High Resolution Detailed Hydrocarbon Analyses by Capillary Column Gas Chromatography

In the petrochemical industry, samples such as petroleum naphthas and gasolines routinely must be separated – quantitatively – into their individual components. Because these petroleum-derived samples consist of hundreds of compounds, petroleum analysts require chromatography columns that offer high resolution. We have developed polar and nonpolar capillary gas chromatography columns to provide the high resolution necessary for detailed hydrocarbon analyses. (ChromFax: 109868)

Key Words:
- detailed hydrocarbon analyses
- hydrocarbons
- gasoline
- naphtha
- reformate
- light hydrocarbons

Before the development of capillary columns, packed GC columns typically were used to perform detailed light hydrocarbon separations (Figures A and B). These packed columns are still useful for specific applications. The development of capillary columns, however, enabled analysts to more efficiently separate complex mixtures.

One of the first capillary columns used to analyze a complex hydrocarbon mixture was a 60m x 0.75mm ID glass column coated with a nonpolar, bonded stationary phase (SPB™-1). This column separated commercial gasoline in a relatively short time, and resolved C3-C12 hydrocarbons (Figure C). Narrower bore (0.25mm ID) fused silica capillary columns coated with SP™-2100, a nonpolar, nonbonded stationary phase similar to SPB-1, improved resolution for fingerprinting complex mixtures, such as jet kerosene (Figure D).

Aromatics

Because aromatic and nonaromatic compounds have similar boiling points, they are hard to resolve on nonpolar columns. Therefore, analysis of aromatics in gasoline has been a difficult application. Using a narrow bore polar capillary column simplifies quantitative analysis of aromatic compounds. When gasoline is analyzed on a polar 30m x 0.20mm ID SUPELCOWAX™ 10 column, benzene and higher molecular weight aromatics are retained until after most nonpolar components (up to n-nonane) elute (Figure E).

The same SUPELCOWAX 10 column can be used for xylene analysis (Figure F). Trace components that elute immediately after the major component can be difficult for a petrochemical analyst to quantify on a wider bore column, but the 0.20mm ID column performs the separation quickly and easily. The SUPELCOWAX 10 column resolves para-xylene and meta-xylene isomers to baseline in less than 10 minutes – even though their boiling points differ by only 1°C.

When compounds are present in balanced concentrations, xylene analysis can be accomplished more quickly by raising the column temperature. Analyzing benzene, toluene, and xylene on a SUPELCOWAX 10 column, using an isothermal starting temperature of 75°C, reduces analysis time by approximately 2 minutes (Figure G).

If the speed of separation is of primary concern, the greater efficiency of a narrow bore column allows the analyst to trade that efficiency for faster analysis time. Using a shorter column is another way to decrease analysis time.

PNA - PONA - PIANO Analyses: 50-Meter Nonpolar Column

During the past few years, much effort has been devoted to developing rapid, reliable gas chromatographic methods for compositional analyses of naphthas, gasolines, reformates, and other complex hydrocarbon mixtures. Quantitative separation of the paraffin, isoparaffin, aromatic, naphthenic, and olefin* content of many samples is critical for process control and product quality testing.

Good results have been obtained with 50m x 0.20mm ID fused silica capillary columns coated with 0.50µm of nonpolar methyl silicone phase. Developed specifically for this type of application, 50m x 0.20mm ID Petrocol™ DH 50.2 columns are high efficiency columns that typically offer 5000 plates/meter (250,000 plates/column). This high efficiency permits separation of all of the major components present in these complex hydrocarbon mixtures. Analysts can then categorize the components into the appropriate class: paraffin, isoparaffin, aromatic, naphthene, or olefin (PIONA analysis).

PONA Analyses

In analyses of the paraffin, olefin, naphthene, and aromatic composition of complex hydrocarbon mixtures, a temperature program consisting of a 30 minute hold at 35°C, followed by an increase to 200°C at a rate of 2°C/minute, has proven useful. Under this program, a Petrocol DH 50.2 column resolves the lighter weight components in naphthas, gasolines, alkylates, reformates, and other complex mixtures very well (Figures H-J). The long hold time at essentially ambient temperature provides maximum separation of these early eluting components (through toluene). An important separation, m-xylene from p-xylene, is approximately 75% to baseline.

In addition to complex mixtures, relatively simple hydrocarbon mixtures, such as butane lighter fuel, petroleum ether, and C6 feedstock streams, can be analyzed on a Petrocol DH 50.2 column

* Often referred to as PNA, PONA, and PIANO analyses.
under the same conditions. Light components are retained sufficiently well for separation, without the need for a subambient initial temperature.

Alternatively, if the initial hold time is reduced from 30 minutes to 5 minutes, a Petrocol DH 50.2 column can provide much faster separations of the same samples – with virtually the same resolution. This program is very useful when speed of analysis is most important, or when there is less emphasis on the lighter hydrocarbons. The faster program also is more appropriate for samples containing greater proportions of heavier components, such as C8 streams, turpentine, charcoal lighter fluid, and mineral spirits. The maximum operating temperature for Petrocol DH 50.2 columns is 320°C. Hence, under other temperature programs, they can be used for analyses of lubricating oils and other mixtures containing hydrocarbons through C30 and above.

**Analyses on a 60-Meter Nonpolar Column**

The high alkyl content of the SPB-Octyl stationary phase (50% methyl/50% n-octyl polysiloxane), provides a polarity lower than the 100% dimethylsilicone phase, SPB-1. As a result, greater interaction with hydrocarbon-like analytes is possible while, at the same time, polar analytes can interact with the long alkyl chains to induce the phase to behave in a somewhat polar manner. These interactions influence the separation mechanism and bring about some unique separations of importance to petrochemical and environmental analysts which are not possible using the SPB-1 column.

**Gasoline**

Figure K shows the analysis of a premium unleaded gasoline on a 60-meter SPB-Octyl column. The elution order of the components is similar to that of dimethylsilicone phases, but aromatic and other polar compounds exhibit subtle shifts that can be useful in detailed analyses of these complex samples. Two such important separations are shown in Figure L. Benzene/1-methylcyclopentene and toluene/2,3,3-trimethylpentane are two pairs of hydrocarbons that co-elute or are only partially resolved by SPB-1. Both pairs are resolved to baseline on the SPB-Octyl column. Because the compounds represent different classes of hydrocarbons, separations of these pairs improves the accuracy of PNA, PONA, and PIANO analyses of gasoline and similar hydrocarbon mixtures.

**Analyses on a 100-Meter Nonpolar Column**

The small sample capacity of Petrocol DH 50.2 columns (0.20mm ID) typically requires high split ratios (500:1). To enable petrochemical analysts to use lower split ratios and obtain greater resolution, we developed a longer, wider bore Petrocol column. Providing approximately 400,000 plates, the high efficiency 100m x 0.25mm ID Petrocol DH column can be used to achieve difficult separations, ranging from resolving light hydrocarbon gases or closely eluting isomers to detailed separations of highly complex mixtures such as petroleum naphthas, reformates, and liquified coal fractions.

**Gasoline**

Using an ambient initial column temperature, C3-C12 hydrocarbons in a gasoline are well resolved and easily quantified (Figure M). The 100m x 0.25mm ID column also can be used in place of a 50m x 0.20mm ID column for PONA and PIANO analyses of gasolines and other samples.

**Cyclopentane – 2,3-Dimethylbutane**

A Petrocol DH column can perform one of the more difficult separations in analyses of complex hydrocarbon mixtures. Separation of cyclopentane from 2,3-dimethylbutane is important when performing a PONA or PIANO analysis. The 100-meter column sufficiently resolves these compounds at 35°C to permit quantification. Baseline separation is achieved at 25°C (Figure N).

When used with a moderately subambient initial temperature, a Petrocol DH column provides the more difficult separations of many light hydrocarbon gases, including olefins, diolefins, paraffins, isoparaffins, and acetylenes.

**Isobutylene – 1-Butene**

By using an initial temperature of -20°C, isobutylene and 1-butene can be separated with a 65% return to baseline – enough resolution to allow quantification (Figure O). Propylene and propane are separated to baseline under these conditions.

If a lower initial temperature (-50°C) is used, separation of the C1-C5 hydrocarbons is improved. Ethylene, acetylene, and ethane are resolved to the baseline, and isobutylene and 1-butene are approximately 90% separated (Figure P). Propylene and propane also are resolved to baseline.

**Dicyclopentadiene**

Dicyclopentadiene (DCPD), a highly reactive cyclic diolefin dimer, is commonly used in manufacturing petroleum resins and other specialty products. Crude DCPD usually is monitored for breakdown products, because it often is thermally cracked (intentionally or unintentionally) to yield cyclopentadiene (CPD). Because DCPD is thermally unstable, mild analytical conditions and an inert column are essential to prevent sample decomposition during the analysis. In an experiment to monitor the effect of injection port temperature, we analyzed neat DCPD using both mild (130°C) and severe (250°C) injection port temperature. With the lower temperature, essentially no CPD monomer was seen (Figure Q). At the higher injection port temperature, DCPD was partially decomposed to the monomer. Thus, the milder conditions are best suited to this analysis. The Petrocol DH column provided excellent resolution of the analogs, decomposition products, and impurities, allowing the sample composition to be determined.

**Olefin (Hexene) Isomerization**

Olefin isomerization studies usually require a high resolution capillary column to separate the variety of isomeric starting materials and reaction products. Used with an ambient initial temperature, a Petrocol DH column resolves hexene isomerization products, although the boiling points of some of these compounds differ by only 2°C (Figure R). 2-Methyl-2-pentene and cis-3-methyl-2-pentene, which differ by only four retention index units, are separated to baseline.
**RETENTION INDICES**

With each Petrocol DH column we include a table of retention indices for more than 400 compounds, obtained by using the 100-meter column under temperature-programmed conditions. The table can be used to help identify unknown compounds in complex samples. To identify an unknown compound, first identify the normal hydrocarbons that bracket the unknown, then calculate the retention index of the unknown and compare the value to those in the table.

**ANALYSES ON A 150-METER NONPOLAR COLUMN**

Some petrochemical analyses, especially in the light hydrocarbon range, demand even more separating ability from a capillary column. A 150-meter Petrocol DH 150 column is 50% longer than a Petrocol DH column, and has a film thickness twice as great (1.0µm), to ensure highly effective separations of light hydrocarbons.

Petrocol DH 150 columns have very high efficiency (typically 550,000 theoretical plates) and a low phase ratio (0.25mm ID, 1.0µm phase film; β = 63). These important characteristics enable these columns to separate light hydrocarbons significantly better than shorter columns with thinner phase films.

Highly versatile Petrocol DH 150 columns will separate hydrocarbon mixes ranging from the light hydrocarbon gases to the higher boiling components of gasolines, naphthas, coal liquidification products, and other samples of comparable boiling range. Most of these analyses can be performed using ambient (25°C-35°C) or mildly subambient (0°C or -20°C) initial temperatures. The 150-meter column requires a head pressure of approximately 75psi of helium for optimum linear velocity. The head pressure requirement can be reduced to approximately 50psi by using hydrogen as the carrier gas.

**GASOLINE**

Using an ambient initial temperature, gasoline analyzed on a Petrocol DH 150 column shows near baseline resolution of the light hydrocarbons cyclopentane and 2,3-dimethylbutane, and the heavier m-xylene and p-xylene isomers (Figure W). Under these conditions, separations of the light hydrocarbons through toluene are optimized by using the isothermal hold period. The subsequent temperature program enables analysts to obtain excellent detail for the heavier compounds. Conditions can be varied (e.g., analysis time shortened) to meet specific needs.

**XYLENE ISOMERS**

A Petrocol DH 150 column separates m-xylene and p-xylene nearly to baseline under isothermal conditions (Figure X). This separation usually is difficult to achieve on a nonpolar column, and requires a second analysis on a polar column. The Petrocol DH 150 column saves the time and expense of a second analysis.

**GASEOUS – LIQUID HYDROCARBON SEPARATIONS**

A Petrocol DH 150 column is versatile, because it can resolve gaseous hydrocarbons from liquid hydrocarbons. In natural gas, small amounts of C2-C5 hydrocarbons are easily separated from high concentrations of methane – under ambient conditions (Figure Y). The components can be quantified. In liquid petroleum gas analyses, small amounts of propylene are baseline separated from the major (propane) peak.

**LIGHT n-PARAFFINS AND 1-OLEFINS**

A Petrocol DH 150 column separates C1-C6 paraffins and olefins, including C2 compounds, using an ambient initial temperature. Peaks in Figure Z represent approximately 20-50rpm of each compound. The ethylene-ethane and propylene-propane pairs are approximately 75% separated and all other compounds are resolved to baseline.
Oxygenated Compounds – C4 Gas Streams
A Petrocol DH 150 column also can separate oxygenated hydrocarbons, including C1 and C2 alcohols, dimethylether, and methyl tert-butylether (MTBE), from the hydrocarbons commonly present in some C4 gas streams. The oxygenates are used as alternative fuels and as performance enhancers when added to other fuels. Used with an ambient, isothermal temperature, the 150-meter column separates ethanol, dimethylether, and MTBE from all other compounds present (Figure AA). Isobutane and methanol are separated to baseline and isobutylene is partially separated from 1-butene. With an initial temperature of 0°C, the column separates isobutylene and 1-butene almost to baseline.

Light Hydrocarbons
A Petrocol DH 150 column resolves isobutylene from 1-butene, using moderately subambient initial temperatures – the separation at 0°C is almost as good as at -20°C (Figure AB). Propylene and propane are resolved to baseline with initial temperatures as high as 35°C. If column temperatures are reduced, the 150-meter column can be used to accomplish many difficult light hydrocarbon separations. With an initial temperature of -50°C, the column resolves C2 hydrocarbons very well, and separates methylacetylene from propadiene (Figure AC). The peaks in Figure AC represent concentrations of approximately 5ppm (10ppm for propadiene). Other difficult separations that can be performed include analyzing ppm levels of acetylene in ethylene streams and separating and quantifying methylacetylene and propadiene in analyses of Mapp® gases.

Summary
Detailed analyses of complex hydrocarbon mixtures are best performed on high resolution capillary columns. The type of analysis and the degree of resolution required determine the most appropriate column.

Polar, narrow bore SUPELCOWAX 10 columns are well suited for analyses of aromatic compounds in complex matrices and for determining the purity of aromatic samples. Versatile Petrocol DH series columns are designed and tested specifically for analyses of petroleum and other complex hydrocarbon mixtures. Columns are individually tested, to ensure consistent coating efficiency, column activity levels, and k’ values for nonpolar hydrocarbons. Narrow bore Petrocol DH 50.2 columns offer an excellent combination of quality and economy. They are effective for compound class analyses, including PNA, PONA, and PIANO analyses of naphthas, reformates, and gasolines. When greater separating ability or sample capacity are required, use a versatile 100-meter Petrocol DH column to perform the same types of analyses, on samples containing light gases through gasoline range components, with good results. For maximum resolution, especially for light hydrocarbons, a 150-meter Petrocol DH 150 column will separate compounds that otherwise require special conditions or unusual columns.

If you monitor the composition of complex hydrocarbon mixtures, we highly recommend SUPELCOWAX 10 and Petrocol DH series columns.

Figure A.Hydrocarbons on a Carbopack™ C/Picric Acid Packed Column

Figure B. C2-C6 Saturated and Unsaturated Hydrocarbons
**Figure C. Gasoline on a Capillary Column in a Packed Column Chromatograph**

- Column: SPB-1, 60m x 0.75mm ID, 1.0µm film
- Cat. No.: 23720
- Oven: 35°C (12 min) to 200°C at 4°C/min, hold
- Carrier: helium, 5cc/min (flow controlled)
- Det.: TCD
- Inj.: 0.4µL gasoline, direct injection

**Figure D. Jet Kerosene**

- Column: SP-2100, 30m x 0.25mm ID, 0.25µm film
- Cat. No.: 24007
- Oven: 50°C to 200°C at 2°C/min
- Carrier: helium, 20cm/sec
- Det.: FID
- Inj.: 0.1µL kerosene, split (100:1)
Figure E. Aromatics in Gasoline

| Column: SUPELCOWAX 10, 30m x 0.20mm ID, 0.20µm film |
| Cat. No.: 24169 |
| Oven: 60°C (8 min) to 210°C at 8°C/min |
| Carrier: helium, 25cm/sec |
| Det.: FID |
| Inj.: 0.1µL gasoline, split (150:1) |

Analysis Completed in Less Than 30 Minutes

Figure F. Xylene Isomers

| Column: SUPELCOWAX 10, 30m x 0.20mm ID, 0.20µm film |
| Cat. No.: 24169 |
| Oven: 60°C |
| Carrier: helium, 25cm/sec |
| Det.: FID |
| Inj.: 0.1µL p-xylene product, split (150:1) |

Figure G. Xylene Isomers and Other Aromatic Compounds

| Column: SUPELCOWAX 10, 30m x 0.20mm ID, 0.20µm film |
| Cat. No.: 24169 |
| Oven: 75°C |
| Carrier: helium, 25cm/sec |
| Det.: FID |
| Inj.: 0.1µL hexane (1.7% each analyte), split (150:1) |
Figure H. Gasoline on a 50-Meter Petrocol DH 50.2 Column

Column: Petrocol DH 50.2, 50m x 0.20mm ID, 0.50µm film
Cat. No.: 24133
Oven: 35°C (30 min) to 200°C at 2°C/min
Carrier: helium, 19-21 cm/sec
Det.: FID (225°C)
Inj.: 225°C

Figure I. Reformate on a Petrocol DH 50.2 Column

Column: Petrocol DH 50.2, 50m x 0.20mm ID, 0.50µm film
Cat. No.: 24133
Oven: 35°C (30 min) to 200°C at 2°C/min
Carrier: helium, 19-21 cm/sec
Det.: FID (225°C)
Inj.: 225°C
Figure J. Detailed Analysis of Naphtha Column: Petrocol DH 50.2, 50m x 0.20mm ID, 0.50µm film
Cat. No.: 24133
Oven: 35°C (30 min) to 200°C at 2°C/min
Carrier: helium, 19-21cm/sec
Det.: FID (225°C)
Inj.: 225°C

1. nC3 11. nC7
2. iC4 12. Methylcyclohexane
3. nC4 13. Toluene
4. iC5 14. nC8
5. nC5 15. m-Xylene
6. 2-Methylpentane 16. p-Xylene
7. nC6 17. nC9
8. Methylcyclopentane 18. nC10
9. Benzene 19. nC11
10. Cyclohexane 20. nC12

Figure K. Premium Unleaded Gasoline Column: SPB-Octyl, 60m x 0.25mm ID, 1.0µm film
Cat. No.: 24233
Col. Temp.: 35°C (15 min) 1°C/min to 200°C (15 min)
Carrier: helium, 20cm/sec (at 60°C)
Det.: FID, 250°C
Inj.: 1µL premium gasoline, split (100:1), 250°C

1. Isopentane 12. 2,3-Dimethylpentane 28. Isopropylbenzene
2. n-Pentane 13. 2,2,4-Trimethylpentane 29. n-Propylbenzene
3. Methyl tert-butyl ether 14. n-Heptane 30. 1-Methyl-3-ethylbenzene
4. Cyclopentane 15. Methylcyclohexane 2,3-Dimethyltoluene
5. 1-Hexene 16. 2,5-Dimethylhexane 31. 1-Methyl-2-ethylbenzene
6. n-Hexane 17. 2,4-Dimethylhexane 32. Isobutylbenzene
7. tert-Butyl ethyl ether 18. Toluene 33. Isobutylcyclohexane
8. cis-2-Hexene 19. Ethylcylopetanete 34. n-Decane
9. n-Butanol 20. 2-Methylpentane 35. 1-Methyl-4-isopropylbenzene
10. 1-Methylcyclopentene 21. 3-Methylpentane 36. 1-Methyl-4-n-propylbenzene
11. 2-Methylhexane 22. n-Octane 37. 1,3-Dimethyl-5-ethylbenzene
12. 3-Methylpentane 23. Ethylbenzene 38. 1,4-Dimethyl-2-ethylbenzene
13. 2,2,4-Trimethylpentane 24. p-Xylene 39. 1,2-Dimethyl-4-ethylbenzene
14. n-Heptane 25. m-Xylene 40. n-Lindane
15. Methylcyclohexane 26. n-Xylene 41. 1,2-Dimethyl-3-ethylbenzene
16. 2,5-Dimethylhexane 27. n-Nonane 42. 2-Methylbutylbenzene
17. 2,4-Dimethylhexane
18. Toluene
19. Ethylcyclopentane
20. 1-Methyl-3-ethylbenzene
21. Isobutylbenzene
22. Isobutylcyclohexane
23. n-Decane
24. 1-Methyl-4-isopropylbenzene
25. 1-Methyl-4-n-propylbenzene
26. 1,3-Dimethyl-5-ethylbenzene
27. 1,4-Dimethyl-2-ethylbenzene
28. 1,2-Dimethyl-4-ethylbenzene
29. 1,2-Dimethyl-3-ethylbenzene
30. 2-Methylbutylbenzene

Figure L. Hydrocarbon Pairs Resolved to Baseline Column: SPB-Octyl, 60m x 0.25mm ID, 1.0µm film
Cat. No.: 24233
Col. Temp.: 35°C (15 min) 1°C/min to 200°C (15 min)
Carrier: helium, 20cm/sec (at 60°C)
Det.: FID, 250°C
Inj.: 1µL benzene/1-methylcyclopentene mix (2:1), split (100:1), 250°C

1. Benzene
2. Toluene
3. 2,3,3-Trimethylpentane
4. 1-Methylcyclopentene
5. Ethylbenzene
6. n-Octane
7. 1-Methyl-3-ethylbenzene
8. 1-Methyl-4-isopropylbenzene
9. 1-Methyl-4-n-propylbenzene
10. 1,3-Dimethyl-5-ethylbenzene
11. 1,4-Dimethyl-2-ethylbenzene
12. 1,2-Dimethyl-4-ethylbenzene
13. 1,2-Dimethyl-3-ethylbenzene
14. 2-Methylbutylbenzene
15. 2,3,3-Trimethylpentane
16. 1-Methylcyclopentene
17. Ethylbenzene
18. n-Octane
19. 1-Methyl-3-ethylbenzene
20. 1-Methyl-4-isopropylbenzene
21. 1-Methyl-4-n-propylbenzene
22. 1,3-Dimethyl-5-ethylbenzene
23. 1,4-Dimethyl-2-ethylbenzene
24. 1,2-Dimethyl-4-ethylbenzene
25. 1,2-Dimethyl-3-ethylbenzene
26. 2-Methylbutylbenzene

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Figure M. Components of Premium Unleaded Gasoline

Column: Petrocol DH, 100m x 0.25mm ID, 0.50µm film
Cat. No.: 24160
Oven: 35°C (15 min) to 200°C at 2°C/min, hold 5 min
Carrier: helium, 20cm/sec
Det.: FID
Inj.: 0.1µL gasoline, split (100:1)

1. Isobutane
2. n-Butane
3. Isopentane
4. n-Pentane
5. 2,3-Dimethylbutane
6. 2-Methylpentane
7. 3-Methylpentane
8. n-Hexane
9. 2,4-Dimethylpentane
10. Benzene
11. 2-Methylhexane
12. 3-Methylhexane
13. 2,2,4-Trimethylpentane
14. n-Heptane
15. 2,5-Dimethylhexane
16. 2,4-Dimethylhexane
17. 2,3,4-Trimethylpentane
18. Toluene
19. 2,3-Dimethylhexane
20. Ethylbenzene
21. m-Xylene
22. p-Xylene
23. o-Xylene
24. 1-Methyl-3-ethylbenzene
25. 1,3,5-Trimethylbenzene
26. 1,2,4-Trimethylbenzene
27. 1,2,3-Trimethylbenzene
28. Naphthalene
29. 2-Methylnaphthalene
30. 1-Methylnaphthalene
31. Dimethylnaphthalenes
Figure P. C1-C5 Hydrocarbons

Column: Petrocol DH, 100m x 0.25mm ID, 0.50µm film
Cat. No.: 24160
Oven: -50°C (10 min) to 75°C at 5°C/min
Carrier: helium, 20cm/sec
Det.: FID
Inj.: 250µL nitrogen
   (5-10ppm each analyte), split (100:1)

1. Propylene
2. Ethylene
3. Acetylene
4. Ethane
5. Propane
6. Propene
7. Propadiene
8. Isobutane
9. Isobutylene
10. 1-Butene
11. 1,3-Butadiene
12. n-Butane
13. trans-2-Butene
14. cis-2-Butene
15. Isopentane
16. 1-Pentene
17. n-Pentane

Figure Q. Dicyclopentadiene (DCPD) Monitored for Breakdown Products

Column: Petrocol DH, 100m x 0.25mm ID, 0.50µm film
Cat. No.: 24160
Oven: 35°C (15 min) to 230°C at 2°C/min, hold 15 min
Carrier: helium, 20cm/sec
Det.: FID
Inj.: 0.1µL DCPD, split (100:1)

130°C Injection Temperature
   ! DCPD
   ! Essentially No
   ! CPD Monomer
   ! Higher Analogs

250°C Injection Temperature
   ! DCPD
   ! CPD Monomer

Figure N. Cyclopentane and 2,3-Dimethylbutane Resolved

Column: Petrocol DH, 100m x 0.25mm ID, 0.50µm film
Cat. No.: 24160
Oven: 35°C or 25°C (15 min) to 200°C at 2°C/min, hold 5 min
Carrier: helium, 20cm/sec
Det.: FID
Inj.: synthetic blend (1% cyclopentane,
   2% 2,3-dimethylbutane), split (100:1)

1. Cyclopentane
2. 2,3-Dimethylbutane

Figure O. A Difficult Separation – Isobutylene from 1-Butene

Column: Petrocol DH, 100m x 0.25mm ID, 0.50µm film
Cat. No.: 24160
Oven: -20°C (10 min) to 200°C at 2°C/min
Carrier: helium, 19cm/sec
Det.: FID
Inj.: 25µL Phillips L6 blend, split (100:1)

1. Propylene
2. Propane
3. Isobutane
4. 1,3-Butadiene
5. n-Butane
6. trans-2-Butene
7. cis-2-Butene
**Figure R. Closely Eluting Olefin (Hexene) Isomerization Products**

- **Column:** Petrocol DH, 100m x 0.25mm ID, 0.50µm film
- **Cat. No.:** 24160
- **Oven:** 35°C (15 min) to 45°C at 2°C/min, hold 30 min
- **Det.:** FID
- **Inj.:** 3µL mixed hexene isomers, split (100:1)

1. cis-4-Methyl-2-pentene
2. trans-4-Methyl-2-pentene
3. 2-Methyl-2-pentene
4. cis-3-Methyl-2-pentene
5. trans-3-Methyl-2-pentene

**Figure S. ENB Isomers and VNB Isomers Can Be Quantified**

- **Column:** Petrocol DH, 100m x 0.25mm ID, 0.50µm film
- **Cat. No.:** 24160
- **Oven:** 35°C (15 min) to 200°C at 2°C/min
- **Det.:** FID
- **Inj.:** 0.05µL ENB/VNB mix, split (100:1)

1. endo-VNB
2. exo-VNB
3. trans-ENB
4. cis-ENB

**Figure T. Petroleum Reformate**

- **Column:** Petrocol DH, 100m x 0.25mm ID, 0.50µm film
- **Cat. No.:** 24160
- **Oven:** 35°C (15 min) to 200°C at 2°C/min
- **Det.:** FID (sensitivity in Fig. S = 4X sensitivity in Fig. R)
- **Inj.:** 0.1µL reformate, split (100:1)

1. Benzene
2. Toluene
3. Ethylbenzene
4. m-Xylene
5. p-Xylene
6. o-Xylene
7. 1-Methyl-3-ethylbenzene
8. 1,2,4-Trimethylbenzene
9. Naphthalene
10. 2-Methylnaphthalene
11. 1-Methylnaphthalene
12. Dimethylnaphthalenes

Better Than 40% Return to Baseline

C9-C10 Aromatics Well Resolved

Enlarged in Figure U
Figure U. High Resolution of Polynuclear Aromatic Hydrocarbons in Petroleum Reformer

Column: Petrocol DH, 100m x 0.25mm ID, 0.50µm film
Cat. No.: 24160
Oven: 35°C (15 min) to 200°C at 2°C/min
Det.: FID (sensitivity in Fig. S = 4X sensitivity in Fig. R)
Inj.: 0.1µL reformate, split (100:1)

9. Naphthalene
10. 2-Methylnaphthalene
11. 1-Methylnaphthalene
12. Dimethylnaphthalenes

Figure V. MTBE Contaminants Standard Resolved

Column: Petrocol DH, 100m x 0.25mm ID, 0.50µm film
Cat. No.: 24160
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. 4-7942) split (200:1) (250°C)

1. Methanol
2. Isopentane
3. n-Pentane
4. trans-2-Pentene
5. tert-Butanol
6. cis-2-Pentene
7. 2-Methyl-2-butenone MTBE
8. tert-Butyl ethyl ether
9. tert-Amyl methyl ether (TAME)
10. 2,4,4-Trimethyl-1-pentene
Triisobutylene Isomers:
11. 4,4-Dimethyl-2-neopentyl-1-pentene
12. 2,2,4,6,6-Pentamethyl-3-heptene

MTBE

Column: Petrocol DH, 100m x 0.25mm ID, 0.50µm film
Cat. No.: 24160
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. 4-7942) split (200:1) (250°C)

1. Methanol
2. Isopentane
3. n-Pentane
4. trans-2-Pentene
5. tert-Butanol
6. cis-2-Pentene
7. 2-Methyl-2-butenone MTBE
8. tert-Butyl ethyl ether
9. tert-Amyl methyl ether (TAME)
10. 2,4,4-Trimethyl-1-pentene
Triisobutylene Isomers:
11. 4,4-Dimethyl-2-neopentyl-1-pentene
12. 2,2,4,6,6-Pentamethyl-3-heptene

Column: Petrocol DH, 100m x 0.25mm ID, 0.50µm film
Cat. No.: 24160
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. 4-7942) split (200:1) (250°C)

1. Methanol
2. Isopentane
3. n-Pentane
4. trans-2-Pentene
5. tert-Butanol
6. cis-2-Pentene
7. 2-Methyl-2-butenone MTBE
8. tert-Butyl ethyl ether
9. tert-Amyl methyl ether (TAME)
10. 2,4,4-Trimethyl-1-pentene
Triisobutylene Isomers:
11. 4,4-Dimethyl-2-neopentyl-1-pentene
12. 2,2,4,6,6-Pentamethyl-3-heptene
Figure W. Detailed Analysis of Gasoline, Using Ambient Initial Temperature

Column: Petrocol DH 150, 150m x 0.25mm ID, 1.0µm film
Cat. No.: 24155
Oven: 35°C (125 min) to 200°C at 2°C/min
Carrier: helium, 20cm/sec
Det.: FID
Inj.: 0.1µL unleaded gasoline, split (100:1)

1. n-Butane
2. Isopentane
3. n-Pentane
4. 2,2-Dimethylbutane
5. Cyclopentane
6. 2,3-Dimethylbutane
7. 2-Methylpentane
8. 3-Methylpentane
9. n-Hexane
10. 2,4-Dimethylpentane
11. Benzene
12. 2-Methylhexane
13. 2,3-Dimethylpentane
14. 3-Methylhexane
15. 2,2,4-Trimethylpentane
16. n-Heptane
17. 2,5-Dimethylhexane
18. 2,4-Dimethylhexane
19. 2,3,4-Trimethylpentane
20. Toluene
21. 2,3,3-Trimethylpentane
22. 2,4-Dimethylpentane
23. 2-Methylheptane
24. 3-Methylheptane
25. 2-Methyl-1-heptene
26. n-Octane
27. Ethylbenzene
28. m-Xylene
29. p-Xylene
30. o-Xylene
31. 1-Nonene
32. n-Nonane
33. Isopropylbenzene
34. 3,3,5-Trimethylpyridine
35. 2,4,5-Trimethylpyridine
36. n-Propylbenzene
37. 1-Methyl-3-ethylbenzene
38. 1-Methyl-4-ethylbenzene
39. 1,3,5-Trimethylbenzene
40. 3,3,4-Trimethylpyridine
41. 1-Methyl-2-ethylbenzene
42. 1,2,4-Trimethylbenzene
43. Isobutylbenzene
44. sec-Butylbenzene
45. n-Decane
46. 1,2,3-Trimethylbenzene
47. Indane
48. 1,3-Diethylbenzene
49. n-Butylbenzene
50. 1,4-Dimethyl-2-ethylbenzene
51. 1,3-Dimethyl-4-ethylbenzene
52. 1,2-Dimethyl-4-ethylbenzene
53. 1,2,4-Trimethylbenzene
54. 1,2,3,5-Tetramethylbenzene
55. Naphthalene
56. 2-Methylnaphthalene
57. 1-Methylnaphthalene
58. Dimethylnaphthalenes
Figure X. Xylene Isomers, Using Isothermal Temperature

Column: Petrocol DH 150, 150m x 0.25mm ID, 1.0µm film
Cat. No.: 24155
Oven: 75°C
Carrier: helium, 20cm/sec
Det.: FID
Inj.: 0.1µL cyclohexane
(4% m-xylene, 2% p-xylene), split (100:1)

1. m-Xylene
2. p-Xylene

Figure Z. Light n-Paraffins and 1-Olefins, Using Ambient Initial Temperature

Column: Petrocol DH 150, 150m x 0.25mm ID, 1.0µm film
Cat. No.: 24155
Oven: 25°C (15 min) to 200°C at 5°C/min
Carrier: helium, 20cm/sec
Det.: FID
Inj.: 250µL nitrogen (approx. 50ppm each analyte), split (100:1)

1. Methane
2. Ethylene
3. Ethane
4. Propylene
5. Propane
6. 1-Butene
7. n-Butane
8. cis-2-Butene
9. 1-Pentene
10. n-Pentane
11. 1-Hexene
12. n-Hexane

Figure Y. Gaseous and Liquid Hydrocarbons Resolved

Column: Petrocol DH 150, 150m x 0.25mm ID, 1.0µm film
Cat. No.: 24155
Oven: 35°C
Carrier: helium, 20cm/sec
Det.: FID
Inj.: 25µL natural or liquified petroleum gas, split (100:1)

Natural Gas Standard
1. Methane
2. Ethane
3. Propane
4. Isobutane
5. n-Butane
6. Isopentane
7. n-Pentane

Figure AA. Oxygenated Compounds in a C4 Gas Stream, Using Ambient Isothermal Temperature

Column: Petrocol DH 150, 150m x 0.25mm ID, 1.0µm film
Cat. No.: 24155
Oven: 25°C
Carrier: helium, 20cm/sec
Det.: FID
Inj.: 50µL nitrogen (0.1-2% each analyte), split (100:1)

1. Ethane
2. Propylene
3. Propane
4. Dimethylether
5. Isobutane
6. Methanol
7. Isobutylene
8. 1-Butene
9. n-Butane
10. trans-2-Butene
11. cis-2-Butene
12. Ethanol
13. n-Pentane
14. Methyl tert-butylether

Liquified Petroleum Gas Standard
1. Ethane
2. Propylene
3. Propane
4. Isobutane
5. n-Butane
6. Isopentane
Figure AB. Light Hydrocarbons, Using Moderately Subambient Initial Temperature

<table>
<thead>
<tr>
<th>Column:</th>
<th>Petrocol DH 150, 150m x 0.25mm ID, 1.0µm film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat. No.:</td>
<td>24155</td>
</tr>
<tr>
<td>Oven:</td>
<td>-20°C (30 min) to 75°C at 5°C/min</td>
</tr>
<tr>
<td>Carrier:</td>
<td>helium, 20cm/sec</td>
</tr>
<tr>
<td>Det.:</td>
<td>FID</td>
</tr>
<tr>
<td>Inj.:</td>
<td>250µL nitrogen (0.1-1% each analyte), split (100:1)</td>
</tr>
</tbody>
</table>

Isobutylene and 1-Butene Are Well Resolved at 0°C Initial Temperature

1. Ethane
2. Propylene
3. Propane
4. Isobutane
5. Isobutylene
6. 1-Butene
7. n-Butane
8. trans-2-Butene
9. cis-2-Butene
10. Isopentane
11. 1-Pentene

Figure AC. C1-C3 Hydrocarbons

<table>
<thead>
<tr>
<th>Column:</th>
<th>Petrocol DH 150, 150m x 0.25mm ID, 1.0µm film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat. No.:</td>
<td>24155</td>
</tr>
<tr>
<td>Oven:</td>
<td>-50°C (25 min) to 75°C at 5°C/min</td>
</tr>
<tr>
<td>Carrier:</td>
<td>helium, 20cm/sec</td>
</tr>
<tr>
<td>Det.:</td>
<td>FID</td>
</tr>
<tr>
<td>Inj.:</td>
<td>250µL nitrogen (5-10ppm each analyte), split (100:1)</td>
</tr>
</tbody>
</table>

Ordering Information:

Capillary Columns for Detailed Hydrocarbon Analyses

- **SPB-1 Wide Bore Column**
  - 60m x 0.75mm ID glass, 1.0µm film
  - Cat. No.: 23720-U

- **SP-2100 Column**
  - 30m x 0.25mm ID, fused silica, 0.25µm film
  - Cat. No.: 24007

- **SUPELCOWAX 10 Column**
  - 30m x 0.20mm ID fused silica, 0.20µm film
  - Cat. No.: 24169

- **Petrocol DH 50.2 Column**
  - 50m x 0.20mm ID fused silica, 0.50µm film
  - Cat. No.: 24133-U

- **Petrocol DH Column**
  - 100m x 0.25mm ID fused silica, 0.50µm film
  - Cat. No.: 24160-U

- **Petrocol DH 150 Column**
  - 150m x 0.25mm ID fused silica, 1.0µm film
  - Cat. No.: 24155

- **SPB-Octyl Column**
  - 60m x 0.25mm ID fused silica, 1.0µm film
  - Cat. No.: 24233-U

Test Mixes

- **Polar Test Mix**, 2mL
  - For evaluating performance of SUPELCOWAX 10 capillary columns
  - Cat. No.: 47302

- **Nonpolar Test Mix**, 2mL
  - For evaluating performance of Petrocol DH 50.2 (50-meter) and Petrocol DH 150 (150-meter) capillary columns
  - Cat. No.: 47300-U

- **Petrocol DH Test Mix**, 1mL
  - nC6 through nC9, benzene, and toluene (1% each), m-xylene (4%), and p-xylene (2%) in cyclohexane.
  - For evaluating performance of Petrocol DH (100-meter) capillary columns.
  - Cat. No.: 48872

Petrochemical Standards for Hydrocarbon Analyses

- **n-Paraffin Standards**
  - For determining retention indices.
  - Neat, total 500mg
    - C5, C6, C7, C8
    - Cat. No.: 47100
    - C7, C8, C9, C10
    - Cat. No.: 47101
    - C10, C12, C14, C16
    - Cat. No.: 47102
  - Mixes, total 250mg/5mL n-octane
    - C18, C20, C22, C24
    - Cat. No.: 47108
    - C22, C24, C28, C32
    - Cat. No.: 47106
    - C24, C28, C32, C36
    - Cat. No.: 47107

Qualitative Reference Standards

- 6 x 1mL
  - **Naphtha**
    - Cat. No.: 48265-U
  - **Reformate**
    - Cat. No.: 48266
  - **Alkylate**
    - Cat. No.: 48267-U
  - **Refinery Kit (2 x 1mL of each of above)**
    - Cat. No.: 48268
Quantitative Reference Standards

<table>
<thead>
<tr>
<th>Composition</th>
<th>Retention Indices</th>
<th>Cat. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins Mix, 0.1mL</td>
<td>500.0-1500.0</td>
<td>44585-U</td>
</tr>
<tr>
<td>(11 n-paraffins)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isoparaffins Mix, 0.1mL</td>
<td>483.4-974.2</td>
<td>44586-U</td>
</tr>
<tr>
<td>(35 isoparaffins)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aromatics Mix, 0.1mL</td>
<td>638.6-1247.2</td>
<td>44587</td>
</tr>
<tr>
<td>(37 aromatics)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthenes Mix, 0.1mL</td>
<td>549.0-1146.9</td>
<td>44588</td>
</tr>
<tr>
<td>(29 naphthenes)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Olefins Mix, 0.1mL</td>
<td>457.4-988.7</td>
<td>44589</td>
</tr>
<tr>
<td>(28 olefins)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-I-A-N-O Mix, 0.1mL</td>
<td>457.4-1500.0</td>
<td>4-4593-U</td>
</tr>
<tr>
<td>(140 components in 5 class mixes above)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-I-A-N-O Kit (0.1mL P-I-A-N-O Mix, 0.1mL each of 5 class mixes)</td>
<td>457.4-1500.0</td>
<td>4-4594-U</td>
</tr>
</tbody>
</table>

For additional hydrocarbon standards, please see the latest Supelco Catalog.

Useful Information

**Chromatography in Petroleum Analysis**

Chromatography Science Series (Vol. II)

Edited by K.H. Altgelt and T.H. Gouw

Marcel Dekker, Inc. · 1979 · 500pp

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