Simultaneous Analysis of Trace Oxygenates and Hydrocarbons in Ethylene Feedstocks Using Agilent 7890A GC Capillary Flow Technology

Application Brief

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The presence of trace hydrocarbons in ethylene can have damaging effects on both the process catalysts and the final polymer products. Test methods such as ASTM D6159 are used to ensure the quality of these feedstocks [1]. However, the analysis of other key contaminants, such as oxygenates, requires GC methods that run on separate instruments. This can be time consuming and expensive for the process analysis lab.

The Agilent 7890A GC serves as the ideal platform when analyzing different classes of trace compounds in ethylene. Maximum productivity can be realized by:

- Using Capillary Flow Technology to perform analysis of trace oxygenates and hydrocarbons in a single run through 2-D Deans switch chromatography.
- Automating the preparation of multilevel calibration standards using the new auxiliary electronic pneumatics control (EPC) modules.
- Protecting the sensitive and expensive alumina PLOT column by preventing polar oxygenates from entering the column.

Enhancing ASTM Method D6159 with Capillary Flow Technology 2-D GC

ASTM Method D6159 uses a methyl silicon column in series with an alumina PLOT column to resolve light hydrocarbons in ethylene. Polar oxygenated compounds cannot be analyzed on this column set because methyl silicon has insufficient selectivity and the alumina column will adsorb oxygenates, resulting in column damage. Wax-type liquid phases such as HP-INNOWax can easily separate polar compounds from light hydrocarbons using 2-D GC [2]. A wax column placed before an alumina column will retain polar compounds while the light hydrocarbons elute near the void volume. Therefore, if a Deans switch is placed between the columns, the hydrocarbons can be heart-cut from the wax to the alumina columns while oxygenates are held by the wax column. The optimized thermal and pneumatic performance of the Agilent 7890A Deans switch is a result of Capillary Flow Technology. This provides the high levels of retention time precision and narrow peak shape needed for optimal heart-cutting 2-D GC (Figure 1).

Highlights

- The Agilent 7890A GC Capillary Flow Technology combined with enhanced electronic pneumatics control (EPC) provide greater productivity and flexibility in the analysis of trace contaminants in ethylene.
- Multiple auxiliary EPC channels provide the ability to automatically generate gas calibration standards for trace level impurities.
- Enhancement of ASTM D6159 method with 2-D GC Deans switching measures trace oxygenates and hydrocarbons in a single run.

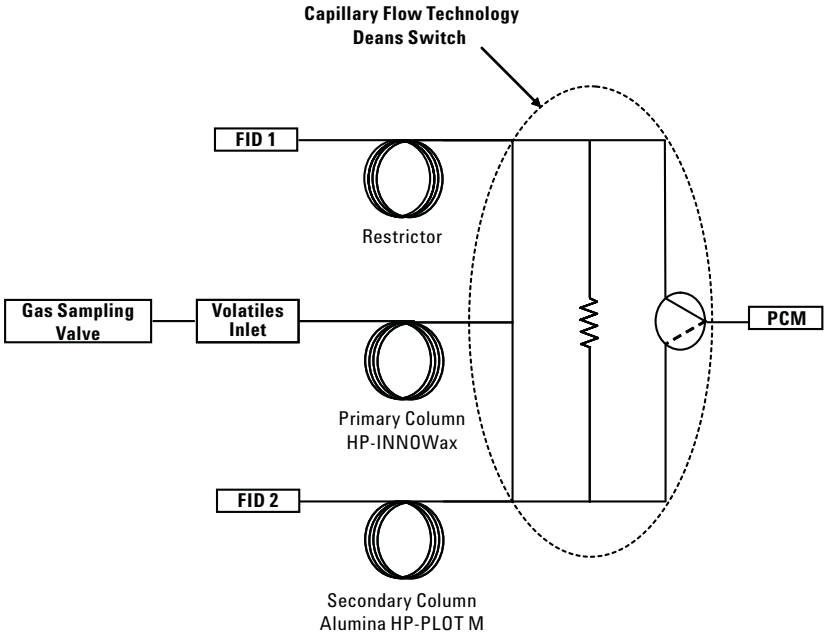

Figure 1. Configuration of Agilent 7890A for the 2-D GC analysis of trace oxygenates and hydrocarbons in ethylene.

Method Parameters for Enhanced ASTM D6159 Method

Primary column:	HP-INNOWax, 30 m × 0.32 mm id × 0.5 µm film (19091N-213)
Primary column flow:	Helium at 2.5 mL/min
Secondary column:	Alumina HP-PLOT M, 30 m × 0.53 mm id × 15 µm (19095P-M23)
Secondary column flow:	Helium at 6 mL/min
Oven temperature program:	40 °C for 6 min, 4 °C/min to 125 °C
Volatiles inlet conditions:	150 °C, 5:1 split
Sample loop:	250 µL at 65 °C
Detector temperature:	250 °C
Capillary Flow Technology: Deans switch cut time	2.3 to 4.5 min

Automating the Preparation of Trace-Level Calibration Standards

Another advantage of the Agilent 7890A GC is the expanded capabilities in EPC. These extra channels of auxiliary EPC are used with the dynamic blending system hardware to allow automated preparation of ppmV gas standards for calibration. This approach has been described for the automated preparation of trace sulfur compounds in various gas matrices [3].

Results

Figure 2 shows the 2-D GC analysis of methanol and C1 to C4 hydrocarbons in a sample of technical grade ethylene. The HP-INNOWax column first separates the polar methanol from the unresolved hydrocarbon peaks. The Deans switch transfers the hydrocarbons to the Agilent alumina HP-PLOT M column, where the C1 to C4 hydrocarbons are easily separated. This column is also shown to provide better separation of trace hydrocarbons from the large ethylene peaks, while maintaining excellent peak shape and intensity for the acetylene. The performance of this alumina column is maintained over many injections since the HP-INNOWax column prevents polar oxygenates (water, alcohols) from damaging the sensitive stationary phase. Table 1 shows very good precision using this method for a sample containing approximately 2 ppmV.

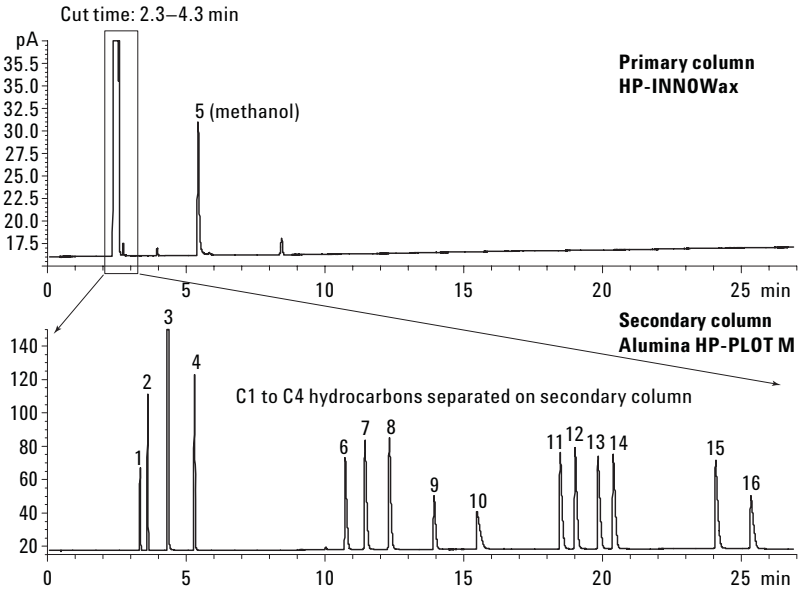

Figure 2. Capillary Flow Technology Deans switch used to separate 100 ppmV oxygenate and hydrocarbon impurities in ethylene.

Table 1. Method Precision for 2-D GC Analysis of Ethylene Impurities

Peak No.	Name	Avg. (ppmV)*	Std Dev*	%RSD*
1	Methane	2.1	0.011	0.5
2	Ethane	21.5	0.049	0.2
3	Ethylene	Balance	Balance	Balance
4	Propane	2.1	0.062	3.0
5	Methanol	2.1	0.081	3.8
6	Propylene	2.1	0.023	1.1
7	Isobutane	2.1	0.015	0.7
8	n-Butane	2.0	0.011	0.5
9	Propadiene	2.1	0.025	1.2
10	Acetylene	1.9	0.036	1.9
11	Tran-2-butene	2.1	0.011	0.5
12	1-Butene	2.0	0.013	0.7
13	Isobutylene	2.1	0.016	0.8
14	cis-2-butene	2.1	0.017	0.8
15	1,3-Butadiene	2.1	0.018	0.9
16	Methylacetylene	2.0	0.015	0.7

*Sample run 20 times

References

1. Annual Book of ASTM Standards, Vol. 05.03, “Petroleum Products and Lubricants (III), D5303 - D6553,” ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428 USA.
2. J. D. McCurry, “Fast Determination of Denatured Fuel Ethanol Purity by Two-Dimensional Gas Chromatography,” Agilent Technologies publication 5988-9460EN, April 2003.
3. R. L. Firor and B. D. Quimby, “Automated Dynamic Blending System for the Agilent 6890 Gas Chromatograph: Low Sulfur Detection,” Agilent Technologies publication 5988-2465EN, April 2001.

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