Analysis and Chromatographic Separation of Oxygenates in Hydrocarbon Matrices

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October 11th, 2007

Agenda

- WCOT vs. PLOT columns
- OxyPlot – A Unique stationary phase
  - Trace oxygenates in reformulated gasoline
- Capillary Flow Technology (CFT)
  - Heart cutting and back-flushing

WCOT vs. PLOT

Type	Stationary Phase	Chromatographic Process	Stationary Phases
WCOT	Liquid or gum	Gas / Liquid partition	Polysiloxanes PEG
PLOT	Solid	Gas solid adsorption	Porous Polymers, Al_2O_3, Zeolites, etc.

Film Thickness and Retention (WCOT): Isothermal

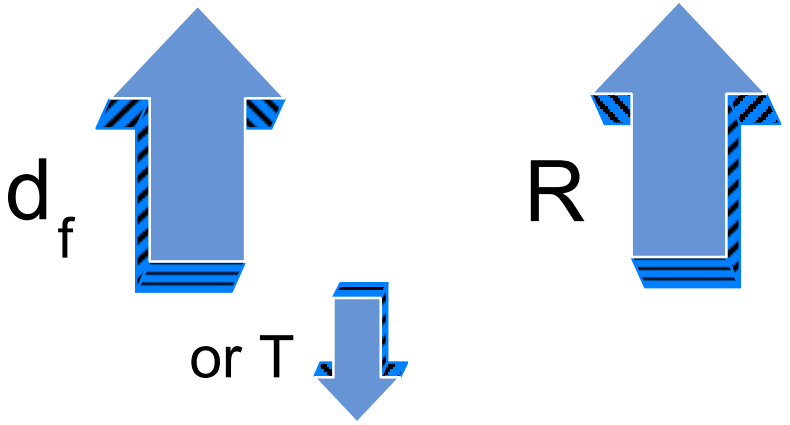
Thickness (µm)	Retention Change
0.10	0.40
0.25	*1.00*
1.0	4.00
3.0	12.0
5.0	20.0

Constant Diameter
Normalized to 0.25 µm

Film Thickness and Resolution

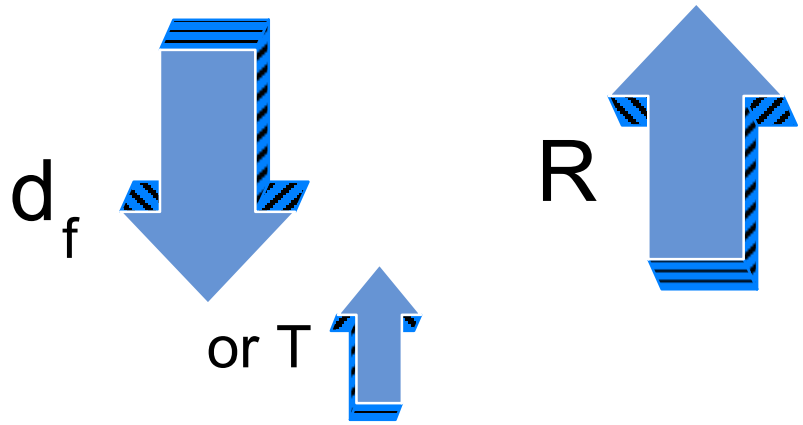
When solute k < 5

(early eluters)

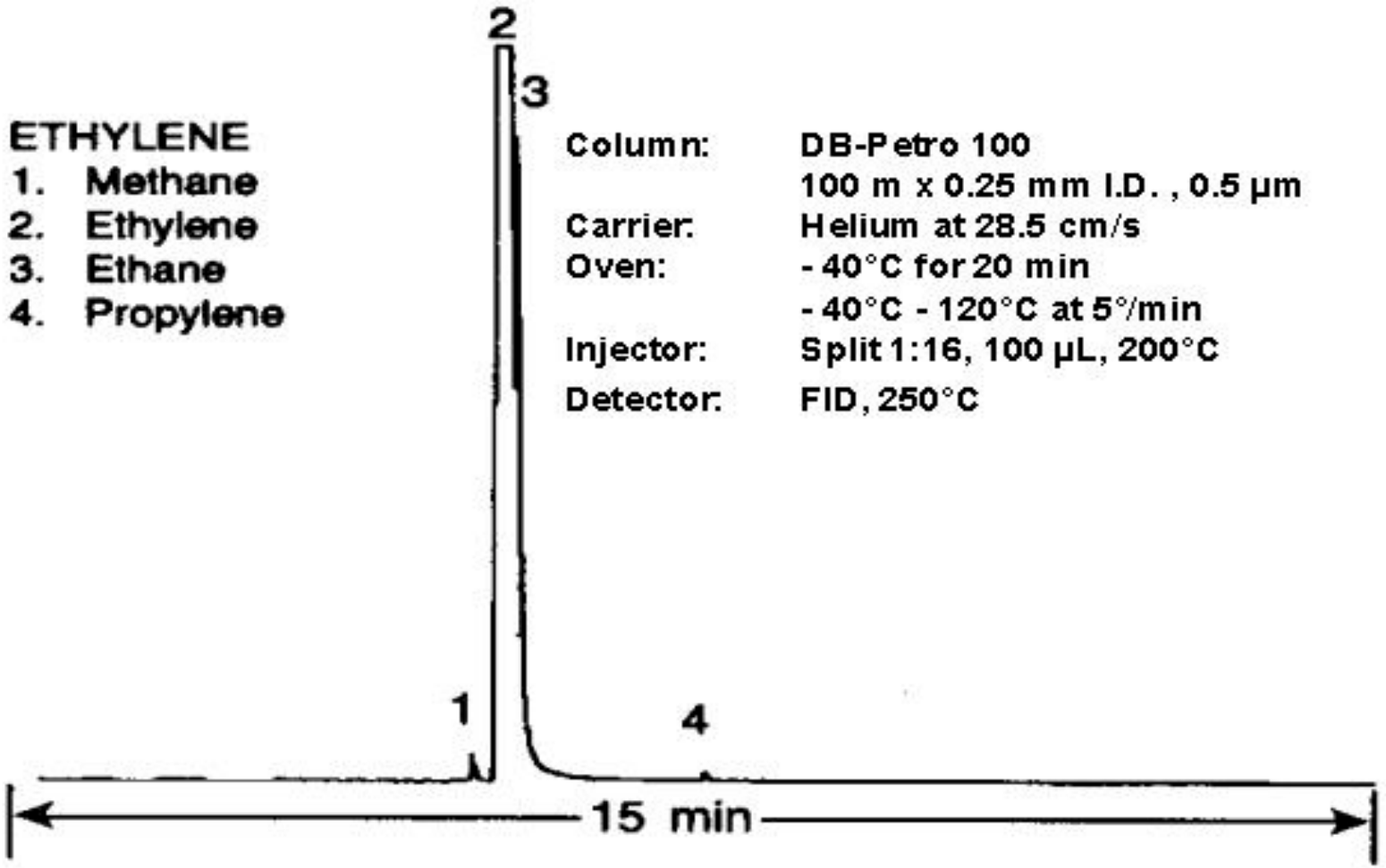


When solute k > 5

(later eluters)



WCOT Ethylene Analysis

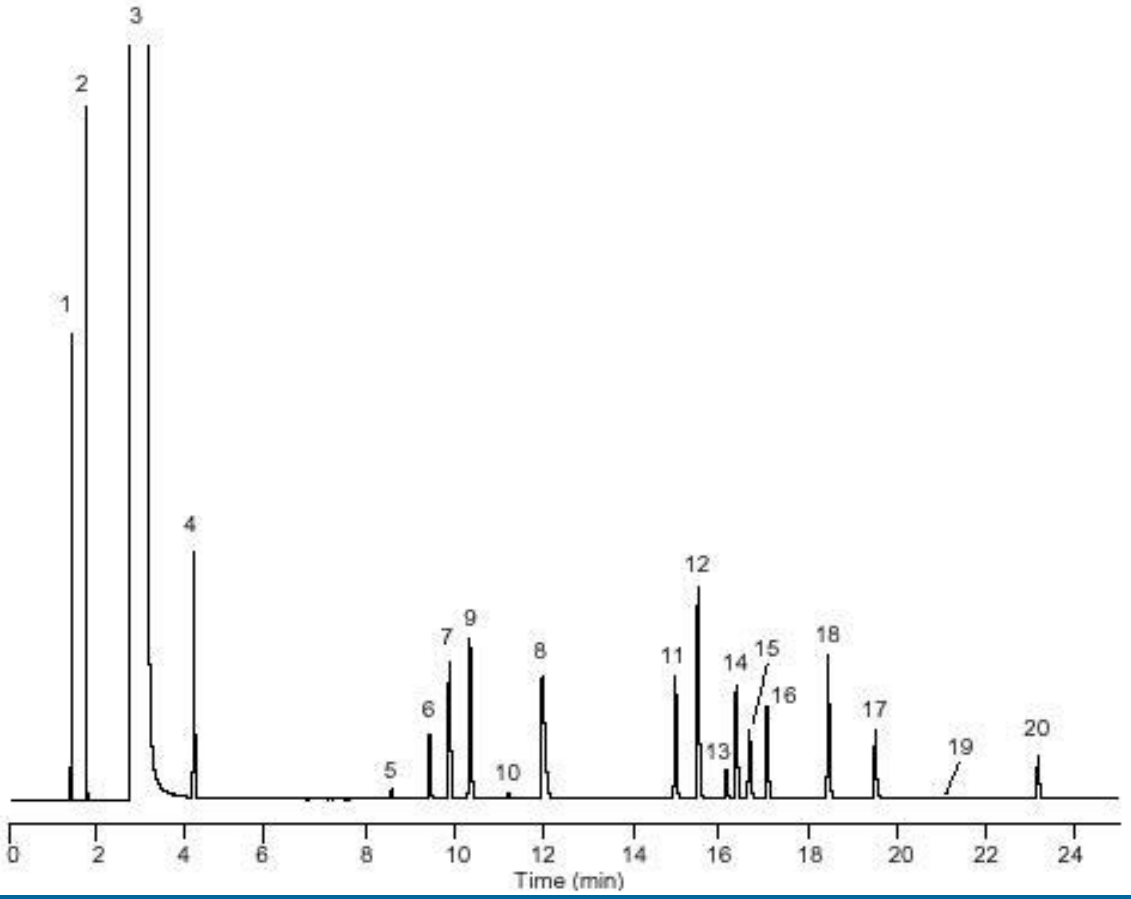


PLOT Ethylene Analysis

Ethylene

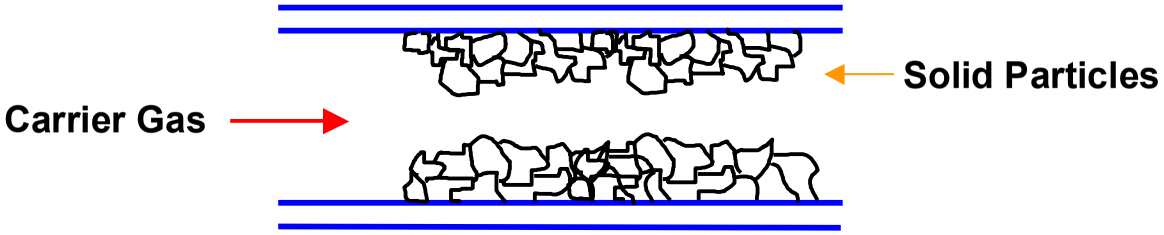
Column: **GS-Alumina**
50 m x 0.53 mm I.D.
J&W P/N: **115-3552**
Carrier: Helium at 11 mL/min, measured at 35°C
Oven: 35°C for 2 min
35-190°C at 6°/min
190°C for 3 min
Injector: Split 1:30, 200°C
0.2 mL of trace hydrocarbons in ethylene
Detector: FID, 200°C
Nitrogen makeup gas at 20 mL/min

1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Cyclopropane
6. Propylene
7. Isobutane
8. Acetylene
9. *n*-Butane
10. Propadiene
11. *trans*-2-Butene
12. 1-Butene
13. Isobutylene
14. *cis*-2-Butene
15. Isopentane
16. *n*-Pentane
17. Propyne
18. 1,3-Butadiene
19. 1-Pentene
20. *n*-Hexane

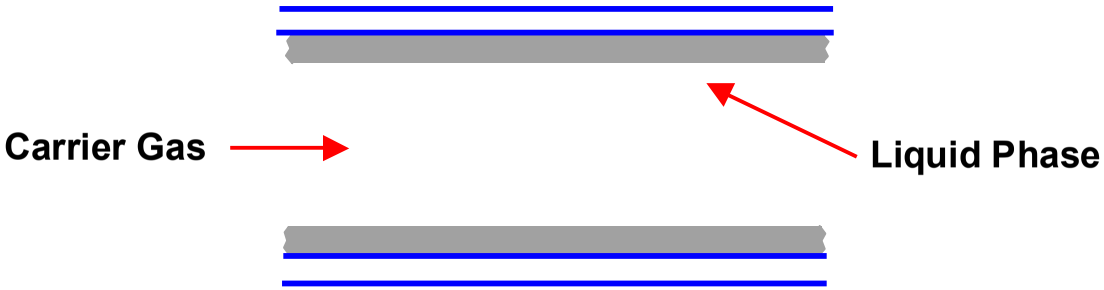


C585

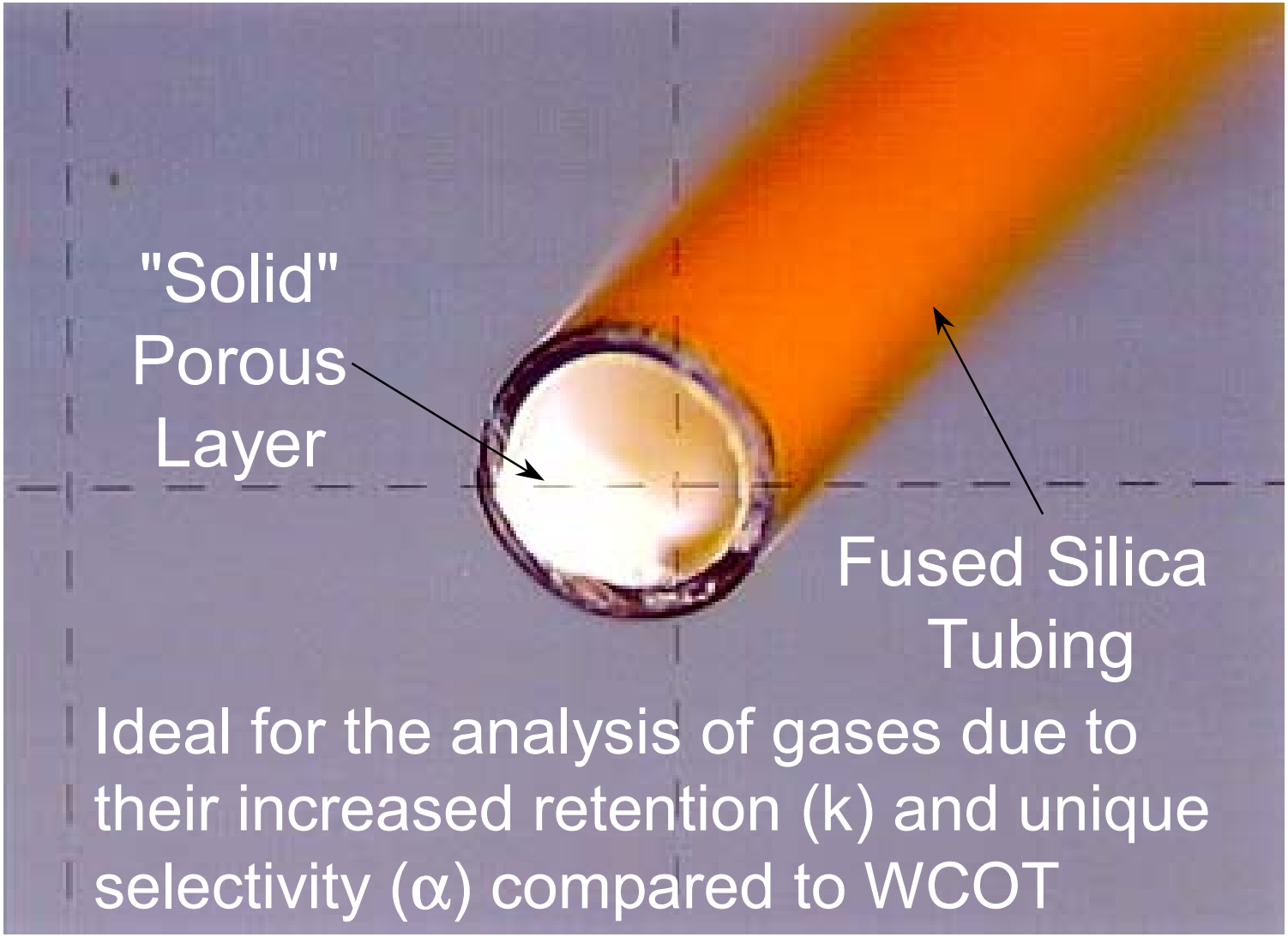
Capillary Column Types



Wall Coated Open Tube (WCOT)



PLOT Columns



Selectivity Interactions in PLOT Phases

Shape / Size

Surface

Zeolites

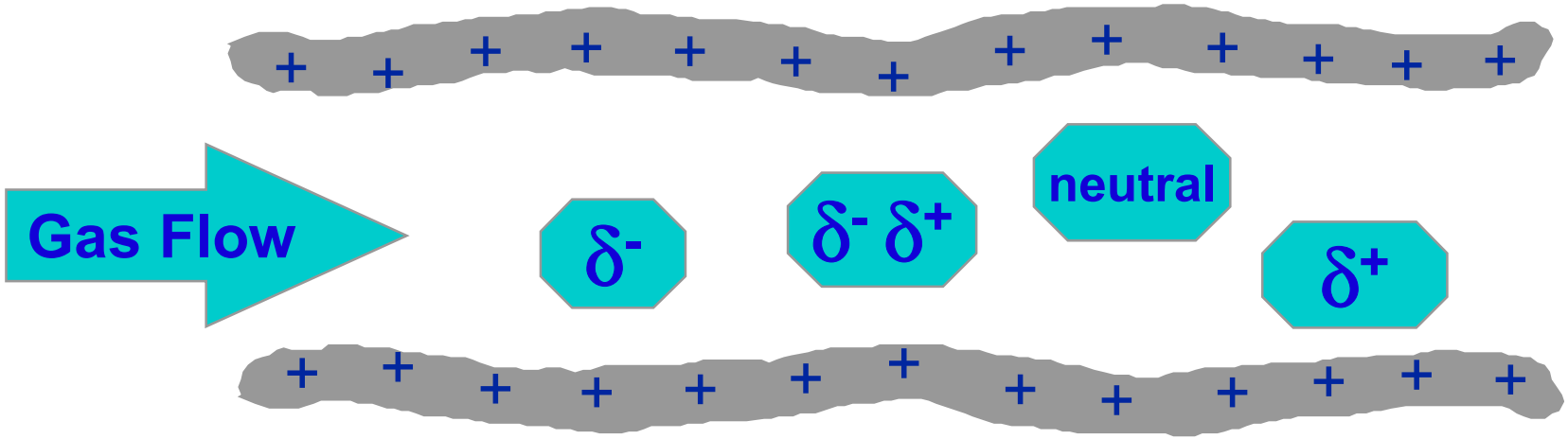
Al_2O_3

Porous Polymers

Bonded Carbon Molecular Sieves

Bonded Silica

Surface Interactions in PLOT Columns



Vapor pressure always plays a leading role in solute interactions

Considerations for PLOT Column Analysis

- Inlet issues
  - split versus direct injection
  - gas sampling valves
  - low dead volume
  - column ID and flow rate
- Detector issues
  - particle generation or “spiking”; particle traps
  - column ID and flow rate

Considerations for PLOT Column Analysis

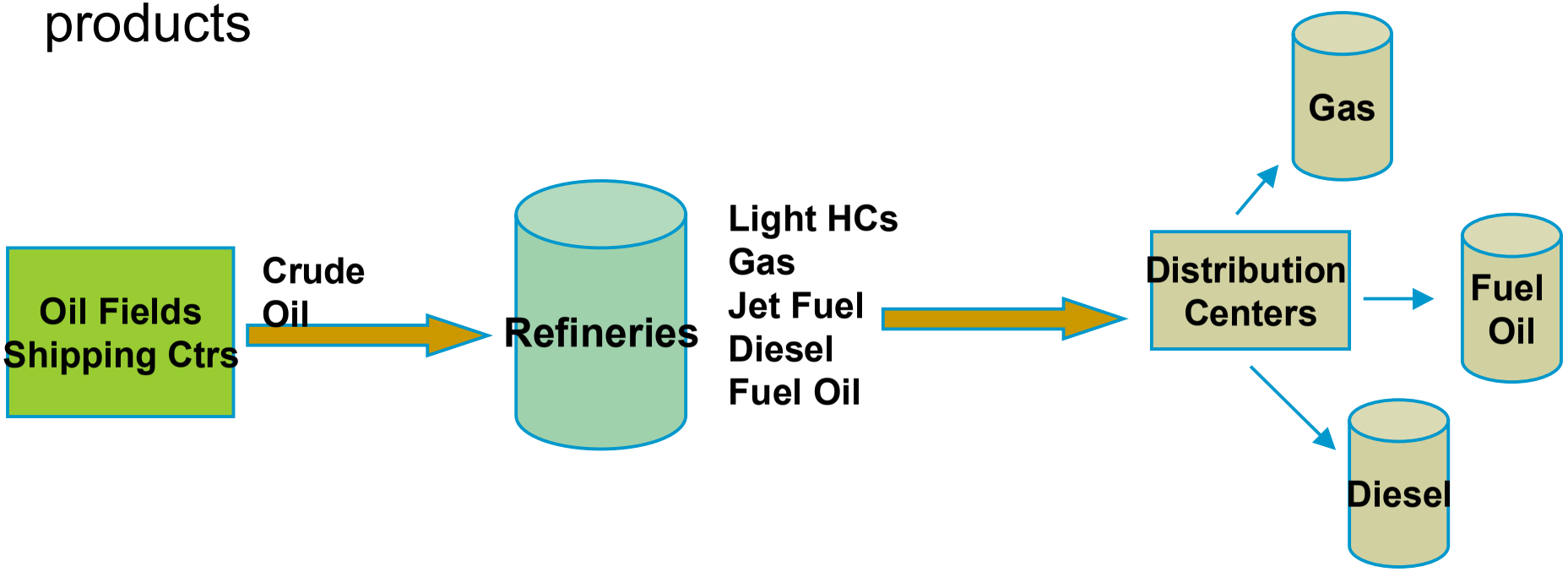
- Column issues
  - selectivity
  - capacity; overloaded peaks
  - inertness
  - temperature limits
  - Elution order of major peak
- Column contamination
  - efficiency loss; “ghost peaks”; increase in bleed
  - water, CO_2, high molecular weight hydrocarbons?
  - Carrier gas purifiers

J&W / Agilent PLOT Columns

- **GS-OxyPlot**
- GS-Alumina
- HP-PLOT Al_2O_3 “M”
- HP-PLOT Al_2O_3 “S”
- HP-PLOT Al_2O_3 “KCl
- HP-PLOT MoleSieve
- GS-CarbonPLOT
- HP-PLOT Q
- HP-PLOT U
- GS-GasPro

Application Summary

Petrochemical and Chemical companies have a need to quantitatively measure low level oxygenates in petroleum products



Application Summary

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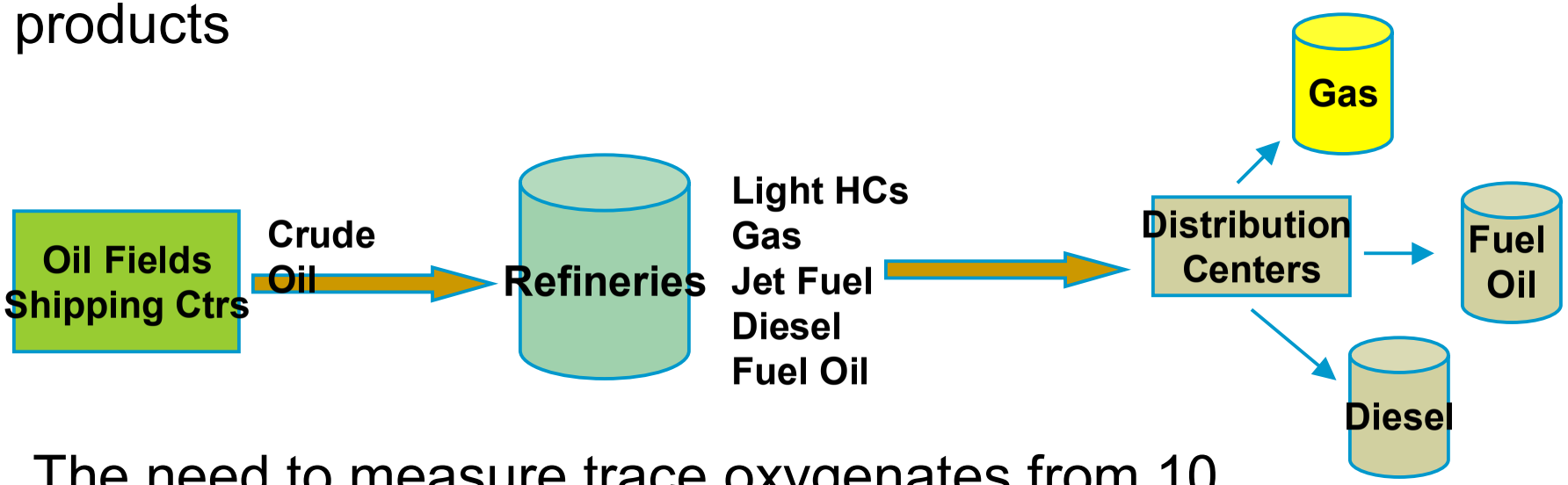


The need to measure trace oxygenates from 10 to 1000 ppm in Gasoline

- Problems with MTBE in reformulated gasoline
  - MTBE causing groundwater contamination
  - Desire to use ethanol as a renewable, green fuel additive

Oxygenates in Gasoline and Naphtha

Why is this measurement needed

- Oxygenated additives in reformulated gasoline
  - Needed for clean air regulations and petroleum fuel extenders
    - Problems with groundwater contamination
      - Ethers in gasoline (MTBE, ETBE, TAME) in underground tanks
      - Greater toxicity than alcohol additives
  - Move toward biofuels
      - Fuels derived from renewable agricultural products
      - Ethanol from fermentation of biomass
      - Lower toxicity than other alcohols
- Improve quality of feedstocks
  - Gasoline and naphtha used as feedstock for other HPI products
  - Traces of oxygenates poison catalyst
    - lower production yields
    - lower product quality

Traditional Oxygenates Methods

ASTM D4815

- Valve based using TCEP packed/ DB-1 capillary column
- Used to measure oxygenated additives (0.1 wt% to 15 wt%)
- ASTM study shows that D4815 has interference problems
  - TCEP column cannot separate trace oxygenates from trace olefins

ASTM D5599

- Single column method using oxygen selective detector (OFID)
- Expensive system that is dedicated to only one application
- Selectivity and sensitivity may not be good enough for low ppm

New Method Under Development by ASTM D2

Method Scope

- Trace oxygenates in finished gasoline from 10 ppm to 1000 ppm (wt/wt)
- Oxygenates include:
  - methanol, n-propanol, i-propanol, n-butanol, s-butanol, t-butanol, s-butanol, t-pentanol
  - MTBE, ETBE, DIPE, TAME
  - Ethanol additive from 1 to 15 wt%
  - Internal standard: 1,2-dimethoxyethane (DME)

Other capabilities

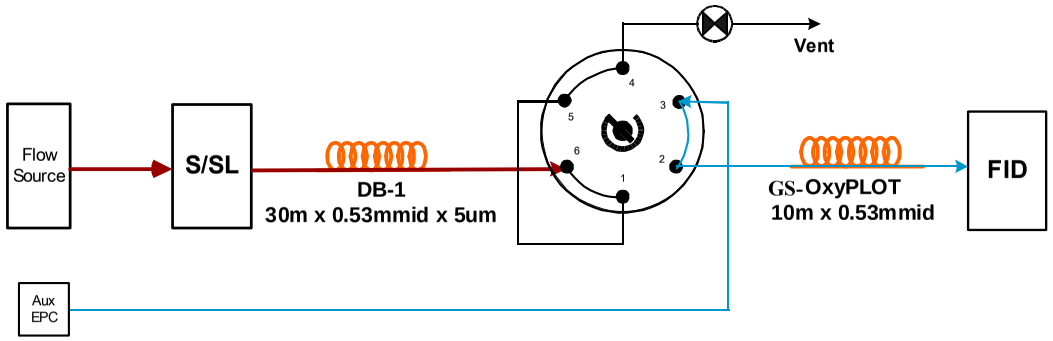
- can measure other oxygenate contaminants
  - ketones and other alcohols and ethers
- can be used for naphthas
- sensitivity range can be lowered to 1 ppm with no changes in method conditions

New Proposed ASTM Method Instrumentation Configuration

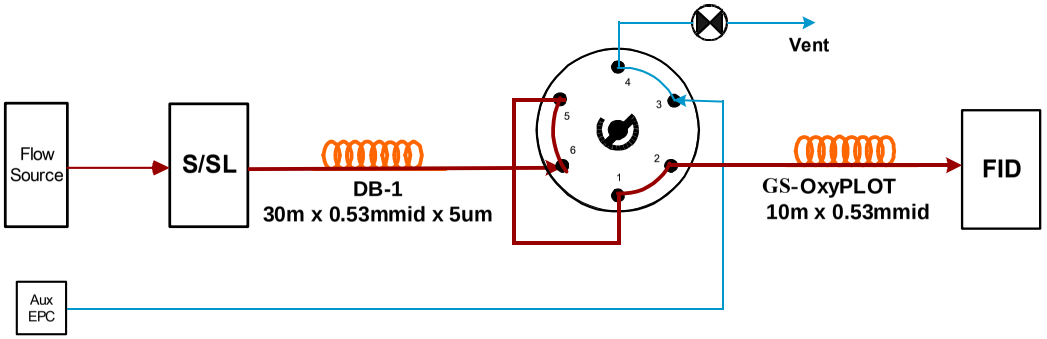
- Uses valve switching 2-D GC
- DB-1 column separates oxygenates/light hydrocarbons from heavy hydrocarbons
- New Agilent GS-OxyPLOT column separates light hydrocarbons from oxygenates

Proposed ASTM Methods Uses 2-D GC with Oxygenate Selective PLOT column

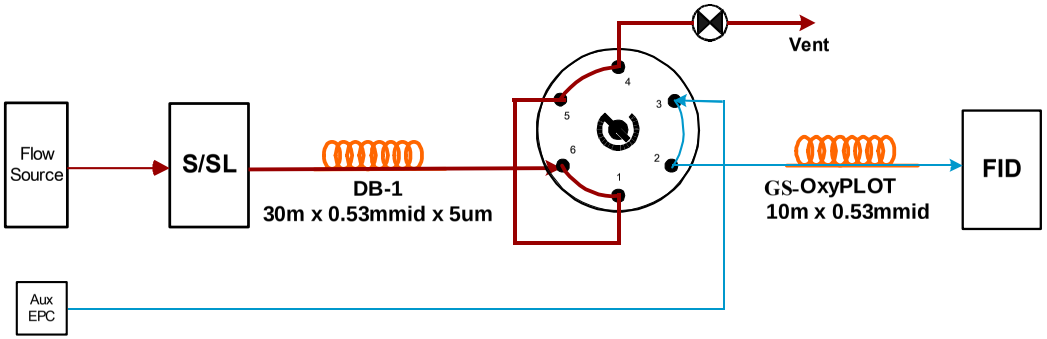
1. Sample introduction of gasoline onto DB-1 pre-column.



2. Oxygenates and light hydrocarbons transfer to GS-OxyPlot. Heavy hydrocarbons remain on DB-1 pre-column.



3. Heavy hydrocarbons vented from DB-1 pre-column. Oxygenates resolved on GS-OxyPlot column.



What Is GS-OxyPLOT?

- A 10 m x 0.53 mm I.D., 10 µm film thickness, Porous Layer Open Tubular (PLOT) Capillary Column. New Agilent p/n 115-4912.
- The stationary phase is a "proprietary, salt deactivated adsorbent".
- Key characteristics are:
  - Strong selectivity to oxygenated hydrocarbons.
  - Methanol (BP 65 °C) elutes ***after*** Tetradecane (BP 254°C)

Solute	MTBE	Iso-Butylaldehyde	Methanol	Acetone
RI*	1236	1368	1418	1450

**150°C*

  - Upper temperature limit 350°C with no column bleed
  - Stabilized phase coating, minimizing particle generation and detector spiking

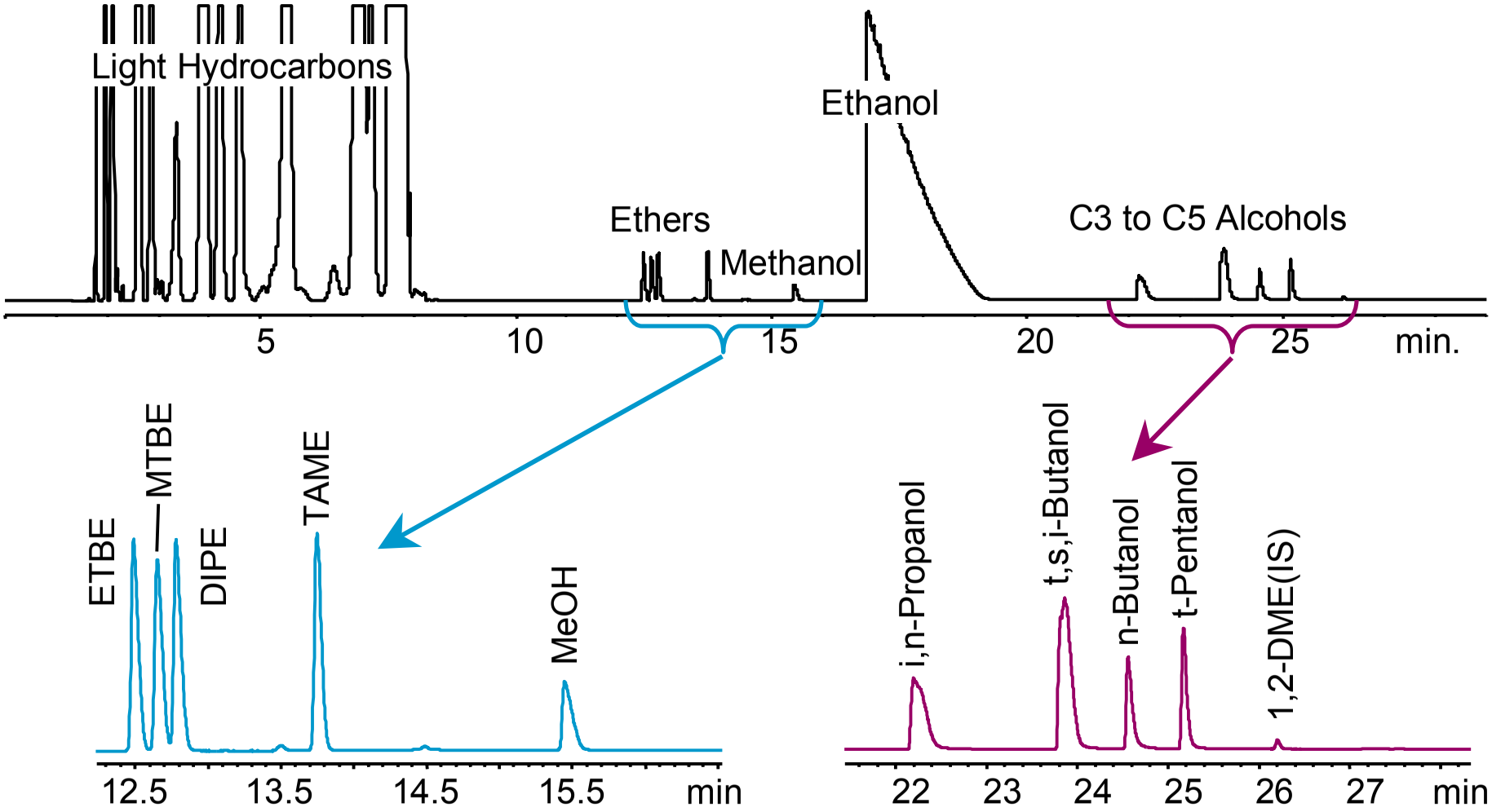
GS-Oxy-PLOT “Electronic” Selective Interactions

Distinct Advantages

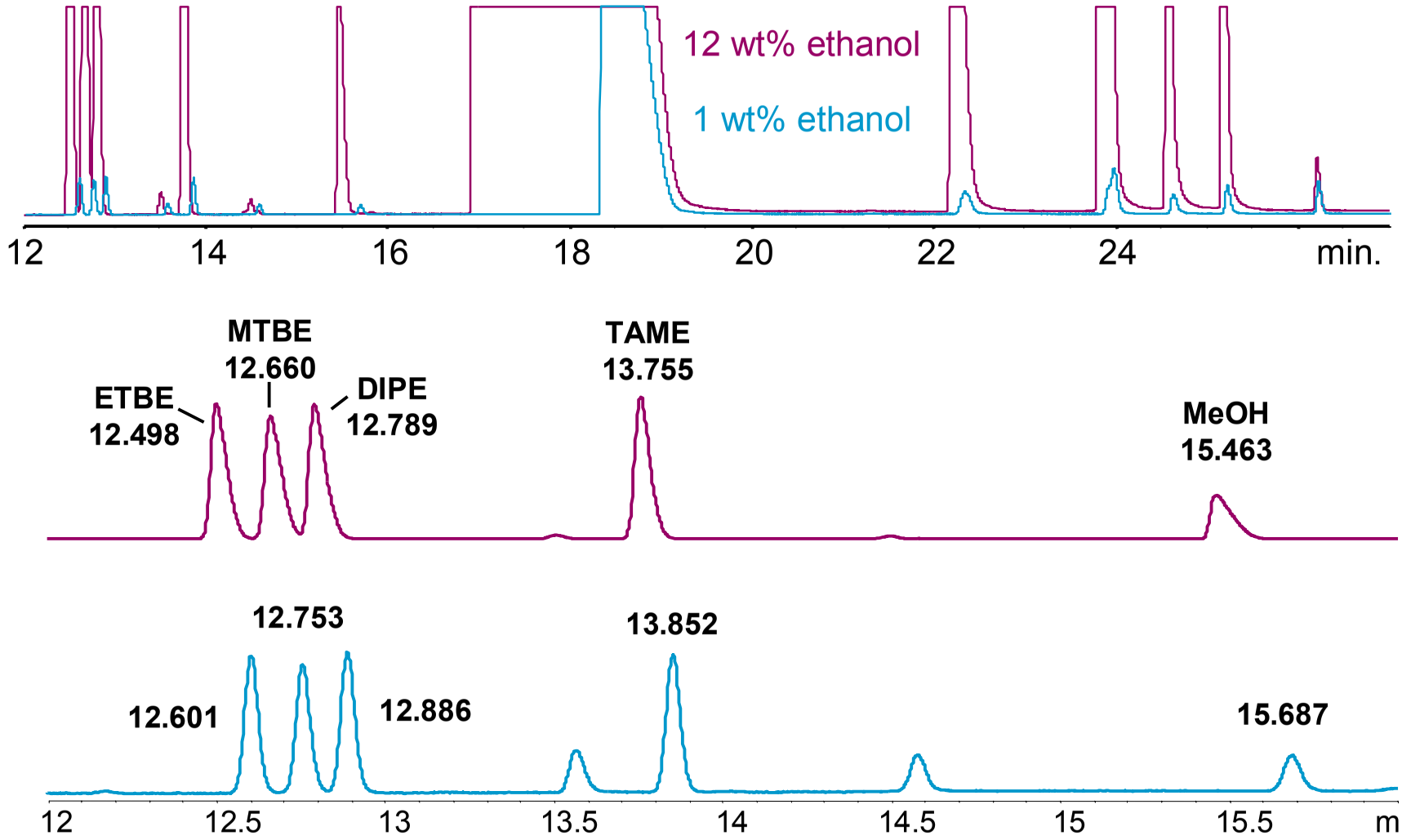
- Adsorption interactions are much stronger than the polar/non-polar interactions in “liquid” stationary phases.
  - Oxygenated hydrocarbons, un-retained in a WCOT column even at sub-ambient temperatures can exhibit high retention in a PLOT column at GC oven temperatures above ambient
  - Non-polar solutes are essentially un-retained except for their vapor pressure interaction at a given oven temperature.
  - Ideal column for selective solute-value cut applications

- Column phase is surprisingly inert to the polar compounds it so strongly interacts with.
  - Good for low concentration, quantitative GC analysis

OxyPlot Column Separation of Trace Oxygenates and Ethanol Additive in Reformulated Gasoline



Ethanol Influenced Retention Time Shifts



Excellent Quantitative Precision

High Concentration QA/QC Check Sample

	Expected (ppm)*	Avg (ppm)*	Std Dev (ppm)*	RSD
ETBE	780	758	1.3	0.2%
MTBE	795	816	1.5	0.2%
DIPE	795	758	1.1	0.2%
TAME	779	779	1.4	0.2%
Methanol	802	759	1.6	0.2%
Ethanol*	12.0%	11.3%	0.0	0.4%
i,n-Propanol	1619	1566	14.7	0.9%
t,s,i-Butanol	2399	2372	4.4	0.2%
n-Butanol	798	791	1.7	0.2%
t-Pentanol	801	766	0.6	0.1%

Low Concentration QA/QC Check Sample

	Expected (ppm)*	Avg (ppm)*	Std Dev (ppm)*	RSD
ETBE	49	48	0.7	1.4%
MTBE	49	46	1.0	2.1%
DIPE	49	93	0.7	0.8%
TAME	48	48	0.3	0.6%
Methanol	50	67	0.6	0.8%
Ethanol*	1.0%	0.9%	0.0	2.2%
i,n-Propanol	101	95	1.3	1.4%
t,s,i-Butanol	150	152	2.4	1.6%
n-Butanol	50	47	0.8	1.6%
t-Pentanol	50	47	0.2	0.5%

*ethanol results are in wt%

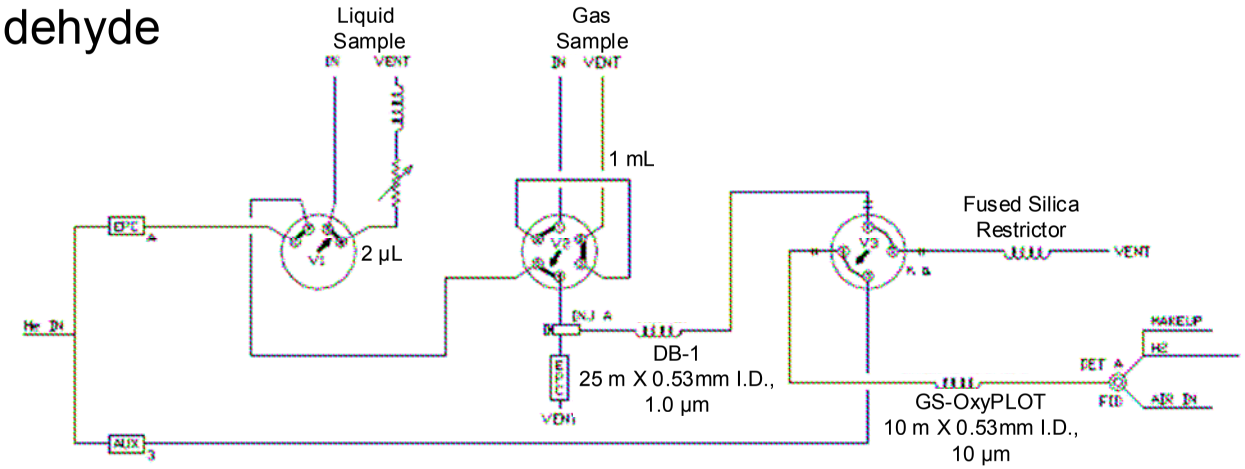
Each QA/QC sample prepared in reformulated gasoline
Five consecutive runs of each sample

New Method Under Development by ASTM D2 for Analysis of Oxygenates in Ethene, Propene, C4 and C5 Hydrocarbon Matrices

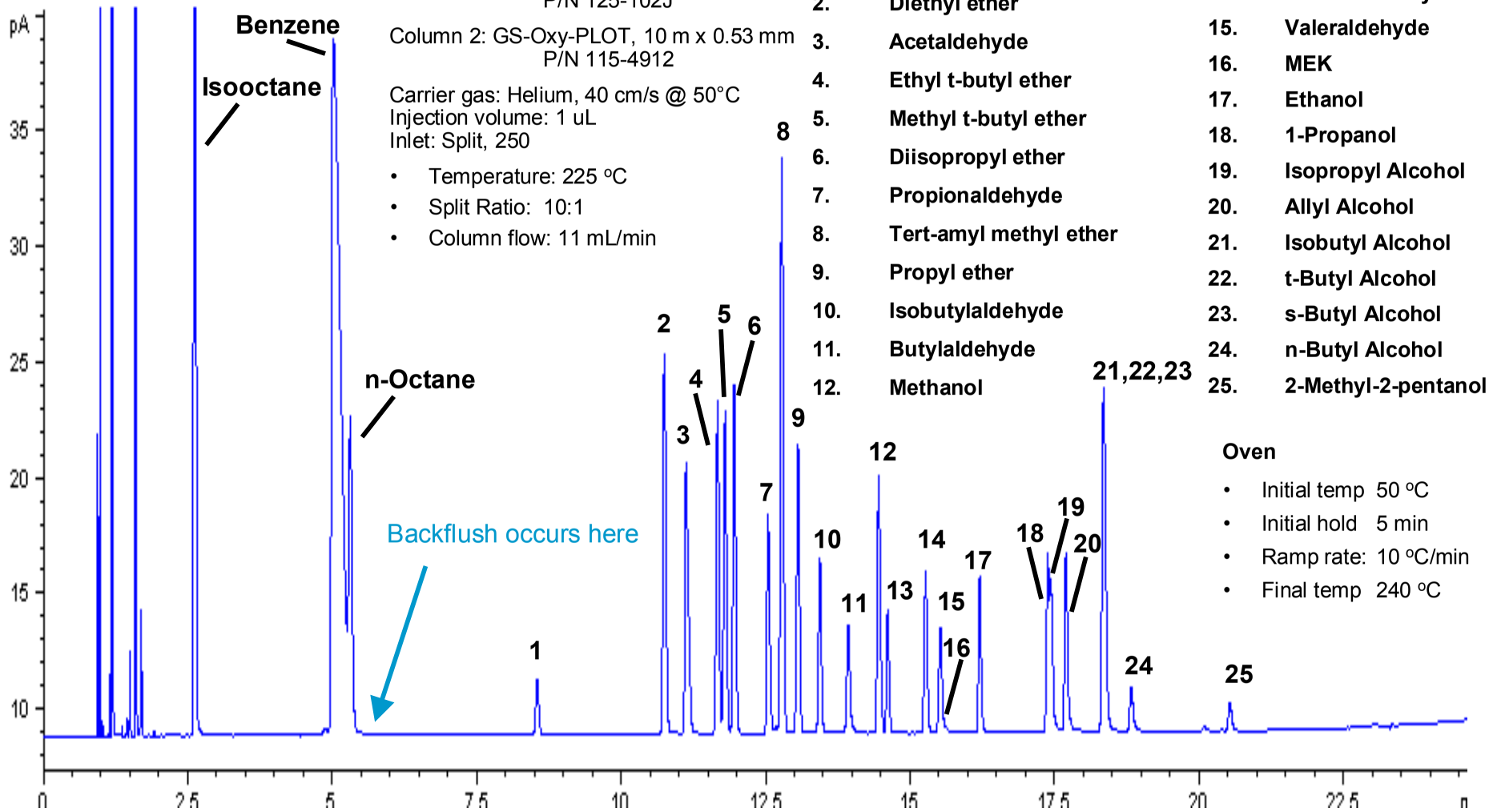
Method Scope

- Oxygenates in these light hydrocarbon matrices from 500 ppb to 100 ppm (wt/wt)
- Oxygenates include 25 alcohols, ketones, aldehydes and ethers (e.g.):
  - –methanol, ethanol, n-propanol, n-butanol, s-butanol, t-butanol, s-butanol
  - –DME, MTBE, DIPE, TAME
  - –Acetone, acetaldehyde

Similar in principle to the oxygenates in gasoline method



Hydrocarbons and Oxygenates Separation using DB-1 Stripper Column and GS-OxyPLOT Separation Column



Column 1: DB1, 25 m x 0.53 mm x 1 um
P/N 125-102J

Column 2: GS-Oxy-PLOT, 10 m x 0.53 mm
P/N 115-4912

Carrier gas: Helium, 40 cm/s @ 50°C
Injection volume: 1 uL
Inlet: Split, 250

- Temperature: 225 °C
- Split Ratio: 10:1
- Column flow: 11 mL/min

1. **Dimethyl ether**
2. **Diethyl ether**
3. **Acetaldehyde**
4. **Ethyl t-butyl ether**
5. **Methyl t-butyl ether**
6. **Diisopropyl ether**
7. **Propionaldehyde**
8. **Tert-amyl methyl ether**
9. **Propyl ether**
10. **Isobutylaldehyde**
11. **Butylaldehyde**
12. **Methanol**
13. **Acetone**
14. **Isovaleraldehyde**
15. **Valeraldehyde**
16. **MEK**
17. **Ethanol**
18. **1-Propanol**
19. **Isopropyl Alcohol**
20. **Allyl Alcohol**
21. **Isobutyl Alcohol**
22. **t-Butyl Alcohol**
23. **s-Butyl Alcohol**
24. **n-Butyl Alcohol**
25. **2-Methyl-2-pentanol**

Oven

- Initial temp 50 °C
- Initial hold 5 min
- Ramp rate: 10 °C/min
- Final temp 240 °C

Summary

A New Proposed ASTM Method for Trace Oxygenates in Reformulated Gasoline

- designed to measure 10 to 1000 ppm oxygenates in gasoline with 1 to 15 wt% ethanol additive

Agilent 7890A GC System with GS-OxyPlot Column meets method requirements

- excellent separation of oxygenates from light hydrocarbons
- resolves all ethers (ETBE, MTBE, DIPE, and TAME)
- high quantitative precision for both high and low concentrations in the presence of percent ethanol

A New Proposed ASTM Method for Trace Oxygenates in Light Hydrocarbon Matrices

- designed to measure 500 ppb to 100 ppm oxygenates in matrices with BPts less than 200°C

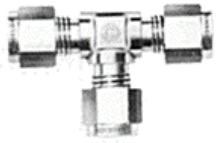
Old vs. New Switching Technology

- Previous Slides depicted “Old-school” method of switching column flow
- Newer method uses Capillary Flow Technology (CFT)
  - No moving parts
  - Low dead volume
  - Low thermal mass

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**

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

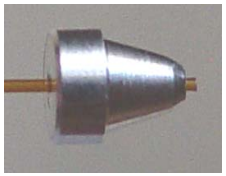
IF We Only Had A Technology That Provided Easy, Reliable Flow Structures In The GC Oven...

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.**

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

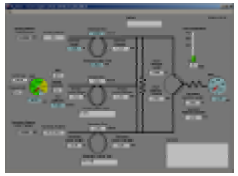
Deactivation of Metal

Makes metal surfaces as inert as column

EPC

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

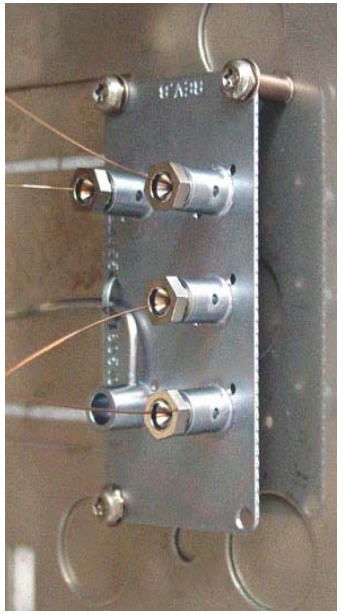
Calculators



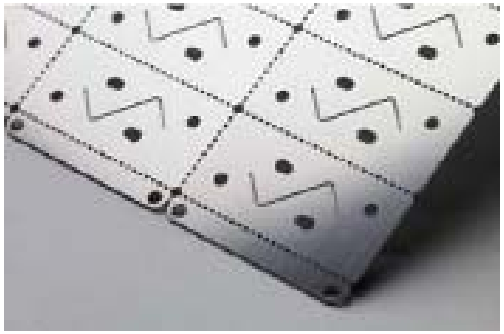
Accurately predict flows and pressures BEFORE installing devices

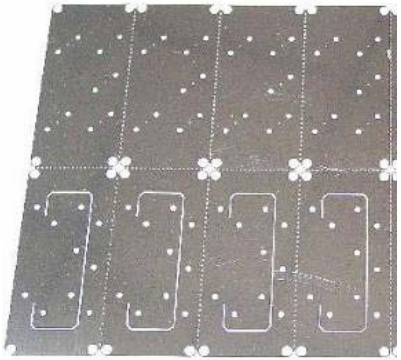
Capillary Flow Technology- Design

… 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

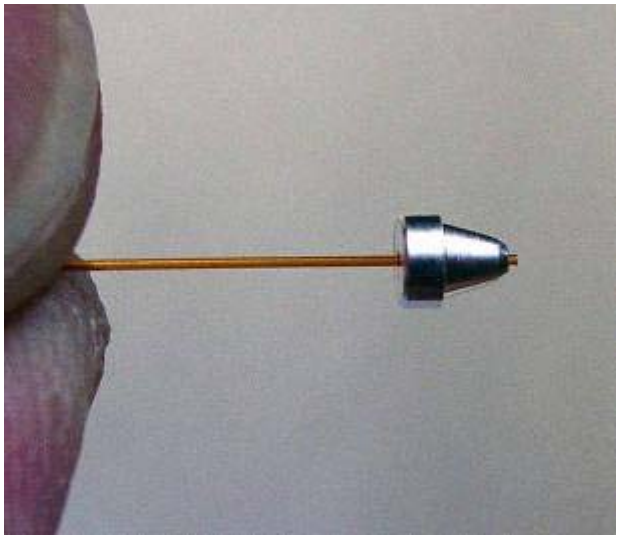


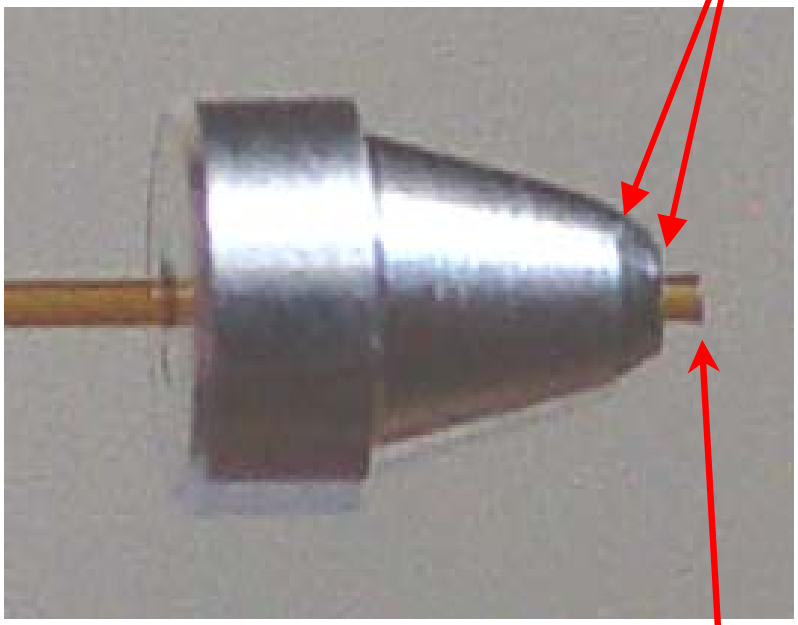


The Metal Ferrule

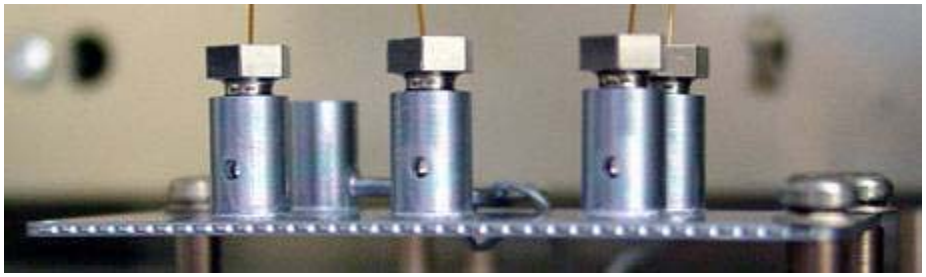
Does not loosen (leak) even with *thousands* of runs to 350C

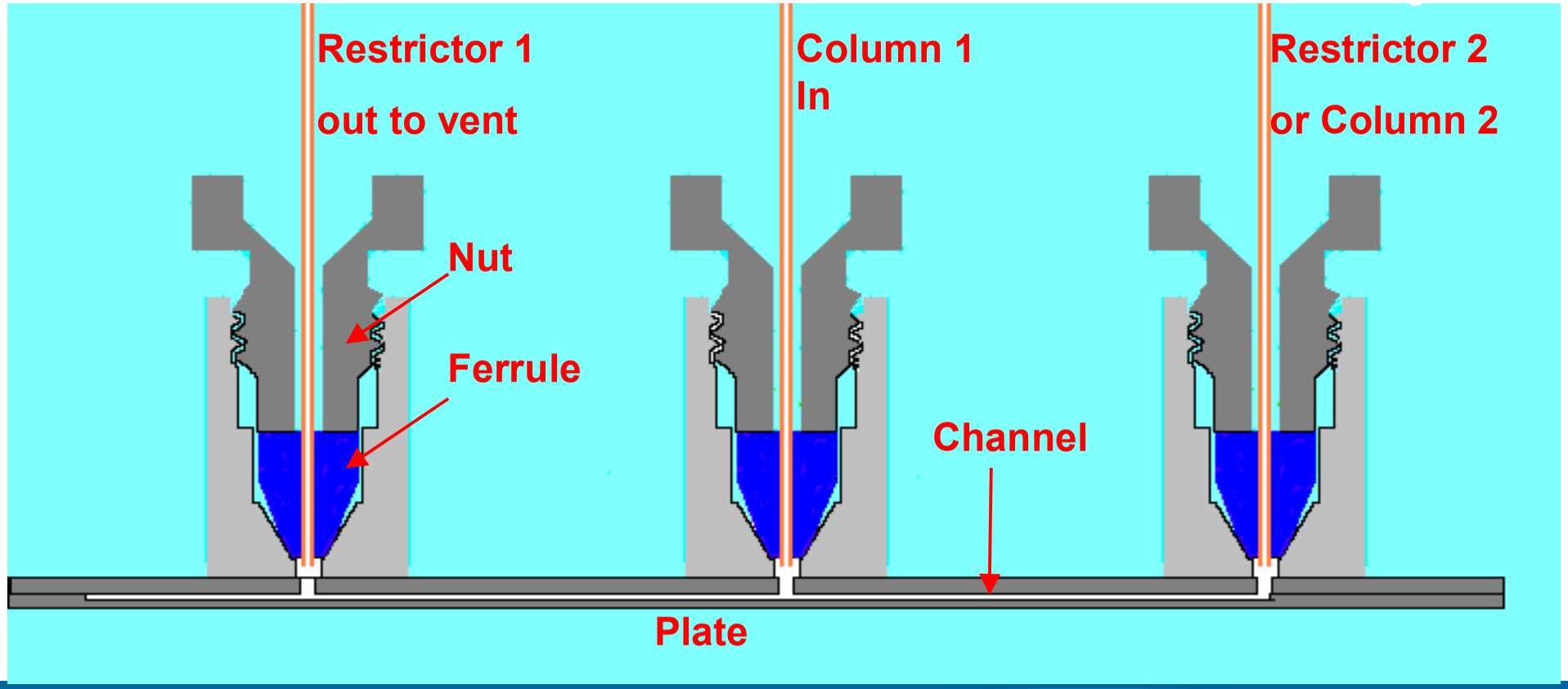
Does not shed particles





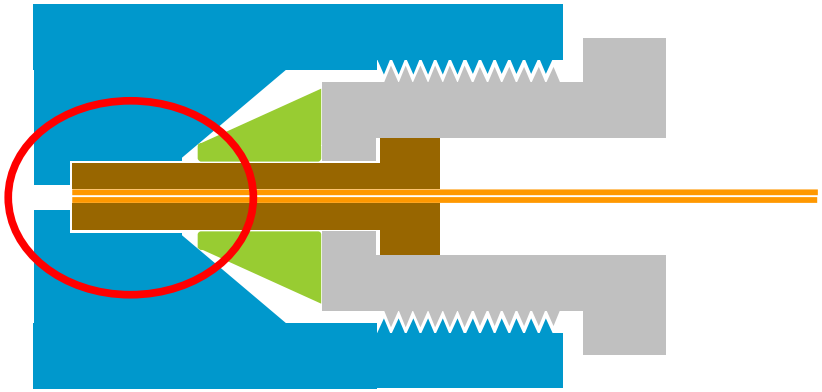
Capillary Flow Technology





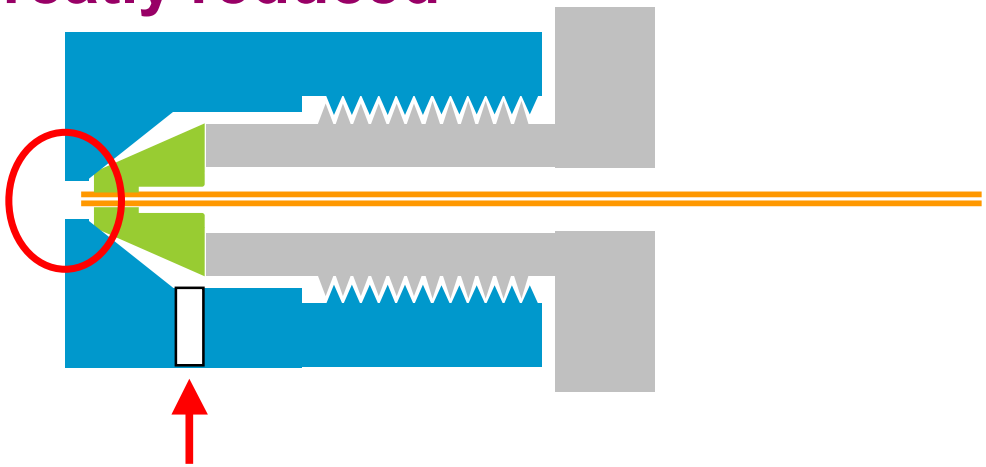
Comparison of New Fitting with Polyimide Fitting

Polyimide Fitting



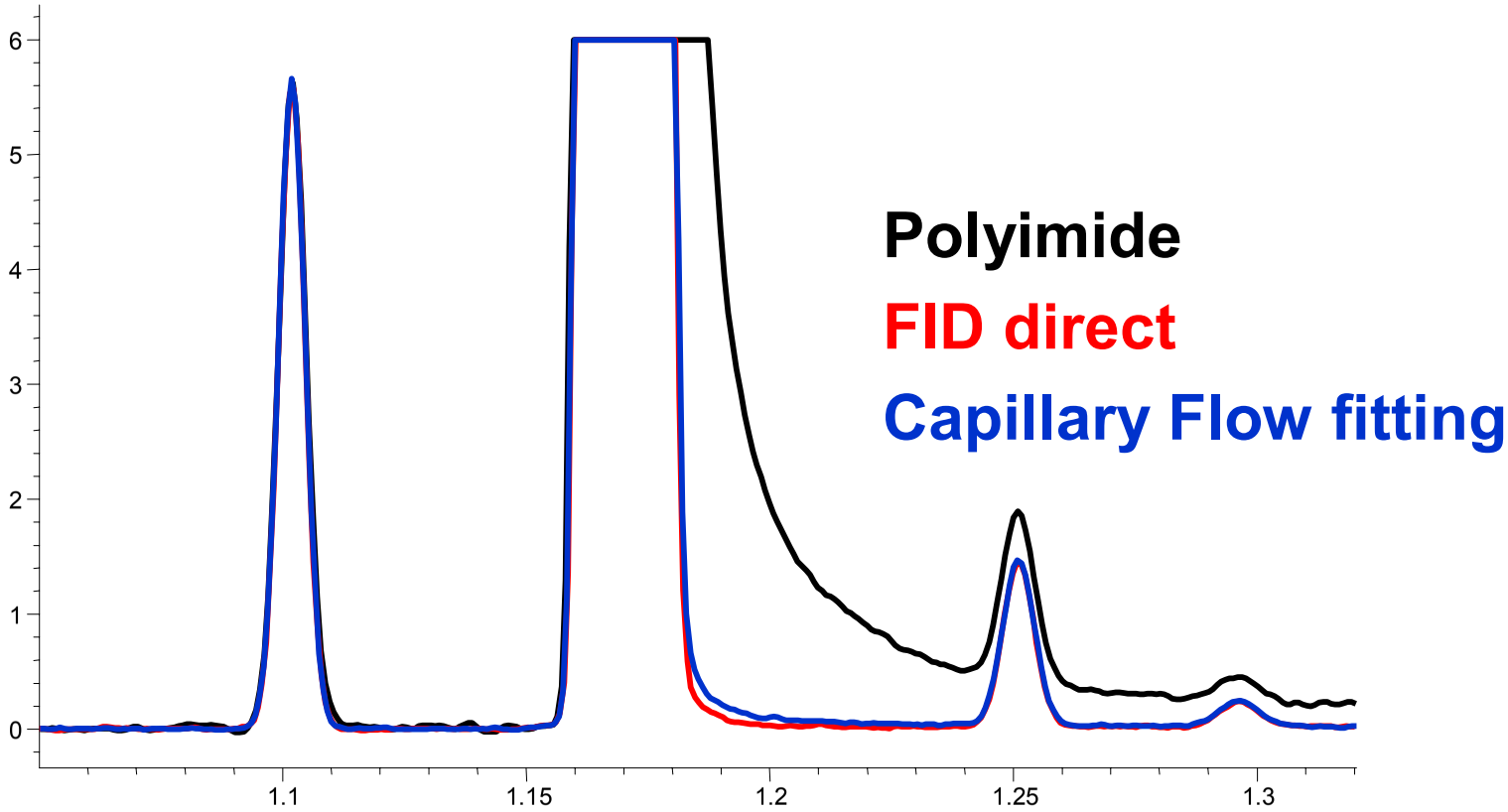
Exposure to polyimide and unpurged annular spaces is greatly reduced

New Fitting



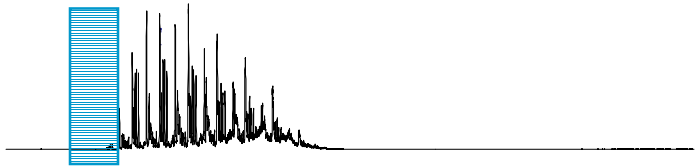
Fitting Design Minimizes Tailing

Pentane test chromatogram

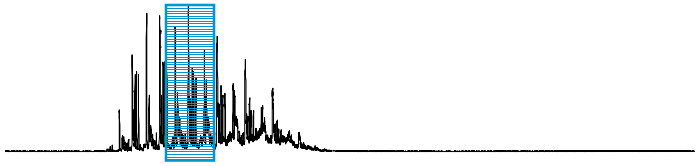


Capillary Flow Technology fittings avoid tailing with small but well swept dead volume

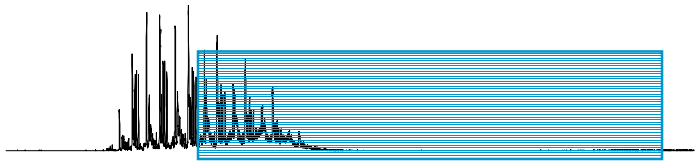
Capillary Flow Technology- Capabilities



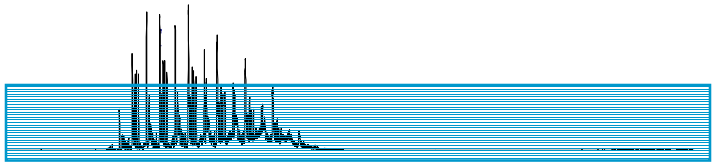
Solvent Bypass



Heart Cutting (Deans Switch)

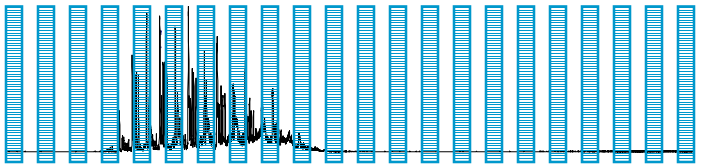


Backflush



Detector Splitting

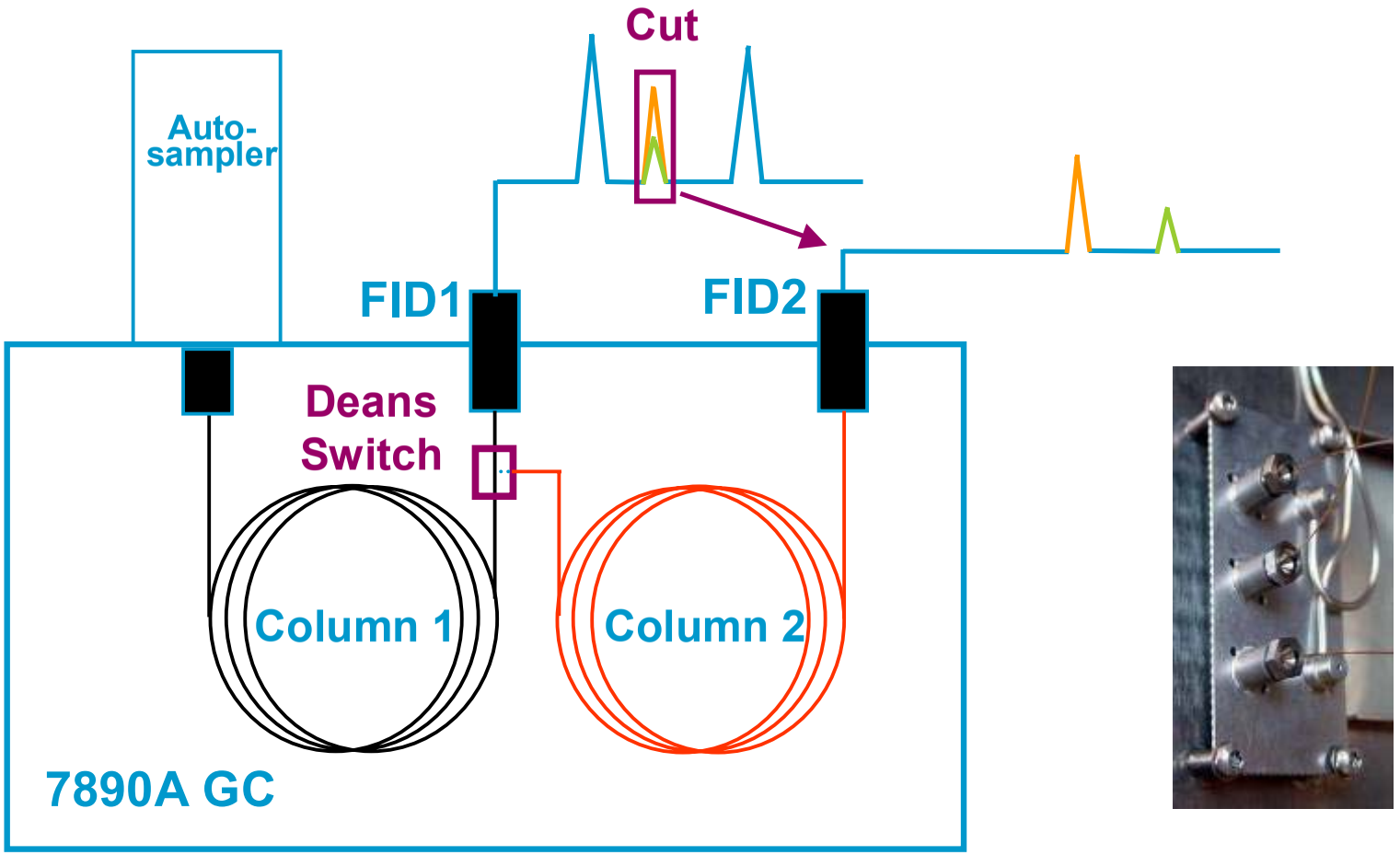
QuickSwap



Modulation (GCXGC)

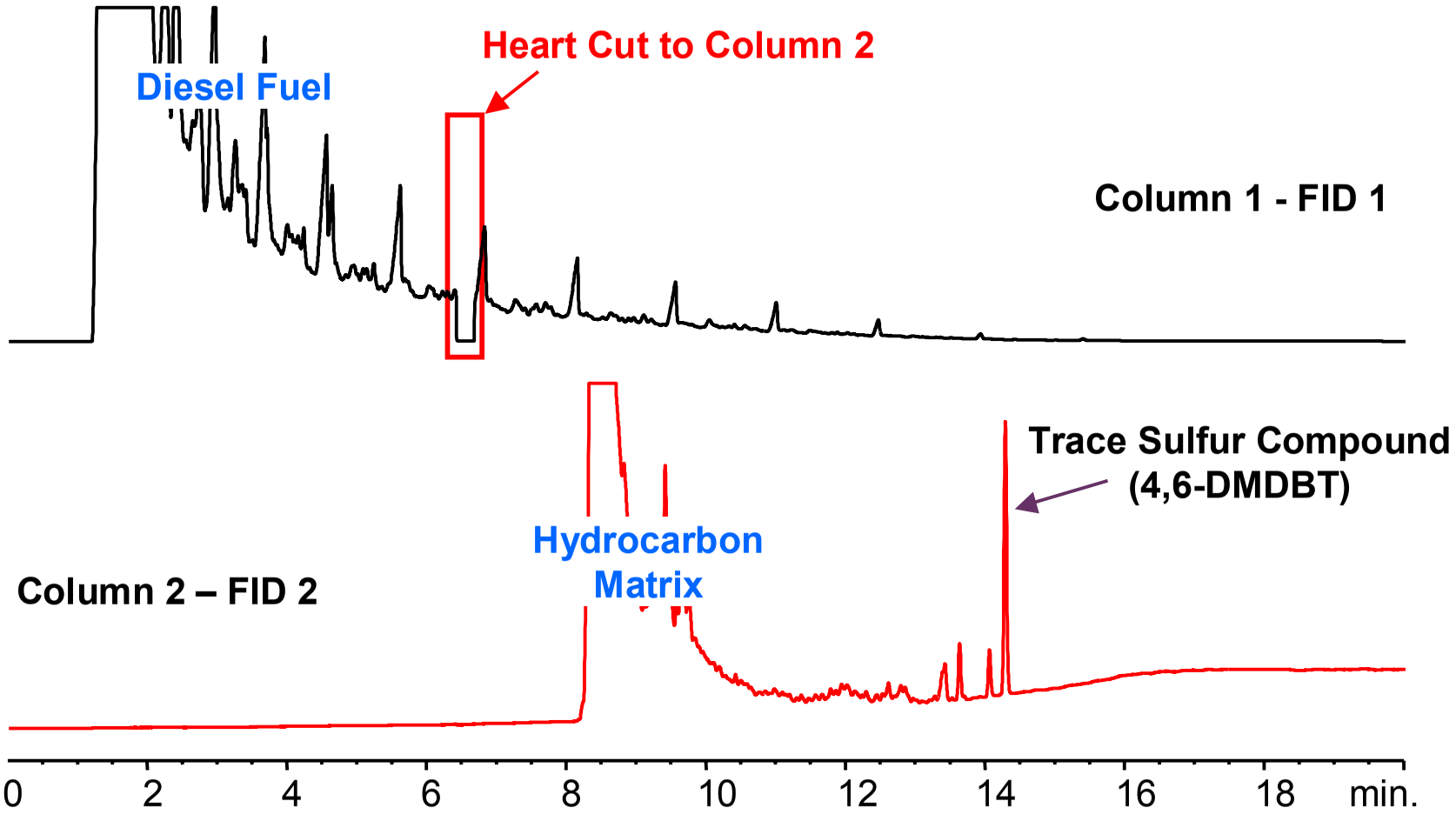
Dean Switch

Heartcutting 2-D GC provides extremely high chromatographic resolution



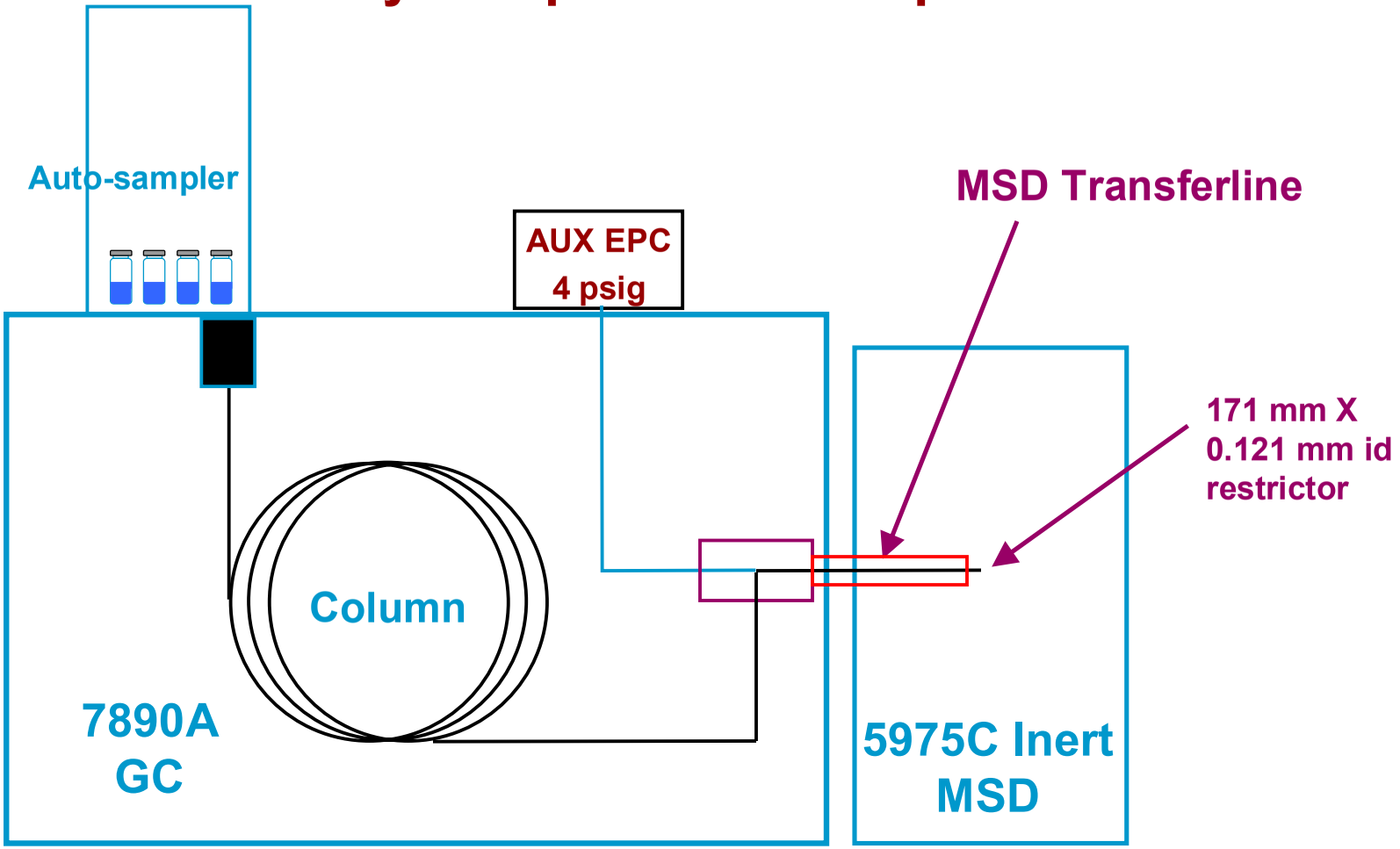
2-D Separation of Sulfur Compound in Diesel Fuel

Compound is completely resolved and can be analyzed with FID



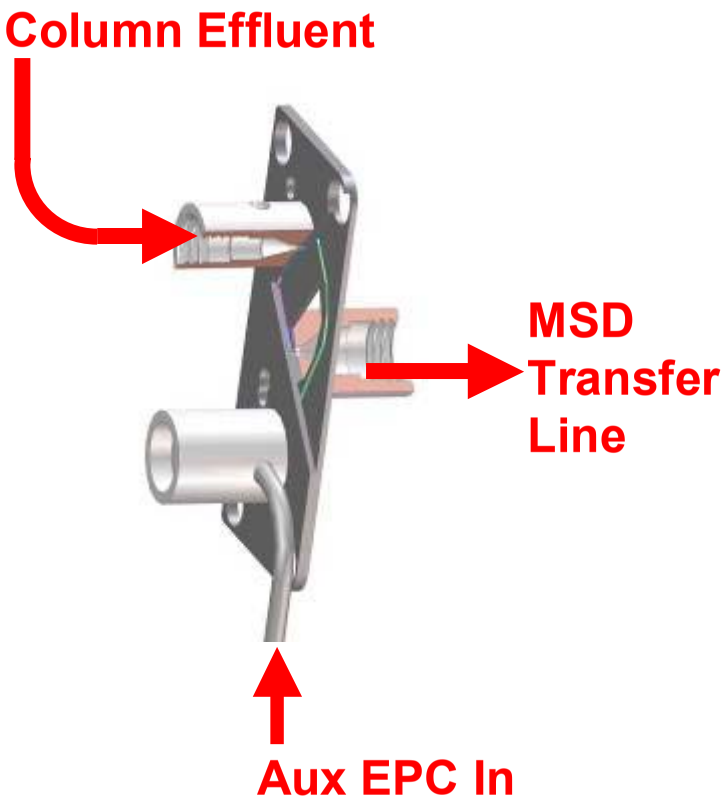
QuickSwap

Change MSD columns without venting
Backflush heavy components out split vent



QuickSwap MSD Interface

- **Remove column w/o venting**
  - Air & H_2O 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)

Thank you!

Questions?

Feel free to contact Agilent Application support at:

1-800-227-9770 Option 41….or…..

Via e-mail at:

gc-column-support@agilent.com