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Separation of Volatile Organic Hydrocarbons with Agilent J&W PLOT GC Columns and Selectivity Tuning

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Abstract

This application note demonstrates the separation characteristics of a series of divinylbenzene-based porous layer open tubular columns. With the incorporation of functional groups, the porous polymer's selectivity and polarity used as a stationary phase can be adjusted to tailor for different applications. Selectivity tuning is illustrated as a viable strategy to alter the overall separation characteristic and offer separation that cannot be achieved with a single column. Improvements in manufacturing processes for porous polymers have led to columns with higher stability, robustness, inertness, and reduced spiking.

Introduction

Volatile organic compounds (VOCs) are often encountered in the manufacturing and processing of hydrocarbons. The separation of VOCs is critical in many industrial applications such as feedstock screening, product quality control, and environmental monitoring. Gas chromatography (GC) is a versatile analytical technique widely used to analyze volatile compounds. Based on the principle of separation, there are two main approaches: gas-liquid chromatography (GLC) and gas-solid chromatography (GSC).[1,2] When the stationary phase is a liquid deposited on an inert support or coated as a thin film onto a capillary column wall, it is referred to as GLC. The separation is mainly by the partition process; therefore, it is also called partition chromatography. In GSC, a solid adsorbent serves as the stationary phase. The primary separation mechanism is adsorption; thus it is referred to as adsorption chromatography. Although GLC is prominent in many GC applications, it is not a universal solution. There are growing interests in GSC from research to industrial applications, especially with the introduction of Porous Layer Open tubular (PLOT) columns. For PLOT columns, stable layers of adsorbents are coated on the inner wall of fused silica capillary tubing.[2,3] These highly retentive stationary phases enable effective separation of gaseous molecules and volatile liquids, such as fixed gases and light hydrocarbons, above ambient temperature. These solid phases can be an inorganic material such as alumina, zeolite, molecular sieve, or organic porous polymers.

Porous polymers have become popular because of the high retention and the selectivities these materials provide. The polymer materials are usually made of divinylbenzene (DVB) polymer or DVB-based copolymers. Different functional groups can be incorporated with this base material to adjust the column selectivity and optimize separation. Several types of porous polymers are commercially available under different names. The most widely known Q-type polymer consists of styrene-divinylbenzene and is considered nonpolar. DVB-vinyl pyridine copolymer is classified as S type. U type is most polar with DVB-ethylene glycol methacrylate copolymer.[4–6] In this study, a series of Agilent J&W PoraPLOT Q, S, and U GC columns were chosen to illustrate how the functional groups affect the separation and elution order of hydrocarbons.

Despite the many stationary phases that are available, a single column's selectivity may not be sufficient in specific applications with increasing sample complexity or the need to resolve isomers. Selectivity tuning, introduced by Grob and Sandra, is an efficient and cost-effective strategy to achieve unique selectivity.[7–9] Selectivity tuning can be performed by different means, e.g., series coupling columns of different selectivities, using mixed phases, using specially synthesized phases, or using temperature-dependent relative retention.[9–11] The concept of selectivity tuning through series column coupling was demonstrated with the J&W PoraPLOT GC columns.

The latest advancement in the column manufacturing process has developed more stable and robust PLOT phases, called PoraBOND.[12–16] For example, a PoraBOND Q column can be used up to a temperature of 300 °C, an increase of 50 °C over a PoraPLOT Q column. Particle shedding from the polymer is also reduced with the improved binding technology. Column performance, including selectivity and inertness, was compared between PoraBOND Q and PoraPLOT Q columns in this study.

Experimental

An Agilent 7890B GC/FID equipped with a split/splitless inlet, and an Agilent 7693 automatic liquid sampler with control software Agilent OpenLab (software version A.02.05.021) was used for GC/FID experiments. For the gas samples, 0.5 mL manual injections were conducted using a 1 mL Hamilton Gas Tight Syringe (Hamilton Company, Reno, NV, USA). For liquid samples, an Agilent 7693 autosampler with a 10 μL syringe was used for sample introduction with an injection volume of 1 μL. Two columns were coupled using an ultra-inert press-fit column connector (part number 5190-6979) to conduct a selectivity tuning study.

Carrier and utility gases such as helium, nitrogen, hydrogen, and air used were acquired from Linde (Edmonton, Canada). Gas standards for system performance studies were purchased from Air Liquide (Edmonton, Canada). Chemicals and reagents were purchased from Fisher Scientific (Edmonton, Canada).

Results and discussion

Agilent J&W PoraPLOT GC column selectivity comparison

PoraPLOT columns are a series of divinylbenzene (DVB) based porous polymer columns with unique retention characteristics for polar and apolar volatile compounds. With the incorporation of different functional groups, the stationary phase offers different polarities and selectivities to achieve the desired separation. PoraPLOT Q is the most nonpolar column with 100% polystyrene-divinylbenzene. PoraPLOT S has medium polarity with a divinylbenzene/vinyl pyridine copolymer. PoraPLOT U is the most polar among the three, with ethylene glycol dimethyl acrylate (EGDMA). Figure 1 compares the separation of saturated and unsaturated C_1 to C_3 hydrocarbons on these three columns. As shown in Figure 1A, on a PoraPLOT Q column, ethylene and acetylene coelute, while propylene and propane are baseline separated. The higher polarity of PoraPLOT S leads to increased retention of acetylene and the separation of acetylene from ethylene; however, acetylene partially coelutes with ethane as illustrated in Figure 1B. With a further increase in polarity, baseline separation is achieved for C_2s (ethane, ethylene, and acetylene) on a PoraPLOT U column; however, the coelution of propylene and propane occurs.

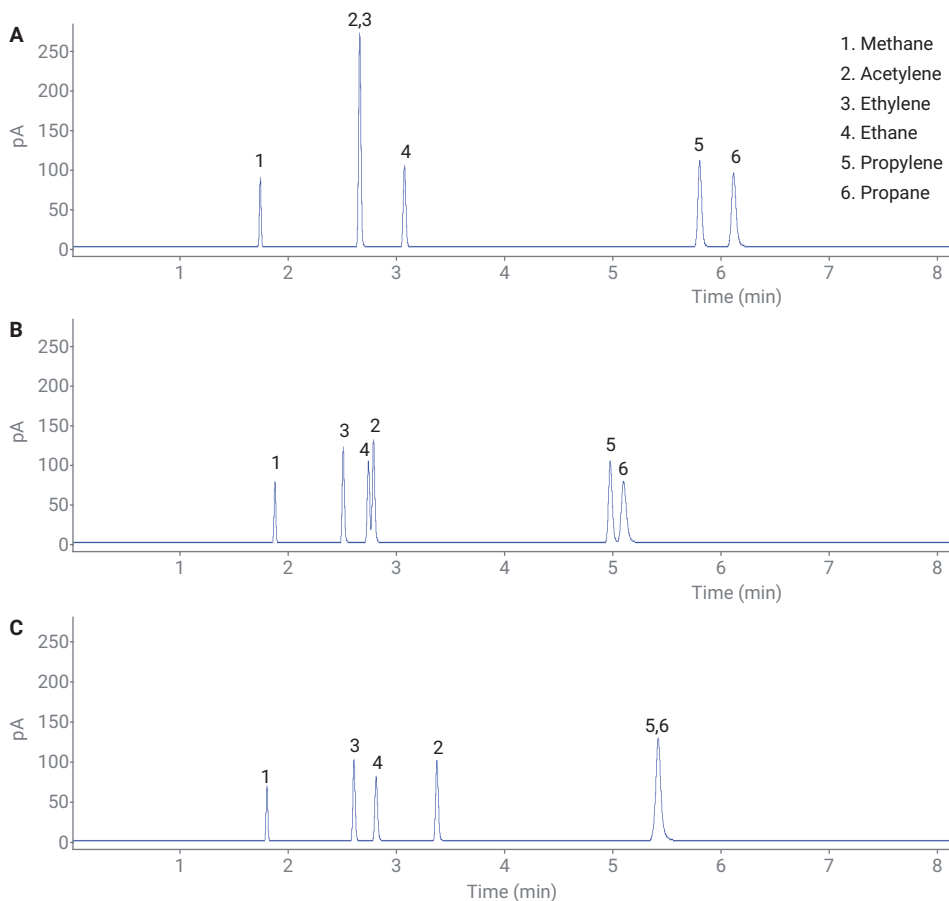| GC Conditions	
Columns	Agilent J&W PoraPLOT Q, 25 m × 0.53 mm × 20 μm (p/n CP7554) Agilent J&W PoraPLOT S, 25 m × 0.53 mm × 20 μm (p/n CP7574) Agilent J&W PoraPLOT U, 25 m × 0.53 mm × 20 μm (p/n CP7584) Agilent J&W PoraPLOT Q, 10 m × 0.53 mm × 20 μm (p/n CP7553) Agilent J&W PoraBOND Q, 25m × 0.53 mm × 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

Figure 1. Separation of saturated and unsaturated C_1 to C_3 hydrocarbons on (A) Agilent J&W PoraPLOT Q, (B) Agilent J&W PoraPLOT S, and (C) Agilent J&W PoraPLOT U columns.

System repeatability

System repeatability was assessed with repeated injections of a 1,000 ppm v/v C_1 to C_6 n-alkane standard. Figure 2 shows an overlay of chromatograms from 12 injections of the gas standard, demonstrating the repeatability of the manual injection technique as well as the chromatographic platform. A slow but steady manual injection technique was used to eliminate the possibility of overpressurization of the inlet. Overpressurization could result in the sample coming into contact with the septum or being diverted through the septum vent stream. Relative standard deviations of retention time for model compounds from methane to hexane were found to be less than 0.2% (n = 12) and less than 5% for area counts, as summarized in Table 1.

Selectivity tuning

Two PoraPLOT columns with different stationary phases were coupled in series to illustrate the concept of selectivity tuning. All six combinations (PoraPLOT Q + U, PoraPLOT U + Q, PoraPLOT U + S, PoraPLOT S + U, PoraPLOT Q + S, PoraPLOT S + Q) were tested and compared. In selectivity tuning with column coupling, the columns' order plays a critical role in determining the overall selectivity. Because the pressure drop across the column increases along the column, the linear velocity through the first column is as expected, and lower than expected through the second column. As a result, the column at the front has a greater influence in tuning the relative retention and selectivity.

For example, a PoraPLOT Q column joined to a PoraPLOT U column yields a column combination with unique selectivity, as shown in Figure 3. With the addition of PoraPLOT U at the back as illustrated in Figure 3A, acetylene is retained more and is separated from ethylene, as compared to PoraPLOT Q
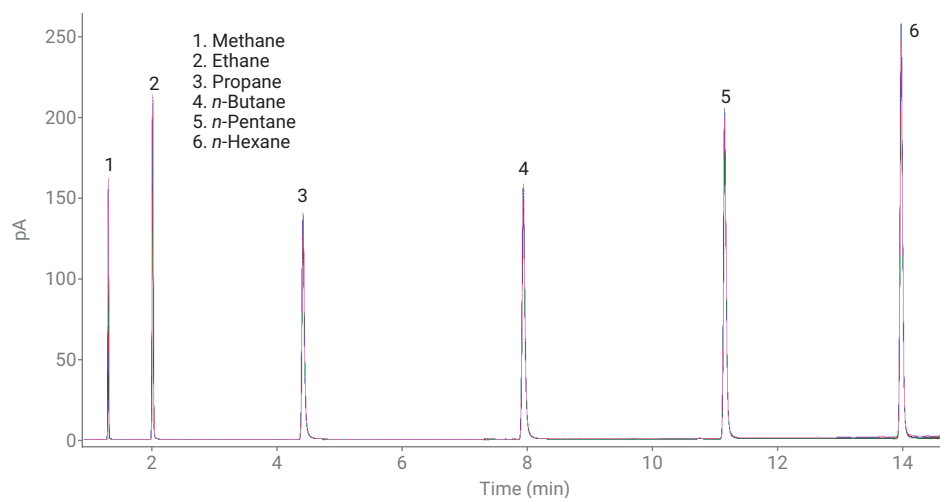

Figure 2. An overlay of chromatograms from 12 injections of 1,000 ppm v/v C_1 to C_6 n-alkane standard on an Agilent J&W PoraPLOT Q column.

Table 1. Retention times, area counts, and their relative standard deviations (RSDs) for model n-alkane compounds.

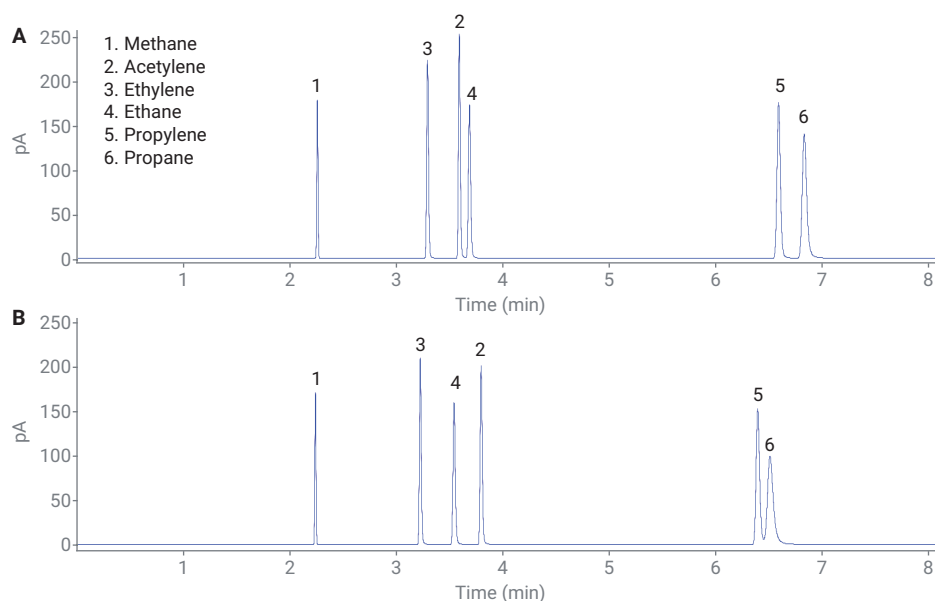| Compounds	t_R (min)	RSD (n = 12)	Area Counts	RSD (n = 12)
Methane	1.32	0.16%	135.9	4.6%
Ethane	2.03	0.10%	263.4	4.6%
Propane	4.43	0.04%	396.0	4.6%
n-Butane	7.95	0.02%	518.2	4.5%
n-Pentane	11.16	0.01%	638.7	4.3%
n-Hexane	13.98	0.01%	762.6	4.6%

Figure 3. Separation of saturated and unsaturated C_1 to C_3 hydrocarbons on (A) Agilent J&W PoraPLOT Q + U and (B) Agilent J&W PoraPLOT U + Q columns.

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alone in Figure 1A. Propylene and propane are still separated; however, resolution decreases from 4.4 for PoraPLOT Q only to 3.5 for PoraPLOT Q + U. In contrast, when PoraPLOT U was placed in front of PoraPLOT Q as shown in Figure 3B, PoraPLOT U plays a dominant role, resulting in even higher retention of acetylene, baseline resolution of C_2s (ethane, ethylene, acetylene), but partial coelution of C_3s (propylene and propane). The change of elution order is also observed with acetylene eluting after ethane.

Figure 4 shows the comparison of separation of C_1 to C_3 hydrocarbons on all six column combinations. Table 2 summarizes the resolution calculated between C_2s and C_3s. A column or column combination can be chosen based on the requirements for separation in specific applications. For example, PoraPLOT S + Q provides the best overall separations for both C_2s and C_3s. When aiming to separate C_2s only, PoraPLOT U, or PoraPLOT U + Q, or PoraPLOT U + S can be good options. Therefore, to choose a column that suits a specific application, it is vital to understand the chemistry related to the stationary phase, the sample matrix, and target compounds of interest.

Note that in coupling two columns, great care must be taken to ensure a low-dead-volume connection so that the chromatographic performance will not be compromised by extra band broadening. In these experiments, a press-fit connector with a low void volume was used to connect the two columns.
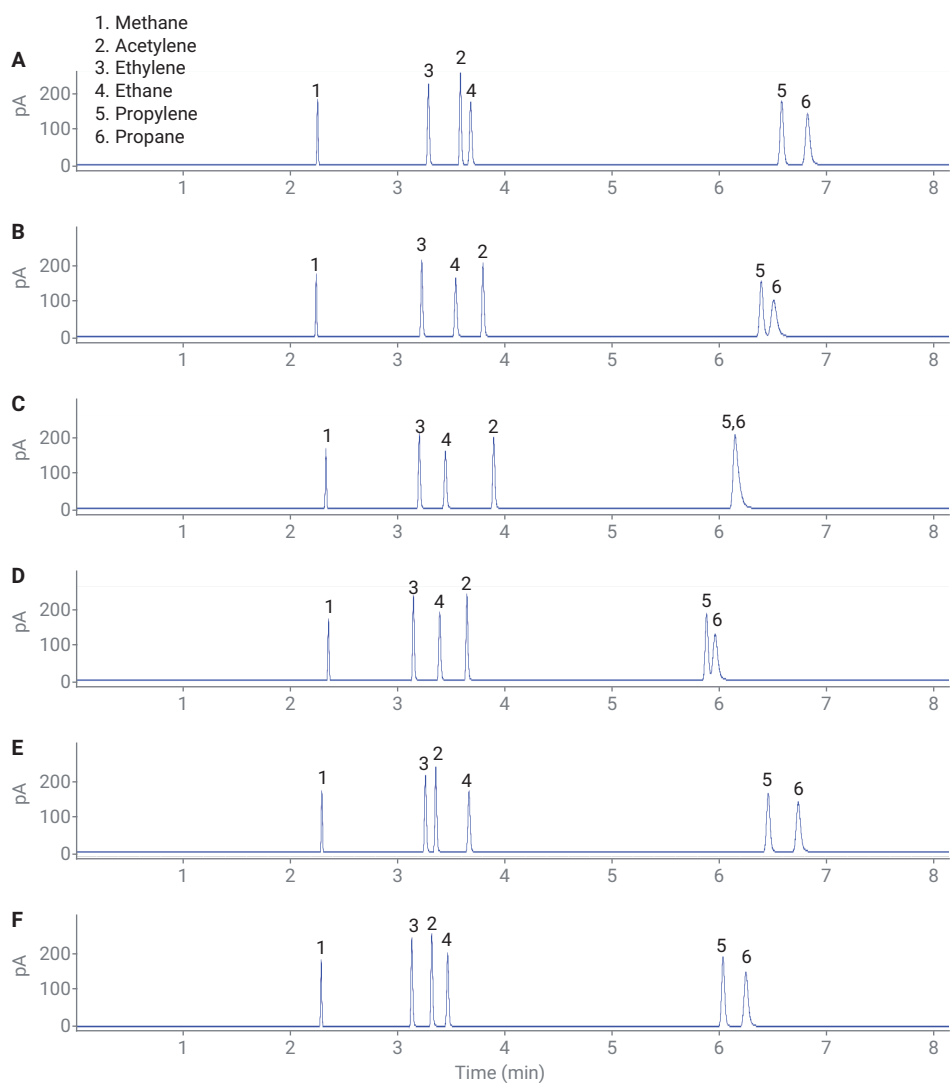

1. Methane
2. Acetylene
3. Ethylene
4. Ethane
5. Propylene
6. Propane

Figure 4. Separation of saturated and unsaturated C_1 to C_3 hydrocarbons on Agilent J&W PoraPLOT GC column combinations: (A) PoraPLOT Q + U, (B) PoraPLOT U + Q, (C) PoraPLOT U + S, (D) PoraPLOT S + U, (E) PoraPLOT Q + S, (F) PoraPLOT S + Q columns.

Table 2. Resolution obtained on Agilent J&W PoraPLOT GC columns and combinations tested.

PoraPLOT	Resolution			
	Ethylene - Acetylene	Ethylene - Ethane	Acetylene - Ethane	Propylene − Propane
Q	0.0	9.7	9.7	4.4
S	6.9	5.7	1.1	1.6
U	17.6	4.7	11.9	0.0
Q + U	9.0	16.2	2.6	3.5
U + Q	16.5	8.9	6.5	1.4
U + S	19.4	6.7	11.4	0.0
S + U	15.6	7.4	7.5	1.2
Q + S	2.9	11.1	8.5	4.1
S + Q	5.9	10.2	4.4	3.4

Applications – analysis of light hydrocarbons and aromatics

As an example, Figure 5 shows a chromatogram from the analysis of 18 light-saturated, unsaturated hydrocarbons, and aromatics. Figure 5 demonstrates that respectable separation of these compounds with a broad boiling point range from −161 °C (methane) to 110 °C (toluene) can be achieved within 20 min.

Comparison of Agilent J&W PoraPLOT Q and PoraBOND Q columns

The PoraPLOT columns are useful for the separation of volatile compounds. However, the overall utilization of traditional PLOT columns is hindered by the lack of stability of the porous layer coated on the inner wall. Free particles can form with pressure shocks or during column transport. Loose particles shed from the porous layer can create retention time drift, plugged column, and random spikes. Before use, it is recommended to precondition columns at a flow rate 50% higher than that to be used for analysis. A particle trap can be added at the detector end to prevent particulates from reaching the detector and reduce spikes. These limitations became the driving force to develop new bonded PLOT columns. One of the advancements is in the column manufacturing technology. With the in-situ polymerization technique, highly stable and pure porous polymer phases called PoraBOND were developed. Improved bonding technology results in significantly reduced particle shedding and higher mechanical stability. Stabilized particle layers offer improved robustness and reproducibility. Higher purity of the polymer material renders a more inert column for analyzing volatile polar compounds and active analytes such as oxygenated and sulfur compounds. The increased maximum temperature widens the application range.
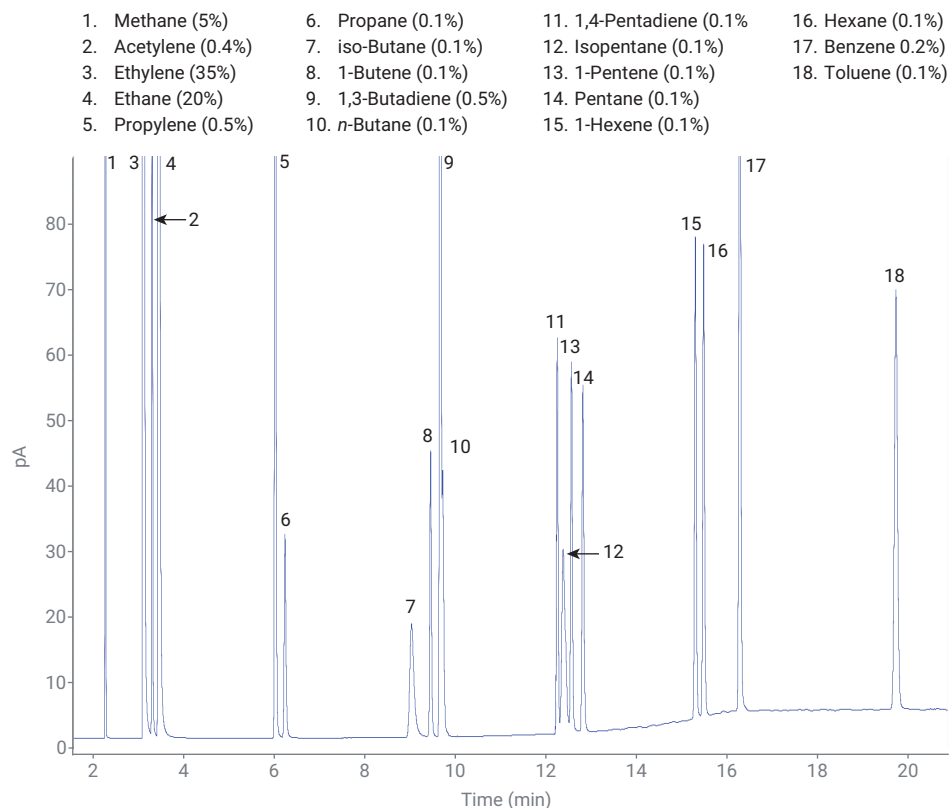
1. Methane (5%)
2. Acetylene (0.4%)
3. Ethylene (35%)
4. Ethane (20%)
5. Propylene (0.5%)
6. Propane (0.1%)
7. iso-Butane (0.1%)
8. 1-Butene (0.1%)
9. 1,3-Butadiene (0.5%)
10. n-Butane (0.1%)
11. 1,4-Pentadiene (0.1%
12. Isopentane (0.1%)
13. 1-Pentene (0.1%)
14. Pentane (0.1%)
15. 1-Hexene (0.1%)
16. Hexane (0.1%)
17. Benzene 0.2%)
18. Toluene (0.1%)

Figure 5. Separation of 18 saturated and unsaturated hydrocarbons and aromatics on an Agilent J&W PoraPLOT S + Q column combination.

A
1. Methane
2. Acetylene
3. Ethylene
4. Ethane
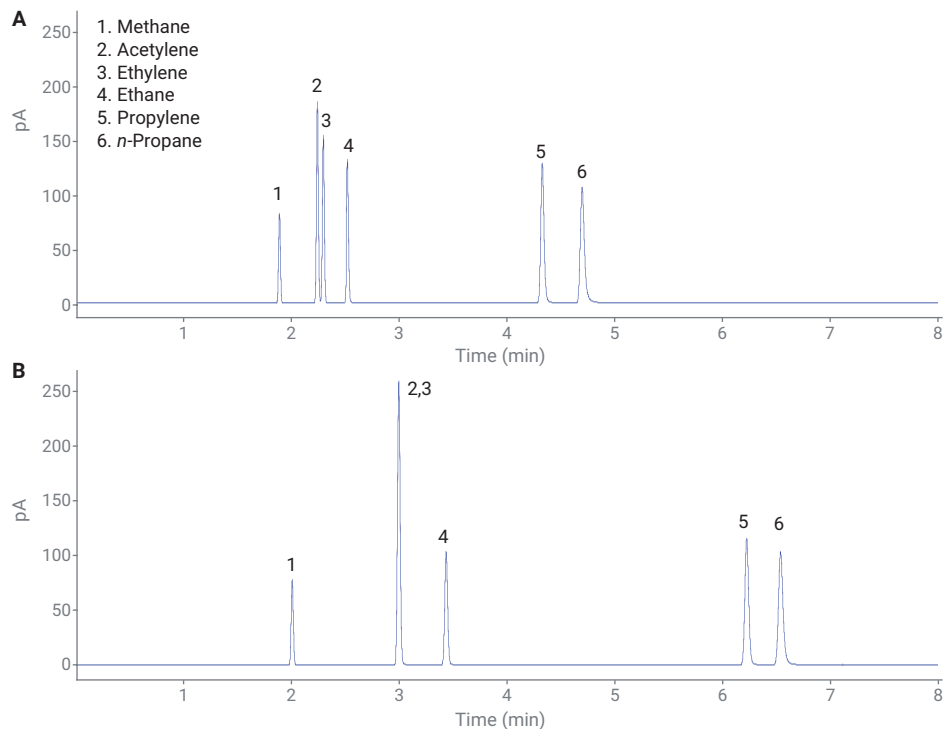5. Propylene
6. n-Propane

B

Figure 6. Separation of saturated and unsaturated C_1 to C_3 hydrocarbons on (A) Agilent J&W PoraBOND Q and (B) Agilent J&W PoraPLOT Q columns.

This study compared the performance of PoraPLOT Q and PoraBOND Q using various model compounds of different classes. Figure 6 shows the analysis of saturated and unsaturated C_1 to C_3 hydrocarbons on these two columns. A slight difference can be seen in the selectivity as a result of the different column manufacturing processes. On a PoraBOND Q column, acetylene and ethylene are almost baseline separated, while on a PoraPLOT Q, coelution is observed. Also, higher retention is observed on PoraPLOT Q due to the thicker film thickness.

Light sulfur compounds can be active and adsorptive, making the analysis of these molecules problematic, with tailing peaks and response loss. An inert column is critical for accurate quantification, especially for components at trace levels. Figure 7 compares the analysis of 100 ppm v/v sulfur compound standard containing four mercaptans. Figure 7A demonstrates that the PoraBOND Q column offers a higher degree of inertness with sharper and more symmetrical peaks for these compounds, compared to the tailing peaks with a reduced response on a PoraPLOT Q column as illustrated in Figure 7B. Similarly, the PoraBOND column offers better inertness for oxygenated compounds, as illustrated in Figure 8.
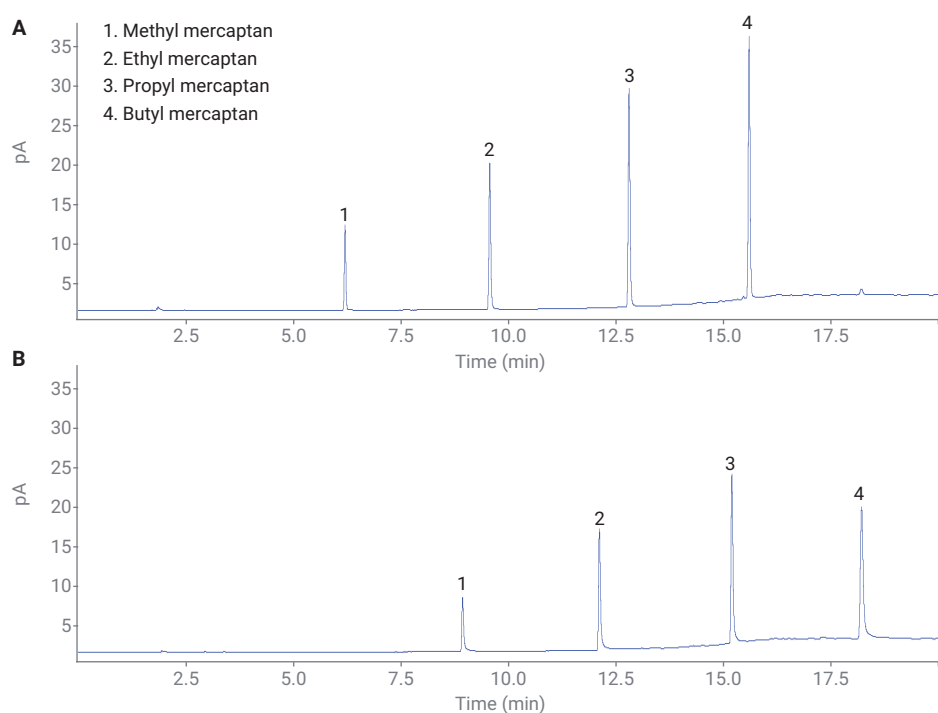

1. Methyl mercaptan
2. Ethyl mercaptan
3. Propyl mercaptan
4. Butyl mercaptan

Figure 7. Analysis of 100 ppm v/v sulfur compounds on (A) Agilent J&W PoraBOND Q and (B) Agilent J&W PoraPLOT Q columns.

1. Methanol
2. Ethanol
3. 2-Propanol
4. 1-Propanol
5. *tert*-Butanol
6. 2-Butanol
7. *iso*-Butanol
8. 1-Butanol
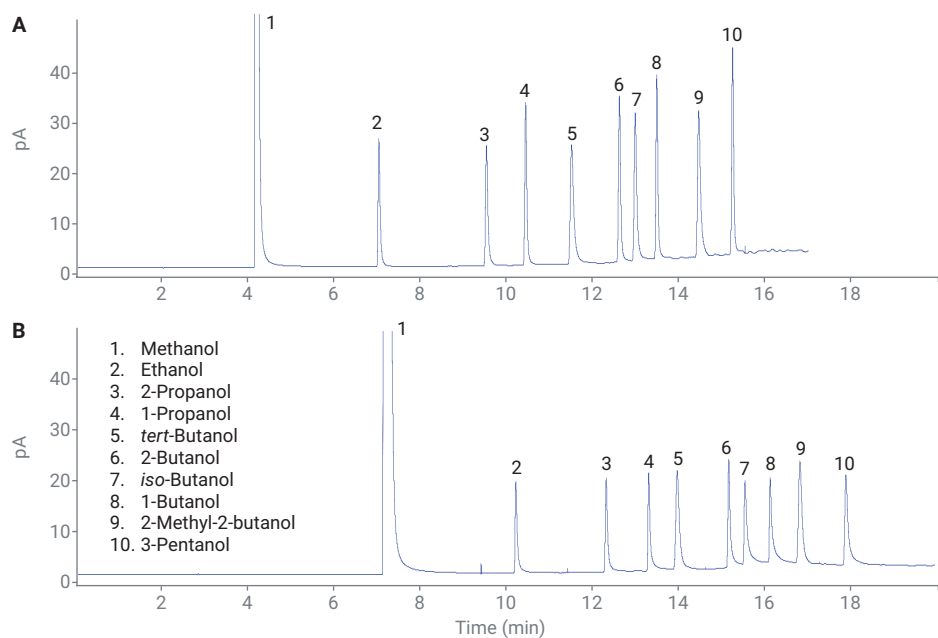9. 2-Methyl-2-butanol
10. 3-Pentanol

Figure 8. Analysis of 1% w/w oxygenated compounds in methanol on (A) Agilent J&W PoraBOND Q and (B) Agilent J&W PoraPLOT Q columns.

The analysis of highly basic compounds, such as amines, is a challenging chromatographic application due to their reactivity and adsorption to active surfaces. As demonstrated in Figure 9, active amine compounds such as mono-ethanolamine (MEA) and n-methylethanolamine (NMEA) exhibit severe peak tailing on a PoraBOND Q column due to the interaction between analytes and the stationary phase. On PoraPLOT Q, MEA and NMEA are undetectable even at a high concentration level of 1% w/w. As such, both columns are not suited for active amine compound analysis.

Conclusion

Porous polymers are unique, highly retentive stationary phases with a wide application range for both polar and nonpolar compounds. With these porous polymer phases, volatile components can be separated without cryogenic cooling. These polymers are classified as Q, S, or U-type, based on the monomers used and the functional groups incorporated. The polarity of these phases is in the order of Q < S < U. The column selectivity changes were illustrated with the separation of light hydrocarbons. Also, by series coupling columns with different selectivities, selectivity tuning is a practical and low-cost approach to achieve separations when a single column selectivity is inadequate. Despite the broad applications, these columns have limitations, such as random spikes resulting from particle dislodging. A particle trap can mitigate this issue.
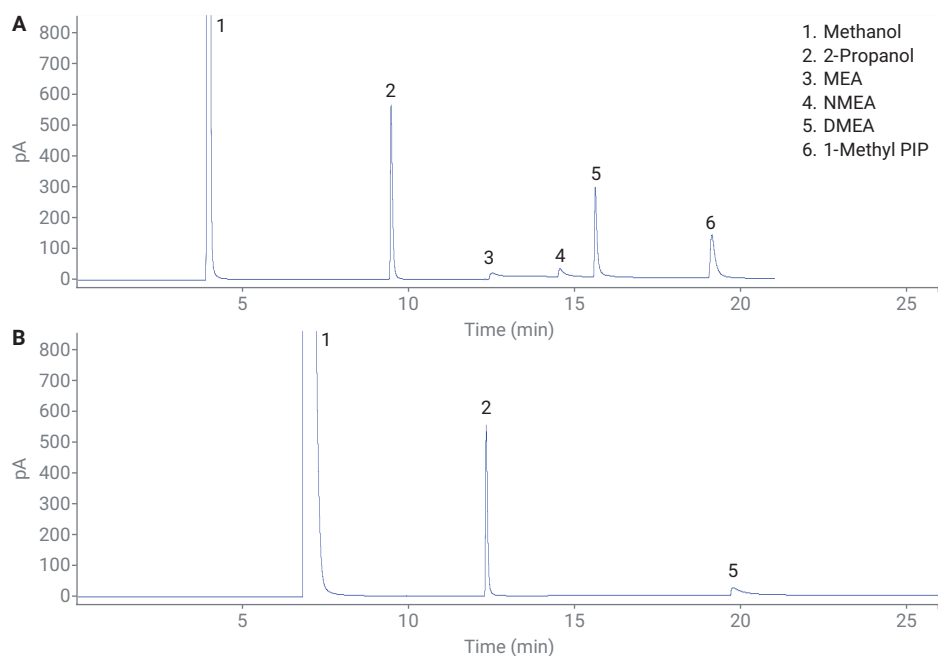

Figure 9. Separation of 1% w/w amine compounds in methanol on (A) Agilent J&W PoraBOND Q and (B) Agilent J&W PoraPLOT Q columns.

Modern manufacturing processes with in-situ polymerization have resulted in porous polymer phases such as the Agilent J&W PoraBOND series with improved stability and reduced spiking. This type of PLOT column also offers better inertness for analyzing volatile polar compounds and active analytes.

Acknowledgments

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