SUPERCRITICAL FLUID CHROMATOGRAPHY: A POWERFUL TOOL FOR HYDROCARBON TYPE ANALYSIS

Supercritical Fluid Chromatography (SFC) is a chromatographic technique in which the mobile phase, typically carbon dioxide, is employed at pressures and temperatures above its critical point. A supercritical fluid exhibits both gas and liquid like properties that makes it a unique carrier fluid for chromatographic separations. It is gas like in that it is a compressible fluid that fills its container and is liquid like in that it has comparable densities and solvating power.

These gas/liquid like properties lead to several important advantages in chromatographic applications including: -

- Controllable Solvating power: - the solvent strength of a supercritical fluid is a function of its density which in turn can be easily controlled by its temperature and pressure.
- High mass transfer rates: - high rates of diffusion (typically an order of magnitude higher than liquids) lead to higher chromatographic efficiency.
- Low viscosity: - supercritical fluids exhibit significantly lower viscosities than liquids (typically an order of magnitude) which provides favourable flow properties in chromatographic systems.
- Compatibility with a wide range of Detectors: commonly used fluids such as carbon dioxide can be readily employed with GC detectors such as the Flame Ionisation Detector (FID) and many common HPLC detectors.

Carbon dioxide is the most common supercritical fluid in use today as it has readily achievable critical pressure and temperature, is inert and non-toxic, and is widely available in high purity at low cost. The solvating power of pure supercritical carbon dioxide at liquid like densities has often been compared to hexane and therefore it is well suited to normal phase chromatographic separations of hydrocarbon samples, especially when used with an FID. In recent years, due to the helium supply shortage for GC separations and the "green" solvent properties of carbon dioxide, SFC has become an attractive alternative separation technique in many application areas.

Hydrocarbon Group Type Analysis and Fluorescence Indicator Adsorption (FIA)

ASTM International, formerly known as American Society for Testing and Materials, is an international standards organization that develops and publishes voluntary consensus technical standards for a wide range of materials, products, systems, and services including hydrocarbon process streams and refined products such as gasoline, diesel and jet fuel. Hydrocarbon group type analysis, where components are grouped and classified as saturates, olefins and aromatics is one of the most common methods of characterising hydrocarbon streams and products. The current ASTM referee method for testing aromatics and olefins in aviation turbine fuels and gasoline is ASTM D1319 -18 the Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption (1).

ASTM D1319 was originally developed in the early 1940s and approved as a standard method by ASTM in 1954. The method employs a calibrated glass column, typically about 4 ft in length, which is packed with activated silica gel and topped with a mixture of fluorescent indicator dyes. The sample is adsorbed onto the silica gel and the hydrocarbon types are then separated on the column using alcohol as the eluant. The fluorescent dyes are separated selectively between the hydrocarbon types and quantification is dependent on the accuracy of the observation and recording of the fluorescent bands. The method is tedious and labour intensive as sample preparation is time consuming, the chromatographic run is lengthy, and the column requires constant monitoring. Other limitations include poor reproducibility and the method is subject to operator bias as it relies on the analyst correctly identifying and physically measuring the separated bands.

In the past few years there has been manufacturing issues producing the fluorescent indicator dye for D1319 and the ASTM have had workgroups looking into the implications of this and proposing method modifications and developments. As a result, the ASTM committee D02 on Petroleum Products has approved SFC methods for testing gasoline, diesel and aviation products. These methods take advantage of the unique ability of SFC to achieve hydrocarbon group type separation using the most common universal detector in GC, the flame ionization detector (FID).

The SFC ASTM methods that are currently being used for gasolines and diesels are separations that resemble ASTM D1319. ASTM D6550 is the Standard Test Method for the Determination of Olefin Content in Gasolines by Supercritical-Fluid Chromatography (2) and ASTM D5186 is the Standard Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels by Supercritical Fluid Chromatography (3).

Both ASTM D5186 and D6550 have been used as the regulatory method in the state of California since 2000 and the US EPA adopted ASTM D6550 as an alternative to D1319 in 2013. The methods have been proven to be more accurate than the alternative ASTM D1319.

The Selerity Technologies Series 4000 SFC: Designed to meet the needs of the Petroleum Industry

Selerity Technologies is the market leader in SFC systems for the petroleum industry and their Series 4000 is a "turn-key", completely automated system that uses supercritical carbon dioxide as a mobile phase for analytical separations. It is designed specifically to meet the needs of methods such as ASTM D6550 and ASTM D5186 for final product testing of gasoline, aviation turbine and diesel fuels.

The Series 4000 SFC is equipped with a syringe pump for a continuous pulse free stream of supercritical carbon dioxide as the carrier fluid; a flame ionization detector for the identification of hydrocarbon group types; Valco injection valves for repeatable sample introduction to the column; Valco switching valves to direct the carrier flow to the appropriate columns as per the method specifications and a positive pressure autosampler. This instrument is also uniquely designed to accommodate proprietary 1 mm packed columns that are manufactured and tested in house by Selerity. These columns were designed to specifically meet the requirements of ASTM D5186 and ASTM D6550 and provide resolution factors significantly higher than specified in D5186. Performance is especially enhanced when used with Selerity's zero dead-volume Secure-FitTM connectors and each column is individually conditioned and tested under the SFC conditions recommended in Method D5186.

Figure 1:- The Selerity Technologies 4000 SFC

This "gas chromatograph" like SFC instrument and column combination has been experimentally demonstrated for application to ASTM D6550 and ASTM D5186 using the following set up :-

All chromatographic analyses were performed using a Series 4000 SFC (Selerity Technologies, Salt Lake City, Utah) equipped with an internal loop injection and two six-port switching valves,

(Valco Instruments, Houston, Texas) and a flame ionization detector. SFC-grade carbon dioxide was used as mobile phase in combination with a 50 cm X 1 mm silica gel and a 5 cm X 1 mm silver-loaded silica column (Selerity). HPLC grade iso-octane and toluene were used for timing solutions (Sigma-Aldrich, St. Louis, Missouri) and technical grade air to actuate the injection and switching valves.

This SFC instrument and column combination easily meets the rigorous performance requirements of ASTM D6550 and ASTM D5186.

The Selerity 4000 Series SFC performance study for ASTM D6550

The ASTM D6550 SFC method separates the three compound classes of gasoline — aromatics, saturates and olefins — using a combination of an analytical silica gel column, a silver-loaded silica gel column, and two six-port switching valves. The switching valves connect the two columns and can be systematically actuated to direct the supercritical carbon dioxide flow through each column in both foreflush and backflush modes. The injected sample passes through the silica column, separating the olefins and saturates from the polar and aromatic compounds. The aromatic and polar species are retained in the silica column and the olefinic and saturate compounds pass onto the silver-loaded silica column where the olefinic species are trapped and the saturates continue through to the detector. The valves are then actuated to backflush the polar and aromatic compounds to the detector. This is followed by returning the valves to their original position and forward flushing the silver-loaded column to remove any remaining saturates. At this point the olefinic species are the only compounds still retained, and the valves are actuated to backflush them from the silver-loaded silica gel column to the detector.

Experimental Results: A typical chromatogram obtained from the ASTM D6550 method using supercritical carbon dioxide (at 200 atm) as the mobile phase, with an oven temperature of 70 °C and a flame ionization detector temperature at 400 °C is shown in Figure 2. The chromatogram shows a class-type separation of the three components found in gasoline in under 12 minutes with clear baseline separation between the saturates, aromatics, and olefin groups.

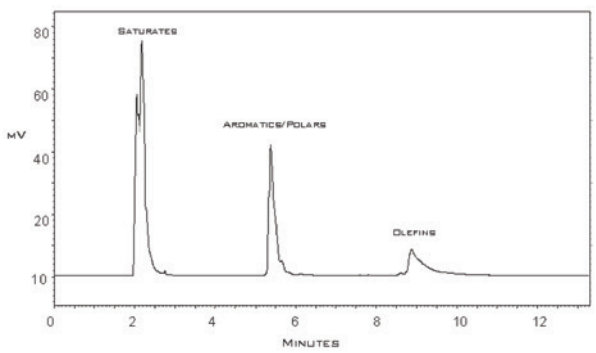


Figure 2: Chromatogram of gasoline separated into saturates, aromatics and olefins by ASTM D6550.

ASTM D6550 Comments and recent developments: The instrumentation used in this study complies with ASTM D6550 standards. The columns have been optimized for SFC and are individually tested for the determination of the olefin content in gasoline. Further developments for this method have been identified including temperature controls for the silver column to produce sharper olefin peak and the use of the integral temperature-controlled pressure transducer to ensure that the temperature of the environment does not affect the pressure of the carbon dioxide being delivered to the columns.

This work clearly demonstrated that the use of SFC for olefin determination overcomes many of the disadvantages of, and offers a viable alternative to, older traditional analysis methods.

The Selerity 4000 Series SFC performance study for ASTM D5186

The ASTM D5186 SFC method uses an analytical silica gel packed column to separate and quantify the three compound classes of diesel — saturates, mono aromatics and polynuclear aromatic hydrocarbons. It is a normalized method making it very straight forward and simple method to use. However, before samples can be analysed the system performance must be optimized including

- the determination of a relative FID response factor for aromatics to saturated hydrocarbons.

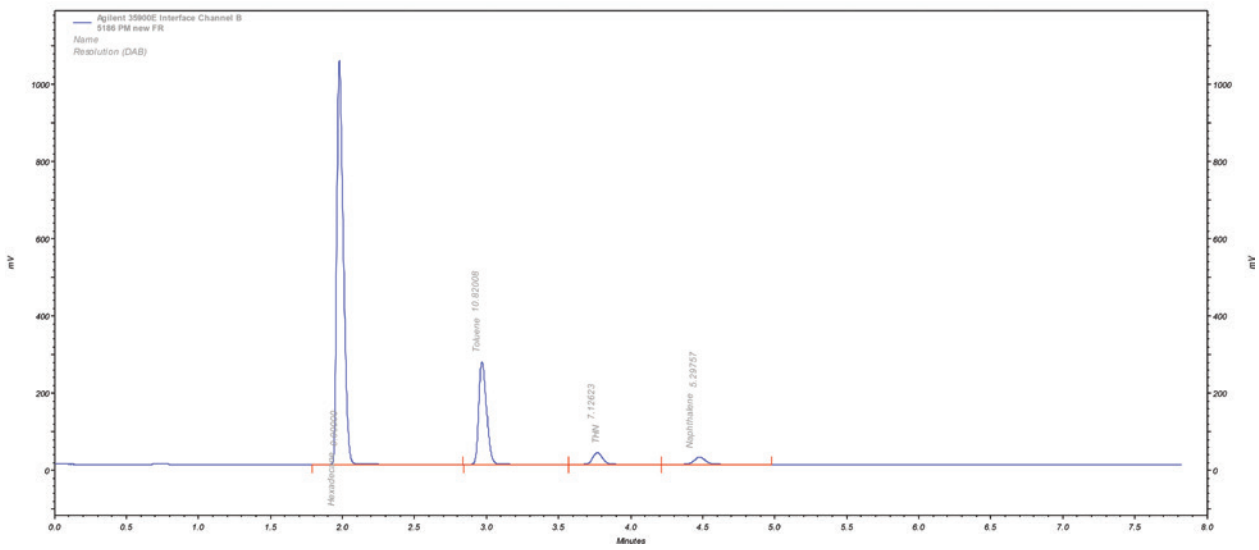
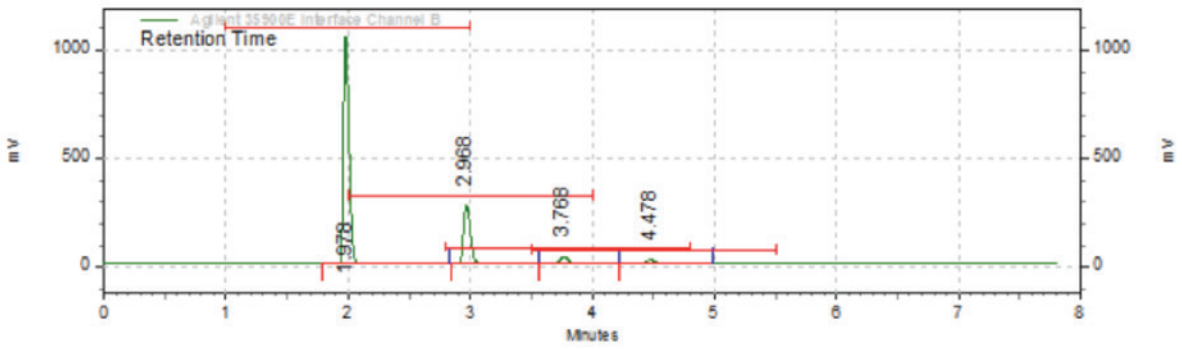


Figure 3:- Chromatogram obtained for the ASTM D5186 performance standard using the Selerity 4000 SFC

System Performance Report

Data File: PM
Method: C:\Users\Test Bench 1\Desktop\Method\5186PM.met
Acquired: 5/19/2019 11:25:43 PM (GMT -06:00)
Printed: 5/19/2019 11:28:17 PM (GMT -06:00)



Agilent 35900E Interface Channel B Results

Name	Retention Time	Area	Area Percent	Resolution (DAB)	Asymmetry
Hexadecane	1.978	332160383	72.733	0.00000	1.46382
Toluene	2.968	99874046	21.869	10.82008	1.30886
THN	3.768	14527150	3.181	7.12623	1.12625
Naphthalene	4.478	10123564	2.217	5.29757	1.10554
Totals		456685143	100.000		

Figure 4. System Performance Report for the ASTM D5186 performance standard using the Selerity 4000 SFC

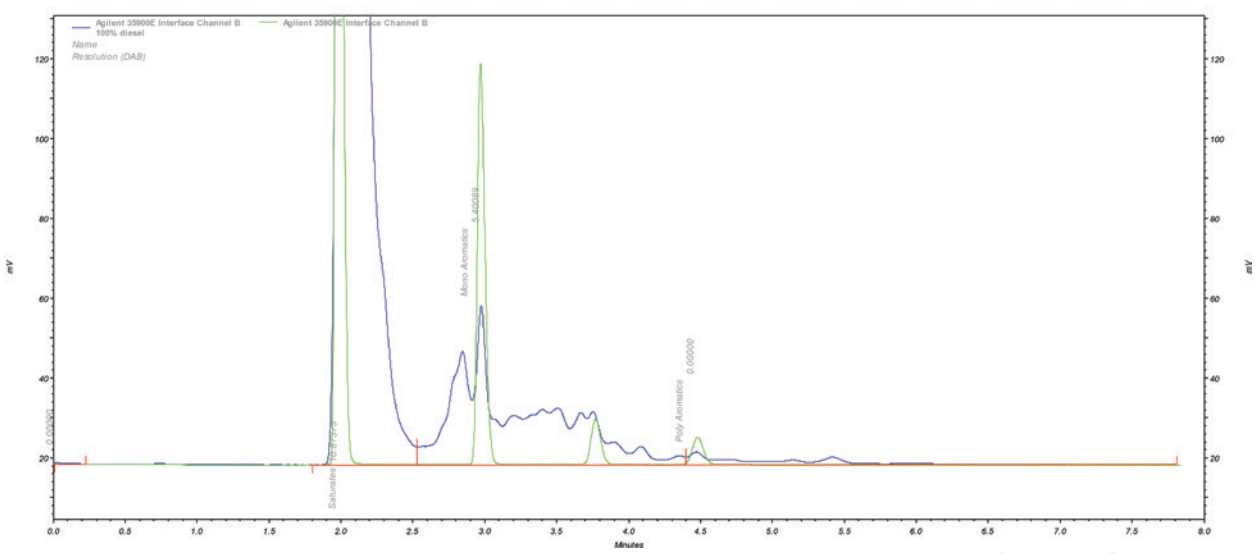


Figure 5:- Chromatogram obtained using the Selerity 4000 SFC for a typical diesel sample (blue) overlaid with the ASTM D5186 performance standard chromatogram (green).

- demonstrating a retention time repeatability of 0.5% to ensure that an accurate cut time of the polynuclear aromatics is maintained.
- a detector linearity calculation to check for bias from high aromatic to low aromatic hydrocarbon samples.
- determining minimum chromatographic resolution requirements can be met.

This is achieved using a performance standard solution containing 75 mass percent of hexadecane, 20 mass percent of toluene, 3 mass percent of tetralin and 2 mass percent of naphthalene which is analysed and the relative response ratios measured. The hexadecane represents the saturated hydrocarbons, toluene and tetralin represent the mono aromatic hydrocarbons and naphthalene represents the polyaromatic hydrocarbons. If the relative response ratio passes the method parameters, then the total area can be summed and split into the compound classes, the cut point for the poly aromatics begins when the naphthalene marker peak rises off the baseline.

Experimental Results

All chromatograms were obtained using supercritical carbon dioxide (at 200 atm) as the mobile phase, with an oven temperature of 40 °C and a flame ionization detector temperature at 400 °C. A typical performance mix chromatogram is shown in Figure 3 and the resulting system performance report is shown in Figure 4.

A typical chromatogram of a diesel sample and an overlay of the performance mix is shown in Figure 5.

ASTM D5186 Comments

The instrumentation and methods used in this study has been developed to comply with ASTM D5186 standards. The columns and chromatographic conditions have been optimized to exceed method performance requirements for both peak tailing and resolution and to provide repeatable results with a sample run time of less than 10 minutes. This work has demonstrated that the SFC method D5186 offers a viable alternative to the FIA method for common middle distillate fuels.

Closing Comments and Conclusions

Supercritical Fluid Chromatography using the Selerity 4000 SFC instrument with carbon dioxide mobile phase, optimised silica based 1mm id packed columns and FID detection has been demonstrated to fully meet and exceed the performance specifications set by ASTM hydrocarbon group type methods for both gasoline and middle distillate samples. The analyses are fast, highly automated, produce minimal solvent waste and can be run unattended thus improving lab efficiency and sample turnaround times when compared to other hydrocarbon group type methods.

1. ASTM D1319-18, Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption, ASTM International, West Conshohocken, PA, 2018, www.astm.org
2. ASTM D6550-15, Standard Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography , ASTM International, West Conshohocken, PA, 2015, www.astm.org
3. ASTM D5186-15, Standard Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels By Supercritical Fluid Chromatography, ASTM International, West Conshohocken, PA, 2015, www.astm.org

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