

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

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### 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 semivolatile 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, and helium is used as the carrier gas for the method<sup>1</sup>. 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 reduced the GC run time to less than 2 min using either helium (He) or hydrogen (H<sub>2</sub>) carrier gas. This establishes a high throughput alternative to conventional methods for DRO and ORO quantification.

### 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 (purchased from Vici) for this analysis. The FTP column and transfer lines were covered in resistively heated coils and independently controlled by the FTP controller (Vici) 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<sub>2</sub>) as the carrier gas.

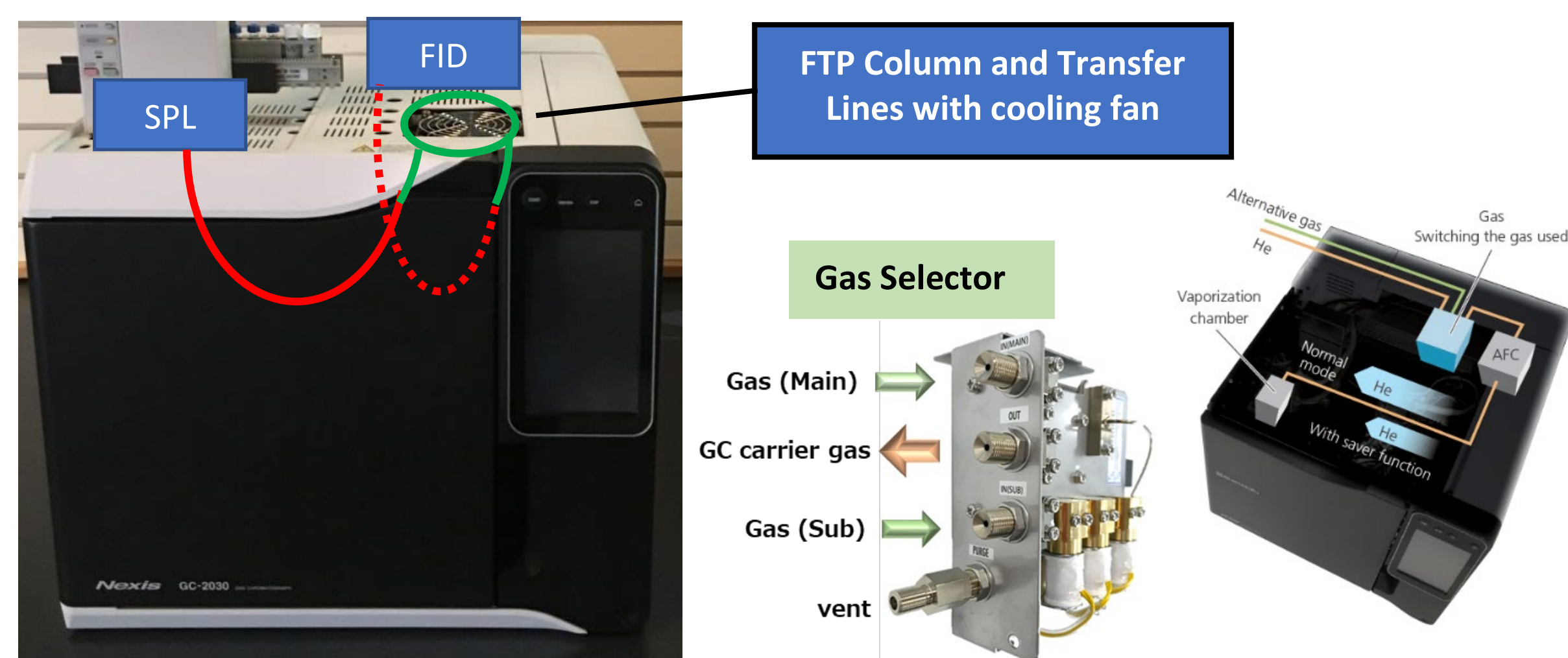


Figure 1: The setup of ultrafast GC system with FTP column and gas selector.

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 <sub>2</sub> , switching controlled by Gas Selector
Flow mode	Constant flow of 10 mL/min
FID Detector	370 °C, sampling rate 16 ms

### Ultrashort GC run time

Typically, analysis of semivolatiles (C10 to C40) takes 20 minutes or longer<sup>1</sup>. 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.

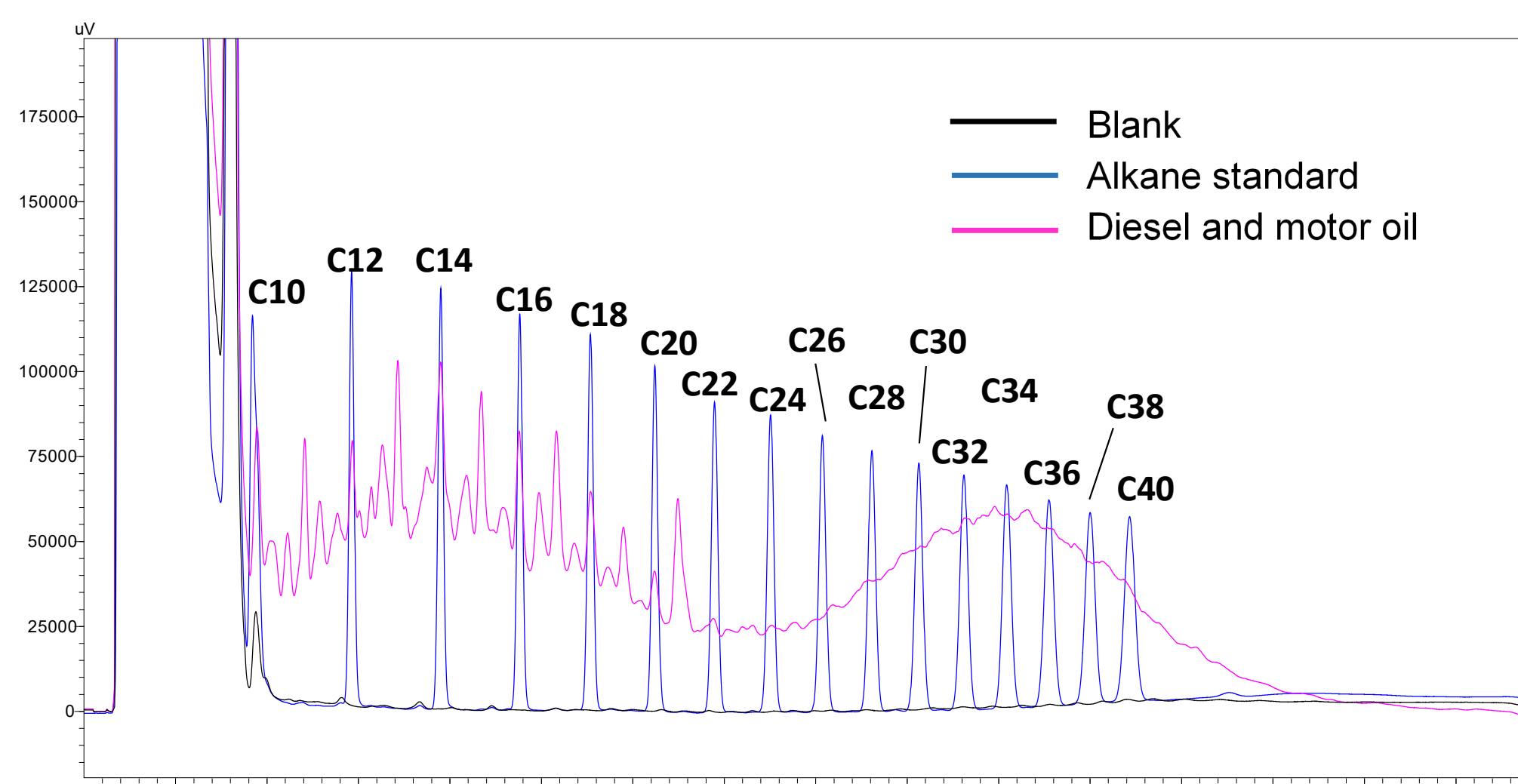


Figure 2: The Chromatograms of blank (dichloromethane), alkane standard (C10-C40) and a mix of diesel #2 and motor oil. He carrier gas was used.

### 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<sub>2</sub> carrier gas for easy comparison. The chromatograms obtained with H<sub>2</sub> carrier gas were compared to those obtained with He carrier gas. The retention times of each alkane compound using H<sub>2</sub> or He carrier gas were shown in Table 2 below. Since H<sub>2</sub> is a smaller molecule than He, when column flow is set to be the same, linear velocity is higher with H<sub>2</sub> carrier gas. Therefore, the retention times were shifted slightly earlier with H<sub>2</sub> carrier gas. The detector response and resolution are similar between the two carrier gases. So, it was demonstrated that H<sub>2</sub> is a suitable alternative gas to He for this application.

Table 2: Retention times and peak resolution for alkanes using either He or H<sub>2</sub> carrier gas

Compound	Ret. Time (min)		Resolution	
	He	H <sub>2</sub>	He	H <sub>2</sub>
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

### Calibration Curves

Purchased diesel #2 standard and motor oil standard were diluted in dichloromethane to prepare the calibration standards, with concentrations 10, 25, 50, 100 and 500 ppm. Five-point calibrations for DRO and ORO were constructed using either He or H<sub>2</sub> carrier gas. DRO was identified using C10 and C28 as bracketing markers, and ORO was identified using C28 and C40 as bracketing markers. The *r*<sup>2</sup> values for all curves were > 0.997. Deviation of each concentration (percent difference from expected value) was also shown (Table 3). All values were within 15% of expected concentrations.

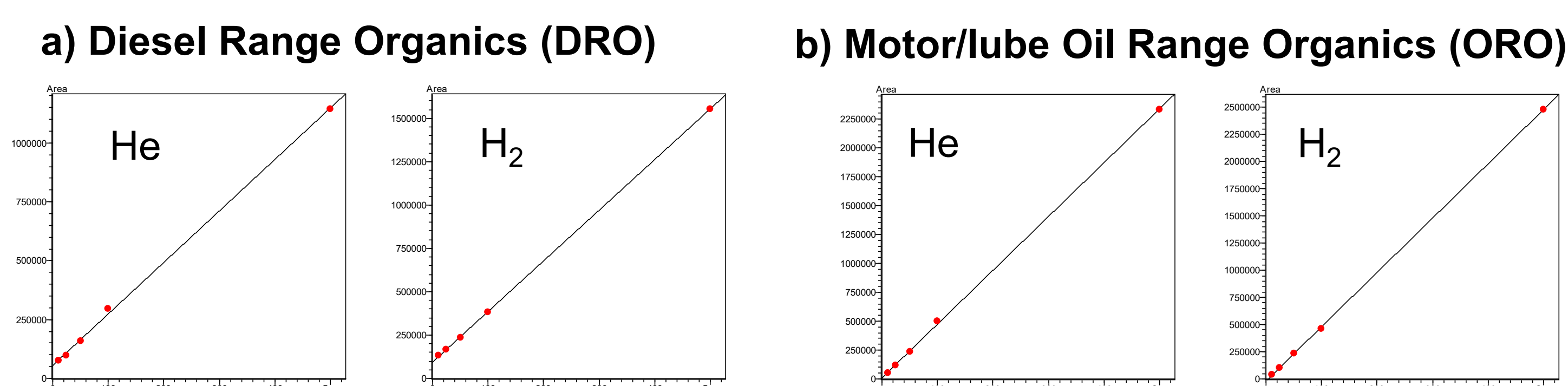


Figure 3: Five-point calibration curves for DRO (a) or ORO (b) using He or H<sub>2</sub> carrier gas. Linear fitting with 1/A weighting was used for each calibration curve.

Table 3: Calibration curve accuracy. Deviation of measured concentrations from expected concentrations are shown for each concentration using either He or H<sub>2</sub> carrier gas. The numbers shown are percent differences.

Expected conc.	10 ppm	25 ppm	50 ppm	100 ppm	250 ppm					
Carrier gas	He	H <sub>2</sub>	He	H <sub>2</sub>	He	H <sub>2</sub>	He	H <sub>2</sub>	He	H <sub>2</sub>
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 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 (hydrogen) and helium were 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<sub>2</sub> carrier gas were comparable, confirming that H<sub>2</sub> is a suitable alternative gas for this analysis. Given the high cost of He nowadays, H<sub>2</sub> 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 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.

### References

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