Determination of Olefin Content in Denatured Ethanol According to ASTM D7347

Application Note

Energy & Chemicals

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Abstract

This Application Note demonstrates the determination of the olefin content in denatured ethanol using the Agilent 1260 Infinity Analytical SFC system together with the SIM Flame Ionization Detector (FID). Combining the 1260 Infinity Analytical SFC system with this FID meets all requirements of the ASTM D7347-07 method such as the required retention time precision for time-based column switching, good area precision, and calibration function.

SIM Scientific Instruments Manufacturer GmbH

Agilent Technologies

Introduction

Denatured ethanol is used as an oxygenate additive in spark ignition engine fuel. It is added to fuel at the terminals, and can contain olefinic species, which contribute to the total olefins content. Olefinic hydrocarbons have been demonstrated to contribute to photochemical reactions in the atmosphere. This can result in the formation of smog in susceptible urban areas. Therefore, the California Air Resources Board (CARB) has specified a maximum allowable limit of total olefins in spark ignition engine fuel[1,2].

An analytical method is necessary to determine the amount of olefins in denatured ethanol intended for spark ignition engine fuel, as described in ASTM method D7347-07. Regulators and producers must abide by this method[2]. An appropriate analytical test method for the determination of total olefins in gasoline is described in ASTM D6550[3,4].

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 D5186 for the determination of aromatic compounds in diesel fuels[5,6].

This Application Note demonstrates the determination of the olefin content in denatured ethanol using the 1260 Infinity Analytical SFC system together with the SIM Flame Ionization Detector. It is shown that the SFC/FID system meets all requirements of ASTM D7347-07. The test method is automated, does not require any sample preparation, and has a relatively short analysis time of approximately 10 minutes. The application range is from 0.1 to 1.0 mass% total olefins. For the final method, the retention time (RT) and area precision, the accuracy of olefin quantification, and detector linearity is demonstrated. Finally, a denatured ethanol sample is measured.

Experimental

Instrument

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 Agilent InfinityLab Quick Change valves
- Agilent 1260 Infinity SFC Control Module
- CTC Analytics LC-Injector HTC PAL (50 cm width) modified with 4-port valve (internal 1-µL loop) and DLW or Agilent 1260 Infinity Standard Autosampler (alternative)
- SIM Flame Ionization Detector
- Restrictor for hexane purging path: PEEKsil, 100 µm id, 20 cm

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

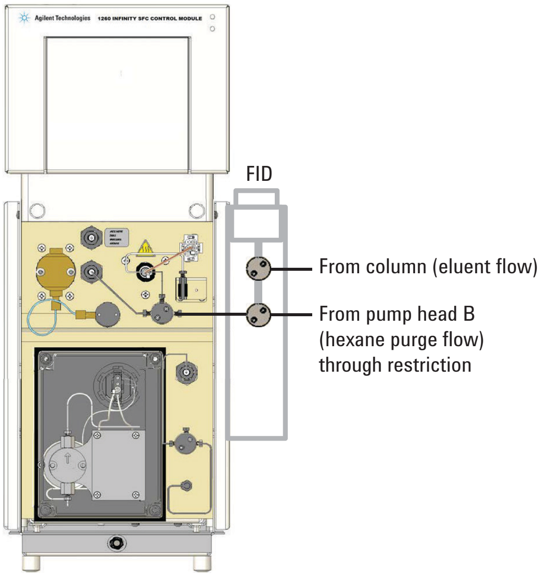

Figure 1. Connection of the SFC/FID module with the LC instrument.

Analytical column

- Agilent ChromSpher 5 Lipids (silver loaded), 4.6 × 30 mm (p/n G7601-85000)
- YMC-PACK-SIL-06, 4.6 × 250 mm, S-5 µm, 6 nm (p/n SL06S05-2546WT)
- YMC-Pack-PVA-Sil, 4.0 × 50 mm, S-5 µm, 12 nm (p/n PV12S05-0504QT)

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.

Column and valve configuration

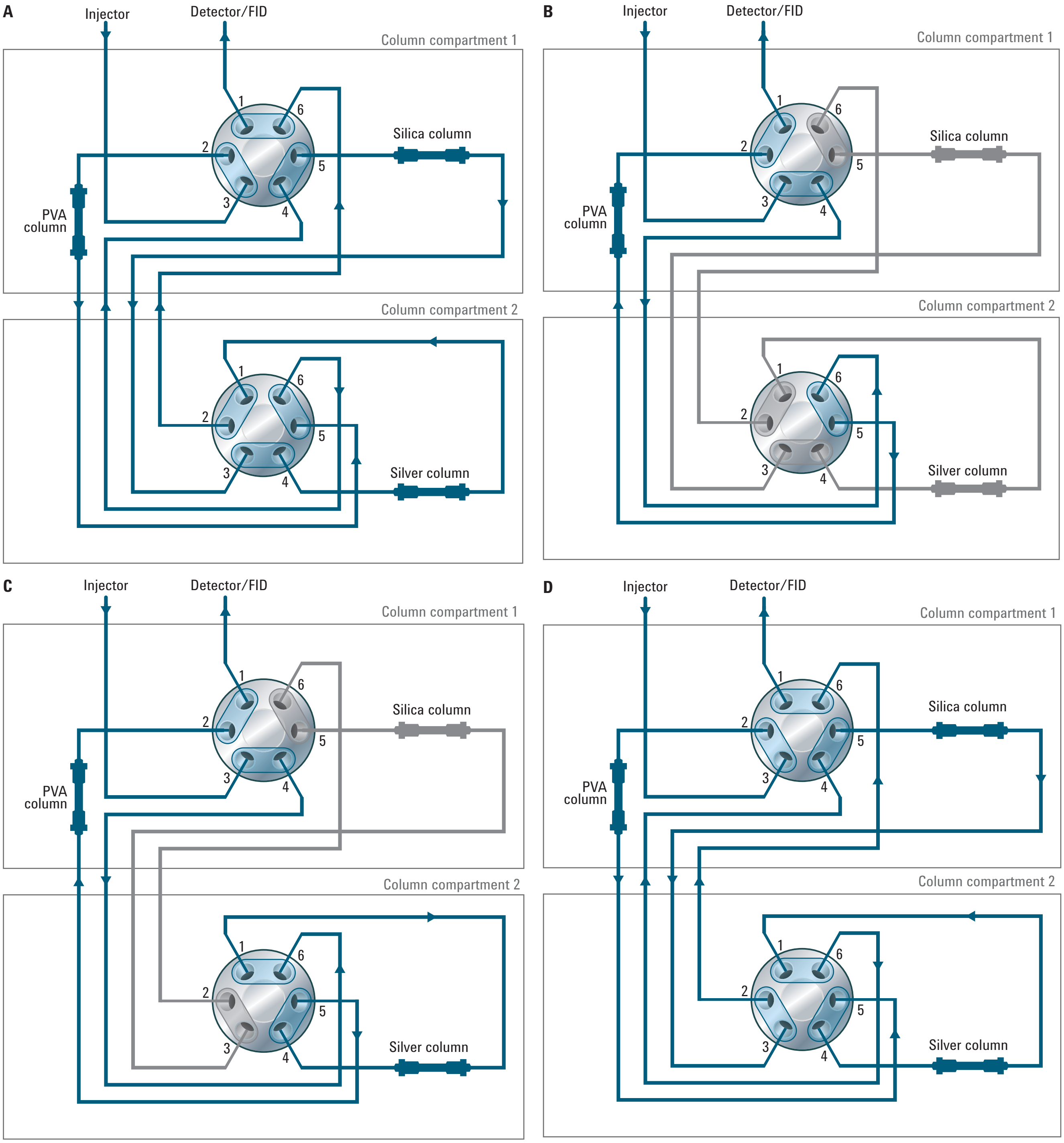

Figure 2. Column and valve configurations. Position A) PVA column, silica column, and silver-loaded column in forward-flush mode, connected in series. Injection of the sample onto the three columns retains the ethanol on the PVA column. After elution of the ethanol (position B), this position will be used to elute the saturates, load olefins onto the silver-loaded column, and retain the aromatics. Position B) Backflush of the ethanol from the PVA column. The silica and the silver-loaded column are not in the flow path. Position C) Backflush of the silver-loaded column to elute the olefins. The silica column is not in the flow path. Position D) The flow enters the PVA column first, then the silver-loaded column, and last the silica column in forward-flush mode to elute the aromatics off the silica column to the detector.

Determination of valve switching times (ASTM D7347, section 9)

The times for valve switching were determined by the experiments described below by means of the loading-time mixtures A to C. This procedure has to be done at initial system setup, or whenever something was changed such as columns, capillaries, and so on.

- For the determination of the sample loading time, t_L, the valves were switched to positions described in Figure 2B; loading-time mixture A was used. This valve position only allows use of the PVA column, while the silica column is protected from ethanol, and the silver-loaded column is protected from aromatics (Figure 3A, t_L = 0.75 minutes).
- Pure ethanol was used to determine the time to backflush the ethanol, t_E, from the PVA column after the loading time, t_L. The ethanol was injected with the valves in the positions shown in Figure 2A, and the valves were switched to the positions shown in Figure 2B at t_L = 0.75 minutes. The time t_E was determined when the ethanol peak returned to the baseline (Figure 4, t_E = 3.0 minutes).
- Loading-time mixture B was used for the determination of the loading time of the olefinic compounds, t_O, from the silicia column onto the silver-loaded column (Figure 5, t_O = 5.15 minutes).
- Loading-time mixture C was used to determine the time period, t_{BO}, necessary for the complete elution of the olefins from the silver-loaded column in backflush mode (Figure 6, t_{BO} = 7.5 minutes).

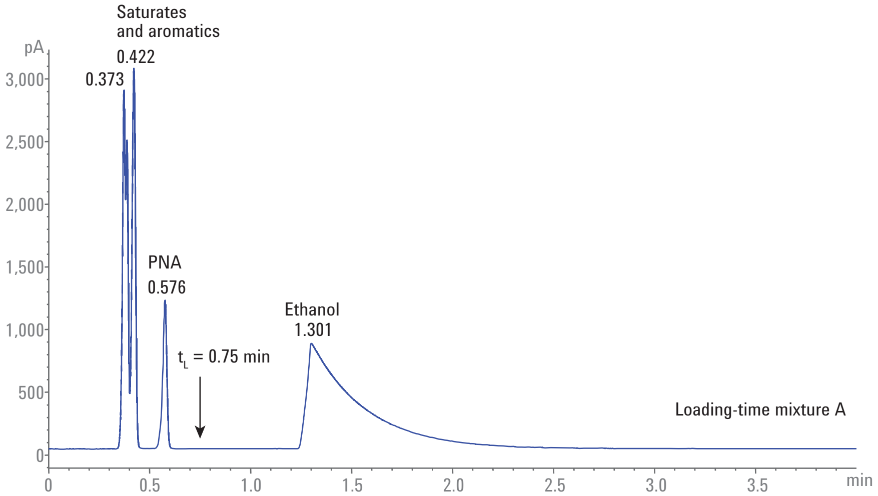

Figure 3. Determination of the sample loading time, t_L. Valves were switched to positions described in Figure 2B. Loading-time mixture A was used. The loading time t_L is determined when the aromatic and saturate compounds exit the PVA column, and the signal is back to baseline (t_L = 0.75 minutes).

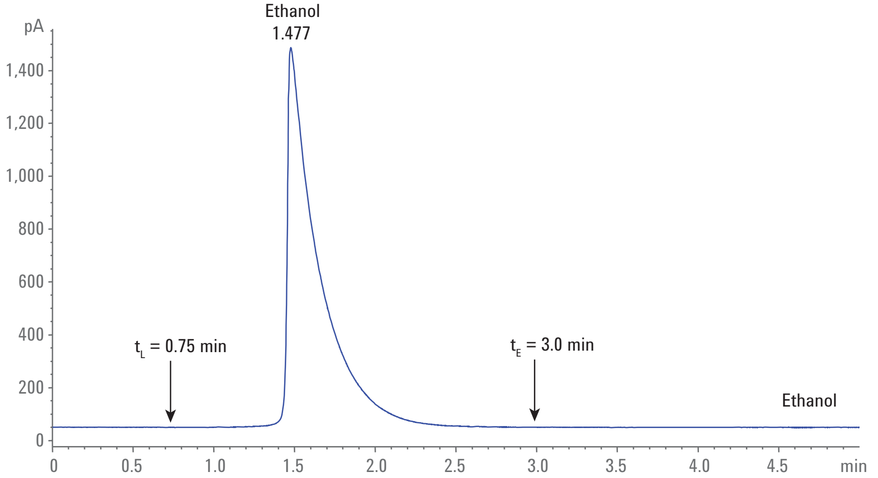

Figure 4. Determination of the backflush time for ethanol, t_E, after loading time, t_L. Ethanol was injected in valve position 2A, switching to position 2B (t_L = 0.75 minutes). The backflush time t_E is determined when the ethanol peak returns to the baseline (t_E = 3.0 minutes).

- Loading-time mixture B was used for the determination of the elution time of the aromatics, t_A. After the time period t_{BO}, the aromatics were eluted from the silica column by switching to the valve positions shown in Figure 2D. After elution of the mono-aromatics and the polynuclear aromatics (PNA), the run can be stopped (t_A = 9.5 minutes). Figure 7 shows the complete chromatogram.
- Loading-time mixtures D and E can be used to show whether there are saturates or aromatics eluted onto the silver-loaded column. They can be used to optimize the valve switching time point t_O (chromatograms not shown).

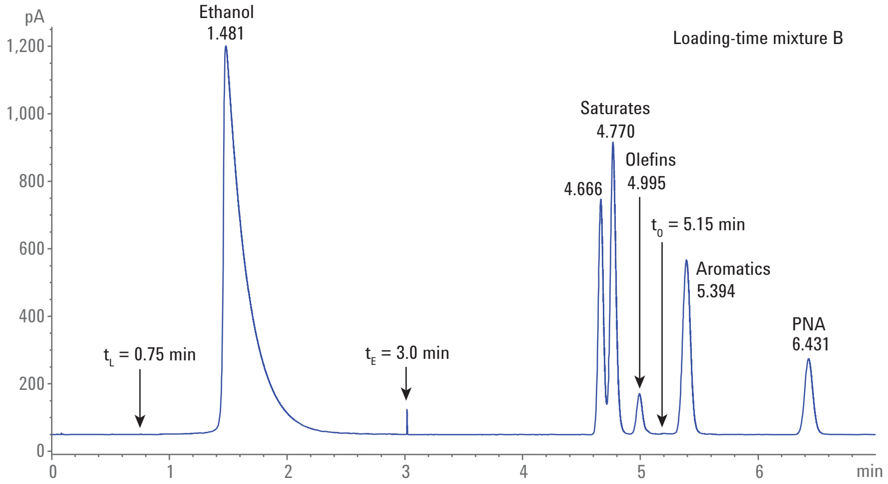

Figure 5 Determination of the loading time of the olefinic compounds, t_O, onto the silver-loaded column. Loading-time mixture B was used. To determine t_O, the loading-time mixture B was injected with the valve positions given in Figure 2A. After t_L, the valves were switched to positions shown in Figure 2B to backflush the ethanol. At t_E, the valves were switched to positions shown in Figure 2D. This configuration elutes saturates, olefins, and aromatics directly to the detector without contaminating the silver-loaded column (t_O = 5.15 minutes).

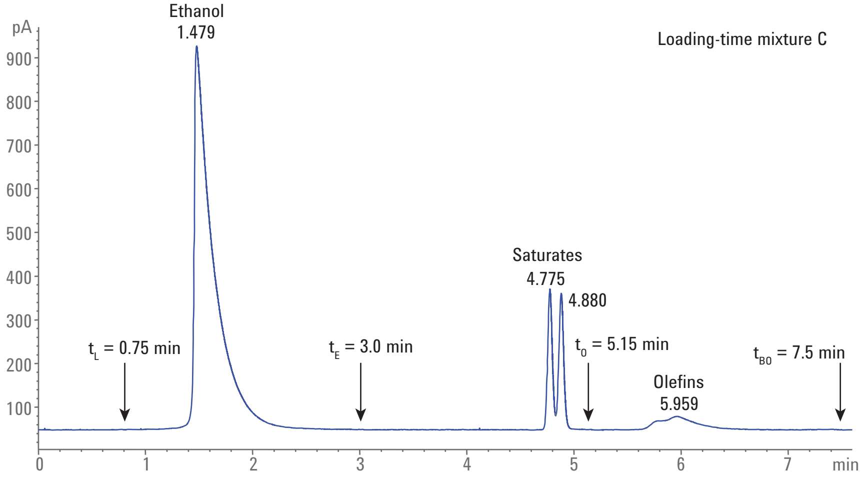

Figure 6 Determination of the time period t_{BO} necessary for the complete elution of the olefins from the silver-loaded column in backflush mode. Loading-time mixture C was used. This sample was injected by means of valve positions according to Figure 2A. At t_L, the valves were switched to the positions according to Figure 2B to backflush the ethanol. At t_E, the valves were switched back to the initial positions until saturates were eluted from the silica column through the silver-loaded column to the detector, until time t_O. The valves are now actuated to the position shown in Figure 2C, and the retained olefins are eluted from the silver-loaded column in backflush mode (t_{BO} = 7.5 minutes).

Chemicals and solutions

Samples and standards were prepared according to guidance published in ASTM D7347. All chemicals: benzene, toluene, naphthalene, hexane, cyclohexane, cyclohexene, 2-pentene, 1-hexene, and petrol (gasoline, puriss., bp 90 to 100 °C) were purchased from Sigma-Aldrich, Taufkirchen, Germany. Ethanol was HPLC grade, and was purchased from Carl Roth, Germany.

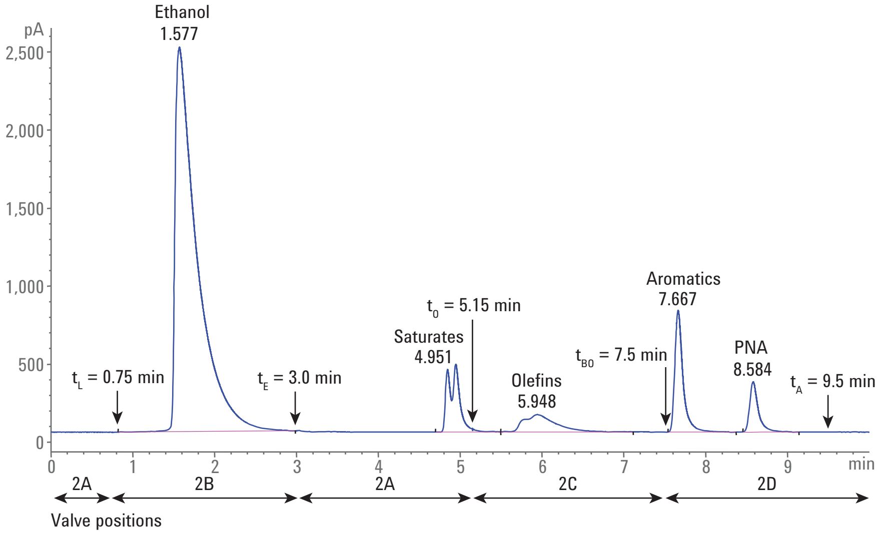

Figure 7. Performance test for the measurement of olefins in denatured ethanol. Valve switching time points and time ranges are indicated. The respective flow paths are shown in Figure 2.

Component	Composition
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).
Loading-time mixture A	10 % Alkanes (*n*-hexane and cyclohexane), 10 % aromatics (benzene, toluene, and naphthalene), and 80 % ethanol were used to determine the loading time of saturates and aromatics on the silica column while the silica column is protected from ethanol by the PVA column (ASTM D7347, section 7.5.1).
Loading-time mixture B	10 % Alkanes (*n*-hexane and cyclohexane), 7 % aromatics (benzene, toluene, and naphthalene), 3 % olefins (2-pentene, 1-hexene, and cyclohexene), and 80 % ethanol were used to determine the loading time of saturates and olefins on the silver-loaded column without aromatic contamination (ASTM D7347, section 7.5.2).
Loading-time mixture C	7 % Alkanes (*n*-hexane and cyclohexane), 3 % olefins (2-pentene, 1-hexene, and cyclohexene), and 90 % ethanol were used to determine the elution time of the olefins from the silver-loaded column (ASTM D7347, section 7.5.3).
Loading-time mixture D	10 % Alkanes (*n*-hexane and cyclohexane) and 90 % ethanol were used to check the absence of saturates on the silver-loaded column (ASTM D7347, section 7.5.4).
Loading-time mixture E	10 % Aromatics (benzene, toluene, and naphthalene) and 90 % ethanol were used to check the absence of aromatics on the silver-loaded column (ASTM D7347, section 7.5.5).
Performance Test Mixture (PTM)	Alkanes (*n*-hexane and cyclohexane), mono-aromatics (benzene and toluene), and polynuclear aromatic (naphthalene) at no more than 10 % by weight and mono-olefins (2-pentene, 1-hexene, and cyclohexene) at no more than 3 % by weight in ethanol (ASTM D7347, section 7.7).
Quality control mixture	Ethanol containing olefins at a known concentration to monitor the precision of the analytical SFC system (ASTM D7347, section 7.8).
Calibration mixture	10 % Alkanes (hexane and cyclohexane) by weight and 2 % olefins (2-pentene, 1-hexene, and cyclohexene) by weight with 88 % ethanol by weight (ASTM D7347, section 8.5). This stock solution was diluted 1:1 with ethanol containing 10 % alkanes (hexane and cyclohexane) by weight. The resulting 1 % olefin solution was diluted to calibration solutions with olefin content down to 0.1 % in steps of 0.1 %.
Spiked sample	Ethanol (denatured with no more than 10 % petrol) containing mono-olefins (2-pentene, 1-hexene, and cyclohexene) at no more than 1 %.

Results and Discussion

This ASTM D7347 test method for the determination of the total amount of olefins in denatured ethanol is based on a chromatographic SFC LC system with three columns and two six-port switching valves. Step by step, the olefins are separated from ethanol, aromatics, and saturates; an FID is used for quantification of the olefins. It is important to determine the valve switching times thoroughly to protect the column from ethanol, and the silver-loaded silica column from ethanol and aromatics, and to guarantee the absence of aromatics and saturates on the silver-loaded column at the time of the olefin elution.

At the beginning, the valve switching times were determined as described in the experimental section, then the Performance Test Mixture (PTM) was measured. This mixture comprised saturated hydrocarbons, olefins, mono-aromatics, and PNAs. This mixture was used to evaluate the accurateness of valve switching, and to ensure that all compounds were eluted in time from their respective columns to meet the required retention time (RT) (Figure 7).

SFC Method

Agilent 1260 Infinity Binary SFC Pump	
Solvent A	CO_2 (precompressed), 99.998 %
Solvent B	Hexane, 0.5 % (used for purging the backpressure regulator (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	1.5 mL/min
BPR temperature	40 °C
BPR pressure	170 bar
Agilent 1290 Infinity Thermostatted Column Compartment	
Column temperature PVA and silica column	40 °C
Column temperature silver-loaded column	70 °C
Valve positions (Figure 2)	
Valve position A	At 0 minutes
Valve position B	At 0.75 minutes
Valve position A	At 3.0 minutes
Valve position C	At 5.15 minutes
Valve position D	At 7.5 minutes
CTC Analytics LC-Injector HTC PAL	
Injection volume	1.0 µL loop, 30-times overfill, wash in port with hexane
Preclean with solvent 1	1
Preclean with sample	1
Filling speed	5 µL/s
Filling strokes	3
Inject to	LCVlv1
Injection speed	10 µL/s
Pre-injection delay	500
Postinjection delay	500
Postclean solvent 1	2
Valve clean solvent 1	2
Agilent 1260 Infinity Injector (alternative)	
Injection volume	1.0 µL loop, 10-times overfill, wash in vial with hexane
FID	
Temperature	300 °C
Gases	Hydrogen (H_2) 50 mL/min Air 500 mL/min Make-up gas (N_2) 50 mL/min

In the first step, ethanol has to be removed from the hydrocarbons. While they have entered the silica column completely at t_L (0.75 minutes), ethanol is retained in the PVA column and eluted by backflush until t_E (3.0 minutes). The valve positions are assigned at the bottom of Figure 7. Figure 2 shows their respective flow paths. After elution of the saturates and olefins from the silica column, the olefins are retained on the silver-loaded column, and the saturates are guided through to the detector (4.95 minutes). At t_0 = 5.15 minutes, the silver-loaded column is switched to backflush for the elution of the olefins. The aromatics are still retained on the silica column, which is in bypass mode. The olefins elute from the backflushed silver-loaded column in a broader peak with the maximum at 5.95 minutes. After complete elution and flushing of the silver-loaded column, the aromatics are eluted from the silica column by switching it back into the flow path at 7.5 minutes. The mono-aromatics elute at 7.67 minutes, and the PNAs at 8.58 minutes. Figure 8 shows an overlay of 20 repeating measurements of PTM to show that the time-based valve switching is working well. The resolution between the olefins and the mono-aromatic peak is around 6 (required > 4).

For the measurement of real samples, it is necessary to generate a calibration curve with calibration points from 0.1 to 1.0 % olefins dissolved in denatured ethanol. The calibration showed good linearity with a correlation better than 0.99 (Figure 9). Figure 9 also displays an overlay of the 0.1 to 1.0 % calibration concentrations of the olefin peak.

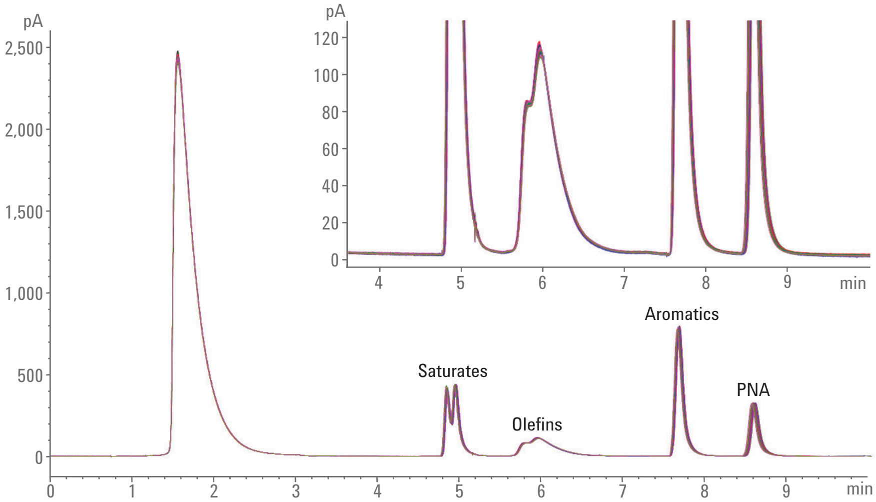

Figure 8. Performance test with PTM for the olefin measurement in denatured ethanol with zoom in (overlay; n = 20).

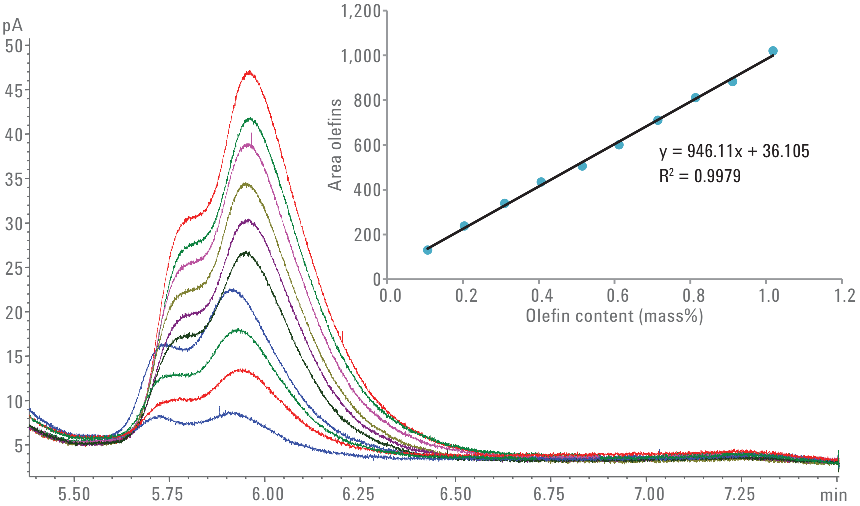

Figure 9. Overlay of 0.1 to 1.0 mass% content of olefin and calibration curve for the measurement of olefins in denatured ethanol with linearity correlation 0.9979.

Together with the calibration curve, a performance sample (PTM), a quality control (QC) sample, and a spiked sample of denatured ethanol (with 9.5 % petrol) were measured. Figure 10 shows a sample of denatured ethanol spiked with 0.5 % olefin. All samples were injected 20 times for a statistical evaluation of the olefin peak (Table 1). The relative standard deviation (RSD) of the RT is typically below 0.2 % (required < 0.5 %), and the peak area RSDs were typically below 2 %. The repeatability limit was calculated according to ASTM D7347-07, section 13.1.1. All samples met this criterion as the difference between successive results did not exceed the calculated limit.

Table 1. RT, area, concentration, and repeatability values for the PTM, QC, and spiked sample (n = 20) in accordance to ASTM 7347-07, section 13.1.1.

Sample	PTM 3.0 % olefin			Quality control 0.25 % olefin			Spiked sample 0.5 % olefin		
Olefin content by weight (mass%)	3.027			0.257			0.527		
	RT	Area	Amount	RT	Area	Amount	RT	Area	Amount
Average (mass%)	5.95	3,024.21	3.158	5.93	271.70	0.249	5.95	482.90	0.472
SD	0.01	26.57	0.03	0.01	4.80	0.01	0.01	5.19	0.01
RSD (%)	0.13	0.88	0.89	0.14	1.77	2.04	0.14	1.07	1.16
Repeatability*(Δ_{max})			0.107			0.022			0.023
Repeatability limit*			0.216			0.065			0.077

* calculated according to ASTM D7347-07, section 13.1.1

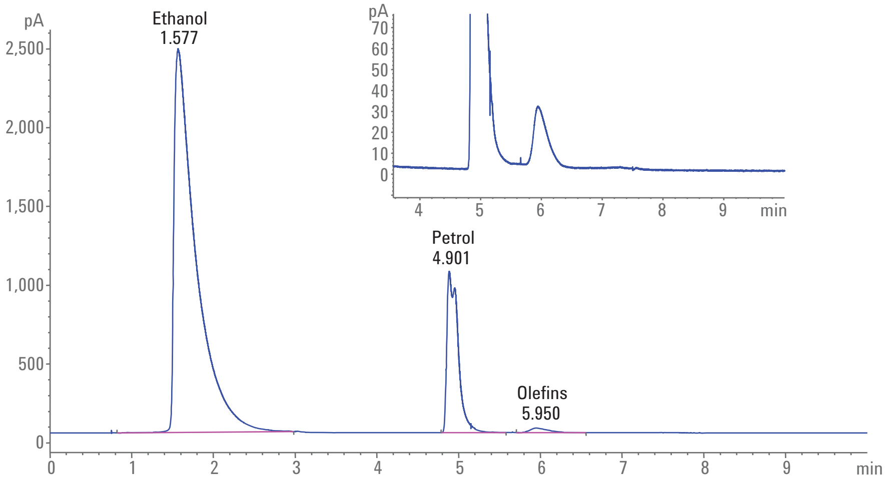

Figure 10. Sample of denatured ethanol (9.5 % petrol) spiked with 0.5 % olefins.

Conclusions

This Application Note demonstrates the improved capabilities of the Agilent 1260 Infinity Analytical SFC system in combination with the SIM/FID for the determination of olefins in denatured ethanol according to ASTM D7347-07.

The olefin content of a denatured ethanol sample was separated from saturated and aromatic hydrocarbons as well as from the ethanol itself by means of three different columns, and a valve switching solution for separation in forward-flush and elution in backflush mode. The olefins were quantified between 0.1 and 1.0 mass%, with good linearity. RT precision, which is important for time-based column switching, was within the given limits. The difference between the successive results agree to the repeatability limits stated in section 13.1.1 of ASTM D7347-07.

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