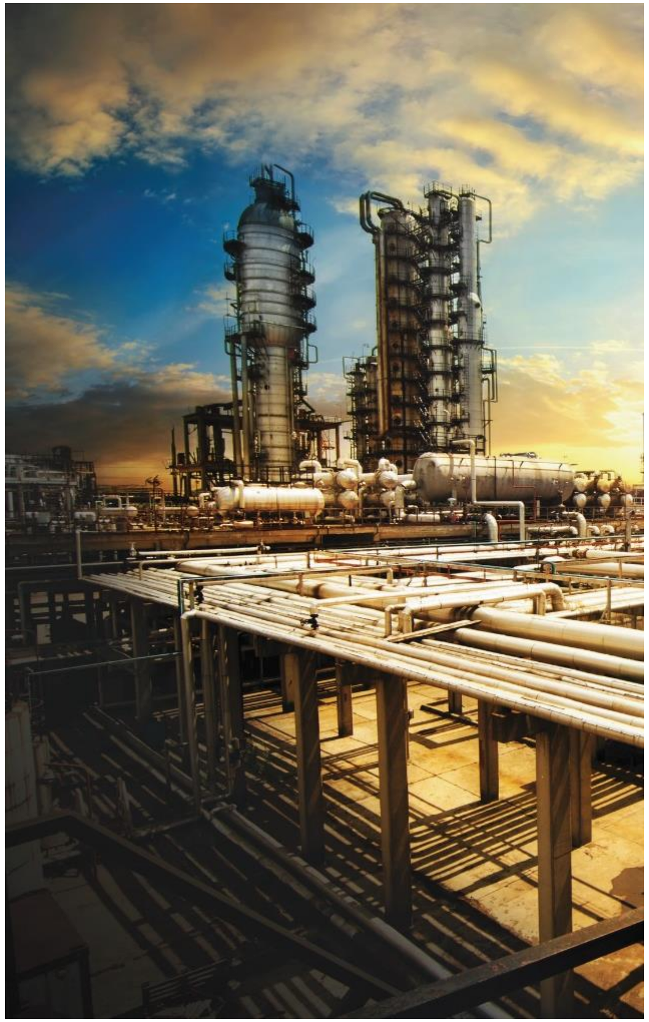
Separation Superhero Seminar Tour

Battle the villains of bad chromatography

Solutions for light hydrocarbons and gasses: PLOT columns

Agilent

Solutions for Light Hydrocarbons and Gasses: PLOT Columns



Allen K. Vickers

Agilent Technologies

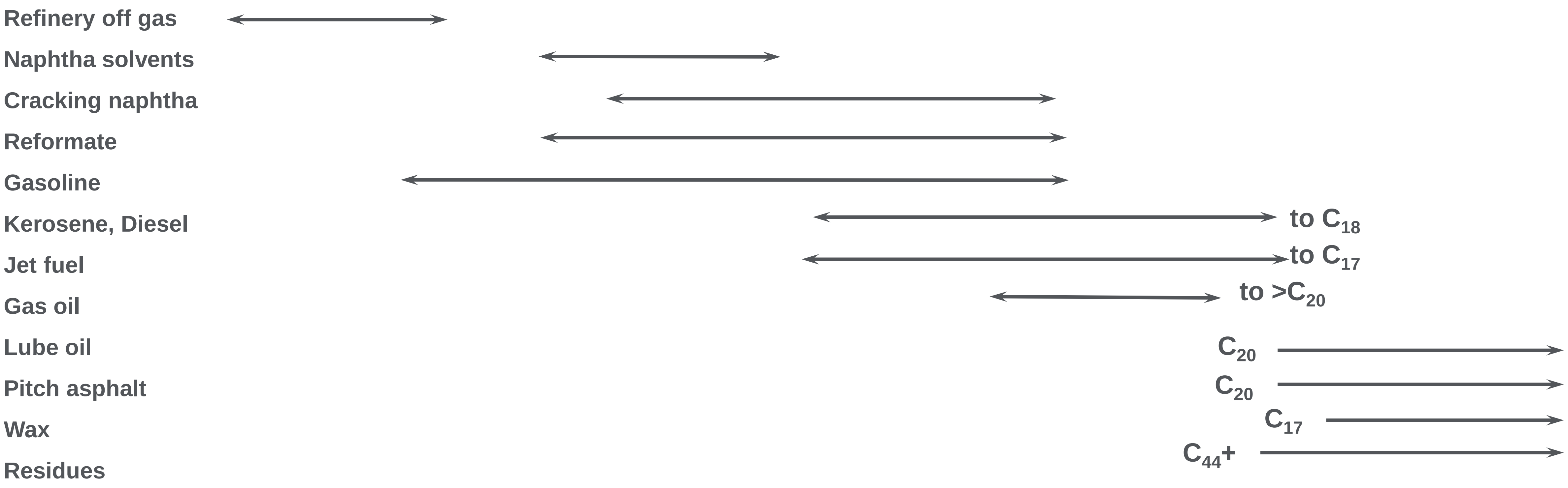
Folsom Technology Center

California, USA

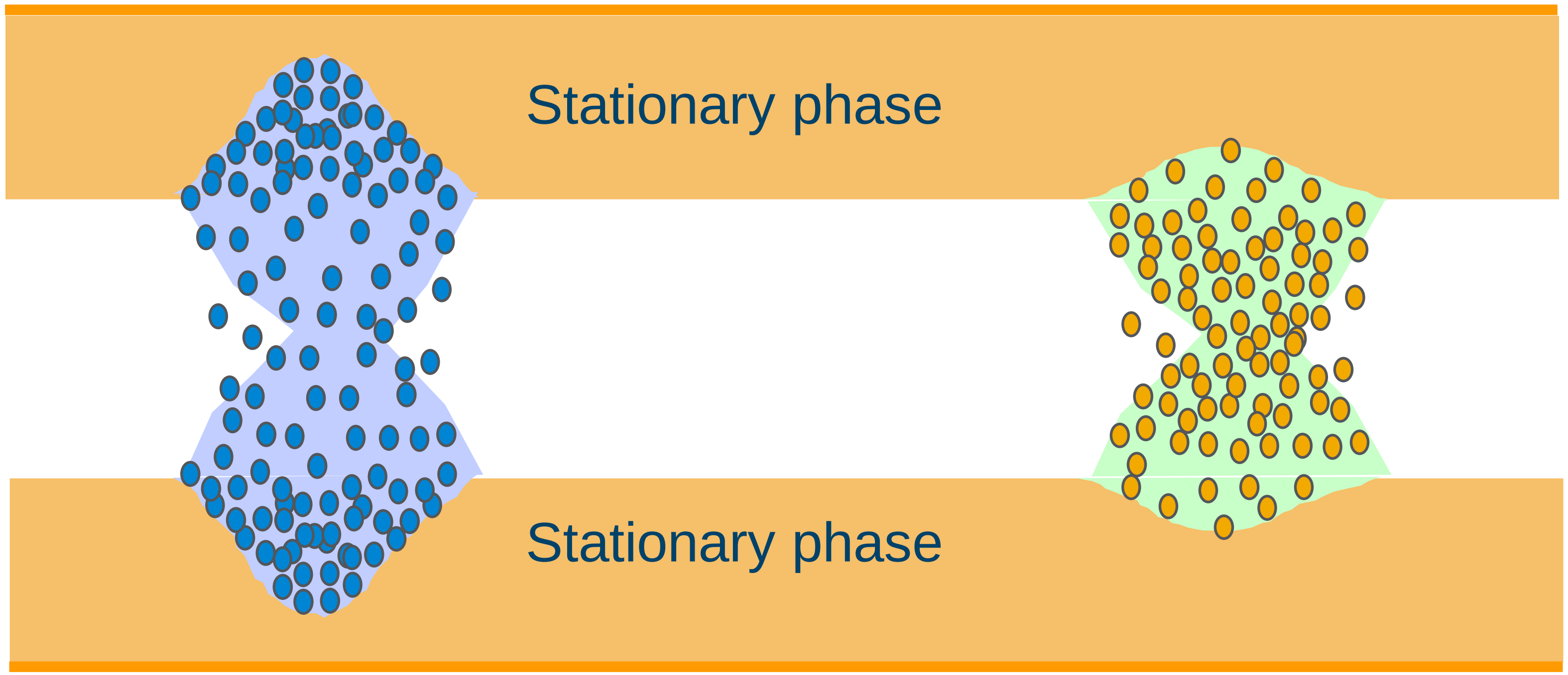
April 18, 2019

Table of Boiling Point Fractions

Carbon No.	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 at 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



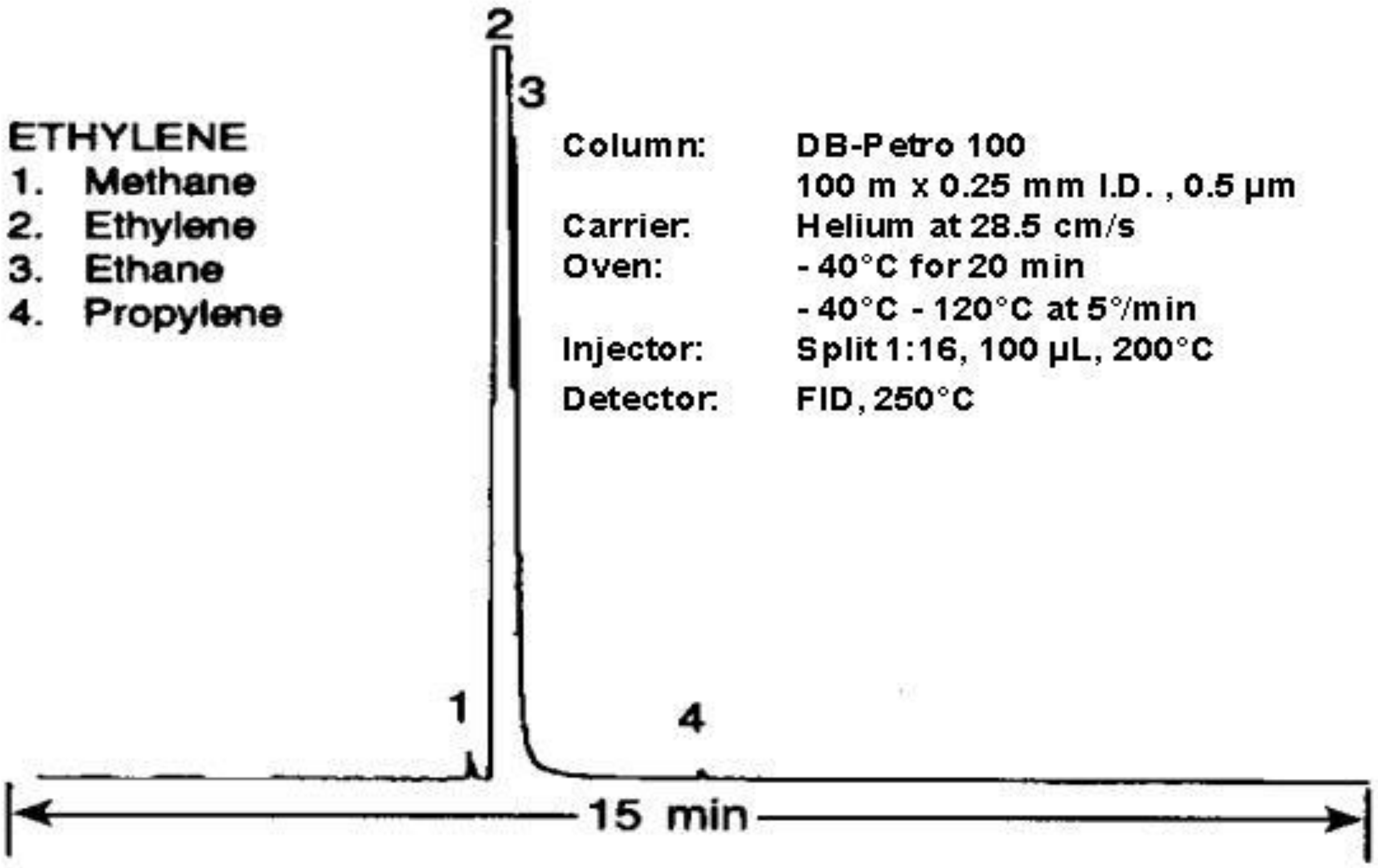
Wall Coated Open Tubular (WCOT) Columns



K_c => Large

K_c => Small

WCOT Ethylene Analysis



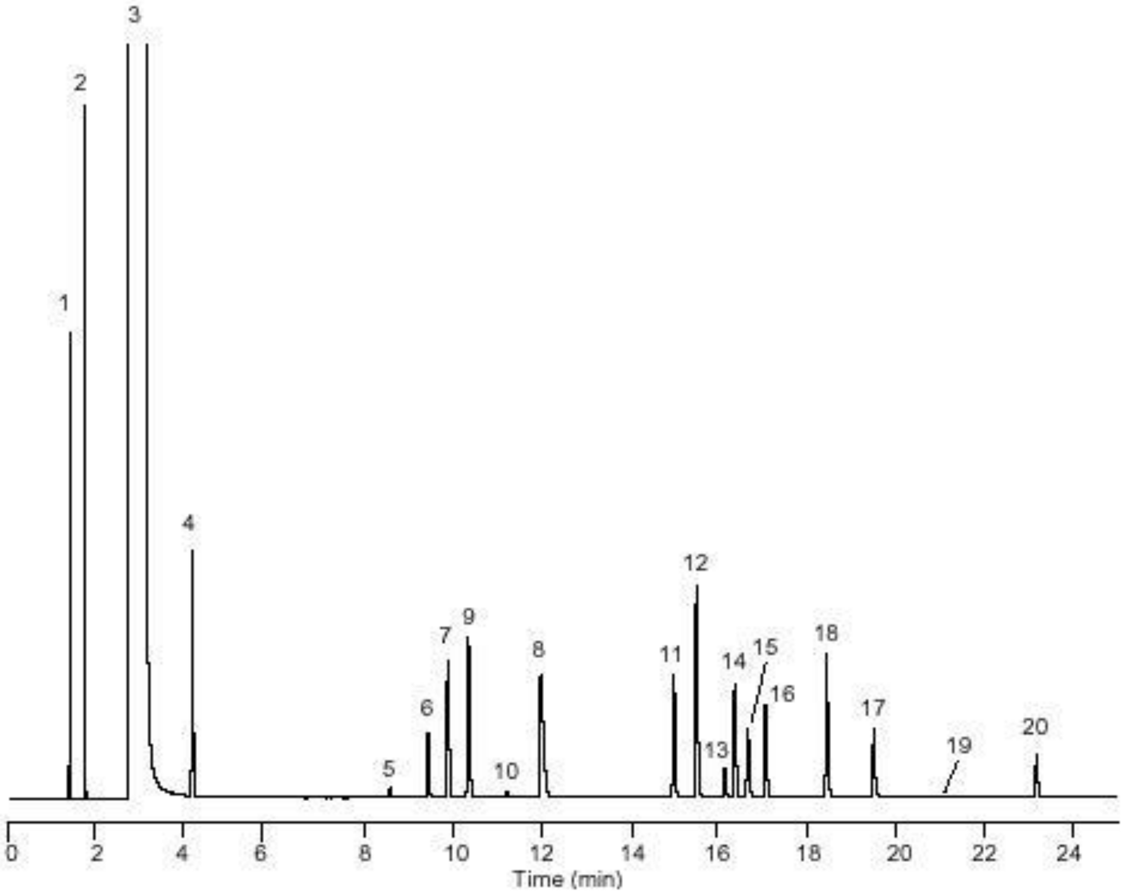
PLOT Ethylene Analysis

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



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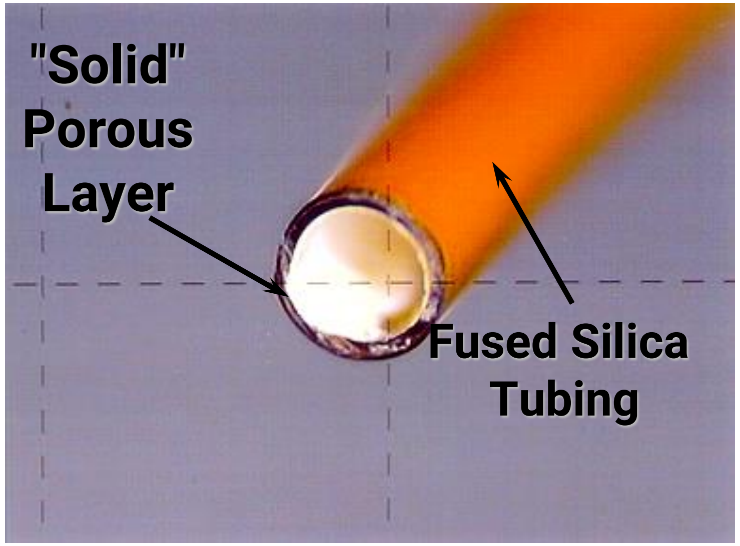
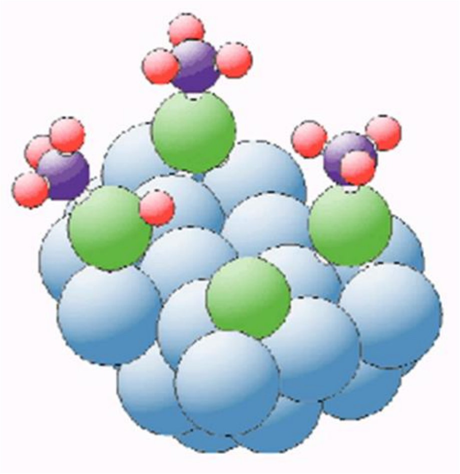
What Is a PLOT Column?

- Porous layer (surface) on the inner wall of the capillary
- Porosity achieved by the deposition of porous particles on the wall from a suspension
- Porous layer serves as stationary phase
- Separation mechanism (gas-solid chromatography) differences in analyte distribution between carrier gas and the surface of the adsorbent (stationary phase)
- Separation mechanism for gas-liquid chromatography differences in analyte solubility in liquid phase (stationary phase)
- Benefit is higher selectivity (α) and retention (k) of highly volatile solutes





Selectivity Interactions in PLOT Phases

Shape/size ⟷ **Surface**

Zeolites

Al_2O_3

Porous polymers

Bonded carbon
Molecular sieves

Bonded silica

Porous Layer Open Tubular (PLOT) Columns

Advantages

- Retention for high vapor pressure solutes
  - No cryogenics needed
  - Useful for multicolumn and valve switching, heart cutting techniques.
- Variety adsorbents
  - Porous polymers, alumina, molecular sieve, and so on
  - Selectivity for isomeric compounds
  - Gases and solvents separations
- Efficiency capillary PLOT
  - Preferred over packed
  - Packed benefits in specific applications

Agilent PLOT Columns Portfolio

Porous Polymers

- HP-PLOT Q, U
- PoraBOND Q, U
- PoraPLOT Q, U, S
- GS-Q
- PoraPLOT Q-HT

Zeolites

- HP-Molesieve
- CP- Molsieve 5A

Oxygenates

- Lowox
- GS-OxyPLOT

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

Silica Porous

- GS-GasPro
- SilicaPLOT

Graphitized Carbon

- CarboPLOT P7
- CarboBOND
- GS-CarbonPLOT

Compounds and Columns

- Permanent gases
  - Noble gases, O_2, N_2, H_2, CO, CO_2, CH_4
- Light hydrocarbons
  - C1 – C8, saturated, unsaturated
  - Aromatics, natural gas, C2, C3, C4 streams
- Volatile sulfur compounds
  - H2S, COS, mercaptans
  - Sulfides, disulfides
- Oxygenates
  - Alcohols, ketones, ethers
- Solvents
  - Oxygenates, aromatics, alkanes
  - Chlorinated hydrocarbons
- Chlorinated and fluorinated hydrocarbons

Molsieve **Select Perm. Gases**

Alumina **Silica**

Carbon **Porous polymers**

Select Low Sulfur **Silica**

Porous polymers

Lowox **OxyPLOT**

Porous polymers

Silica **Porous polymers**

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Porous Polymer PLOT Columns

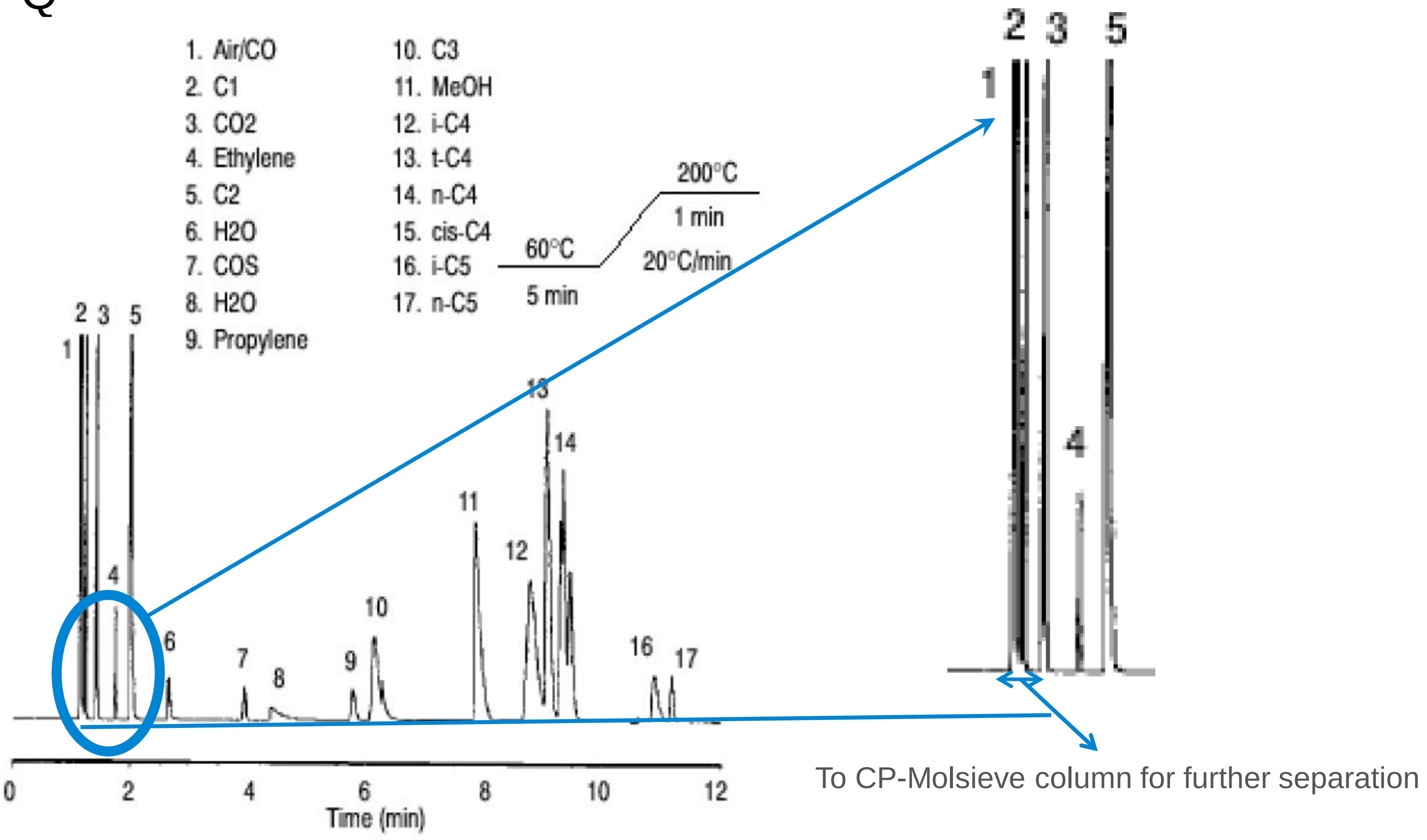
- Analyses of polar and nonpolar volatile compounds
  - Oxygenates, gases, halogenated compounds, hydrocarbons C1 – C6, ketones, solvents
- Most versatile adsorbent materials
- Suitable for aqueous injections
- Elution of water as a sharp peak + quantification of water
- Recommended for column switching systems
- Divinyl benzene copolymer = nonpolar Q type
- Styrene-glycol methacrylate copolymer = polar U type

Porous Polymer PLOT Columns

- HP-PLOT Q, GS-Q and PoraPLOT Q
  - Separation ethane/ethylene, propane/propylene
  - % levels, not ppm impurities in C2, C3 matrix
- H_2S and COS
  - Refinery gas analysis
  - 100 ppm – %, not low ppm
- Precolumn with CP-Molsieve columns for O_2, N_2, CH_4, CO
- Poor C4 isomer separation
  - Alumina preferred
- Not sensitive to moisture
- Good choice for solvents and CFCs

Refinery Fuel Gas and Porous Polymer Separation

HP- PLOT Q



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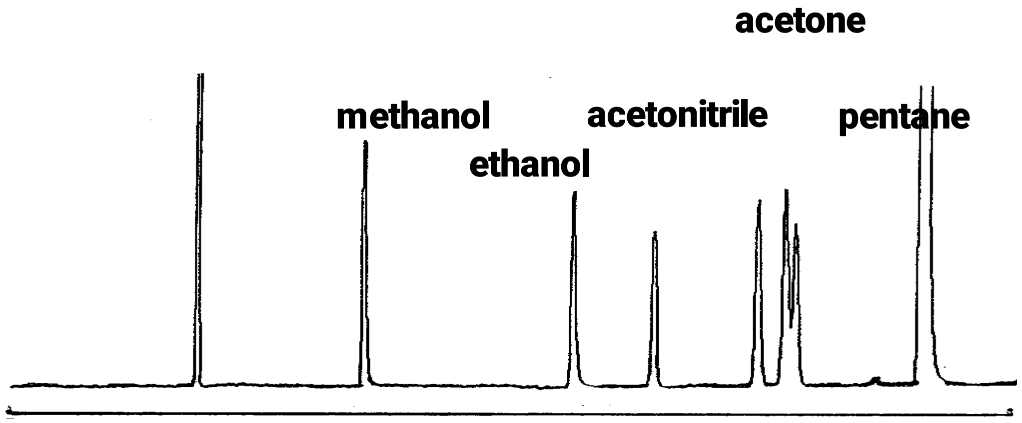
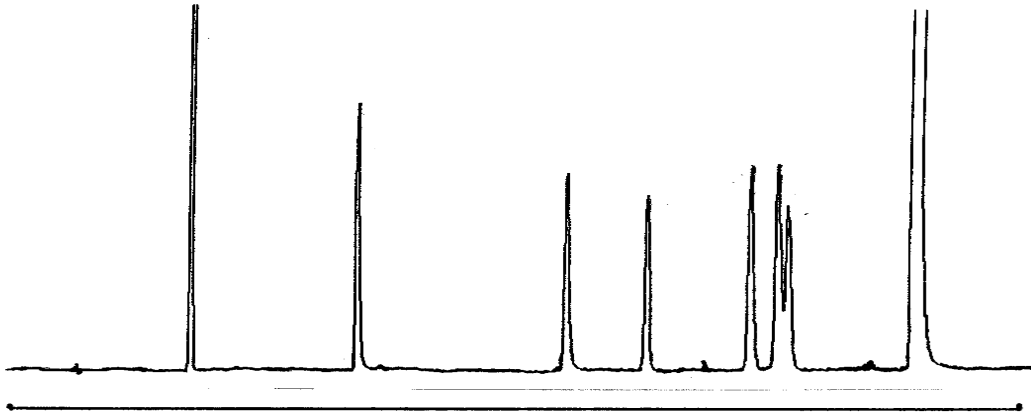
Porous Polymer PLOT, Aqueous Injections

Before



After

5 x 5 µL water, **splitless,** at 80 °C



Retention times are the same for all compounds

Samples containing water can be analyzed

Isothermal and short cycle time

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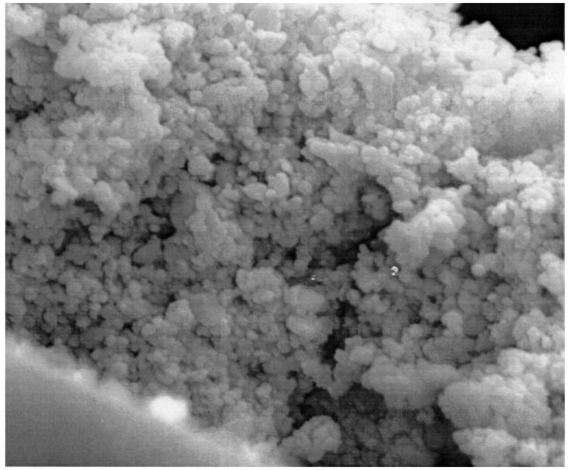
Agilent “BOND” Technology

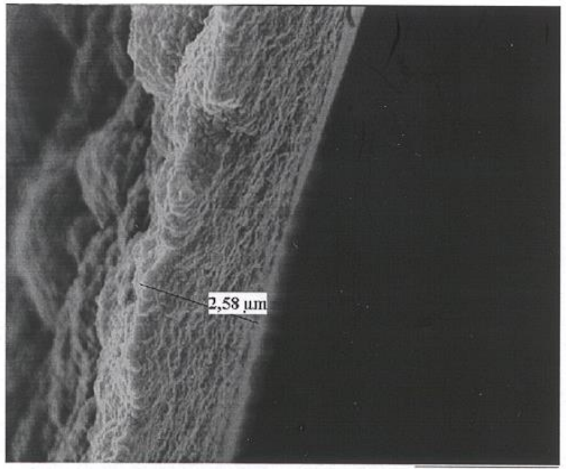
Particle PLOT Q



Particle size: 0.1 - 2 µm

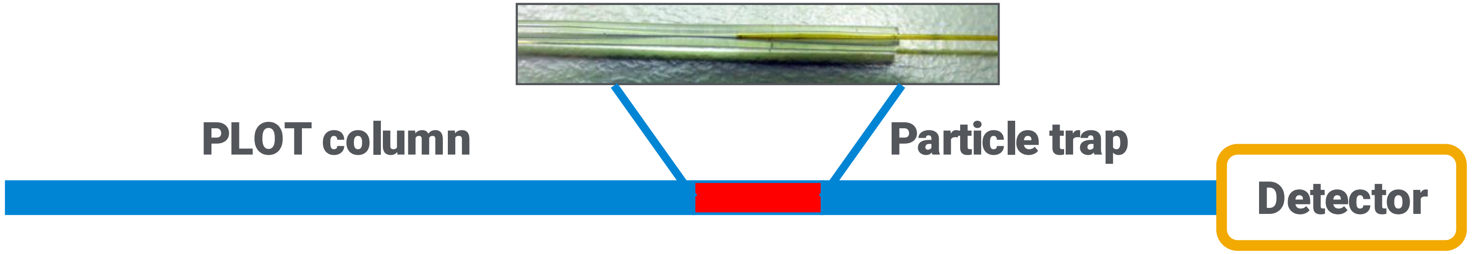
Number: >10^{12}

PoraBOND Q



Bonded polymer layer

No particle traps

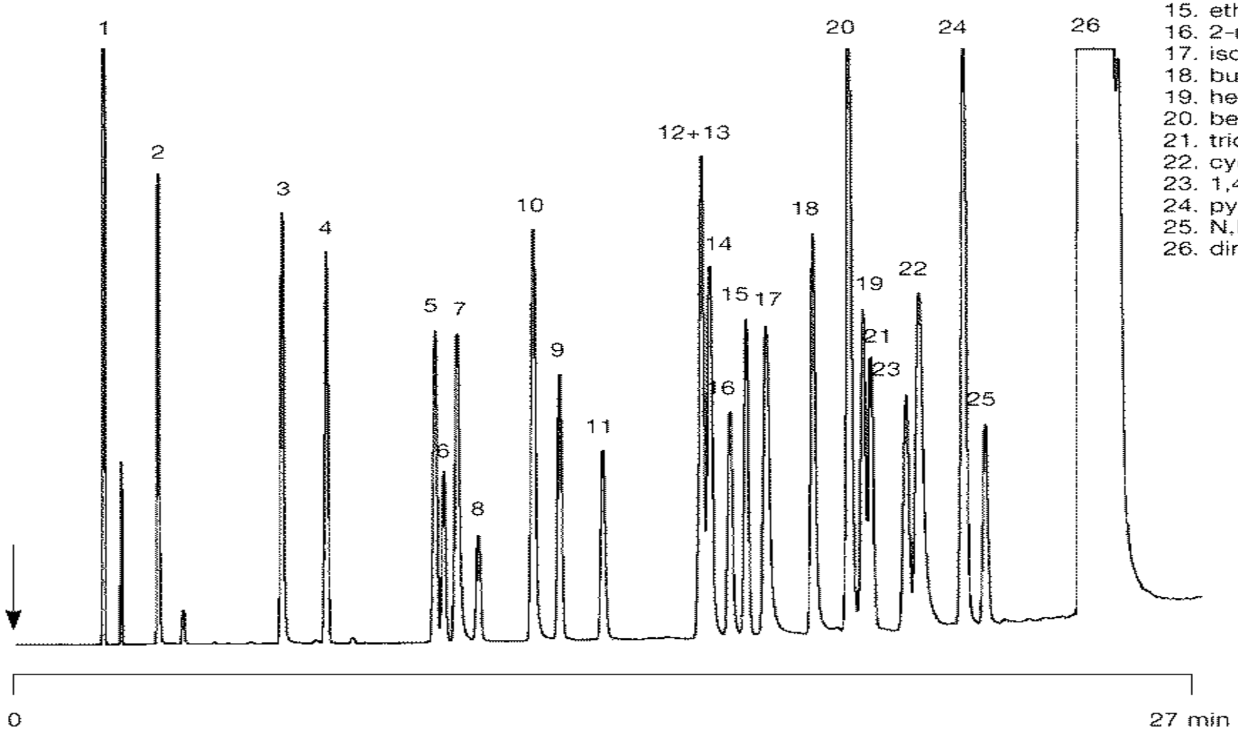


Solvent Analysis on PoraBOND Q

Column	:	CP-PoraBOND Q fused silica PLOT 25 m x 0.53 mm, df = 10 µm, Cat. no. 7354
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



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Alumina Adsorbent and PLOT Columns

Best selectivity for hydrocarbon separations

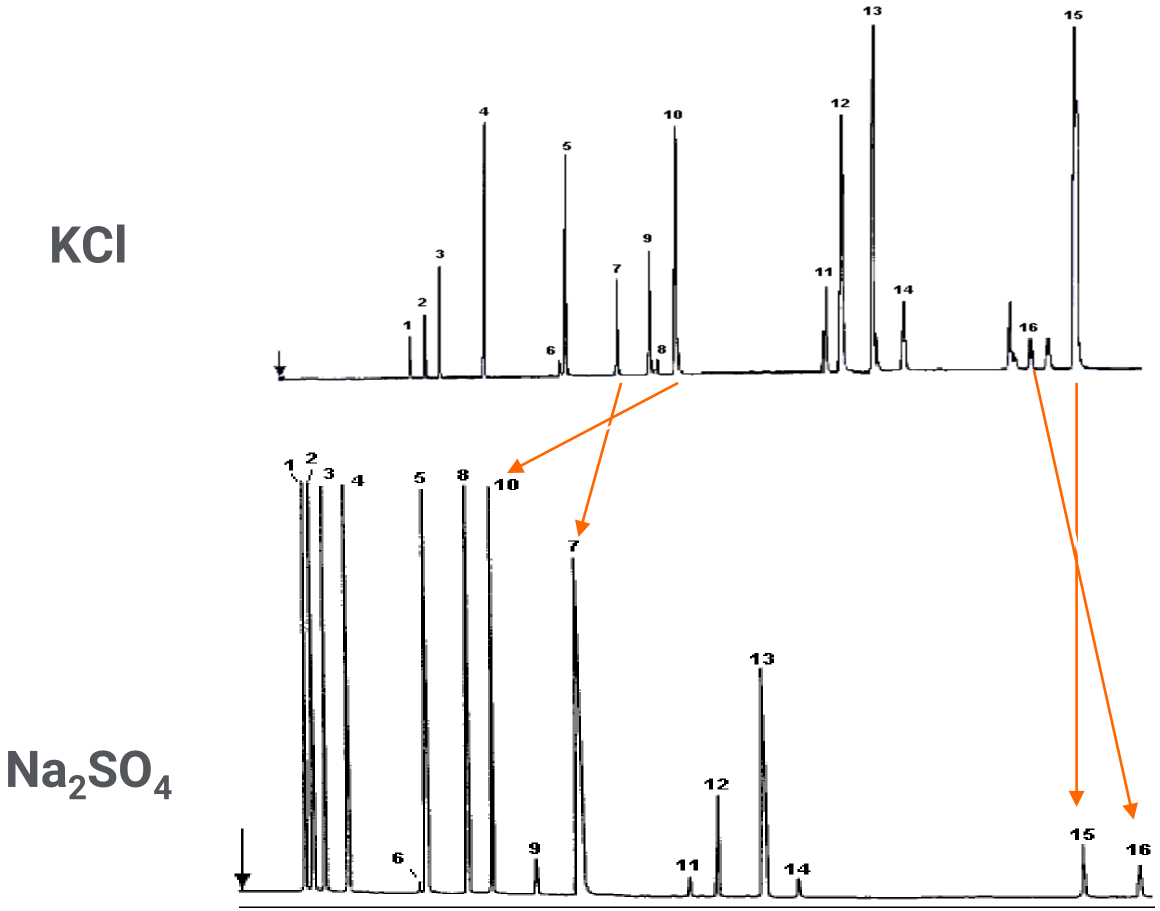
- General C1 – C6 (C9) hydrocarbons
- Natural gas
- Ethylene streams, impurities
- Impurities in propylene
- Butylene streams, impurities and complex C4 composition
- Environmental hydrocarbons distributions

Alumina Adsorbent and Columns

Separation depends on:

- **Degree of hydrocarbon saturation**
  - Elution order: alkane, alkene, alkyne, (dialkenes)
- **Types of deactivation**
  - KCl, Na_2SO_4 and proprietary
- **Operating conditions**
  - Column flow and oven temperature
- **Presence of water**
  - Al_2O_3 columns are sensitive to moisture in carrier gas: Gas Clean filters

Selectivity Difference KCl and Na_2SO_4

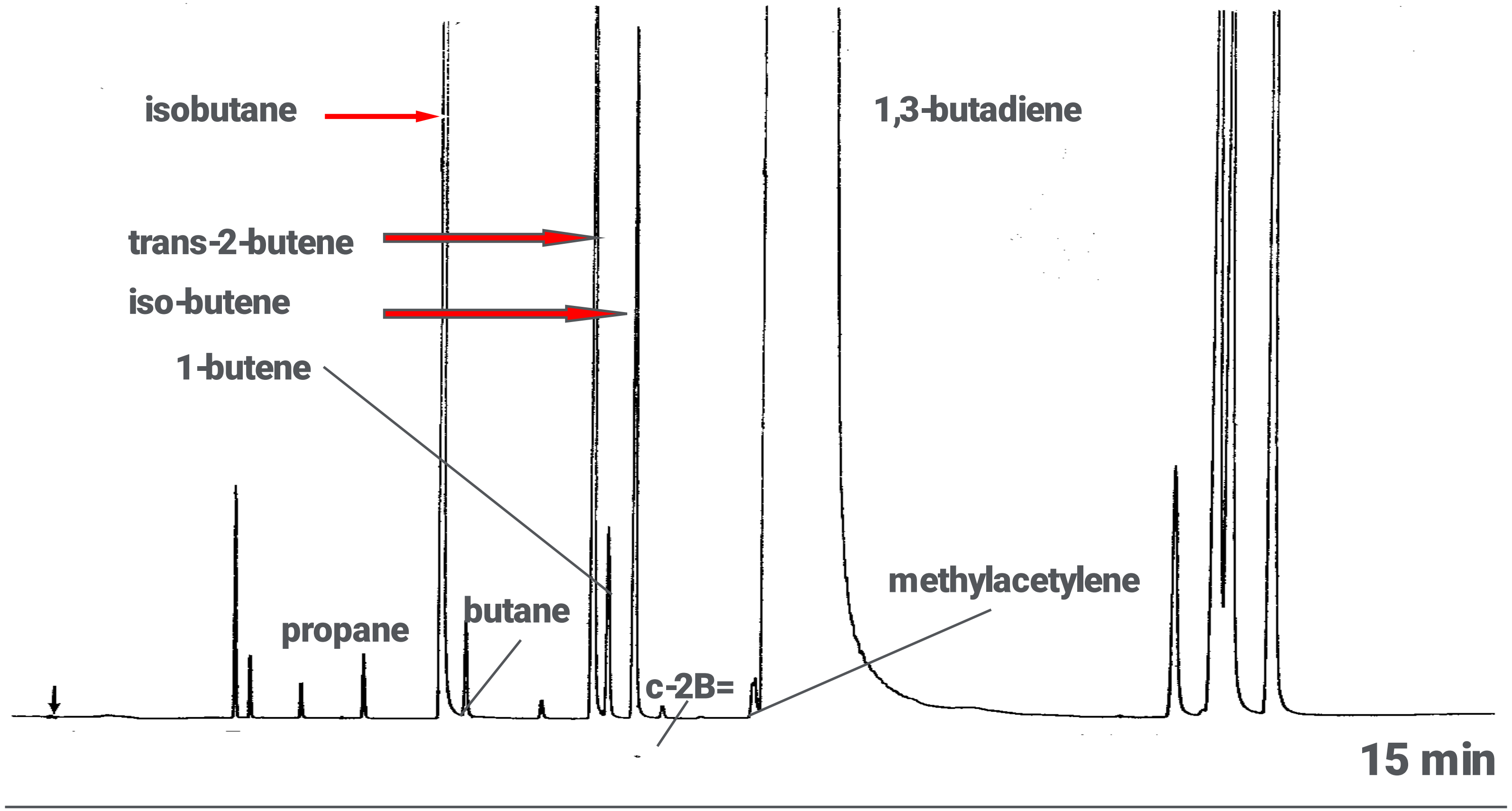


1. Methane
2. Ethane
3. Ethene
4. Propane
5. Propene
6. Cyclopropane
7. Ethyne
8. Iso-butane
9. Propadiene
10. n-Butane
11. t-2-Butene
12. 1-Butene
13. Iso-butene
14. c-2-Butene
15. 1,3-Butadiene
16. Propyne

Impurities in 1,3 Butadiene

50 m x 0.32 mm Al2O3/KCl, 5 µm

100 °C – 200 °C, 6 °C/min



Select Alumina Column

MAPD

Methyl Acetylene PropaDiene

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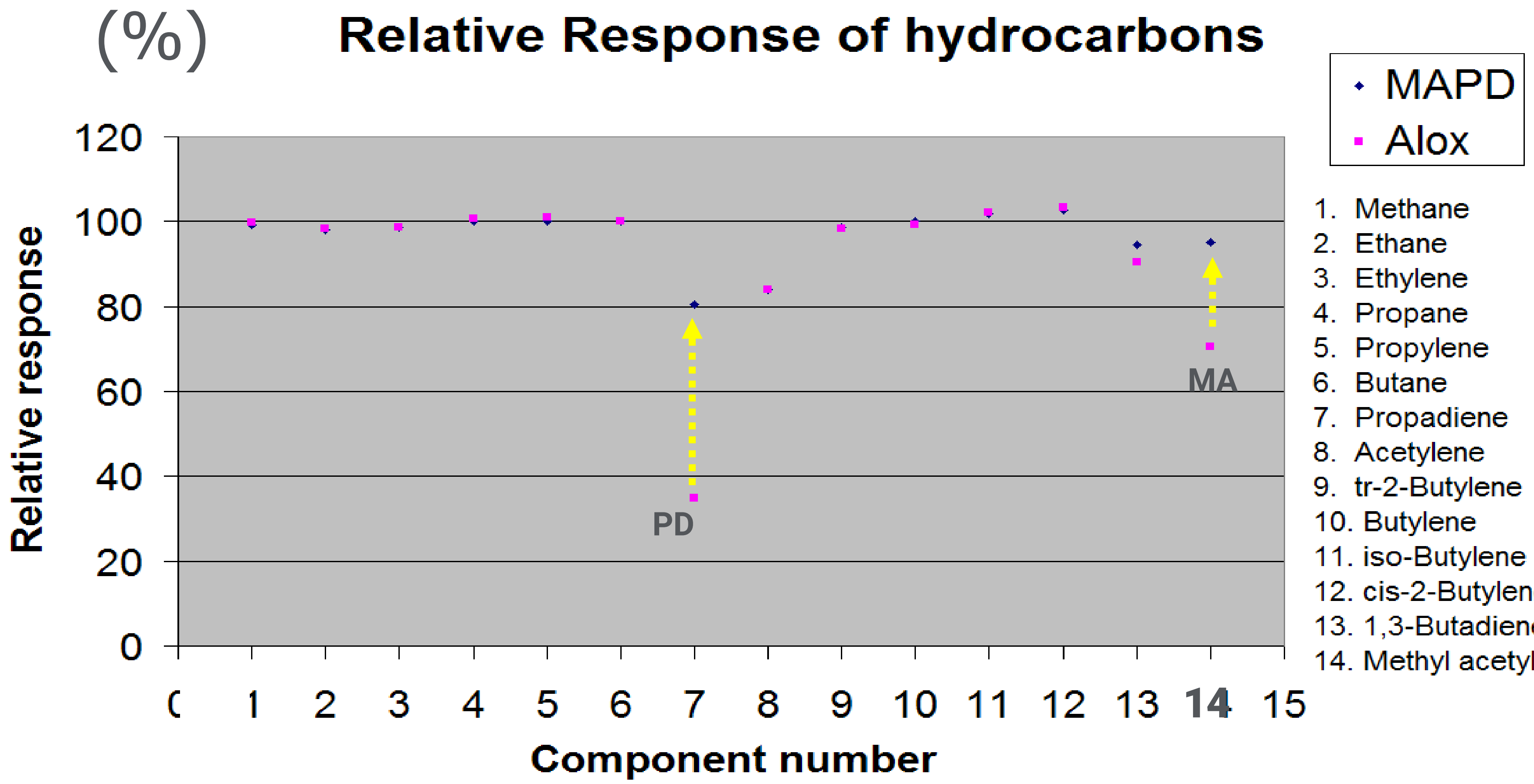
Response of Hydrocarbons

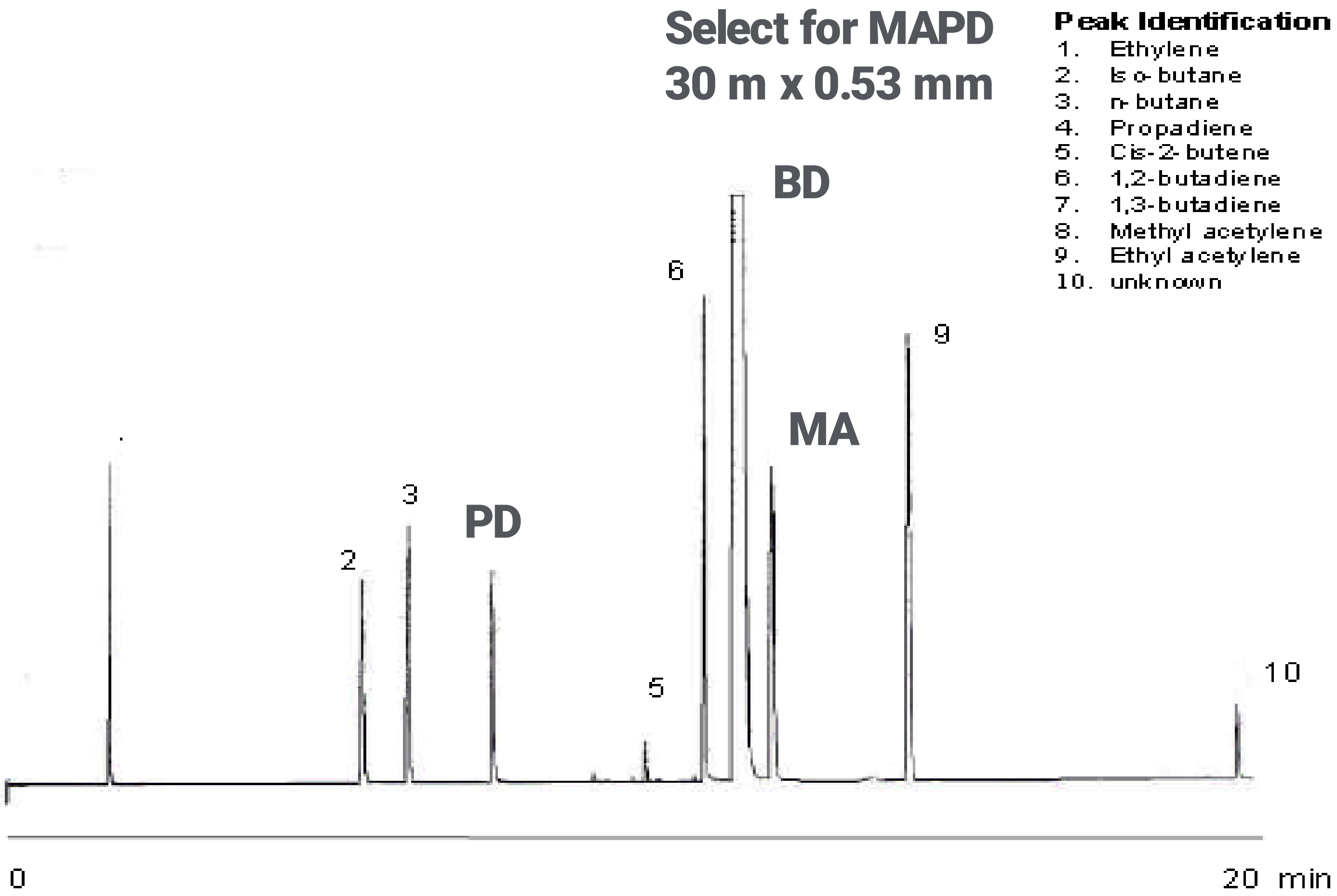
Standard Al2O3

Select Al2O3 MAPD



1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Propylene
6. Butane
7. Propadiene
8. Acetylene
9. tr-2-Butylene
10. Butylene
11. iso-Butylene
12. cis-2-Butylene
13. 1,3-Butadiene
14. Methyl acetylene

Improved Response on Select for MAPD

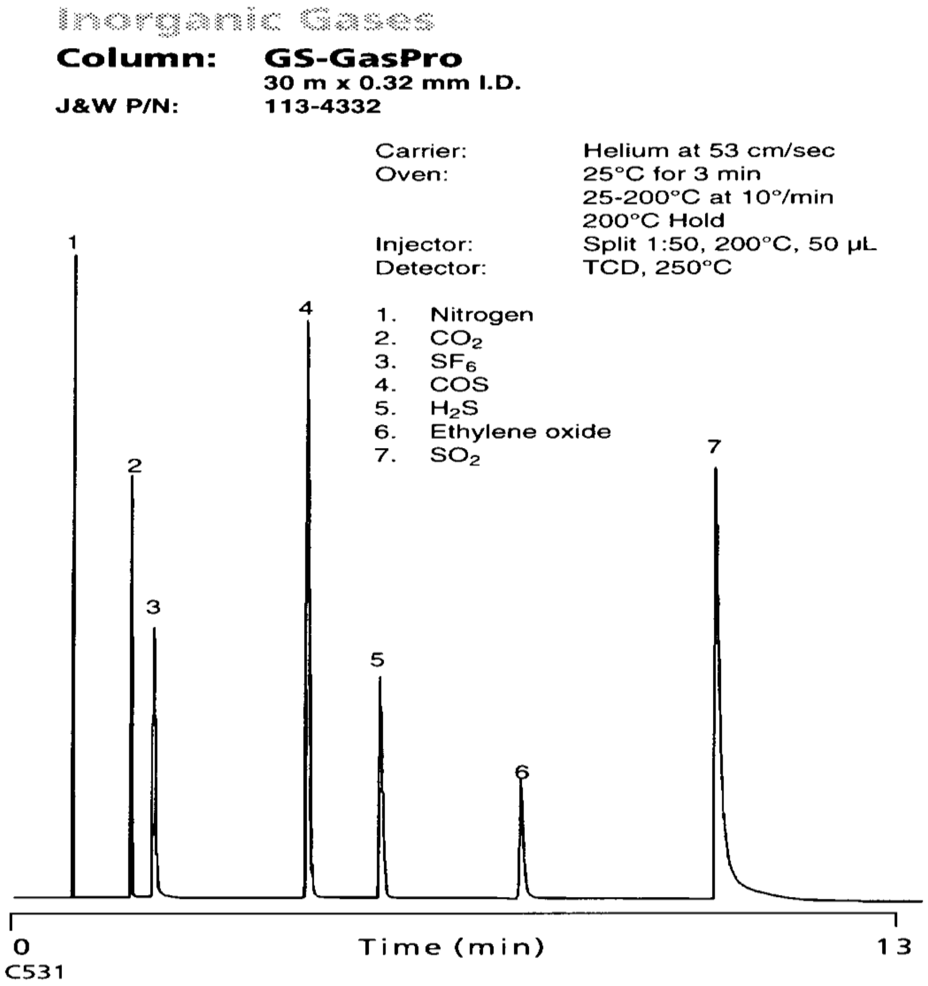


Courtesy: J. Luong, Dow Chemical Canada

Silica

- Light hydrocarbon separation, C1 – C4
- Extended hydrocarbon range compared to other PLOT substrates (+C10)
- Inert enough for light sulfurs, H_2S, COS, mercaptans
- CFCs
- GS-GasPro
- CP-SilicaPLOT
- Not sensitive to moisture in carrier gas
- MSD compatible

GS-GasPro: Inorganic Gases

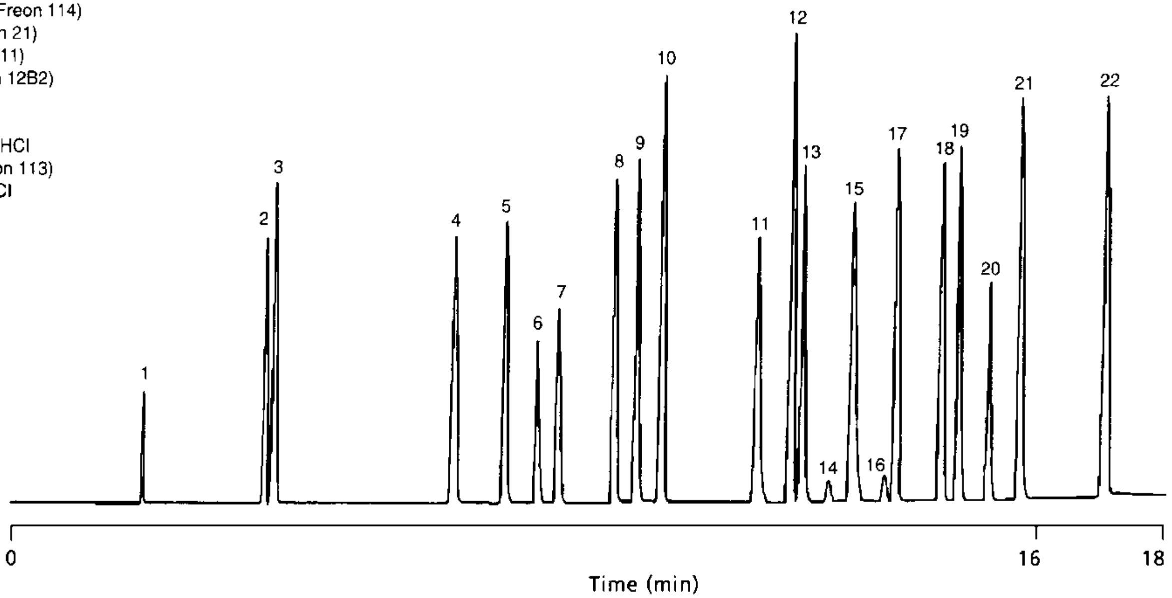


GS-GasPro: Halocarbons

Halocarbons

Column: **GS-GasPro**
30 m x 0.32 mm I.D.
J&W P/N: **113-4332**
Carrier: Helium at 30 cm/sec
Oven: 130°C for 4 min
130-225°C at 10°/min
225°C Hold
Injector: Split 1:67, 1 µL, 250°C
Detector: FID, 250°C

1. CH_4
2. $CHClF_2$ (Freon 22)
3. CCl_2F_2 (Freon 12)
4. $ClCF_2CF_2Cl$ (Freon 114)
5. $CHCl_2F$ (Freon 21)
6. CCl_3F (Freon 11)
7. CF_2Br_2 (Freon 12B2)
8. CH_3I
9. CH_2Cl_2
10. *trans*-ClCH=CHCl
11. CF_3CCl_3 (Freon 113)
12. *cis*-ClCH=CHCl
13. $CHCl_3$
14. ? from CCl_4
15. CCl_4
16. ? from CCl_4
17. CH_3CH_2I
18. CH_2Br_2
19. $CHCl_2Br$
20. C_4F_9I
21. $CHClBr_2$
22. $CH_3CH_2CH_2I$



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Molecular Sieves

- Noble gases, Kr, He, Ar, Xe
- N2, O2, $H_{2,}$ $CH_{4,}$ CO (not CO_2)

- CP-Molsieve 5 A
- HP-Molesieve

- Very sensitive to moisture/CO_2 in carrier gas/sample
  – Conditioning needed
  – Gas Clean moisture filters in carrier gas essential

PLOT Columns for Oxygenate Analysis

- Light oxygenates in hydrocarbon streams (ppm)
- C1 – C5 alcohols, ethers, ketones
- One column solution for ethylene, propylene, butylene feeds

- CP-Lowox
- GS-OxyPLOT

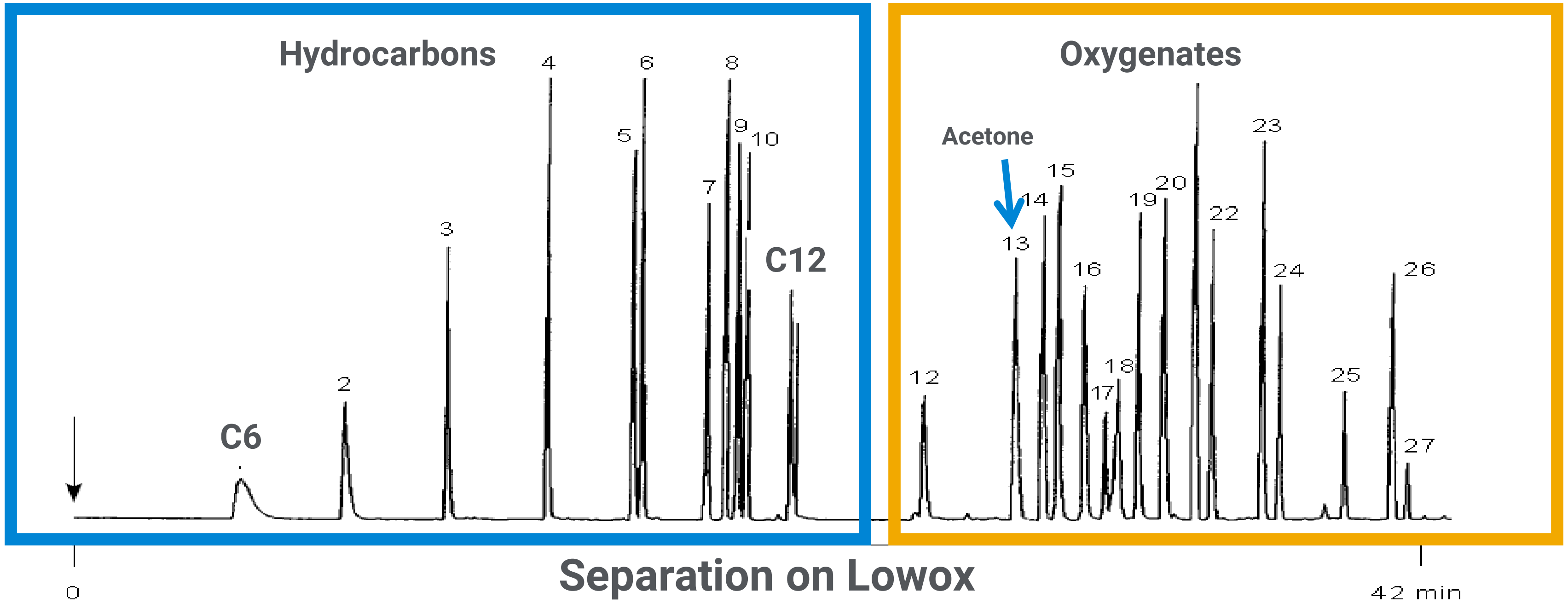
- Highly sensitive to moisture in carrier gas
  - Conditioning needed
  - Gas Clean moisture filters essential

Oxygenates in Hydrocarbons

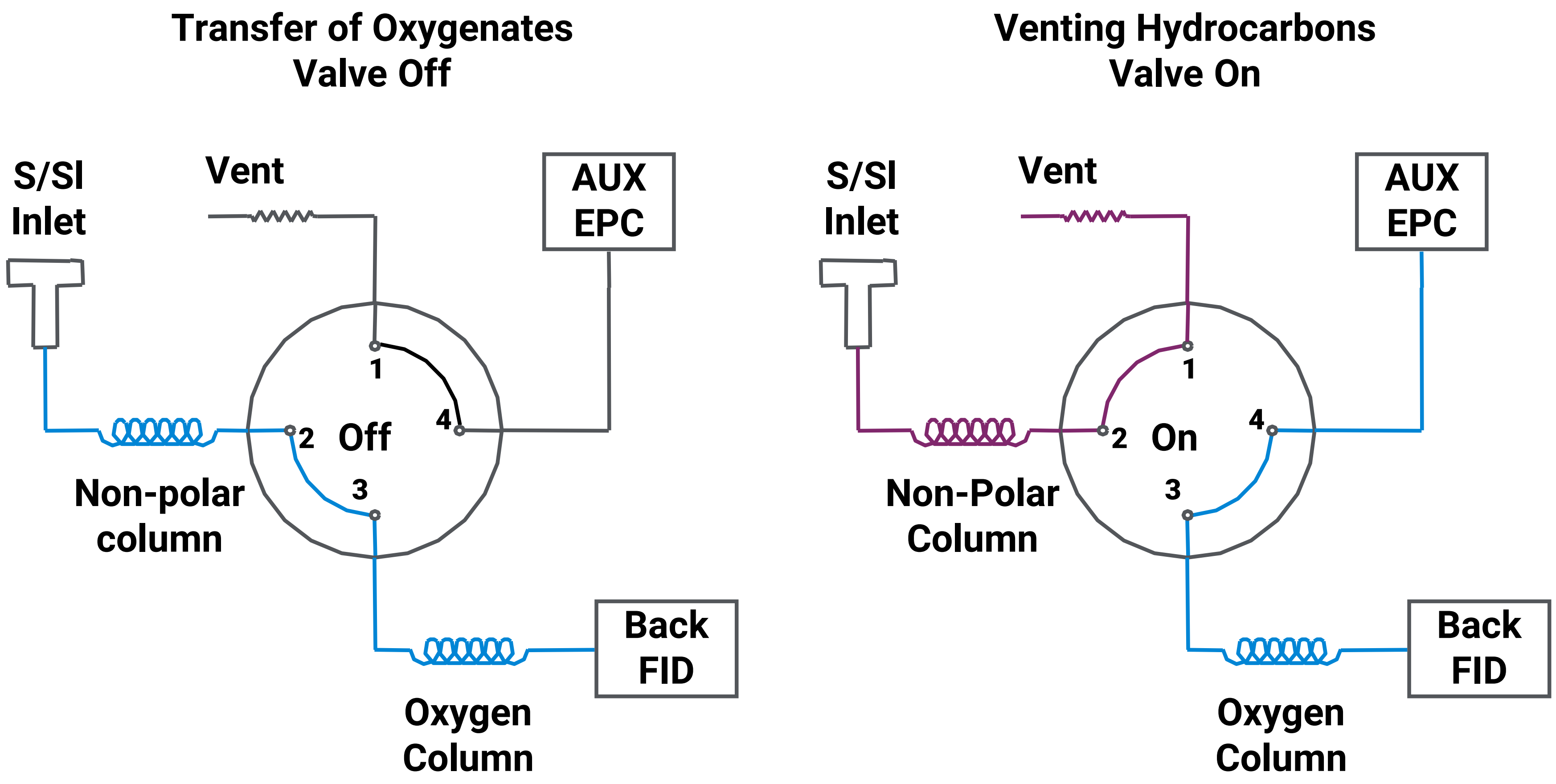
- Oxygenates blended in gasoline
  - Additives to boost octane content, prevent engine "knocking"
  - MTBE, ETBE, ethanol
  - % level oxygenates
  - GC analyses on WAX or TCEP polar liquid phase columns
- Oxygenate in intermediates (monomers, naphthas)
- Lower catalyst effectiveness, lower yield
  - Higher catalyst costs
  - More refinery downtime
  - ppm level oxygenates
  - GC analyses on Lowox, OxyPLOT columns, Agilent exclusives

Analyzing Oxygenates in Hydrocarbon Matrix

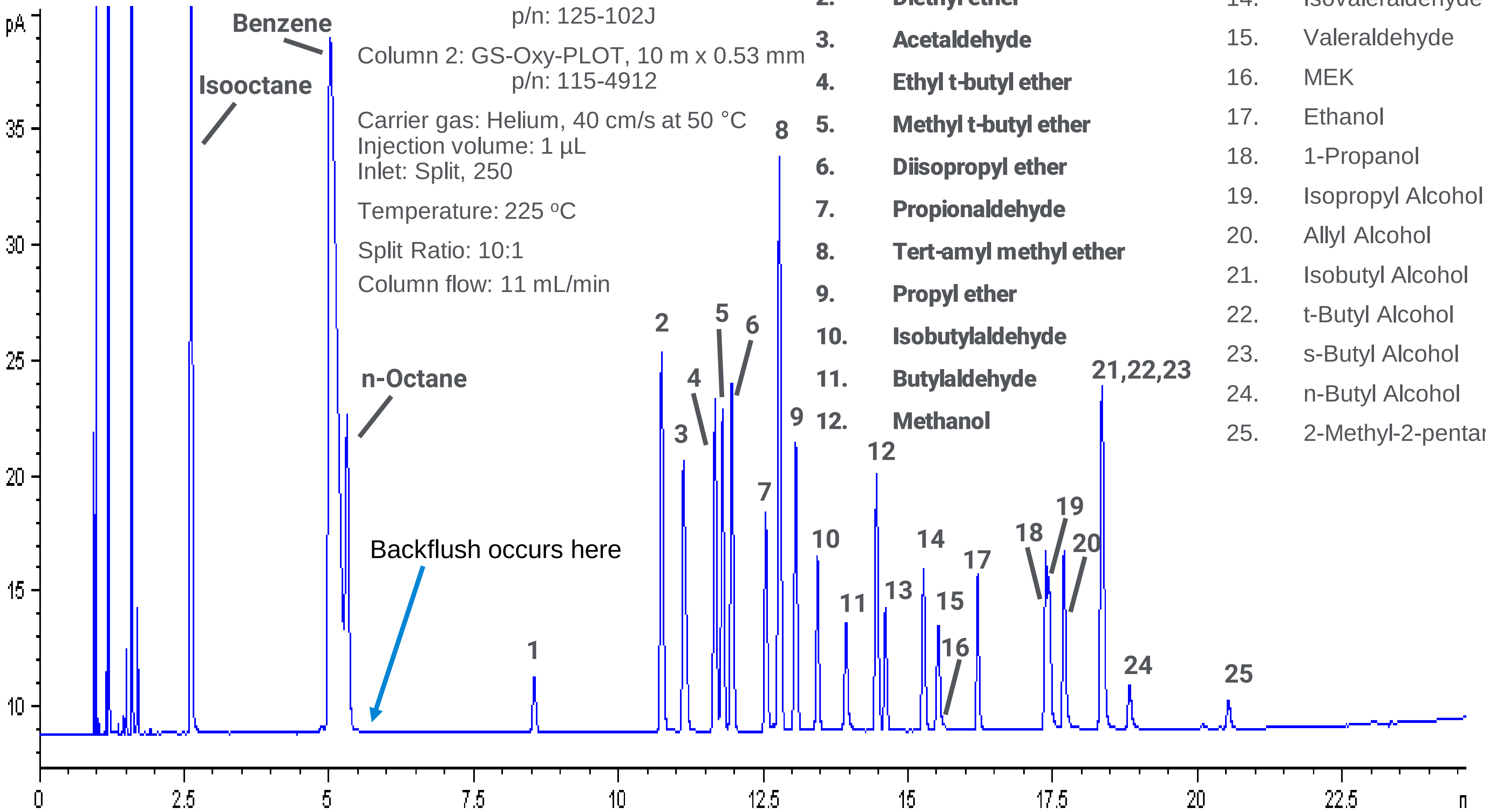
- Low ppm concentration level oxygenates
- FID detection (MS rarely)
- High selectivity columns hydrocarbons/oxygenates



Rotary Valve Configuration for ASTM Trace Oxygenate Analysis Methods



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 µm
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 at 50 °C
Injection volume: 1 µL
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

GS-CarbonPLOT

Monolithic carbon molecular sieve

Phase formed *in situ*

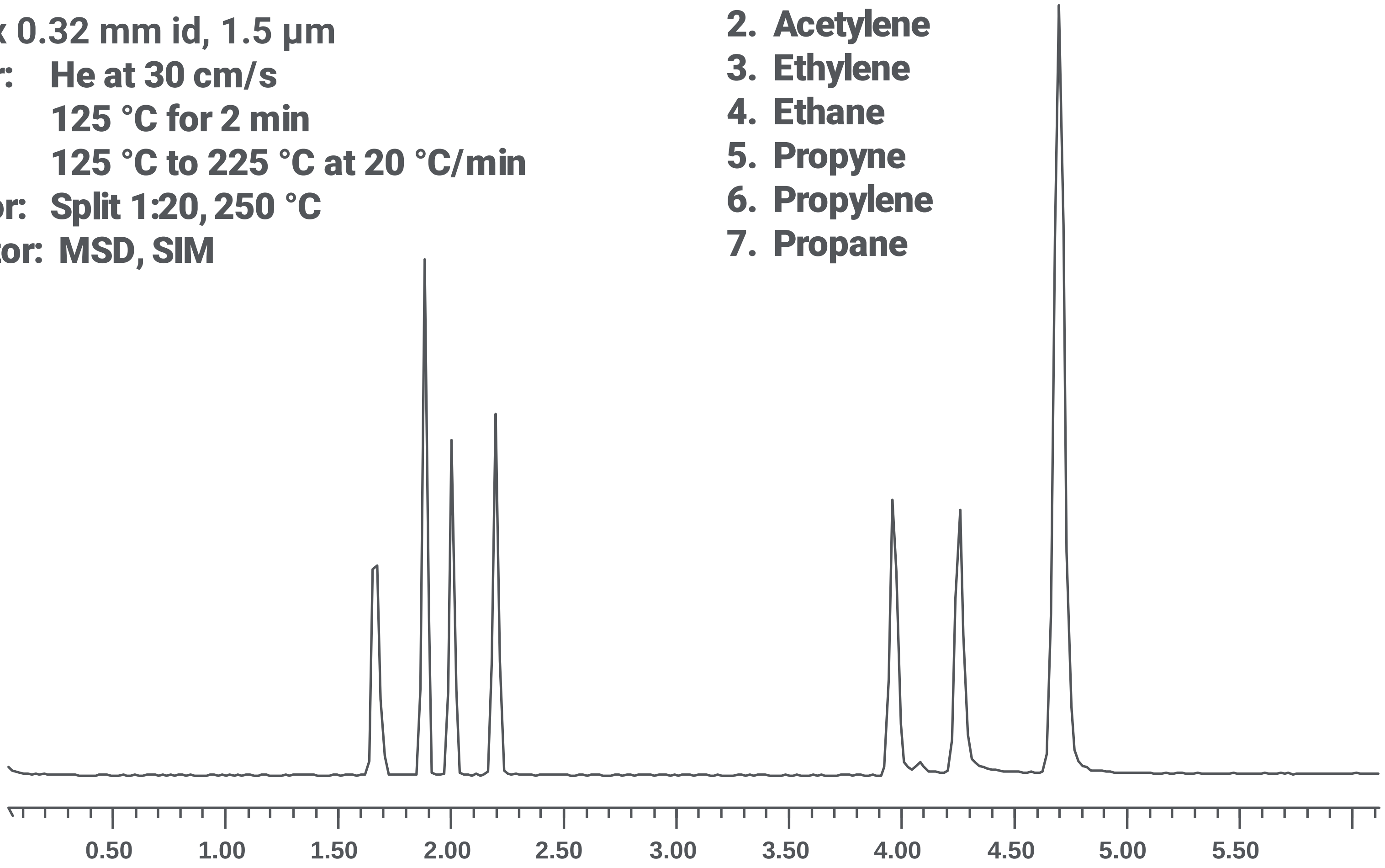
Extended temperature limit of 360 ºC

Unique selectivity

C1 to C3 Hydrocarbon Split Injector

GS-CarbonPLOT
30 m x 0.32 mm id, 1.5 µm
Carrier: He at 30 cm/s
Oven: 125 °C for 2 min
125 °C to 225 °C at 20 °C/min
Injector: Split 1:20, 250 °C
Detector: MSD, SIM

1. Methane
2. Acetylene
3. Ethylene
4. Ethane
5. Propyne
6. Propylene
7. Propane

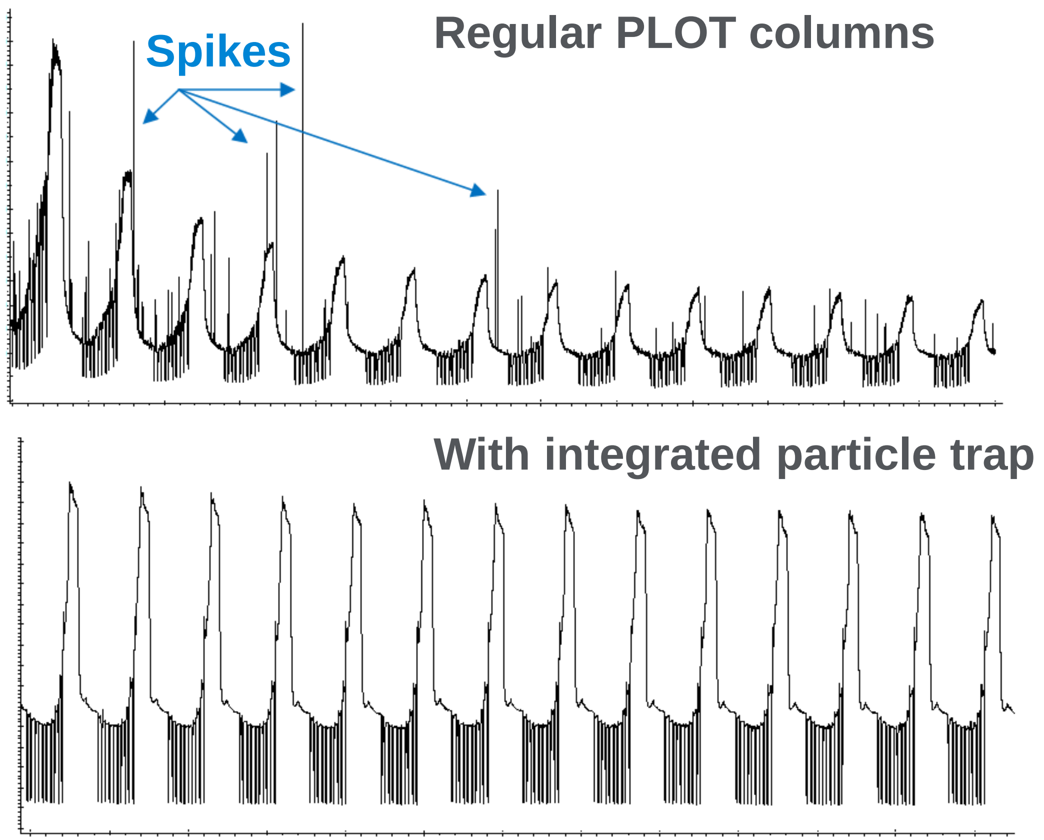


PLOT Column with Integrated Particle Trap

- **Zero particle shedding when using steep temperature gradients and pressure ranges**
- **Integrated to column – no unions and fittings**
- **Compatible with multicolumn valve switching systems and systems with CFT technology**
  - **Particle traps integrated on both ends – supports backflush apps**
- **Similar selectivity, plates, and peak shape performance to existing Agilent porous polymer PLOT columns**
  - **Minimum method redevelopment required**
  - **Available in a wide variety of our most popular porous polymer PLOT columns configurations**

Proof of Agilent PLOT PT Column Performance

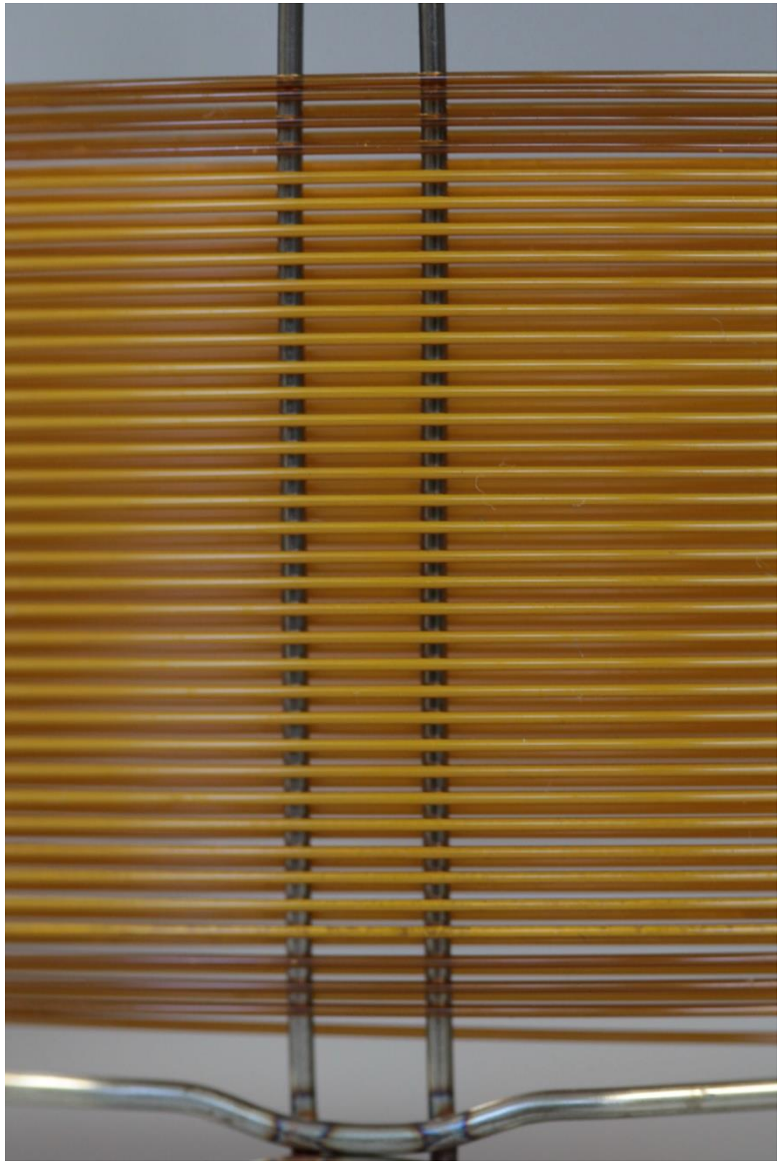
- 150 °C to 250 °C at 20 °C/min
- Pressure 3x higher than optimal pressure
- 15 cycles
- Carrier gas off and on 10 times



PLOT Column with Integrated Particle Trap

Integrated particle trap at front and back of the column

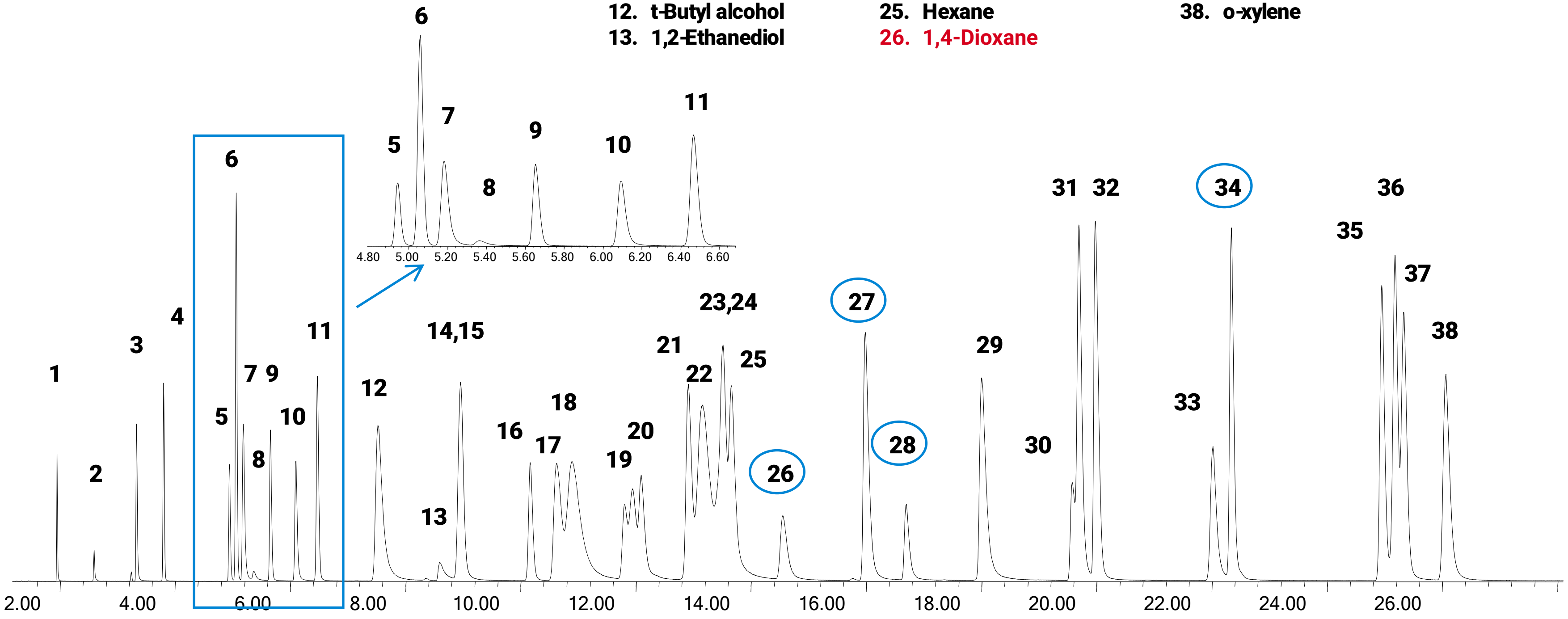
PLOT column part



Example of Chromatographic performance

Column: PoraBond Q PT, 30 m × 0.25 mm, 3 µm
Carrier : Helium, 43 cm/s at 90 °C
Oven: : 90 °C – 140 °C at 10 °C/min
140 °C for 6 min
140 °C – 200 °C at 5 °C/min
200 °C for 10 min
Injection: Split, 250 °C, split ratio 1:160
Detector: MSD, 280 °C
Transfer line, full scan at 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



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

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

Gas Clean Offer More Reliable Data

Bottom Line:

By removing impurities from the carrier gas stream, Gas Clean filters improve separation and repeatability while using PLOT columns.

We suggest:

For a 7890 GC:

CP17988 Gas Clean carrier gas kit (1/8 in fittings)

For a 6890 GC:

CP17974 Gas Clean carrier gas kit (1/8 in fittings)

Agilent 7890 Gas Clean carrier gas kit installed on a 7890B GC

Summary

- Agilent supplies the largest selection of PLOT columns in the market for all gases and volatiles applications. Agilent has dedicated columns for challenging analyses in the petrochemical industry.
- Fully QC tested to assure column-to-column reproducibility with 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.
- The PLOT-PT columns with integrated particle traps to assure “spike free” detection, mass spectrometer compatibility, and improved system performance with complex valve applications.

Contact Agilent Chemistries and Supplies Technical Support

1-800-227-9770 option 3, option 3:

Option 1 for GC and GC/MS columns and supplies

Option 2 for LC and LC/MS columns and supplies

Option 3 for sample preparation, filtration and QuEChERS

Option 4 for spectroscopy supplies

Option 5 for chemical standards

Available in the USA and Canada 8-5 all time zones

gc-column-support@agilent.com

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