PLOT Columns
Separation Solutions for Light Hydrocarbons & Gases

Porous Layer Open Tubulars

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Training & Development
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Agilent CrossLab
From Insight to Outcome

Agilent

Table of Boiling Point Fractions

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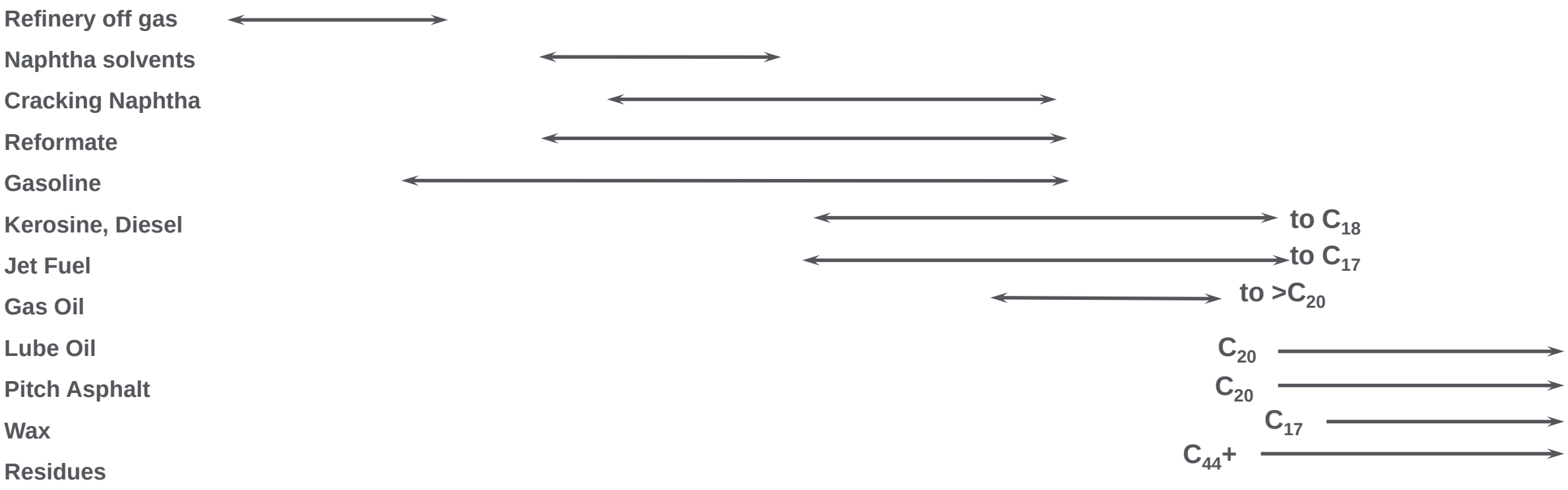
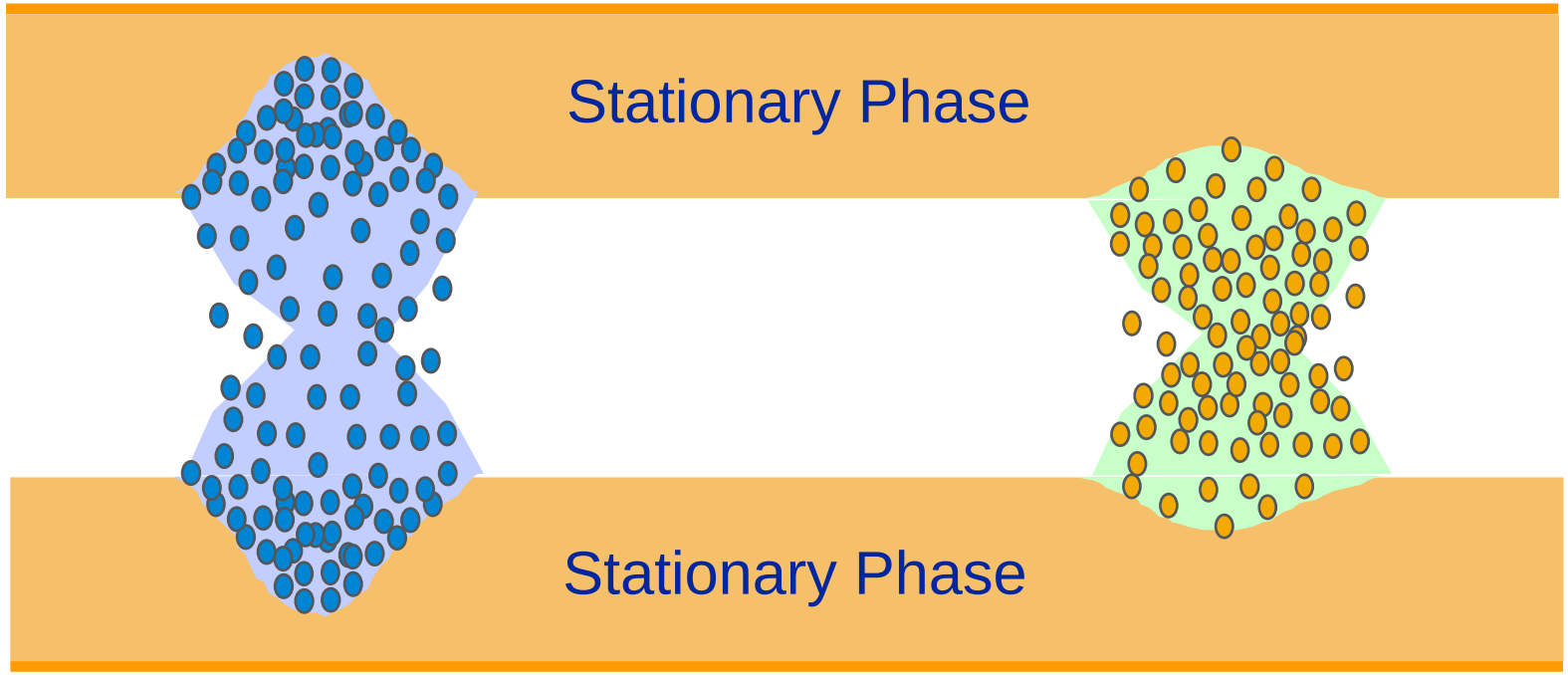
Carbon #	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}
Bpt of n-Paraffin @ 760 mm Hg																
Centigrade	-161	-89	-42	-0.5	+36	69	98	126	151	174	196	216	235	253	270	287
Fahrenheit	-259	-127	-44	+31	97	156	209	258	303	345	384	421	421	488	519	548



Wall Coated Open Tubular (WCOT) Columns

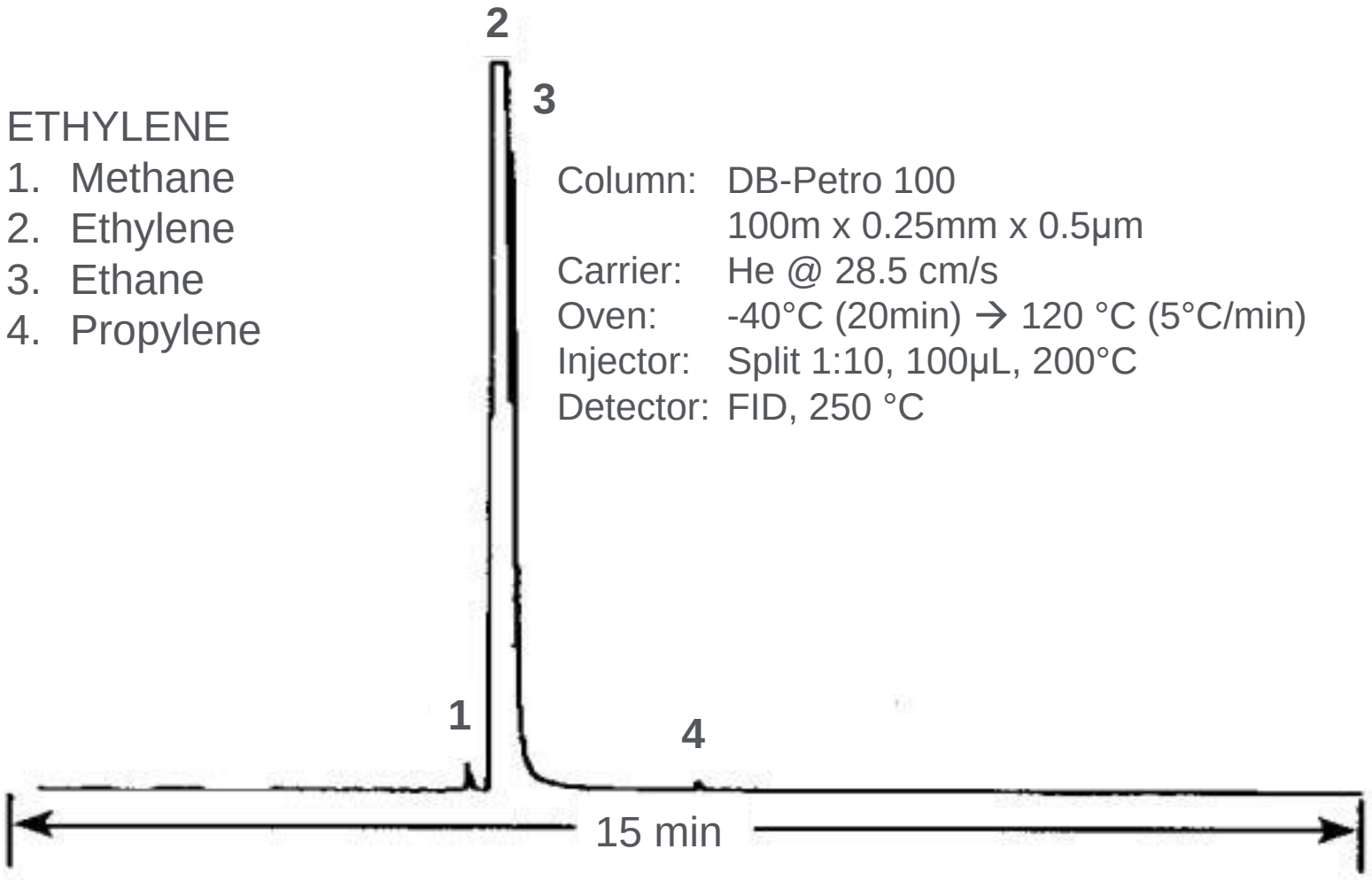


K_c => Large

K_c => Small

Ethylene Analysis on non-polar WCOT

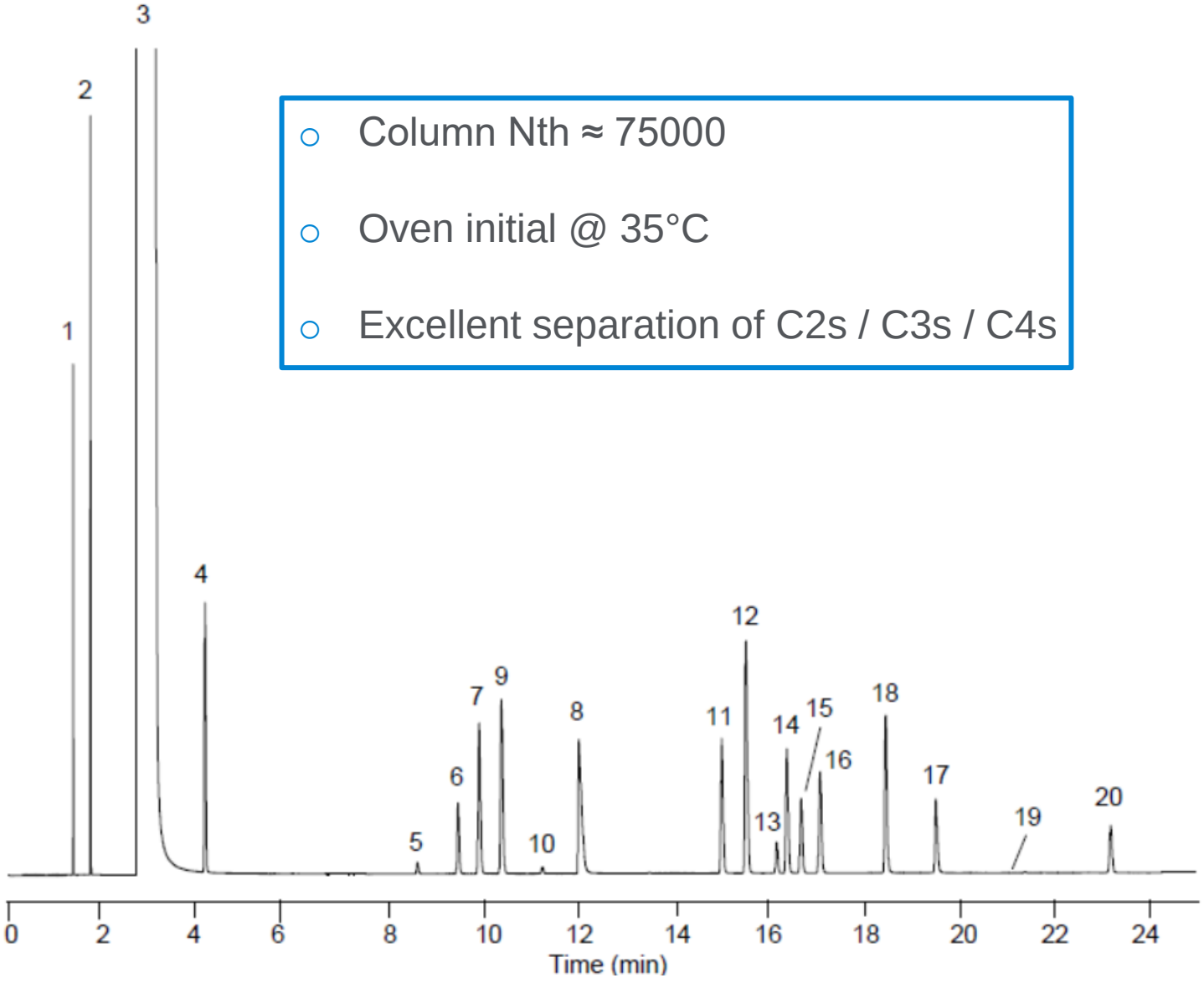
ETHYLENE
1. Methane
2. Ethylene
3. Ethane
4. Propylene



Column: DB-Petro 100
100m x 0.25mm x 0.5µm
Carrier: He @ 28.5 cm/s
Oven: -40°C (20min) → 120 °C (5°C/min)
Injector: Split 1:10, 100µL, 200°C
Detector: FID, 250 °C

- ❑ Column Nth = 350000
- ❑ Oven start @ -40°C
- ❑ Poor separation of C2s
- ❑ Poor separation of C3s

Ethylene Analysis on Alumina PLOT



- Column Nth ≈ 75000
- Oven initial @ 35°C
- Excellent separation of C2s / C3s / C4s

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

What is a PLOT column?

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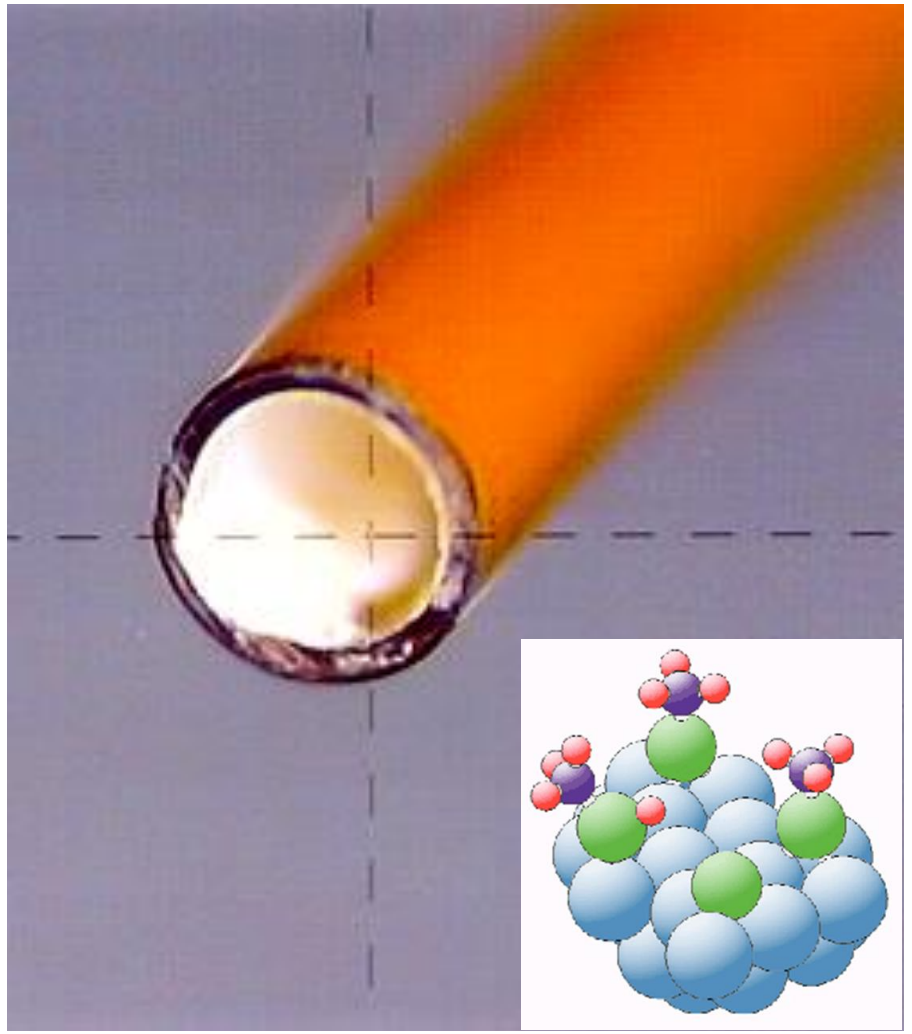
- Porous layer (surface) on the inner wall capillary
- Deposition of porous particles on the wall from suspension
- Porous layer serves as stationary phase
- Gas-Solid Chromatography - PLOT
  Differences in analyte distribution between carrier gas & surface of the adsorbent (stationary phase)
- Gas-Liquid Chromatography - WCOT
  Differences solubility in liquid phase (stationary phase)



Advantages of GSC:
- Improved selectivity (α)
- Retention (k) of highly volatile solutes

Selectivity Interactions in PLOT Phases

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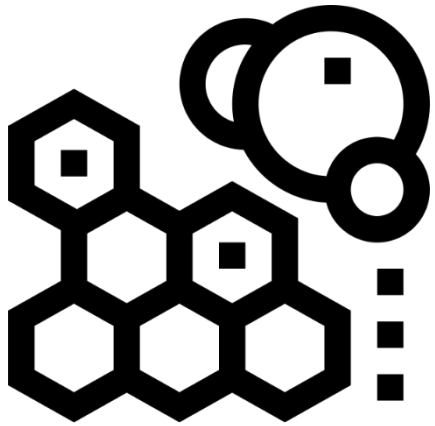
Shape / Size ⟷ **Surface**

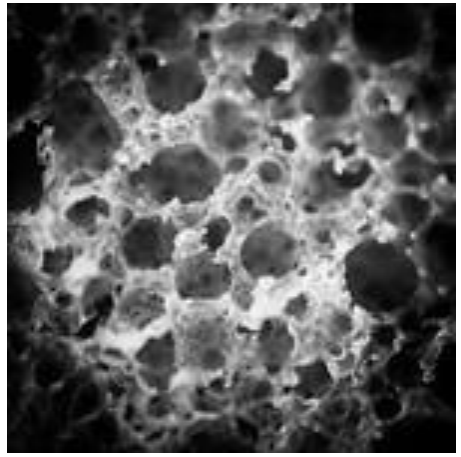
Zeolites

Porous Polymers

Al_2O_3

Bonded Carbon Molecular Sieves





Bonded Silica

*Molecular sieve by Bearfruitidea from the Noun Project

Creative Commons: Daniel Kulinski

Porous Layer Open Tubular (PLOT) Columns
-- Advantages --

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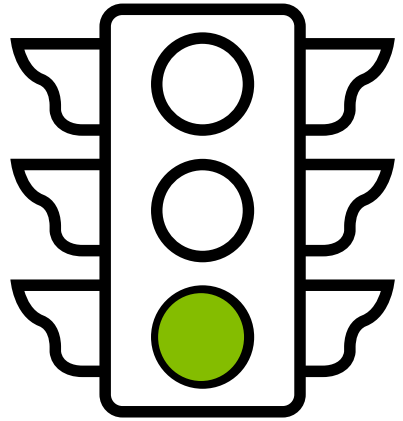
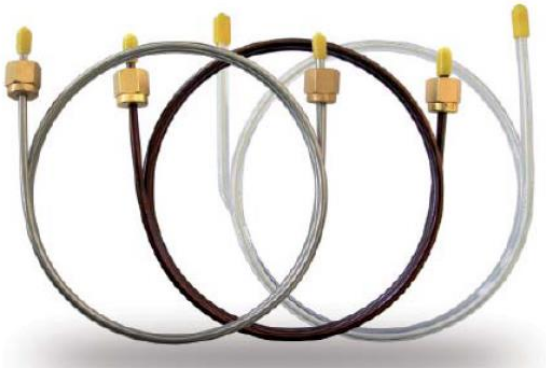


- Retention for high vapor pressure solutes
  - No cryogenics needed
  - Useful for multi-column & valve switching & heart cutting techniques
- Variety adsorbents
  - Porous polymers, alumina, molecular sieve, silica
  - Selectivity for isomeric compounds (HC isomers)
  - Gases & solvents separations
- Efficiency of a capillary
  - Preferred over packed
  - Packed columns have advantages in specific applications



PLOT -- Some Limitations & Considerations --

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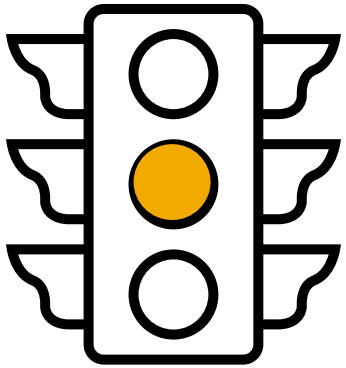

- Lower sample capacity than thick film (1 – 5µm) liquid phase columns
  0.53mm PLOT offers highest loadability
- More limited maximum temperatures than siloxanes – limiting analyte scope
- Highly active -- some compounds do not elute
  or require extensive column conditioning (CO_2 / H_2O)
- Molecular rearrangements above MAOT – selectivity might change
  Do not exceed MAOT!

- Particles may dislodge under mechanical / flow stress – but solutions do exist

Agilent J&W PLOT Column Portfolio

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Porous Polymers
- HP-PLOT Q & U
- PoraBOND Q & U
- PoraPLOT Q, U & S
- GS-Q
- PoraPLOT Q-HT

Alumina
- Al_2O_3/KCl, HP-PLOT Al_2O_3/KCl
- Al_2O_3/Na_2SO_4 , HP-PLOT Al_2O_3 S
- GS-Alumina
- Select MAPD

Zeolites
- HP-Molesieve
- CP-Molsieve 5A

Porous Silica
- GS-GasPro
- SilicaPLOT

Oxygenates
- CP-Lowox
- GS-OxyPLOT

Graphitised Carbon
- CarboPLOT P7
- CarboBOND
- GS-CarbonPLOT

Compounds & PLOT Column Selection

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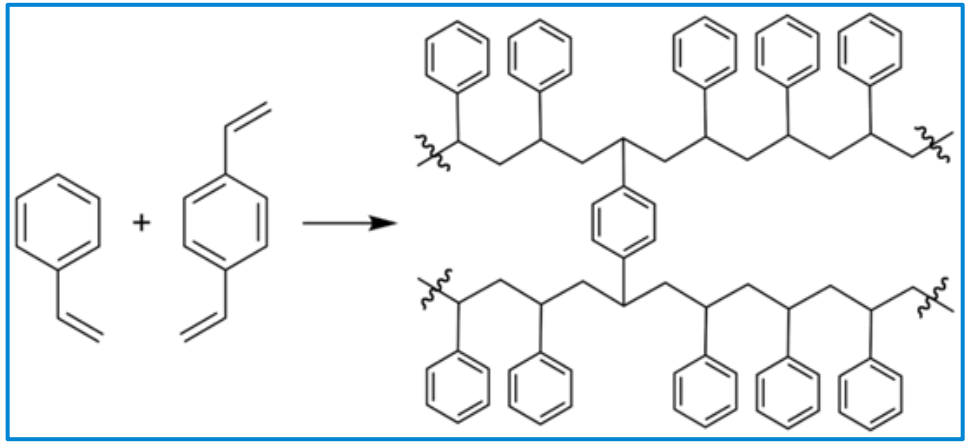
○ Permanent gases - Noble gases, O_2, N_2, H_2, CO, CO_2, CH_4	Molsieve	Select Permanent Gases
○ Light hydrocarbons - C1 – C8, saturated, unsaturated, - Aromatics, natural gas, C2, C3, C4 streams	Alumina Silica	Porous carbon Porous polymers
○ Volatile sulfur compounds - H_2S, COS, mercaptanes, sulfides, disulfides	Select Low Sulfur Silica	Porous polymers
○ Oxygenates - Alcohols, ketones, ethers	Lowox	OxyPLOT
○ Solvents - Oxygenates, aromatics, alkanes, - Chlorinated hydrocarbons	Porous polymers	
○ Chlorinated and fluorinated hydrocarbons	Silica	Porous polymers

Porous Polymer PLOT Columns

- Analyses of polar and non-polar volatile compounds
  Oxygenates, gases, halogenated compounds, hydrocarbons C1 –C6, ketones, solvents
- Most versatile of adsorbent materials
- Suitable for aqueous injections
  (in split & direct mode through inlet)
- Elution of water as a sharp peak + quantification of water
  (on the polar U type)
- Recommended for column switching systems
- Styrene/divinyl benzene polymer = Non-polar “Q type”
- Styrene-glycol methacrylate co-polymer = Polar “U type”
- Divinylbenzene/vinylpyridine polymer = Mid-Polar “S type”

Styrene/divinylbenzene polymer



Porous Polymer PLOT columns

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HP-PLOT Q, GS-Q & PoraPLOT Q

- Separation ethane/ethylene, propane/propylene
  - % levels, not ppm impurities in C2, C3 matrix
- H_2S and COS
  - Refinery gas analysis (RGA)
  - 100 ppm - %, **but not low ppm due to strong surface interactions for H_2S**
- Pre-column for O_2, N_2, CH_4, CO separations on Molsieve column
- Poor C4 isomer separation
  - Alumina preferred
- Not sensitive to moisture -- Stable retention -- No selectivity changes
- Good choice for solvents and CFCs

Refinery fuel gas, porous polymer separation
-- HP- PLOT Q --

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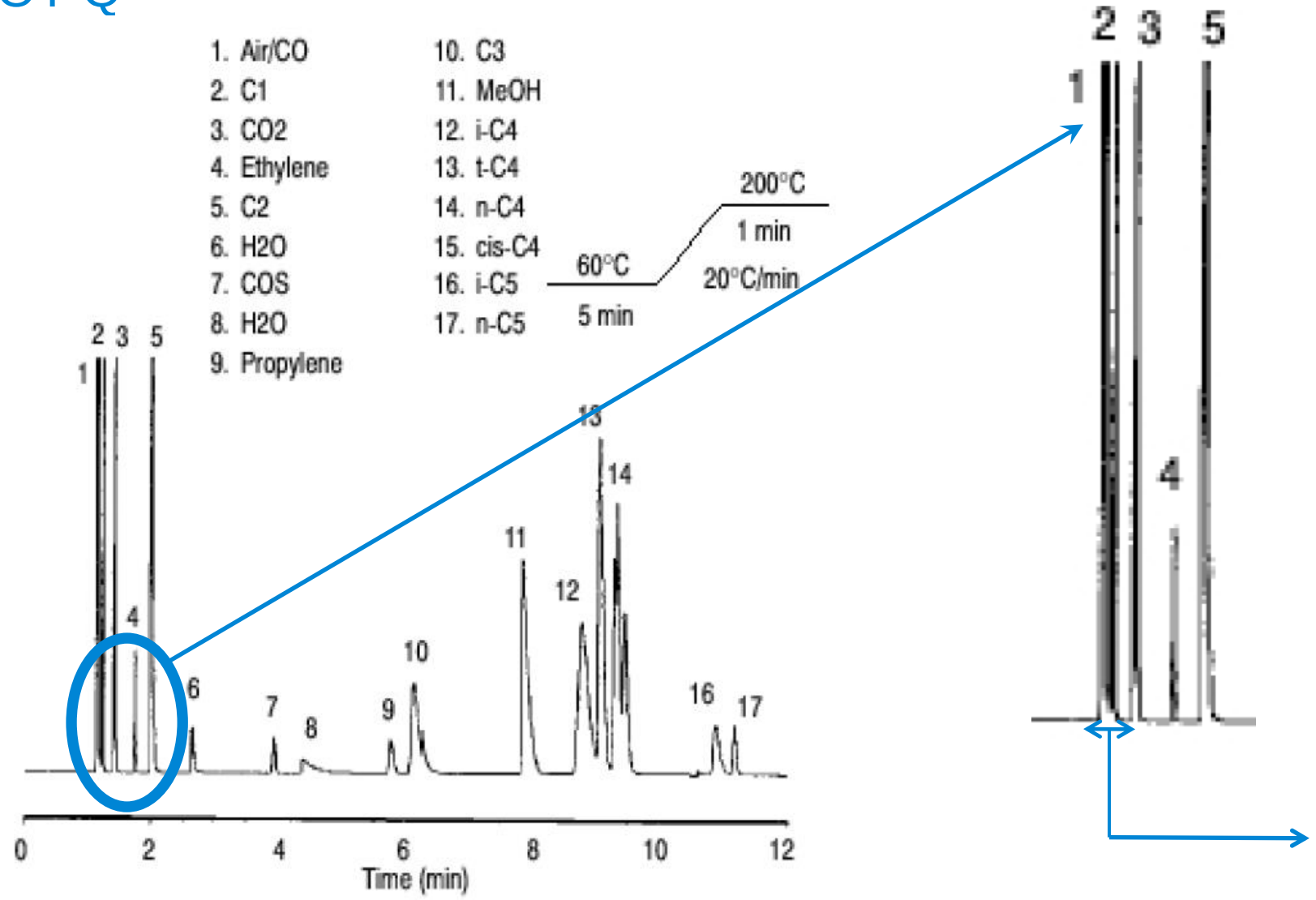

To Molsieve column for further separation

Aqueous Injections on Porous Polymer Q-PLOT

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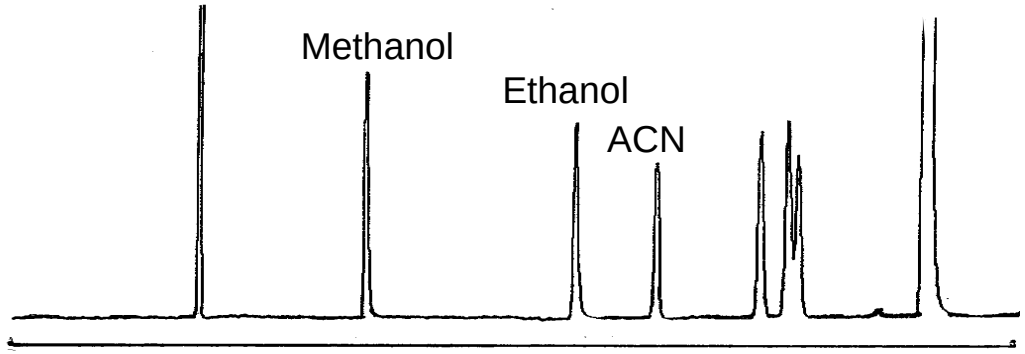
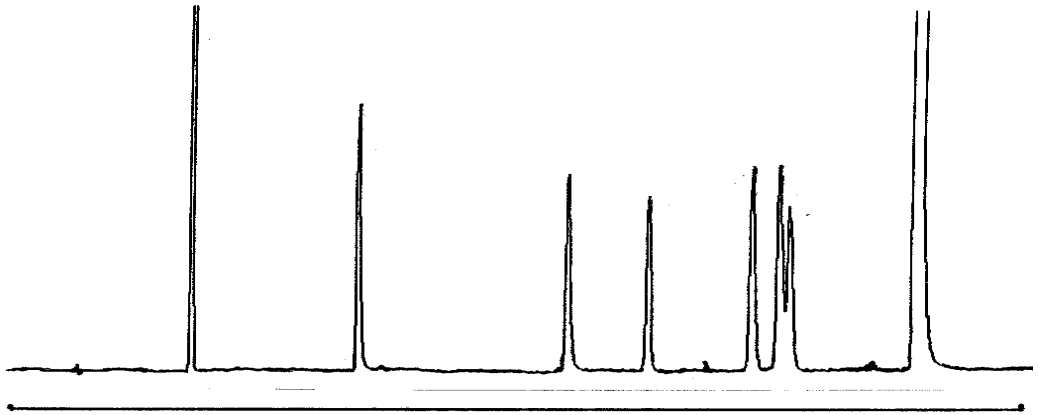
Before



After 5 x 5 µl water, **Splitless** at 80°C



Retention times
unchanged
for all compounds

Samples containing water can be analyzed

Isothermal & short cycle time

Agilent “BOND” Technology & Traditional Particle Traps

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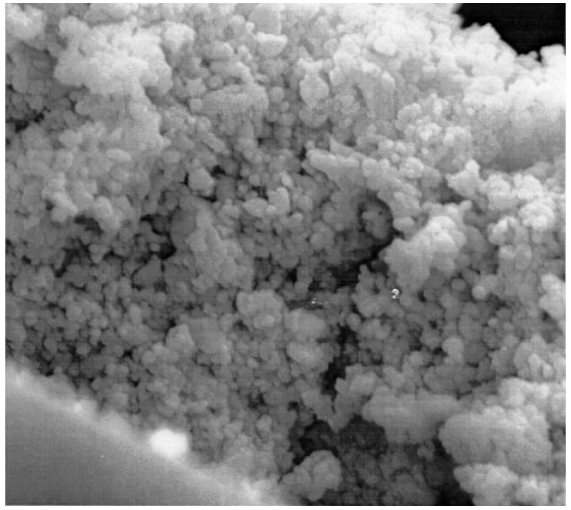
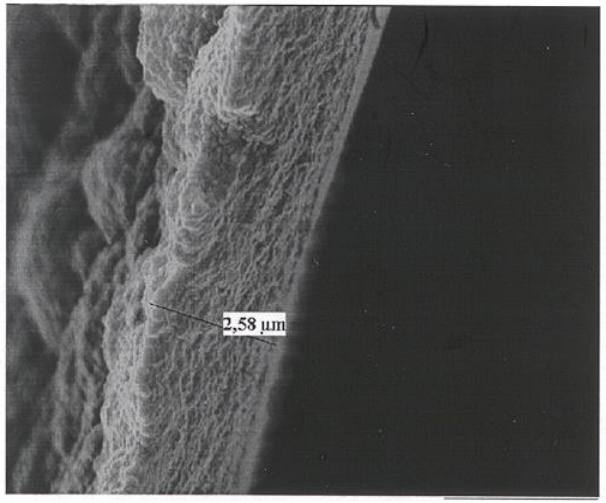
Particle PLOT Q

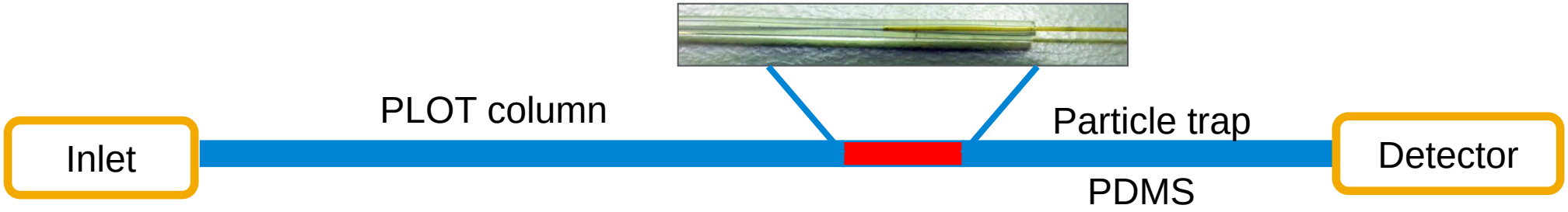


Particle size: 0.1- 2 um
Number: > 10^{12}

PoraBOND Q



Bonded polymer layer
Reduced need particle trap



Solvent Analysis on PoraBOND Q

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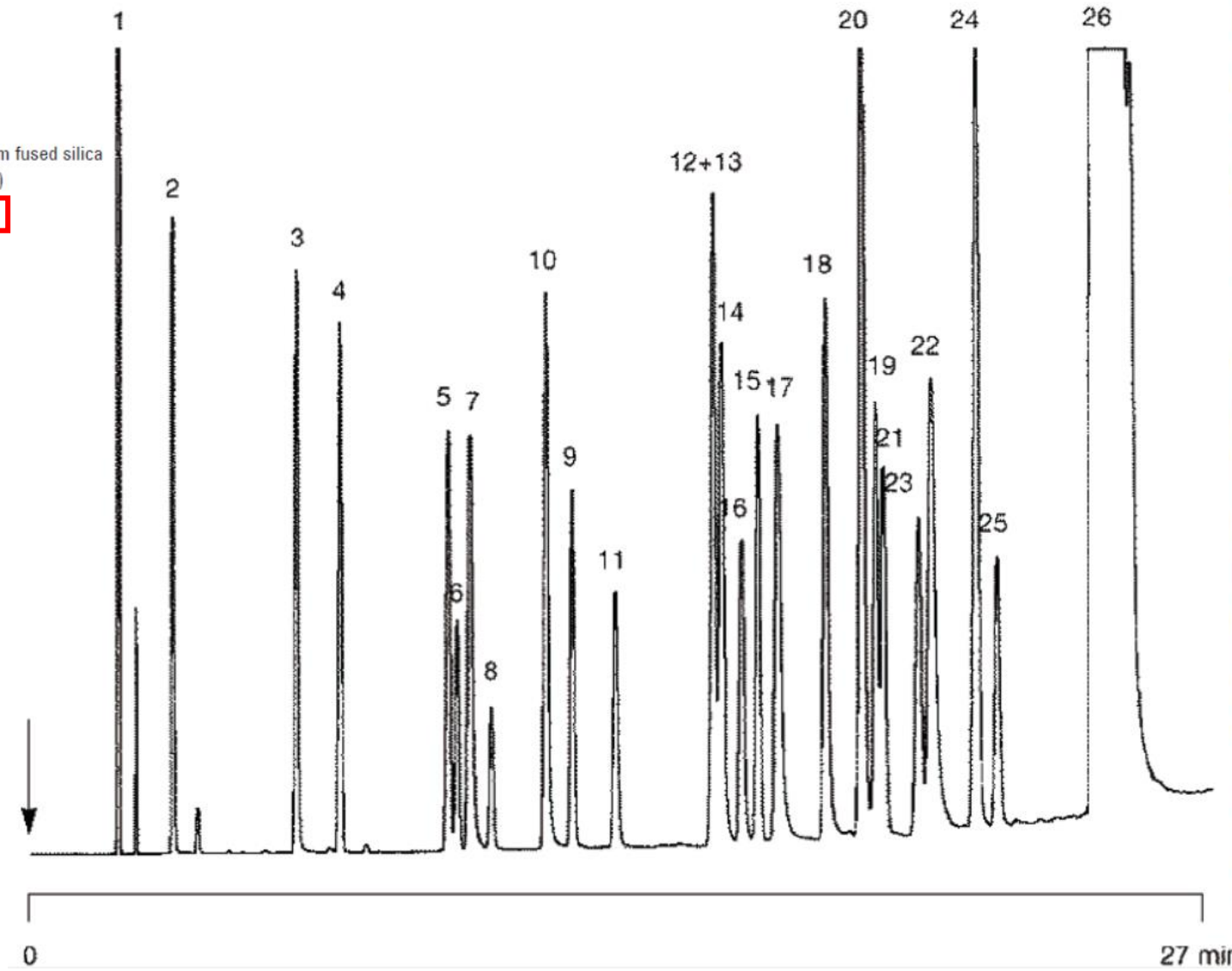
Conditions

Technique	:	GC-wide-bore
Column	:	Agilent PoraBOND Q, 0.53 mm x 25 m fused silica PLOT (df = 10 µm) (Part no. CP7354)
Temperature	:	100 °C (2 min) ⟶ 300 °C. 5 °C/min
Carrier Gas	:	He, 25 kPa (0.25 bar, 3.5 psi)
Injector	:	Split, T = 250 °C
Detector	:	FID, T = 250 °C
Sample Size	:	0.5 µL
Concentration Range	:	0.1% per compound
Solvent Sample	:	DMSO



Peak identification

1. methane
2. methanol
3. ethanol
4. acetonitrile
5. acetone
6. dichloromethane
7. 2-propanol (isopropanol)
8. dimethyl sulfide
9. diethyl ether
10. 1-propanol
11. pentane
12. 2-butanone
13. trichloromethane
14. tetrahydrofuran
15. ethyl acetate
16. 2-methoxyethanol
17. isobutanol
18. butanol
19. hexane
20. benzene
21. trichloroethylene
22. cyclohexane
23. 1.4-dioxane
24. pyridine
25. N,N-dimethylformamide
26. dimethyl sulfoxide

Integrated Particle Trap (PT)

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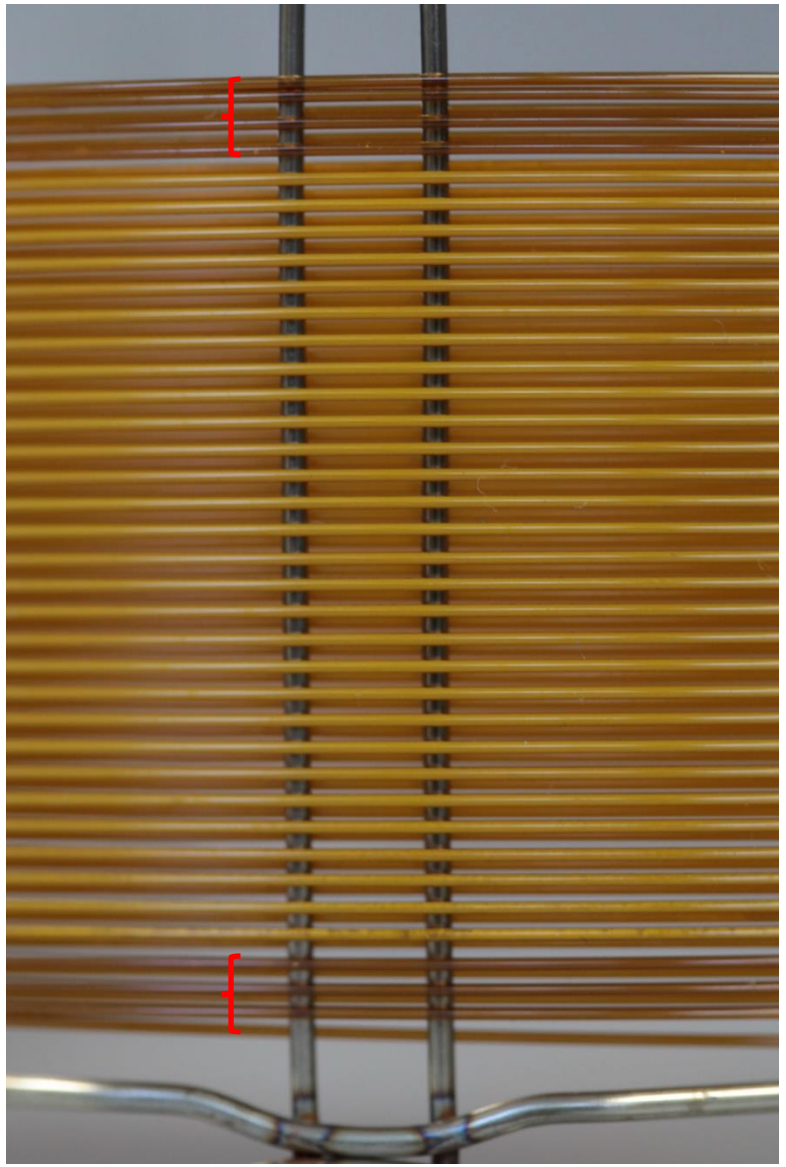
Integrated particle trap at front & back of the column

PLOT column



Assurance & Safety
for valves & detectors
in
for- and backflush modes

Proof of Agilent PLOT-PT Column Performance

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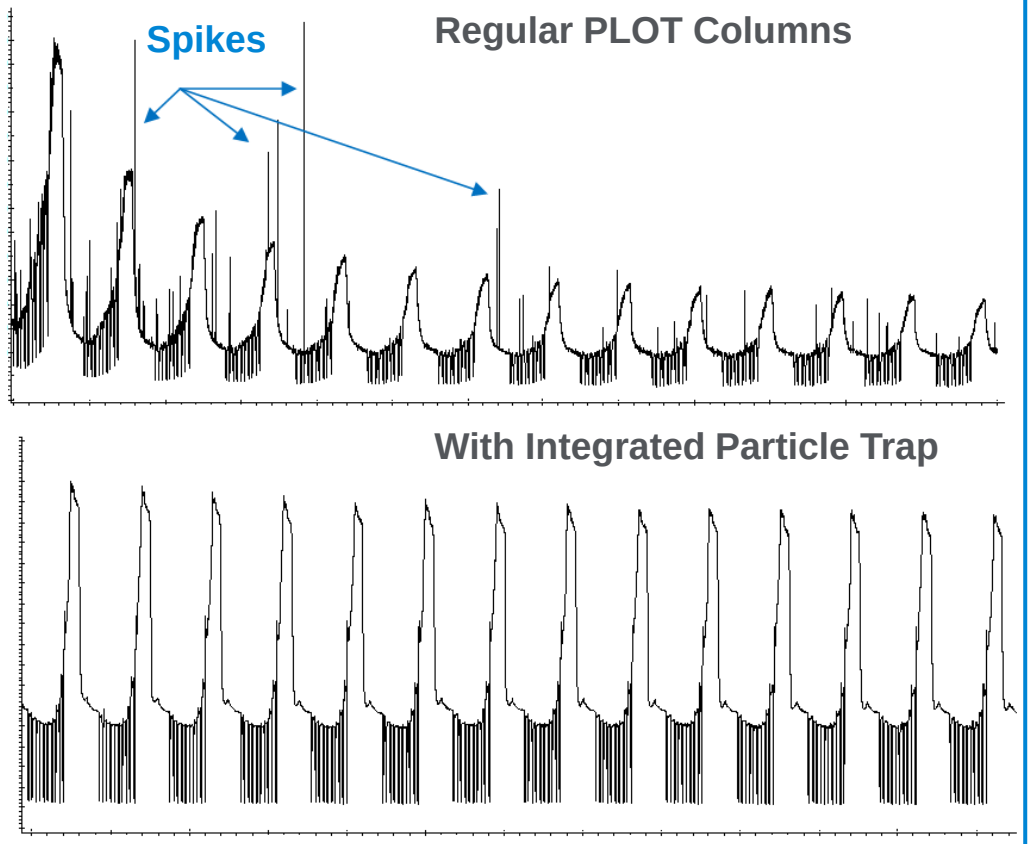
- 150°C → 250°C @ 20 °C/min
- Pressure 3x higher than optimal
- 15 cycles
- 10 x Carrier gas off / on



Agilent PLOT-PT

- Zero particle shedding
- No unions and fittings – No blockage
- Multi column valve switching
- Particle traps integrated on both ends – supports back flush & CFT technology
- Similar selectivity, efficiency & peak shape performance to existing Agilent porous polymer PLOT columns
- Minimum method redevelopment required
- Available for most popular porous polymer PLOT columns

PLOT-PT Chromatographic Performance

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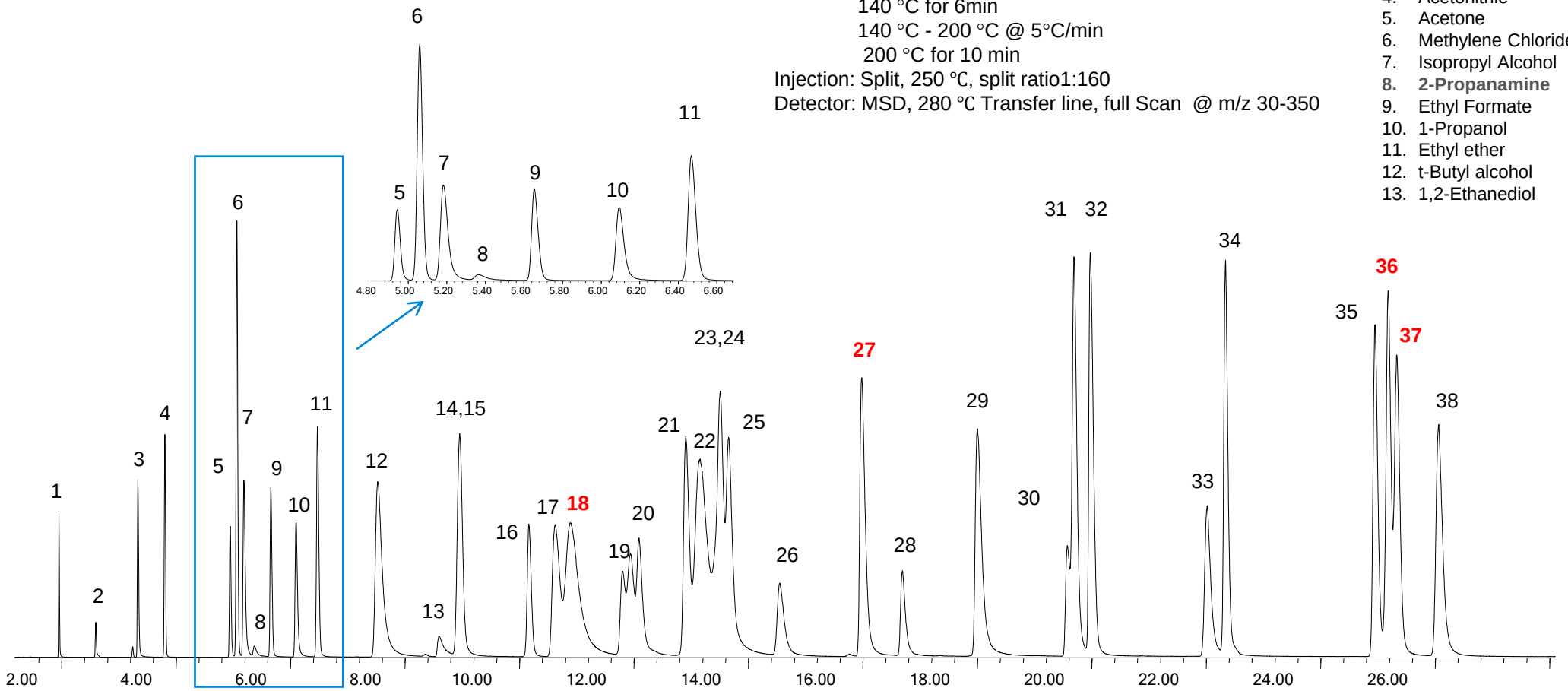
Column: PoraBond Q PT, 30m×0.25mm,3um
Carrier : Helium, 43cm/s @ 90 ℃
Oven: : 90 °C- 140 °C at 10°C/min
140 °C for 6min
140 °C - 200 °C @ 5°C/min
200 °C for 10 min
Injection: Split, 250 ℃, split ratio1:160
Detector: MSD, 280 ℃ Transfer line, full Scan @ m/z 30-350



1. Methyl Alcohol
2. **Acetaldehyde**
3. Ethanol
4. Acetonitrile
5. Acetone
6. Methylene Chloride
7. Isopropyl Alcohol
8. **2-Propanamine**
9. Ethyl Formate
10. 1-Propanol
11. Ethyl ether
12. t-Butyl alcohol
13. 1,2-Ethanediol
14. Trichloromethane
15. 2-Butanone (MEK)
16. Ethyl Acetate
17. sec-Butyl alcohol
18. **MTBE**
19. 2-chlorobutane
20. 1-Butanol
21. Benzene
22. 1,1,1-Trichloroethane
23. 1-chlorobutane
24. Carbon Tetrachloride
25. Hexane
26. 1,4-Dioxane
27. Pyridine
28. Dimethyl Formamide (DMF)
29. Isoamyl Alcohol
30. Dimethyl Sulfoxide (DMSO)
31. Toluene
32. Heptane
33. Paraldehyde
34. **Chlorobenzene**
35. Ethylbenzene
36. m-Xylene
37. p-Xylene
38. o-xylene

Selectivity Comparison of Porous Polymer PLOT

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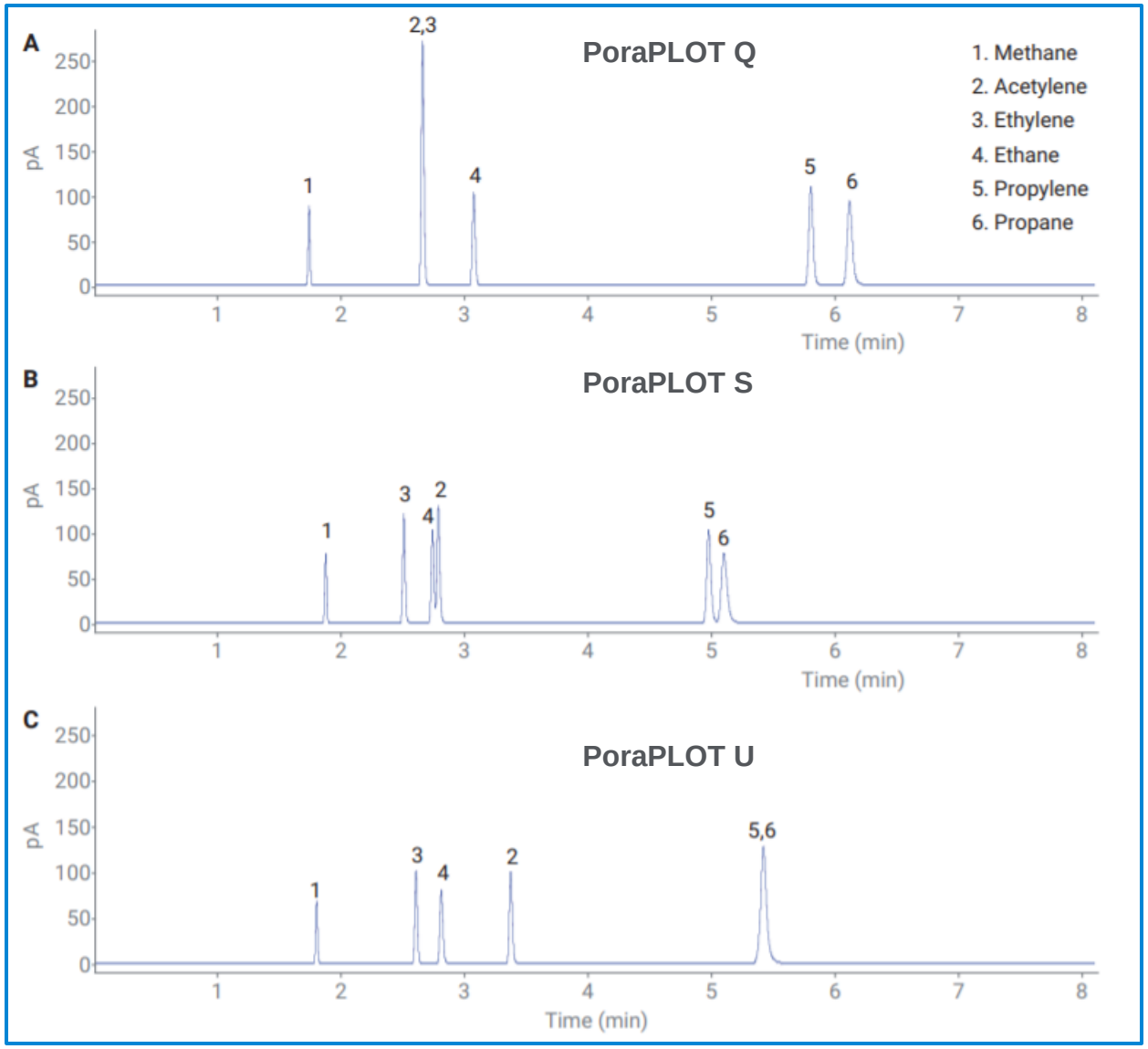

GC Conditions	
Columns	Agilent J&W PoraPLOT Q, 25 m × 0.53 mm × 20 µm (p/n CP7554) Agilent J&W PoraPLOT S, 25 m × 0.53 mm × 20 µm (p/n CP7574) Agilent J&W PoraPLOT U, 25 m × 0.53 mm × 20 µm (p/n CP7584) Agilent J&W PoraPLOT Q, 10 m × 0.53 mm × 20 µm (p/n CP7553) Agilent J&W PoraBOND Q, 25m × 0.53 mm × 10 µm (p/n CP7354)
Carrier	Helium, constant flow, 5 mL/min
Oven	50 °C (1.0 min), Ramp 10 °C/min to 200 °C (2 min) *Ramp to 180 °C for the J&W PoraPLOT U
Inlet	SSL Inlet, split mode, 200 °C, split ratio 20:1
Inlet Liner	Ultra Inert, split, low pressure drop, glass wool (p/n 5190-2295)
GC/FID	Agilent 7890B GC equipped with FID
Sampler	Agilent 7693 automatic liquid sampler
FID Conditions	
Temperature	200 °C
Hydrogen	30 mL/min
Air	350 mL/min
Col + Make Up	25 mL/min

5994-3485EN

Alumina Adsorbent and PLOT Columns
-- Best selectivity for light hydrocarbon separations --

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Applications

- General C1 – C6 (C9) hydrocarbons
- Natural Gas
- Ethylene streams, impurities
- Impurities in propylene
- Butylene streams, impurities
  complex C4 composition
- Environmental hydrocarbon distributions

Separation & Conditions

- Degree of saturation
  Elution: alkane, alkene, alkyne, (dialkenes)
- Selectivity: types of deactivation
  KCl, Na_2SO_4 and Proprietary
- Selectivity: column flow & temperature

- Moisture carrier gas (& sample)
  Retention & selectivity impacted
  Gas Clean moisture filters recommended!

Selectivity Difference between KCl and Na_2SO_4

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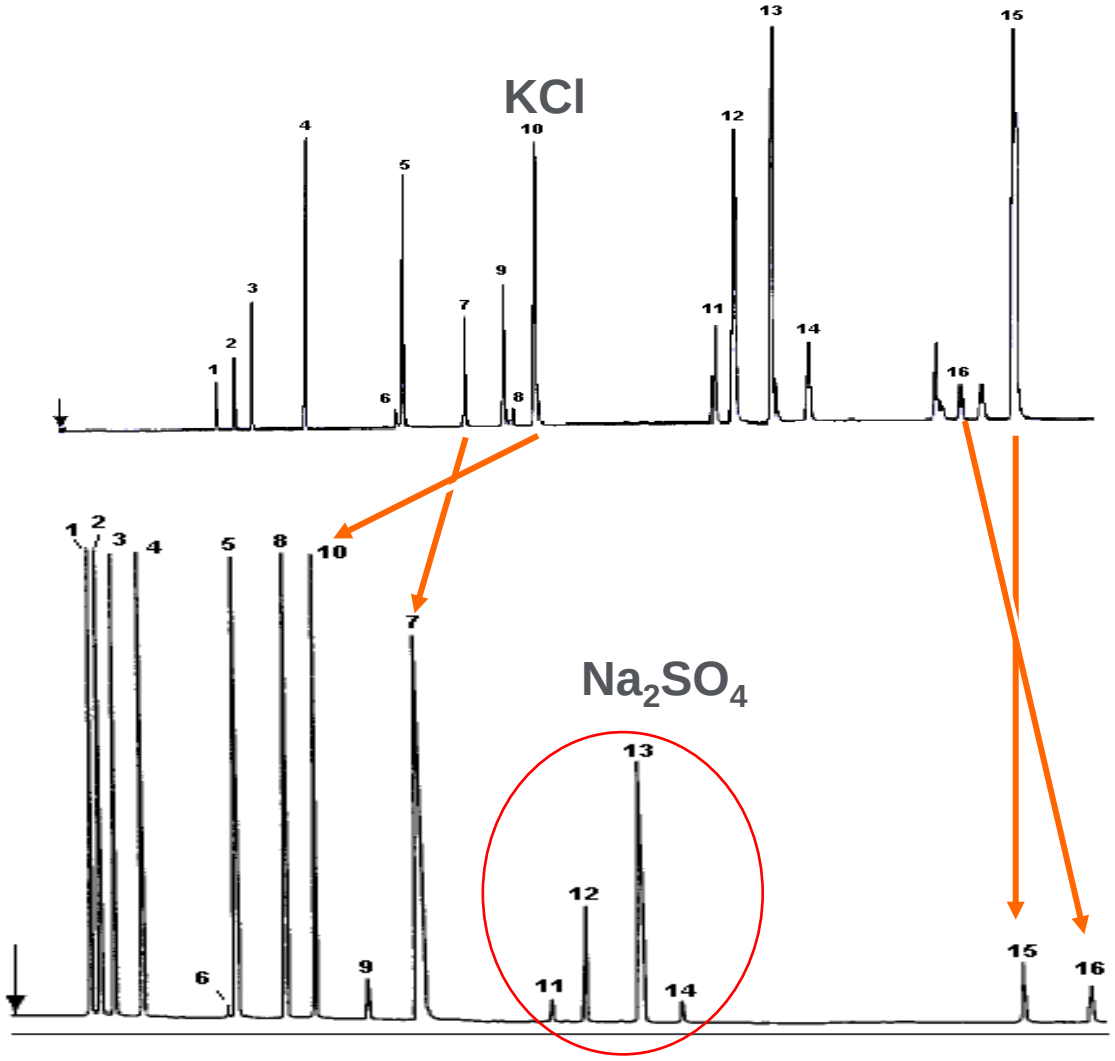
1. methane
2. ethane
3. ethene
4. propane
5. propene
6. cyclopropane
7. ethyne
8. iso-butane
9. propadiene
10. n-butane
11. t-2-butene
12. 1-butene
13. iso-butene
14. c-2-butene
15. 1,3-butadiene
16. propyne



KCl for
- Impurities in Ethylene
- Impurities Propylene
- Impurities in 1,3 Butadiene

Na_2SO_4 for C4 feeds

Alumina columns tend to exhibit overload for highly unsaturated analytes more quickly

Impurities in 1,3-Butadiene

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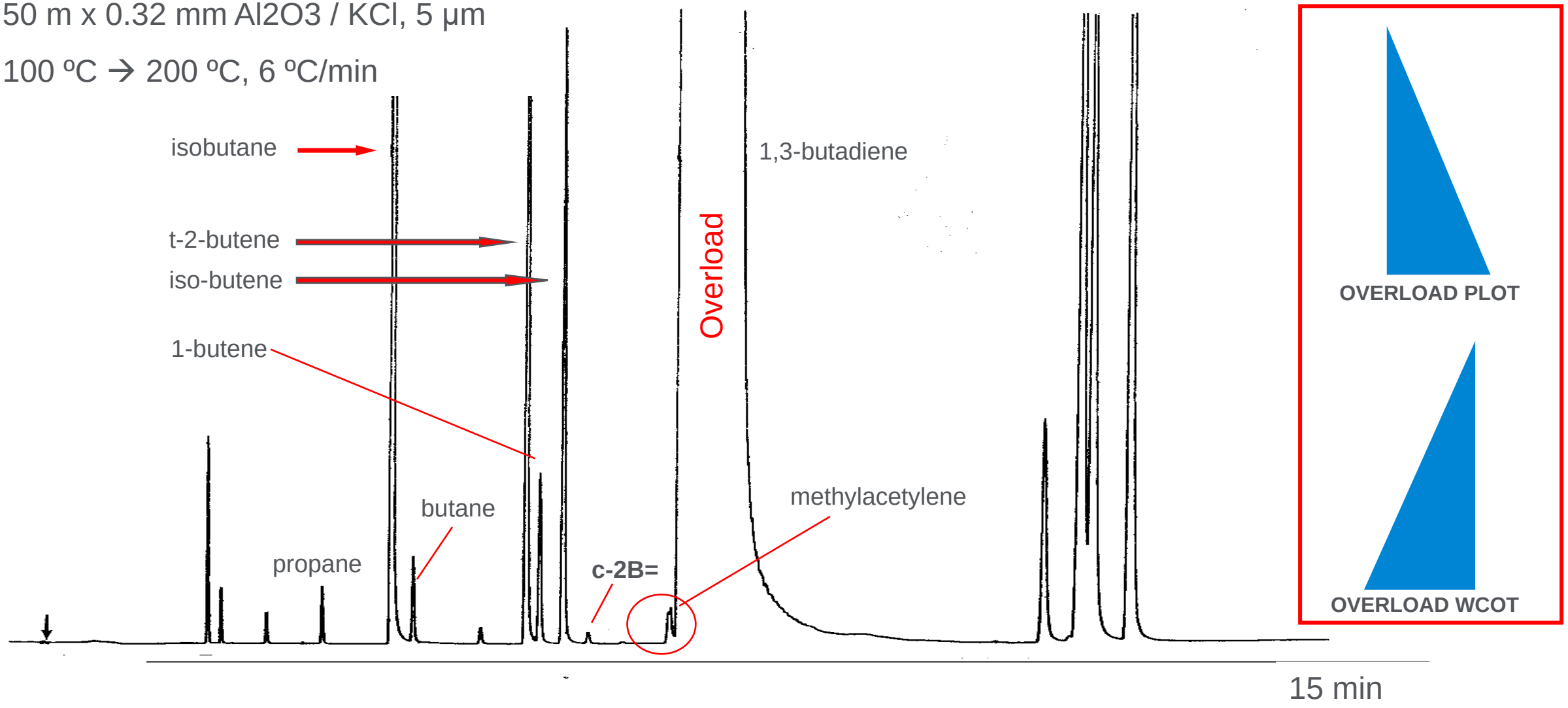
50 m x 0.32 mm Al2O3 / KCl, 5 µm

100 ºC → 200 ºC, 6 ºC/min



Absorption and Response of Hydrocarbons
-- The Case for Al_2O_3 MAPD --

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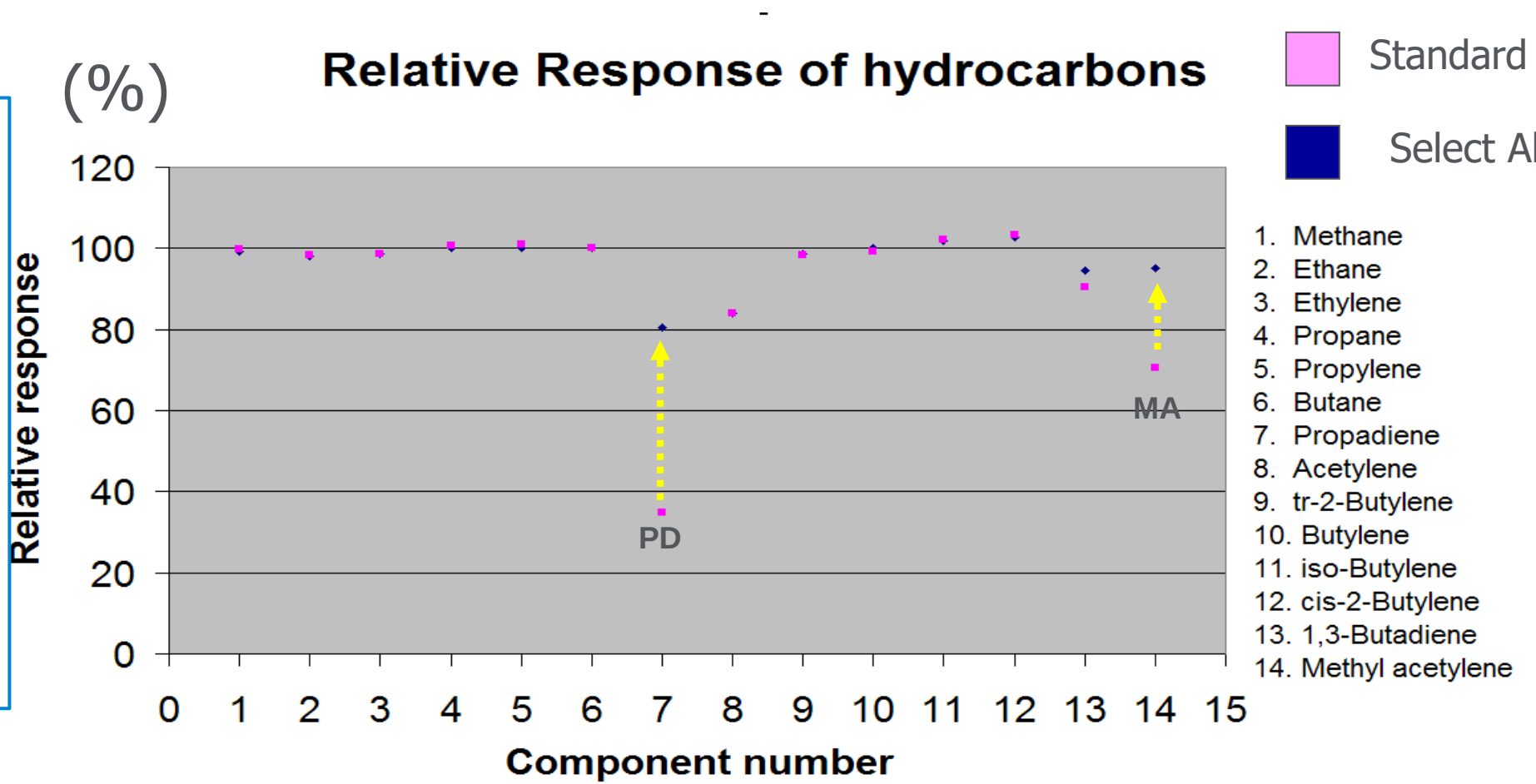
BE AWARE

Alumina columns exhibit partial irreversible absorption of highly unsaturated HC

-

No 100% level calibration!



Silica based PLOT

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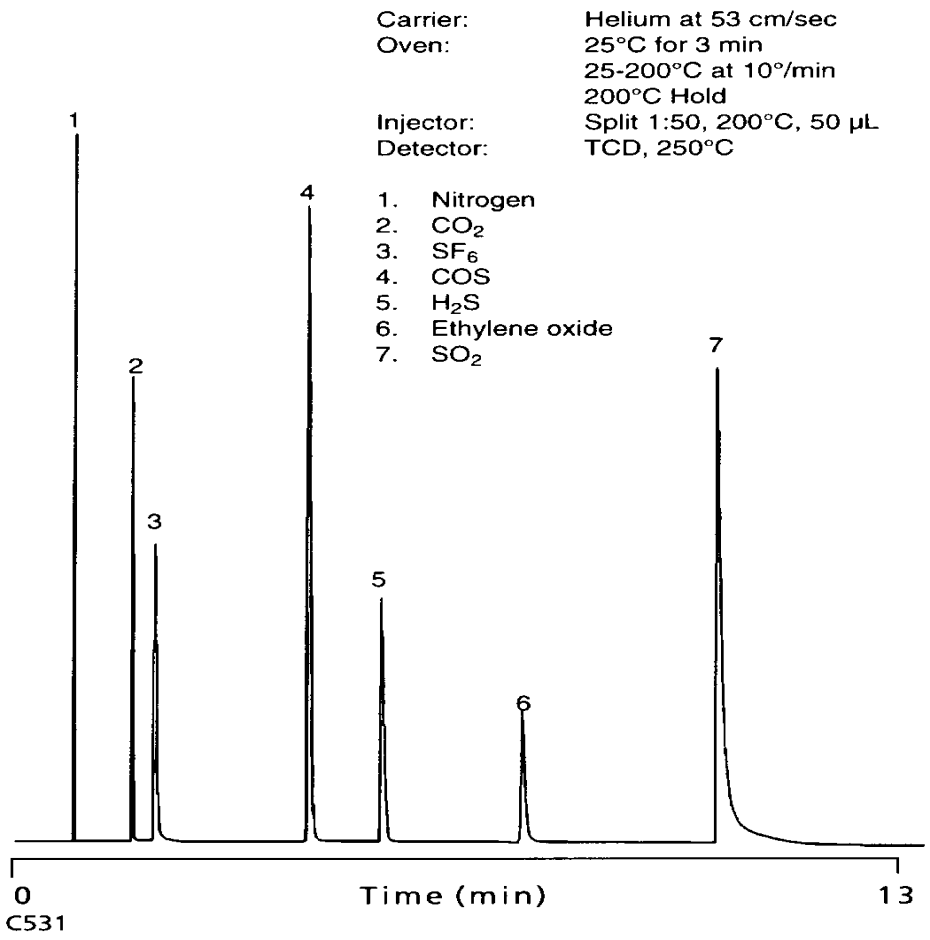
Inorganic Gases on GC-GasPro

30m x 0.32mm



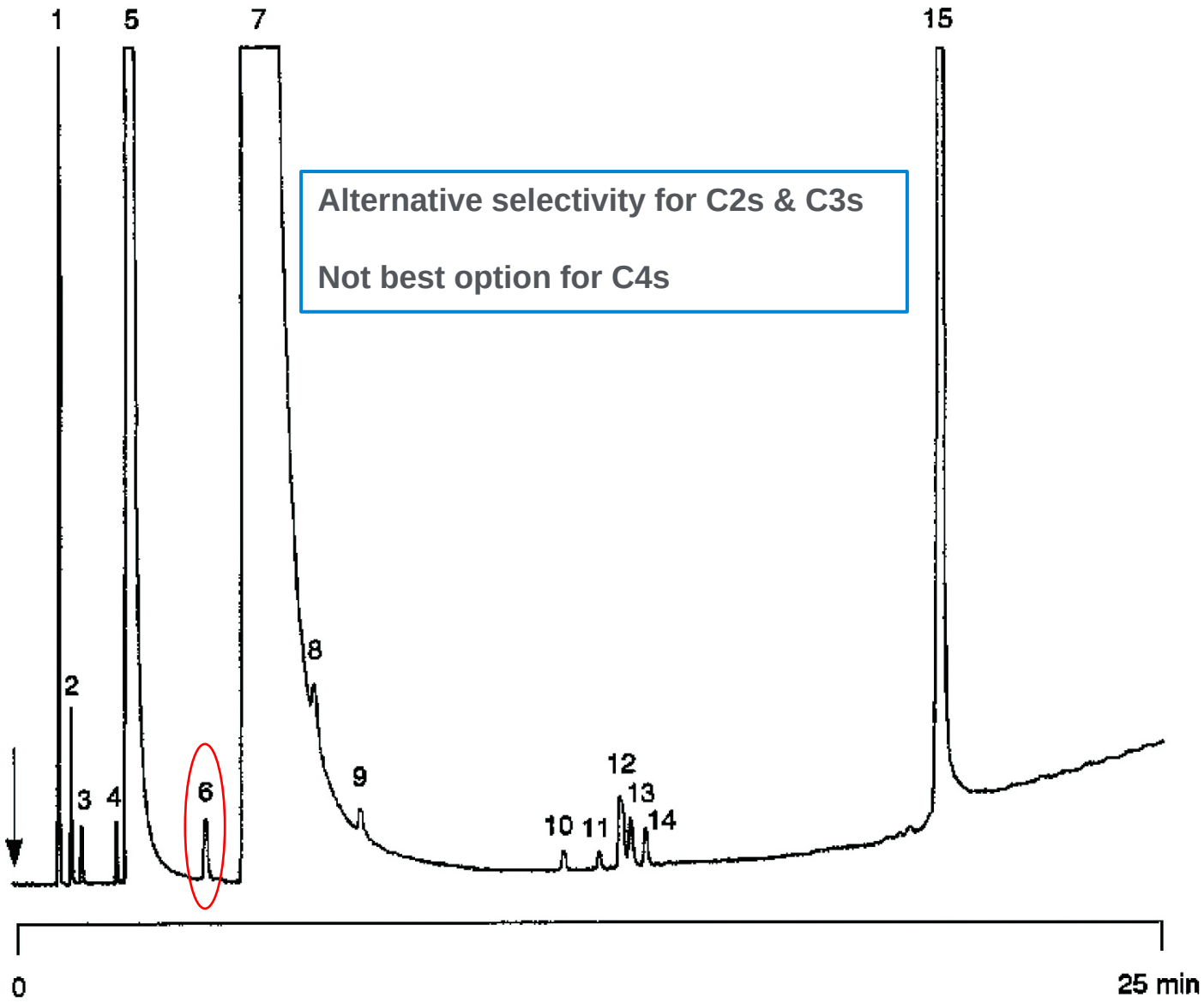
- GS-GasPro & CP-SilicaPLOT
- Light hydrocarbon separation: C1 – C4
- Extended hydrocarbon range compared to other PLOTs
- Inert enough for low ppm light sulfurs, H_2S, COS, mercaptans
- CFC's
- Not sensitive to moisture in carrier gas
- MSD compatible
- MAOT of 200°C

CP-SilicaPLOT -- Hydrocarbons

Column	:	Agilent CP-SilicaPLOT, 0.53 mm x 30 m, fused silica PLOT CP-SilicaPLOT (df = 6 µm) (Part no. CP8570)
Temperature	:	50 °C (5 min) → 225 °C, 5 °C/min
Carrier Gas	:	He, 20 kPa (0.2 bar, 2.9 psi)
Injector	:	Direct T = 225 °C
Detector	:	FID T = 250 °C
Sample Size	:	2 µL
Concentration Range	:	ppm %

Peak identification

1. methane
2. ethane
3. ethylene
4. acetylene
5. propane
6. cyclopropane
7. propylene
8. isobutane
9. butane
10. 1-butene
11. propyne (methylacetylene)
12. 1,3-butadiene
13. isobutene
14. cis-2-butene
15. hexane



Alternative selectivity for C2s & C3s

Not best option for C4s

Permanent Gases on Parallel Column Solution

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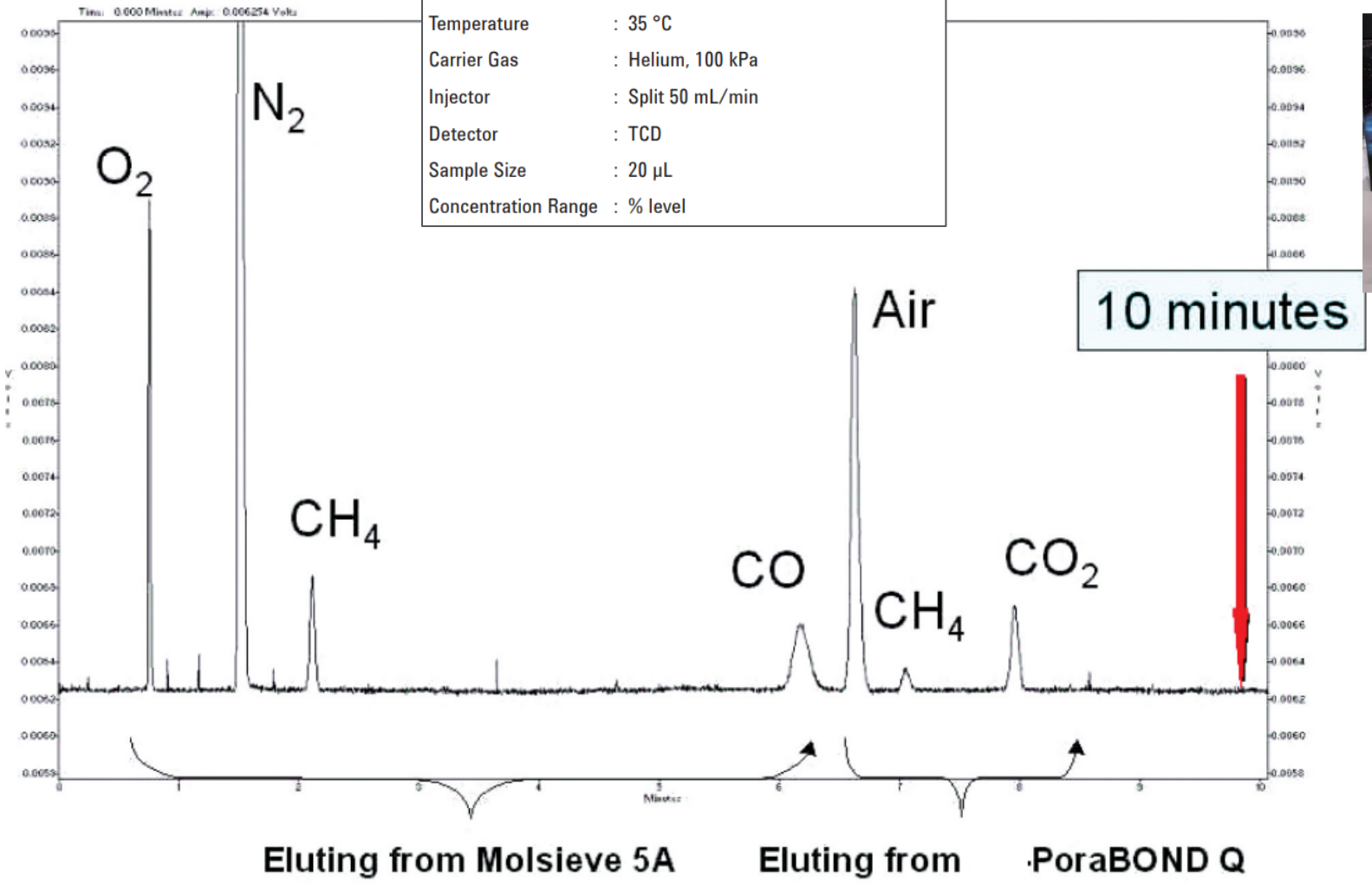
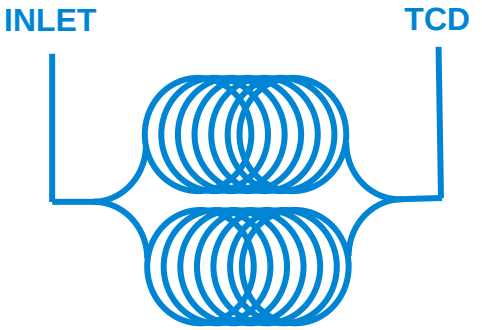
Column	:	Agilent Select Permanent Gases/CO_2 Part no. CP7429
Temperature	:	35 °C
Carrier Gas	:	Helium, 100 kPa
Injector	:	Split 50 mL/min
Detector	:	TCD
Sample Size	:	20 µL
Concentration Range	:	% level





- **Application**: All permanent gases incl. CO2, water, ethane, ethylene

- Optimized dimensions for fast analysis

- PoraBOND Q allows high temperature bake-out (300°C) of CO_2& H_2O

Oxygenates in Hydrocarbons

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Oxygenates blended in gasoline

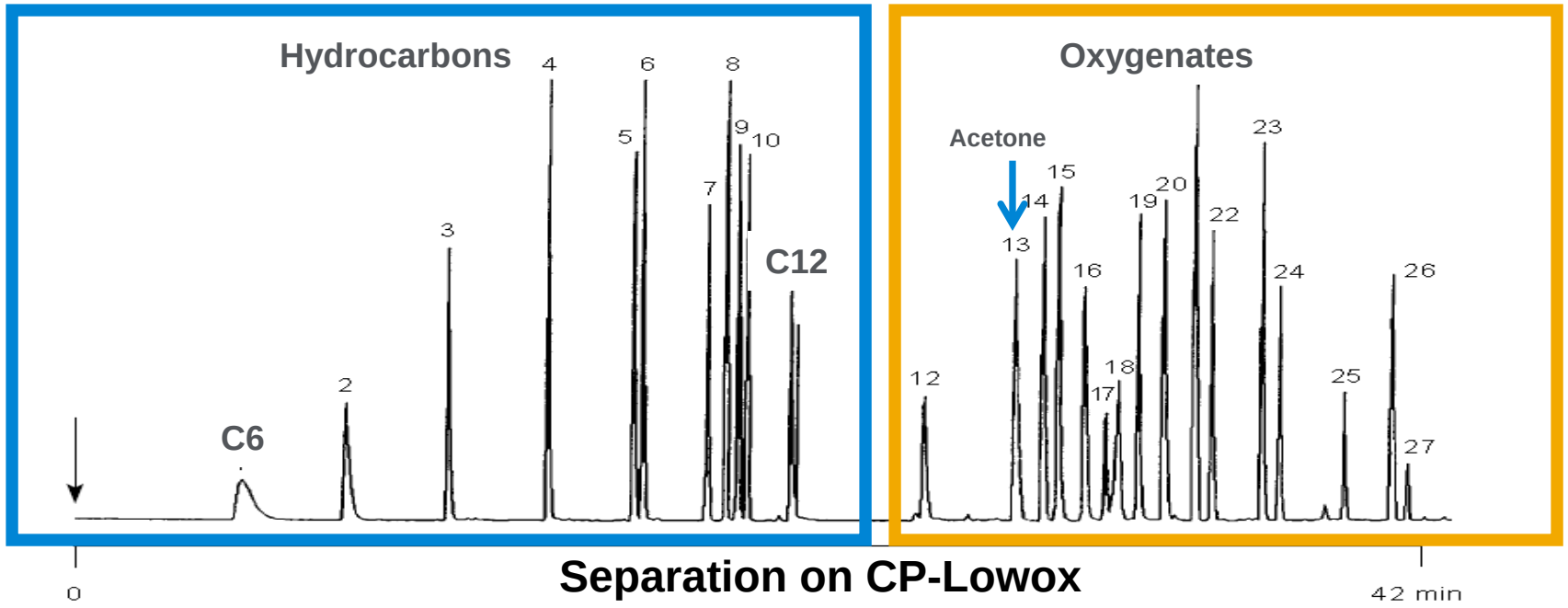
- Additives to boost octane content, prevent engine “knocking”
- MTBE, ETBE, Ethanol
- **% level oxygenates**
- **GC analyses on Wax or TCEP polar liquid phase columns**

Oxygenate in intermediates (monomers, naphtha’s)

- Lower effectiveness catalysts - lower yield
- Higher costs of catalysts
- More refinery downtime
- **ppm level oxygenates**
- **GC analyses on Lowox, OxyPLOT columns, Agilent exclusives**

Analyzing Oxygenates in Hydrocarbon Matrix

- Low ppm concentration level oxygenates – Low analyte capacity of stationary phase
- FID detection (MSD uncommon)
- Agilent columns with high selectivity hydrocarbons/oxygenates: CP-Lowox / OxyPLOT
- Very moisture sensitive ⚠ Use Gas Clean moisture filters in carrier gas



ASTM Trace Oxygenate Analysis Methods
-- Valve Configuration --

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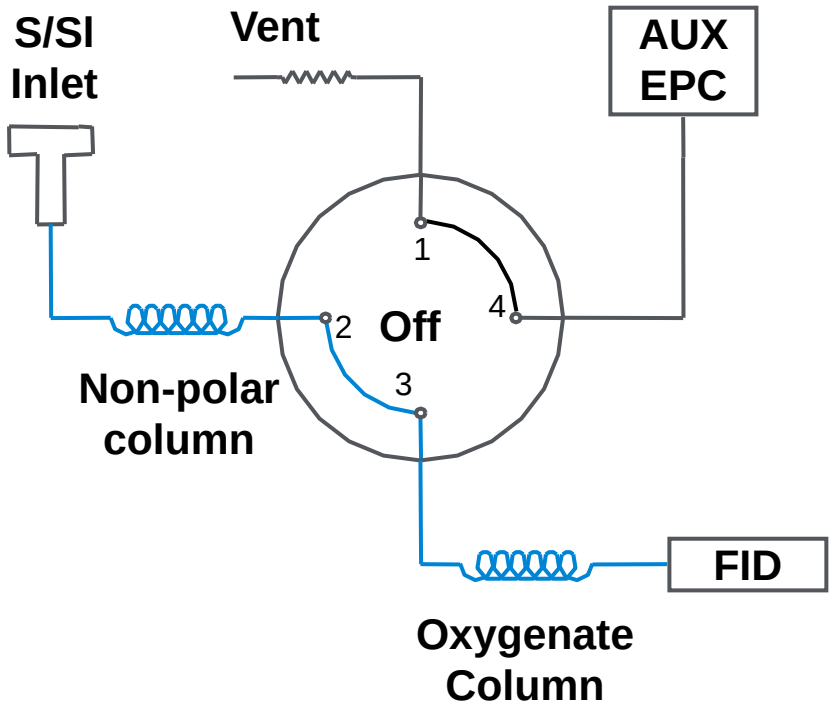
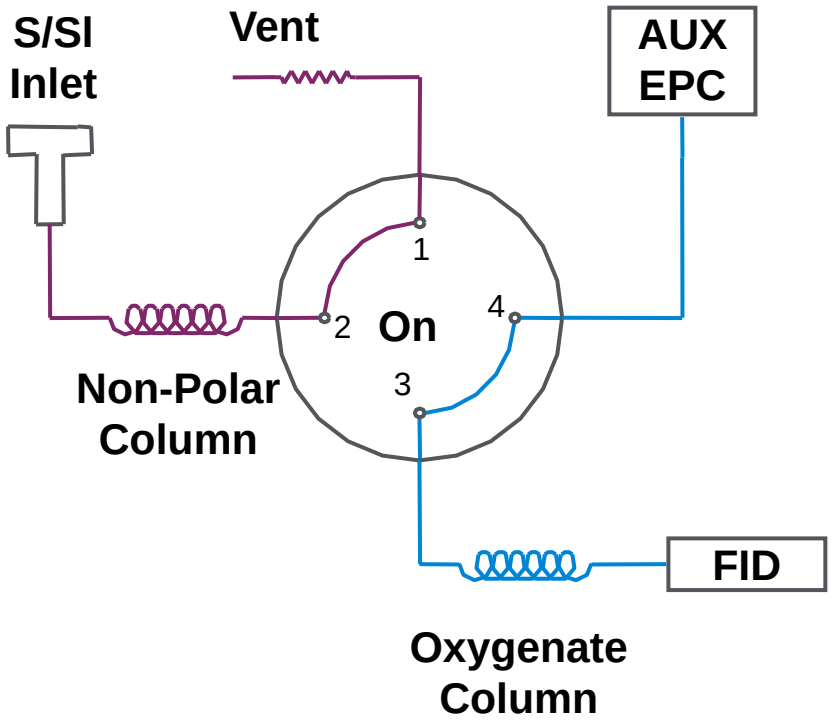
Transfer of Oxygenates
Valve Off



Venting Hydrocarbons
Valve On



Oxygenate Analysis

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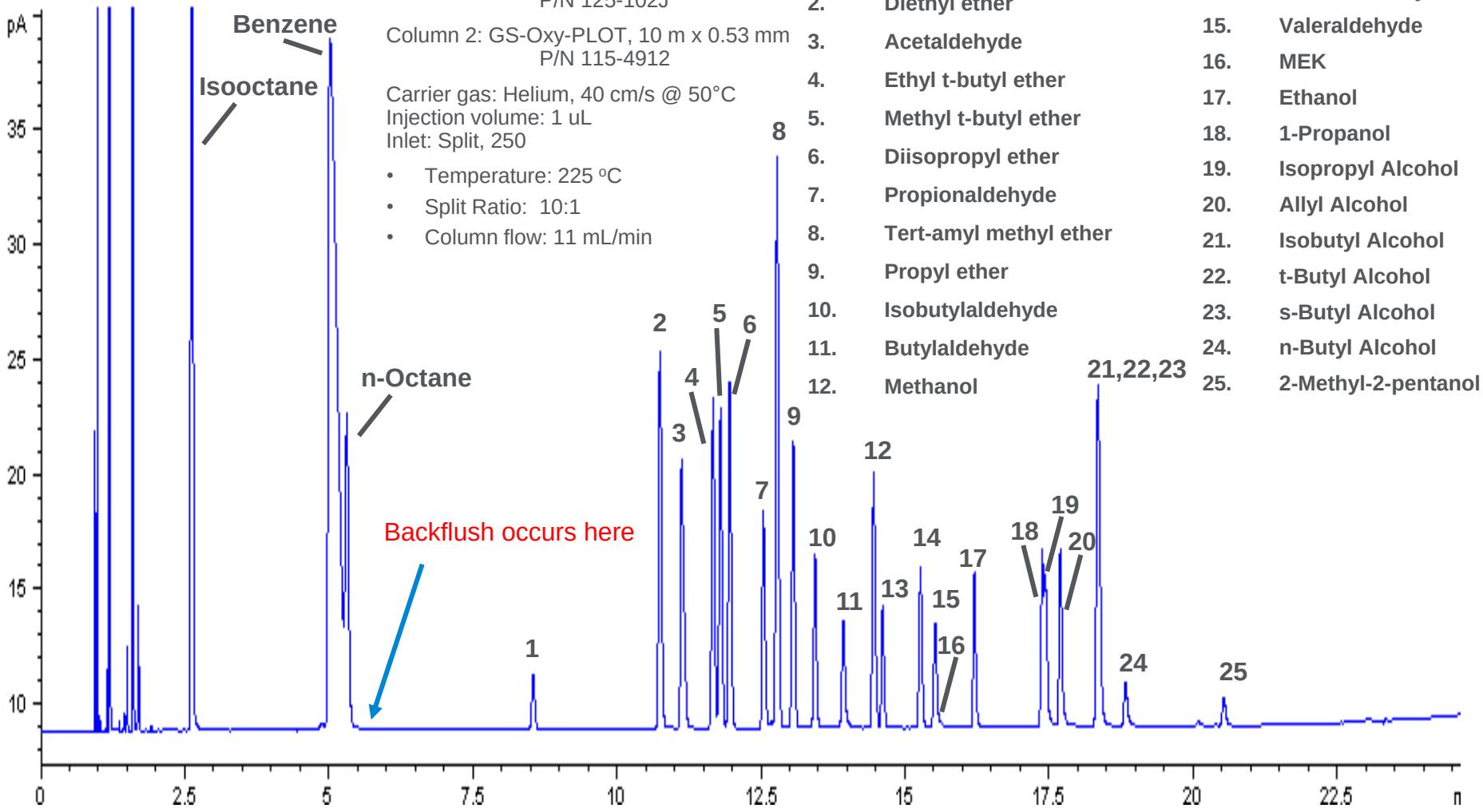


Column 1: DB1, 25 m x 0.53 mm x 1 um
P/N 125-102J

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

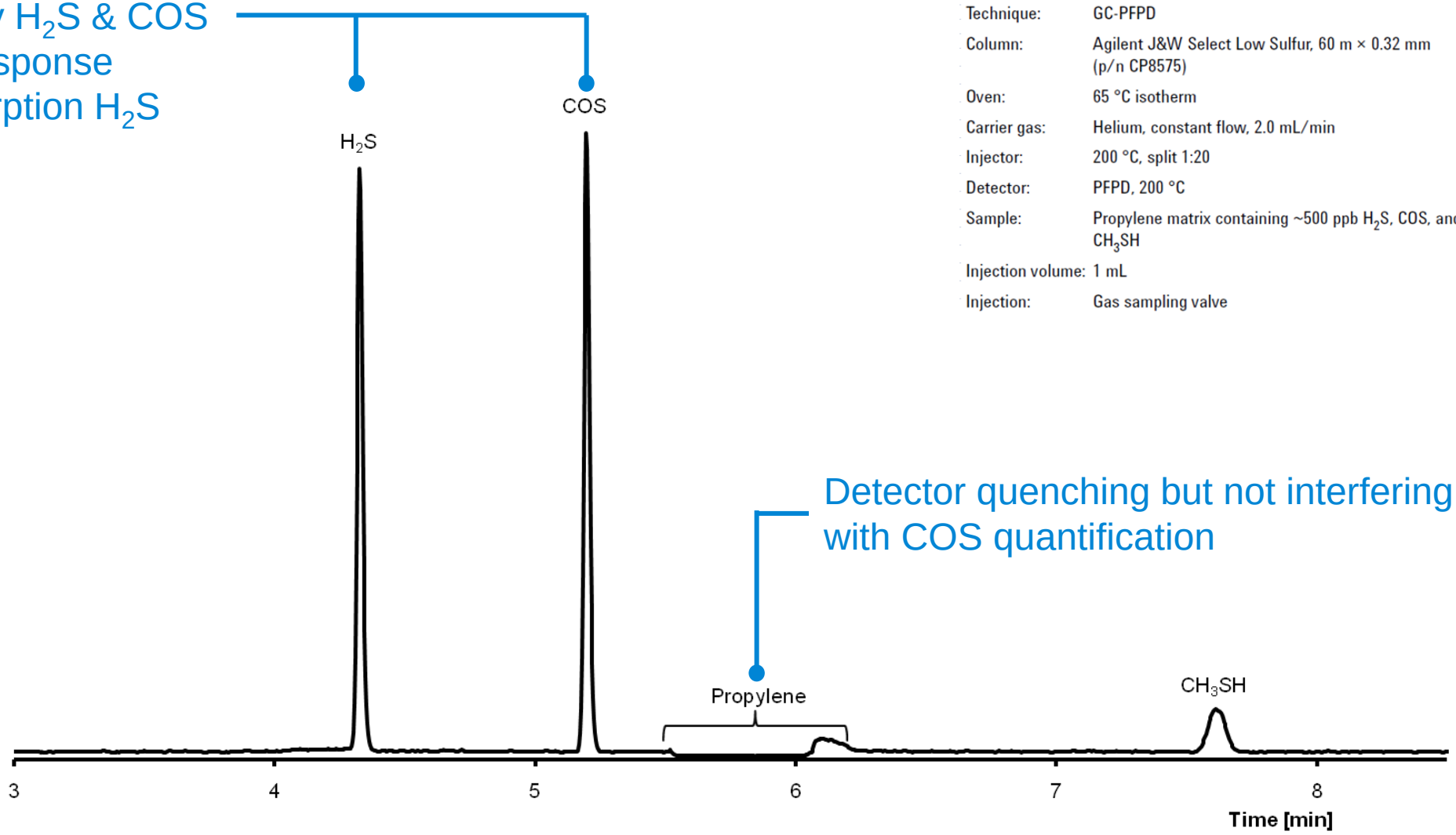
Select Low Sulfur - PLOT

- Super permeable & porous stationary phase
  - Proprietary material
- Unique selectivity characteristics for volatile sulfurs/hydrocarbons
  - No detector quenching for propane/propylene matrix
- Highly inert for volatile sulfurs, H_2S, Methyl mercaptane
- One part number: 60m x 0.32mm, p/n CP8575
- Near 100% recovery for H_2S at 20 – 100 ppb levels
- Zero particle loss
- FPD, PFPD, SCD, AED Compatible

Sulfur components in propylene by PFPD

- 500 ppbv H_2S & COS
- Same response
- No absorption H_2S

Technique:	GC-PFPD
Column:	Agilent J&W Select Low Sulfur, 60 m × 0.32 mm (p/n CP8575)
Oven:	65 °C isotherm
Carrier gas:	Helium, constant flow, 2.0 mL/min
Injector:	200 °C, split 1:20
Detector:	PFPD, 200 °C
Sample:	Propylene matrix containing ~500 ppb H_2S, COS, and CH_3SH
Injection volume:	1 mL
Injection:	Gas sampling valve



Detector quenching but not interfering with COS quantification

Considerations for PLOT Column Analysis

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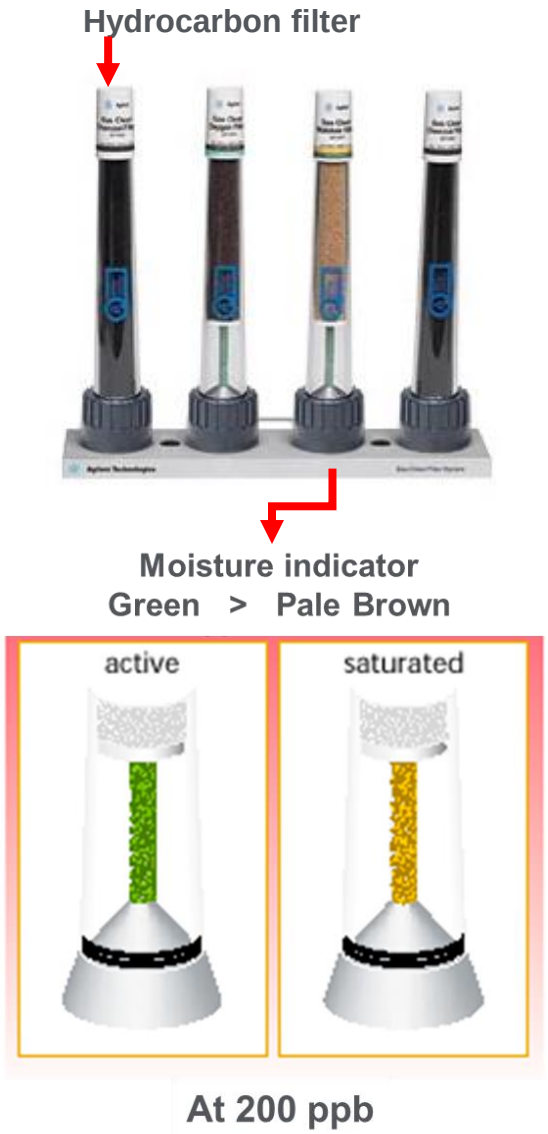
Columns

- Selectivity – Consider elution pattern
- Capacity – Overloading – 0.53mm --
- Inertness (low conc. sulfurs)
- Temperature limits

Contamination

- Efficiency loss; “ghost peaks”; increase in bleed
- Water, CO_2, high molecular weight hydrocarbons
- Carrier gas purifiers highly recommended



Summary

- Agilent supplies largest selection of PLOT columns in the market for all gases and volatiles applications with dedicated columns for challenging analyses in the petrochemical industry.
- Fully QC tested to assure column to column reproducibility with the excellent peak shape performance and separation for the best data accuracy.
- Agilent PLOT columns come with the lowest levels of particle shedding for better baseline stability and trouble-free analyses.
- Exclusive to Agilent, are the PLOT-PT columns with integrated particle traps to assure “spike free” detection, mass spectrometer compatibility and improved system performance with complex valve applications.

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