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Important Petroleum Separations Using a New SPB™-Octyl Capillary Column

M.V. Robillard, N.G. Ervin, and L.M. Sidisky

The newly-developed SPB-Octyl stationary phase, a bonded nonpolar silicone polymer containing 50% methyl and 50% n-octyl substituted groups, displays a polarity lower than the widely used polydimethylsiloxane phases such as SPB-1 and approaches that of squalane. The potential for using the SPB-Octyl phase in important petroleum applications is demonstrated through a number of key separations which differentiate it from other nonpolar phases.

Squalane is the "zero" polarity reference in the Rohrschneider and McReynolds systems for characterizing stationary phase polarity (Reporter Vol. 13, No. 3, page 10). In the past, petroleum analysts typically used squalane as the standard nonpolar stationary phase for detailed separation of complex hydrocarbon samples such as naphthas, reformates, and gasolines. But the use of squalane had disadvantages. As a nonbonded phase, it had a very low maximum operating temperature. Applying a thick film of the phase on a capillary column resulted in major loss of chromatographic coating efficiency, adversely affecting high resolution detailed hydrocarbon analysis.

Polydimethylsiloxane (PDMS) replaced squalane as a nonpolar stationary phase. However, PDMS columns such as SPB-1 and SPB-5, while being classified as nonpolar, have a measurably higher polarity than squalane.

Our new SPB-Octyl columns are coated with an extremely nonpolar bonded stationary phase containing 50% octyl/50% methyl polysiloxane. The SPB-Octyl phase displays a polarity lower than PDMS phases and approaches that of squalane. This new phase offers a wide temperature range (-60°C to 280°C) and provides several unique hydrocarbon separations important to petroleum analysts. It is particularly useful for separating aromatics and oxygenates from compounds of other classes with which they coelute or are only partially resolved on other nonpolar columns.

Benzene and 1-methylcyclopentene, and toluene and 2,3,3-trimethylpentane, are two pairs of compounds of different class frequently present at high levels in petroleum streams. Because of their different compound classes, separation is often critical. These two pairs coelute on SPB-1 type phases. As shown in Figure A, they are more than baseline resolved on the SPB-Octyl column.

A method recently developed by the American Society for Testing and Materials (ASTM D5441, *Test Method for Analysis of Methyl tert-Butyl Ether (MTBE) by Gas Chromatography*) specifies the use of a long SPB-1 type column to resolve several key oxygenate/hydrocarbon pairs, specifically tert-butanol and cis/trans-2-pentene (Reporter Vol. 13, No. 2, page 8). Figure B compares a 100m Petrocol™ DH column (coated with an SPB-1 stationary phase) with an SPB-Octyl column in separating part of a calibration standard. On the Petrocol DH column, tert-butanol elutes between cis- and trans-2-pentene. On the SPB-Octyl column, tert-butanol elutes well before both cis- and trans-2-pentene. Other hydrocarbons in this calibration standard maintain the same relative elution order on these two columns.

Figure A. Key Hydrocarbon Pairs Completely Resolved on a 100-Meter SPB-Octyl Column

Column: **SPB-Octyl, 100m x 0.25mm ID, 0.5µm film**
Cat. No.: **24282**
Oven: 35°C (15 min) to 200°C at 1°C/min, hold 15 min
Carrier: helium, 50psig
Det.: FID, 250°C
Inj.: 0.1µL, split 215:1, 250°C

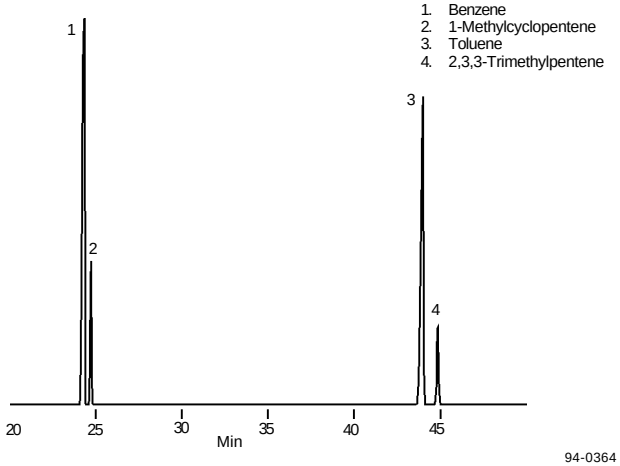
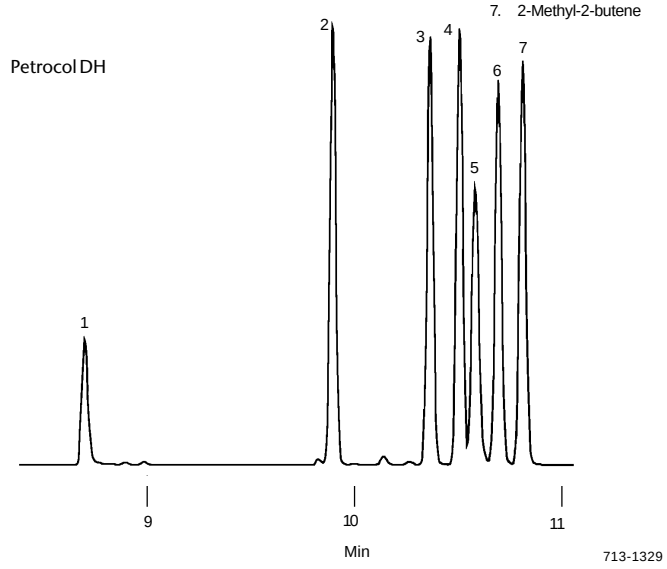


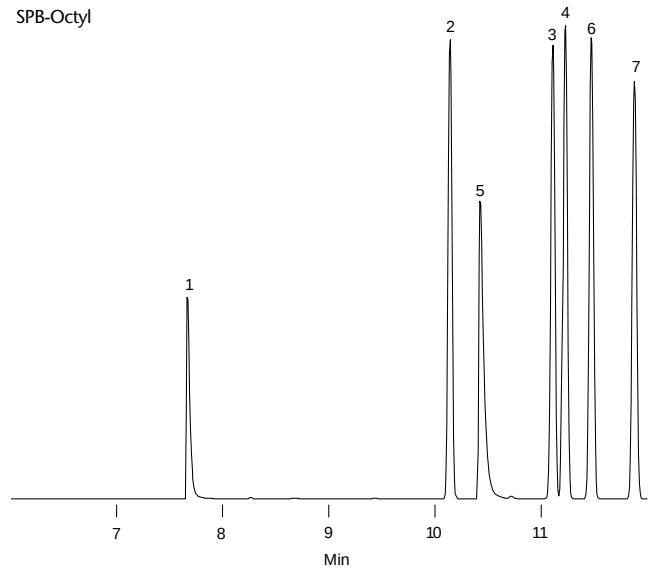
Figure B. MTBE Contaminants

Column: **Petrocol DH, 100m x 0.25mm ID, 0.5µm film**
Cat. No.: **24160-U**
Oven: 50°C (13 min) to 180°C at 10°C/min
Carrier: helium, 20cm/sec; vent flow 140mL/min
Det.: FID, 310°C
Inj.: 1µL MTBE containing 1% each analyte (MTBE Contaminants Mix A, Cat. No. 47942), split 200:1, 250°C

Column: **SPB-Octyl, 100m x 0.25mm ID, 0.5µm film**
Cat. No.: **24282**
Oven: 35°C (15 min) to 200°C at 1°C/min, hold 15 min
Carrier: helium, 50psig
Det.: FID, 250°C
Inj.: 0.1µL, split 215:1, 250°C

1. Methanol
2. Isopentane
3. n-Pentane
4. trans-2-Pentene
5. tert-Butanol
6. cis-2-Pentene
7. 2-Methyl-2-butene





Methanol and isobutane can be separated easily on the SPB-Octyl column through shifting of oxygenates earlier in relative retention time (Figure C). This separation is important for purity analysis of methyl tert-butyl ether (MTBE) as well as several other important applications. To achieve the methanol/isobutane separation on a 100-meter SPB-1 column, a subambient initial temperature must be used, especially if disproportionate concentrations are encountered.

Figure C. Methanol and Isobutane Separated at 35°C on a 100-Meter SPB-Octyl Column

Column: **SPB-Octyl, 100m x 0.25mm ID, 0.5µm film**
Cat. No.: **24282**
Oven: 35°C (15 min) to 200°C at 1°C/min, hold 15 min
Carrier: helium, 50psig
Det.: FID, 250°C
Inj.: 0.1µL, split 215:1, 250°C

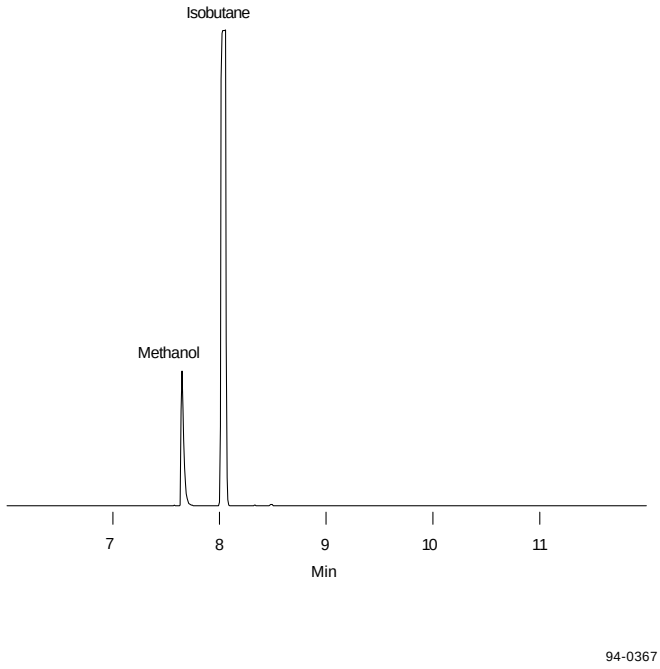
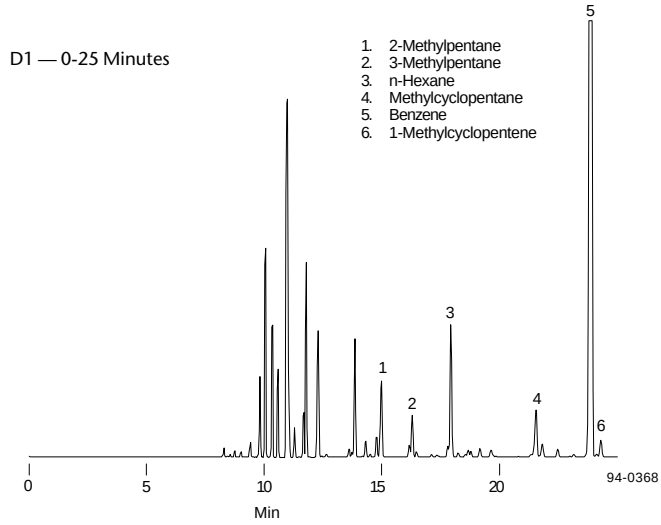


Figure D1 shows the first 25 minutes of an analysis of a pyrolysis gasoline (py gas) sample containing very high concentrations of olefinic, aromatic and styrenic compounds. The SPB-Octyl column baseline resolves disproportionate concentrations of benzene (>30%) and 1-methyl-cyclopentene. The 50-75 minute region of the chromatogram in Figure D2 shows that the xylene isomers, in addition to styrene, all are resolved.

Figure D. Pyrolysis Gasoline on a 100-Meter SPB-Octyl Column

Column: **SPB-Octyl, 100m x 0.25mm ID, 0.5µm film**
Cat. No.: **24282**
Oven: 35°C (15 min) to 200°C at 1°C/min, hold 15 min
Carrier: helium, 50psig
Det.: FID, 250°C
Inj.: 0.1µL, split 215:1, 250°C



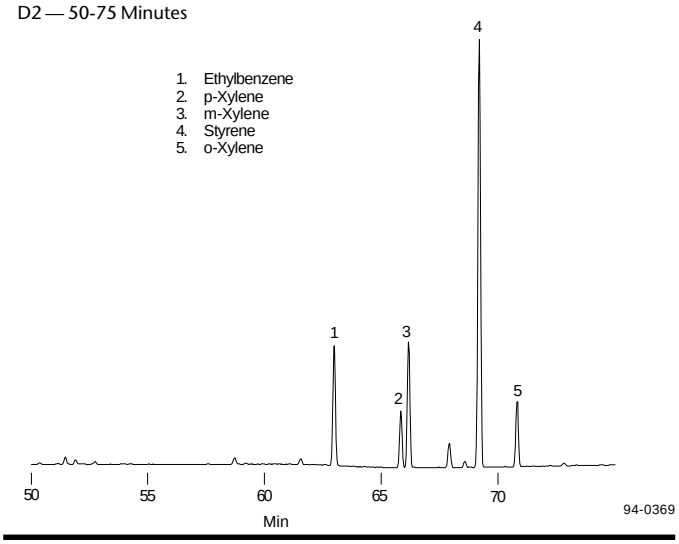
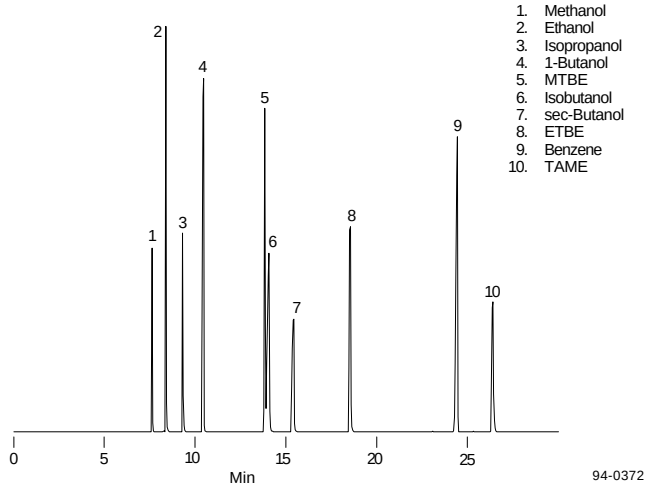


Figure E. Oxygenates Mix on a 100-Meter SPB-Octyl Column

Column: **SPB-Octyl, 100m x 0.25mm ID, 0.5µm film**
Cat. No.: **24282**
Oven: 35°C (15 min) to 200°C at 1°C/min, hold 15 min
Carrier: helium, 50psig
Det.: FID, 250°C
Inj.: 0.1µL, split 215:1, 250°C



Ordering Information:

Fused Silica Capillary Columns

SPB-Octyl
100m x 0.25mm, 0.5µm film **24282**

Petrocol DH
100m x 0.25mm, 0.5µm film **24160-U**

SPB-1
100m x 0.25mm, 0.25µm film **24198**
100m x 0.25mm, 1.0µm film **24220-U**
100m x 0.32mm, 0.25µm film **24228-U**
100m x 0.32mm, 1.0µm film **24213-U**

Highly Characterized Reference Materials

Petroleum Refinery Reformate
1mL **47489**

Petroleum Refinery Pyrolysis Gasoline (Py Gas)
1mL **47490-U**

Petroleum Refinery Heavy Straight Run Naphtha
1mL **47488**

P-I-A-N-O Mix
Quantitative mix of 140 n-paraffins, isoparaffins, aromatics, naphthenes, and olefins.
0.1mL **44593-U**

P-I-A-N-O Kit
0.1mL of each of the following mixes: P-I-A-N-O, n-paraffins, isoparaffins, aromatics, naphthenes, and olefins.
44594-U

MTBE Contaminants Mix A
12 components at 1% w/w in MTBE.
1mL **47942**

Figure E shows some common oxygenates analyzed on a 100-meter SPB-Octyl column. Elution order is the same as on an SPB-1 column. However, there are significant differences in retention indices of these compounds with respect to hydrocarbons.

The SPB-Octyl column provides excellent resolution and efficiency for separating petroleum mixtures. The unique nonpolar functionality of this bonded phase also is useful for a wide range of food, fragrance, pharmaceutical, and environmental applications.