APPLICATION NOTE

Gas Chromatography

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EPA Method 8015C for Diesel Range Organics

Introduction

EPA 8015C is a gas chromatographic method used to establish concentrations of a variety of non-halogenated volatile organic compounds, semivolatile organic compounds, and petroleum hydrocarbons. For the purpose of this application, a Clarus® 690 GC was used for the analysis of petroleum hydrocarbons, specifically Diesel Range Organics (DRO). The Clarus 690 GC uses a Wide Range Flame Ionization Detector (WR-FID), which is designed with a large dynamic range to be able to detect high and low concentrations of analytes during a single chromatographic run. TotalChrom® chromatography data system (CDS) software will calculate the hydrocarbon envelope between nC10 and nC28 to accurately quantitate the DRO concentration in each sample. Equipped with a 0.011" jet ID, the wide range FID offers more sensitive detection of analytes and can cover a broad range of reporting limit requirements.

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Diesel Range Organics (DRO)

Diesel Range Organics exist in in the hydrocarbon range of nC10 to nC28. Retention times are established through the analysis of a known n-hydrocarbon standard with a broad range of nC6 to nC44 (Figure 1). The DRO calibration curve is prepared at concentrations according to procedural or specific state required reporting limits. The EPA requires analysis of a minimum five point curve with a % RSD of ≤20%. Standard concentrations should cover the expected sample concentrations being analyzed with at least one level at or below the required reporting limit. The wide-range FID's increased dynamic range will continue to meet method criteria at extended concentration ranges. However, there is a trade-off of large concentration ranges versus carryover contamination. Using a plunger in needle style can increase the performance by reducing carryover with the understanding that the needle may be more prone to plugging.

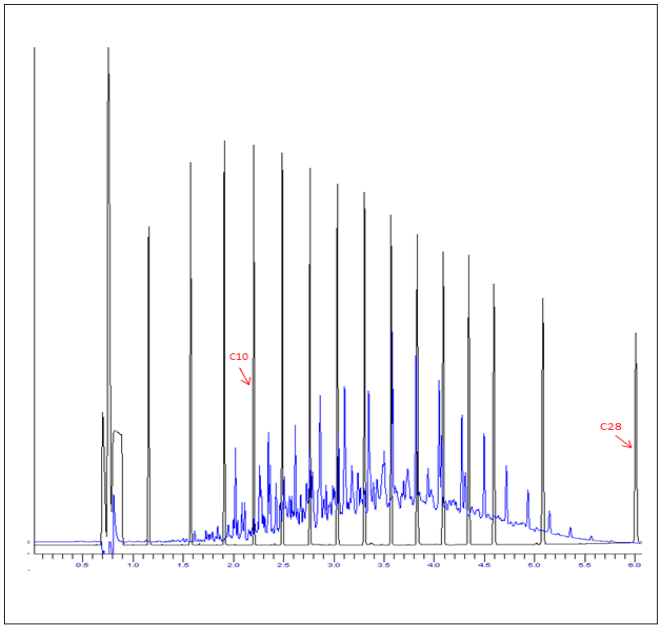

Figure 1. nC6-nC44 range overlay with #2 Fuel Oil (2500 ug/ml).

For the needs of this application note, the method listed below (Table 1) was used to generate a five point curve run at concentrations of 25, 250, 500, 1000, 2500 ug/mL and resulted in a % RSD of 3.44%. The % RSD is an average response factor calculation across all levels in the curve.

Prior to running the curve, a clean GC system needs to be established. A solvent blank is run to verify that the GC system does not contain contaminants (peaks of interest within the DRO range) greater than half of the lowest level of the reporting limit. An Elite-1 15 m x 0.25 mmID x 1 um column was used and a runtime of 15 minutes was established. However, alternate columns such as a PerkinElmer Elite-1 15 m .32 mmID, .25 umdf (part no. N9316017) can be used for even quicker runtimes with only minor method modifications. The Clarus 690 GC has a typical cool down time of less than three minutes as well as the capability of pre-rinsing the syringe while the system is equilibrating to reduce injection to injection time.

The wide rage FID has all of the same desirable attributes as the standard FID that allows for successful determination of DRO. The wide range FID now allows a larger dynamic range to be able to detect low to high concentrations of analytes. This wide dynamic range gives more confidence to an analyst to determine dilutions more accurately. Although it is best to analyze samples within the curve range for system cleanliness, we all know that unexpectedly high sample concentrations can sneak in when least expected. The wide range FID will provide the analyst with true concentrations even when it is over the curve range to allow them to make more accurate judgments on the dilutions required for re-analysis. This could eliminate, or at least decrease, performing multiple dilutions to bring the sample within the analyzed curve range.

Table 1. GC Chromatographic method used for EPA 8015C DRO analysis.

Autosampler Settings	• 1.0 uL Injection (Methylene Chloride) • Injection Speed normal • Viscosity Delay 0** • Pre-Injection Solvent Washes 2 (methylene chloride) • Post-Injection Solvent Washes 9 (methylene chloride) • Pre-Injection Sample Washes 1
Injector Settings	• Carrier Flow 3 ml/min Helium (PPC) hold for 1.0 min then 1.0 /min to 4.0 ml/min hold for 999.0 min • Split mode (30 ml/min) • Inj Temp = 275°C
Oven Settings	• 40°C for 1.0 minute; 140°C/min to 70°C, Hold for 0 min, 105°C/min to 115°C, hold for 0 min, 85°C/min to 175°C, hold for 0 min, 55°C/min to 300°C hold 0 min, 35°C/min to 320°C hold for 10 min. • Oven equilibration = 1.0 min
FID Settings	• Detector temperature 320°C • Air = 450 ml/min • Hydrogen = 30 ml/min • Data Rate = 6.25 pts/sec • Attn -6 / Time constant 200

**Viscosity delay should be modified based on the type of samples you are analyzing. More viscous samples should have a higher viscosity delay to allow the sample to fully pull up into the syringe.

The attenuation values can be used at one optimized setting to ensure all peaks are detectable and on-scale, from the lowest to highest concentrations. An attenuation setting of 64x will allow the analyst to see from the lowest possible concentration level to seven orders of magnitude higher, resulting in never seeing a saturated detector signal. The curve range can be lowered to see very low levels of DRO if samples are expected to be clean.

Conclusion

With the new broader detection capabilities of the wide range FID working in tandem with the pre-existing attributes of the Clarus 690 GC cool down time, analysis has taken a leap forward in ease of use, accuracy, and speed. For clients with quick turnaround times, fast and effective results are vital in the success of DRO analysis.

References

Method 8015C: Nonhalogenated Organics by Gas Chromatography, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (PDF) (36 pp, 313 K, February 2007)

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