

Analysis of Alcohols and Aromatics in Gasoline and Fuel Ethanol by a Two-Dimensional GC Method

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Introduction

Oxygenated compounds such as alcohols and ethers are blended into reformulated gasoline to improve octane ratings and reduce emissions of smog producing combustion products. Alcohols have largely replaced ethers such as MTBE, ETBE, or TAME for this application due to problems with groundwater contamination and toxicity concerns from these compounds in gasoline in underground tanks. In addition, legislation promoting the use of biofuels derived from renewable agricultural products has provided incentives for petroleum companies to switch to ethanol produced by fermentation of biomass. Analysis of these compounds is critical to ensure correct blending ratios, to confirm conformance to specifications, and to ensure that they are not present in hydrocarbon products going into non-transportation applications. For example, traces of oxygenates in gasoline and naphtha used as feedstock for other petrochemical products can produce catalysts that lower production yields and product quality.

The measurement of trace oxygenates in hydrocarbon products presents a challenge to the chromatographer. Chromatographic resolution can be a problem since oxygenates are low boiling compounds that tend to coelute with the bulk of the hydrocarbons typically found in gasoline. Therefore, these alcohols cannot be separated using nonpolar, "boiling point" type columns such as DB1 or DB5. In addition, oxygenates are not all very polar and cannot use traditional polar phases such as DB-Wax or TCEP since they coelute with the "polar" hydrocarbons such as olefins and aromatics. Sensitivity and dynamic range is also an issue since oxygenates need to be measured down to the 1 ppm level with good peak shape for petrochemical feedstock and up to 12 wt.% for ethanol in gasoline. The solution is to use 2D GC with a sensitive, dynamic detector to achieve the resolution, sensitivity, and large dynamic range required for the analysis.

Experimental

A two-dimensional GC uses a fluidic switch device that selectively diverts the primary column flow from the detector to a second column without allowing the sample to contact the switching hardware. This technique has numerous advantages such as high resolution of target compounds in complex matrices, improvement in speed of analysis, high level of precision, ease of setup, and use of readily available capillary columns and hardware. The fluidic switch device is called a Deans Switch and is the basis of two methods published by the European Committee for Standardization (CEN) for determination of oxygenates and benzene in gasoline. The scope of these methods covers benzene concentration of 0.05% (v/v) to 6% (v/v) and individual organic oxygenates from 0.17% (m/m) to 15% (m/m). Figures 1 and 2 show an Agilent 7890 GC System configured with the Deans Switch hardware.

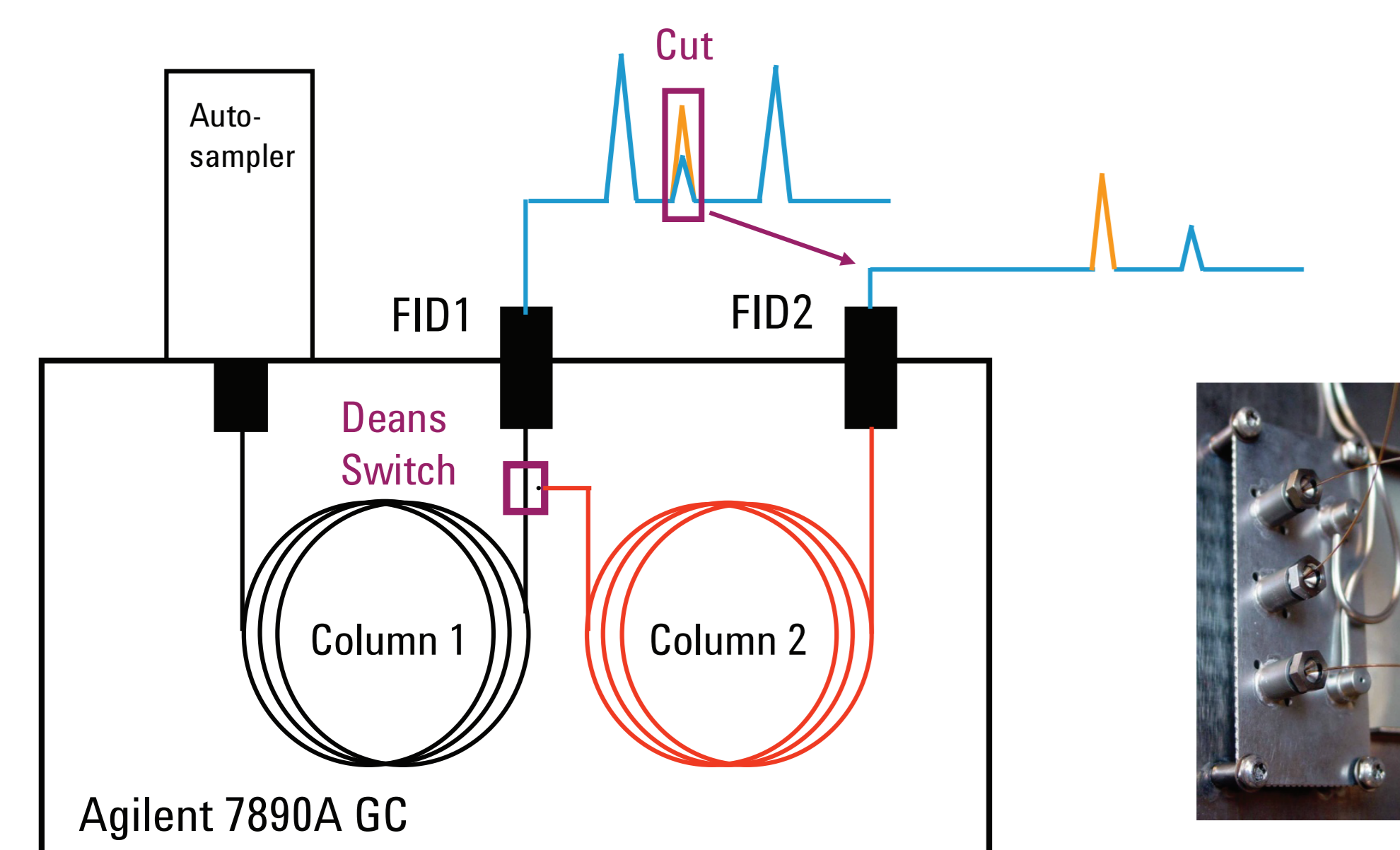


Figure 1. Deans Switch Heart-cutting 2-D GC provides extremely high chromatographic resolution

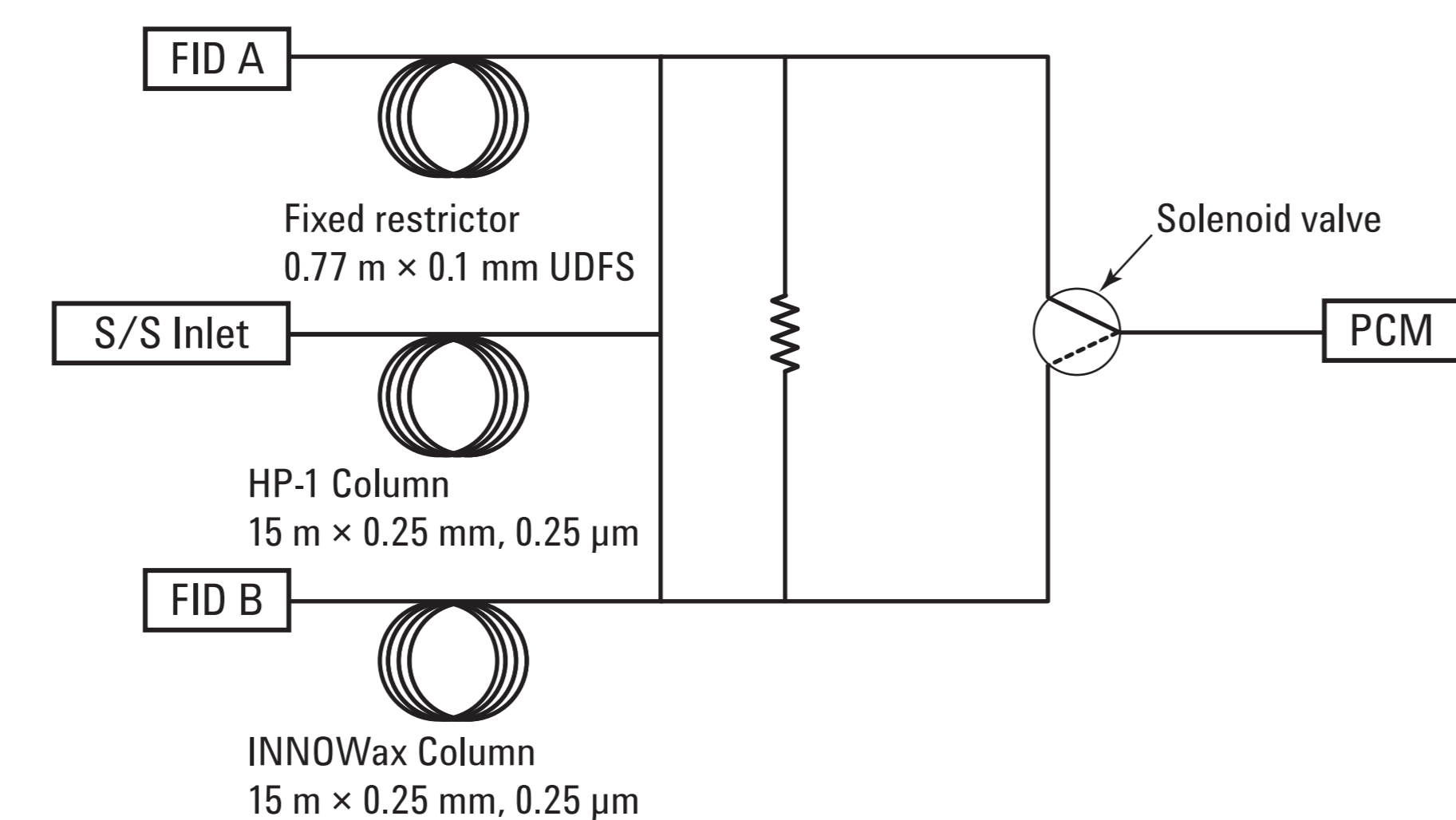


Figure 2. Deans Switch configuration for the fast analysis of oxygenated additives in gasoline.

Figure 3 shows the chromatographic conditions used for the analysis of oxygenates in gasoline. The gasoline sample is injected into split/splitless inlet and is initially separated on the HP-1 column. Just before the peaks of interest elute from this column, the fluidic switch transfers the flow to the INNOWax column for improved separation of the oxygenates and then switches back to the original flow path. This technique is referred to as "heartcutting". This switching process is repeated several times during the analysis to achieve the resolution needed for the compounds of interest. The entire process is automatically controlled by the Agilent OpenLab chromatography data system.

Oven program: 40 °C for 4 minutes
Ramp 1: 20 °C/min to 250 °C for 0 minutes
Ramp 2: 100 °C/min to 250 °C for 0 minutes

Injection volume: 0.1 μL
Inlet: 250 °C, split ratio 400:1

Column 1: HP-1 (30 m x 0.25 mm, 0.25 μm)
Column 1 flow: 3 mL/min, post run backflush for 2.36 minutes at -7.77 mL/min

Column 2: INNOWax (30 m x 0.25 mm, 0.25 μm)
Column 2 flow: 4 mL/min
Heart-cut times adjusted accordingly.

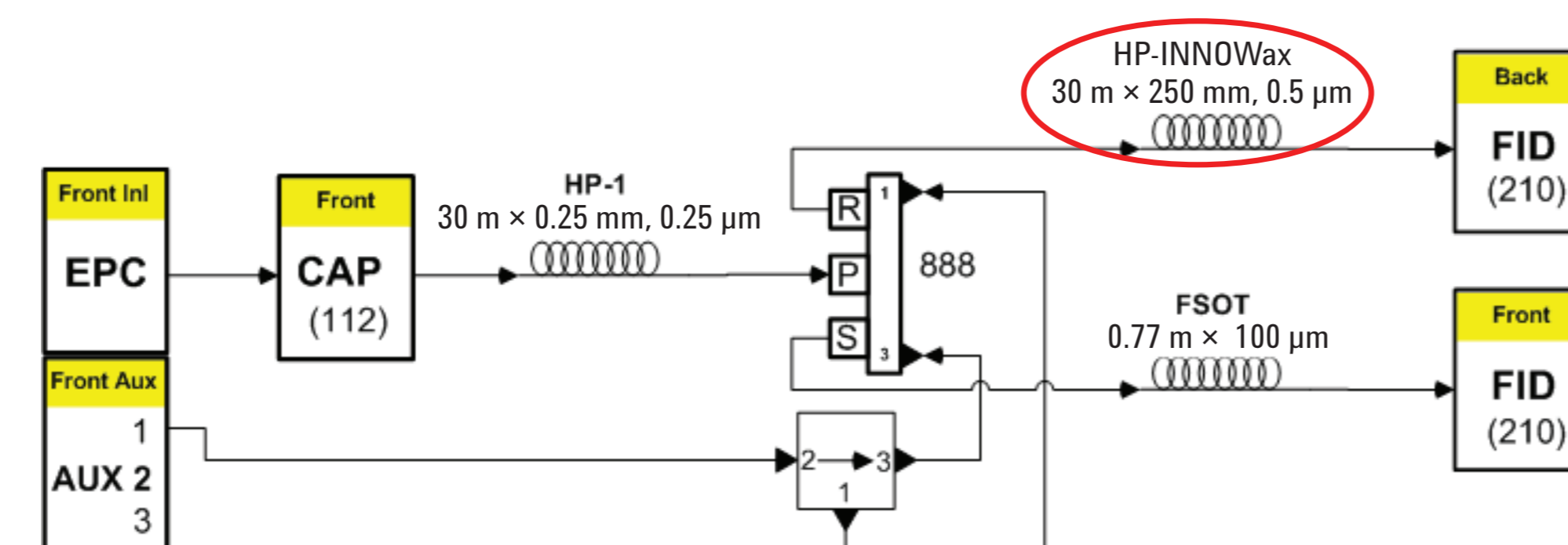


Figure 3. GC setup to improve separation on secondary column.

When setting the cut times, it is important to use a standard that contains the highest concentration of target compounds that will be expected in the samples without overloading the column. If the column is overloaded, then the split ratio, injection volume, or both should be adjusted to maintain good peak shape. This ensures that the cut times will accommodate the maximum peak widths encountered.

When the retention times and cut times for an analyte are determined, a gasoline blank is run using these cut times. This will determine any potential interference from the matrix that is not resolved by the secondary column. Quantitative analyses for oxygenates are performed by analyzing commercially prepared calibration standards.

Results and Discussion

An oxygenate standard was initially analyzed to determine the retention times of each component. Figure 4 shows a typical chromatogram of this analysis. A gasoline standard containing no oxygenates was then analyzed to determine potential interferences. Figure 5 shows this chromatogram. Using these standards to set appropriate cut times, the commercial gasoline sample was analyzed, and the chromatograms obtained are shown in Figures 6 and 7. The base line is stable with oxygenate compounds well resolved with good peak shape that is easily quantitated.

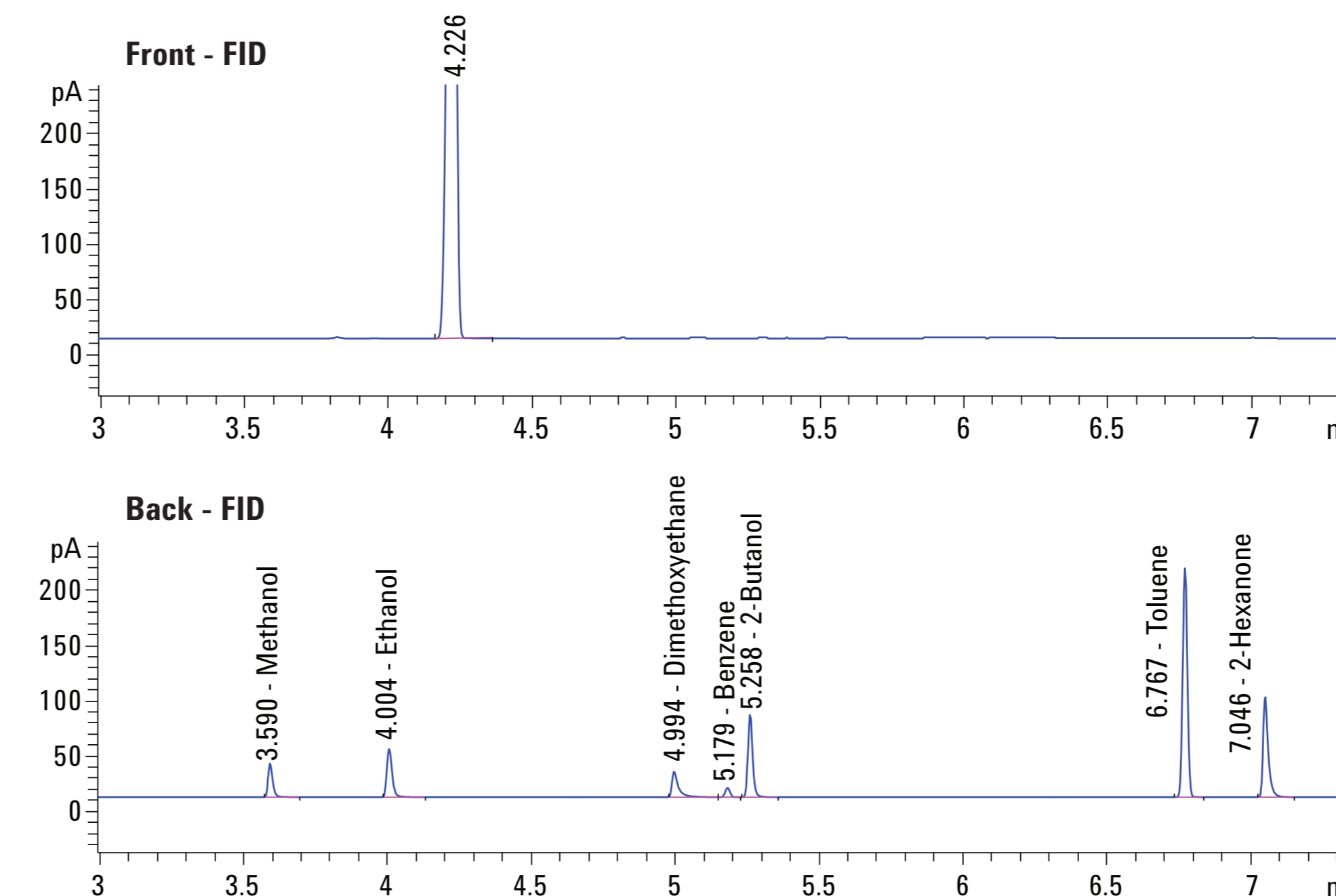


Figure 4. Chromatograms of the retention time standard.

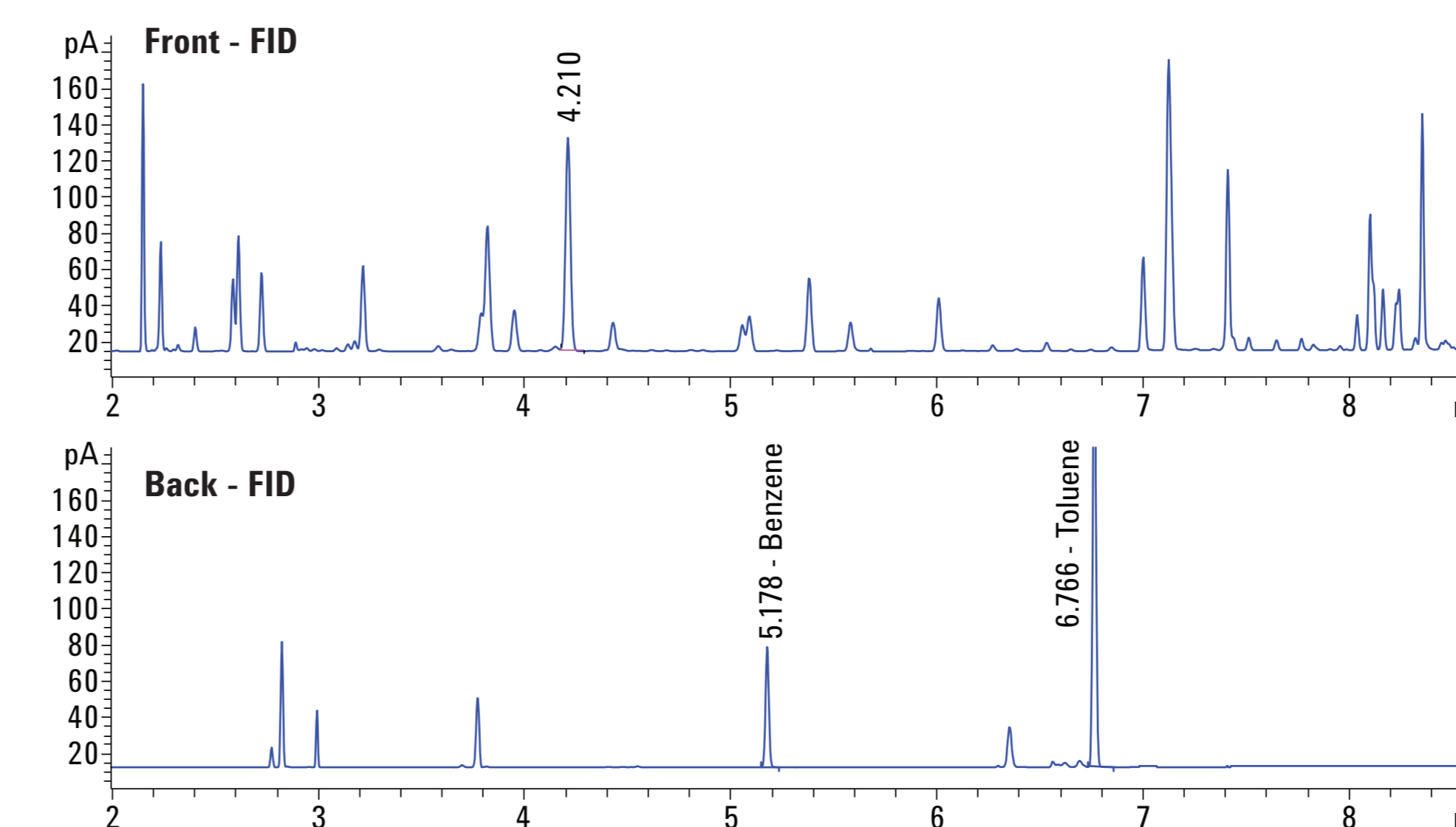


Figure 5. Chromatograms of gasoline containing no oxygenates.

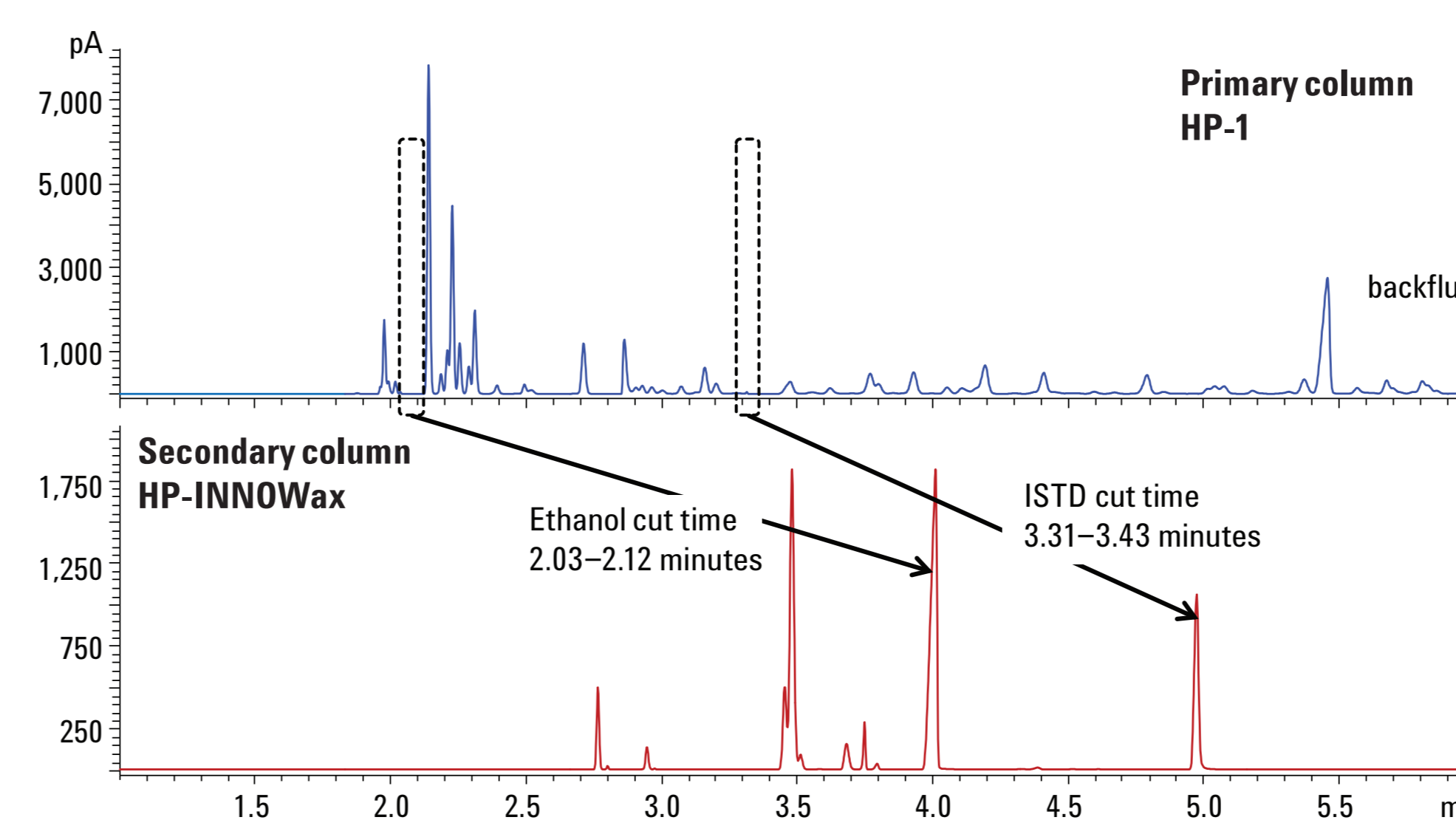


Figure 6. 2D GC analysis of ethanol in gasoline using the Agilent 7890 CFT Deans Switch with backflush.

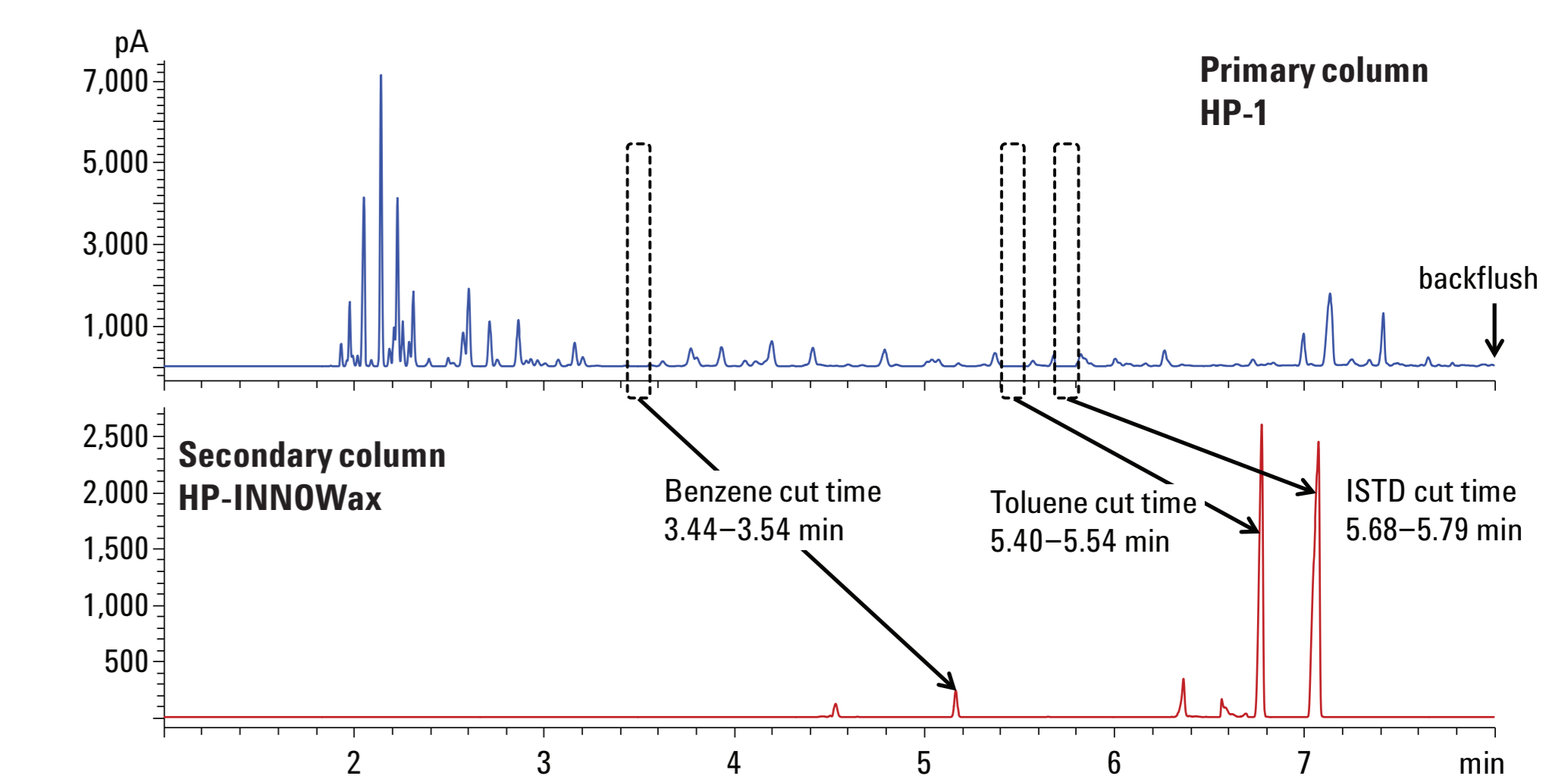


Figure 7. 2D GC analysis of benzene and toluene in gasoline using the Agilent 7890 CFT Deans Switch with backflush.

As an extension of this work, gasoline samples were prepared for analysis using the Agilent 7696A Sample Prep WorkBench with weigh option to evaluate reproducibility of the method. The results tabulated in Figure 8 show that the 2D method, combined with the automated sample preparation, gives results superior to the precision required by the ASTM Standard D4815.

The Deans Switch plumbing design used for this work offers several advantages for method development and performance. The restrictor used between the HP-1 column and the front FID is designed to provide the same backpressure to the HP-1 column as the INNOWax column. This allows for consistent retention times when the fluidic switch is in both the off and on positions which helps maintain reproducible start and stop times for heart cutting. Another advantage is the "trickle purge" between the upper and lower legs of the flow path. This low flow of helium eliminates any unswept volumes that can adversely affect the analysis.

Run	Sample	Weigh station weight (g) Istd	Wt% Ethanol
1	0.69587	0.04517	12.644
2	0.69456	0.04526	12.640
3	0.69400	0.04517	12.606
4	0.69416	0.04501	12.584
5	0.69240	0.04514	12.638
6	0.69252	0.04527	12.610
7	0.69298	0.04523	12.718
8	0.69052	0.04538	12.693
9	0.69080	0.04536	12.672
10	0.69043	0.04519	12.578
Mean:			0.68282 0.04521 12.629
STDEV:			0.00185 0.00018 0.043
RSD:			0.26741% 0.21160% 0.338%
ASTM r:			0.140
ASTM r (spcc):			0.282

< 0.4% RSD for weighing and final results
Exceeds ASTM D4815 single lab precision requirements

Figure 8. High precision ethanol results for Agilent WorkBench prepared gasoline samples.

Conclusions

The two-dimensional GC method for the analysis of oxygenates in gasoline was shown to give complete chromatographic separation of all target compounds from the hydrocarbon matrix. The unique plumbing design used on the Agilent 7890 GC system provided easier method setup and reliable performance by eliminating carryover and minimizing peak tailing for very polar compounds.

- A single Deans Switch method can be used for analysis of methanol, ethanol, benzene, toluene, and internal standards in spark ignition fuels.
- Using a 30 m secondary capillary column avoids oxygenate interferences with 7 minutes runtime.
- The method using the Agilent 7696A WorkBench for automated sample preparation exceeds ASTM precision requirements.

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