

Abstract

The analysis of diesel fuel and jet fuel samples presents some unique challenges for the analyst. Variances in the source or type of fuel depends on many factors, most of which are not controllable, and may have significant effects on the fuel over time. These factors may include the degree of evaporation during weathering, microbial degradation, and migration through the matrix from where the sample was taken. In addition the source of the crude oil varies, as does the refinery practices throughout the country and at different times of the year. Compound this with the differences in the fuel specifications due to latitude, elevation and seasonal changes that refineries have to account for in their markets means that the analyst may have a hard time identifying a fuel source. However, by selecting the appropriate standards and analysis techniques accurate determination of fuel type and source can be achieved.

Introduction

In the following study several diesel fuels were analyzed to measure some of their different attributes by gas chromatography. Most of the diesel fuels were obtained from sources within Pennsylvania, but fuels from California and Alaska are also represented. All of the fuels are those marketed as diesels for cars or trucks (see Table 1).

We used Restek's diesel composite standard (part #31258) as a control standard for this exercise. It is made up of a representative of diesel fuels from the central Pennsylvania region, and although it may not represent the fuels available in other regions of North America, a bench-mark fuel is needed for a study of this type, if only for comparisons sake.

Experimental

Each of the diesel fuel standards was made up at 50,000 ppm in methylene chloride, except the unweathered and weathered samples in Figure 3. For that study we used stock standards at 5,000 ppm in methylene chloride (Restek part #31233, 31234, 31235 and 31236, for the unweathered, 25% weathered, 50% weathered and 75% weathered, respectively).

Each of the samples was analyzed by GC-FID using an Rtx-5 column (30m x 0.25 mm x 0.5 μm, Restek part #10238). An injector temperature of 250°C, a detector temperature of 330°C, split of 40 cc/min and carrier gas (H₂) flow of 40 cm/sec was used. We used a temperature program of 40°C (hold 2 minutes) to 330°C at 10°C/min (hold 5 minutes).

Aliphatic peak identification was performed using a DRO test standard with n-alkanes from C₁₀-C₂₅ (Restek part #31214). Naphthalene and methyl-naphthalenes peak identification was performed using selective ion extraction on GC-MS following the same GC temperature program conditions as used for the GC-FID analyses.

Results and Discussion

A comparison of the results from the GC analysis of the diesel fuels in this study is shown in Figures 1, 2 and 3. It can be observed that diesel fuels obtained from different areas of the United States show markedly different chromatographic and molecular differences.

In Figure 1 the diesel fuel from Alaska has a greater proportion of lighter boiling material than the other fuels. This fuel is a #1 diesel fuel and is derived from a slightly lower boiling range than conventional #2 diesel fuel oil. The fuel needs to have this lower boiling range in order to avoid solidification and deposition in the very cold winters that the fuel may experience. In the summer Alaskans may switch to #2 diesel to avoid volatility problems.

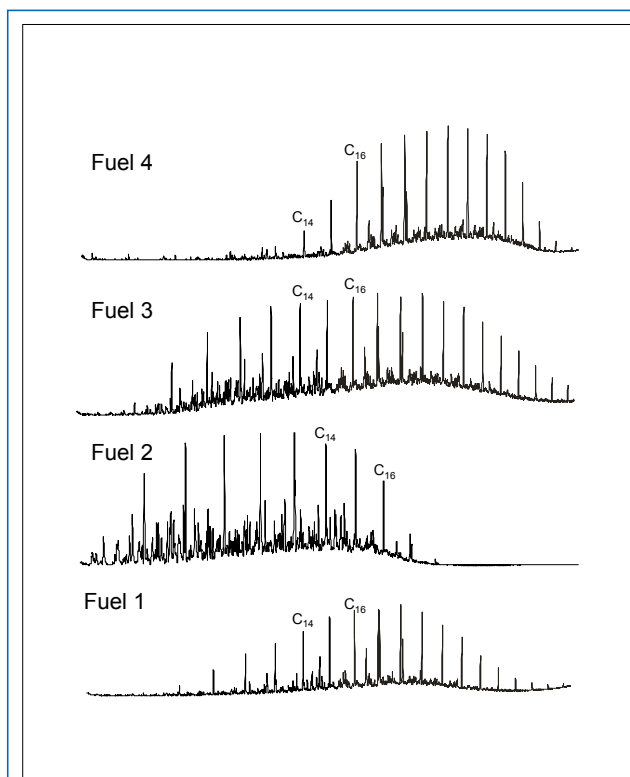


Figure 1. Comparison of geographically diverse diesel fuels.

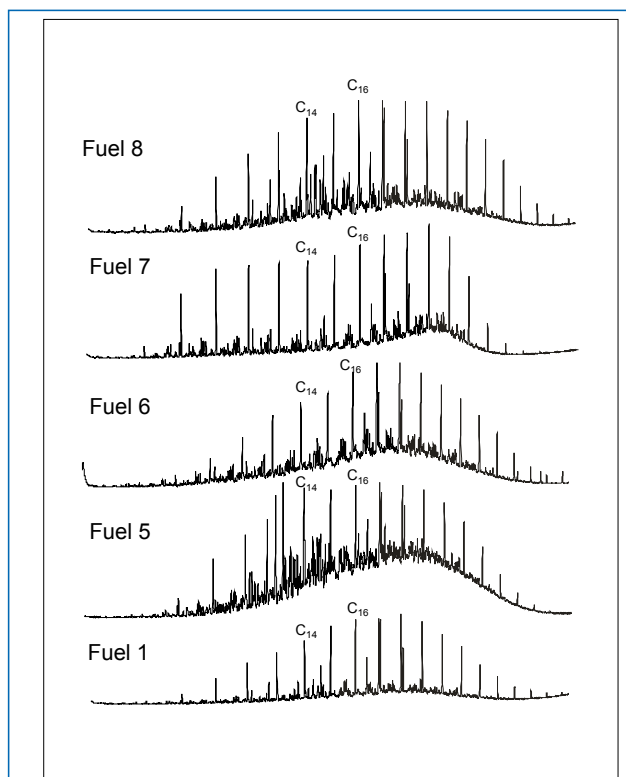


Figure 2. Comparison of Pennsylvania diesel fuels.

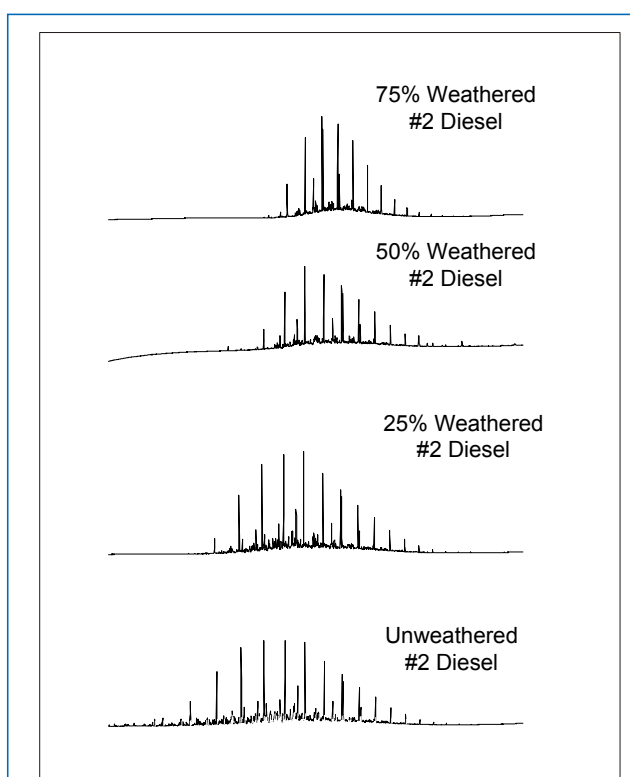


Figure 3. Comparison of artificially weathered diesel fuels.

The difference seen in the two Californian diesels is due to the processing that the fuels have experienced after fractionation. In order to attain the low sulfur levels required for fuels in California, it is necessary for some distillates to undergo catalytic hydrocracking. This process not only removes the heterocyclic sulfur from such species as dibenzothiophenes, but the excessive temperatures and hydrogen pressures used tend to crack the aliphatic components within the fuel. Thus we see an increase in low boiling material (cracking) and higher boiling material (polymerization) in the low sulfur fuel, compared with the straight #2 diesel. The wider boiling range is needed for the low sulfur fuel in order for it to maintain the desired physical properties of the fuel; cetane number, lubricity, cloud point, etc.

At first glance there seems to be little difference between the five Pennsylvania diesel fuels analyzed in this study. However, if you focus on the component ratio analyses performed we begin to see some quite marked differences (see Table 2). The results show that there is little variance in the ratios of the aromatic and alkyl-aromatic compounds, but significant differences in the aliphatic ratios. Techniques such as these could be used, in conjunction with other tests to fingerprint specific sources of fuel.

An interesting observation is the difference between the low sulfur fuels analyzed in this study. As we noted before, low sulfur fuels have to undergo catalytic hydroprocessing in order to meet the specific sulfur specifications for the region in which they are being sold. However, diesel fuels 3, 5 and 7 are considerably different. The major contributing factor to these differences is the type of crude oil used in the fractionation of the diesel fuel. Pennsylvania crude is typically very high in aliphatic components and low in aromatics. It is typically these aromatic components, especially the dibenzothiophenes, which contain the sulfur within diesel fuels. The crude oils used in Californian refineries may come from California, Texas, Oklahoma, or even Mexico and Venezuela. These types of crude oil are typically much higher in aromatic content and possibly sulfur content, and as such must undergo more severe hydroprocessing to remove the sulfur. The more severe hydroprocessing in turn can affect the other components of the fuel, as was mentioned earlier.

Figure 3 shows a comparison of the weathered diesel fuel standards sold by Restek. It can clearly be seen that as the fuels are weathered the lighter boiling components are being driven off, thus concentrating the boiling range towards the higher boiling material. Typically, diesel fuels have a boiling range from C₉-C₂₄. Therefore, if a fuel or extracted sample is analyzed that shows signs of a shorter boiling range, the analyst should start asking questions about the fuel and the time and conditions under which the fuel may have been spilled. Also the medium into the fuel was spilled may effect the fuels characteristics. For example, a fuel spilt on macadam surface in a warm environment will weather quicker than a fuel spilt onto soil or sand in a cool environment. Fuel that has seeped into the ground may over time be exposed to microbial degradation too. This may not be obvious by glancing at the chromatogram. Microbes tend to degrade sulfur-containing compounds, therefore, selective ion extraction MS or GC-FPD may play a key role in determining microbial degradation, if it is an analysis of interest.

Table 1. Diesel fuels used in this study.

Fuel	State	Designation
1	PA	#2 Diesel Composite Standard (Restek part # 31258) - Control
2	AK	#1 Diesel fuel
3	CA	#2 Diesel - Low sulfur
4	CA	#2 Diesel - Los Angeles Area
5	PA	#2 Diesel - Low sulfur
6	PA	#2 Diesel
7	PA	#2 Diesel - Low sulfur
8	PA	#2 Diesel

Table 2. Component ratio analysis results.

Fuel	Naphthalene/ 1-Methylnaphthalene Ratio	Naphthalene/ 2-Methylnaphthalene Ratio	C ₁₄ /C ₁₆ Ratio
1	0.61	0.35	0.62
2	1.48	0.32	1.61
3	1.66	1.02	0.90
4	-	-	0.35
5	0.40	0.12	1.16
6	-	-	0.58
7	0.58	0.33	0.77
8	0.55	0.34	1.14

Conclusions

It is fair to say there is probably no one standard that can be successfully used to determine the chromatographic nature of the diesel fuels used in the United States. However, the composite standard that is offered by Restek offers many of the key compositional features exhibited by the majority of diesel fuels sold in the United States. If the diesel fuel that is being analyzed does not look like the fuels composite standard then the analyst should ask some questions: Where was the sample taken from? How long had the sample been in that place? Is a fresh (unweathered) sample available? Is this fuel typical for the geographic region?