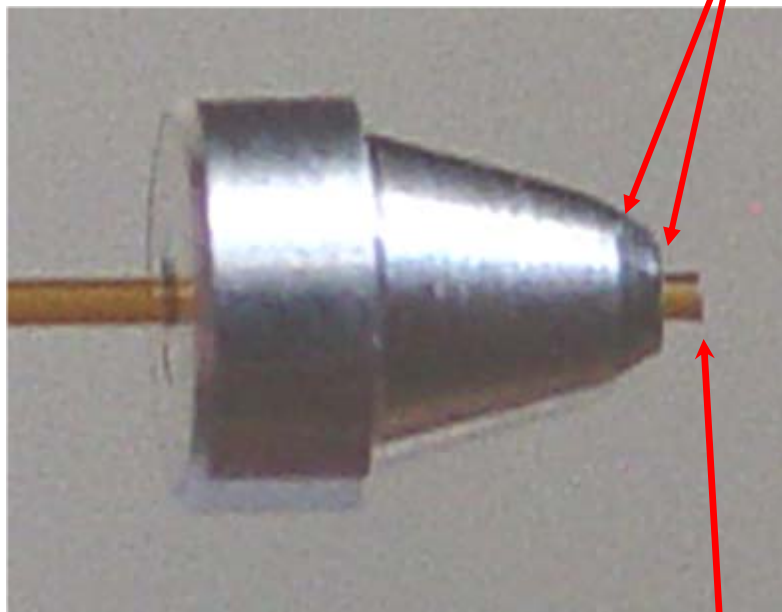
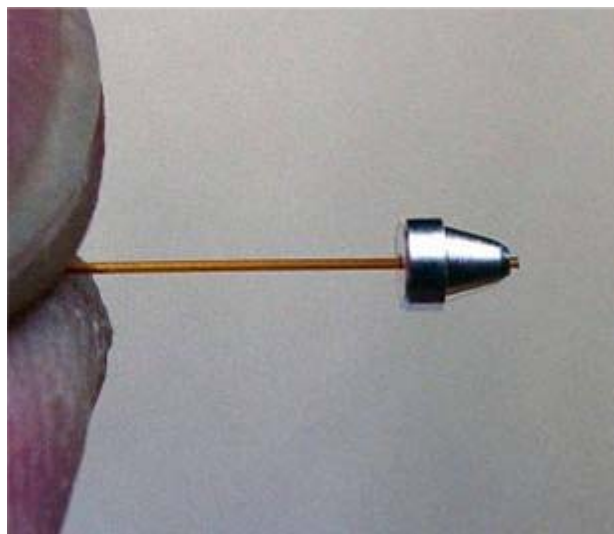
The Metal Ferrule



Does not loosen (leak) even with thousands of runs to 350C

Does not shed particles

Seal region

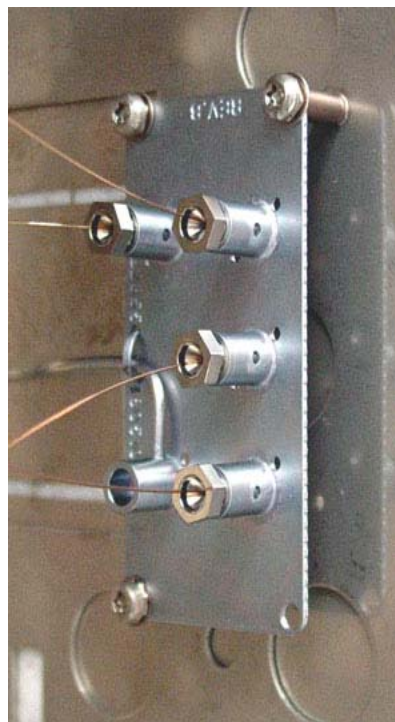
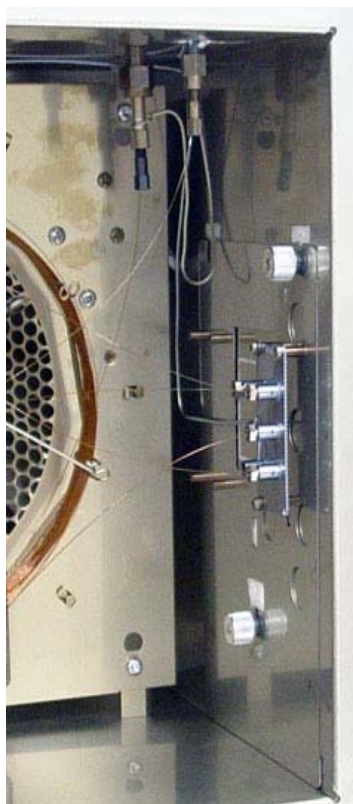


Square cut is not critical

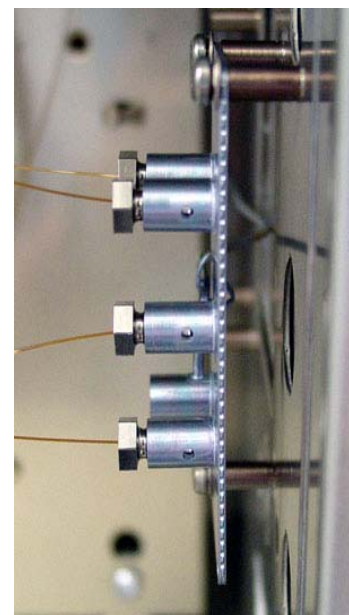
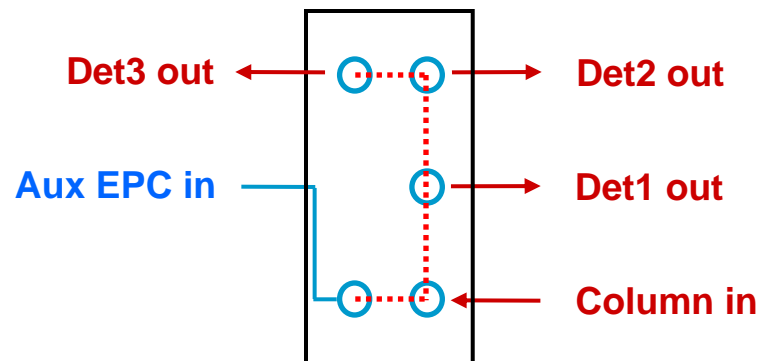




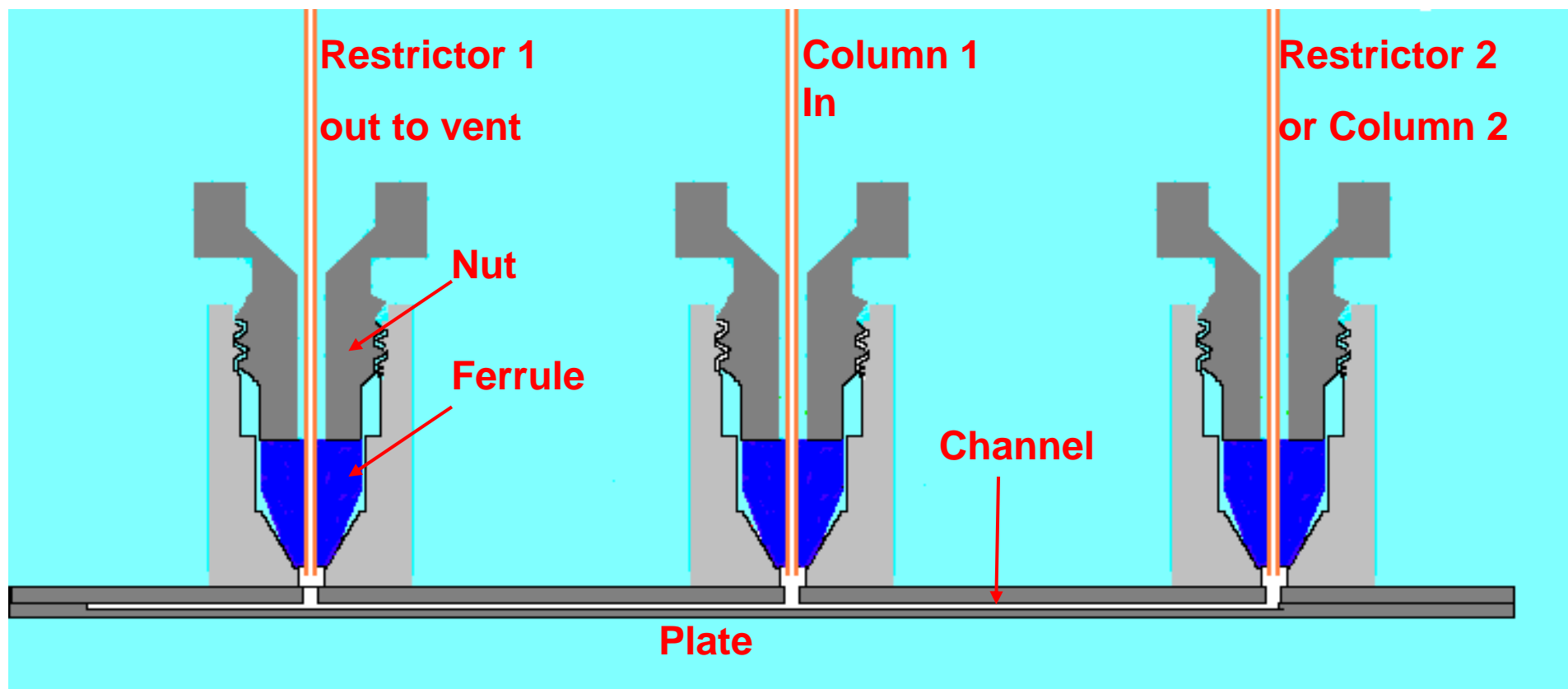
3-Way Splitter With Makeup



Effluent Splitter
(3 Way)



Capillary Flow Technology

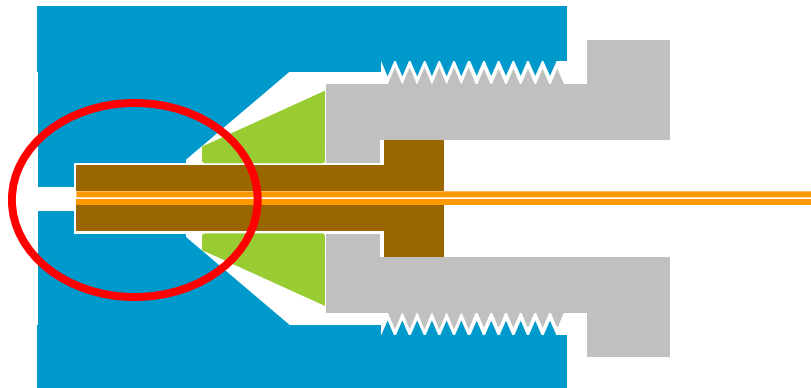




Comparison of New Fitting with Polyimide Fitting

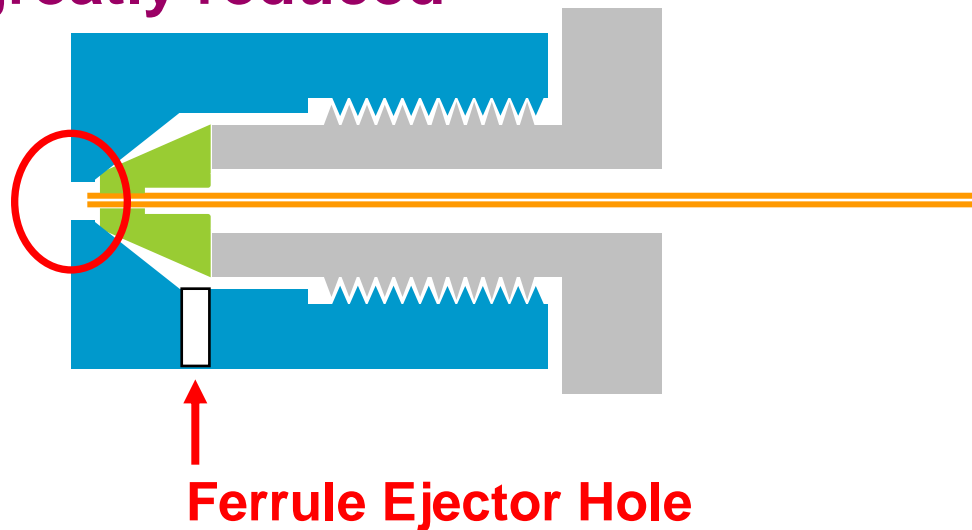


Polyimide Fitting



Exposure to polyimide and unpurged annular spaces is greatly reduced

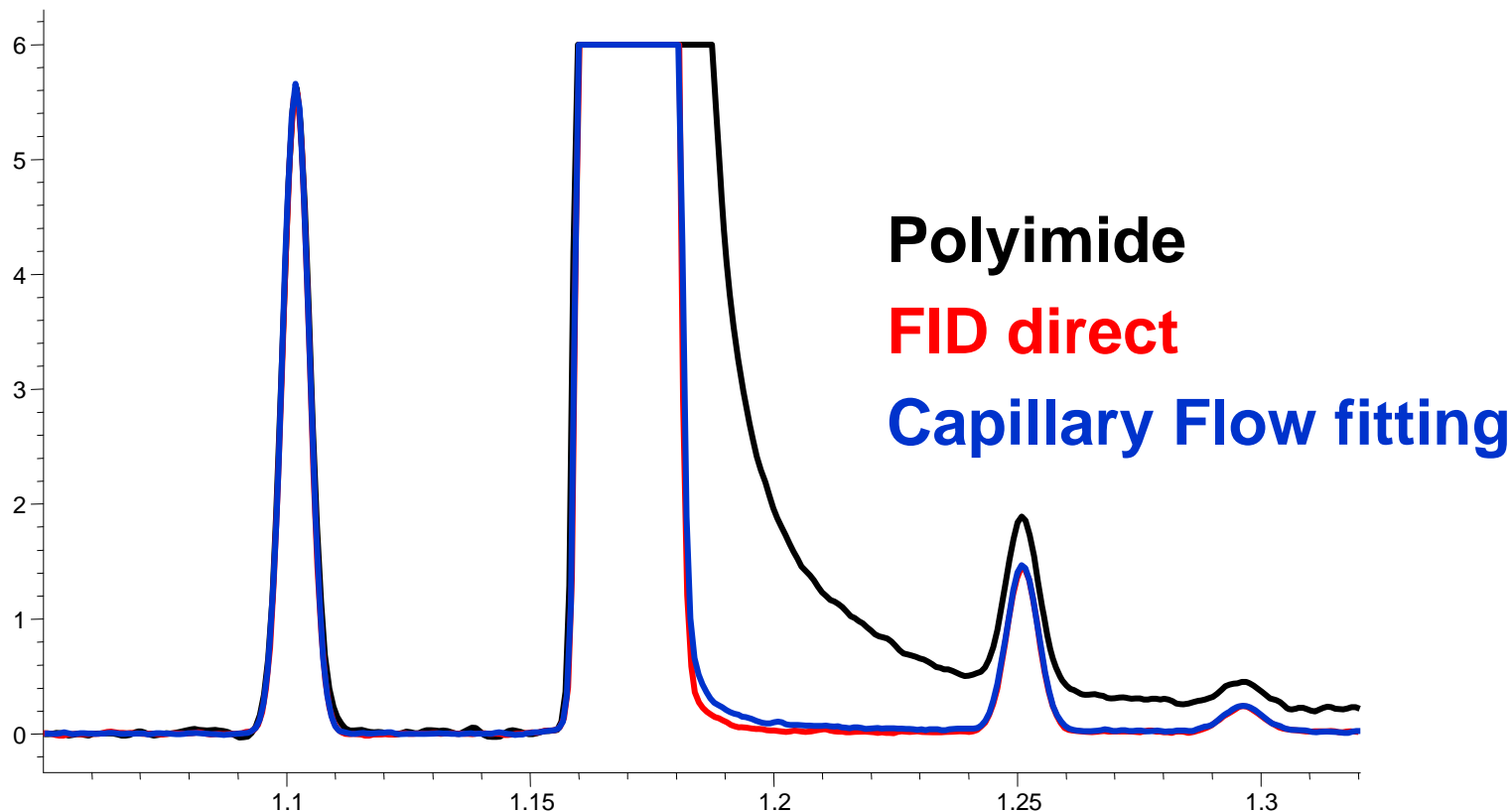
New Fitting





Fitting Design Minimizes Tailing

Pentane test chromatogram



Capillary Flow Technology fittings avoid tailing with small but well swept dead volume





Capillary Flow Technology- Capabilities



Solvent Bypass

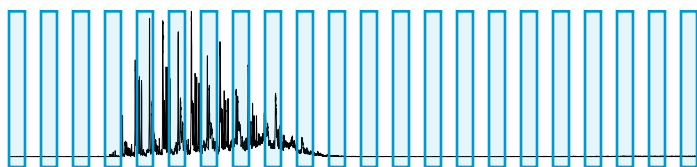
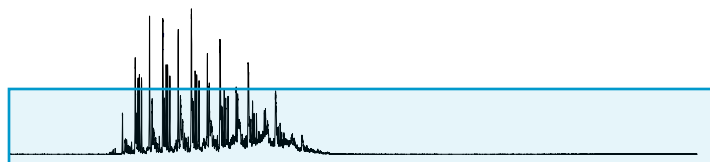
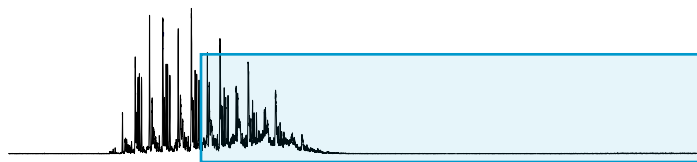
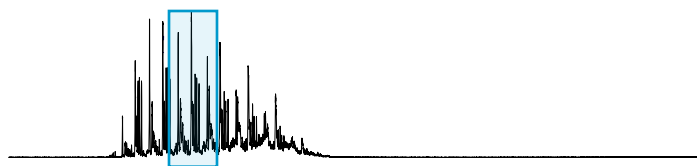
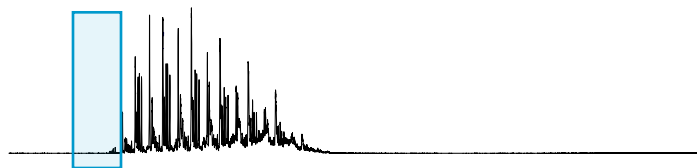
Heart Cutting (Deans Switch)

Backflush

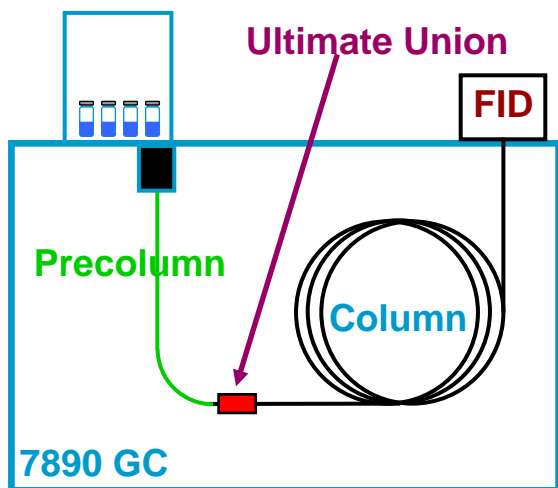
Detector Splitting

QuickSwap

Modulation (GCXGC)



Capillary Flow Technology Devices

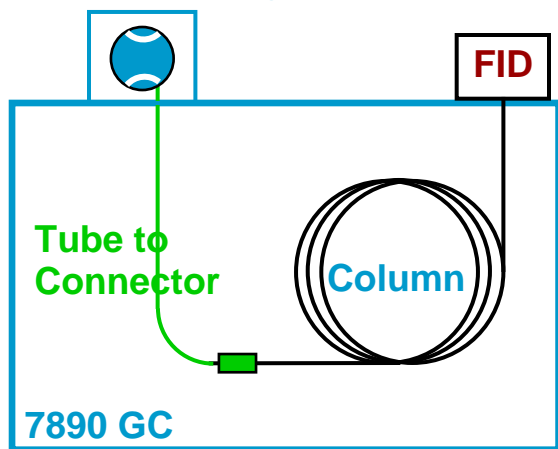


Ultimate Union

Reliable precolumn connector



Gas Sampling Valve



Tube Connector

Easy valve to capillary column connector

Tube is 0.25 mm id and is deactivated



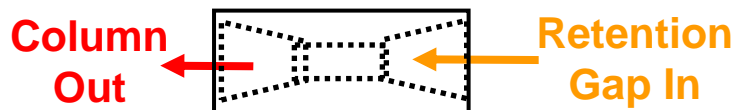
Biodiesel Analysis by EN14105/ASTM D6584

Capillary Flow Technology Ultimate Union

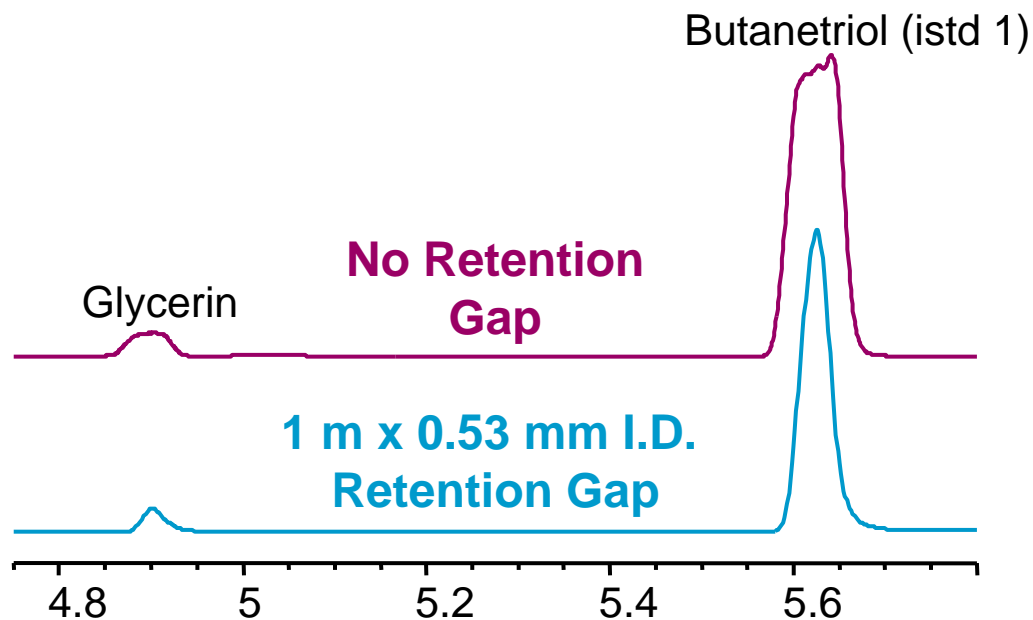


- Use 1 to 5 m, 0.53 mm ID deactivated fused silica tubing
- Improves peak shape
- Ultimate Union
 - easy, robust connection
 - deactivated
 - no-leak metal ferrule
 - optimized for high temperatures

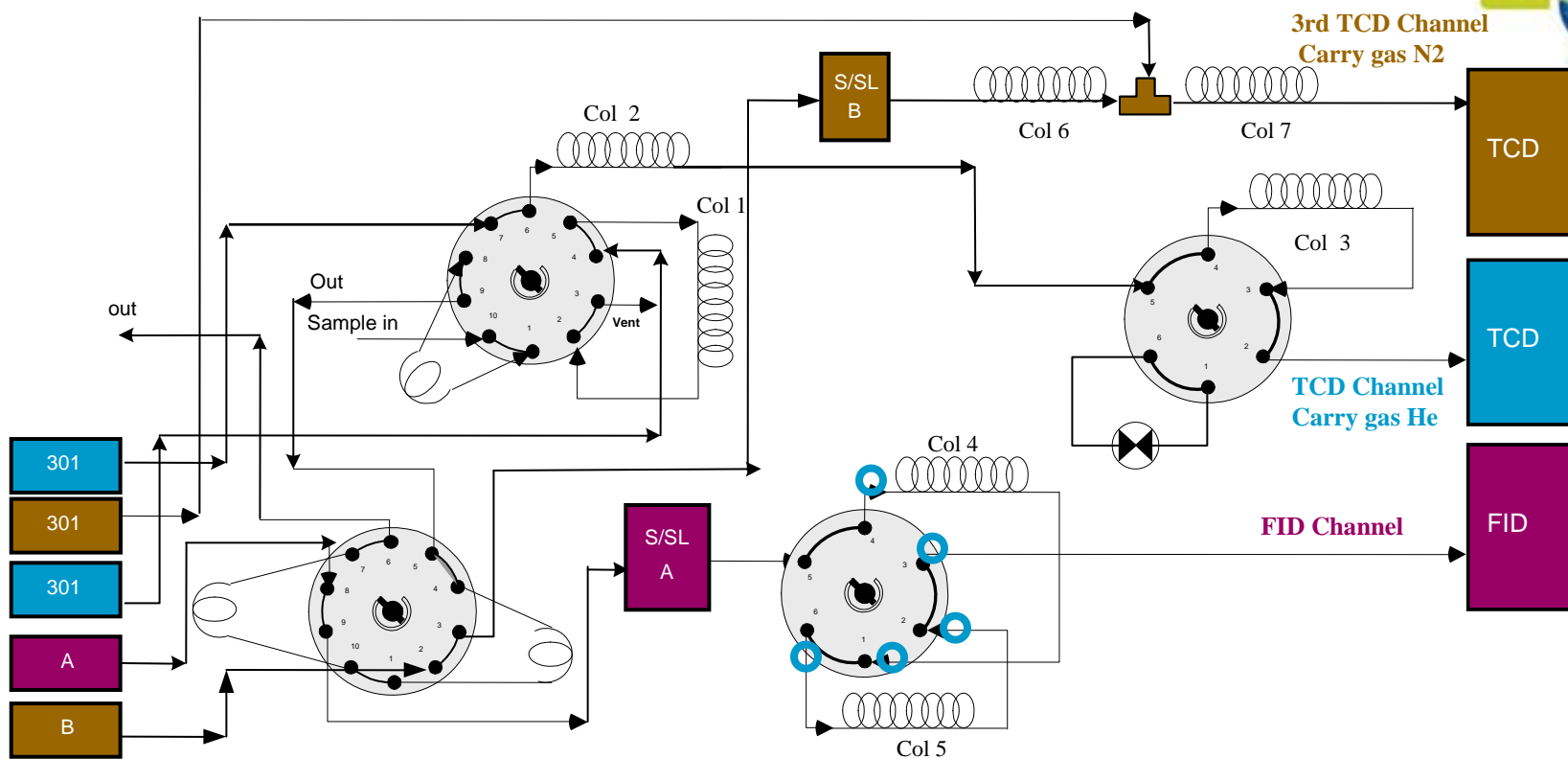
Capillary Flow Technology Ultimate Union



Inert, High Temp Metal Ferrule



Refinery Gas Analysis



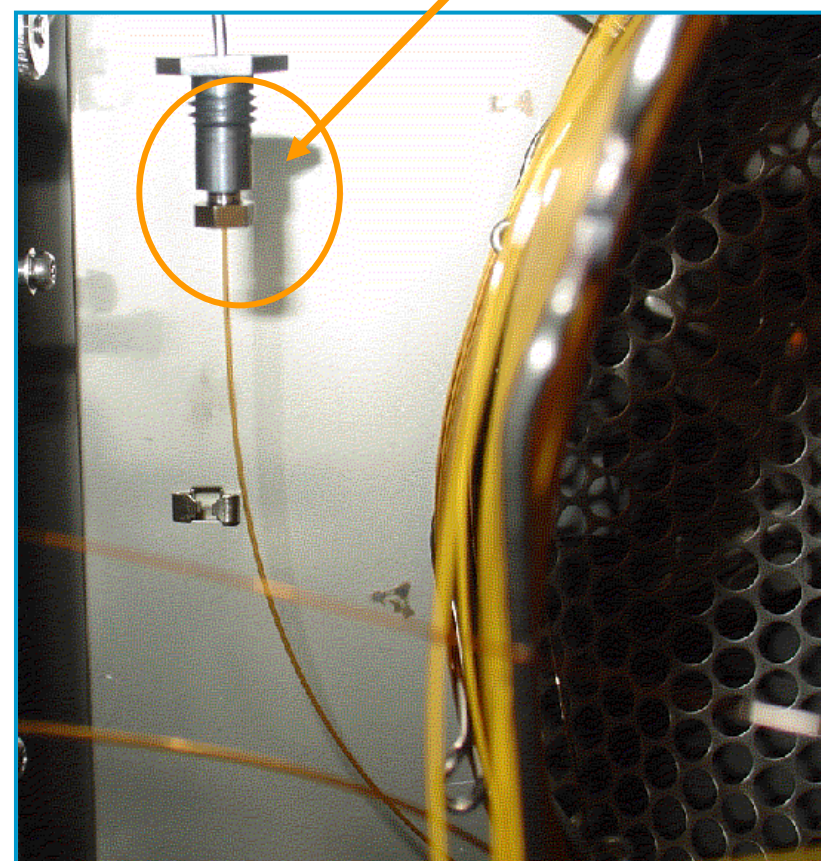
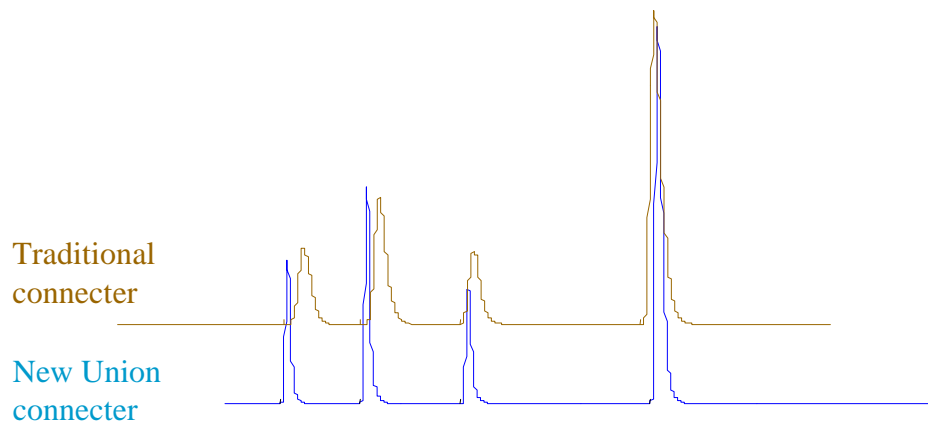
Col 1: Propark Q 80/100, 0.5m
 Col 2: Propark Q, 80/100, 6ft
 Col 3: Molsieve 5A, 60/80, 2m
 Col 4: DB-1, 2m, 0.32mm, 5um

Col 5: HP-AL/S 25m, 0.32mm, 8um
 Col 6: Carbon PL, 15m, 0.53mm, 3um
 Col 7: HP- Molsieve, 15M, 0.53mm, 50um

Enhance Gas Analysis with Ultimate Union



Column Union Connector



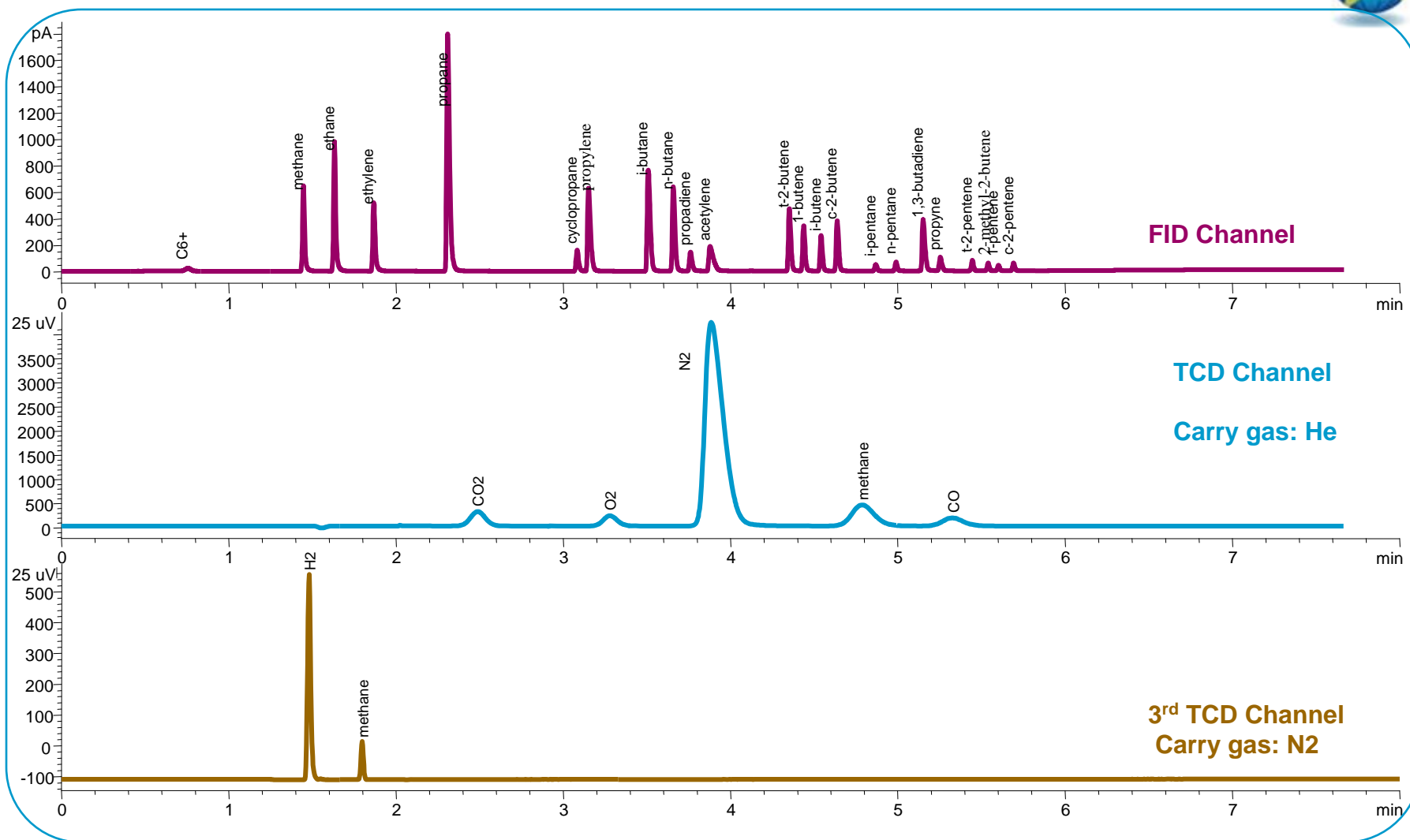
... Peak shape enhancement



Application and Result- RGA standards



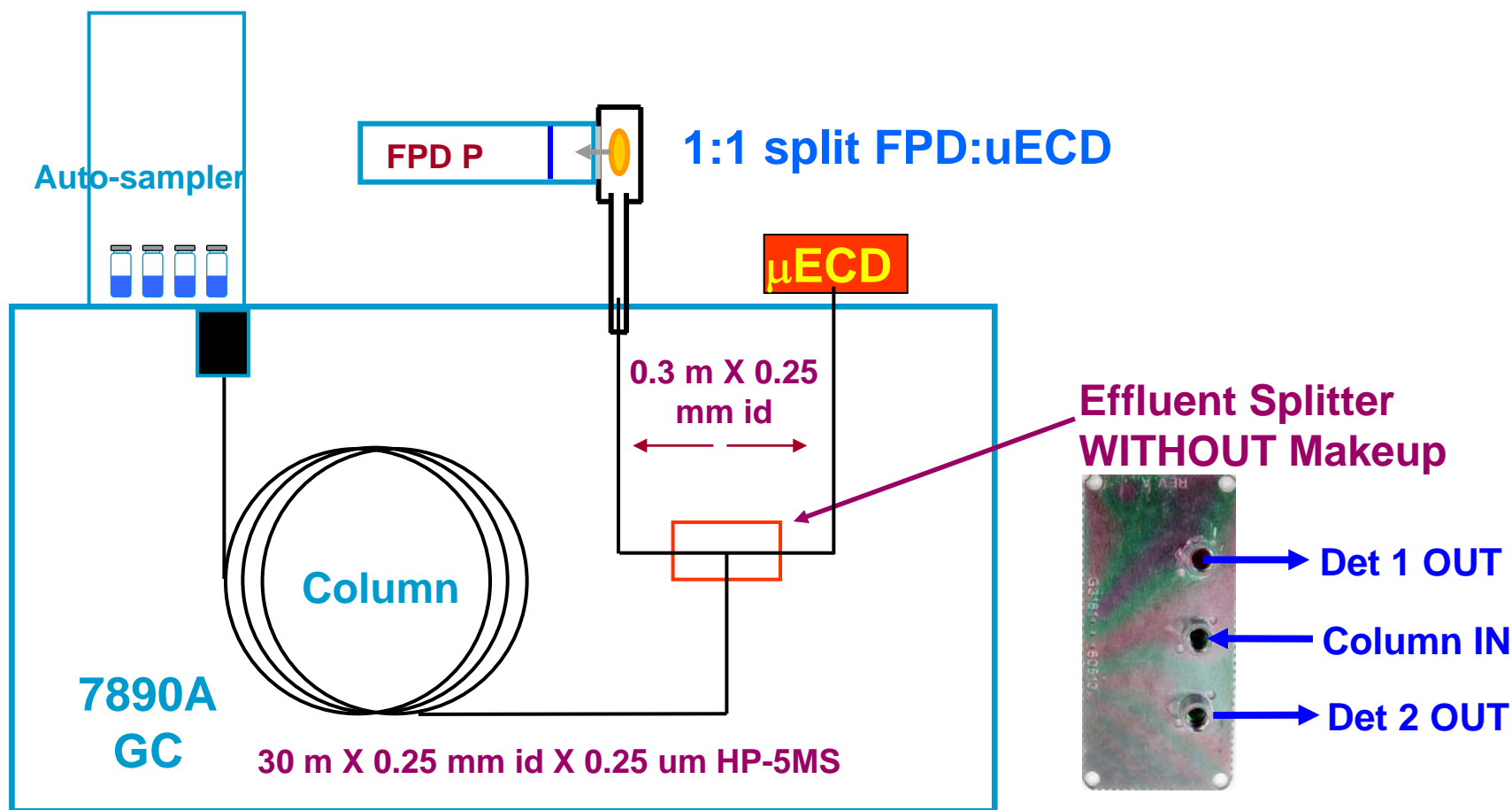
The complete analysis with one injection in 6 minutes



Splitters: Unpurged Tee

Simultaneous detection with 2 detectors (but NOT MSD)

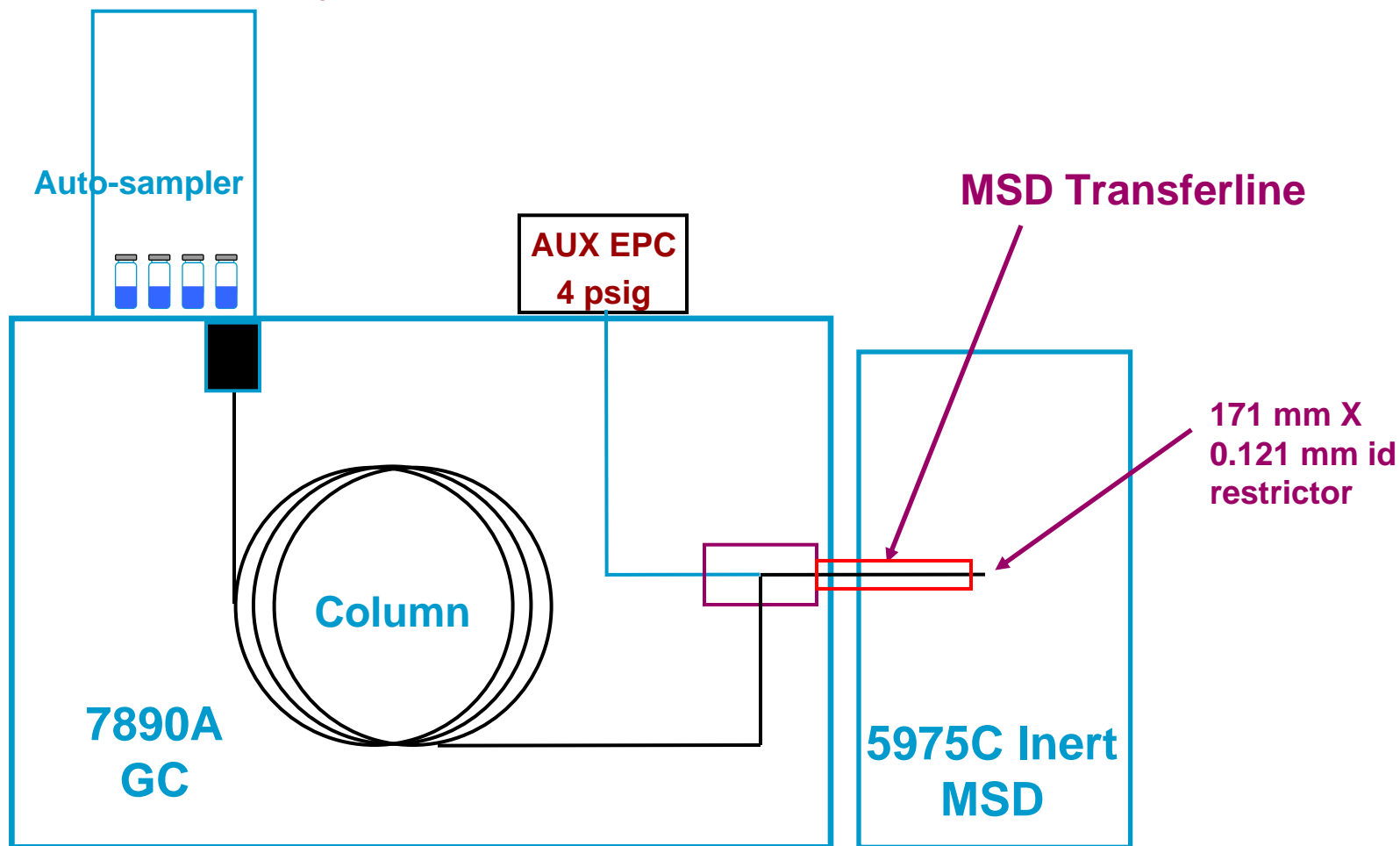
No external pressure source - Cannot do backflushing



QuickSwap



Change MSD columns without venting
Backflush heavy components out split vent



QuickSwap MSD Interface



Remove column w/o venting

- Air & H₂O blocked

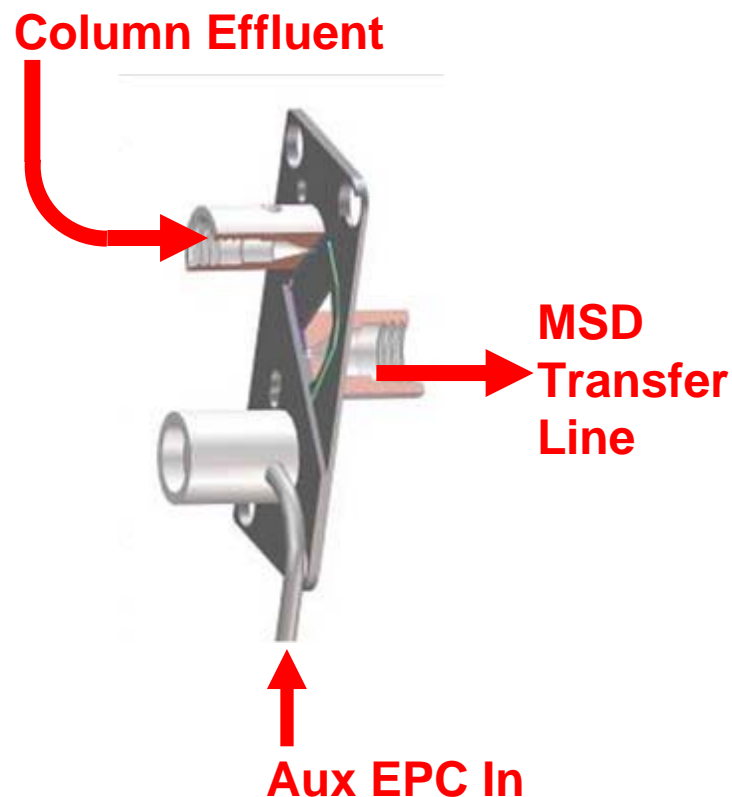
Safe disconnection of column from inlet for inlet maintenance

- Reversed flow through column during inlet maintenance

Backflushing

- Removes heavies from column

Maintain constant flow to MSD



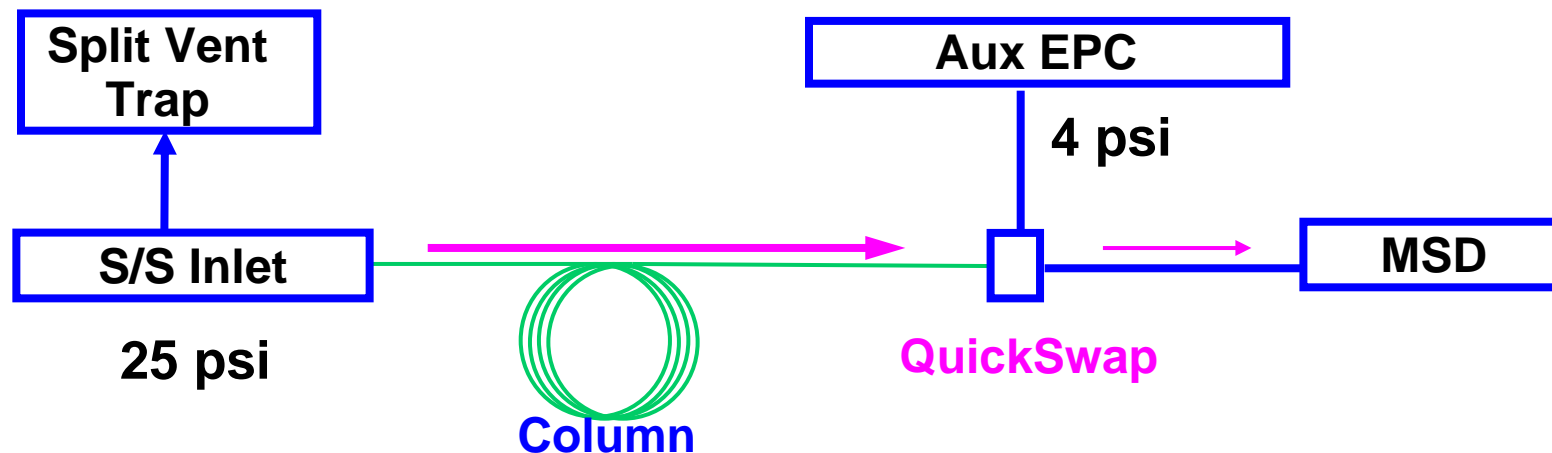
(flow rates exceeding 2 mL/min require an MSD with Performance Turbo)



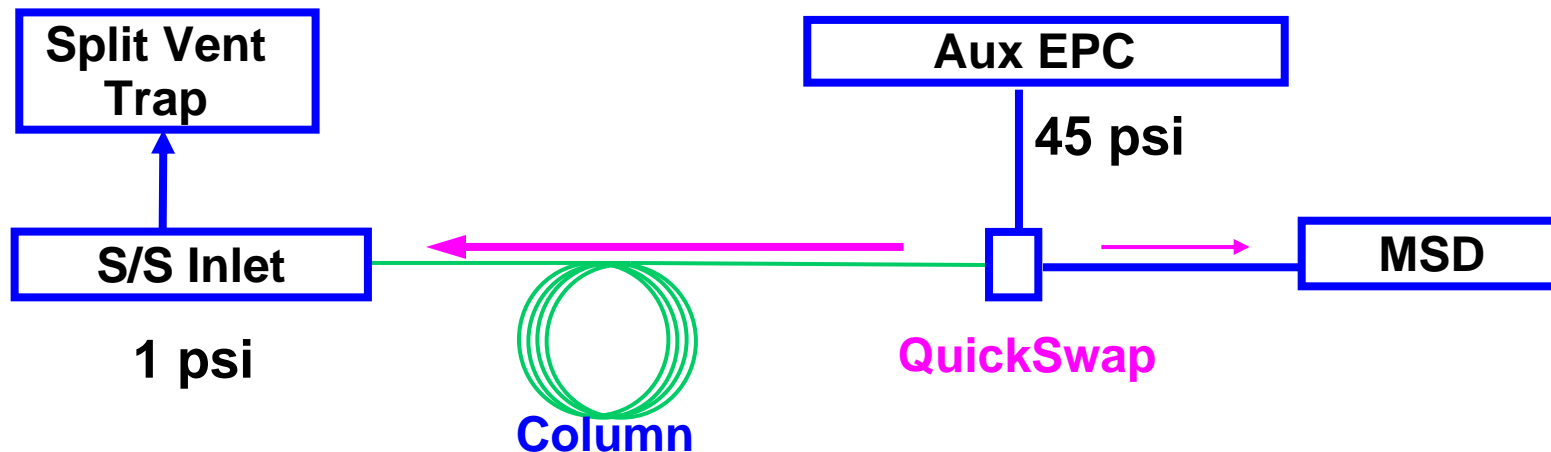


Backflush with QuickSwap

During GC Run



After GC Run





Benefits of Backflushing



- **More samples/day/instrument**
- **Better quality data**
- **Lower operating costs**
- **Less frequent and faster GC & MSD maintenance**
- **Longer column life**
- **Less chemical background**





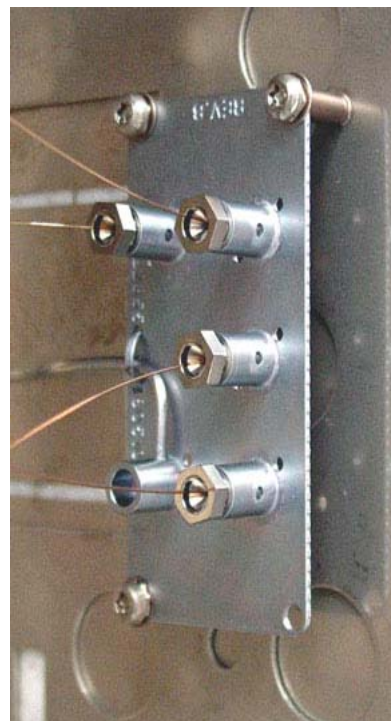
Three Other Devices Provide Backflush Capability



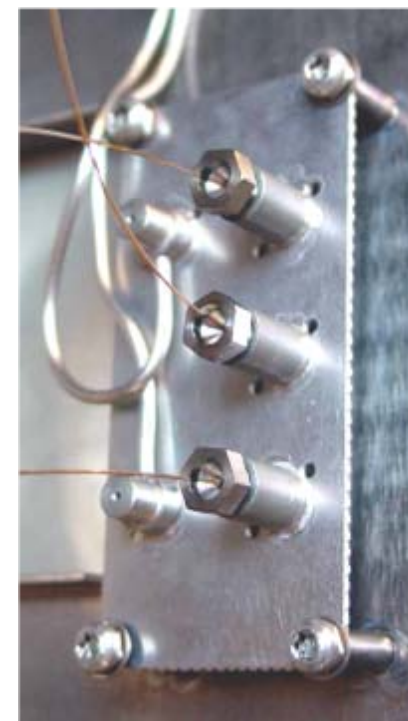
2-Way Splitter with Makeup



3-Way Splitter with Makeup



Deans Switch

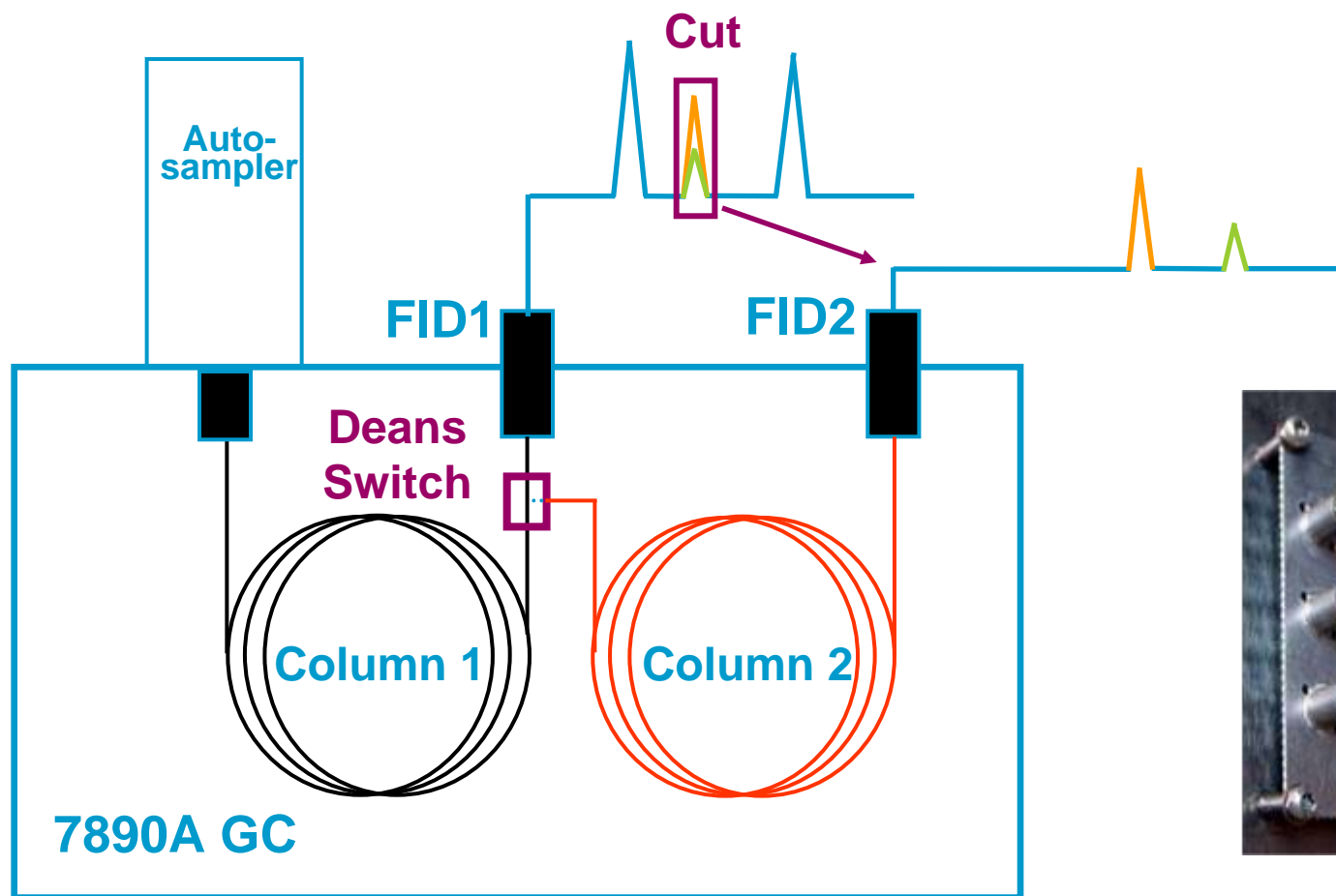




Dean Switch



Heart cutting 2-D GC provides extremely high chromatographic resolution

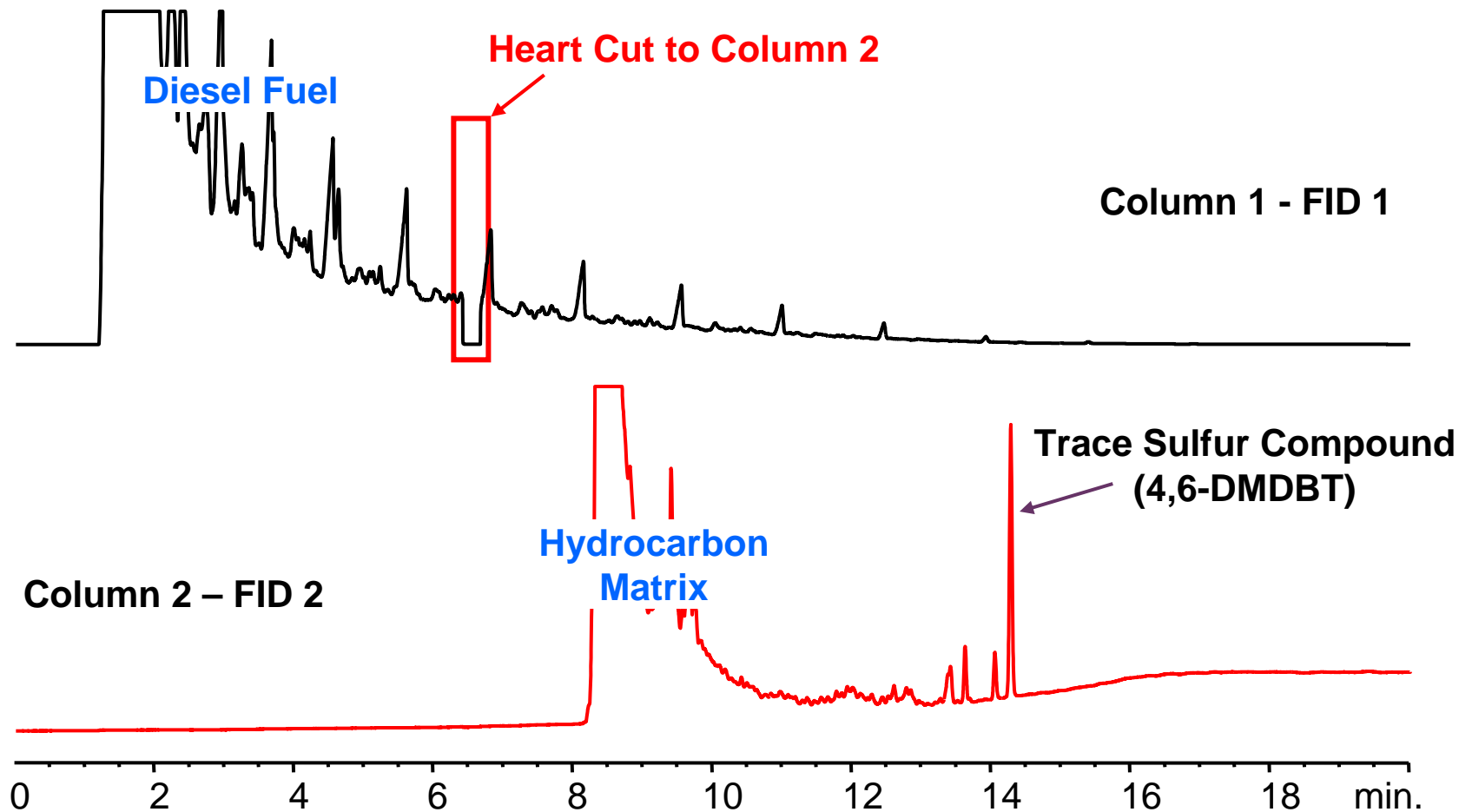




2-D Separation of Sulfur Compound in Diesel Fuel



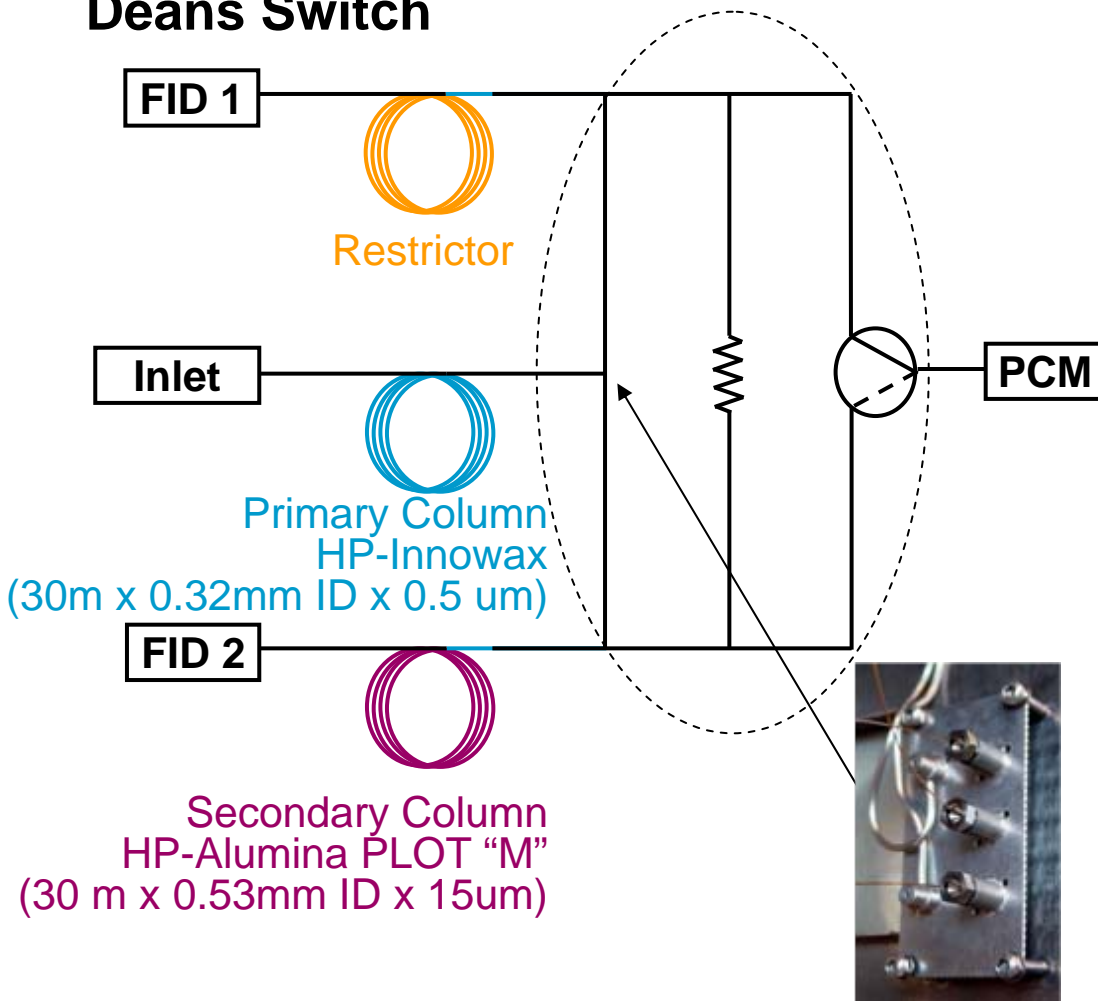
Compound is completely resolved and can be analyzed with FID



Configuration for Enhanced ASTM D6584



Capillary Flow Technology Deans Switch



ASTM D6584 measures trace hydrocarbons

- uses alumina PLOT column

Oxygenates best separated on HP-Innowax column

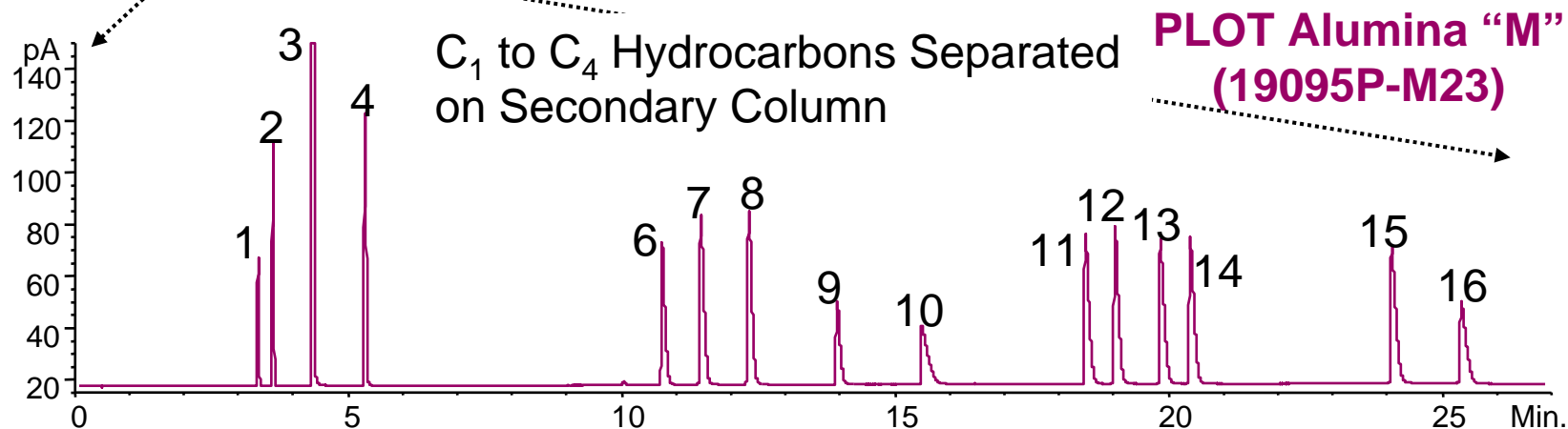
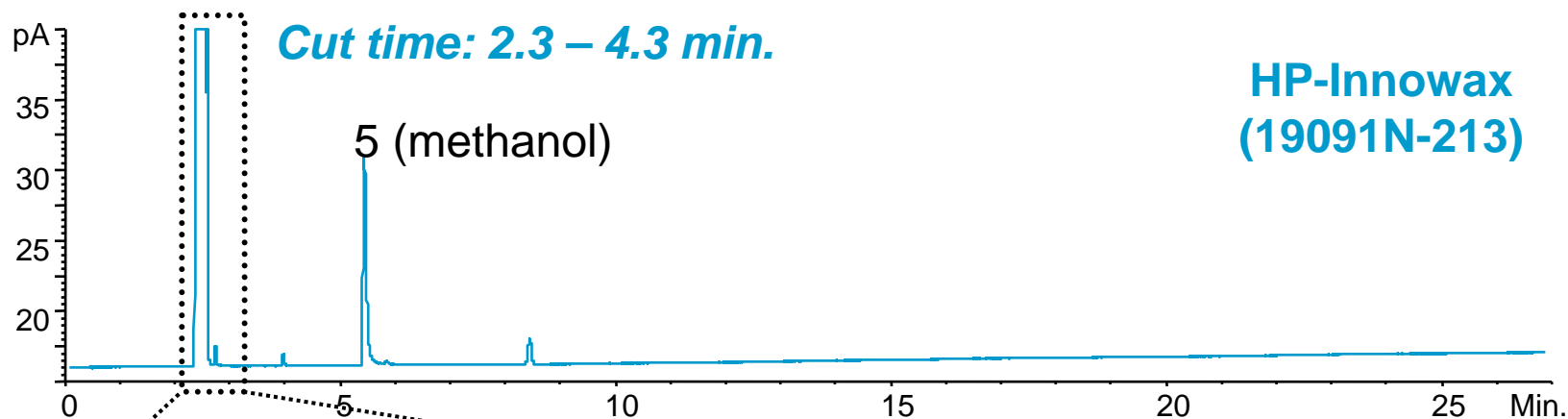
Use Deans switch to combine two methods into one

- primary column separates oxygenates
- Deans switch selectively transfers only the hydrocarbons to alumina PLOT
- HP-Innowax column protects alumina PLOT from damage

Complete Separation of Oxygenates and Hydrocarbons



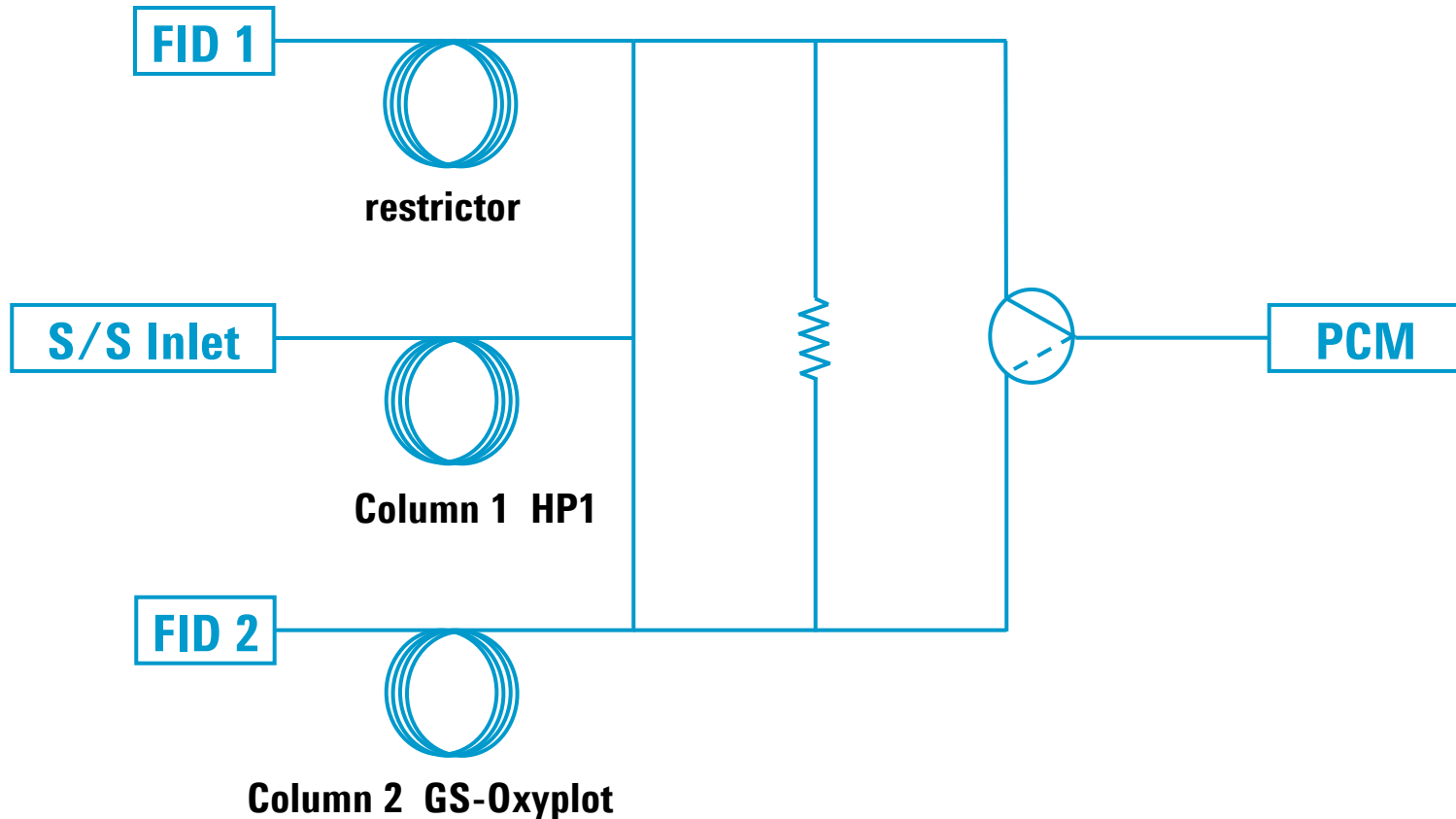
Heart-Cutting 100 ppmV Impurities in Ethylene



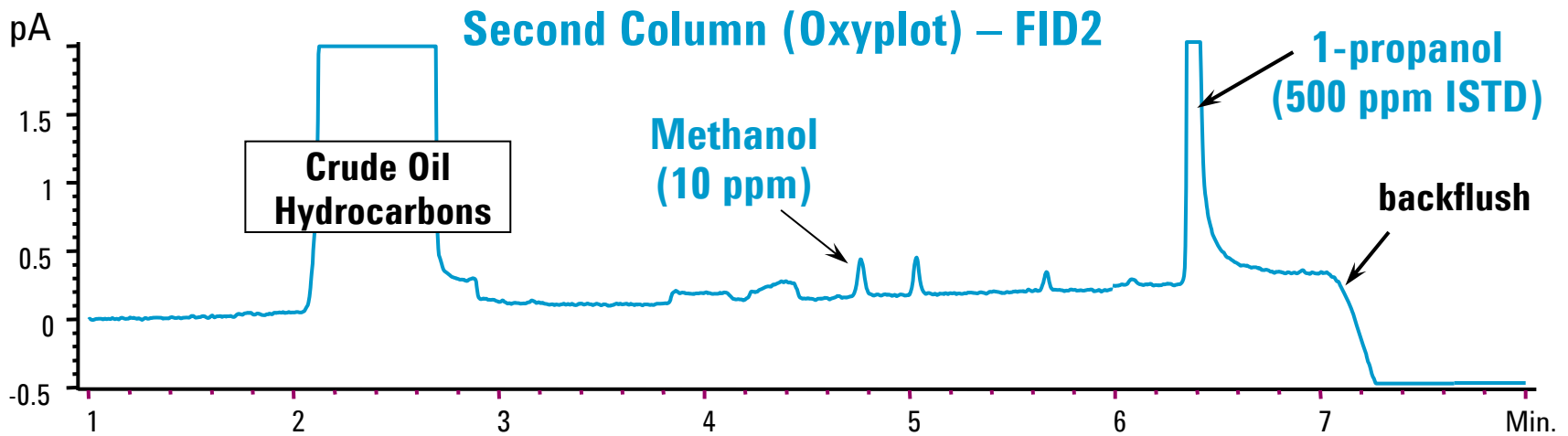
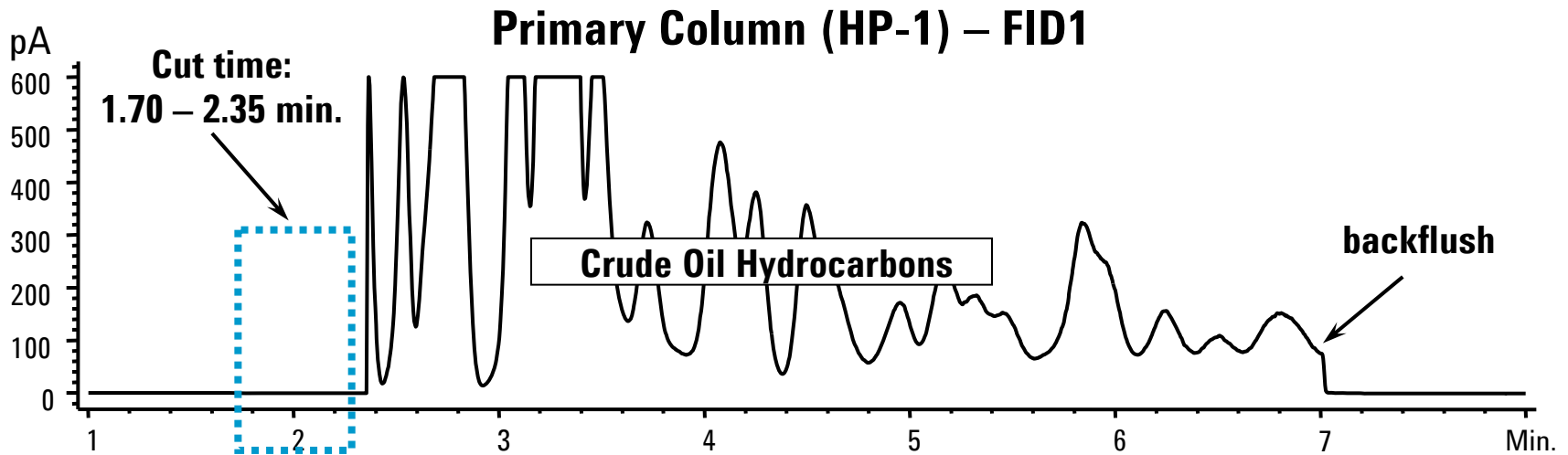
ASTM 7059 - Trace Methanol in Crude by 2-D GC



Used to "heart cut" alcohols from HP-1 column to Innowax



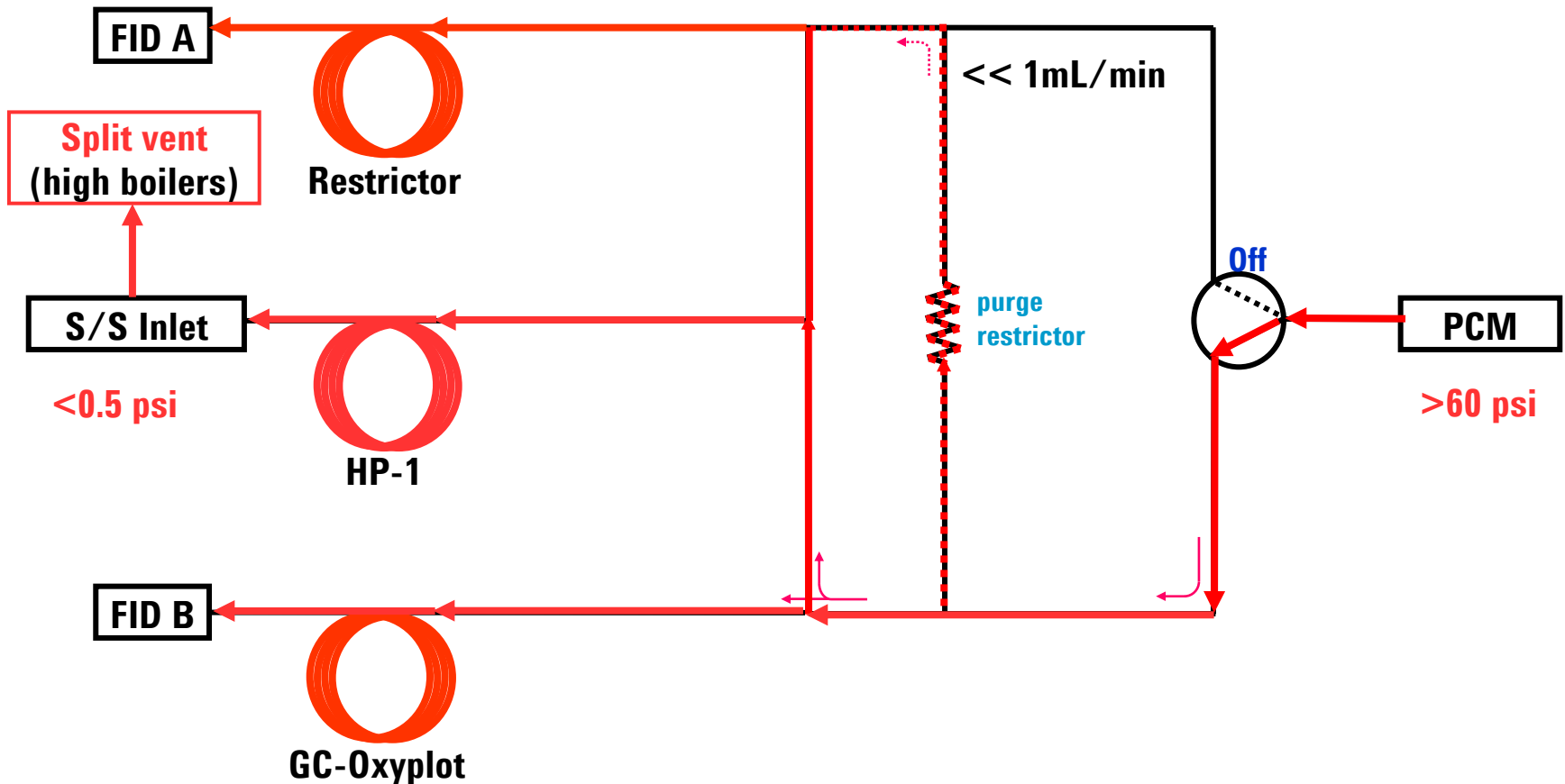
ASTM 7059 - Trace Methanol in Crude by 2-D GC



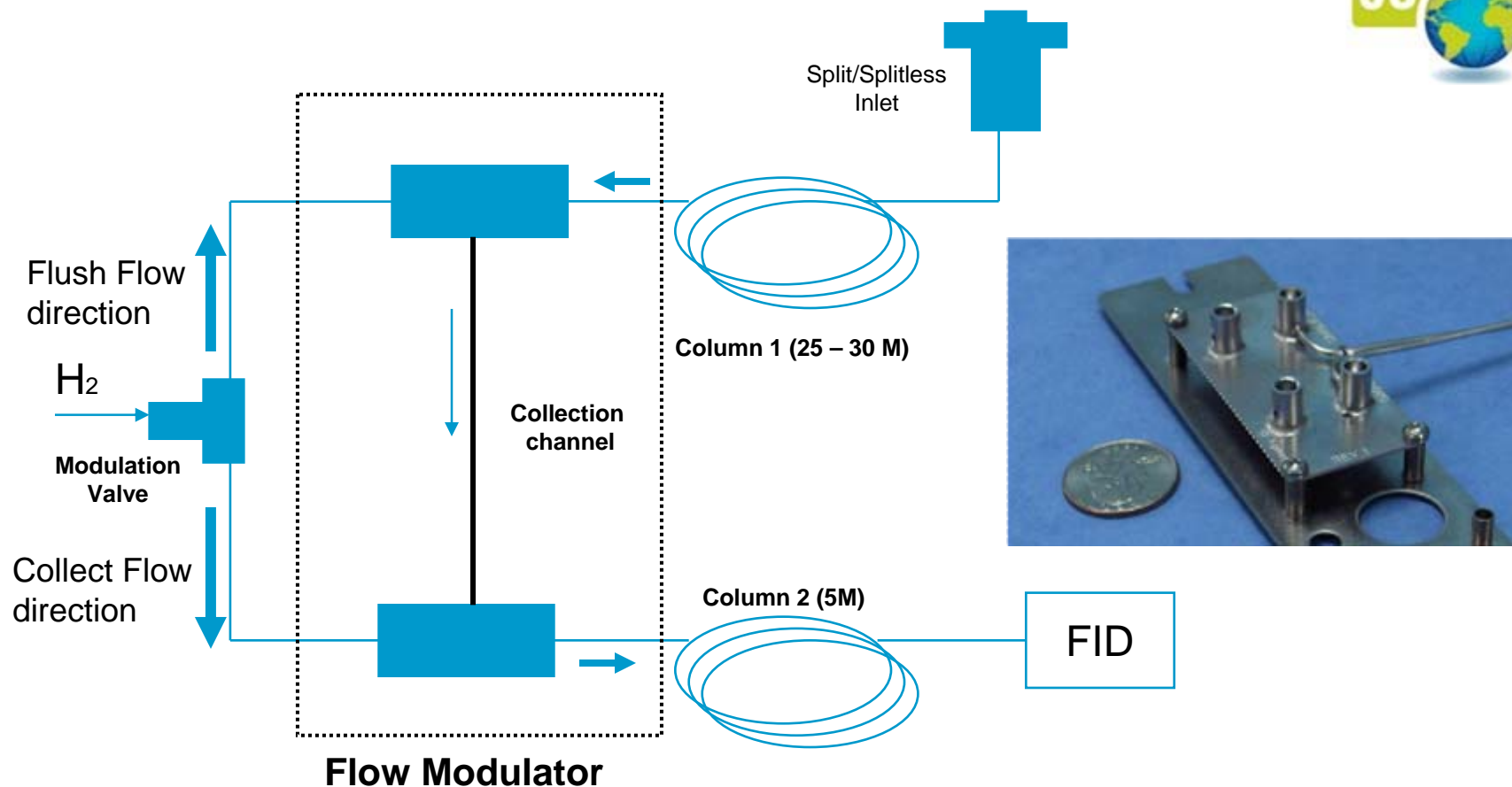
Backflush To Decrease Run Time



Valve off – Lower Inlet pressure, Increase PCM pressure



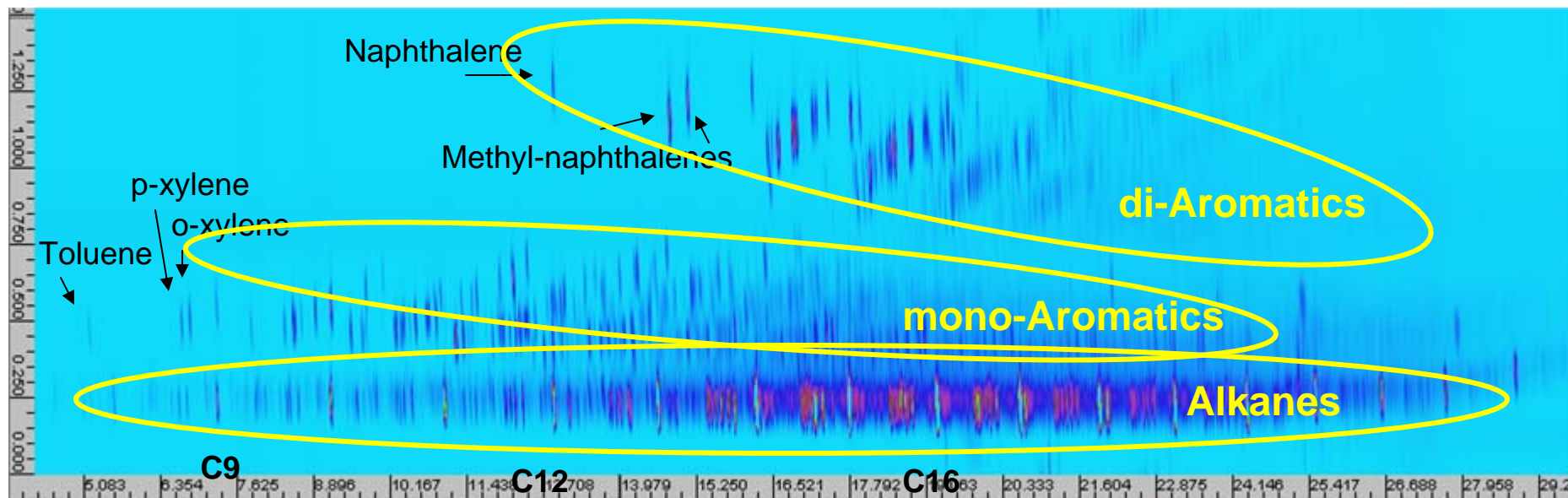
Agilent's flow modulator design : Differential Flow



Differential flow concept is designed by John V. Seeley, Oakland University

Flow modulator eliminates the need for cryo. Sample compression controlled by flow ratios occurs in the collection loop and is quickly injected into the second column, resulting in very narrow and tall peaks.

Flow modulation: (GC x GC) of diesel fuel: 7890A



GC x GC Chromatogram:

- Showing the normal B.P. distribution (1st dimension)
- Also shows hydrocarbon classes in clusters
- Consistent RT for alkanes in 1st dimension showing precise modulation
- Comparable peak in 2nd dimension band shows minimum peak broadening with flow modulation



Agilent Flow Modulation GC x GC



- **Reliable Setup:** Based on capillary-flow- technology, easy to setup, high performance chromatography, and reliable.
- **No Cryogen Required:** Flow modulation means no tanks of Liquid N₂ or CO₂
- **7890A Enabled GC x GC:** Capillary- flow-technology ready, synchronized periodic events ensure precise modulation, control from a modified TCD board
- **Comparable resolution without Liquid N₂:** Cap Flow Technology allows low dead volume and precise flow control, resulting in minimum peak broadening even without cryo-focusing . Peak widths on the second column are typically 70 to 100 ms at half maximum.
- **Sensitivity:** Approaches that obtained by thermally modulated systems





Summary



Capillary Flow Technology solves difficult application problems easily.

It opens up many new (and old) possibilities for GC and GC/MS systems.

