

Determination of Olefin Content in Gasoline According to ASTM D6550

Application Note

Energy & Chemicals

Authors

Martina Noll-Borchers, Timo Hölscher
SIM Scientific Instruments
Manufacturer GmbH
Oberhausen, Germany



Edgar Naegele, Markus Becker
Agilent Technologies, Inc.
Waldbronn, Germany

Abstract

This Application Note demonstrates the determination of the olefin content in gasoline using the Agilent 1260 Infinity Analytical SFC System with the SIM Flame Ionization Detector (FID). Combining the SFC system with this FID meets all requirements of the ASTM D6550 method such as the required retention time precision for time-based column switching, good area precision, and calibration function.



Agilent Technologies

Introduction

Olefinic hydrocarbons present in gasoline contribute to photochemical reactions in the atmosphere. This results in the formation of photochemical smog in susceptible urban areas. A specification of the maximum allowable limit of olefins in motor gasoline was defined by the California Air Resources Board (CARB)¹. An appropriate analytical test method that can be used by regulators and producers² for the determination of total olefins is described in ASTM D6550.

SIM Scientific Instruments Manufacturer GmbH (Germany) has developed a flame ionization detector (FID) for the Agilent 1260 Infinity Analytical SFC System to enhance the range of applications, for example, to meet petrochemical requirements described in ASTM method D5186. The starting point of the FID development was the determination of aromatic compounds in diesel fuels, as published in ASTM method D5186. The system performance could be verified according to the requirements in this test method that enables the separation of mono- and polynuclear aromatics in fuel samples using a FID^{3,4}.

This Application Note demonstrates the determination of the olefin content in gasoline using the 1260 Infinity Analytical SFC System with the SIM FID. The ASTM D6550 requires an SFC analysis with a set of two chromatographic columns connected in series, and a valve switching solution. Together with specified column switching times, the olefins can be separated and quantified. The first column is packed with high-surface-area silica particles, and the second column contains silver ions. In the forward-flow mode, saturates pass through both columns, whereby the olefins are trapped on the silver-loaded column, and the aromatics and oxygenates are retained on the silica column. Aromatic compounds and oxygenates are then eluted from the silica column to the detector in backflush mode. Finally, the olefins are backflushed from the silver-loaded column to the detector.

Experimental

Instrumentation

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

- Agilent 1260 Infinity Binary SFC Pump
- Two Agilent 1290 Infinity Thermostatted Column Compartments with valve drives and 2-position/6-port Quick-Change valves
- Agilent 1260 Infinity SFC Control Module
- CTC Analytics LC-Injector HTC PAL (50 cm width) modified with 4-port valve (internal 0.5 μ L loop) and DLW
- SIM Flame Ionization Detector
- Restrictor for hexane purging path: PEEKsil, 100 μ m id, 20 cm

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

Analytical column

Pursuit XR5 5 Si, 4.6 \times 250 mm (p/n A6006250X046)

ChromSpher 5 Lipids (silver loaded), 4.6 \times 30 mm (G7601-85000)

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 to the FID (Figure 1). For purging the backpressure regulator (BPR), hexane is permanently pumped from pump head 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.

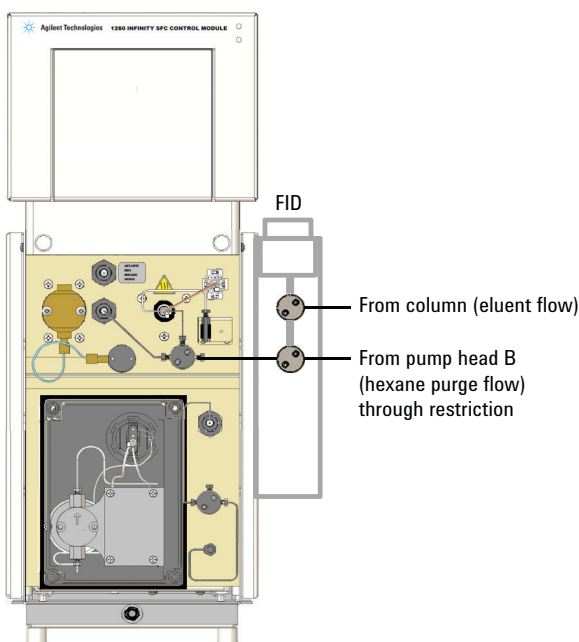


Figure 1. Connection of the SFC/FID module with the LC instrument.

Column and valve configuration

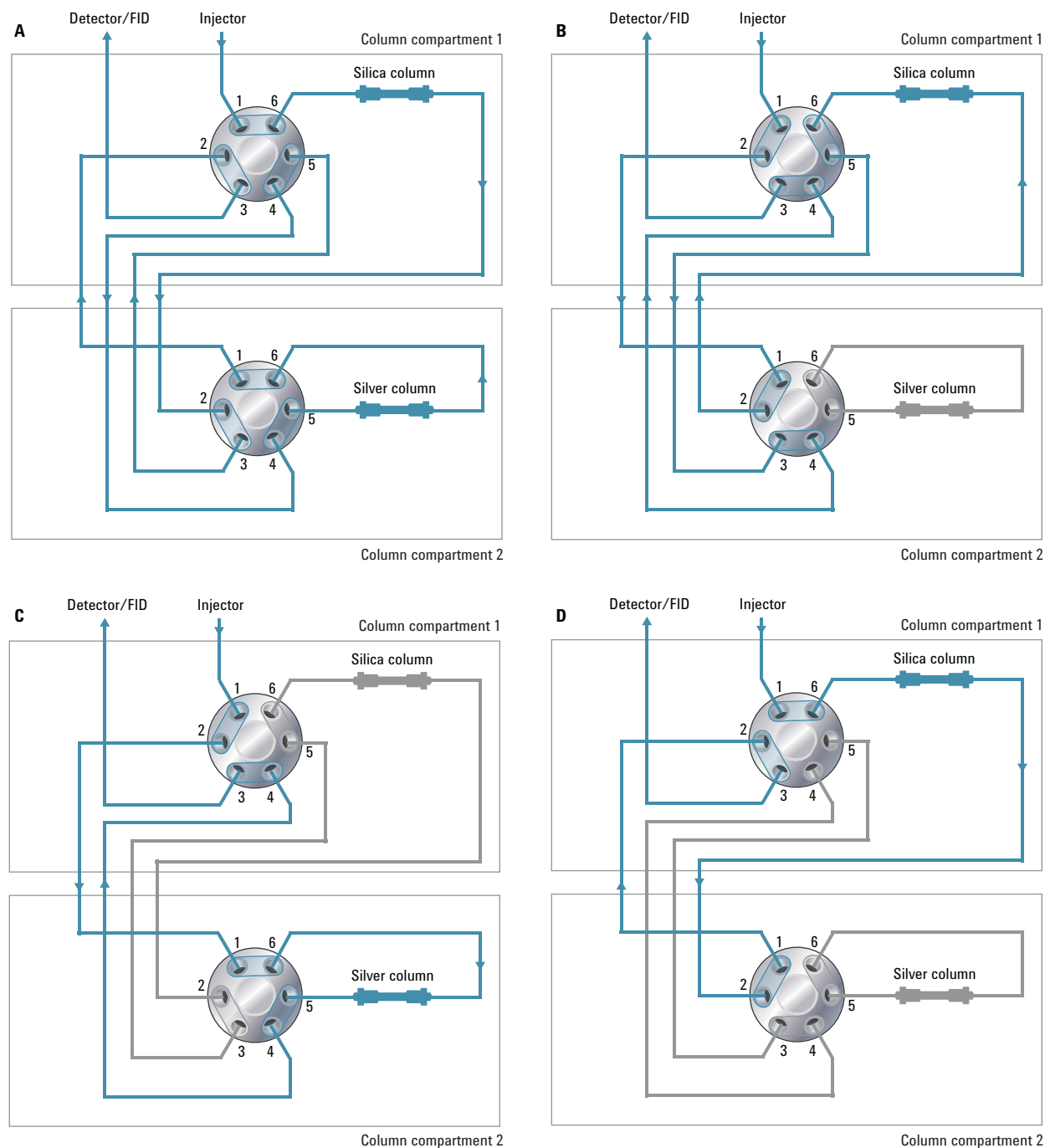


Figure 2. Column and valve configuration.

Position A: The silica column and the silver-loaded column are in forward-flush mode. The sample is injected on the two columns, the saturates are eluted from both columns, the olefins are trapped on the silver-loaded column, and the aromatics are retained on the silica column.

Position B: The silica column is switched to backflush mode, the silver-loaded column is not in the flow path. This position is used to elute aromatics.

Position C: The silica column is not in the flow path and the silver-loaded column is in backflush mode to elute the olefins.

Position D: The silica column is in forward-flush mode and the silver-loaded column is not in the flow path. This position is used to optimize the separation. This position enables ASTM D5186.

SFC Method

Agilent 1260 Infinity Binary SFC Pump	
Solvent A	CO ₂ (precompressed), 99.998 %
Solvent B	Hexane, 0.5 % (used for purging the BPR only, not used 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	2.2 mL/min
Agilent 1260 Infinity SFC Control Module	
BPR temperature	25 °C
BPR pressure	150 bar
Agilent 1290 Infinity Thermostatted Column Compartment	
Column temperature silica column	25 °C
Column temperature silver-loaded column	80 °C
Valve positions (Figure 2)	
Valve position A	At 0 minutes
Valve position B	At 2.0 minutes
Valve position A	At 6 minutes
Valve position C	At 6.5 minutes
CTC Analytics LC-Injector HTC PAL	
Injection volume	0.5 µL (loop)
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 (ms) 500 Post inject delay (ms) 500 Post clean with solvent 1 (hexane) 2 Valve clean with solvent 1 1 (all other parameters not listed are set to zero)
FID	
Temperature	300 °C
Gases	Hydrogen (H ₂) 50 mL/min Air 500 mL/min Make-up gas (N ₂) 50 mL/min

Chemicals and solutions

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

Component	Description
FID gases	Hydrogen, air, and nitrogen (as make-up gas)
Eluent	Carbon dioxide (purity > 99.998 %, pressurized in a cylinder without DIP tube according to the specifications of the SFC module)
Purge solution for backpressure regulator	Hexane (not used as modifier, pumped with channel B of the binary pump)
Performance Test Mixture (PTM)	Quantitative mixture prepared according to section 7.7 of the ASTM method from fine chemicals (Sigma-Aldrich) with the following composition (approximate values): 80 mass% hexane (n-C ₆) 10 mass% toluene (T) 10 mass% 3-methyl-2-pentene, <i>cis/trans</i> -mixture (3M2PE)
Calibration mixture	A) Quantitative mixture prepared from fine chemicals (Sigma-Aldrich) with the following composition (approximate values): 70 mass% hexane (n-C ₆) 10 mass% toluene (T) 20 mass% 3-methyl-2-pentene, <i>cis/trans</i> -mixture (3M2PE) B) Quantitative mixture prepared according to section 8.2.4 of the ASTM method from fine chemicals (Sigma-Aldrich) with the following composition (approximate values): 70 mass% gasoline 20 mass% mixture of olefins (for example, Olefin Mix, Sigma-Aldrich p/n 44589, suitable for ASTM methods) 10 mass% toluene (T) These stock solutions were diluted in a 1:2 pattern down to 1.25 % olefin with gasoline: olefin content 20, 10, 5, 2.5, 1.25 mass%.
Petrol (gasoline)	Puriss., b.p. 90–100 °C
Gasoline	Obtained from a local gas station

Results and Discussion

The Performance Test Mixture (PTM), comprising toluene and olefin with 10 mass% each, was used to create the separation method. The valve switching times for changes in flow directions were determined according to ASTM D6550. First, the PMT was injected in valve position D when only the silica column is in the flow path (valve position D, Figure 2) to measure the resolution between olefinic and aromatic compounds (R_{AO} , see Figure 3, blue chromatogram). The resolution R_{AO} was 6.2, and exceeded the required value of 3, so that a quantitative separation between the olefins and aromatics could be achieved.

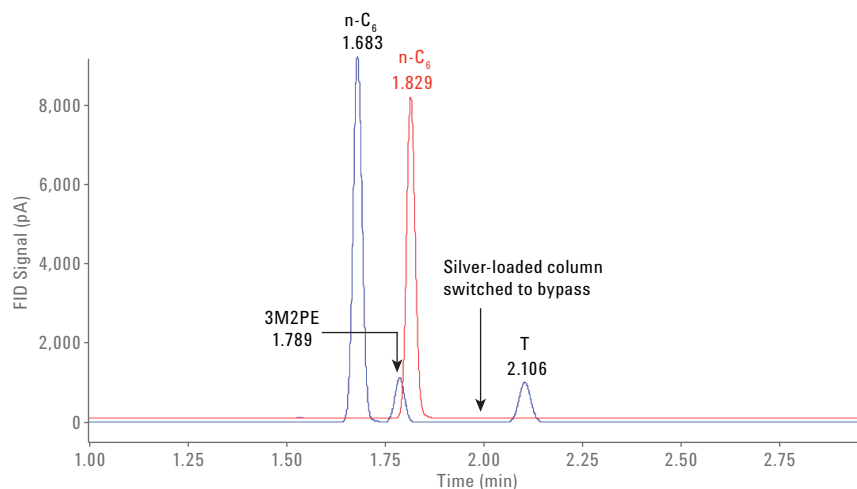


Figure 3. Separation of the PTM on the silica column (blue), and chromatogram of hexane on the silica and silver-loaded columns in series (red). The silver-loaded column can be switched to bypass at 2.0 minutes when the saturates arrive at the FID.

In the second step, valve position A was used to find the retention time of the saturated hydrocarbons (hexane) from the silica and the silver-loaded column in forward-flush mode (Figure 3, red chromatogram). As a result of these chromatograms, the time point to switch the silica column to backflush mode (valve position B) was determined to be 2.0 minutes, so that the aromatics can be eluted by backflush mode before they enter the silver-loaded column.

Subsequent switching times were determined according to the requirements in the ASTM standard. After elution of the aromatics from the silica column in backflush mode, the columns were switched back to starting position A for 0.5 minutes to clean off saturated and polar residues. Then, the valves were switched to position C at 6.5 minutes for the elution of the olefins from the silver-loaded column in backflush mode (Figure 4). In the final method, the olefin compound eluted at 7.166 minutes.

The performance of the system was tested by 10 injections of the PTM and calculation of the retention time and area precision of the three substances representative for saturates (*n*-hexane), aromatics (toluene) and olefins (3M2PE) (Figure 5 and Table 1). For the olefin representative, the retention time repeatability was 0.04 % and the area repeatability was 1.26 %.

Good retention time repeatability is important for the quantification of the olefins because column switching is performed on a time basis. The values over a period of several days were also significantly below the limit of 0.5 %.

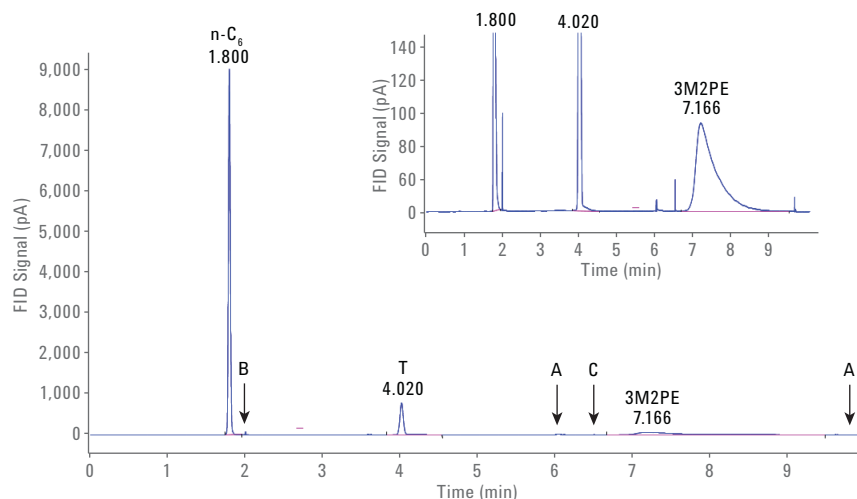


Figure 4. Separation of the PTM with the final method. The letters signify the valve position chosen at that time (*n*-hexane: retention time with both columns in-series 1.800 minutes, toluene: retention time with silica column backflush mode 4.020 minutes, olefin: retention time with silver-loaded column in backflush mode at 7.166 minutes (see inset).

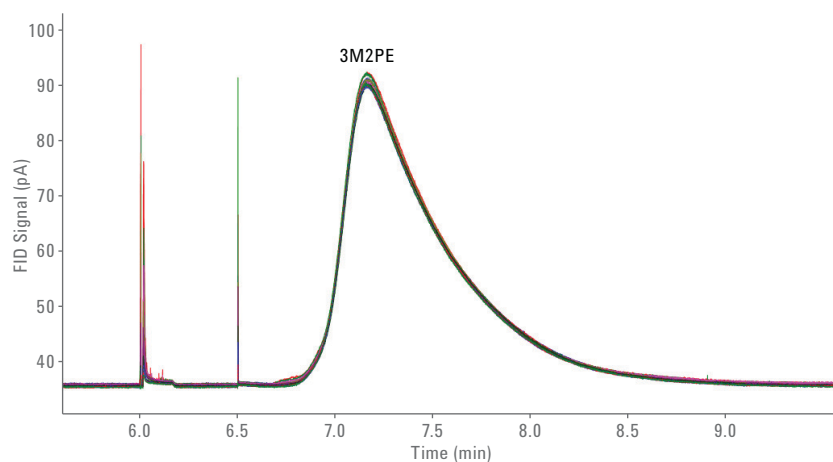


Figure 5. Overlay of 10 injections of the PTM (detailed display of the olefin region of the chromatogram) to show retention time and area precision performance of the separated olefin 3M2PE.

Table 1. Retention time (RT) and area RSD (%) performance.

	Hexane		Toluene		Olefin 3M2PE	
	RT	Area	RT	Area	RT	Area
Average	1.80	16161	4.02	2198.6	7.16	2059.5
SD	0.002	130.6	0.002	17.7	0.003	26.0
RSD (%)	0.13	0.81	0.04	0.80	0.04	1.26

The compounds of the PTM (calibration mixture A, see Chemicals and solutions) were also used to generate a calibration function. A dilution of this mixture containing 20 mass% olefin by a 1:2 dilution pattern was used to generate the calibration levels at 20, 10, 5, 2.5, and 1.25 mass% olefin in hexane, that itself was free from aromatics and olefins (Figure 6A). Together with a blank, each calibration level was injected nine times. The calculated calibration function had a linearity of 0.99997 (Figure 6B). This complied with the calibration shown in ASTM D6550, which shows a linearity of 0.997².

To obtain proof of the method, a multi-olefin sample was measured with a second SFC/FID system. The multi-olefin sample, comprising 25 olefins, was diluted in pure gasoline (petrol) to 20 mass%, and injected directly (Figure 7). The petrol used for the dilution was completely free of olefinic residues and aromatic residues. This obtained mixture (calibration mixture B) was also suitable to calibrate the SFC/FID instrument, as described above with comparable results (data not shown).

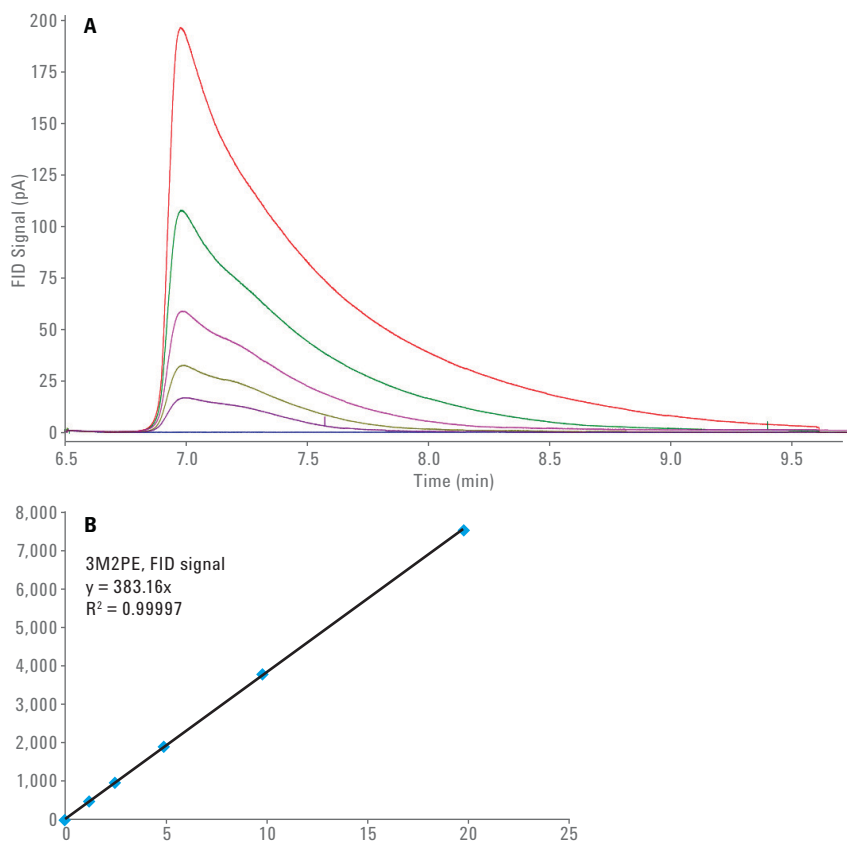


Figure 6. Calibration of the SFC/FID for the determination of olefins. A) Chromatograms of blank and the five calibration levels of the olefin 3M2PE in the PTM. B) Related calibration function for the olefin 3M2PE (calculated from six measurements of each level).

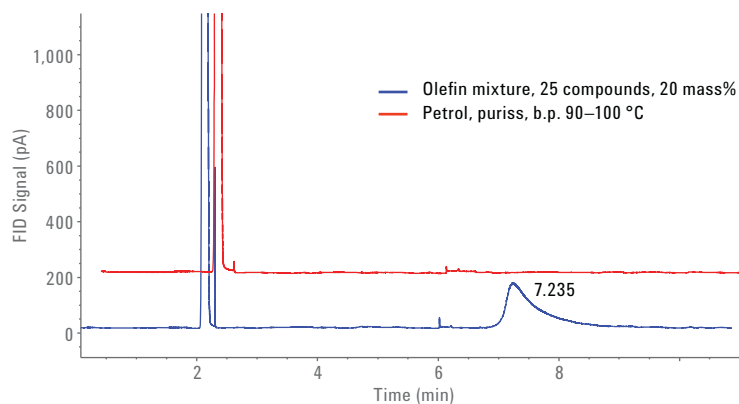


Figure 7. Multi-olefin sample comprising 25 olefins (20 mass%), diluted in pure gasoline (petrol).

Finally, an actual gasoline sample was analyzed with the first SFC/FID instrument (20 times, Figure 8A). The olefins at 7.02 minutes, the olefin content, determined directly from the calibration function, was 12.8 mass% with 1.54 % RSD (equaling 0.2 mass% olefin). The repeatability limit for this concentration stated in the ASTM standard is 0.7 mass%. This value shall not be exceeded in more than one case in twenty. The plot of the individual results shows that 19 results were within a difference of 0.6 mass%, which agreed to this requirement (Figure 8B).

Conclusion

This Application Note demonstrates the usability of the Agilent 1260 Infinity Analytical SFC System in combination with the SIM-FID for the determination of olefins in gasoline according to ASTM D6550. The olefin content of a gasoline sample was separated from saturated and aromatic hydrocarbons by means of two different columns, and a valve-switching solution for separation in forward flush and elution in backflush mode. The olefins were quantified between 1.25 and 20 mass% with good linearity. In addition to test solutions, real gasoline samples were measured to confirm the repeatability limits of the ASTM method.

References

1. California Air Resources Board, The California Reformulated Gasoline Regulations, Title 13, California Code of Regulations, Sections 2250-2273.5 Reflecting Amendments Effective August 29, 2008.
2. American Society for Testing and Materials (ASTM): ASTM D6550-10 (2009), Standard Test Method for Determination of Olefin Content of Gasoline by Supercritical-Fluid Chromatography, <http://www.astm.org/Standards/D6550.htm> (accessed June 1, 2015).

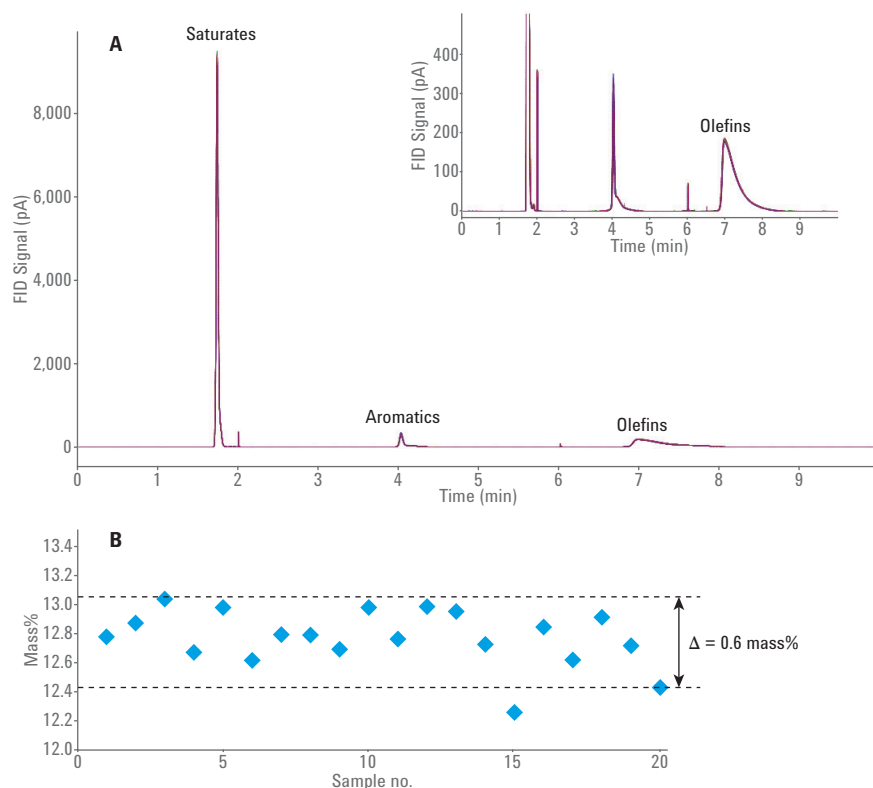


Figure 8. Real gasoline sample analyzed according to the final test method. A) Overlay of 20 injections. B) Olefin content of 20 successive analyses to prove the repeatability limit.

3. American Society for Testing and Materials (ASTM): ASTM D 5186-03 (2009), Standard Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels By Supercritical Fluid Chromatography, <http://www.astm.org/Standards/D5186.htm> (accessed June 1, 2015).
4. Noll-Borchers, M., Hölscher, T., Naegele, E., Becker, M., Determination of Aromatic Content in Diesel Fuel According to ASTM D5186, *Agilent Technologies Application Note*, publication number 5991-5682EN, 2015.

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