Separation of Hydrocarbons by Packed Column GC

This bulletin deals with the separation of hydrocarbons by gas chromatography using packed columns. The first section contains information regarding the various types of column materials and also lists important literature references pertaining to hydrocarbon separation. Other sections deal with specific separations.

Key Words

- aliphatics • aromatics • hydrocarbons
- microcrystalline wax hydrocarbons
- saturated and unsaturated hydrocarbons • standards

Packed GC Columns for Separating Hydrocarbons

A wide variety of gas chromatographic column materials is available for separating hydrocarbon mixtures. The type of packed column chosen depends on the nature of the hydrocarbon mixture to be separated. There are several basic categories of packing, including: (a) gas solid chromatography (GSC), (b) gas liquid/solid chromatography (GLSC), (c) conventional GLC columns (stationary phase coated on a support), and (d) conventional GLC columns with stationary phase plus complexing agent on a support.

Adsorbents

Inorganic adsorbents used in GC include silica gel, alumina, molecular sieves and carbons. Silica gel and alumina can be used to separate hydrocarbons in the C1 to C4 range (1). Molecular sieves are generally limited to separating methane and permanent gases such as H_2, O_2, N_2, and CO. Porous carbon (Carbosieve™ S-II and G and Carboxen™-1000) can be used to separate hydrocarbons in the C1 to C3 range, along with permanent gases such as H_2, O_2, N_2, CO, and CO_2 (2). Organic adsorbents (the so-called porous polymers) are large surface area resins made from such materials as styrene and divinylbenzene. It is the surface of the adsorbent which causes the separation to occur. The porous polymers have been used to separate light hydrocarbons (3, 4, 5).

Modified Adsorbents

The usefulness of a number of adsorbents may be substantially extended by modifying their surfaces. This is done in some cases by bonding the stationary phase to the surface of the adsorbent, or in other cases by merely coating the surface. Halasz (6) modified the surface of a special gel, Porasil® C, by bonding to its surface a series of stationary phases. These are now commercially available as the Durapak® series manufactured by Waters (7). Guillemin et al. (8, 9) have extended this work, using Spherosil®, and have developed a series of bonded Spherosils manufactured by Pechiney-Saint-Gobain (10).

Bruner, Di Corcia, Liberti, and co-workers have studied the graphitized carbons sold by Supelco under the trade names Carbopack™ B and C, after modifying their surfaces with a stationary phase. Their work has shown that not only is the type of stationary phase important, but also the amount used (11, 12).

The Carbopacks are useful for separating the C4 unsaturates as well as various C4 and C5 hydrocarbons (13, 14). Earlier, Eggertsen et al. (15) had reported that a carbon black (Pelletex) modified with 1.5% squalane could be used to separate the C5 and C6 saturates according to their boiling points.

Conventional Packed Columns

A conventional packed column consists of a stationary phase coated on a support. The choice of the type and amount of phase, as well as the type and particle size of the support are governed by the type of sample to be separated. First, consider the boiling point range of the sample when deciding on the nature and the amount of stationary phase to use in the column. A very volatile sample is quickly eluted from a column while a high boiling sample is slowly eluted at the same temperature. Second, the amount of stationary phase in the column is important in the elution of the sample; the greater the amount of stationary phase, the greater will be the elution time. To separate very low boiling compounds, it is necessary to use a relatively high concentration (20-30%) of a very specific stationary phase; a medium boiling sample requires a 10% loading, and a high boiling sample requires a 3% loading of a general purpose stationary phase. A methyl silicone stationary phase is well suited for both medium and high boiling samples (see pages 6 and 11). For very high boiling mixtures such as microcrystalline waxes, a short (18") column filled with 1% Dexsil® 300 is capable of giving rapid separation.

The pink or Chromosorb® P-type supports have twice the density and twice the capacity of the white or Chromosorb W-type supports. As a consequence, the pink supports are favored for those packings which require high (20-30%) loadings. In the case of the medium boiling range samples, either the Chromosorb P- or W-type will suffice. For the high boiling samples, the Chromosorb W-type supports are favored because the samples are more rapidly eluted.

The particle size of the support used is an important factor in the efficiency of the column; the smaller the particle size, the more efficient the column. The most commonly used particle sizes are: 60/80, 80/100, and 100/120 mesh. The 100/120 mesh size will give the most efficient column. It should also be noted that as the particle size of the support is reduced, the column back pressure will increase.

C1 to C5 Hydrocarbons

Many stationary phases have been used for separating C1 to C5 saturated and unsaturated hydrocarbons. Some of these phases, and references for more information, are listed below. The first four phases listed are useful at column temperatures of 0 to 25°C. Above this temperature they have a limited life because of the volatility of the materials. In contrast, SP-1700 can be used at column temperatures of 0°C to 110°C, with most hydrocarbons analyses done at 70°C.

Stationary phase	Reference
Hexamethylphosphoramide (HMPA)■	16
Dimethylsulfolane (DMS)	17
Propylene carbonate/glutaronitrile	18
Ethyl n,n-dimethyloxamate (EDO-1)	19
SP-1700	See Section 4

■Supelco has discontinued supplying HMPA because it is now considered a carcinogen.

Medium Range Hydrocarbons (C6 to C16)

A 10% loading of a dimethyl silicone phase, such as SP™-2100, allows for a good separation of samples containing medium range hydrocarbons, particularly if the need is to obtain a "fingerprint" to characterize the sample. The use of this type of column is described on pages 6 and 7.

High Boiling Hydrocarbons

A 10% loading of a dimethyl silicone (SP-2100) or a 50-50 methyl phenyl silicone (SP-2250) is useful for separating high boiling fractions, such as those found in coal tar. Of the two phases, dimethyl silicone gives the better separation. For details see High Boiling Aromatics (page 11).

Very High Boiling Hydrocarbons

To separate mixtures such as microcrystalline waxes, which contain C30 and larger hydrocarbons, a lightly loaded, short column is needed. 1% Dexsil 300 on SUPELCOPORT™ in an 18" column will readily separate this type of sample. A 1% SE-30 column will also work. See page 12 of this bulletin and request Bulletin 755 for information about high temperature GC separations.

Separating Aromatics

Bentone® 34 is the most widely used complexing agent because it allows for the separation of m- and p-xylene as well as other aromatics. Mortimer and Gent (20), and Spencer (21) demonstrated that combining a stationary phase and Bentone 34 would readily separate m- and p-xylene along with ethylbenzene and o-xylene. For more details regarding Bentone 34 and its use in GC, see pages 8 and 9 of this bulletin and request Bulletin 740.

• German Pat. No. 1935500. Patent holder: Badische Anilin- & Soda-Fabrik Aktiengesellschaft

References

1. Green, S.A. and H. Pust, Anal. Chem., *29*, 1055 (1957).
2. Supelco Bulletin 712.
3. Dave, S.B., J. Chromatog. Sci., *7*, 389 (1969).
4. Hollis, O.L., J. Chromatog. Sci., *11*, 335 (1973).
5. Wilhite, W.F. and O.L. Hollis, J. Gas Chromatog., *6*, 84 (1968).
6. Halasz, I. and I. Sebestian, J. Chromatog. Sci., *12*, 161 (1974).
7. Waters Associates, Bulletin PB 204.
8. Cirendini, S., J. Vermont, J.C. Gressin, and C.L. Guillemin, J. Chromatog., *84*, 21 (1973).
9. Guillemin, C.L., M. Delevil, S. Cirendini, and J. Vermont, Anal. Chem., *43*, 2015 (1971).
10. Pechiney-Saint-Gobain, Bulletin *Spherosil*, Porous Silica Beads for Gas Chromatography.
11. Bruner, F., P. Ciccioll, G. Crescentini, and M.P. Pistolesi, Anal. Chem., *45*, 1851 (1973).
12. Di Corcia, A., A. Liberti, and R. Samperi, Anal. Chem., *45*, 1228 (1973).
13. Di Corcia, A. and R. Samperi, Anal. Chem., *47*, 1853 (1975).
14. Di Corcia, A. and R. Samperi, J. Chromatog., *107*, 99 (1975).
15. Eggertsen, F.T., H.S. Knight, and S. Groennings, Anal. Chem., *28*, 303 (1956).
16. McEwen, D.J., Chem. in Canada 11, No. 10, 35 (1959).
17. Fredericks, E.M. and F.R. Brooks, Anal. Chem., *28*, 297 (1956).
18. McKenna, T.A., Jr. and J.A. Idelman, Anal. Chem., *31*, 2000 (1959).
19. Richmond, A.B., J. Chromatog. Sci., *7*, 321 (1969).
20. Mortimer, J.V. and P.L. Gent, Nature, *197*, 789 (1963).
21. Spencer, S., Anal. Chem., *35*, 592 (1963).

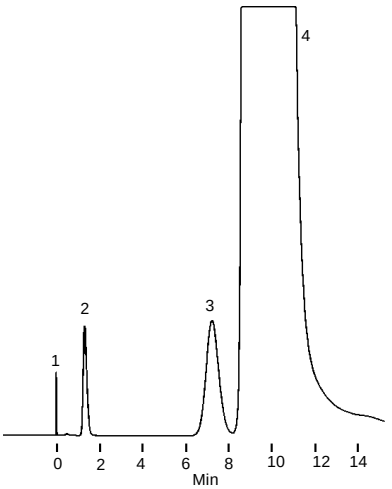
References not available from Supelco.

Separation of C1 to C3 Hydrocarbons

Carbosieve• S-II and G and Carboxen-1000 (high purity carbons) can be used to separate hydrocarbons in the C1 to C3 range. Their unique surface and structure causes separation by degree of unsaturation, with saturated hydrocarbons eluting last. This unique order of elution is useful in the trace analysis of methane and acetylene in ethylene (See Figures A and B).

Figure A. Trace Acetylene and Methane Resolved from Ethylene

Column: **60/80 Carbosieve S-II, 5' x 1/8" SS**
Col. Temp.: 125°C
Flow Rate: 50mL/min, N_2
Det.: FID
Sens.: 4 x 10^{-11} AFS
Sample: 1mL of ethylene containing acetylene and methane, 100ppm each

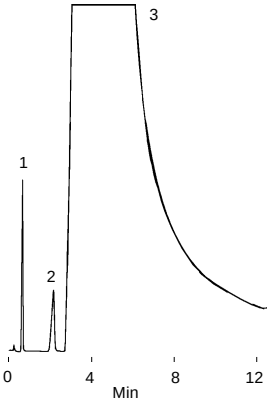


1. Inject
2. Methane (100ppm)
3. Acetylene (100ppm)
4. Ethylene

795-0666

Figure B. Trace Acetylene in Ethylene

Column: **40/60 Carboxen-1000, 5' x 1/8" SS (2.1mm ID)**
Oven: 160°C
Carrier: helium, 30mL/min, N_2
Det.: FID
Sample: 0.5mL ethylene with trace impurities

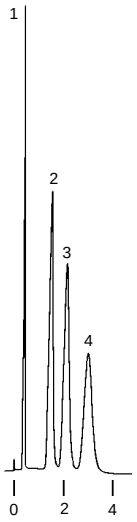


1. Methane
2. Acetylene (14ppm)
3. Ethylene

794-0116

Figure C. Methane and C2 Hydrocarbons Resolved

Column: **60/80 Carbosieve G, 5' x 1/8" SS**
Col. Temp.: 145°C
Flow Rate: 50mL/min, N_2
Det.: FID
Sens.: 2.56 x 10^{-11} AFS
Sample: 0.1mL, 1% each component in N_2



1. Methane
2. Acetylene
3. Ethylene
4. Ethane

795-0667

The C2 hydrocarbons are separated in the following order: acetylene, ethylene, and ethane. These compounds, along with methane, are shown in Figure C.

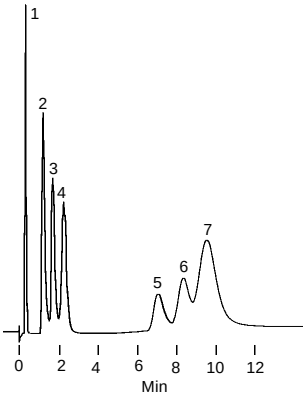
The C3 hydrocarbons are best separated on Carbosieve G or Carboxen-1000. They too elute by degree of unsaturation (propyne, then propylene, then propane). Chromatographers performing this analysis should be sure the chromatograph oven temperature indicator is accurate, because trace concentrations of the C3 unsaturates will be adsorbed if the column temperature exceeds 225°C. To obtain the proper peak shape for propylene, both columns should be primed with propylene before they are used. Priming instructions accompany all of our Carbosieve G products. Figure D shows the resolution of the C3s, along with methane and C2 compounds, on a temperature programmed Carbosieve G column. Figure E shows a shorter Carboxen-1000 column provides a faster analysis.

The C4 and larger molecular weight hydrocarbons are adsorbed on Carbosieve and Carboxen columns under practical analytical conditions.

For further information on the characteristics and applications of Carbosieves, refer to the current Supelco Catalog. For more information on Carboxen-1000, request Application Note 10.

Figure D. C1-C3 Hydrocarbons on Carbosieve G

Column: **60/80 Carbosieve G, 5' x 1/8" SS**
Col. Temp.: 145°C to 195°C at 6°C/min and hold 5 min
Flow Rate: 50mL/min, N_2
Det.: TCD
Sens.: 16 x 10^{-12} AFS
Sample: 1.0mL, approx. 15ppm each component (30ppm propane) in N_2

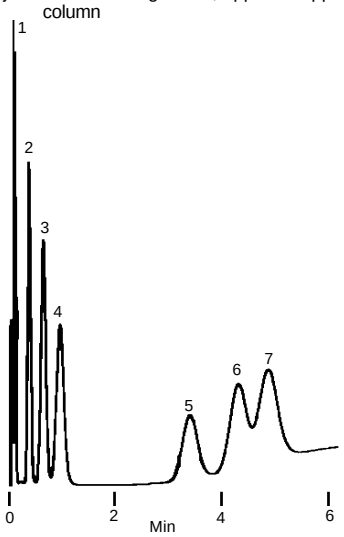


1. Methane
2. Acetylene
3. Ethylene
4. Ethane
5. Propyne
6. Propylene
7. Propane

795-0681

Figure E. C1-C3 Hydrocarbons on Carboxen-1000

Column: **40/60 Carboxen-1000, 2' x 1/8" SS (2.1mm ID)**
Oven: 165°C (1 min) to 220°C at 16°C/min
Carrier: helium, 60mL/min
Det.: FID
Inj.: 0.6mL Scott gas mix, approx. 15ppm each analyte on column



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

795-0115

Ordering Information:

Packings for Carbosieve columns

Mesh Size	Carbosieve S-II Cat. No.	Carbosieve G Cat. No.
45/60	—	**10197**
60/80	**10189**	**10198**
80/100	**10190-U**	**10199**
100/120	—	**10200-U**
120/120	**10192**	—

Carboxen-1000 columns (45/60 mesh)

Instrument ID	2' x 1/8" Cat. No.	5' x 1/8" Cat. No.
General configuration	**12370-U**	**12380**
HP 5700, 5992-3, GC-MS	**12371**	**12381**
HP 5880, 5890, 5987	**12372**	**12382**
PE 900, 3920, Sigma 1, 2, 3	**12373**	**12383**
PE 8300, 8400, 8590, 8600, 8700 Auto System	**13740**	**13742-U**
Varian 3700, Vista series	**12374**	**12384**
Varian 3300/3400, Vista series	**13741**	**13743**

GC Columns for C4 Unsaturates

The C4 unsaturates can be readily separated with our Carbopack C/0.19% picric acid packing. Carbopack C is a graphitized carbon similar to Carbopack A, which was introduced some time ago. The addition of the proper amount of picric acid (0.19%) modifies the surface of the graphite to give the desired separation. Most column packings now used for separating the C4 unsaturates require operation at room temperature or below, but even under these conditions the column has a limited life. In contrast, Carbopack C/0.19% picric acid has a maximum upper limit of 120°C, so we anticipate very long column life at 50°C. A temperature programmed analysis of C1-C5 hydrocarbons, including several unsaturated C4 compounds, is shown in Figure F, and an isothermal analysis of the same compounds is shown in Figure G. The use of the lower initial column temperature in Figure F improves the propane/propylene separation. The isothermal separation shown in Figure G could be improved by reducing the flow rate. To avoid the long retention time for iso- and n-pentane, the column might be back-flushed after the C4s are eluted. Because Carbopack C/0.19% picric acid can be used at 50°C for prolonged periods of time, it is a possible choice for process control use.

Although Carbopack C/0.19% picric acid was designed specifically for the C4s, 1,2-butadiene and n-butane are not separated from each other. The C5s trans-2-pentene and n-pentane are not separated and 2-methyl-butene and cis-2-pentene are only partially separated. The elution order of the C5s is as follows: 3-methyl-1-butene, isopentane, 1-pentene, 2-methyl-1-butene, cis-2-pentene, trans-2-pentene/n-pentane as one peak, and 2-methyl-2-butene. At a higher concentration of picric acid, 0.7%, iso- and n-pentane are eluted more rapidly but the cis- and trans-2-butene are eluted as one peak. The column will not separate the C2s from each other.

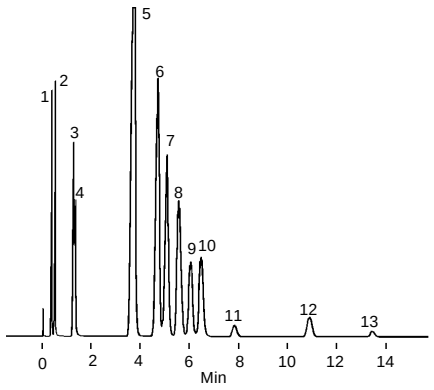
The Carbopack C/picric acid column has a limited capacity for sample. If too large a sample is used, the column is overloaded and poor separation results. For a 2m x 1.8" OD x 0.085" ID stainless steel column, a maximum of 100µL gas sample may be used. Because of the sample size limitation, we suggest that a 1/8" column be used only with a flame ionization detector (FID). If a TC detector is to be used and if it requires more than a 100µL gas sample, then we suggest the use of a 2m x 1/4" OD x 0.0120" ID stainless steel column. With this column a maximum of 550µL of gas sample may be used. Please note that the 100 and 550µL values are approximate, because we find that different syringes deliver different amounts of sample for the same indicated volume.

We recommend that you purchase this packing, rather than prepare it in your laboratory, since it requires considerable practice to obtain reproducible results. Directions for preparing the column are included with the packing. A 2m x 1/8" column requires about 5.5g of the packing while a 2m x 1/4" column requires 34g of packing.

The Carbopack C/picric acid packing for light hydrocarbons was developed by Drs. A. Di Corcia and R. Samperi of the University of Rome (22, 23).

Figure F. C4 Hydrocarbons Separated Through a Temperature-Programmed Analysis

Column: **80/100 Carbopack C/0.19% picric acid, 2m x 1/8" OD SS**
Col. Temp.: hold 1 min at 30°C, then to 100°C at 4°C/min
Flow Rate: 50mL/min, N_2, at 53psi
Det.: FID

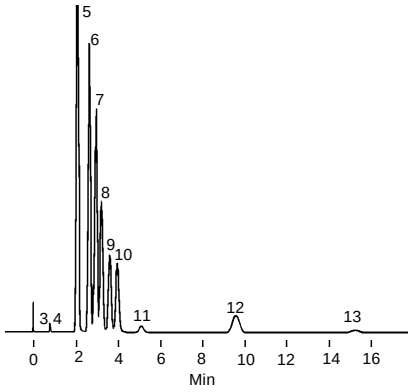


1. Methane
2. Ethane
3. Propane
4. Propylene
5. Isobutane
6. 1-Butene
7. n-Butane
8. Isobutylene
9. cis-2-Butene
10. trans-2-Butene
11. 1,3-Butadiene
12. Isopentane
13. n-Pentane

795-0668

Figure G. C4 Unsaturates Separated Through Isothermal Analysis

Column: **80/100 Carbopack C/0.19% picric acid, 2m x 1/8" OD SS**
Col. Temp.: hold 1 min at 30°C, then to 100°C at 4°C/min
Flow Rate: 50mL/min, N_2, at 53psi
Det.: FID



1. Methane
2. Ethane
3. Propane
4. Propylene
5. Isobutane
6. 1-Butene
7. n-Butane
8. Isobutylene
9. cis-2-Butene
10. trans-2-Butene
11. 1,3-Butadiene
12. Isopentane
13. n-Pentane

795-0669

Ordering Information▲:

Description	Cat. No.
Packing	
Carbopack C GP 80/100, 0.19% picric acid, 15g	**11824**
Column	
1/8" x 2m stainless steel column packed with 0.19% picric acid on 80/100 Carbopack C	**13867**

References

22. Di Corcia, A. and Samperi, R., Anal. Chem., *47*, 1853 (1975).
23. Di Corcia, A. and Samperi, R., J. Chromatog., *107*, 99 (1975).

References not available from Supelco.

GP — Indicates packing has been pretested for specific analysis shown in this section.

▲ For information about ordering packed columns, refer to our latest catalog, or call our Ordering and Customer Service Department at 800-247-6628 or 814-359-3441.

Saturated and Unsaturated C1 - C5 Hydrocarbons

23% SP-1700 on Chromosorb P AW columns separate numerous C1-C5 saturated and unsaturated hydrocarbons. They provide rapid analyses, have a large sample capacity, and withstand the stress of pressure surges from sample valve operation.

Analysts can separate many hydrocarbons using a stock 30' x 1/8" SP-1700 column (Table 1). Figure H shows an isothermal analysis that includes most of the compounds in C1-C6 petroleum streams. At 70°C the C1-C5 components elute from the column in about 21 minutes. Methylhexane, a C7 compound and the heaviest component, elutes in 36 minutes with a symmetrical peak. Even isopentane and 1,3-butadiene, hydrocarbons that coelute with many columns, separate sharply when an SP-1700 column is used.

A chromatographer analyzing hydrocarbon mixtures must operate most columns at 35°C or lower. These are difficult temperatures to maintain in a chromatograph oven. Component retention times vary as a result, and components may be misidentified. Furthermore, these columns are typically operated near their maximum recommended temperature and consequently exhibit high bleed and short life spans. Other columns for hydrocarbon analyses may require temperature programming. When the cool-down and stabilization periods are included, these analyses are often undesirably long.

SP-1700 columns can be used from room temperature to 110°C in isothermal as well as temperature programmed analyses. Time is saved between samples because analysts can perform isothermal separations on these columns, and because SP-1700 columns are conditioned and ready to use within an hour after installation.

Many columns presently being used to separate petrochemicals have inadequate sample capacity. Such columns may separate trace levels of hydrocarbons well: for example, levels in environmental or industrial hygiene samples. But if the sample contains large quantities of some components, these columns become saturated and resolve components poorly. In contrast, the high stationary phase content (23%) of SP-1700 columns provides a large sample capacity: 0.5-2µL for liquid samples, 0.5-10cc for gas samples. In Figure H the difference between the isopentane and hexane concentrations is extremely large, yet both peaks are symmetrical. The symmetry of the hexane peak (sample solvent) shows the column is not overloaded by highly concentrated compounds.

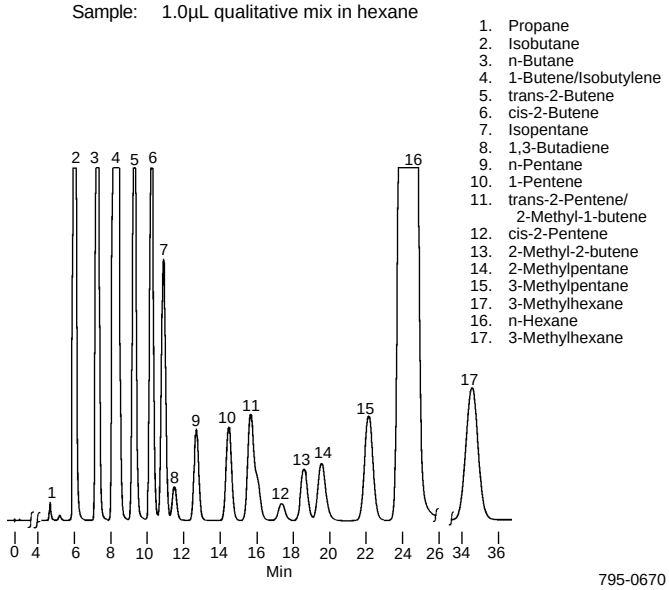
Table 1. Hydrocarbon Retention on 23% SP-1700/Chromosorb P AW

Component	Retention Time At 70°C (min)
O_2, N_2, CO	3.17
CH_4/H_2S	3.27
Ethane	3.67
Ethylene	3.70
CO_2	3.86
Propane	4.73
Propylene	5.04
Acetylene	5.20
Isobutane	6.12
COS	6.58
n-Butane	7.4
Isobutylene/1-Butene	8.34
trans-2-Butene	9.50
cis-2-Butene	10.49
Isopentane	11.18
1,3-Butadiene	11.81
n-Pentane	13.08
Pentene-1	14.92
trans-2-Pentene/2-Methyl-1-butene	16.16
cis-2-Pentene	17.89
2-Methyl-2-butene	19.18
2-Methylpentane	20.19
3-Methylpentane	22.85
n-Hexane	25.13
3-Methylhexane	35.71

Column: **23% SP-1700 on 80/100 Chromosorb P AW, 30' x 1/8" OD SS**
Col. Temp.: 70°C
Inj. Temp.: 100°C
Det. Temp.: 110°C
Flow Rate: 25mL/min
Det.: FID
Sample: composite data

Figure H. Isothermal Separation of ASTM○○ Section L Blend No. 6 Plus C5s

Column: **23% SP-1700 on 80/100 Chromosorb P AW, 30' x 1/8" OD SS**
Col. Temp.: 70°C
Inj. Temp.: 100°C
Det. Temp.: 110°C
Flow Rate: 25mL/min●
Det.: FID
Sens.: 8 x 10^{-10} AFS
Sample: 1.0µL qualitative mix in hexane



795-0670

○○ American Society for Testing and Materials

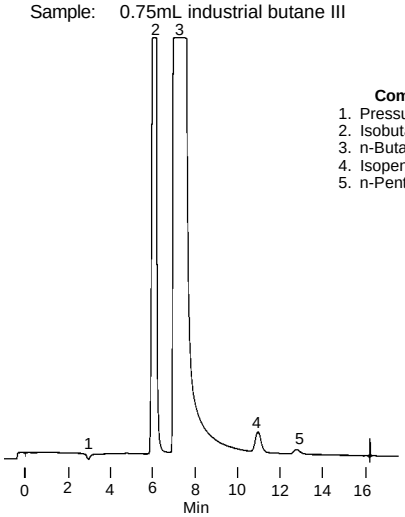
An analysis of an industrial butane sample also reveals that SP-1700 columns separate highly disproportionate concentrations of sample components well (Figure I). Although the components ranged in concentration from 97.9% (n-butane) to 0.01% (n-pentane), all peaks were nearly symmetrical. In addition, the analysis was completed in only 14 minutes. Propane and propylene in liquid propane can be resolved (Figure J) when the concentration ratio is 90:1 or more. ASTM Section L Blend No. 5 and Phillips Petroleum Blend No. 40 also separate extremely well on SP-1700 columns. Although several pairs of compounds elute at the same or similar times from SP-1700 column (Table 1), the coelution of isobutylene and 1-butylene is the only significant column limitation.

These examples illustrate general hydrocarbon analyses performed using stock 30' SP-1700 columns. To meet unique requirements, we also offer custom SP-1700 columns and 23% SP-1700/ Chromosorb P AW packing. (SP-1700 phase is not available separately.)

Figure I. Symmetrical Peaks From Major and Trace Components of Industrial Butane III

Column: **23% SP-1700 on 80/100 Chromosorb P AW, 30' x 1/8" OD SS**
Col. Temp.: 70°C
Inj. Temp.: 100°C
Det. Temp.: 110°C
Flow Rate: 25mL/min•, He
Det.: FID
Sens.: 32 x 10^{-10} AFS
Sample: 0.75mL industrial butane III

Component	Wt. %
1. Pressure Disturbance	
2. Isobutane	2.02
3. n-Butane	97.92
4. Isopentane	0.05
5. n-Pentane	0.01

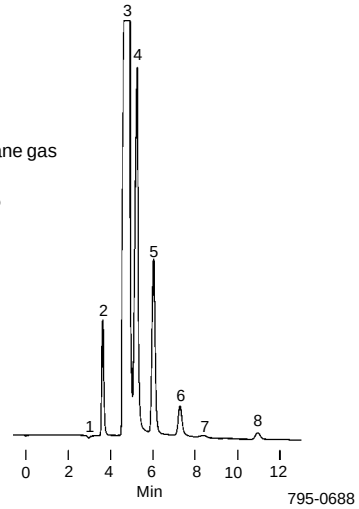


795-0687

Figure J. Propane and Propylene Peaks Resolved at Highly Disparate Ratios

Column: **23% SP-1700 on 80/100 Chromosorb P AW, 30' x 1/8" OD SS**
Col. Temp.: 70°C
Inj. Temp.: 100°C
Det. Temp.: 150°C
Flow Rate: 25mL/min•, He
Det.: FID
Sens.: 128 x 10^{-11} AFS
Sample: 0.5mL liquid propane gas

Component	Wt. %
1. Pressure Disturbance	
2. Ethane	3.42
3. Propane	96.75
4. Propylene	1.72
5. Isobutane	0.93
6. n-Butane	0.17
7. 1-Butene/Isobutylene	trace
8. Isopentane	trace



795-0688

Ordering Information:

Description	Cat. No.
Packing	
23% SP-1700 on 80/100 Chromosorb P AW, packing 25g (21-22g will fill a 30' x 1/8" column)	**11865**
Stock Packed Stainless Steel Columns▲	
30' x 1/8" columns filled with 23% SP-1700 on 80/100 Chromosorb P AW General configuration (6' coil with 8" arms), conditioned	**12809-U**
Coiled to any other configuration◆, conditioned	**custom**

Separation of Aliphatic Hydrocarbons

10% SP-2100 can be used to separate various complex mixtures such as naphtha, gasoline, kerosene in order to characterize them, i.e., to obtain a "spectrum" for comparison purposes. Figure K shows chromatograms of a number of petroleum products analyzed under the same set of conditions. The column consisted of 10% SP-2100 on 100/120 SUPELCOPORT, 10' x 1/8" stainless steel. (To obtain an idea of the range of carbon numbers, we calibrated the column using a mixture of n-hydrocarbons.)

SP-2100, Supelco's dimethyl silicone stationary phase, is a low viscosity fluid usable from 0°C to 350°C. It has the same separating characteristics as DC-200, SF-96, SE-30, and UC W98. The low viscosity of SP-2100 allows it to be used to prepare columns of high efficiency. The 10' x 1/8" column described above had an efficiency of 7500 plates.

For naphtha, gasoline, kerosene, and others, a 10% stationary phase loading is recommended. Higher amounts of stationary phase produce columns of poorer efficiency. We also recommend using 100/120 mesh SUPELCOPORT to obtain the maximum efficiency. Coarser fractions such as 80/100 and 60/80 mesh will give columns of lower efficiency.

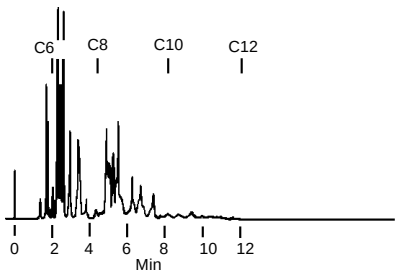
In Figure K no attempt was made to obtain maximum resolution. This can be done by reducing the initial column temperature and by temperature programming the column at a slower rate.

- • A head pressure of about 70lbs is typically observed when producing the desired 25mL/min flow rate. To avoid flow controller problems, we recommend an instrument supply pressure of 90psi.
- ▲ For information about ordering packed columns, refer to our latest catalog, or call our Ordering and Customer Service Department at 800-247-6628 or 814-359-3441.
- ◆ Specify instrument model for which column is to be coiled.

Figure K. Aliphatic Hydrocarbons

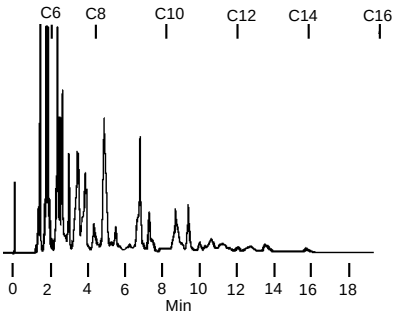
Column: **10% SP-2100 on 100/120 SUPELCOPORT, 10' x 1/8" SS**
Col. Temp.: 75°C to 200°C at 8°C/min
Flow Rate: 20mL/min, N_2
Det.: FID
Sample: 0.1µL

Naphtha



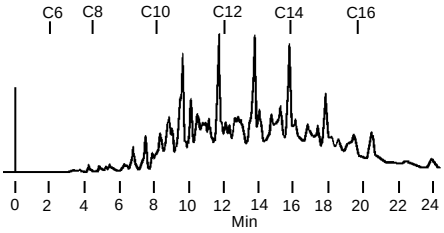
711-0087

Regular Gasoline



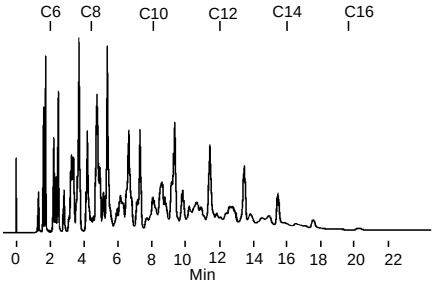
711-0088

Kerosene Jet A



711-0089

Kerosene Jet B

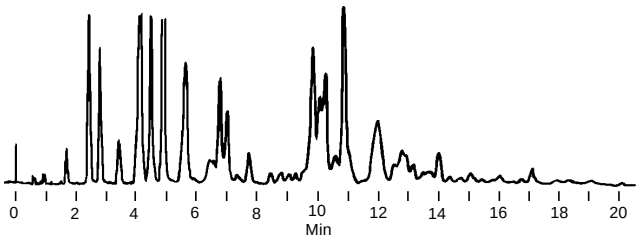


795-0671

Figure L shows the separation of the naphtha sample shown earlier in Figure K, but under conditions modified to obtain better resolution. To obtain maximum separation of a gasoline sample, use a high resolution capillary column rather than a packed column. For details on the complete separation of gasoline samples, see W.N. Sander and J.B. Maynard (24).

Figure L. Naphtha, Highly Resolved

Column: **10% SP-2100 on 100/120 SUPELCOPORT, 10' x 1/8" SS**
Col. Temp.: 30°C to 200°C at 6°C/min
Flow Rate: 20mL/min, N_2
Det.: FID
Sample: 0.1µL



795-0672

Ordering Information:

Description	Cat. No.
Packings	
10% SP-2100 on 80/100 SUPELCOPORT, 20g	**12140**
GP 10% SP-2100 on 100/120 SUPELCOPORT, 20g	**11989**
Stock Packed Stainless Steel Columns▲	
10' x 1/8" column filled with 10% SP-2100 on 100/120 SUPELCOPORT	
General configuration	**12717**
HP 5700, 5992-3, GC-MS	**12739**
HP 5880, 5890, 5987	**12803-U**
PE 900, 3920, Sigma 1, 2, 3	**12750-U**
PE 8300, 8400, 8590, 8600, 8700	
Auto System	**13771**
Varian 3700, Vista series	**12772**
Varian 3300/3400, Vista series	**13772**
10' x 1/8" column filled with 10% SP-2100 on 80/100 SUPELCOPORT	
General configuration	**13766**
HP 5700, 5992-3, GC-MS	**12529**
HP 5880, 5890, 5987	**12530-U**
PE 900, 3920, Sigma 1, 2, 3	**12526**
PE 8300, 8400, 8590, 8600, 8700	
Auto System	**13767-U**
Varian 3700, Vista series	**12527**
Varian 3300/3400, Vista series	**13768**

▲ For information about ordering packed columns, refer to our latest catalog, or call our Ordering and Customer Service Department at 800-247-6628 or 814-359-3441.

GP — Indicates packing has been pretested for specific analysis shown in this section.

Reference

24. Sanders, W.N. and Maynard, J.B., Anal. Chem., *40*, 527 (1968).

Reference not available from Supelco.

Separation of Aromatics from Aliphatics

In many instances it is necessary to determine benzene, toluene, xylenes, and other aromatics in the presence of a number of aliphatic hydrocarbons. With most columns the aliphatics are eluted together, making it difficult or impossible to determine the aromatics. By using certain highly polar stationary phases, aliphatics are separated from aromatics.

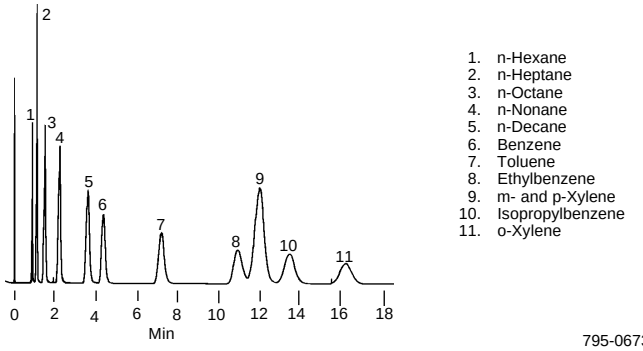
For example, by using 1,2,3-tris(2-cyanoethoxy) propane (TCEP) as the stationary phase, one can retard the aromatics relative to the alphatics with n-decane (C10) eluted before benzene. the column will then separate benzene, toluene, and ethylbenzene, and partially separate the xylenes (m- and p-xylene coelute). In Figure M we show the separation of the C6-C10 aliphatics and the aromatics using 10% TCEP on 100/120 Chromosorb P AW. The use of 100/200 mesh support gives better column efficiency and improves the ethylbenzene/m, p-xylene separation. If the ethylbenzene/xylene separation is not critical, then 80/100 mesh support can be used, with a 25% savings in time.

The separation shown in Figure M is based on the work of C.L. Stuckey (25) who used a 300-foot capillary coated with the stationary phase to separate C6-C10 aromatics in the presence of C1-C11 saturated hydrocarbons. TCEP has an upper temperature limit of 175°C and, for this application, could be conditioned overnight at 100°C.

BC-120 and BC-150 are two other highly polar phases that retard the aromatics relative to the aliphatics (Figure N). BC-120 is limited to a maximum temperature of 125°C, and CBC-150 has a temperature limit of 240°C.

Figure M. Aromatic/Aliphatic Separation

Column: **10% TCP on 100/120 Chromosorb P AW, 8' x 1/8" SS**
Col. Temp.: 80°C
Flow Rate: 20mL/min●, N_2
Sample: 0.2µL



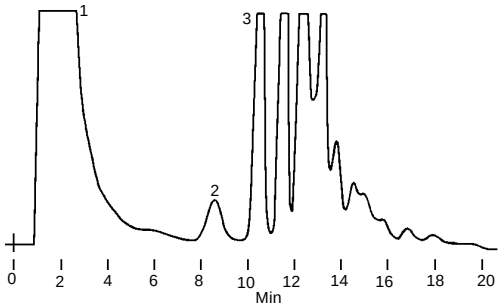
1. n-Hexane
2. n-Heptane
3. n-Octane
4. n-Nonane
5. n-Decane
6. Benzene
7. Toluene
8. Ethylbenzene
9. m- and p-Xylene
10. Isopropylbenzene
11. o-Xylene

795-0673

Figure N. Benzene in Gasoline

Column: **35% BC-150 on 100/120 Chromosorb P AW-DMCS, 10' x 1/8" SS**
Col. Temp.: hold 8min at 110°C, then 220°C at 32°C/min and hold
Flow Rate: 20mL/min, N_2
Det.: FID
Sens.: 256 x 10^{-10} AFS
Sample: 0.5µL gasoline

1. C1-C12 Aliphatic hydrocarbons
2. Benzene
3. Toluene



795-0674

Ordering Information:

Description	Cat. No.
Packings	
GP 10% 1,2,3-tris (2-cyanoethoxy) propane on 100/120 Chromosorb P AW, 20g	**12106-U**
GP 10% 1,2,3-tris (2-cyanoethoxy) propane on 80/100 Chromosorb P AW, 20g	**12122**
GP 35% BC-150 on 100/120 Chromosorb P AW-DMCS, 20g	**11840-U**
GP 35% BC-120 on 100/120 Chromosorb P AW-DMCS, 20g	**11834**
Custom packed stainless steel columns▲	
8 x 1/8" column filled with 10% 1,2,3-tris (2-cyanoethoxy) propane on 80/190 Chromosorb P AW	**custom**

▲ For information about ordering columns with other dimensions, refer to our latest catalog, or call our Ordering and Customer Service Department at 800-247-6628 or 814-359-3441.

GP — Indicates packing has been pretested for specific analysis shown in this section.

Reference

25. Stuckey, C.L., J. Chromatog. Sci., 7,177 (1968).

Reference not available from Supelco.

Note: For details on analysis of industrial solvents, request Bulletin 824.

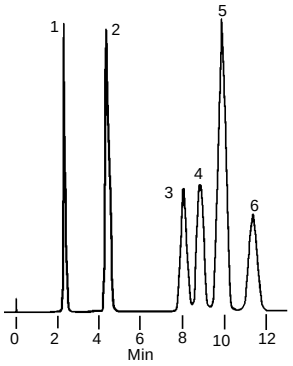
Separation of Xylene Isomers, Styrene, Cumene, etc.

To separate m- and p-xylene on a packed column, it is necessary to use a column which contains a stationary phase plus Bentone 34 (26, 27). Spencer (27) developed a column consisting of 5% didecyl phthalate/5% Bentone 34 to separate benzene, toluene, ethylbenzene and the three xylene isomers as shown in Figure O. To reduce the analysis time by 50% (Figure P), we developed a column consisting of 5% SP-1200/5% Bentone 34 on 100/120 SUPELCOPORT. With both the SP-2100 and phthalate column, isopropylbenzene and o-xylene are eluted.

To separate the xylenes, styrene, and the propyl benzenes, Ottenstein et al. (28) developed a packing consisting of 5% SP-2100/1.75% Bentone 34. The separation of these components on this packing is shown in Figure Q. Table 2 lists the retention values obtained with the packing for the aromatics and for a number of paraffins. To obtain the best efficiency with an SP-1200/1.75% Bentone 34 column, we recommend using a small sample such as 0.1µL of the neat material. As an alternative, the sample could be diluted with a suitable solvent. For more details on the use of Bentone 34 and a literature review on the topic, request Bulletin 740.

Figure O. Xylenes Resolved

Column: **5% DIDP/5% Bentone 34 on 80/100 Chromosorb W NAW, 6' x 1/8" SS**
Col. Temp.: 75°C
Inj. Temp.: 100°C
Det. Temp.: 100°C
Flow Rate: 20mL/min, N_2

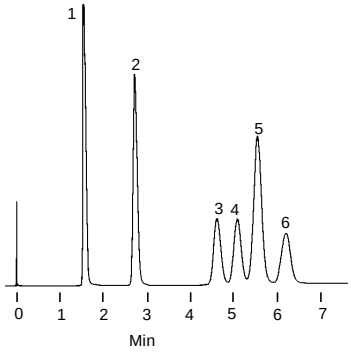


1. Benzene
2. Toluene
3. Ethylbenzene
4. p-Xylene
5. m-Xylene
6. o-Xylene

795-0675

Figure P. Rapid Analysis of Xylenes Isomers

Column: **5% SP-1200/5% Bentone 34 on 100/120 SUPELCOPORT, 6' x 1/8" SS**
Col. Temp.: 100°C
Flow Rate: 20mL/min, N_2
Sample: 0.05µL

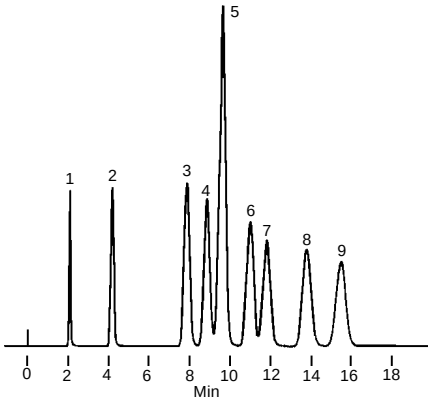


1. Benzene
2. Toluene
3. Ethylbenzene
4. p-Xylene
5. m-Xylene
6. o-Xylene

795-0676

Figure Q. Aromatics

Column: **5% SP-1200/1.75% Bentone 34 on 100/120 SUPELCOPORT, 6' x 1/8" SS**
Col. Temp.: 75°C
Flow Rate: 20mL/min, N_2
Sample: 0.10µL



1. Benzene
2. Toluene
3. Ethylbenzene
4. p-Xylene
5. m-Xylene
6. o-Xylene
4. Isopropylbenzene
5. Styrene
6. n-Propyl benzene

711-0094

Table 2. Corrected Retention, Minutes

(5% SP-1200/1.75% Bentone 34)

Component	Retention Time (min)
n-Hexane	0.40
n-Heptane	1.10
Benzene	1.50
n-Octane	2.65
Toluene	3.55
n-Nonane	6.20
Ethylbenzene	7.25
p-Xylene	8.27
m-Xylene	9.00
o-Xylene	10.35
Isopropylbenzene	11.20
Styrene	13.25
n-Decane	14.20
n-Propyl benzene	14.85

Ordering Information:

Description	Cat. No.
Stationary Phases	
Bentone 34, 50g	**21013-U**
SP-1200, 10g	**21263**
Stock Packings	
GP 5% SP-1200/5% Bentone 34 on 100/120 SUPELCOPORT, 20g	**12133**
GP 5% SP-1200/1.75% Bentone 34 on 100/120 SUPELCOPORT, 20g	**12134**
Custom Packing	
5% didecyl phthalate/5% Bentone 34 on 80/100 Chromosorb W AW, 20g	**custom**
Stock Packed Stainless Steel Columns▲	
6' x 1/8" columns filled with GP 5% SP-1200/5% Bentone 34 on 100/120 SUPELCOPORT	
General configuration	**12721**
HP 5700, 5992-3, GC-MS	**12743**
HP 5880, 5890, 5987	**12798-U**
PE 900, 3920, Sigma 1, 2, 3	**12754**
PE 8300, 8400, 8590, 8600, 8700 Auto System	**13757**
Varian 3700, Vista series	**12776**
Varian 3300/3400, Vista series	**13758**
Custom Packed Stainless Steel Columns▲	
6' x 1/8" column filled with GP 5% SP-1200/5% Bentone 34 on 100/120 SUPELCOPORT	**custom**
6' x 1/8" column filled with 5% didecyl phthalate/5% Bentone 34 on 80/100 Chromosorb W AW	**custom**

▲ For information about ordering columns with other dimensions, refer to our latest catalog, or call our Ordering and Customer Service Department at 800-247-6628 or 814-359-3441.

References

26. Mortimer, J.V. and Gent, P.L., Natuer, *197*, 789 (1963).
27. Spencer, S., Anal. Chem., *35*, 592 (1963).
28. Ottenstein, D.M., Bartley, D.A., and Supina, W. R., Anal. Chem., *46*, 2225 (1974).

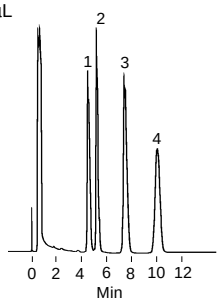
References not available from Supelco.

Separations of Aromatics with Carbopack C Butyl Benzene Isomers

Carbopack C/0.1% SP-1000 can be used to separate mixtures of lower molecular weight aromatics. Because of its unusual separating properties it can be used to separate mixtures of isomers such as the butylbenzenes shown in Figure R. This mixture is difficult to separate and usually requires a capillary column. The test mixture used here consists of 0.1% of each butylbenzene in chloroform, with 1.0µL injected. If the sample is injected neat, it must be reduced to approximately 0.05µL to avoid overloading the column. If excessively large samples are used, broadened peaks, some tailing, and a general reduction in resolution are seen.

Figure R. Butylbenzene Isomers Resolved

Column: **Carbopack C/0.1% SP-1000, 6' x 1/8" SS**
Col. Temp.: 225°C
Flow Rate: 20mL/min, N_2, at 42psi
Det.: FID
Sample: 1.0µL



1. tert-Butylbenzene
2. sec-Butylbenzene
3. Isobutylbenzene
4. n-Butylbenzene

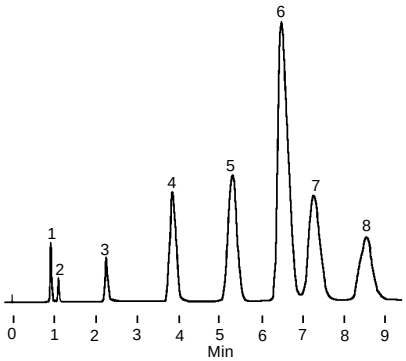
795-0677

Determination of Purity

Figure S shows the separation of a variety of lower molecular weight aromatics and retention values are tabulated in Table 3. The somewhat unusual order of elution of these aromatics makes the packing valuable for determination of purity of certain of the aromatics. Figure T shows a chromatogram of technical ethylbenzene.

Figure S. Aromatics

Column: **Carbopack C/0.1% SP-1000, 6' x 1/8" SS**
Col. Temp.: 200°C
Flow Rate: 20mL/min, N_2, at 42psi



1. Benzene
2. n-Hexane
3. Toluene
4. Ethylbenzene
5. Isopropylbenzene
6. m- and p-Xylene
7. o-Xylene
8. n-Propylbenzene

711-0096

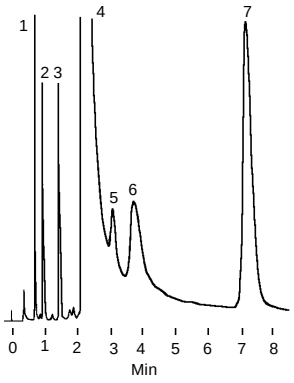
Table 3. Retention Times of Lower Molecular Weight Aromatics

Aromatics	Retention Time (in minutes) at 200°C	at 225°C
n-Hexane	1.15	0.80
n-Heptane	2.30	1.45
n-Octane	5.30	3.00
n-Nonane	12.80	6.70
Benzene	0.95	0.70
Toluene	2.28	1.47
Ethylbenzene	3.90	2.38
Isopropylbenzene	5.36	3.15
m- and p-Xylene	6.60	3.60
o-Xylene	7.30	4.00
n-Propylbenzene	8.56	4.70
1,3,5-Trimethylbenzene	—	9.95
1,2,4-Trimethylbenzene	—	12.10
1,2,3-Trimethylbenzene	—	13.30
tert-Butylbenzene	—	4.55
sec-Butylbenzene	—	5.25
Isobutylbenzene	—	7.45
n-Butylbenzene	—	10.05

Column: **Carbopack C/0.1% SP-1000, 6' x 1/8" SS**
Flow Rate: 20mL/min, N_2, at 42psi

Figure T. Impurities in Ethylbenzene

Column: **Carbopack C/0.1% SP-1000, 6' x 1/8" SS**
Col. Temp.: 225°C
Flow Rate: 20mL/min, N_2, at 42psi



1. Benzene
2. Unknown
3. Toluene
4. Ethylbenzene
5. Isopropylbenzene
6. Xylenes
7. Unknown

711-0097

Ordering Information:

Description	Cat. No.
Packings	
GP 80/100 Carbopack C/0.1% SP-1000	**11820**
Stock Packed Stainless Steel Columns▲	
6' x 1/8" columns filled with GP 80/100 Carbopack C/0.1% SP-1000	
General configuration	**12495-U**
HP 5700, 5992-3, GC-MS	**12499**
HP 5880, 5890, 5987	**12500-U**
PE 900, 3920, Sigma 1, 2, 3	**12496**
PE 8300, 8400, 8590, 8600, 8700 Auto System	**13736-U**
Varian 3700, Vista series	**12497**
Varian 3300/3400, Vista series	**13737**

▲ For information about ordering columns with other dimensions, refer to our latest catalog, or call our Ordering and Customer Service Department at 800-247-6628 or 814-359-3441.

High Boiling Aromatics

Creosote

Higher boiling aromatics can be separated on several column packings. Among these are SP-2100 (a methyl silicone), SP-2250 (a 50:50 methyl phenyl silicone), and a combination of SP-2100 and p-methoxybenzlidene-α,α′-bi-p-toluidene (BMBT). The BMBT, a liquid crystal developed by Janini et al. (29) has the ability to separate phenanthrene and anthracene, which is not normally separated with a conventional stationary phase. The performance of the three columns is compared in Figures U, V, and W for the separation of a commercial sample of creosote (30). In each case a 10′ x 1/8″ stainless steel column was used.

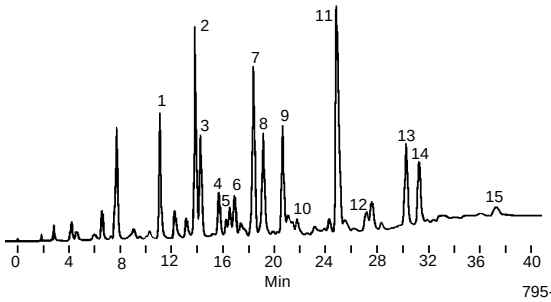
Methylbenzenes

The tri- and tetramethylbenzenes can be separated using 10% SP-2250, as shown in Figure X. We find that most columns will not separate the 1,2,4,5- and 1,2,3,5-tetra pair.

Figure U. Creosote on SP-2100

Column: **10% SP-2100 on 100/120 SUPELCOPORT, 10'x 1/8" SS**
Col. Temp.: 100°C to 300°C at 6°C/min
Flow Rate: 20mL/min, N_2
Det.: FID
Sample: 0.1µL

1. Naphthalene
2. 2-Methylnaphthalene
3. 1-Methylnaphthalene
4. Biphenyl
5. 2,6-Dimethylnaphthalene
6. 2,3-Dimethylnaphthalene
7. Acenaphthalene
8. Dibenzofuran
9. Fluroene
10. Methyl fluorenes
11. Phenanthrene and Anthracene
12. Carbazole
13. Fluoranthene
14. Pyrene
15. Chrysene

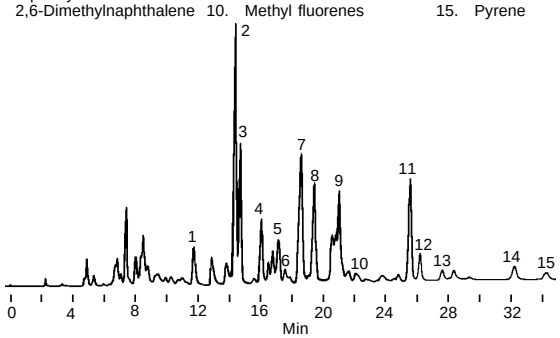


795-0678

Figure V. Creosote on SP-2100/BMBT

Column: **5% SP-2100/1% BMBT on 100/120 SUPELCOPORT, 10' x 1/8" SS**
Col. Temp.: 85°C to 225°C at 6°C/min
Flow Rate: 20mL/min, N_2
Det.: FID
Sample: 0.1µL

1. Naphthalene
2. 2-Methylnaphthalene
3. 1-Methylnaphthalene
4. Biphenyl
5. 2,6-Dimethylnaphthalene
6. 2,3-Dimethylnaphthalene
7. Acenaphthalene
8. Dibenzofuran
9. Fluroene
10. Methyl fluorenes
11. Phenanthrene
12. Anthracene
13. Carbazole
14. Fluoranthene
15. Pyrene

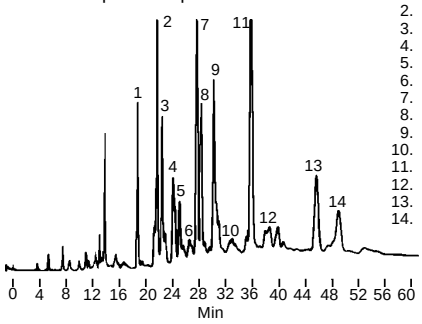


795-0682

Figure W. Creosote on SP-2250

Column: **10% SP-2250 on 100/120 SUPELCOPORT, 10' x 1/8" SS**
Col. Temp.: 100°C to 300°C at 6°C/min
Flow Rate: 20mL/min, N_2
Det.: FID
Sample: 0.1µL

1. Naphthalene
2. 2-Methylnaphthalene
3. 1-Methylnaphthalene
4. Biphenyl
5. 2,6-Dimethylnaphthalene
6. 2,3-Dimethylnaphthalene
7. Acenaphthalene
8. Dibenzofuran
9. Fluroene
10. Methyl fluorenes
11. Phenanthrene and Anthracene
12. Carbazole
13. Fluoranthene
14. Pyrene

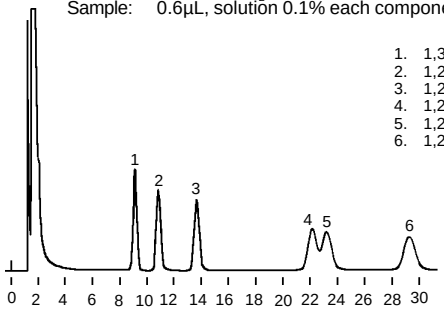


711-0099

Figure X. Tri- and Tetramethylbenzenes

Column: **10% SP-2250 on 100/120 SUPELCOPORT, 10' x 1/8" SS**
Col. Temp.: 110°C
Flow Rate: 20mL/min, N_2
Sample: 0.6µL, solution 0.1% each component in $CHCl_3$

1. 1,3,5-Trimethylbenzene
2. 1,2,4-Trimethylbenzene
3. 1,2,3-Trimethylbenzene
4. 1,2,4,5-Tetramethylbenzene
5. 1,2,3,5-Tetramethylbenzene
6. 1,2,3,4-Tetramethylbenzene



711-0100

Ordering Information:

Description	Cat. No.
Packings	
10% SP-2100 on 100/120 SUPELCOPORT, 20g	**11989**
10% SP-2250 on 100/120 SUPELCOPORT, 20g	**12132**
5% SP-2100/1% BMBT on 100/120 SUPELCOPORT, 20g	**custom**
Custom Packed Stainless Steel Columns▲	
Specify the instrument for which the column is to be coiled:	
10' x 1/8" column filled with 10% SP-2250 on 100/120 SUPELCOPORT	**custom**
10' x 1/8" column filled with 5% SP-2100/1% BMBT on 100/120 SUPELCOPORT	**custom**
Stock packed stainless steel columns▲	
10' x 1/8" column filled with 10% SP-2100 on 100/120 SUPELCOPORT	
Listed in "Separation of Aliphatic Hydrocarbons."	

▲ For information about ordering columns with other dimensions, refer to our latest catalog, or call our Ordering and Customer Service Department at 800-247-6628 or 814-359-3441.

For information on analyzing polynuclear aromatic hydrocarbons, request Bulletin 773.

References

29. Janini, G.M., Johnston, K., and Zielinski, W.L., Jr., Anal. Chem., *47*, 670 (1975).
30. Nestler, F.H.M., Anal. Chem., *46*, 46 (1974).

References not available from Supelco.

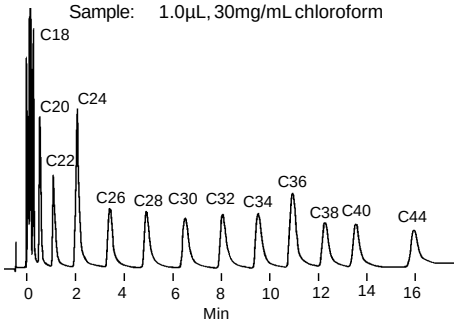
Separation of Microcrystalline Wax Hydrocarbons

Altgelt and Guow (31) have reviewed the topic of heavy petroleum fractions. This review deals with the use of GC for analyzing these higher boiling petroleum fractions, and the use of stimulated distillation to determine the boiling range of the fraction. Other references (32-35) discuss these analyses in detail.

One can obtain a "fingerprint" of microcrystalline waxes using a short (18" x 1/8") stainless steel column filled with 1% Dexsil 300 on 100/120 SUPELCOPORT. Separation of a mixture of known n-hydrocarbons up to C44 is shown in Figure Y. Wax sample separations are shown in Figure Z using the same column and operating conditions.

Figure Y. Standard n-Hydrocarbons

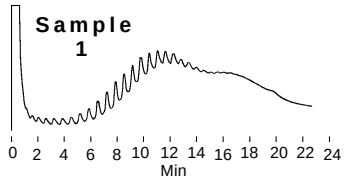
Column: **1% Dexsil 300 on 100/120 SUPELCOPORT, 18' x 1/8" SS**
Col. Temp.: 175°C to 350°C at 8°C/min
Inj. Temp.: 325°C
Det. Temp.: 350°C
Flow Rate: 20mL/min, N_2
Sens.: 16 x 10^{-11} AFS
Sample: 1.0µL, 30mg/mL chloroform



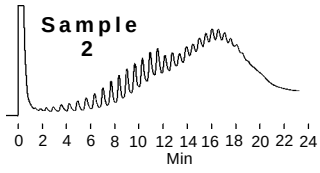
795-0679

Figure Z. Microcrystalline Wax

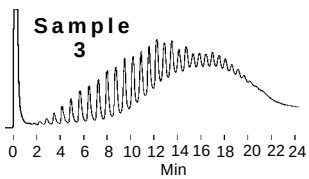
Column and operating conditions, see Figure Y.



795-0680



795-0685



795-0686

Wax samples 1, 2, and 3 represent the range in melting points and molecular weights for microcrystalline waxes. These samples were obtained by solvent fractionation of the "long residuum" fraction in petroleum production. The approximate melting points (ASTM D-127 MP) of 1, 2, and 3 are 65-70°C, 76-82°C, and 88-96°C, respectively. The number average molecular weights (M_N) of 1, 2, and 3 are approximately 745, 760, and 820, respectively. Waxes 1 and 2 are predominantly (~75 and 65% respectively) isoparaffin molecules; while Wax 3 is predominantly n-paraffin molecules (~85 - 98%). One can get an idea of the molecular weight distribution of each wax sample by comparing the sample to the standard mixture. The wax samples were kindly supplied by Gilbert Palmgren of Witco Chemical Corp., Petrolia, Pennsylvania, USA.

When working with a 1% Dexsil column, one should not use too large a sample because the column will overload and the resolution will decrease. The samples used in this study were dissolved in chloroform at a concentration of 30mg/cc, and 1.0µL samples were injected into the column.

In dealing with high temperature, programmed temperature column operation, extraneous peaks often result, caused by bleed from the septum. This problem can be reduced or eliminated by using high temperature septa. For more details, request Bulletins 755 and 780.

Ordering Information:

Description	Cat. No.
Packing	
1% Dexsil 300 on 100/120 SUPELCOPORT, 20g	**11972**
Custom Packed Stainless Steel Columns	
18" x 1/8" column filled with 1% Dexsil 300 on 100/120 SUPELCOPORT	**custom**

References

31. Altgeld, K.H., and Gouw, T.H., "Heavy Petroleum Fraction," *13*, Advances in Chromatography, Marcel Dekker, New York, NY, 1975.
32. ASTM D288-70T, "1971 Annual Book of ASTM Standards," part 17, p. 1072, American Society for Testing and Materials, Philadelphia, PA 19103.
33. Gouw, T.H., Anal. Chem., *45*, 987 (1973).
34. Gouw, T.H., Henkins, R.L., and Jentoft, R.E., J. Chromatog., *28*, 219 (1967).
35. Green, L.S., Schmauch, L.J., and Worman, J.C., Anal. Chem., *36*, 1512 (1964).

References not available from Supelco.