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Bulletin 868A

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.

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 60 m x 0.75 mm I.D. 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 (0.25 mm I.D.) 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 30 m x 0.20 mm I.D. 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 0.20 mm I.D. 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, naphthene, and olefin* content of many samples is critical for process control and product quality testing.

Good results have been obtained with 50 m x 0.20 mm I.D. fused silica capillary columns coated with 0.50 µm of nonpolar methyl silicone phase. Developed specifically for this type of application, 50 m x 0.20 mm I.D. 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 (PIANO 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 methylsilicone 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 coelute 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 (0.20 mm I.D.) 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 100 m x 0.25 mm I.D. 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 100 m x 0.25 mm I.D. column also can be used in place of a 50 m x 0.20 mm I.D. 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 accurately 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.

ENB – VNB Isomers

5-Ethylidene-2-norbornene (ENB) is a cyclic diolefin monomer used in vulcanizing ethylene and propylene terpolymer rubber. ENB typically consists of *cis* and *trans* isomers, and can also contain quantities of the endo and exo forms of 5-vinyl-2-norbornene (VNB). VNB isomers are particularly difficult to separate, usually requiring an exotic stationary phase. A Petrocol DH column easily separates the ENB isomers from each other and from the VNB isomers (Figure S). The VNB isomers are separated with approximately 40% return to baseline – sufficient for reasonably accurate measurements of individual isomer levels.

Reformates

Aromatics-rich petroleum fractions, such as reformates, commonly are added to gasoline to boost its octane value. C8-C12 range aromatic fractions are complex, due to the large number of isomers present. In addition, many reformates contain high boiling components, such as dimethylnaphthalenes. Under ambient conditions, a Petrocol DH column partially separates the m-xylene and p-xylene isomers (better than 40% return to baseline) – compounds that boil only 1 °C apart (Figure T). Thus, a Petrocol DH column will ensure reasonably accurate quantification of these isomers, which most nonpolar capillary columns cannot separate at all.

Peaks representing C9-C10 aromatics are well resolved, and many of these compounds can be identified from the retention index data included with each Petrocol DH column. A Petrocol DH column also separates most dimethylnaphthalene isomers. The polynuclear aromatic hydrocarbon region of a reformate sample is highlighted in Figure U, to show the high degree of resolution of these components.

MTBE Product

The analysis of methyl tert-butyl ether (MTBE) product, an important performance-enhancing oxygenated additive for gasoline, requires high resolution capillary columns in order to resolve several key impurities that may be found in the product. American Society for Testing and Materials (ASTM) Method D5441 specifies Petrocol columns as capable in providing sufficient resolution of these impurities. Figure V shows the separation of a synthetic MTBE standard containing many of the common impurities found in MTBE product. The 100 m x 0.25 mm I.D. x 0.5 µm Petrocol DH column provides sufficient resolution of trans-2-pentene, tert-butanol, and cis-2-pentene to meet the stringent requirements of the method.

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 (1.0 µm), 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 (0.25 mm I.D., 1.0 µm phase film; $\beta = 63$). 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 liquifaction 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 75 psi of helium for optimum linear velocity. The head pressure requirement can be reduced to approximately 50 psi 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 20-50 ppm 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 5 ppm (10 ppm 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

column: 80/100 Carbopack C/0.19% picric acid, 2 m x 1/8" stainless steel (11824, 15 g)
oven: 35 °C to 70 °C at 6 °C/min.
det.: FID
carrier gas: nitrogen, 30 mL/min.

1.	Methane	10 ppm
2.	Acetylene	15 ppm
	Ethylene	10 ppm
	Ethane	10 ppm
3.	Cyclopropane	
4.	Propane	10 ppm
5.	Propylene	5 ppm
6.	Propyne	12.6 ppm
7.	Isobutane	365 ppm
8.	1-Butene	210 ppm
9.	n-Butane	130 ppm
10.	1-Butyne	13 ppm
11.	Isobutylene	120 ppm
12.	cis-2-Butene	60 ppm
13.	trans-2-Butene	70 ppm
14.	2-Butene	10 ppm
15.	1,3-Butadiene	10 ppm
16.	Isopentane	15 ppm
17.	n-Pentane	5 ppm

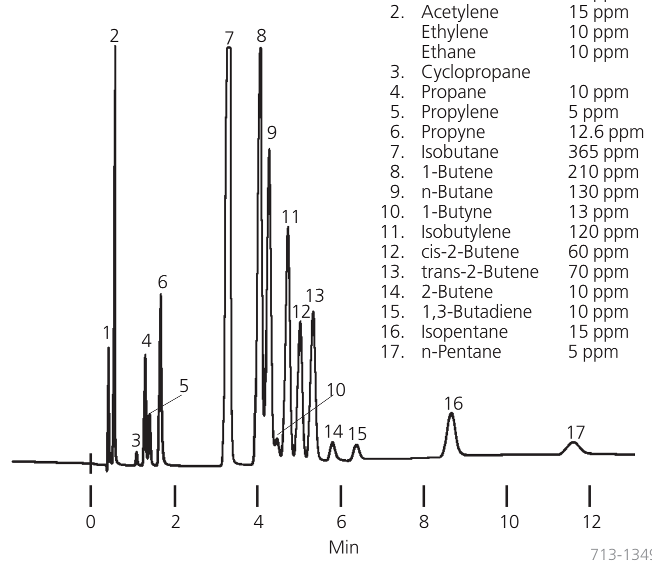

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Figure B. C2-C6 Saturated and Unsaturated Hydrocarbons

column: 23% SP-1700 on 80/100 Chromosorb® P AW, 30' x 1/8" stainless steel (11865, 25 g)
oven: 70 °C
det.: FID
carrier gas: helium, 25 mL/min.
injection: 0.6 µL ASTM Section L Blend No. 6, plus C5s

1.	Ethane	11.	n-Pentane
2.	Propane	12.	1-Pentene
3.	Propylene	13.	2-Methyl-1-butene
4.	Isobutane		trans-2-Pentene
5.	n-Butane	14.	cis-2-Pentene
6.	1-Butene	15.	2-Methyl-2-butene
	Isobutylene	16.	2-Methyl-1-pentane
7.	trans-2-Butene	17.	3-Methyl-1-pentane
8.	cis-2-Butene	18.	n-Hexane
9.	Isopentane	U	Unknown
10.	1,3-Butadiene	19.	3-Methylhexane

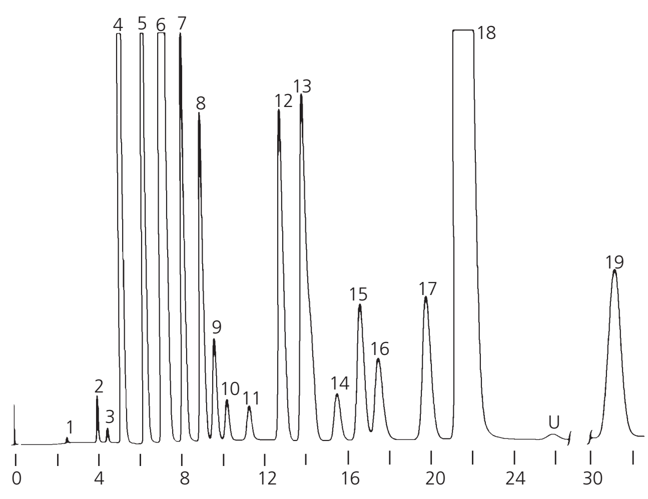

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Figure C. Gasoline on a Capillary Column in a Packed Column Chromatograph

column: SPB-1, 60 m x 0.75 mm I.D., 1.0 µm film (23720)
oven: 35 °C (12 min.) to 200 °C at 4 °C/min., hold
det.: TCD
carrier gas: helium,5 cc/min. (flow controlled)
injection: 0.4 µL gasoline, direct injection

1. Air
2. Propane
3. Isobutane
4. n-Butane
5. Isopentane
6. n-Pentane
7. 2-Methylpentane
8. 3-Methylpentane
9. n-Hexane
10. Methylcyclopentane
11. 2,4-Dimethylpentane
12. Benzene
13. Cyclohexane
14. 2-Methylhexane
15. 3-Methylhexane
16. n-Heptane
17. 2,4-Dimethylhexane
18. Toluene
19. 2-Methylheptane
    4-Methylheptane
20. 3-Methylheptane
21. n-Octane
22. Ethylbenzene
23. m-Xylene
    p-Xylene
24. 2-Methyloctane
25. 3-Methyloctane
26. o-Xylene
27. n-Nonane
28. Propylbenzene
29. n-Decane
30. n-Undecane

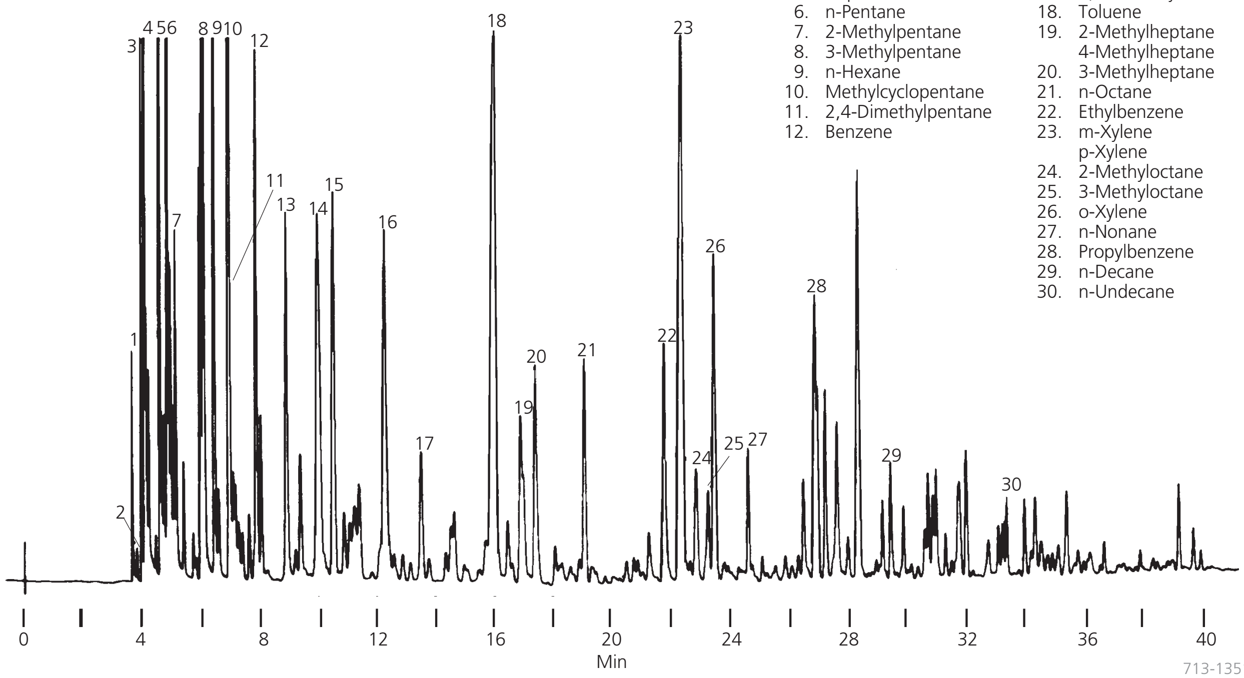

Figure D. Jet Kerosene

column: SP-2100, 30 m x 0.25 mm I.D., 0.25 µm film (24007)
oven: 50 °C to 200 °C at 2 °C/min.
det.: FID
carrier gas: helium, 20 cm/sec.
injection: 0.1 µL kerosene, split (100:1)

1. C9
2. C10
3. C11
4. C12
5. C13
6. C14
7. C15
8. C16
9. C17
10. C18

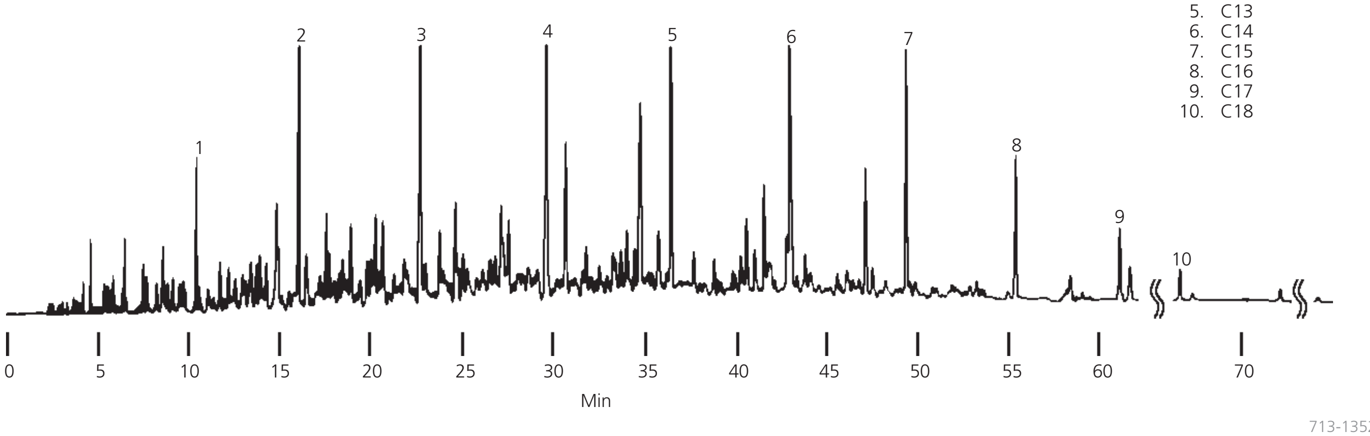

Figure E. Aromatics in Gasoline

column: SUPELCOWAX 10, 30 m x 0.20 mm I.D., 0.20 µm film (24169)
oven: 60 °C (8 min.) to 210 °C at 8 °C/min.
det.: FID
carrier gas: helium, 25 cm/sec.
injection: 0.1 µL gasoline, split (150:1)

1. Benzene
2. Toluene

C8 Aromatics
3. Ethylbenzene
4. p-Xylene
5. m-Xylene
6. o-Xylene

C9 Aromatics
7. Isopropylbenzene
8. n-Propylbenzene
9. 1-Methyl-4-ethylbenzene
10. 1-Methyl-3-ethylbenzene
11. 1,3,5-Trimethylbenzene
12. 1-Methyl-2-ethylbenzene
13. 1,2,4-Trimethylbenzene
14. 1,2,3-Trimethylbenzene
15. Indane

C10 Aromatics
16. tert-Butylbenzene
17. Isobutylbenzene
18. sec-Butylbenzene
19. 1-Methyl-3-isopropylbenzene
20. 1-Methyl-4-isopropylbenzene
21. 1,3-Diethylbenzene
22. 1-Methyl-2-isopropylbenzene
23. 1-Methyl-3-n-propylbenzene
24. 1-Methyl-4-n-propylbenzene
25. 1,4-Diethylbenzene
26. n-Butylbenzene
27. 1,3-Dimethyl-5-ethylbenzene
28. 1,2-Diethylbenzene
29. 1-Methyl-2-n-propylbenzene
30. 1,4-Dimethyl-2-ethylbenzene
31. 1,3-Dimethyl-4-ethylbenzene
32. 1,2-Dimethyl-4-ethylbenzene
33. 1,3-Dimethyl-2-ethylbenzene
34. 1,2-Dimethyl-3-ethylbenzene
35. 1,2,4,5-Tetramethylbenzene
36. 1,2,3,5-Tetramethylbenzene
37. 1,2,3,4-Tetramethylbenzene

Polynuclear Aromatics
38. Naphthalene
39. 2-Methylnaphthalene
40. 1-Methylnaphthalene
41. Dimethylnaphthalenes

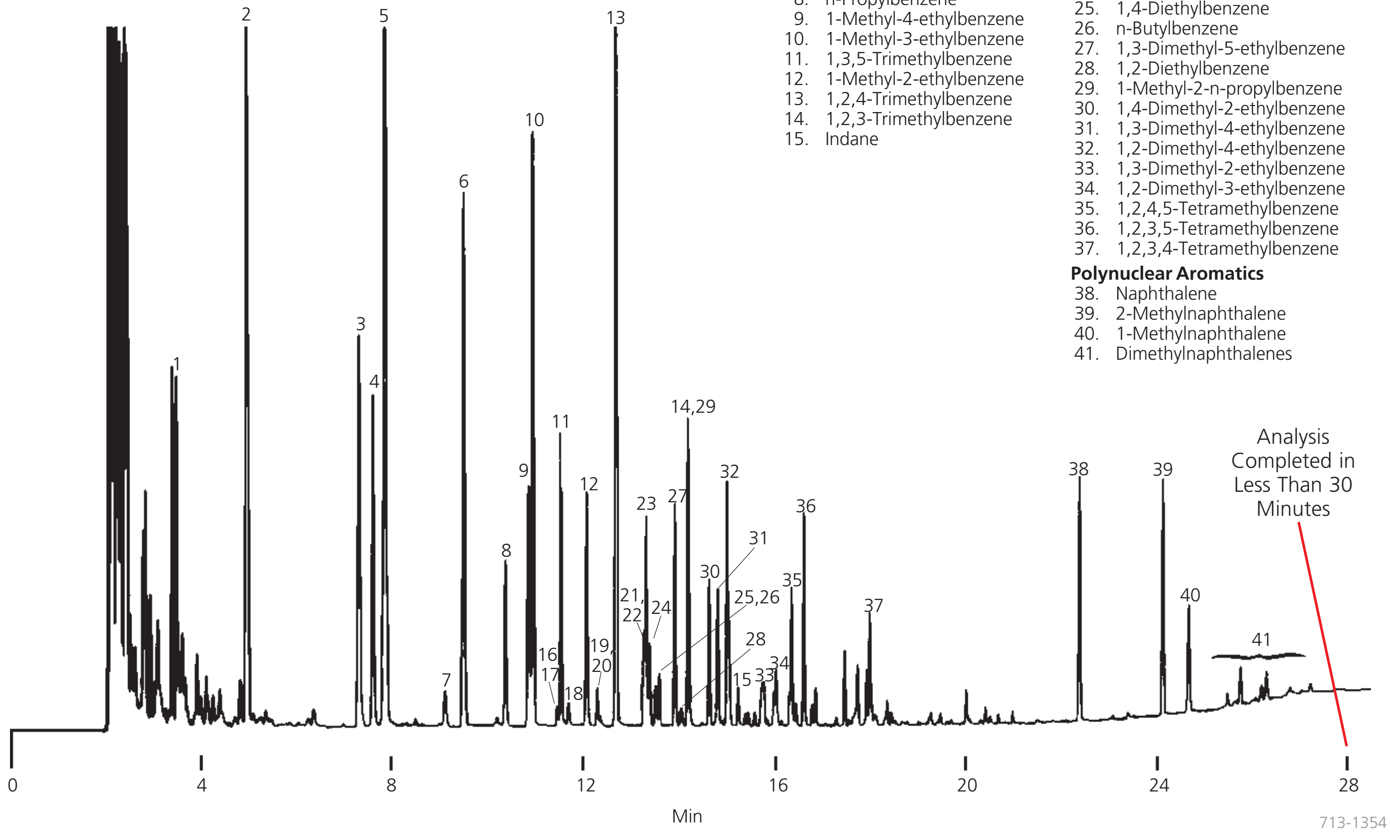

Figure F. Xylene Isomers

column: SUPELCOWAX 10, 30 m x 0.20 mm I.D., 0.20 µm film (24169)
oven: 60 °C
det.: FID
carrier gas: helium, 25 cm/sec.
injection: 0.1 µL p-xylene product, split (150:1)

1. Ethylbenzene
2. Toluene
3. p-Xylene
4. m-Xylene
5. o-Xylene

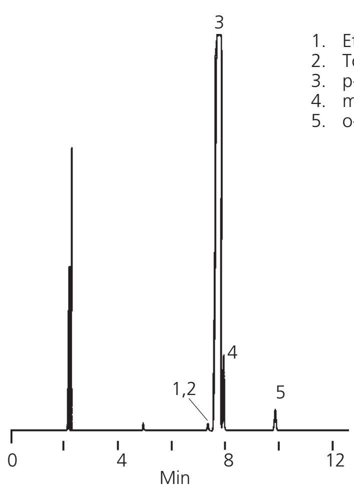

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Figure G. Xylene Isomers and Other Aromatic Compounds

column: SUPELCOWAX 10, 30 m x 0.20 mm I.D., 0.20 µm film (24169)
oven: 75 °C
det.: FID
carrier gas: helium, 25 cm/sec.
injection: 0.1 µL hexane (1.7% each analyte), split (150:1)

1. Benzene
2. Toluene
3. Ethylbenzene
4. p-Xylene
5. m-Xylene
6. o-Xylene

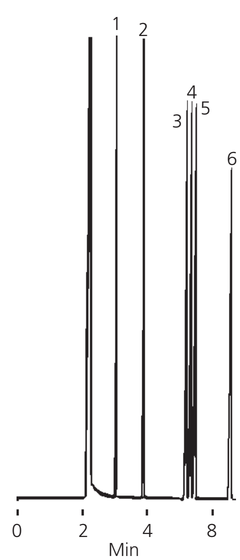

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Figure H. Gasoline on a 50-Meter Petrocol DH 50.2 Column

column: Petrocol DH 50.2, 50 m x 0.20 mm I.D., 0.50 µm film (24133)
oven: 35 °C (30 min.) to 200 °C at 2 °C/min.
det.: FID (225 °C)
carrier gas: helium, 19-21 cm/sec.
injection: 225 °C

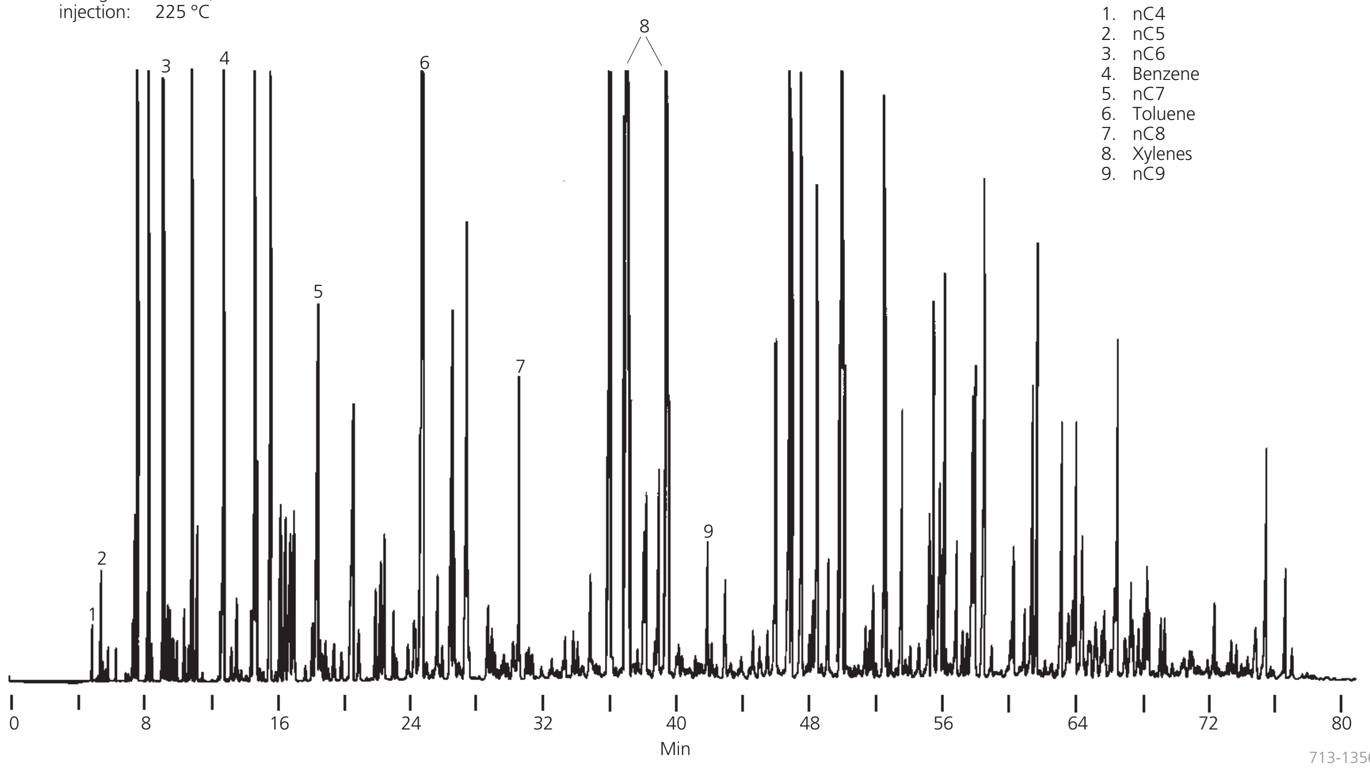


Figure I. Reformate on a Petrocol DH 50.2 Column

column: Petrocol DH 50.2, 50 m x 0.20 mm I.D., 0.50 µm film (24133)
oven: 35 °C (30 min.) to 200 °C at 2 °C/min.
det.: FID (225 °C)
carrier gas: helium, 19-21 cm/sec.
injection: 225 °C

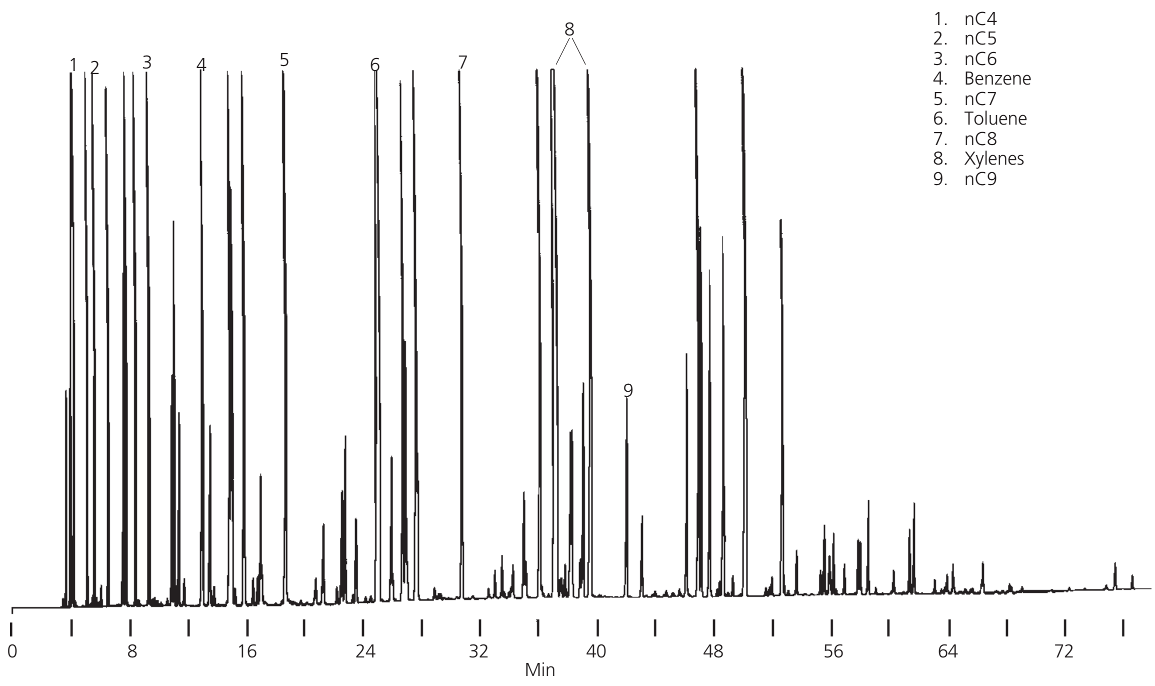


Figure J. Detailed Analysis of Naphtha

column: Petrocol DH 50.2, 50 m x 0.20 mm I.D., 0.50 µm film (24133)
oven: 35 °C (30 min.) to 200 °C at 2 °C/min.
det.: FID (225 °C)
carrier gas: helium, 19-21 cm/sec.
injection: 225 °C

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

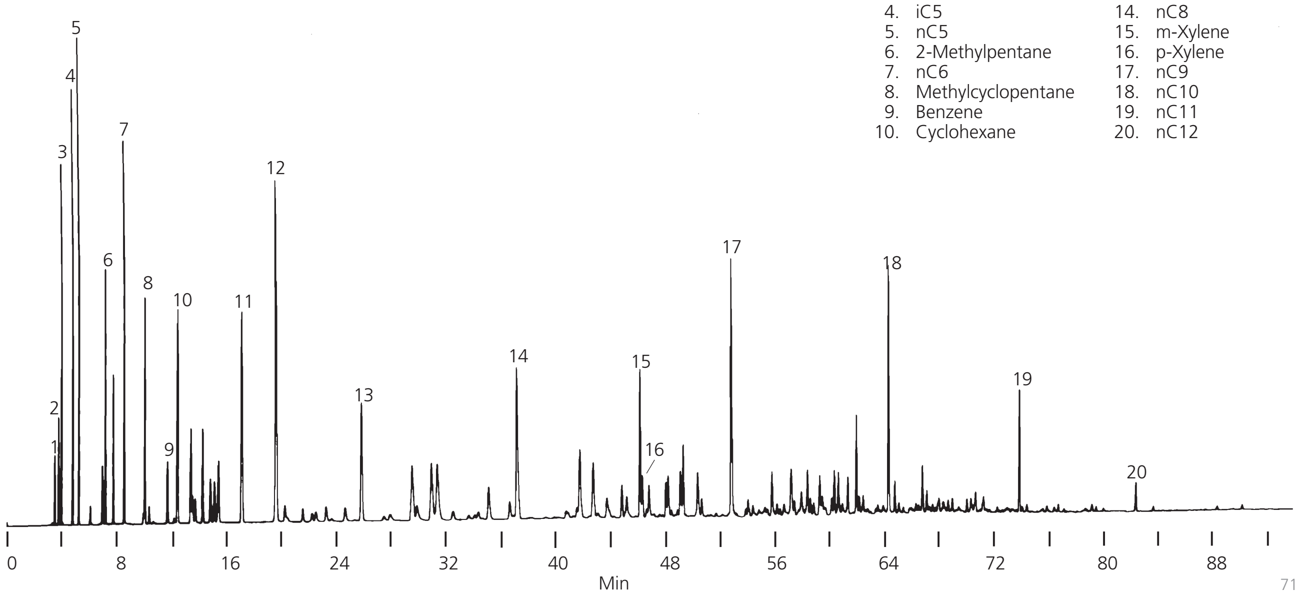


Figure K. Premium Unleaded Gasoline

column: SPB-Octyl, 60 m x 0.25 mm I.D., 1.0 µm film (24233)
oven: 35 °C (15 min.) 1 °C/min. to 200 °C (15 min.)
det.: FID, 250 °C
carrier gas: helium, 20 cm/sec. (at 60 °C)
injection: 1 µL premium gasoline, split (100:1), 250 °C

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

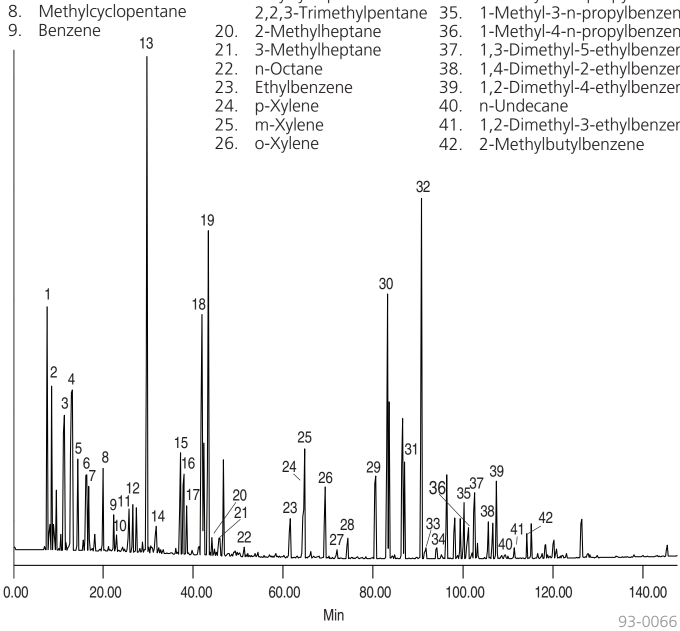


Figure L. Hydrocarbon Pairs Resolved to Baseline

column: SPB-Octyl, 60 m x 0.25 mm I.D., 1.0 µm film (24233)
oven: 35 °C (15 min.) 1 °C/min. to 200 °C (15 min.)
det.: FID, 250 °C
carrier gas: helium, 20 cm/sec. (at 60 °C)
injection: 1 µL benzene/1-methylcyclopentene mix (2:1), 1 µL toluene/2,3,3-trimethylpentane mix (2:1), split (100:1), 250 °C

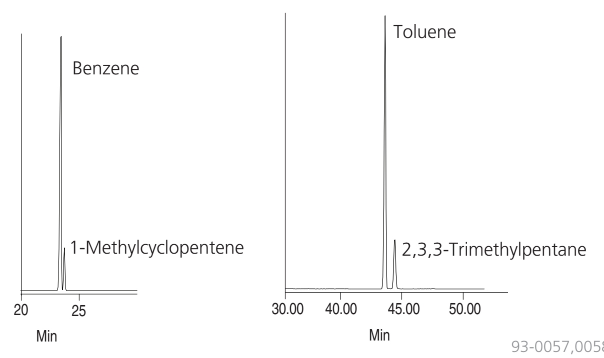
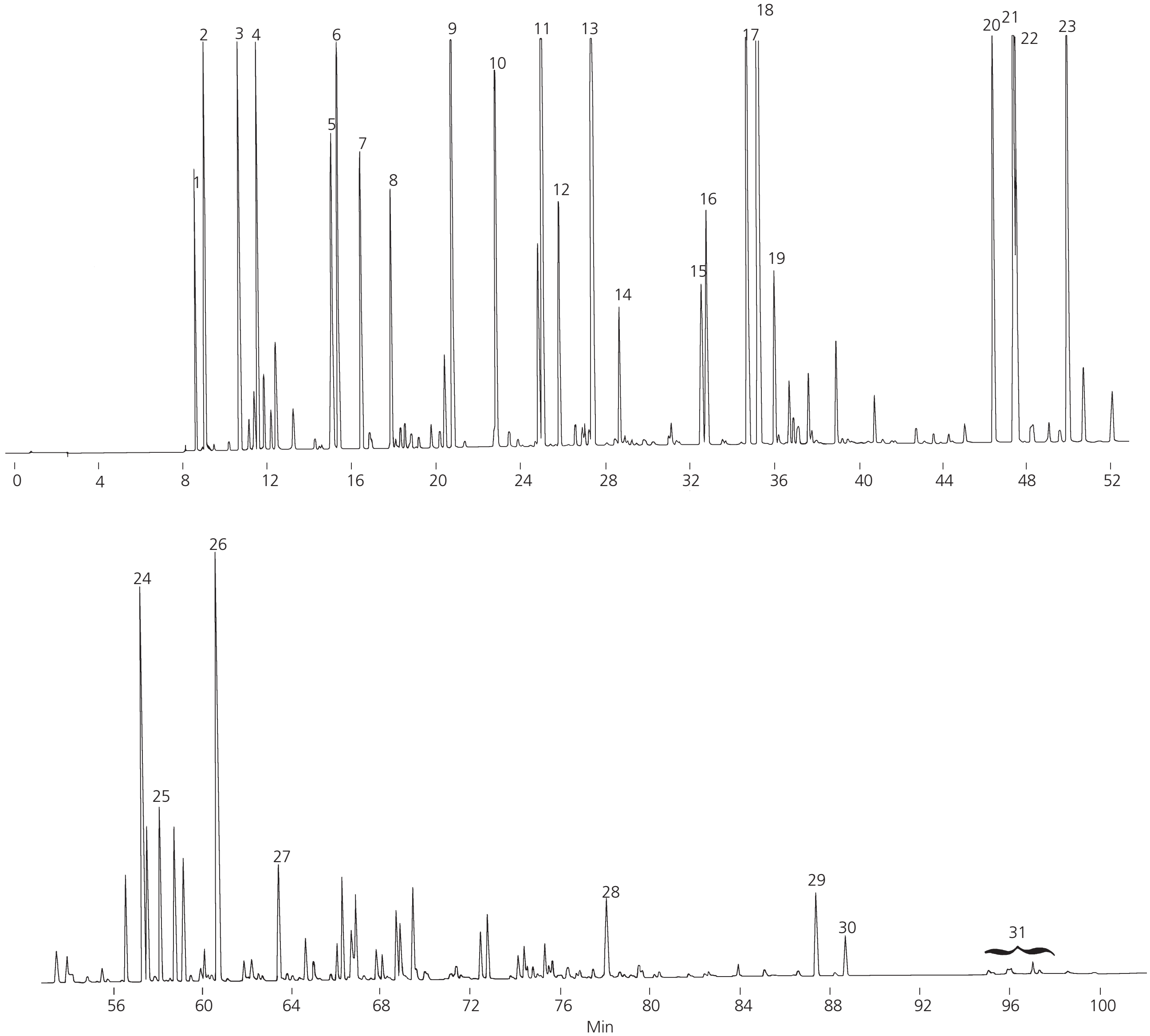


Figure M. Components of Premium Unleaded Gasoline

column: Petrocol DH, 100 m x 0.25 mm I.D., 0.50 µm film (24160)
oven: 35 °C (15 min.) to 200 °C at 2 °C/min., hold 5 min.
det.: FID
carrier gas: helium, 20 cm/sec.
injection: 0.1 µL gasoline, split (100:1)

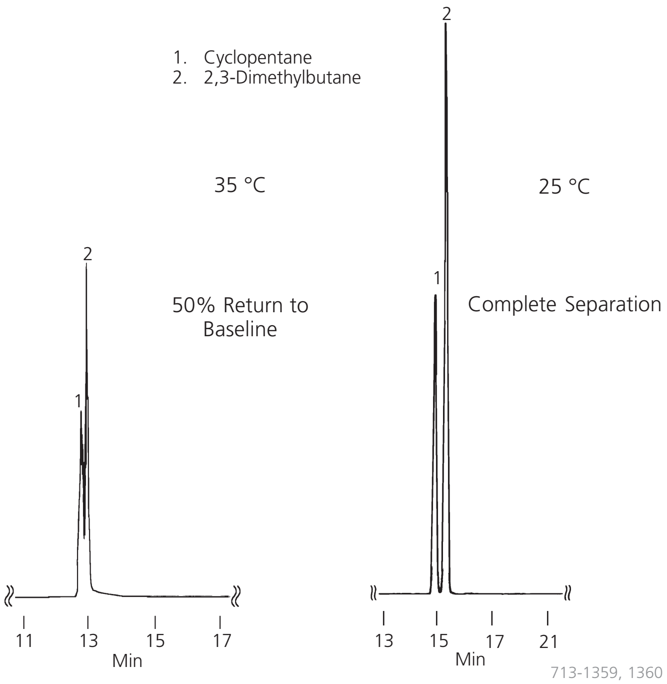
1. Isobutane
2. n-Butane
3. Isopentane
4. n-Pentane
5. 2,3-Dimethylbutane
6. 2-Methylpentane
7. 3-Methylpentane
8. n-Hexane
9.. 2,4-Dimethylpentane
10. Benzene
11. 2-Methylhexane
12. 3-Methylhexane
13. 2,2,4-Trimethylpentane
14. n-Heptane
15. 2,5-Dimethylhexane
16. 2,4-Dimethylhexane
17. 2,3,4-Trimethylpentane
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



713-1274, 0744

Figure N. Cyclopentane and 2,3-Dimethylbutane Resolved

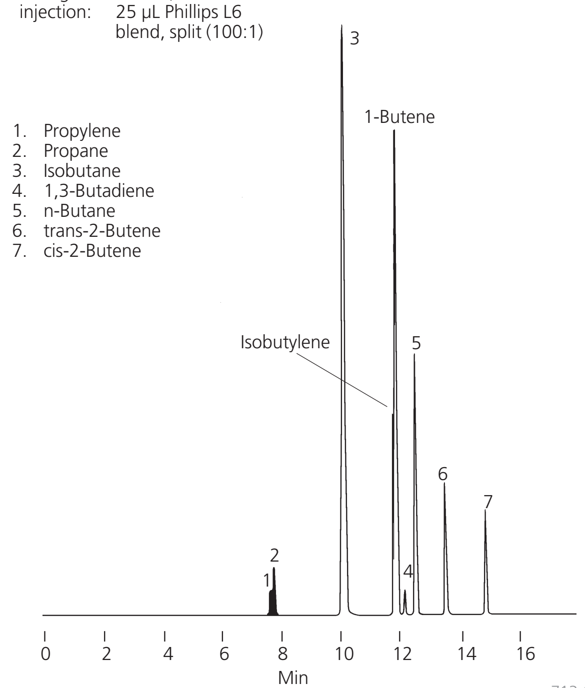
column: Petrocol DH, 100 m x 0.25 mm I.D., 0.50 µm film (24160)
oven: 35 °C or 25 °C (15 min.) to 200 °C at 2°C/min., hold 5 min.
det.: FID
carrier gas: helium, 20 cm/sec.
injection: synthetic blend (1% cyclopentane, 2% 2,3-dimethylbutane), split (100:1)



713-1359, 1360

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

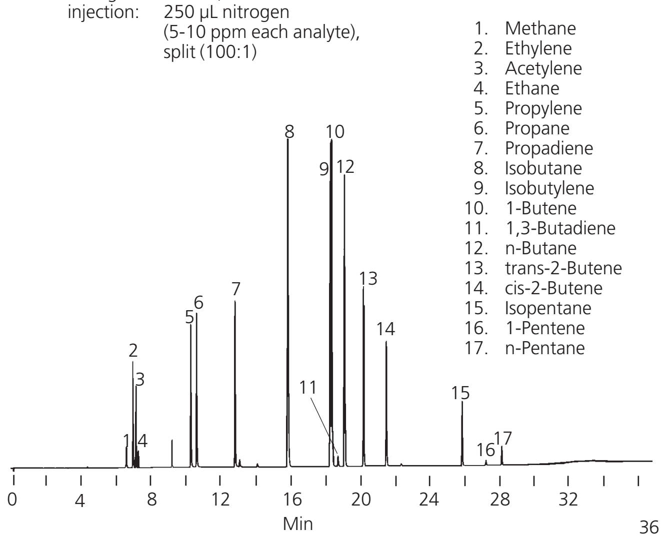
column: Petrocol DH, 100 m x 0.25 mm I.D., 0.50 µm film (24160)
oven: -20 °C (10 min.) to 200 °C at 2 °C/min.
det.: FID
carrier gas: helium, 19 cm/sec.
injection: 25 µL Phillips L6 blend, split (100:1)



713-0740

Figure P. C1-C5 Hydrocarbons

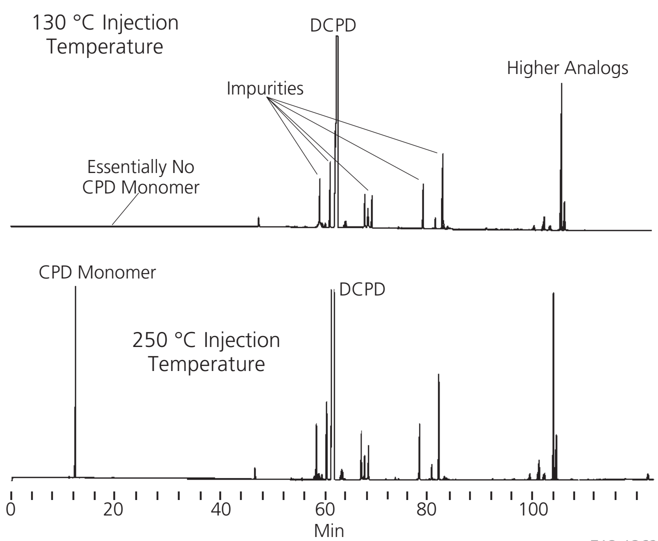
column: Petrocol DH, 100 m x 0.25 mm I.D., 0.50 µm film (24160)
oven: -50 °C (10 min.) to 75 °C at 5 °C/min.
det.: FID
carrier gas: helium, 20 cm/sec.
injection: 250 µL nitrogen (5-10 ppm each analyte), split (100:1)



713-1361

Figure Q. Dicyclopentadiene (DCPD) Monitored for Breakdown Products

column: Petrocol DH, 100 m x 0.25 mm I.D., 0.50 µm film (24160)
oven: 35 °C (15 min.) to 230 °C at 2 °C/min., hold 15 min.
det.: FID
carrier gas: helium, 20 cm/sec.
injection: 0.1 µL DCPD, split (100:1)



713-1362

Figure R. Closely Eluting Olefin (Hexene) Isomerization Products

column:	Petrocol DH, 100 m x 0.25 mm I.D., 0.50 µm film (24160)
oven:	35 °C (15 min.) to 45 °C at 2 °C/min., hold 30 min.
det.:	FID
injection:	3 µL mixed hexene isomers, split (100:1)

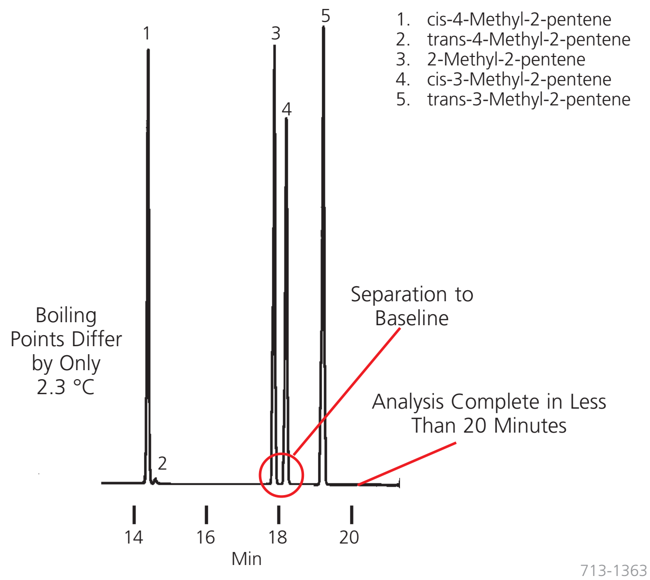


Figure S. ENB Isomers and VNB Isomers Can Be Quantified

column:	Petrocol DH, 100 m x 0.25 mm I.D., 0.50 µm film (24160)
oven:	35 °C (15 min.) to 200 °C at 2 °C/min.
det.:	FID
injection:	0.05 µL ENB/VNB mix, split (100:1)

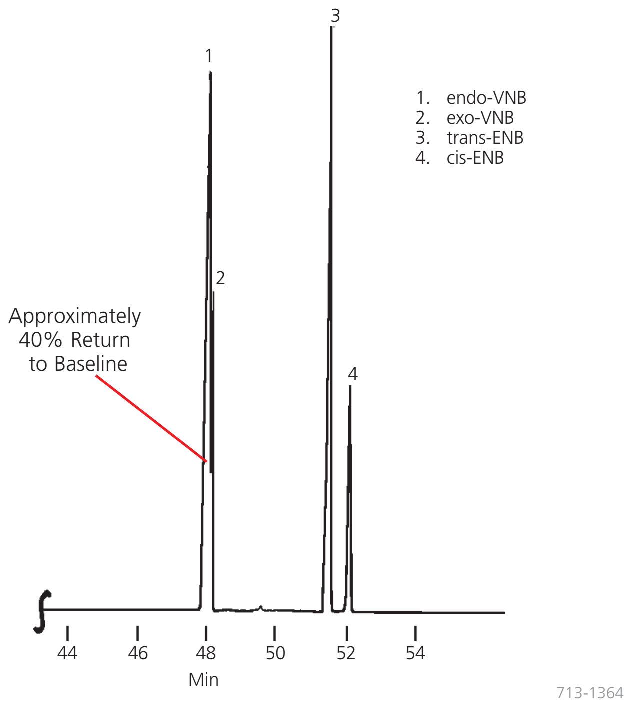


Figure T. Petroleum Reformate

column:	Petrocol DH, 100 m x 0.25 mm I.D., 0.50 µm film (24160)
oven:	35 °C (15 min.) to 200 °C at 2 °C/min.
det.:	FID (sensitivity in Fig. S = 4X sensitivity in Fig. R)
injection:	0.1 µL 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

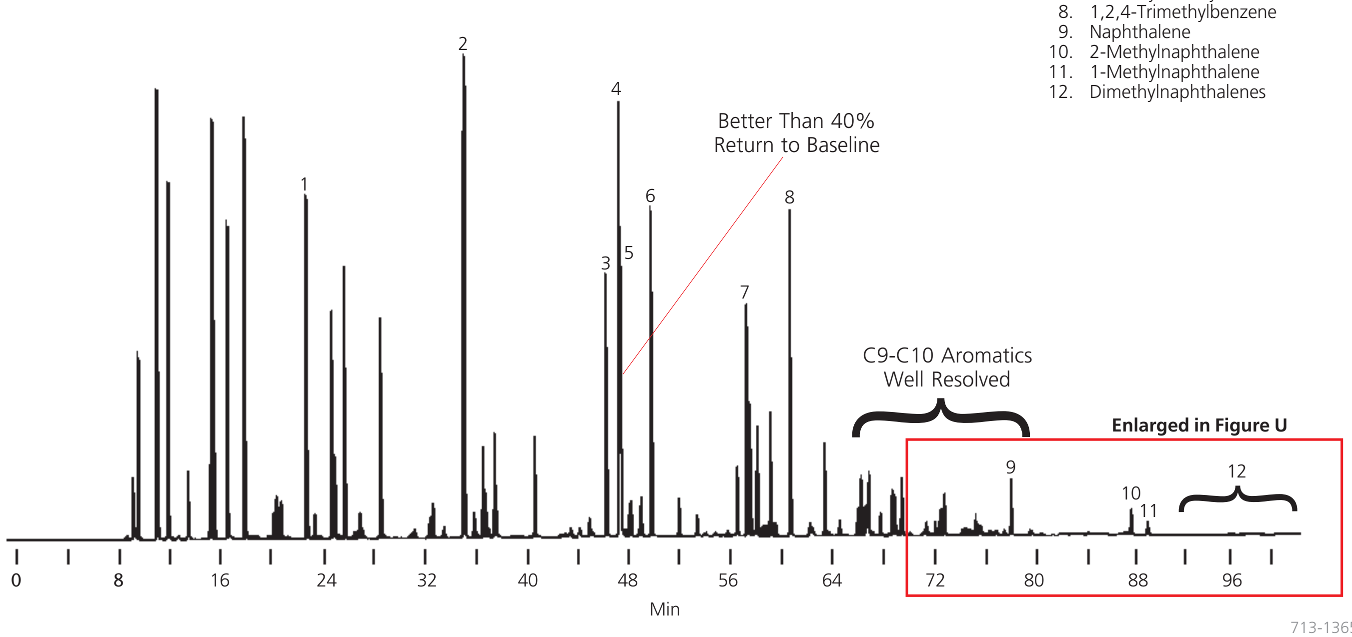
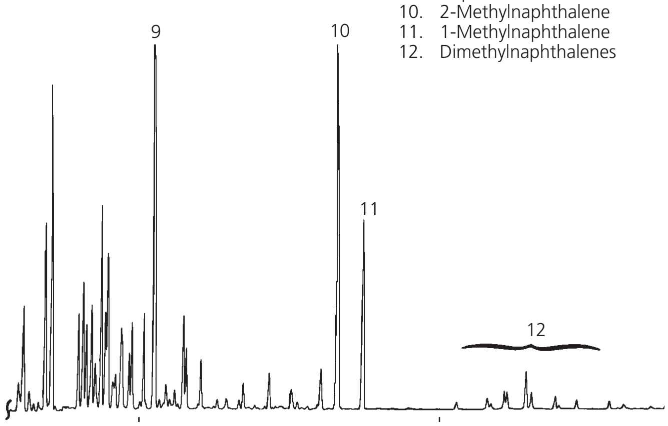


Figure U. High Resolution of Polynuclear Aromatic Hydrocarbons in Petroleum Reformate

column: Petrocol DH, 100 m x 0.25 mm I.D., 0.50 µm film (24160)
oven: 35 °C (15 min.) to 200 °C at 2 °C/min.
det.: FID (sensitivity in Fig. S = 4X sensitivity in Fig. R)
injection: 0.1 µL reformate, split (100:1)

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



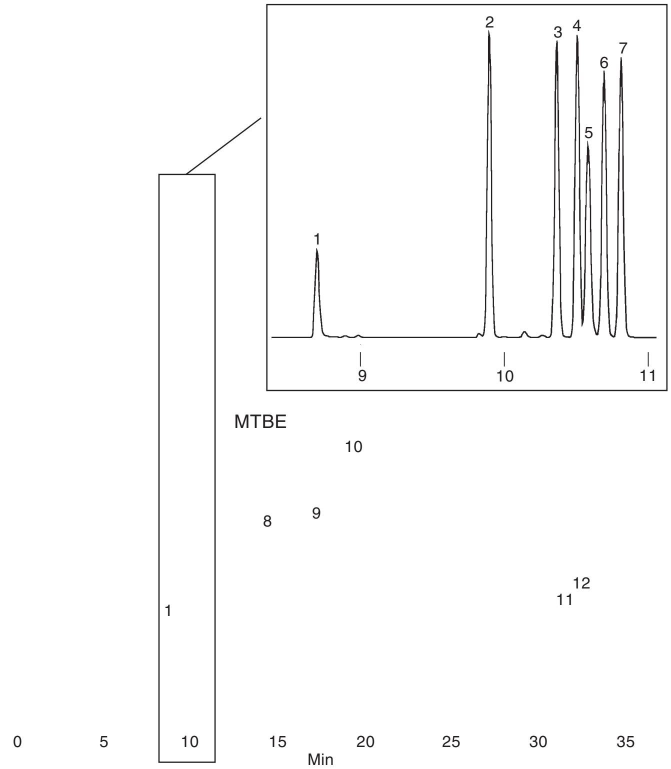
713-1366

Figure V. MTBE Contaminants Standard Resolved

column: Petrocol DH, 100 m x 0.25 mm I.D., 0.50 µm film (24160)
oven: 50 °C (13 min.) to 180 °C at 10 °C/min.
det.: FID (310 °C)
carrier gas: helium, 20 cm/sec.; vent flow 140 mL/min.
injection: 1 µL 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-butene 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

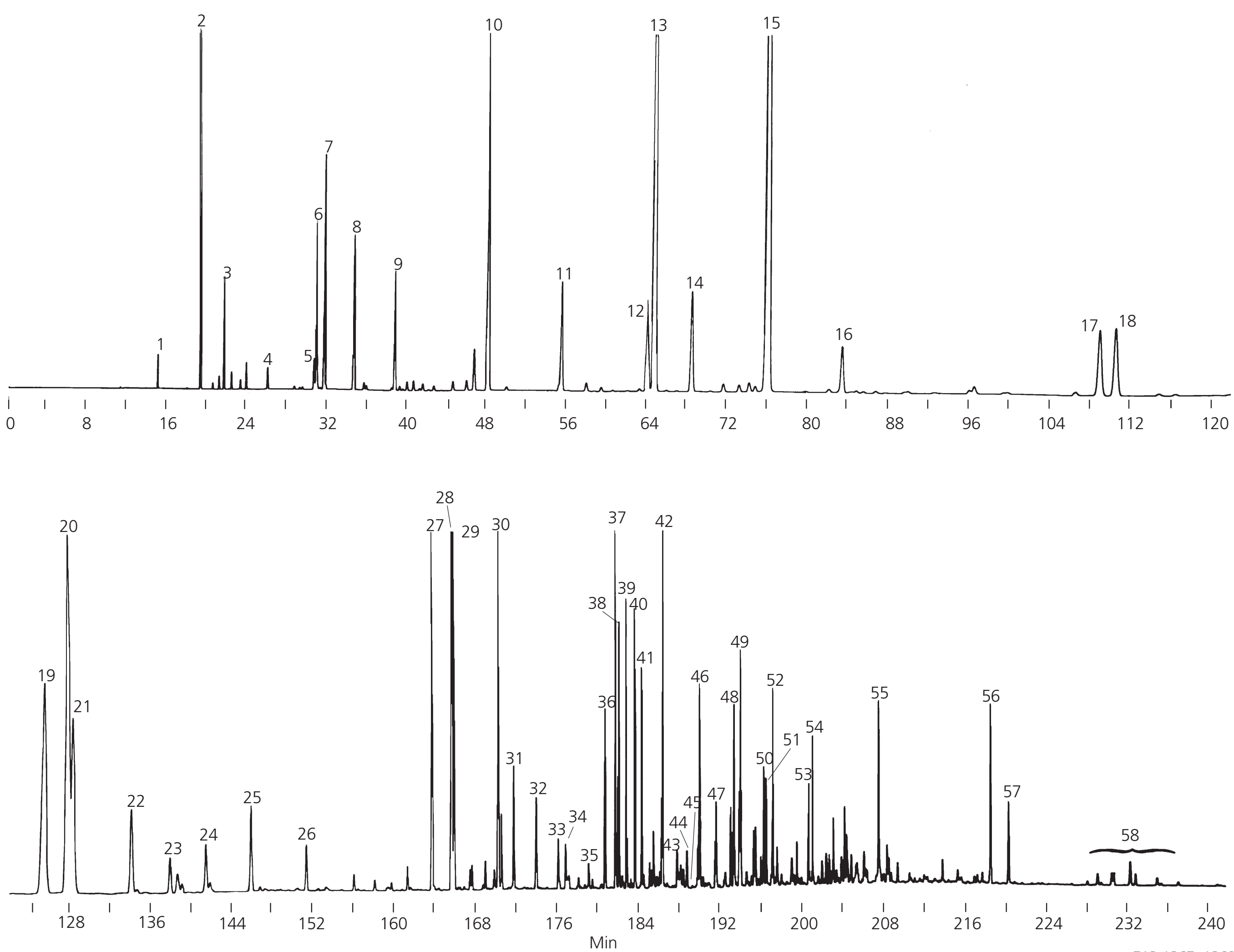


713-1329,1328

Figure W. Detailed Analysis of Gasoline, Using Ambient Initial Temperature

column: Petrocol DH 150, 150 m x 0.25 mm I.D., 1.0 µm film (24155)
oven: 35 °C (125 min.) to 200 °C at 2 °C/min.
det.: FID
carrier gas: helium, 20 cm/sec.
injection: 0.1 µL unleaded gasoline, split (100:1)

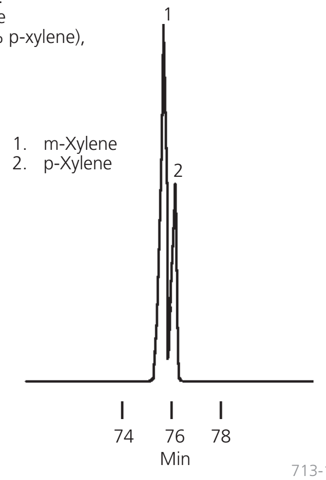
1. n-Butane
2. Isopentane
3. n-Pentane
4. 2,2-Dimethylbutane
5. Cyclopentane
6. 2,3-Dimethylbutane
7. 2-Methylpentane
8. 3-Methylpentane
9. n-Hexane
10. 2,4-Dimethylpentane
11. Benzene
12. 2-Methylhexane
13. 2,3-Dimethylpentane
14. 3-Methylhexane
15. 2,2,4-Trimethylpentane
16. n-Heptane
17. 2,5-Dimethylhexane
18. 2,4-Dimethylhexane
19. 2,3,4-Trimethylpentane
20. Toluene
21. 2,3,3-Trimethylpentane
22. 2,3-Dimethylhexane
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-Trimethylheptane
35. 2,4,5-Trimethylheptane
36. n-Propylbenzene
37. 1-Methyl-3-ethylbenzene
38. 1-Methyl-4-ethylbenzene
39. 1,3,5-Trimethylbenzene
40. 3,3,4-Trimethylheptane
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. 1,2,4,5-Tetramethylbenzene
54. 1,2,3,5-Tetramethylbenzene
55. Naphthalene
56. 2-Methylnaphthalene
57. 1-Methylnaphthalene
58. Dimethylnaphthalenes



713-1367, 1368

Figure X. Xylene Isomers, Using Isothermal Temperature

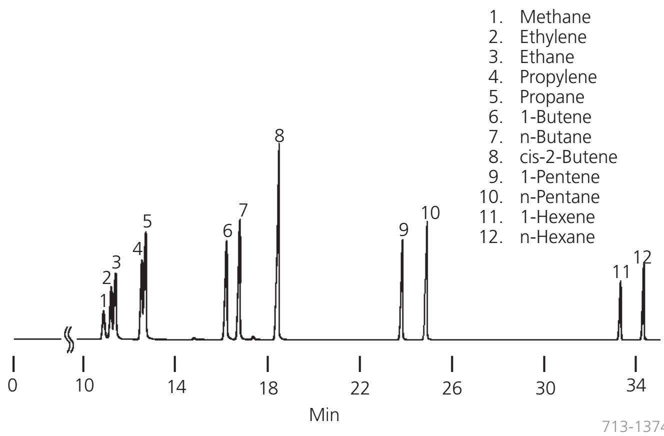
column: Pe trocol DH 150, 150 m x 0.25 mm I.D., 1.0 µm film (24155)
oven: 75 °C
det.: FID
carrier gas: helium, 20 cm/sec.
injection: 0.1 µL cyclohexane (4% m-xylene, 2% p-xylene), split (100:1)



713-1370

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

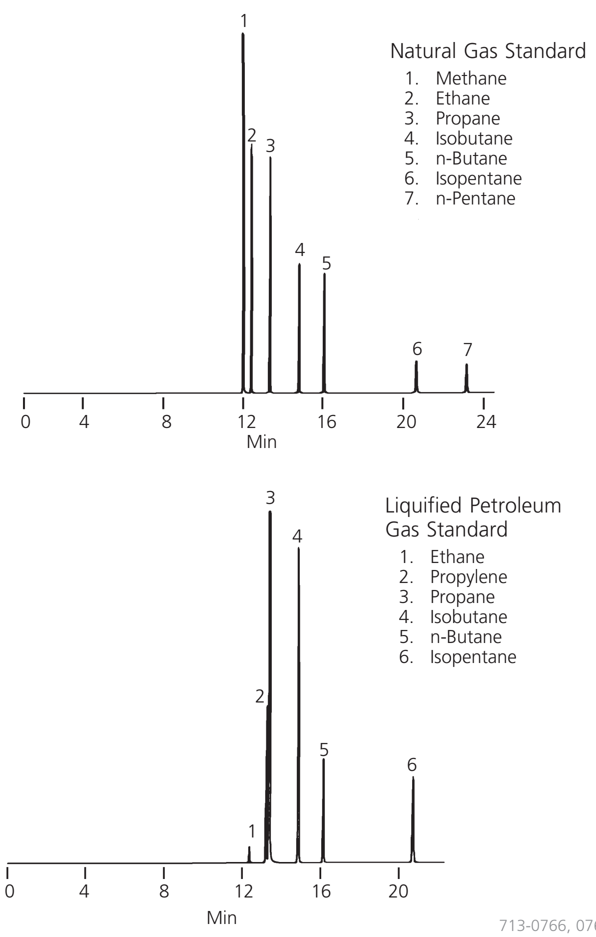
column: Petrocol DH 150, 150 m x 0.25 mm I.D., 1.0 µm film (24155)
oven: 25 °C (15 min.) to 200 °C at 5 °C/min.
det.: FID
carrier gas: helium, 20 cm/sec.
injection: 250 µL nitrogen (approx. 50 ppm each analyte), split (100:1)



713-1374

Figure Y. Gaseous and Liquid Hydrocarbons Resolved

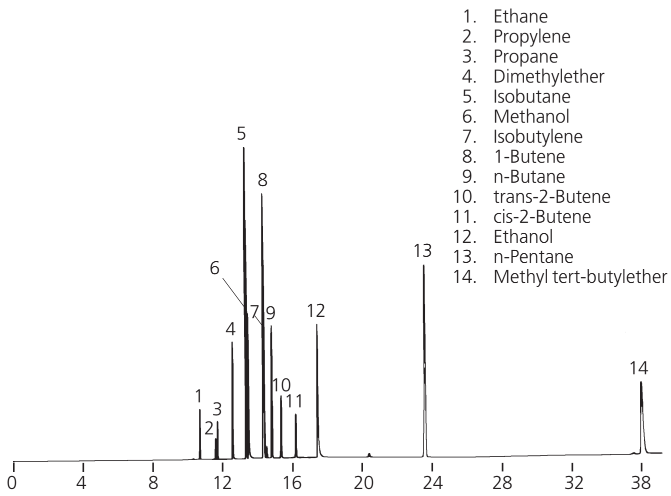
column: Petrocol DH 150, 150 m x 0.25 mm I.D , 1.0 µm film (24155)
oven: 35 °C
det.: FID
carrier gas: helium, 20 cm/sec.
injection: 25 µL natural or liquified petroleum gas, split (100:1)



713-0766, 0767

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

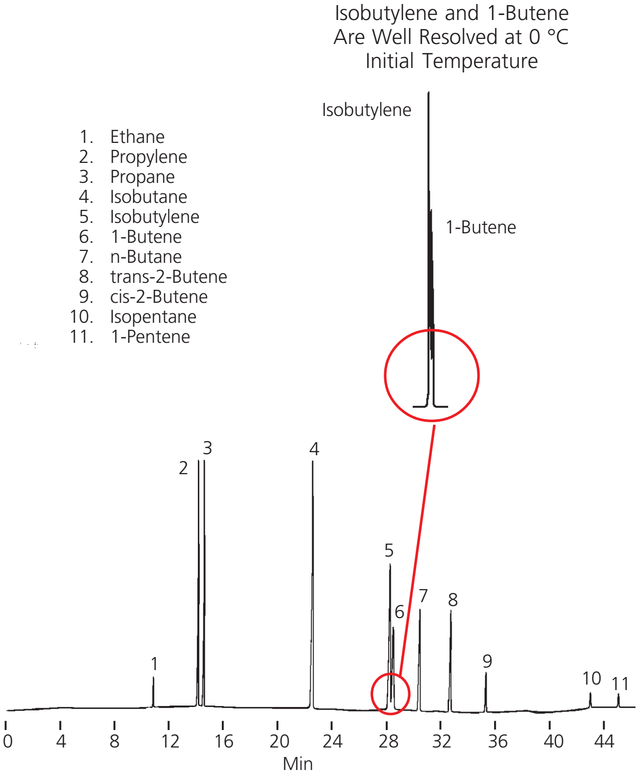
column: Petrocol DH 150, 150 m x 0.25 mm I.D., 1.0 µm film (24155)
oven: 25 °C
det.: FID
carrier gas: helium, 20 cm/sec.
injection: 50 µL nitrogen (0.1-2% each analyte), split (100:1)



713-0765

Figure AB. Light Hydrocarbons, Using Moderately Subambient Initial Temperature

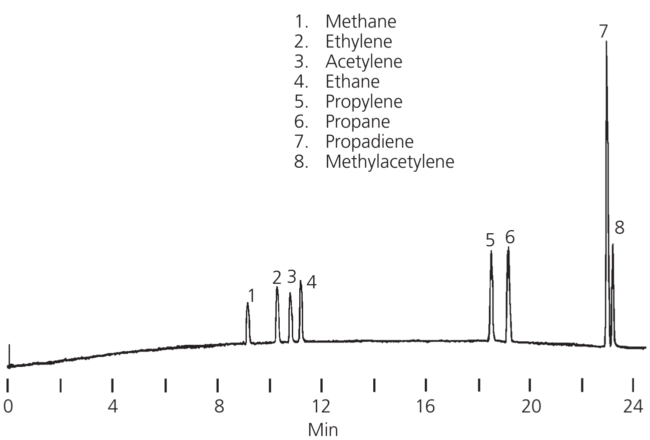
column: Petrocol DH 150, 150 m x 0.25 mm I.D., 1.0 µm film (24155)
oven: -20 °C (30 min.) to 75 °C at 5 °C/min.
det.: FID
carrier gas: helium, 20 cm/sec.
injection: 250 µL nitrogen (0.1-1% each analyte), split (100:1)



713-0764, 1275

Figure AC. C1-C3 Hydrocarbons

column: Petrocol DH 150, 150 m x 0.25 mm I.D., 1.0 µm film (24155)
oven: -50 °C (25 min.) to 75 °C at 5 °C/min.
det.: FID
carrier gas: helium, 20 cm/sec.
injection: 250 µL nitrogen (5-10 ppm each analyte), split (100:1)



713-1375

Ordering Information:

Description	Cat. No.
Capillary Columns for Detailed Hydrocarbon Analyses	
SPB-1 Wide Bore Column	
60 m x 0.75 mm I.D. glass, 1.0 µm film	**custom**
SP-2100 Column	
30 m x 0.25 mm I.D., fused silica, 0.25 µm film	**custom**
SUPELCOWAX 10 Column	
30 m x 0.20 mm I.D. fused silica, 0.20 µm film	**24169**
Petrocol DH 50.2 Column	
50 m x 0.20 mm I.D. fused silica, 0.50 µm film	**24133-U**
Petrocol DH Column	
100 m x 0.25 mm I.D. fused silica, 0.50 µm film	**24160-U**
Petrocol DH 150 Column	
150 m x 0.25 mm I.D. fused silica, 1.0 µm film	**24155**
SPB-Octyl Column	
60 m x 0.25 mm I.D. fused silica, 1.0 µm film	**24233-U**

Fused silica capillary columns manufactured under HP US Pat. No. 4, 293,415.

Test Mixes

Polar Test Mix, 2 mL For evaluating performance of SUPELCOWAX 10 capillary columns	**47302**
Nonpolar Test Mix, 2 mL For evaluating performance of Petrocol DH 50.2 (50-meter) and Petrocol DH 150 (150-meter) capillary columns	**47300-U**

Petrochemical Standards for Hydrocarbon Analyses

n-Paraffin Standards

For determining retention indices.

Neat, total 500 mg	
C5, C6, C7, C8	**47100**
C7, C8, C9, C10	**47101**
C10, C12, C14, C16	**47102**
Mixes, total 250 mg/5 mL n-octane	
C18, C20, C22, C24	**47108**
C22, C24, C28, C32	**47106**
C24, C28, C32, C36	**47107**

Qualitative Reference Standards

6 x 1 mL	
Naphtha	**48265-U**
Reformate	**48266**
Alkylate	**48267-U**
Refinery Kit (2 x 1 mL of each of above)	**48268**

Quantitative Reference Standards

Composition	Retention Indices Range	Cat. No.
Paraffins Mix, 0.1 mL (11 n-paraffins)	500.0-1500.0	**44585-U**
Isoparaffins Mix, 0.1 mL (35 isoparaffins)	483.4-974.2	**44586-U**
Aromatics Mix, 0.1 mL (37 aromatics)	638.6-1247.2	**44587**
Naphthenes Mix, 0.1 mL (29 naphthenes)	549.0-1146.9	**44588**
Olefins Mix, 0.1 mL (28 olefins)	457.4-988.7	**44589**
P-I-A-N-O Mix, 0.1 mL (140 components in 5 class mixes above)	457.4-1500.0	**44593-U**
P-I-A-N-O Kit (0.1 mL P-I-A-N-O Mix, 0.1 mL each of 5 class mixes)	457.4-1500.0	**44594-U**

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 · 500 pp

Eighteen chapters cover a wide range of topics in the application of chromatography to petroleum analyses. Five chapters on analysis of distillates include gas analysis, simulated distillation by GC, and hydrocarbon group analysis by HPLC. Chapters on analysis of heavy distillates, residues, and crudes by GC include identification of oil spills and pyrolysis GC. LC analyses of heavy distillates, residues, and crudes include gel permeation, thin layer, paper, and high performance liquid chromatography. There also is a chapter on supercritical fluid chromatography. Additional chapters describe analysis of polynuclear aromatic hydrocarbons, synthetic fuels, additives in lubricants, and process chromatography. **23585**

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