Analysis of Diesel Range Organics (DRO) and Motor/Lube Oil Range Organics (ORO) in Ultrashort Run Time

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1. Introduction

The remediation of contaminated sites by persistent crude oil and petroleum-based products requires rapid analytical methods to assess the environmental health of soils, sediments and water samples. Petroleum hydrocarbon contaminants encompass a very complex mixture of compounds. A group within these contaminants are semi-volatile compounds, which are aliphatic or aromatic hydrocarbons with ten to forty carbons (C10-C40) and boiling point range of 170-520˚C; this group include diesel range organics (DRO, C10-C28) and motor/lube oil range organics (ORO, also referred to as MRO, C28-C40). These chemicals are typically quantified by gas chromatography equipped with flame ionization detector (GC-FID).

The scope of EPA method 8015 includes the analysis of DRO. The typical analysis time is over 20 min. In this study, analysis of DRO and ORO (C10-C40) were performed using a Shimadzu GC-FID equipped with fast temperature programmable (FTP) column that aim to significantly reduce the run time for this analysis.

2. Experimental

A Shimadzu GC-2030 with split/splitless injector (SPL) and flame ionization detector (FID) was connected to an FTP-MXT-1 column with transfer lines for this analysis. The FTP column and transfer lines were covered in resistively heated coils and controlled by the FTP controller to enable ultrafast ramping of the column temperature.

In addition, a gas selector was installed and connected to SPL to allow automated switching between helium (He) and hydrogen (H_2) as the carrier gas.

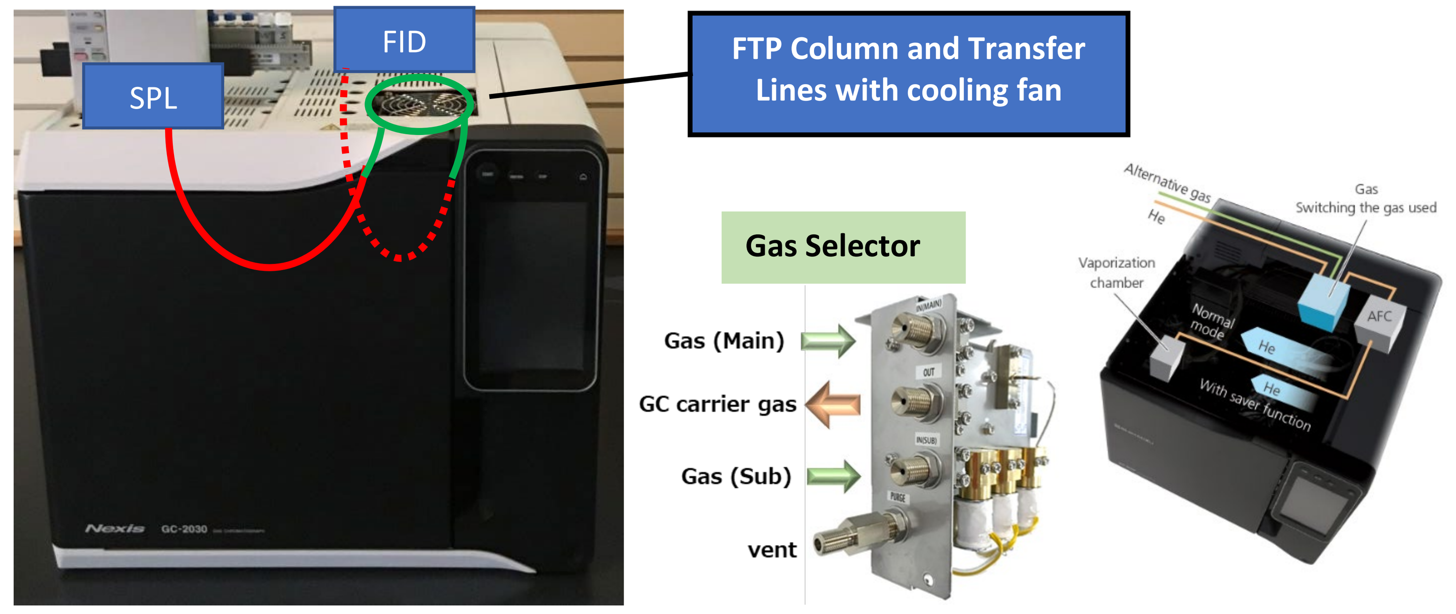

Figure 1: Ultrafast GC system with FTP column and gas selector.

Table 1: Instrument Configuration and Analysis Conditions

GC system	Shimadzu Nexis GC-2030 with SPL, FID, AOC-20 Plus autosampler and Gas Selector
Column	FTP-MXT-1, 5 m x 0.25 mm x 0.25 µm
Column Temp	40 °C, 1 s – 280 °C/min – 350 °C, 16 s
Transfer Line Temp	40 °C, 1 s – 350 °C/min – 360 °C, 28 s
Injection	0.1 µL Splitless
Carrier Gas	He or H_2, switching controlled by Gas Selector
Flow mode	Constant flow of 10 mL/min
FID Detector	370 °C, sampling every 16 ms

3. Results and Discussion

3.1. Ultrashort GC run time

Typically, analysis of semivolatiles (C10 to C40) takes 20 minutes or longer. In the current setup, a short column was heated resistively to allow superfast ramping of the column temperature, which allows separation of C10 to C40 in about one minute. Figure 2 shows overlaid chromatograms of solvent blank, alkane standard (C10-C40) and an oil standard containing diesel and motor oil. All compounds of interest eluted in 1.5 min.

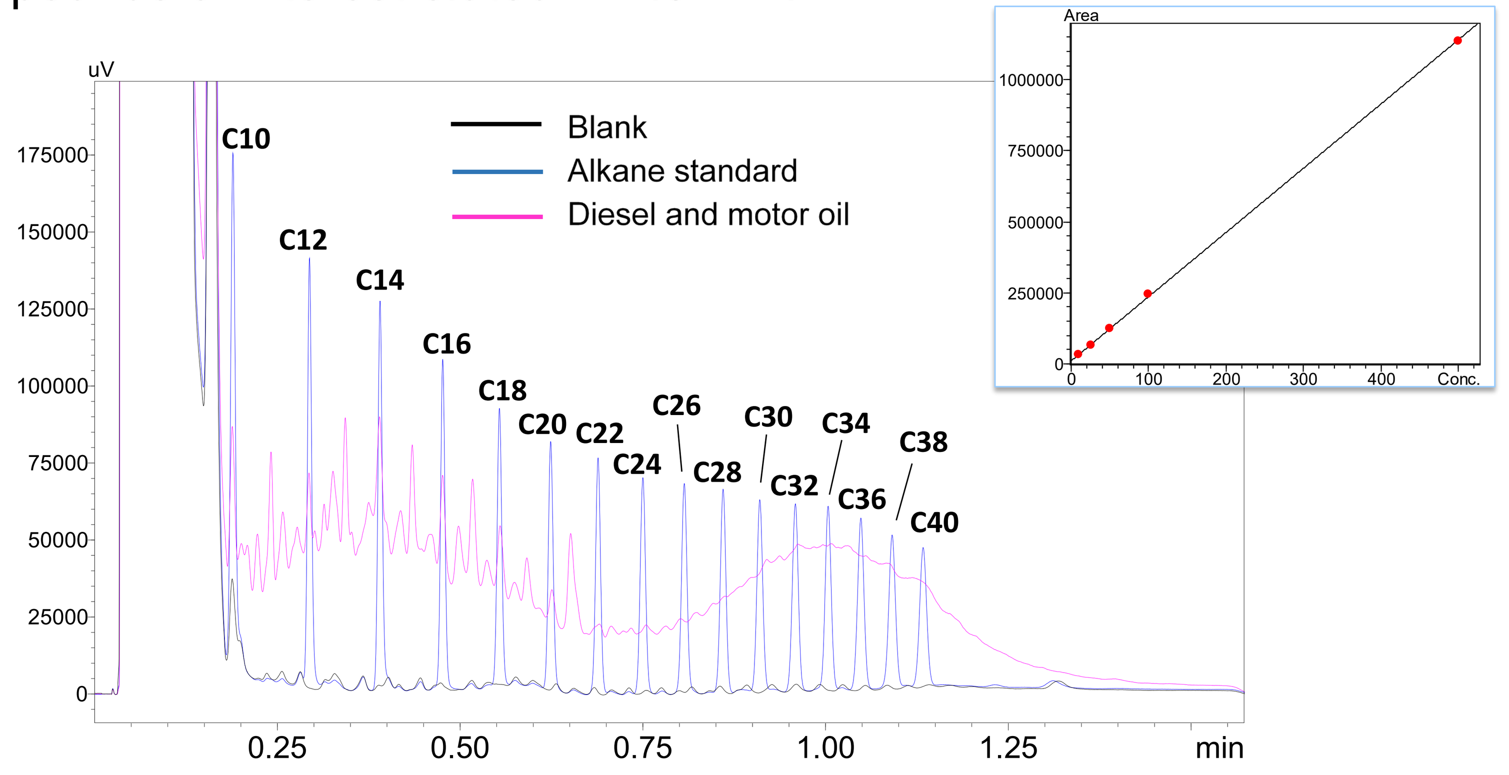

Figure 2. The Chromatograms of blank (dichloromethane), alkane standard (C10-C40) and a mix of diesel #2 and motor oil. He carrier gas was used. Inset shows an example calibration curve for motor oil with He carrier gas.

3.2. Comparison of hydrogen to helium as carrier gas

A gas selector was installed on the GC to allow automated switching between He carrier and H_2 carrier gas for easy comparison. The data obtained with H_2 carrier gas were compared to those obtained with He carrier gas. The retention times of each alkane compound using H_2 or He carrier gas are shown in Table 2.

Table 2: Retention times and peak resolution for alkanes using either He or H_2 carrier gas

	Ret. Time (min)		Resolution	
Compound	He	H_2	He	H_2
C10	0.189	0.166	2.007	1.845
C12	0.294	0.267	1.294	1.450
C14	0.390	0.363	1.688	1.863
C16	0.476	0.449	2.211	2.507
C18	0.554	0.526	1.324	3.153
C20	0.624	0.596	1.473	1.806
C22	0.689	0.660	2.045	2.386
C24	0.750	0.720	1.481	1.480
C26	0.807	0.777	2.015	2.179
C28	0.860	0.830	1.384	1.537
C30	0.910	0.879	1.407	1.739
C32	0.959	0.927	1.680	3.591
C34	1.003	0.973	2.879	3.211
C36	1.048	1.017	1.707	1.709
C38	1.091	1.059	2.532	2.772
C40	1.133	1.102	1.550	2.593

Since H_2 is a smaller molecule than He, when column flow is set to be the same, linear velocity is higher with H_2 gas. Therefore, the retention times were shifted slightly earlier with H_2 carrier gas. The detector response (data not shown) and resolution are similar between the two carrier gases. So, it was demonstrated that H_2 is a suitable alternative gas to He for this application.

3.3. Calibration Curves

Purchased diesel #2 standard and motor oil standard were diluted in dichloromethane to prepare the calibration standards, with concentrations at 10, 25, 50, 100 and 500 ppm. Five-point calibrations for DRO and ORO were constructed using either He or H_2 carrier gas (example curve shown in inset of Figure 2). DRO was identified using C10 and C28 as bracketing markers, and ORO was identified using C28 and C40 as bracketing markers. The r^2 values for all curves were > 0.997.

Deviation of each concentration (percent difference from expected value) is also shown (Table 3). All values were within 15% of expected concentrations.

Table 3: Calibration curve accuracy. % Deviation of measured concentrations from expected concentrations for each concentration using either He or H_2 carrier gas.

Expected conc.	10 ppm		25 ppm		50 ppm		100 ppm		250 ppm	
Carrier gas	He	H_2	He	H_2	He	H_2	He	H_2	He	H_2
DRO (C10-C28)	4.37	14.72	9.72	2.77	0.32	3.17	10.49	0.61	1.35	0.30
ORO (C28-C40)	0.63	13.56	3.64	8.69	0.59	2.56	4.19	7.05	0.57	2.10

4. Conclusion

In this study, DRO and ORO analysis were carried out on an ultrafast setup that allows completion of GC run in less than 2 min. Calibration was linear from 10 ppm to 500 ppm for both DRO and ORO. Alternative carrier gas (hydrogen) and helium were also tested in this study. To minimize disruption and maximize automation during carrier gas switching, a Shimadzu gas selector was employed. Data obtained using He or H_2 carrier gas were comparable, confirming that H_2 is a suitable alternative gas for this analysis. Given the high cost of He nowadays, H_2 would be preferable to use as the carrier gas.

The total analysis time per sample was approximately 3.5 min (including sample preparation and column cool down time); this time can be further optimized to less than 3 min per sample when the autosampler AOC-20 overlapping pretreatment function is enabled. This method significantly increases the throughput (by an order of magnitude) when compared to conditions described in EPA 8015 and allows for the analysis of up to 250 samples in a 12-hr work shift. Coupled with Shimadzu's long-life septa and syringe, up to 1000 injections may be performed without stopping to perform GC maintenance.