

# Total Petroleum Hydrocarbon Analysis by Capillary Gas Chromatography: Decreasing Analysis Times Using Small-Diameter Columns

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## Abstract

The relationship of the injector and column and its influence on GC conditions, method detection limits, resolution, and analysis times for total petroleum hydrocarbon analyses are examined. Decreasing the length and diameter of the capillary column results in a significant analysis time reduction. The resolution of closely eluting peaks is maintained or improved with smaller columns. Even with very short analysis times, the chromatographic profiles or patterns of different petroleum samples are still easily distinguishable. For Megabore direct injectors, the best solvent front shapes and widths are obtained with flash vaporization liners, allowing the resolution of very light hydrocarbons from the solvent front. Packing the liner with glass wool improves the peak shape of the heavier, low-volatility hydrocarbons. The use of split injectors results in increases in method detection limits and injector discrimination. As column diameter decreases, the use of faster ramp rates in the temperature program is required to obtain the shortest analysis times.

## Introduction

Leaking underground petroleum storage tanks contaminate nearby soils and waters, thus creating an environmental problem. Sensitive and specific water and soil analyses are often desired so that the source, type, and level of contamination can be determined. Although techniques such as infrared can be used (1,2), gas chromatography (GC) often provides the higher specificity and sensitivity needed in most cases. Various and diverse sample extraction and concentration techniques have been used to prepare the samples for GC analysis. These techniques include solvent extraction (3–6), distillation (7–8), purge and trap (9–12), headspace (13–14), and supercritical fluid extraction (2,15).

The hydrocarbons typically found in contaminated environmental samples range from very volatile liquids (such as hexane) to low volatility waxes in the  $C_{40}$  or higher range. This wide volatility range forces an analyst to consider a wide variety of column selection and injector related issues. Column dimen-

sions ideal for light hydrocarbons are less than ideal for heavier hydrocarbons and aromatics, and vice versa. The available GC hardware may also place restrictions on the choice of columns and conditions. Also, the column dimensions may place restrictions on the type of injector that can be used.

The performance of total petroleum hydrocarbon (TPH) analyses is significantly influenced by the type of injector and the inner diameter of the capillary column. This paper examines the interconnected relationship of the injector and column and their influence on GC conditions, method detection limits, resolution, and analysis times for TPH analyses.

## Experimental

Megabore™ (J&W Scientific, Folsom, CA) analyses were performed using a Hewlett-Packard (Wilmington, DE) 5890 series II GC. The original packed-column injector was converted using a Megabore conversion kit and flash vaporization liner from J&W Scientific. The fused-silica column was a J&W Scientific DB-1 (30 m × 0.45-mm i.d., 0.42- $\mu$ m film thickness). The narrow-bore and high-speed analyses were performed using a Shimadzu (Kyoto, Japan) 17A version 3 GC. A FocusLiner from SGE (Austin, TX) was used in the split/splitless injector. The fused-silica columns were DB-1 (15 m × 0.25-mm i.d., 0.25- $\mu$ m film thickness) and DB-1 (5 m × 0.10-mm i.d., 0.1- $\mu$ m film thickness) from J&W Scientific. Flame ionization detectors (FIDs) were used for all analyses. Specific analysis conditions are presented with the respective figures. The hydrocarbon characterization, premium gasoline, diesel fuel, and motor oil (30W) standards were prepared and provided courtesy of Accustandard (New Haven, CT).

## Results and Discussion

### Megabore capillary columns

Megabore columns are often used for TPH analyses when ease of use, high carrier gas flow rates, or high sample capacity is

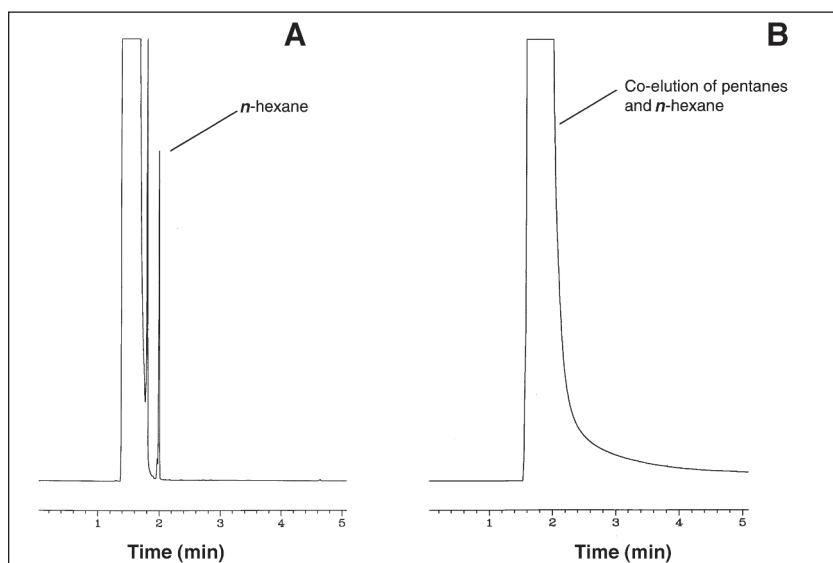
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desired. Many headspace and purge-and-trap samplers require higher carrier gas flow rates to operate properly, thus Megabore columns are needed for these systems. Smaller diameter columns do not tolerate the high carrier gas flow rates needed to successfully operate most headspace and purge-and-trap samplers. In most cases, only 0.45–0.53-mm-i.d. columns can be used with a Megabore direct injector. Using a smaller inner diameter ( $\leq 0.32$  mm) column with a Megabore direct injector invariably results in an excessively broad or distorted peak. Although Megabore columns can be successfully used with a split/splitless injector, there is no compelling chromatographic reason to do so, except for the higher capacity of large diameter columns.

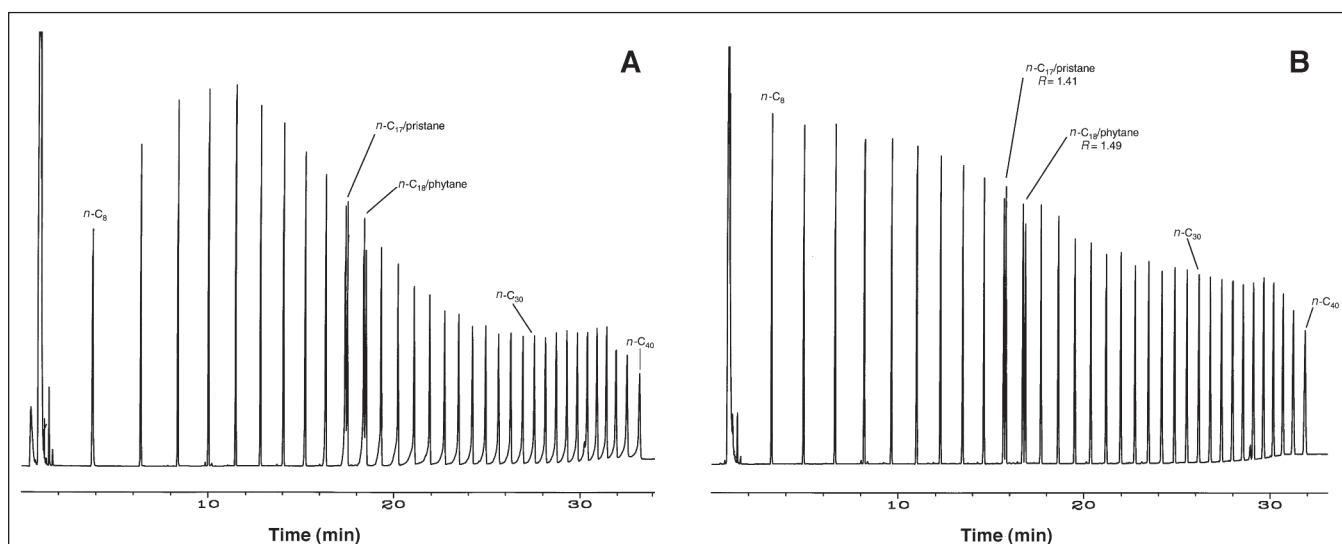
Many Megabore direct injectors are outfitted with a liner that is essentially a straight tube. An alternative Megabore direct liner is commonly called a "flash vaporization liner". It is distinguished by a tapered restriction that is located somewhere between the middle and the bottom of the liner. The diameter of the restriction is smaller than the outer diameter of 0.45- and 0.53-mm-i.d. capillary columns. When a Megabore column is pushed into the liner, it becomes lodged in the restriction. When properly installed, a leak-free seal between the column and liner is obtained. This prevents any carrier gas from traveling past and around the opening of the column. Narrower solvent fronts with less pronounced tails are obtained in comparison with straight tube liners. For TPH analyses requiring the resolution of *n*-hexane from the solvent front (often pentane), a narrow solvent front with minimal tailing is required to meet this directive. Figure 1 shows the superior solvent front obtained with a flash vaporization liner. Flash vaporization liners are not available for every model of Megabore direct injector. This is primarily the case for injectors that use small diameter ( $\leq 0.2$  mm i.d.) liners or glass inserts.

The wide range of volatilities or boiling points of the analytes in many TPH analyses presents a chromatographic challenge. Using thicker film columns to resolve the earlier eluting hydrocarbons from the solvent front results in the very high retention of the heavier, later-eluting hydrocarbons. Using thinner film columns to reduce the retention of the larger hydrocarbons results in resolution losses for the earliest eluting peaks. Compromises and adjustment to the conditions and GC are often necessary.

Upon injection of a hydrocarbon standard ranging from *n*-octane (*n*-C<sub>8</sub>) to tetracontane (*n*-C<sub>40</sub>), peak fronting for the lower volatility

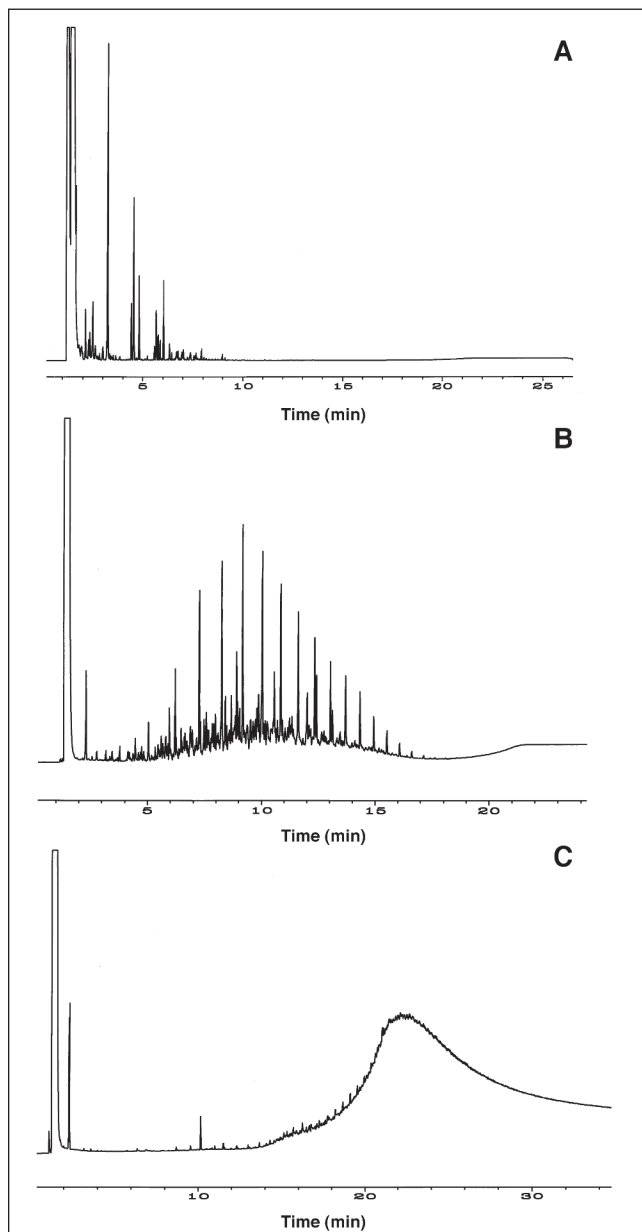


**Figure 1.** Megabore direct injector and 0.45-mm-i.d. column: flash vaporization liner (A) and straight liner (B). 1- $\mu$ L injection of 500-ppm *n*-hexane in pentane. Chromatographic conditions: DB-1 (30 m  $\times$  0.45-mm i.d., 0.42- $\mu$ m film thickness); Megabore direct injector, 300°C; FID detector, 300°C; helium carrier gas at 6.5 mL/min; column temperature, 35°C for 5 min.



**Figure 2.** Megabore direct injector and 0.45-mm-i.d. column: flash vaporization liner (A) and flash vaporization liner with 30 mg of glass wool (B). 1- $\mu$ L injection of 500-ppm hydrocarbon characterization standard. Chromatographic conditions: DB-1 (30 m  $\times$  0.45-mm i.d., 0.42- $\mu$ m film thickness); Megabore direct injector, 300°C; FID detector, 320°C; helium carrier gas at 6.5 mL/min. Column temperature (A): 35°C for 4 min, 35–320°C at 10°/min, 320°C for 3 min. Column temperature (B): 35°C for 2 min, 35–320°C at 10°/min, 320°C for 3 min.

(i.e., higher boiling point) hydrocarbons was observed (Figure 2A). Using different injector temperatures (275, 300, and 325°C) and carrier gas flow rates (4.5, 6.0, and 9.5 mL/min) and adding additional thermal insulation around the injector body did not change the peak shapes. Only the addition of silylated glass wool to the flash vaporization liner corrected the peak fronting problem (Figure 2B). Most flash vaporization liners have an additional upper restriction that acts as a needle guide or backflash barrier. If a flash vaporization liner needs to be packed with glass wool, a liner without an upper restriction is needed. A glass wool plug of 20–40 mg placed immediately above the column restriction provided the best peak shapes. A consistent position,



**Figure 3.** Megabore direct injector and 0.45-mm-i.d. column. 0.5- $\mu$ L injection of 5000-ppm standards of gasoline (A), diesel (B), and motor oil (C). Chromatographic conditions: DB-1 (30 m  $\times$  0.45-mm i.d., 0.42- $\mu$ m film thickness); Megabore direct injector, 300°C with flash vaporization liner packed with 30 mg of glass wool; FID detector, 320°C; helium carrier gas at 6.0 mL/min; column temperature, 35°C for 2 min, 35–320°C at 15°/min, 320°C for 14 min.

amount, and plug size was needed to obtain the best peak area precision.

Column efficiency (i.e., number of theoretical plates per meter;  $N/m$ ) decreases as column diameter increases, thus Megabore columns have the lowest efficiency of the commercially available capillary columns. Sufficient resolution between *n*-heptadecane (*n*-C<sub>17</sub>) and pristane and *n*-octadecane (*n*-C<sub>18</sub>) and phytane was obtained for the chromatogram in Figure 2B. Even though Megabore columns have the lowest efficiency, distinct patterns are still obtained for the petroleum samples encountered in TPH analyses. Figure 3 shows the chromatograms obtained for gasoline, diesel, and motor oil using a 0.45-mm-i.d. Megabore column and a flash vaporization liner packed with 30 mg of glass wool.

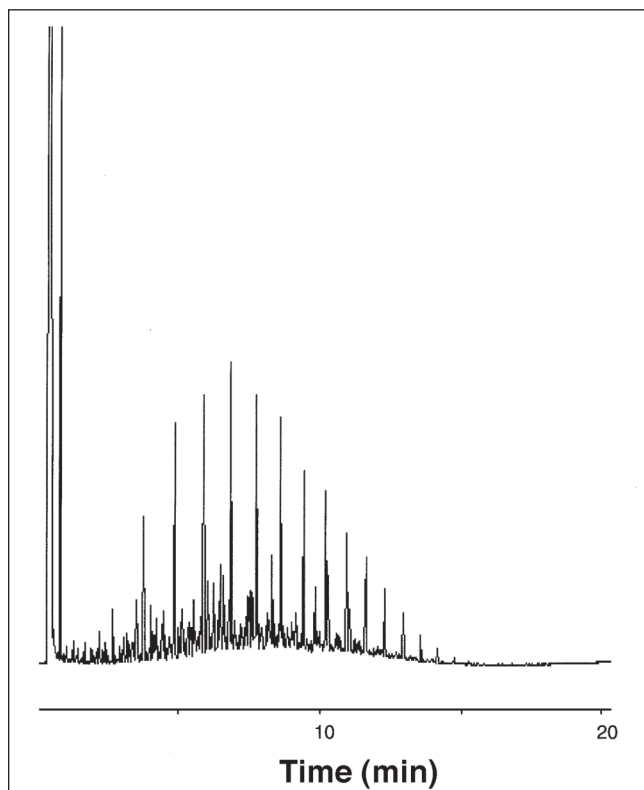
### Narrow bore capillary columns

Narrow bore (0.25–0.32-mm i.d.) columns are often used when better peak resolution is desired. A split/splitless injector (or one specifically designed for small-diameter columns) is required to fully utilize the higher efficiency of smaller diameter columns. Splitless injectors are used when low detection limits are needed, because most of the sample enters the column. For splitless injections, the initial temperature of the temperature program needs to be a minimum of –10°C below the sample solvent's boiling point to obtain acceptable peak shapes for low boiling (i.e., earlier eluting) analytes. Most TPH methods use low-boiling-point sample solvents such as pentane or methylene chloride. With these solvents, initial oven temperatures of 25–35°C are needed. Oven temperatures of 30°C or below can rarely be obtained without the use of cryogenic cooling. Cryogenic cooling adds additional complexity and cost to the analysis and is usually avoided whenever possible. Solvent fronts are typically broad for splitless injections; thus, resolving *n*-hexane from the solvent front becomes difficult. If this requirement needs to be met, using a splitless injection for the TPH analysis may not be feasible.

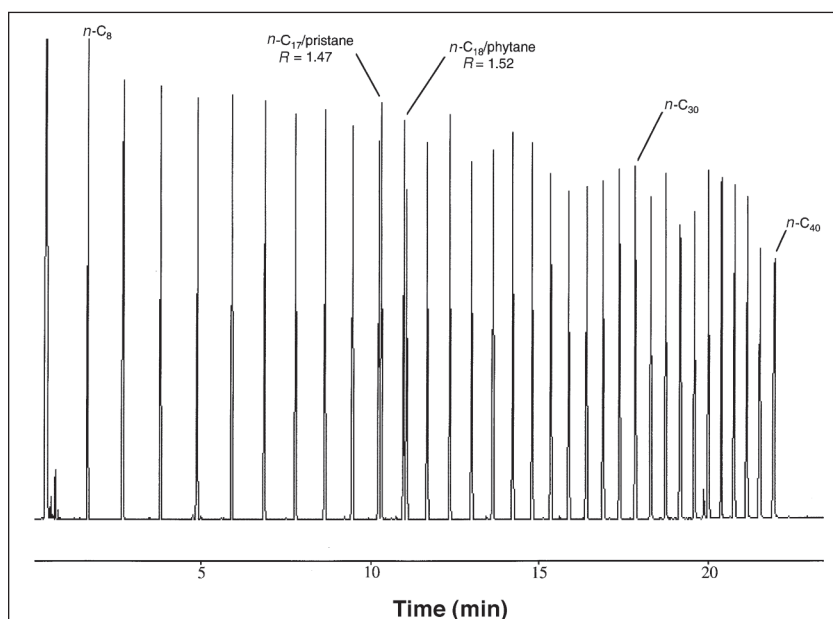
Split injections do not have temperature program restrictions, and the resulting solvent fronts are typically much smaller than for splitless injections. This makes split injections an attractive choice for TPH samples containing low-boiling-point analytes; however, split injectors are not without shortcomings. Split injectors discard a large portion of the injected sample, and only a small amount enters the column. Because of this characteristic, there is an increase in the method detection limit in comparison with a Megabore direct or splitless injection. Although this can be a problem for some very low-level TPH analyses, detection limit losses can be minimized with a proper split injector setup.

Most split injectors require a minimum of 15–20 mL/min of total carrier gas flow (column flow plus split vent flow) in order to obtain acceptable peak shapes, especially for earlier eluting analytes. For a 0.25-mm-i.d. column and helium carrier gas, column flow rates of ~1 mL/min are typical. A split ratio of approximately 1:20 would be needed to obtain good peak shapes. If hydrogen is used as the carrier gas, flow rates of ~3 mL/min are typical. At this column carrier gas flow rate, a split ratio of approximately 1:6 can be successfully used. Using a split ratio of 1:6 would improve detection limits by ~3 times in comparison

with a 1:20 split ratio. Using hydrogen as the carrier gas allows the use of lower split ratios; thus, lower detection limits than with helium are possible. The chromatogram in Figure 4 was generated using a 15-m  $\times$  0.25-mm-i.d. column, hydrogen carrier gas, a 1:6 split ratio, and the same hydrocarbon standard as



**Figure 4.** Split injector and 0.25-mm-i.d. column. 1- $\mu$ L injection of 500-ppm hydrocarbon characterization standard. Chromatographic conditions: DB-1 (15 m  $\times$  0.25-mm i.d., 0.25- $\mu$ m film thickness); split injector, 325°C with a split ratio of 1:6; FID detector, 320°C; hydrogen carrier gas at 3.0 mL/min (80 cm/s); column temperature, 35°C for 1 min, 35–340°C at 15°/min, 340°C for 5 min.



**Figure 5.** Split injector and 0.25-mm-i.d. column. 3- $\mu$ L injection of 500-ppm diesel fuel standard. Chromatographic conditions are the same as Figure 4.

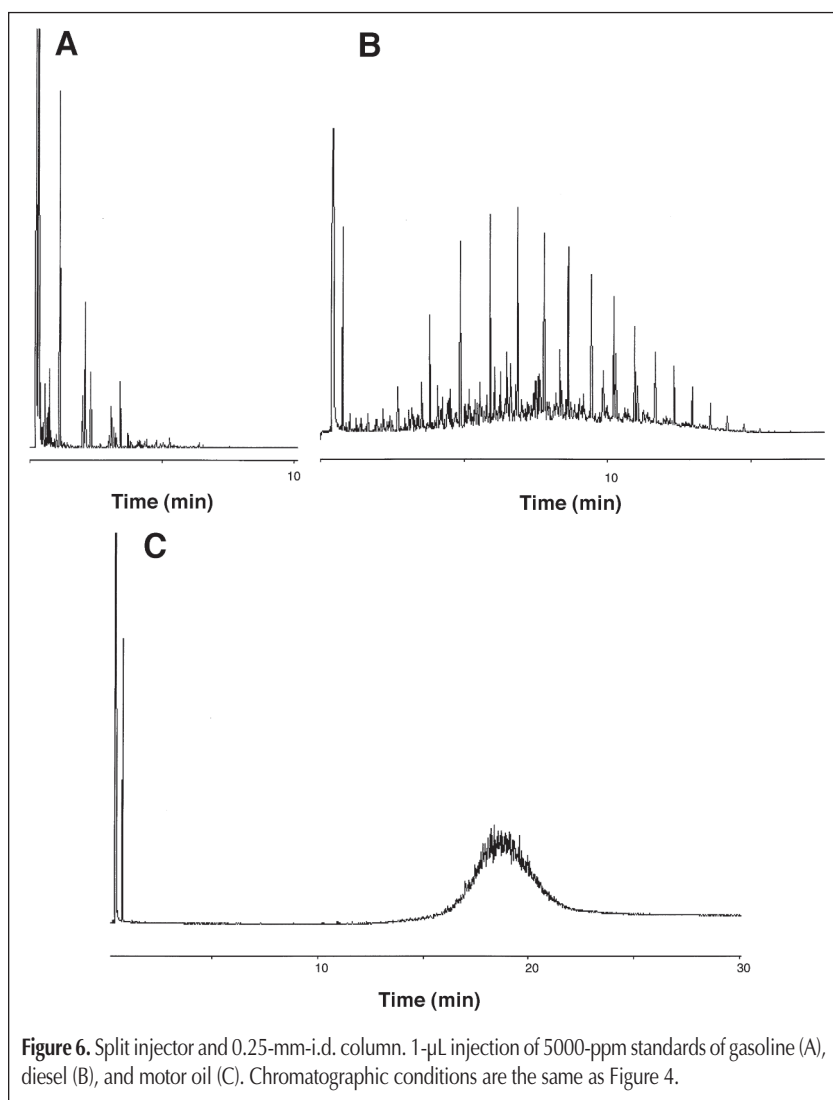
for Megabore direct injection in Figure 2B. Depending on the hydrocarbon, the peak areas were 4–8 times smaller than for the Megabore direct injection. In general, the later eluting hydrocarbons exhibited the largest reductions in peak areas. Even with a 1:6 split ratio, numerous peaks are readily visible for a 500-ppm diesel standard (Figure 5).

The higher efficiency of narrow-bore columns can be used to reduce analysis times. Resolution is a function of peak width and separation. Resolution is increased by decreasing peak widths and increasing peak separation. A 0.25-mm-i.d. column is approximately 2 times more efficient ( $N/m$ ) and retentive than a 0.53-mm-i.d. column with the same stationary phase, film thickness, and length. Similar resolution and retention is obtained with a 0.25-mm-i.d. column that is half the length of a corresponding 0.53-mm-i.d. column. Higher temperatures or faster ramp rates can be used with 0.25-mm-i.d. columns, and the same or better resolution than the 0.53-mm-i.d. column is obtained. The higher temperatures or faster ramps often result in shorter analysis times. Figure 4 shows the chromatogram for the  $n$ -C<sub>8</sub> to  $n$ -C<sub>40</sub> hydrocarbon standard using a 15-m  $\times$  0.25-mm-i.d. column, a 1:6 split ratio, and a more aggressive temperature program. Comparing this chromatogram to the 30-m  $\times$  0.45-mm-i.d. Megabore version (Figure 2B) shows that slightly better resolution between the  $n$ -C<sub>16</sub>/pristane and  $n$ -C<sub>17</sub>/phytane peaks was obtained, along with a 31% decrease in analysis time. Similar results were obtained when comparing the 0.25-mm-i.d. column (Figure 6) to the 0.45-mm-i.d. column (Figure 3) for the same gasoline, diesel, and motor oil standards.

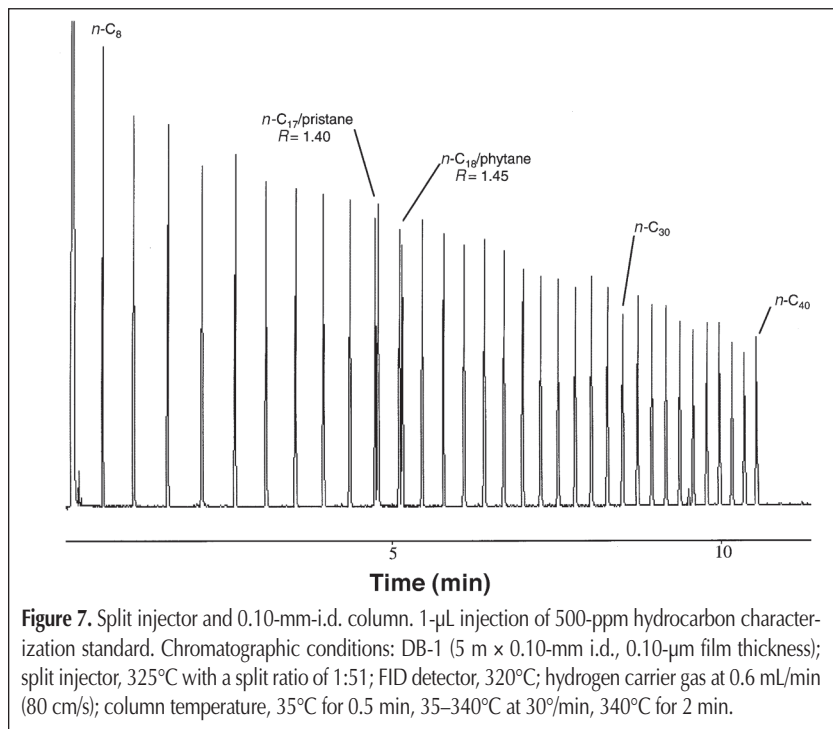
A potential benefit in using small-diameter columns is their lower column bleed levels. Smaller diameter columns usually have thinner films than larger diameter columns used for similar applications. The smaller diameter and thinner film result in less stationary phase in the column and thus lower column bleed at the same or even higher temperature. Column bleed is evident as a sharp rise in the baseline as the column temperature approaches and reaches a column's upper temperature limit. The baseline rise is clearly visible (starting near 28 min) in the Megabore column chromatogram (Figure 2B), whereas the baseline rise is too small to be seen for the 0.25-mm narrow-bore column chromatogram (Figure 5).

In the late 1990's, one of the areas of highest activity in the field of capillary GC is high-speed or fast GC techniques. Columns with inner diameters of 50–100  $\mu$ m and lengths of 1–10 m are being used to achieve high-speed or fast analyses. The very small diameter columns have high numbers of theoretical plates per meter ( $N/m$ ); thus, only short column lengths are able to achieve the resolution obtained with the much longer and larger diameter columns. In turn, the short column lengths result in very short analysis times, hence the achievement of high-speed GC.

As previously discussed, TPH analyses using splitless injectors with small-diameter columns can be problematic. This problem is amplified with 50–100- $\mu$ m columns to a point where splitless injections cannot be used for virtually any



**Figure 6.** Split injector and 0.25-mm-i.d. column. 1- $\mu$ L injection of 5000-ppm standards of gasoline (A), diesel (B), and motor oil (C). Chromatographic conditions are the same as Figure 4.



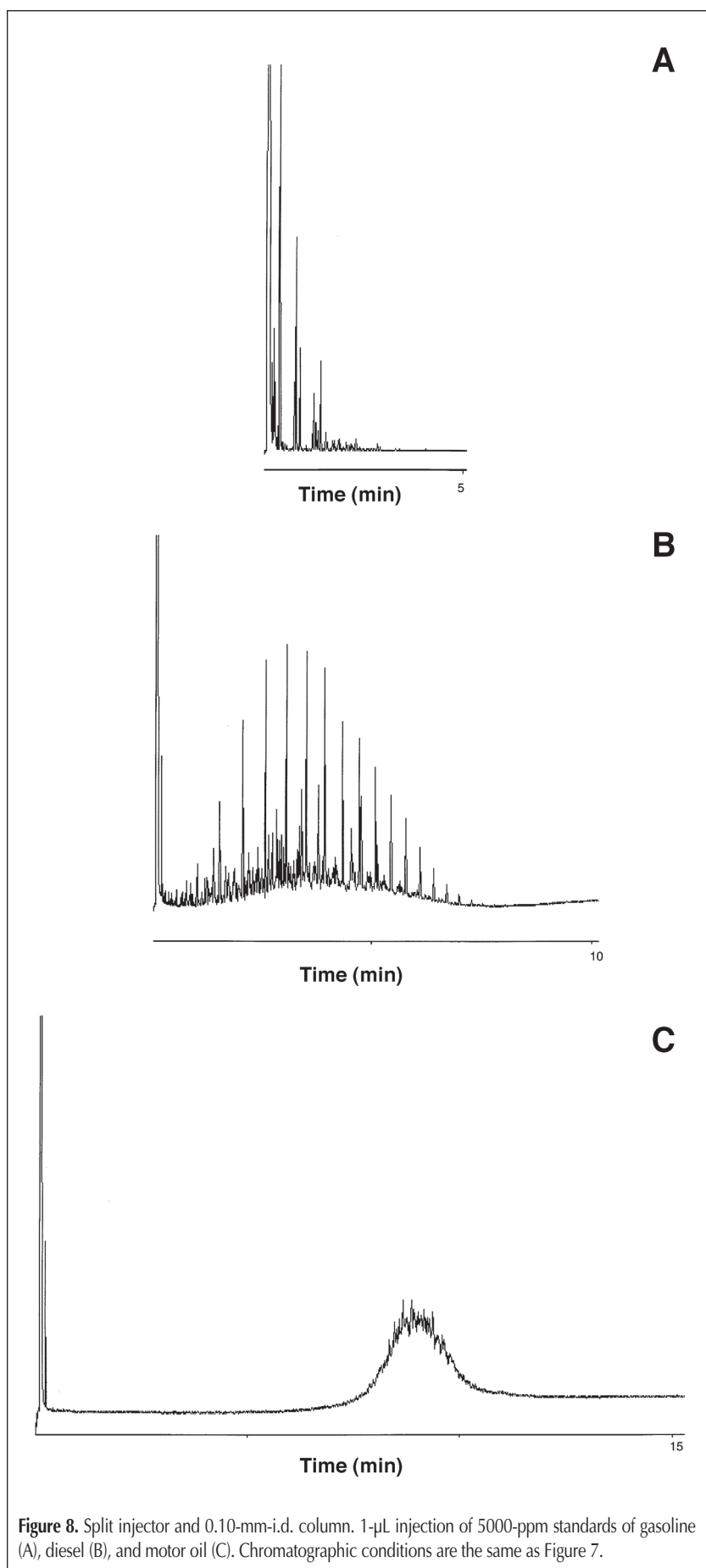
**Figure 7.** Split injector and 0.10-mm-i.d. column. 1- $\mu$ L injection of 500-ppm hydrocarbon characterization standard. Chromatographic conditions: DB-1 (5 m  $\times$  0.10-mm i.d., 0.10- $\mu$ m film thickness); split injector, 325°C with a split ratio of 1:51; FID detector, 320°C; hydrogen carrier gas at 0.6 mL/min (80 cm/s); column temperature, 35°C for 0.5 min, 35–340°C at 30°/min, 340°C for 2 min.

application without cryogenic interfaces or column cooling. The 50–100- $\mu$ m columns require the use of split injectors. The minimum requirement of 15–20 mL/min total carrier gas flow rates still applies for high-speed columns. Using helium as the carrier gas requires a minimum split ratio of approximately 1:65 for a 100- $\mu$ m column, because the column flow rate is typically around 0.3 mL/min. For hydrogen, the minimum split ratio is approximately 1:35 (for column flow rates of  $\sim$ 0.6 mL/min). For 50- $\mu$ m columns, the minimum split ratios are doubled. Although very short analysis times are obtained, detection limits suffer because of the required high split ratios. For this reason, high-speed GC techniques using short and very small diameter columns are often not suited for low-level TPH analyses.

Figure 7 shows the  $n$ -C<sub>8</sub> to  $n$ -C<sub>40</sub> hydrocarbon standard chromatogram obtained using a 5-m  $\times$  0.1-mm-i.d. column, hydrogen carrier gas, and a 1:51 split ratio. Although nearly equivalent resolution to the 0.25- and 0.45-mm-i.d. columns is obtained, the retention time of  $n$ -C<sub>40</sub> is approximately 66% and 50% less than the 0.45- and 0.25-mm-i.d. columns, respectively. Comparable results are obtained for the gasoline, diesel, and motor oil standards (Figure 8).

To obtain the shortest analysis times for high speed columns, very fast temperature program ramp rates are required. Ramp rates of 25–50°C/min are typically used throughout the temperature program for high-speed GC. A ramp rate of 30°C/min was used for the 0.1-mm-i.d. column. This rate is much faster than the ramp rate of 15°C/min used for the 0.25-mm-i.d. and 0.45-mm-i.d. columns. Older model GCs are often unable to maintain ramp rates of 25–50°C/min over their entire oven temperature range; thus, they may be unsuitable or limited for high-speed GC applications. Using slower ramp rates does not fully exploit the very short analysis times possible with 50–100- $\mu$ m diameter columns.

Vaporization injectors such as Megabore direct and split/splitless injectors do not introduce the same fraction or percent of each sample compound into the column. In general, higher amounts of the more volatile sample compounds are introduced into the column than the less volatile compounds. This behavior is called “injector” or “inlet discrimination”. Injector discrimination is evident in chromatograms as a decrease in peak size for the later eluting analytes. Often injector discrimination is not obvious due to differences in analyte concentrations, and detector response discrimination is not obvious due to differences in analyte concentrations and



**Figure 8.** Split injector and 0.10-mm-i.d. column. 1- $\mu$ L injection of 5000-ppm standards of gasoline (A), diesel (B), and motor oil (C). Chromatographic conditions are the same as Figure 7.

detector response factors. Injector discrimination is easily visible in Figure 7. Even though the sample concentration of each hydrocarbon is the same, the peak area for  $n$ -C<sub>40</sub> is 53% of  $n$ -C<sub>8</sub>. If detector response differences are considered, the peak area for  $n$ -C<sub>40</sub> is 11% of  $n$ -C<sub>8</sub> ( $n$ -C<sub>40</sub> is approximately 5 times more responsive than  $n$ -C<sub>8</sub> for a FID). Injector discrimination increases at higher split ratios; thus, lower discrimination is expected and observed for the 0.25-mm-i.d. (Figure 5, 1:6 split ratio) and the Megabore (Figure 2B, no split) columns than for the 0.10-mm-i.d. column (Figure 7, 1:51 split ratio).

## Conclusion

Decreasing the length and diameter of the capillary column resulted in a significant analysis time reduction for TPH analyses. Analysis time reductions of 50–66% were obtained as column diameters and lengths were decreased. The resolution of closely eluting peaks was maintained or improved with the smaller columns. Even with the very short analysis times, the chromatographic profiles or patterns of different petroleum samples were still easily distinguishable.

For Megabore direct injectors, 0.45- or 0.53-mm-i.d. columns are required. The best solvent front shapes and widths were obtained with flash vaporization liners. This allowed the resolution of very light hydrocarbons (such as hexane) from the solvent front. Packing the liner with glass wool improved the peak shape of the heavier, low-volatility hydrocarbons.

Split injectors are required when using 0.25- and 0.10-mm-i.d. columns. The use of a split injector resulted in increases in method detection limits and injector discrimination. As column diameter decreased, the use of faster ramp rates in the temperature program was required to obtain the shortest analysis times.

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