Determination of Aromatic Content in Diesel Fuel According to ASTM D5186

Enhancing the Agilent 1260 Infinity Analytical SFC System with a Flame Ionization Detector

Application Note

Energy & Chemicals

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Abstract

This Application Note describes the determination of the aromatic content of diesel fuel using the Agilent 1260 Infinity Analytical SFC system with the SIM flame ionization detector (FID). Combining the SFC system with this developed FID system meets all requirements of the ASTM D5186 method such as detector accuracy and linearity. This combination offers a cost-effective and fast alternative to the existing normal phase HPLC methods D1319 and D2425.

Introduction

SIM Scientific Instruments Manufacturer GmbH, Oberhausen, Germany, has developed a flame ionization detector (FID) for use with the Agilent 1260 Infinity Analytical SFC system. This combination extends the range of applications, for example, to meet petrochemical requirements as described in the ASTM method D5186. Control of the FID is possible through Agilent OpenLAB CDS ChemStation Edition Software with the appropriate electronic components and the FID software module. The development of the FID was done by taking particular account of detector accuracy and linearity as well as integration in the 1260 Infinity Analytical SFC system. The starting point of the FID development was the determination of aromatic compounds in diesel fuels as published in the ASTM method D5186. This approach was taken so that system performance could be verified according to the requirements in this test method. This enables the separation of monoaromatics and polynuclear aromatics in fuel samples using an FID. An important challenge to be solved was the contamination of the backpressure regulator (BPR) with high-melting compounds such as naphthalene. This challenge was overcome by using Channel B of a binary pump to purge the BPR continuously with hexane.

Diesel and aviation turbine fuels contain nonaromatic, mono- and polyaromatic hydrocarbons. Best performance and maximum lifetime of an engine is achieved when the amount of aromatics is as low as possible. Since the aromatic hydrocarbon content can affect the cetane number of fuels and cause emissions due to incomplete burning, there are different regulations to protect the environment and public health. Examples of such regulations are those from the United States Environmental Protection Agency (USEPA) and the California Air Resources Board (CARB) as well as self-regulation of distilleries for process and quality control.

The American Society for Testing and Materials (ASTM) published the test method D5186 to determine the aromatic and polynuclear aromatic content of diesel fuels and aviation turbine fuels by supercritical fluid chromatography with flame ionization detection. This test method shows clear benefits compared with test methods D1319 and D2425 because it is:

- Applicable for an expanded application range
- Statistically more precise than or at least as precise as other methods
- Unaffected by fuel coloration
- Not as expensive and time-consuming to perform

The method is applicable to samples containing total aromatics in the range of 1 to 75 mass %, and polyaromatics in the range of 0.5 to 50 mass %[1-3].

Instrumentation

An Agilent 1260 Infinity Analytical SFC system with the following configuration was used:

- Agilent 1260 Infinity SFC Control Module
- Agilent 1260 Infinity SFC Binary Pump
- Agilent 1260 Infinity Thermostatted Column Compartment
- CTC Analytics LC-Injector HTC PAL (50-cm width) modified with 4-port valve (internal 0.5-µL loop) and DLW
- SIM flame ionization detector

The complete solution can be ordered through SIM Scientific Instruments Manufacturer GmbH, Oberhausen, Germany.

Experimental

Chemicals and solutions

Samples and standards were prepared according to guidance published in the ASTM method.

FID gases	Hydrogen, air, and nitrogen (as make-up gas)
Eluent	Carbon dioxide (purity > 99.995 %, pressurized in a cylinder without DIP tube, according to the specifications of the SFC module)
Purge solution for back pressure regulator	Hexane (not used as modifier! Pumped with channel B of the binary pump)
Performance mixture	Quantitative mixture prepared according to section 7.6 of the ASTM method from fine chemicals (Sigma Aldrich) with the following composition (approximate values): 75 mass % hexadecane (n-C_{16}) 20 mass % toluene (T) 3 mass % tetralin (1,2,3,4-tetrahydronaphthalene, THN) 2 mass % naphthalene (N)
Diesel sample for linearity check	Diesel sample, aromatic content 21.8 % (according to manufacturer's analysis results)

Analytical column

YMC-PACK-SIL_06, 250 × 4.5 mm, S-6 nm, 5 µm (YMC America, Inc., Allentown, PA, USA), or
Agilent ZORBAX RX-SIL,
4.6 × 250 mm, 5 µm (p/n 880975-901)

Restrictor

PEEKsil, 100-µm inside diameter, 20 cm (for hexane purging path)

Software

Agilent OpenLab CDS ChemStation Edition, Rev. C.01.05

SFC/FID Configuration

The outlet of the column is connected to the upper T-piece of the FID (Figure 1). To purge the backpressure regulator (BPR), hexane is pumped continuously through Channel B of the binary pump. To maintain constant backpressure and a continuously operating system, a restriction capillary is integrated between pump head B and the lower T-piece of the FID (Figure 1).

LC Method

Agilent 1260 Infinity Binary SFC Pump		
Solvent A	CO_2 (precompressed), 99,995 %	
Solvent B	Hexane, 0.5 %, used for purging the backpressure regulator (BPR) only, not as eluent. Depending on the composition of the sample, it might be necessary to purge the BPR with a higher amount of hexane (for example, setting in the software to 50 % eluent B) from time to time.	
Flow rate	1.8 mL/min	
Agilent 1260 Infinity Thermostatted Column Compartment		
Column temperature	25 °C	
LC-Injector HTC PAL		
Injection volume	0.5 µL	
Injection cycle	Preclean with Solvent 1 (hexane)	1
	Preclean with Sample	1
	Filling speed (µL/s)	10
	Filling strokes	3
	Inject to	LC Vlv1
	Injection speed (µL/s)	5
	Pre-inject delay	500 ms
	Post-inject delay	500 ms
	Post clean with Solvent 1 (hexane)	2
	Valve clean with Solvent 1	1
	(all other parameters not listed here have the value zero)	
FID		
Temperature	300 °C	
Gases		
Hydrogen (H_2)	50 mL/min	
Air	500 mL/min	
Make-up gas (N_2)	50 mL/min	

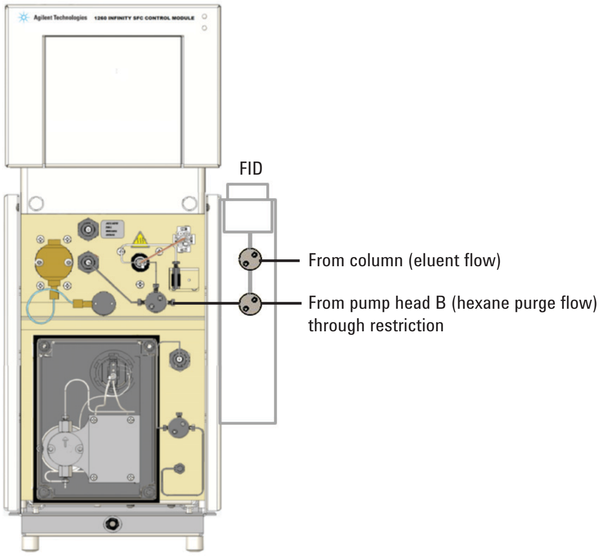

Figure 1. Connection of the SFC/FID module with the LC instrument.

Results and Discussion

In the following, the compliance with the requirements of the system performance listed in section 8.2 of the ASTM test method is shown. The areas in the chromatogram are integrated corresponding to a performance mixture of hexadecane, toluene, tetrahydronaphthalene (THN), and naphthalene (N). The mass % content of each of these groups in the fuel is calculated by area normalization.

FID sensitivity

The first step, according to the ASTM method, was to show that the FID sensitivity is sufficient to detect 0.1 mass % toluene in hexadecane (see ASTM section 6.1). Figure 2 illustrates that the FID exceeds this requirement.

The performance mixture (PFM), according to ASTM section 7.6, is used to determine most of the method acceptance criteria such as resolution, retention time reproducibility, and detector accuracy. Moreover, it is used to determine the integration marks for performing the grouping and integration of the complex fuel samples.

Resolution

Figure 3 shows the resolution between nonaromatics (hexadecane) and monoaromatics (toluene), referred to as R_{NM}. According to ASTM D5186 a R_{NM} value of at least 4 is required, but a value of 10 was determined for the actual experiment. Also, the resolution between mono-(tetralin) and polynuclear (naphthalene) aromatics, referred to as R_{MD}, is twice as high as required (see ASTM method, section 8.2.1).

Retention time reproducibility

Retention-time reproducibility is also determined with the PFM. It should not be higher than 0.5 % RSD for hexadecane and toluene peaks. This is important because the integration marks for the diesel sample are determined from the analysis of the PFM. Figure 4 shows an overlay of five chromatograms as well as the assignment of the areas to the corresponding diesel fractions.

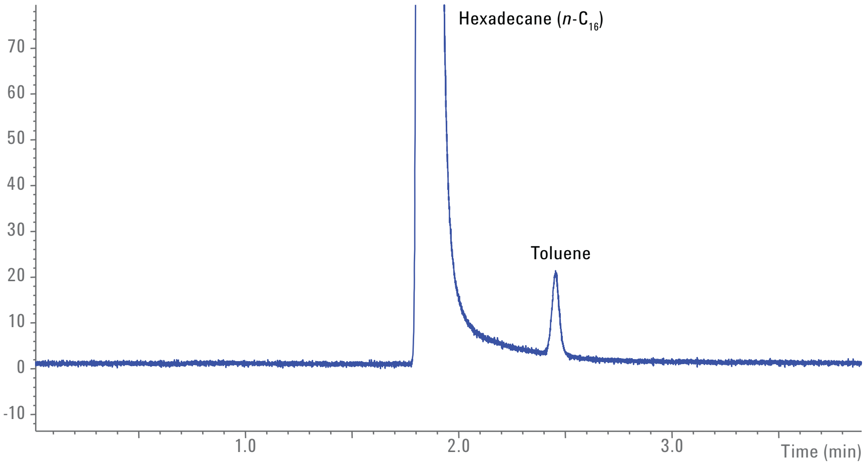

Figure 2. Chromatogram detail of a solution with 0.1 mass % toluene in hexadecane (n-C_{16}).

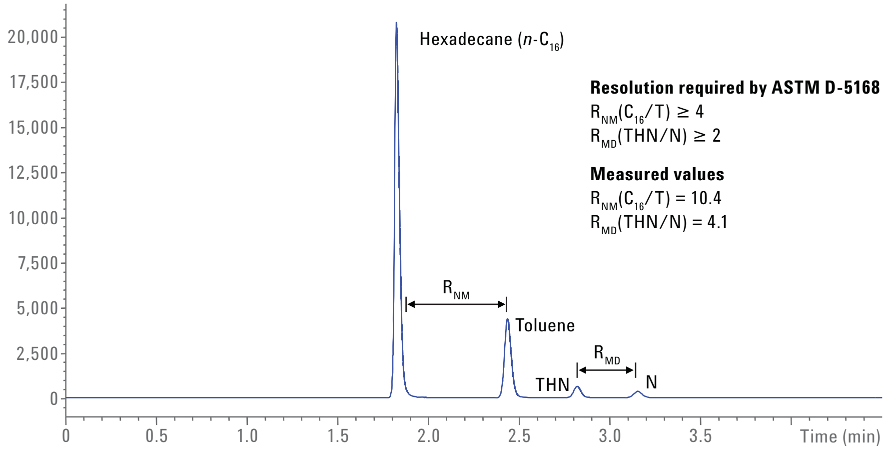

Figure 3. Determination of the resolution values for RNM (hexadecane to toluene) and RMD (THN to N) using the performance mixture.

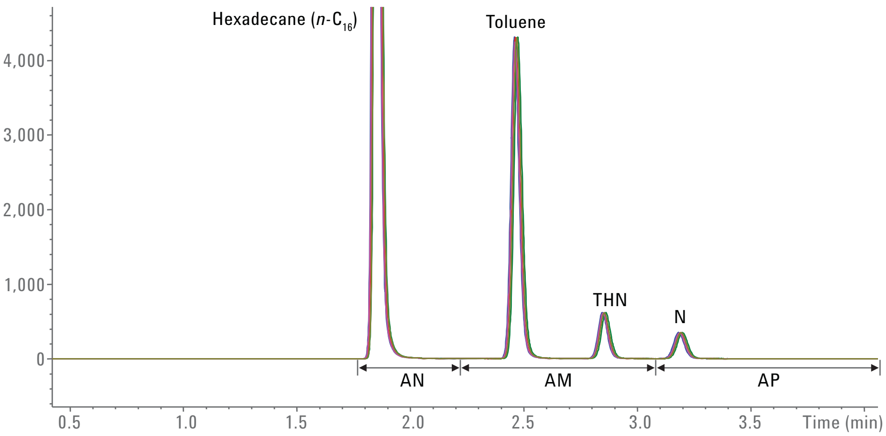

Figure 4. Overlay of five chromatograms of the PFM with the assignment to the fractions of a diesel sample (AN = Area of nonaromatics, AM = Area of monoaromatics, AP = Area of polyaromatics).

Table 1 lists the calculated values for all four substances of the PFM. The relative standard deviations (RSDs) for the retention time (RT) were all in the range of 0.3 %, so that all values fit the acceptance criterion.

Table 1. Retention time reproducibility of PFM (average of 10 runs, *n*-C_{16} = Hexadecane, T= Toluene, THN = 1,2,3,4-tetrahydronaphthalene, N = Naphthalene)

	n-C_{16}	T	THN	N
RT average (n = 10)	1.83	2.44	2.82	3.16
RT SD	0.004	0.007	0.008	0.009
RT RSD %	0.24	0.28	0.29	0.30

Detector accuracy test

To check the assumption that the FID response approximates to the theoretical unit carbon response, the response factors relative to hexadecane (RRF) were calculated for each of the components in the performance mixture. The measured RRF for each component must be within ±10 % of the theoretical value when it is assumed that the FID response approximates to the theoretical unit carbon response. The calculated RRF values were within these limits, as summarized in Table 2.

Table 2. Determination of the relative response factors (RRF) of the performance mixture (average of 10 runs).

RRF value	Minimum	Maximum	Calculated*	Compliance to test method
RRF (toluene)	0.9675	1.1825	1.0753	Yes
RRF (tetrahydronaphthalene)	0.9630	1.1825	1.0420	Yes
RRF (naphthalene)	0.9936	1.2144	1.0840	Yes

* Average based on 10 injections, all within the given limits.

Detector linearity check

A diesel sample was used for this check. Neat fuel and two dilutions (containing fuel and *n*-C_{16} in proportions of 1:1 and 1:3) were analyzed according to ASTM section 9. Determination of the mass % aromatics in the two dilutions, and comparison with their corresponding expected aromatics results was used to verify detector linearity. Figure 5 shows an overlay of these three diesel samples. Integration marks were set according to the chromatogram of the PFM (Figure 4) to determine the content of mono- and polyaromatics. The sum of both areas is the content of total aromatics in the diesel sample (given in mass %).

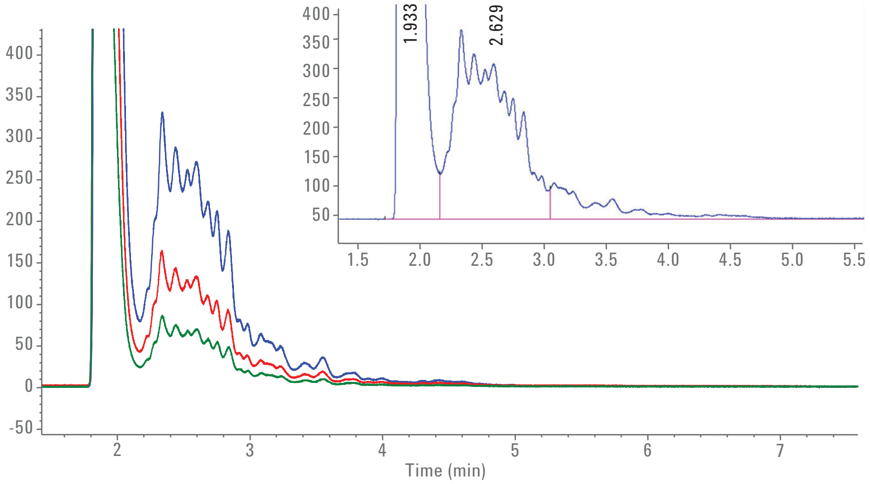

Figure 5. Chromatogram of the diesel sample (blue) and its 1:1 (red) and 1:3 (green) dilution; the inset on the right shows the setting of the integration marks corresponding to the PFM.

Table 3 shows the aromatic content of the diesel sample and its weighed dilutions. The difference between the measured and expected values agree to within the repeatability limits stated in 13.1.1 of the ASTM method, so that the FID linearity could be verified.

Table 3. Total aromatic content of a diesel fuel.

Dilution	Measured aromatics (mass %)*	Expected aromatics (mass %)	Aromatics deviation (mass %)
Neat	21.8		
1:1	11.1	10.8	0.3
1:3	5.9	5.7	0.2

*average based on 10 injections

Analysis of diesel samples

To see the repeatability of the diesel sample measurements, Figure 6 shows an overlay of 10 chromatograms. If fatty acid methyl esters (FAMEs) are present as a biodiesel additive, a longer run time is required to elute the FAMES from the column.

Conclusion

The performance of the Agilent 1260 Infinity Analytical SFC system with the SIM FID meets the requirements of ASTM D5186 for the determination of aromatics in diesel fuel. Specifically, the detector accuracy and linearity tests show the suitability of the SIM FID for the determination of aromatic substances with the 1260 Infinity Analytical SFC system. The system is equipped with continuous purging of the backpressure regulator to ensure trouble-free and reliable operation of the system.

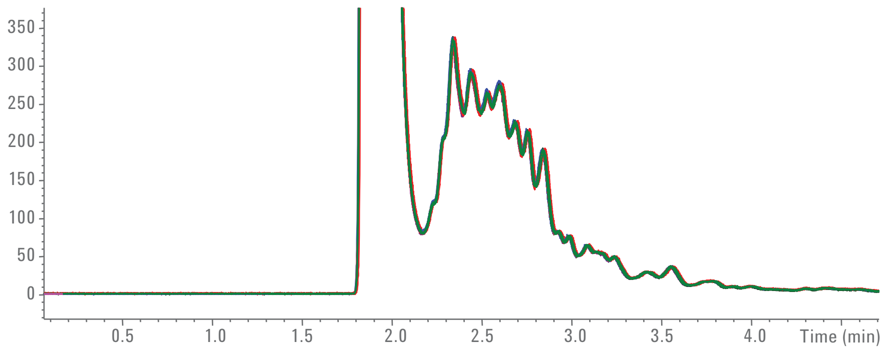

Figure 6. Overlay of 10 chromatograms of a diesel sample.

References

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2. American Society for Testing and Materials (ASTM): ASTM D1319-14, Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption http://www.astm.org/Standards/D1319.htm (accessed April 1, 2015)

3. American Society for Testing and Materials (ASTM): ASTM D2425-04 (2009), Standard Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry http://www.astm.org/Standards/D2425.htm (accessed April 1, 2015)

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