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Application News

No. GC-2105

Gas Chromatography

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

■ Abstract

Petroleum hydrocarbon contaminants are found in environmental samples and can be monitored using gas chromatography. EPA Method 8015 diesel range organics method is widely used to analyze target compounds with boiling points spanning from 170 to 520 °C and it normally takes over 20 min to complete a chromatographic run. In this study, methods to achieve analysis of diesel range organics (DRO) as well as motor/lube oil range organics (ORO) in ultrashort run times were explored using Shimadzu's GC-2030 with a fast temperature programmable (FTP) column. The resistively heated column enables elution of all compounds in less than 2 min, allowing up to 250 samples analyzed per 12-hr shift. This method greatly improves throughput, allowing ultrafast screening of contaminated sites. Furthermore, hydrogen was also evaluated in addition to helium as the carrier gas and was shown to be a suitable cost-effective alternative carrier gas for this method.

■ 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 complex mixture of contaminants. A group within these contaminants are semivolatile compounds, which are aliphatic or aromatic hydrocarbons with ten to forty carbons (C10-C40) and boiling points of 170-520°C; this group includes diesel range organics (DRO, C10-C28) and motor/lube oil range organics (ORO, also referred to as MRO, C28-C40). These chemicals are quantified by gas chromatography equipped with a flame ionization detector (GC-FID).

The scope of EPA Method 8015 includes the analysis of DRO. The typical analysis time is over 20 min, and helium is used as the carrier gas for the method.[1] In this study, analysis of DRO and ORO (C10-C40) were performed using a Shimadzu GC-FID equipped with a fast temperature programmable (FTP) column that reduced the GC run time to 2 min using either helium or hydrogen carrier gas. This establishes a high-throughput alternative to conventional methods for DRO and ORO quantification.

■ Materials and Methods

Dichloromethane (chromatography grade, 99.96%) was purchased from EM Science. Diesel #2 standard, motor oil standard and alkane calibration standard were purchased from Restek. Standards were diluted in dichloromethane to specified concentrations.

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 (purchased from Vici) for this analysis. The FTP column and transfer lines were wrapped in resistively heated coils and independently controlled by the FTP controller (Vici) to enable ultrafast ramping of the column temperature. The FTP column is mounted on the GC top deck and the transfer lines are used to connect the column to SPL and FID inside the GC oven. The column and part of the transfer lines (shown in green in Figure 1) are resistively heated by the FTP controller (Vici) to allow ultrafast ramping of the temperature. The rest of the transfer lines (shown in red in Figure 1) are heated by the GC oven isothermally.

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.

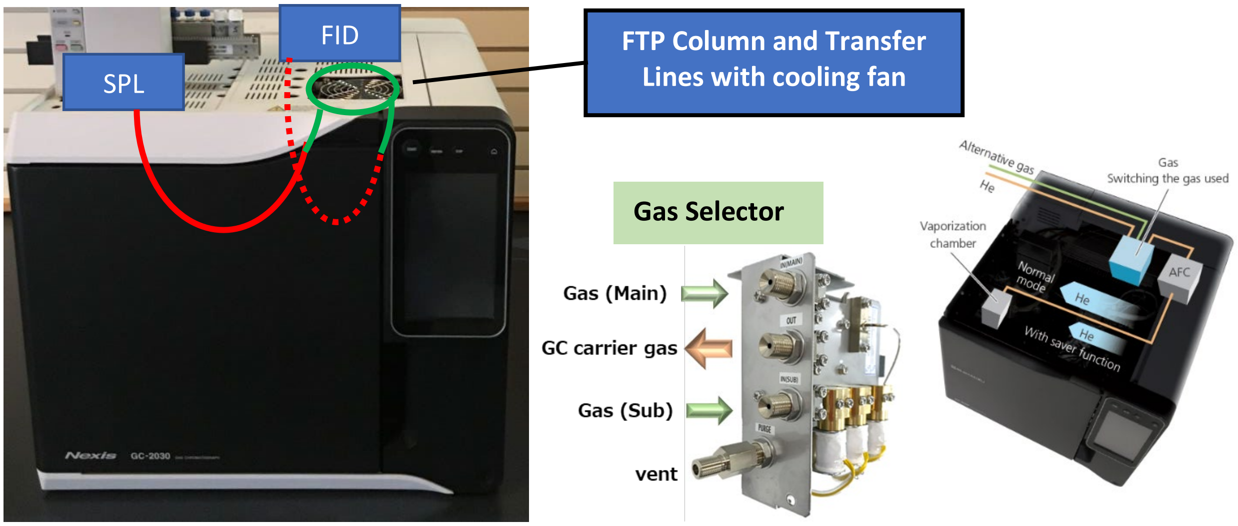


Figure 1: The setup of ultrafast GC system with FTP column and Gas Selector.

Analysis conditions are outlined in Table 1 below. LabSolutions software was used for data acquisition and processing.

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	Helium (He) or Hydrogen (H_2), switching controlled by Gas Selector
Flow Mode	Constant flow of 10 mL/min
FID Detector	370 °C, sampling rate 16 ms
FID Detector Gases	Air 200 mL/min H_2 32 mL/min for He carrier gas, 22 mL/min for H_2 carrier gas N_2 makeup 15 mL/min for He carrier gas, 24 mL/min for H_2 carrier gas

■ Results and Discussion

1. Ultrafast run time for DRO and ORO

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. This significantly reduces GC run time (by an order of magnitude) and allows for the analysis of up to 250 samples in a 12-hr work shift.

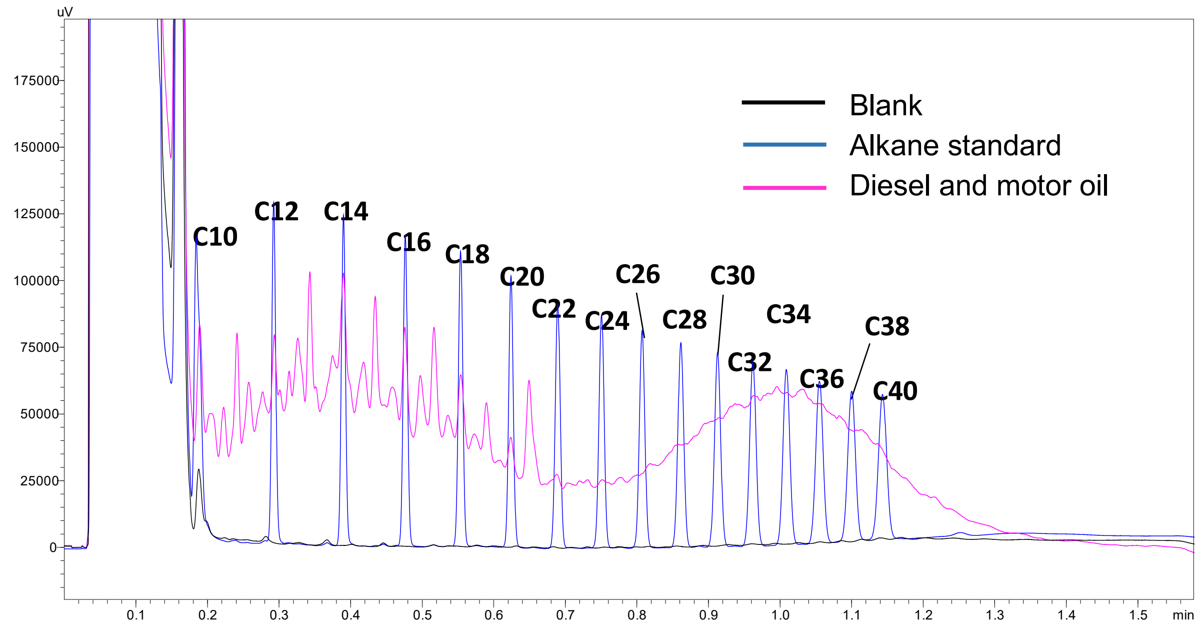


Figure 2: Chromatograms of blank (dichloromethane), alkane standard (C10-C40) and a mix of diesel #2 and motor oil. Helium carrier gas was used in above chromatograms.

2. Comparison of H_2 carrier gas to He 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 chromatograms obtained with H_2 carrier gas were compared to those obtained with He carrier gas. Constant column flow was used for these assays. The retention times of each alkane compound using H_2 or He carrier gas are shown in Table 2 below.

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 carrier gas. Therefore, the retention times were shifted slightly earlier with H_2 carrier gas. The detector response and resolution are similar between the two carrier gases (Figure 3, Table 2). So, H_2 is a suitable alternative gas to He. Given the high cost of He nowadays, H_2 would be preferable to use as the carrier gas.

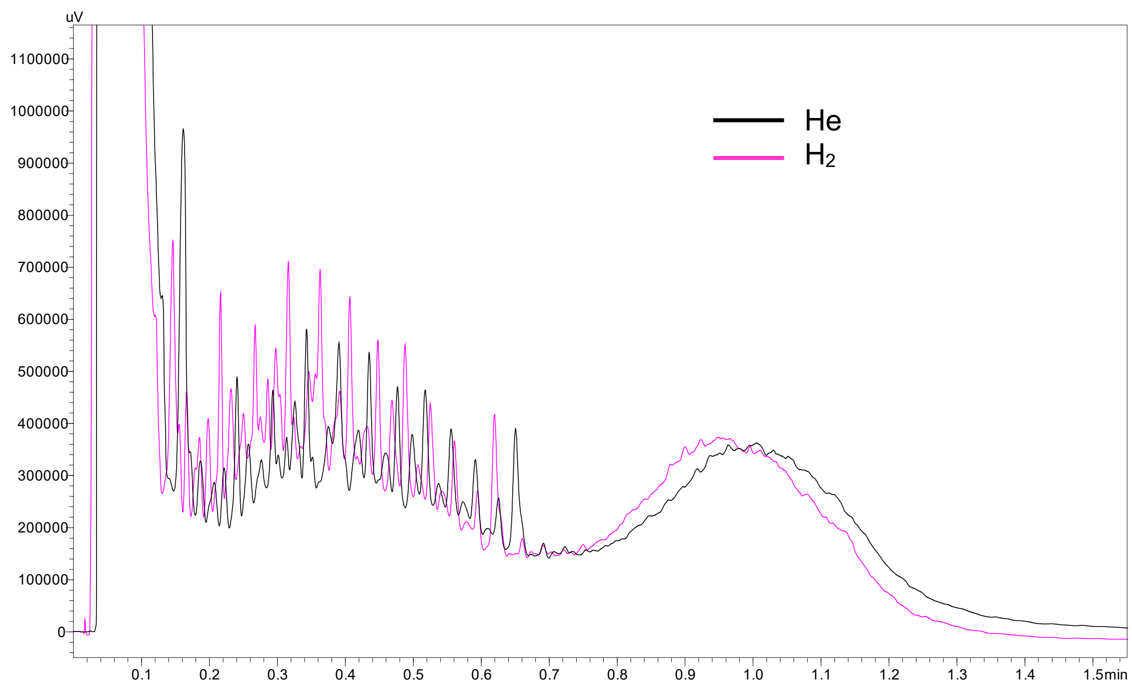


Figure 3: Chromatograms of DRO ORO standard using He (black) or H_2 (pink) carrier gas.

Table 2: Retention times and peak resolution (USP) 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

3. Calibration Curves

Purchased diesel #2 standard and motor oil standard were diluted in dichloromethane to prepare the calibration standards, with concentrations of 10, 25, 50, 100 and 500 ppm. Five-point calibrations for DRO and ORO were constructed using either He or H_2 carrier gas. DRO was identified using C10 and C28 as bracketing markers, and ORO was identified using C28 and C40 as bracketing markers. Linear fitting with 1/A weighting was used for each calibration curve.

The calibration curves and the r^2 values are shown in Figure 4, Figure 5 and Table 3, and the r^2 values for all curves were > 0.997. Deviation of each concentration (percent difference from expected value) is also shown (Table 4). All values were within 15% of expected concentrations.

Diesel Range Organics

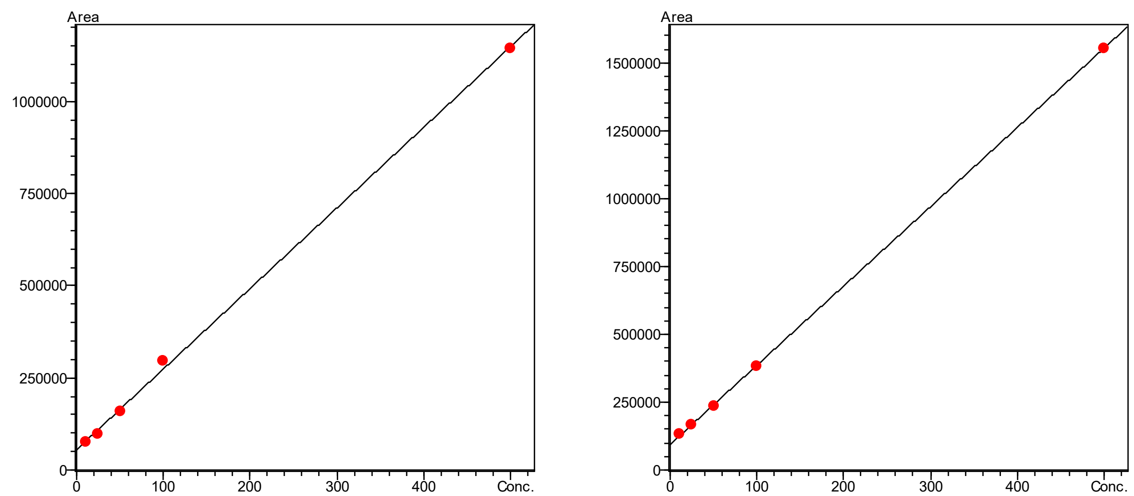
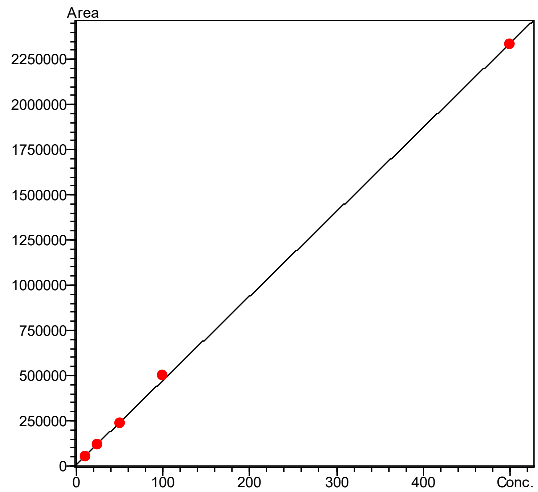


Figure 4: Five-point calibration curves for DRO using He (left) or H_2 (right) carrier gas.

Motor/Lube Oil Range Organics



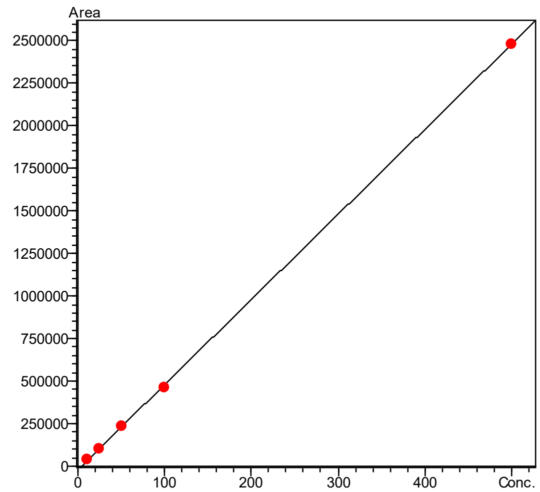


Figure 5: Five-point calibration curves for ORO using He (left) or H_2 (right) carrier gas.

Table 3: Coefficient of determination (r^2) of the calibration curves.

	He	**H_2**
Diesel Range (C10-C28)	0.9978	0.9998
Motor Oil Range (C28-C40)	0.9996	0.9976

Table 4: Calibration curve accuracy. Deviation (percent difference) of measured concentrations from expected concentrations are shown for each concentration using either He or H2 carrier gas.

Expected conc.	**10 ppm**		**25 ppm**		**50 ppm**		**100 ppm**		**250 ppm**	
	He	H_2	He	H_2	He	H_2	He	H_2	He	H_2
Diesel Range (C10-C28)	4.37%	14.72%	9.72%	2.77%	0.32%	3.17%	10.49%	0.61%	1.35%	0.30%
Motor/lube Oil Range (C28-C40)	0.63%	13.56%	3.64%	8.69%	0.59%	2.56%	4.19%	7.05%	0.57%	2.10%

■ Conclusions

In this study, DRO and ORO analysis were carried out on an ultrafast setup that allows completion of a GC run in less than 2 min. Calibration was linear from 10 ppm to 500 ppm for both DRO and ORO, with accuracy within 15%. Alternative carrier gas was also tested in this study. To minimize disruption during carrier gas switching, a Shimadzu gas selector was employed. This allows automated switching of the carrier gas in a sample batch, so results using different carrier gases can be easily compared without having to stop the GC and replumb the system. Furthermore, the type of carrier gas used in the method is automatically documented in the data file, eliminating possible human errors.

Data obtained using He or H_2 carrier gas were comparable, confirming that H_2 is a suitable alternative gas for this analysis.

The total analysis time per sample was about 3.5 min (including sample prep and column cool down time); this time can be further optimized to less than 3 min per sample when the 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 Method 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.

■ Reference

1. U.S. EPA. 2003. "Method 8015D (SW-846): Nonhalogenated Organics Using GC/FID, Revision 4. Washington, DC.

■ Consumables

Part Number	Description	Unit	Instrument
227-35511-01	Xtra life inlet septa	Pk of 25	GC-2030
REST-21719	Uniliner, Single Taper with Wool	Pk of 5	
221-32126-08	Graphite Ferrules for 0.53 mm ID columns	Pk of 10	
221-75597-03	FID jet for GC-2030	each	
227-35401-01	Syringe, 10µL, fixed needle, Xtra life	each	AOC-20i/s
220-97331-31	Sample Vials, 1.5mL Amber Glass with Caps & Septa	Pk of 100	
220-97331-47	Sample Vials, 1.5mL Amber Glass with Caps & Septa	Pk of 1000	
220-97331-62	200µL Glass Inserts for 1.5mL Vials	Pk of 100	
220-97331-23	Wash Vials, 4mL Amber Glass with Caps & Septa	Pk of 100	

The FTP-MXT-1 column is a special-order item. Please contact your Shimadzu sales engineer to purchase the column.

First Edition: March 2021

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