Separation Superhero Seminar Tour

Battle the villains of bad chromatography

Solutions for light hydrocarbons and gasses: PLOT columns
Table of Boiling Point Fractions

<table>
<thead>
<tr>
<th>Carbon No.</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>C₄</th>
<th>C₅</th>
<th>C₆</th>
<th>C₇</th>
<th>C₈</th>
<th>C₉</th>
<th>C₁₀</th>
<th>C₁₁</th>
<th>C₁₂</th>
<th>C₁₃</th>
<th>C₁₄</th>
<th>C₁₅</th>
<th>C₁₆</th>
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<tbody>
<tr>
<td>Bpt of n-Paraffin at 760 mm Hg</td>
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<td>Centigrade</td>
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<td>-89</td>
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<td>Fahrenheit</td>
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<td>303</td>
<td>345</td>
<td>384</td>
<td>421</td>
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<td>488</td>
<td>519</td>
<td>548</td>
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</tbody>
</table>

Refinery off gas
Naphtha solvents
Cracking naphtha
Reformate
Gasoline
Kerosene, Diesel
Jet fuel
Gas oil
Lube oil
Pitch asphalt
Wax
Residues

to C₁₈

to C₁₇

to >C₂₀

C₂₀

C₁₇

C₄₄⁺
Wall Coated Open Tubular (WCOT) Columns

Stationary phase

$K_c \Rightarrow \text{Large}$

$K_c \Rightarrow \text{Small}$
WCOT Ethylene Analysis

**Column:** DB-Petro 100
- 100 m x 0.25 mm I.D., 0.5 μm

**Carrier:** Helium at 28.5 cm/s

**Oven:**
- -40°C for 20 min
- -40°C - 120°C at 5°C/min

**Injector:** Split 1:16, 100 μL, 200°C

**Detector:** FID, 250°C
PLOT Ethylene Analysis

**Ethylene**

**Column:** GS-Alumina  
50 m x 0.53 mm i.D.

**J&W Part:** 115-3552  
**Carrier:** Helium at 11 mL/min, measured at 35°C  
**Oven:**  
30°C for 2 min  
35-190°C at 6°C/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. Propane  
18. 1,3-Butadiene  
19. 1-Pentene  
20. n-Hexane

C585
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 ($\alpha$) and retention ($k$) of highly volatile solutes
Selectivity Interactions in PLOT Phases

- Zeolites
- Porous polymers
- Bonded carbon
- Molecular sieves
- Bonded silica
- Al$_2$O$_3$
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**
- Al₂O₃/KCl, HP-PLOT Al₂O₃/KCl
- Al₂O₃/Na₂SO₄, HP-PLOT Al₂O₃ S
- GS-Alumina

**Select MAPD**

**Silica Porous**
- GS-GasPro
- SilicaPLOT

**Graphitized Carbon**
- CarboPLOT P7
- CarboBOND
- GS-CarbonPLOT
Compounds and Columns

- **Permanent gases**
  - Noble gases, O₂, N₂, H₂, CO, CO₂, CH₄

- **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**
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
- H₂S and COS
  - Refinery gas analysis
  - 100 ppm – %, not low ppm
- Precolumn with CP-Molsieve columns for O₂, N₂, CH₄, 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

To CP-Molsieve column for further separation
Porous Polymer PLOT, Aqueous Injections

Before

methanol  ethanol  acetone  acetonitrile  pentane

Retention times are the same for all compounds

After

5 x 5 µL water, splitless, at 80 °C

Samples containing water can be analyzed

Isothermal and short cycle time
Agilent “BOND” Technology

Particle PLOT Q

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

PoraBOND Q

- Bonded polymer layer
- No particle traps

Diagram showing PLOT column, Particle trap, and Detector.
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: 190 °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 sulfoxide
9. diethyl ether
10. 1-propanol
11. pentane
12. 2-butane
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
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

Separation Superhero Seminar Tour
April 17, 2019
Alumina Adsorbent and Columns

Separation depends on:

• **Degree of hydrocarbon saturation**
  – Elution order: alkane, alkene, alkyne, (dialkenes)

• **Types of deactivation**
  – KCl, Na₂SO₄ and proprietary

• **Operating conditions**
  – Column flow and oven temperature

• **Presence of water**
  – Al₂O₃ columns are sensitive to moisture in carrier gas: Gas Clean filters
Selectivity Difference KCl and Na$_2$SO$_4$

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

- isobutane
- trans-2-butene
- iso-butenes
- 1-butene
- propane
- butane
- c2B=
- methylacetylene
- 1,3-butadiene

15 min
Select Alumina Column

MAPD

Methyl Acetylene  PropaDiene
Response of Hydrocarbons

Relative 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

Select for MAPD
30 m x 0.53 mm

Peak Identification
1. Ethylene
2. Isobutane
3. n-Butane
4. Propadiene
5. C5:2 butene
6. 1,2-butadiene
7. 1,3-butadiene
8. Methyl acetylene
9. Ethyl acetylene
10. Unknown

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, H₂S, COS, mercaptans
- CFCs
- GS-GasPro
- CP-SilicaPLOT
- Not sensitive to moisture in carrier gas
- MSD compatible
Inorganic Gases

Column: GS-GasPro
30 m x 0.32 mm I.D.
J&W P/N: 113-4332

Carrier: Helium at 53 cm/sec
Oven: 25°C for 3 min
25-200°C at 10°C/min
200°C Hold
Injector: Split 1:50, 200°C, 50 μL
Detector: TCD, 250°C

1. Nitrogen
2. CO₂
3. SF₆
4. COS
5. H₂S
6. Ethylene oxide
7. SO₂

Time (min) 0 13
CS31

GS-GasPro: Inorganic Gases
GS-GasPro: Halocarbons

Column: GS-GasPro
J&W P/N: 113-4332
Carrier: Helium at 30 cm/sec
Flow: 130°C for 4 min
225°C Hold
Injector: Split 1:67, 1 μL, 250°C
Detector: FID, 250°C

1. CH₄
2. CH₂F₂ (Freon 22)
3. CCl₂F₂ (Freon 12)
4. C₂F₅Cl (Freon 114)
5. C₂Cl₃F (Freon 11)
6. C₃F₇ (Freon 11
7. CF₂Br₂ (Freon 12B2)
8. CH₂Cl₂
9. CH₃Cl
10. trans-CH₂=CHCl
11. C₁₂H₂₃ (Freon 113)
12. cis-CH₂=CHCl
13. CH₃Br
14. 1 from CCI₄
15. CCl₄
16. 7 from CCl₄
17. CH₂CH₂Cl
18. CH₂Br₂
19. CHCl₃Br
20. CH₂F₂
21. CH₂ClBr₂
22. CH₃CH₂CH₂Cl
Molecular Sieves

- Noble gases, Kr, He, Ar, Xe
- N2, O2, H2, CH4, CO (not CO2)

- CP-Molsieve 5 A
- HP-Molesieve

- Very sensitive to moisture/CO2 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

Separation on Lowox

<table>
<thead>
<tr>
<th>Hydrocarbons</th>
<th>Oxygenates</th>
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<tbody>
<tr>
<td>C6</td>
<td>Acetone</td>
</tr>
<tr>
<td>C12</td>
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</table>
Rotary Valve Configuration for ASTM Trace Oxygenate Analysis Methods

Transfer of Oxygenates Valve Off

Venting Hydrocarbons Valve On

S/Sl Inlet

Vent

AUX EPC

2

S/Sl Inlet

Vent

AUX EPC

4

Non-polar column

1

Oxygen Column

2

3

Off

On

Non-Polar Column

Oxygen Column

Back FID

Back FID
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

Backflush occurs here
GS-CarbonPLOT

Monolithic carbon molecular sieve

Phase formed\textit{ in situ}

Extended temperature limit of 360 °C

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
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 for 6 min
140 °C – 200 °C at 5 °C/min 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. Acetalddehyde
3. Ethanol
4. Acetonitrile
5. Acetone
6. Methylene Chloride
7. Isopropl 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)
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
lc-column-support@agilent.com
spp-support@agilent.com
spectro-supplies-support@agilent.com
chem-standards-support@agilent.com