APPLICATION NOTE

Gas Chromatography

Authors:

William Goodman

Tom Kwoka

Jason Thomas

PerkinElmer, Inc.
Shelton, CT

Accelerating the Analysis of Petroleum Hydrocarbons by Method 8015 with the Application of Novel GC Oven Technology

Introduction

The analysis of diesel range organics (DRO) in soil and water by Environmental Protection Agency (EPA) method 8015 is one of the most frequently performed test methods in environmental analysis laboratories. It is used to test for contamination from leaky underground storage tanks (UST) under the EPA's UST program. Recently, the EPA has prohibited the use of Freon as the solvent for method 1664 total petroleum hydrocarbons; with this, the popularity of testing DRO's by method 8015 has increased dramatically.

In addition, many state environmental agencies now specify their own modified versions of method 8015 to test for DRO's; for example, the state of Florida has the total recoverable petroleum hydrocarbons (TRPH) method and Massachusetts has the volatile petroleum hydrocarbons (VPH) and extractable petroleum hydrocarbons (EPH) methods. For environmental laboratories, the key to this analysis is a method that is both fast and robust, allowing the laboratory to achieve the highest throughput with lowest cost. The purpose of this application note is to apply novel oven technology, a short gas chromatography (GC) column and high oven heating and cooling rates to a modified 8015 DRO method, achieving substantial improvements in sample throughput.

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Experimental

The GC system used in this study was the PerkinElmer Clarus® 680, which is based upon novel oven technology achieving the fastest heating and cooling rates in conventional air bath GC. This oven technology will allow laboratories to begin their analytical run with near ambient oven temperatures and utilize ramp at rates of up to 140 ˚C/min. across a wide temperature range. At the completion of the run, the best in class cooling rates will reduce the oven temperature to 30 ˚C in under six minutes. These heating and cooling capabilities are a result of the radical new oven design, incorporating dual oven walls and creating a unique air flow path. The air flow path of the Clarus 680 GC is single directional and designed to eliminate mixing of heated exhaust and cool ambient air, allowing for the fastest transfer of heat from the GC oven to the room. This high speed cooling allows the user to dramatically decrease the idle time of the instrument between analytical runs.

An additional benefit of fast cooling is the capability to reach near ambient temperatures of 35 ˚C or less within minutes. Near ambient initial oven temperatures will allow improved resolution from a column of standard diameter and film thickness, or adequate resolution from a column of reduced length. In this case, a short column of standard diameter and near ambient oven temperatures will achieve adequate resolution between low molecular weight hydrocarbons (C8) and the solvent (methylene chloride). This combination will improve the peak shape and resolution of the more volatile alkanes, while also achieving the quick elution of the heavier alkanes.

The Clarus 680 GC demonstrated here is configured with a programmable split/split-less (PSS) injector and a flame ionization detector (FID). The injector liner used was a standard 2 mm glass liner packed with a small amount of glass wool; the glass wool will improve vaporization of heavier alkanes. The column used in this example was a PerkinElmer Elite-1 (15 m x 0.25 mm x 0.10 µm). This column was chosen over other smaller diameter columns because it represents a size most laboratories are already comfortable with. The performance and durability of this column will be known to most laboratories.

The instrumental conditions are summarized in Table 1. A 0.5 µL injection was performed into the 330 ˚C injector port; the helium carrier gas was set at 1.8 mL/min., with 10 mL/min. flowing out to split. The GC oven program is: 40 ˚C for 0.75 minutes ramped to 300 ˚C at the maximum oven rate for selected temperature ranges. The total GC oven program time is seven minutes; with an additional five minutes of cool down and ready time, making the total period, injection-to-injection, less than 12 minutes.

Table 1. Summary of the GC conditions used in this study.

Gas Chromatograph	Clarus 680 with FID	
Column:	Elite-1 (15 m x 250 mm x 0.10 µm)	
Injector Type:	Programmable split-splitless	
Injector Temperature:	330 °C	
Injector Liner:	2 mm id glass (w/ glass wool)	
Carrier Gas:	Helium @ 1.8 mL/min.	
Split Flow:	10 mL/min.	
FID Conditions:		
Temperature:	350 °C	
Air Flow:	450 mL/min.	
Hydrogen Flow:	45 mL/min.	
GC Oven Program:	Temperature	
Rate	Set point	Hold Time
	40 °C	0.75
30 °C/min.	65 °C	0.00
140 °C/min.	75 °C	0.00
105 °C/min.	115 °C	0.00
85 °C/min.	180 °C	0.00
55 °C/min.	300 °C	2.02

Results

Under the conditions summarized here, the instrumental throughput is approximately five runs per hour. To demonstrate the improved throughput of the method used here, another popular GC was run under the same analytical conditions, the same exact column was used, and the oven was ramped at its maximum rate. The comparison will demonstrate the results of improved heating and cooling of the Clarus 680 GC. The best time achieved when using the other GC was an analysis time of nearly 10 minutes, a cooling and ready time of an additional 12 minutes, for a combined run time of 22 minutes. With a 22 minute injection-to-injection time, the instrument can complete less than three runs per hour. As you see in Figure 1, the technology demonstrated here allows more than twice as many per hour.

The results reported from an 8015 analysis fall into two categories, a concentration of total petroleum hydrocarbons and the hydrocarbon fingerprint. Calibration of method 8015 is typically performed with a fuel type similar to that found in the environmental sample. For example, if a site is known to have diesel fuel contamination or the contamination fingerprint points to diesel contamination, the calibration curve is prepared from diesel fuel diluted at known concentrations. The total area within a retention time window (for example C10 through C28) is integrated and calculated to determine a total hydrocarbon concentration. Much information can be gathered from the pattern of hydrocarbons in the analysis, which is called the hydrocarbon fingerprint. As you can see, in comparing Figure 1 with the images in Figure 2, the difference between Diesel and motor oil is quite obvious resulting from the dramatically different distribution of hydrocarbons. The comparison of the hydrocarbon pattern or fingerprint is made by the GC analyst to give additional information about the composition of the hydrocarbon contamination.

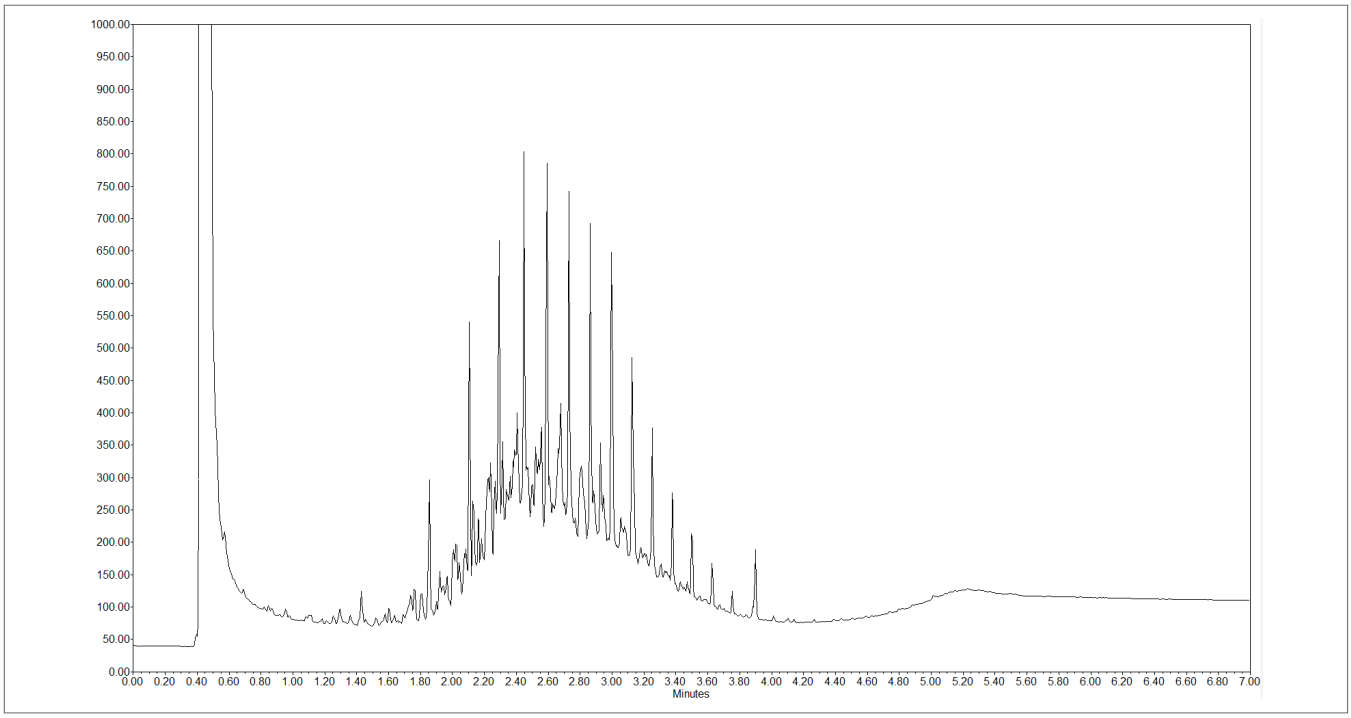

Figure 1. Chromatogram of Diesel fuel standard run under the conditions listed in Table 1.

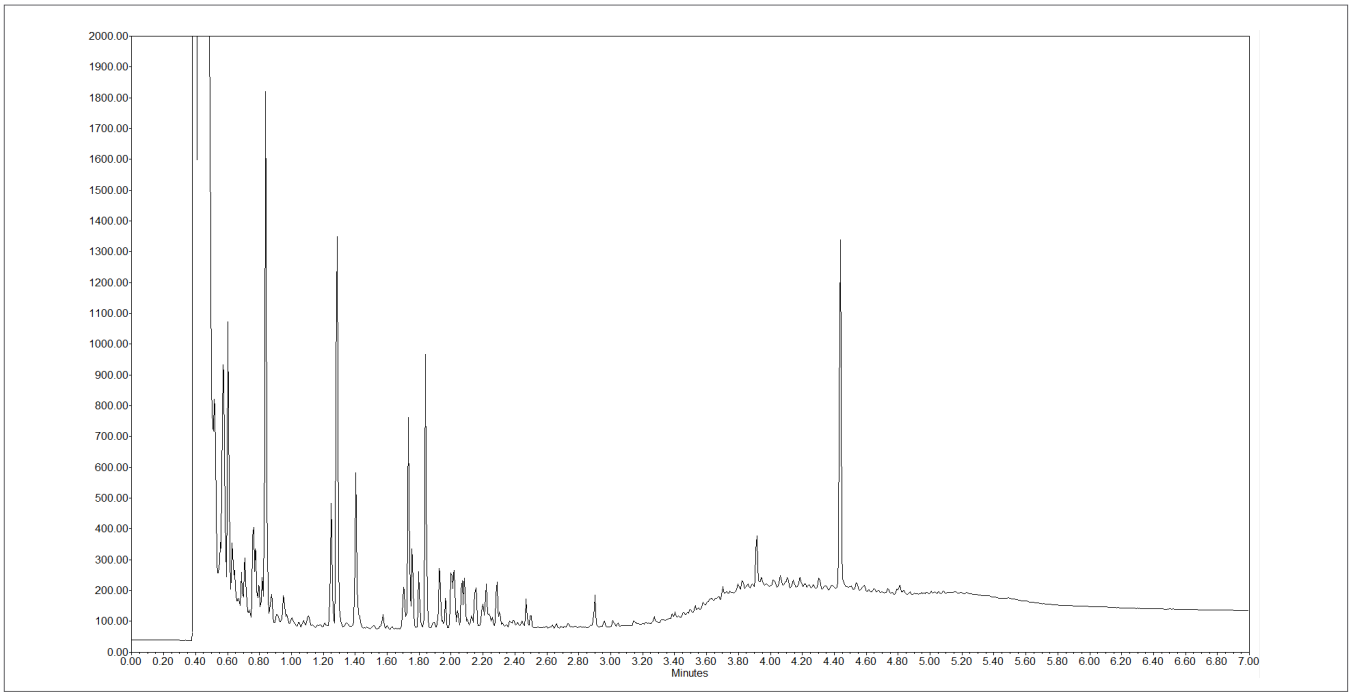

Figure 2. Chromatogram of Gasoline and Motor oil, run under the conditions in Table 1.

The Waters® Empower® 3 Chromatography Data Software (CDS) has several options in the processing method to establish the baseline for correct integration of the EPA 8015 samples.

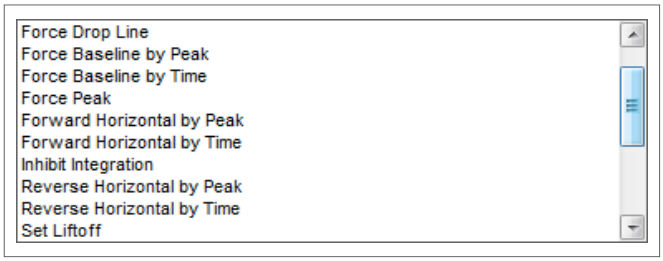

Figure 3. Integration options that are available when using the Traditional integration algorithm.

The option to force by peak or by time identifies when the baseline is to start. In the case of complicated samples it may be desirable to select "by peak" so that the baseline starts once the first peak is detected.

The timed groups for the Diesel Range Organics are set in the processing method as shown in Figure 5. Here it is possible to exclude known peaks, such as the internal standard p-terphenyl, from the group integration.

Conclusion

The novel technology utilized in this study has resulted in an 8015 analysis with an injection-to-injection time of less than 10 minutes. This will increase instrumental throughput by up to two times when compared to other common GC technologies. While increasing throughput, we have maintained the use of a standard diameter GC column. We were able to maintain adequate resolution with a shortened standard diameter column by using a near ambient starting oven temperature. This column was preferred because it will provide the laboratory with a known durability for difficult sample matrices.

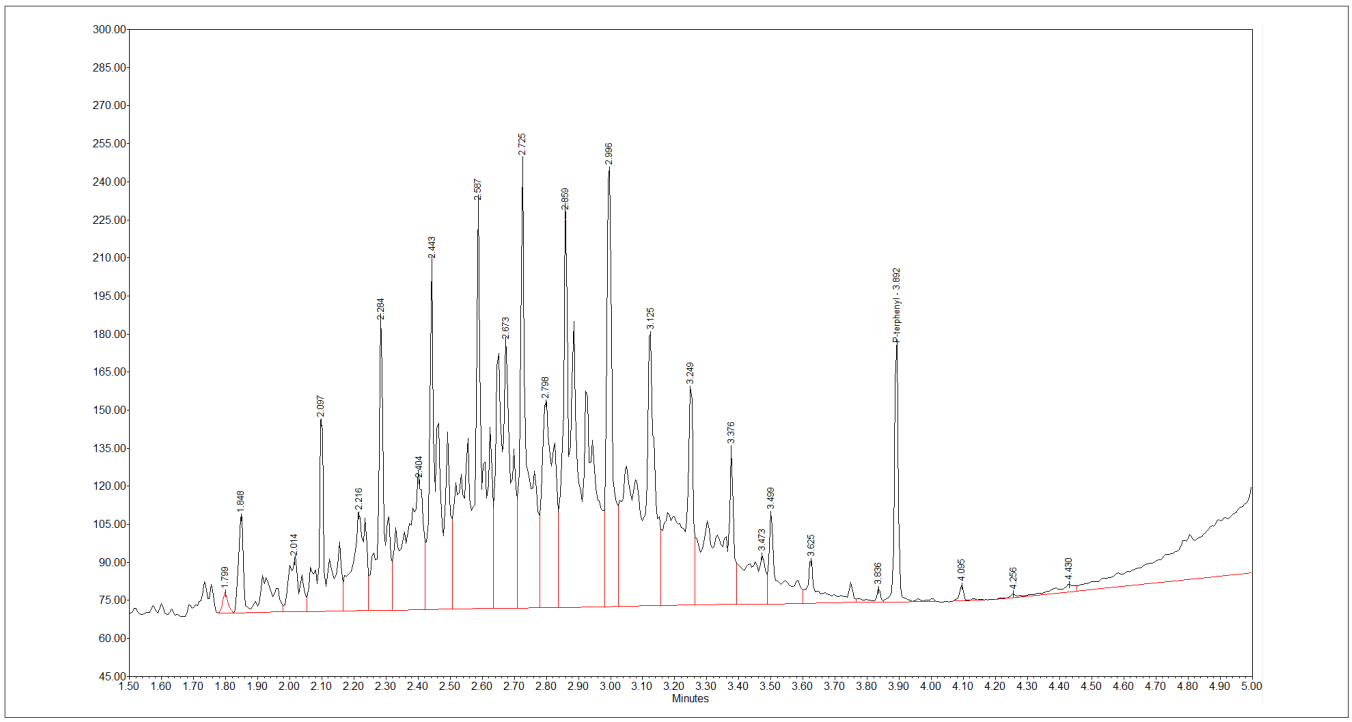

Figure 4. Baseline integration of a DRO standard showing the diesel range organics.

	Name	Start (min)	Stop (min)	Exclude Known Peaks
1	DRO	1.801	4.000	☑
2	ORO	4.001	6.500	☑

Figure 5. Excluding known peaks from the timed groups.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

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