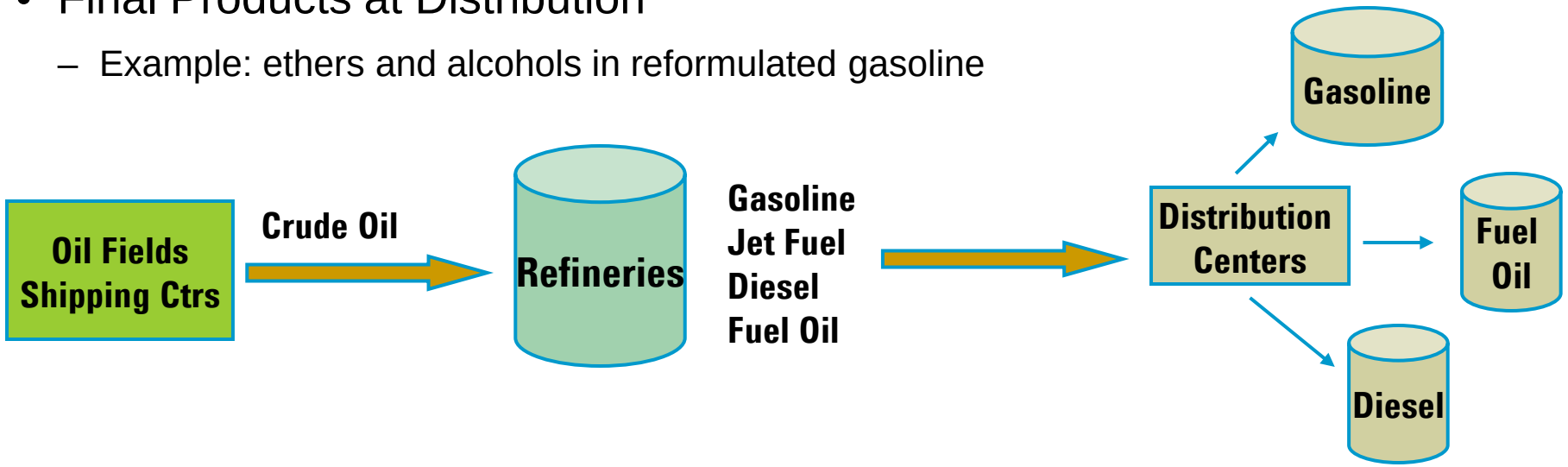
Oxygenates in Fuels – Analysis Solutions From Trace Levels to Ethanol Fuels

James D. McCurry
Senior Scientist
Agilent Technologies
Wilmington, DE USA

Application Summary

There is a need to measure trace oxygenates in:

- Feedstocks
  - Example: denatured fuel ethanol
- Intermediates
  - Example: ethers and alcohols in light hydrocarbons (C_2 to C_5)
- Final Products at Distribution
  - Example: ethers and alcohols in reformulated gasoline



ASTM Methods for Trace Oxygenates

Three recently developed methods

- ASTM D7059 - 09 Standard Test Method for Determination of Methanol in Crude Oils by Multidimensional GC
  - Method scope: 15 mg/kg to 900 mg/kg

- ASTM D7423 - 09 Standard Test Method for Determination of Oxygenates in C2, C3, C4, and C5 Hydrocarbon Matrices by GC and FID
  - Method scope: 0.5 mg/kg to 100 mg/kg

- Proposed Gasoline Method - Standard Test Method for Determination of Trace Oxygenates in Finished Gasoline by Multidimensional GC
  - Method scope: 10 mg/kg to 1000 mg/kg in gasoline containing 1 – 15 wt% ethanol

Each ASTM Methods Uses the Same Approach for Oxygenate Analysis

Problem is to separate and detect ppm level oxygenates from many hydrocarbons in the sample matrix

- Approach: Use oxygenate selective column combined with 2-D GC
  - LowOX and GS-OxyPLOT has strong retention for oxygen containing compounds
    - High boiling and polar hydrocarbons (aromatics) can still interfere
  - Use 2-D GC to eliminate these interfering hydrocarbons

- All three ASTM methods two optional hardware configurations for 2-D GC
  - Rotary valve based
  - Fluidic Switch (Deans switch)

Typical GC Conditions For 2-D GC Analysis of Trace Oxygenates in Hydrocarbons

Column 1: DB-1 (Valve) or HP-5 (Fluidic Switch) 30m x 0.53mm x 1um

Column 2: Oxy-PLOT or LowOX 10m x 0.53mm

Carrier gas: Helium

Injection volume:1 uL

Inlet: Split/splitless

- Temperature: 225 °C
- Split Ratio: 10:1

Oven

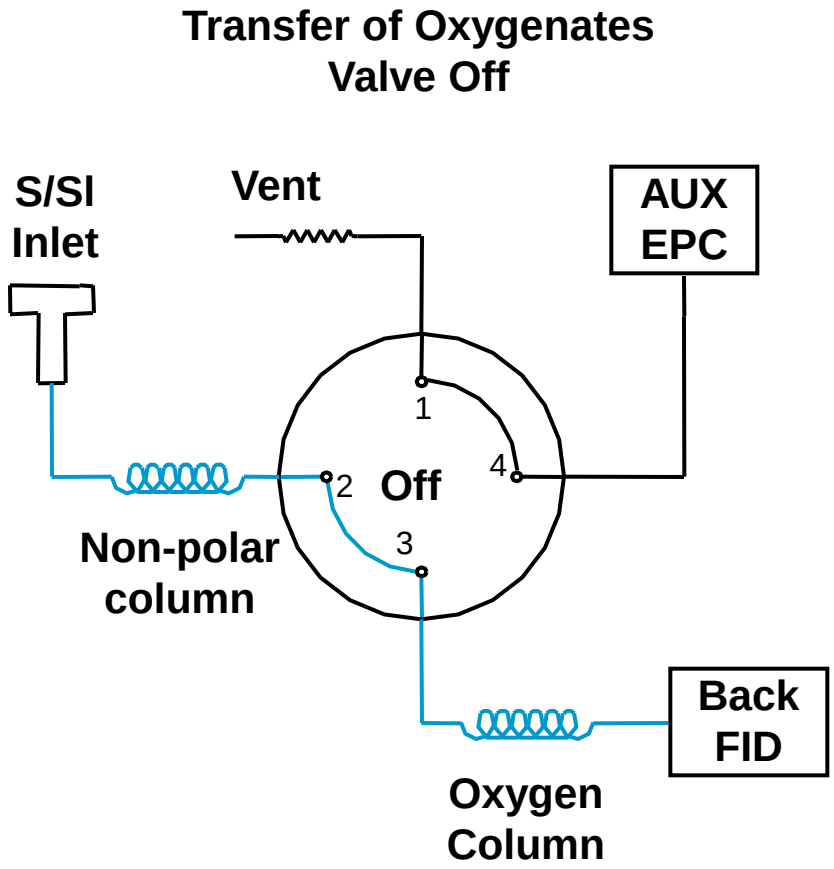
- Initial temp 50 °C
- Initial hold 5 min
- Ramp rate: 10 °C/min
- Final temp 240 °C

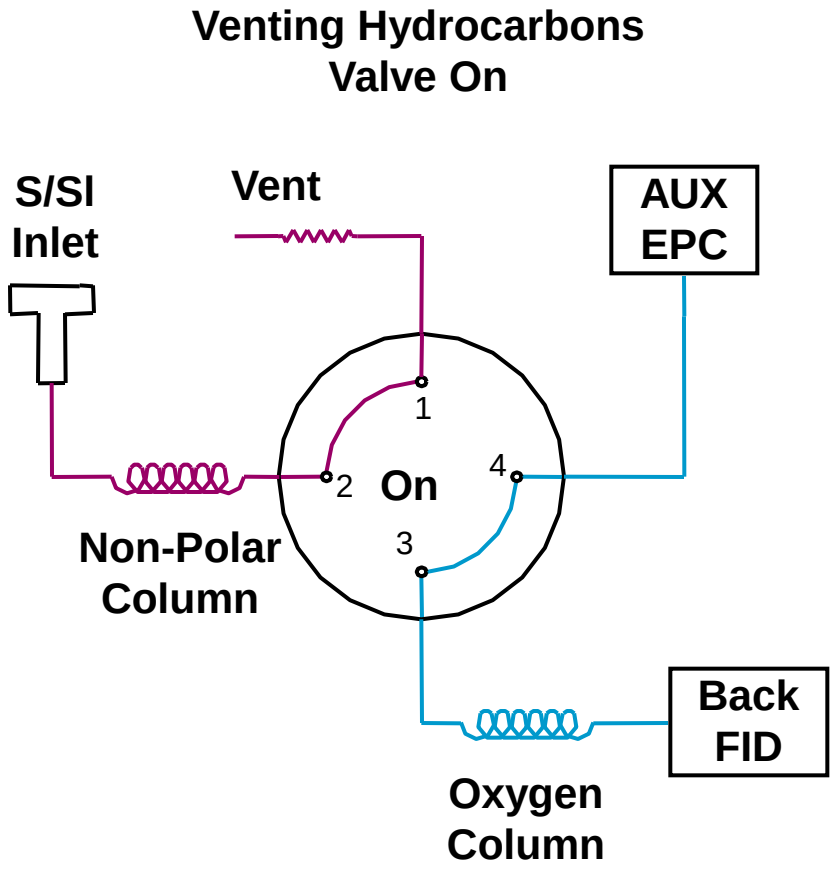
Detector: FID

- Temperature 275 °C

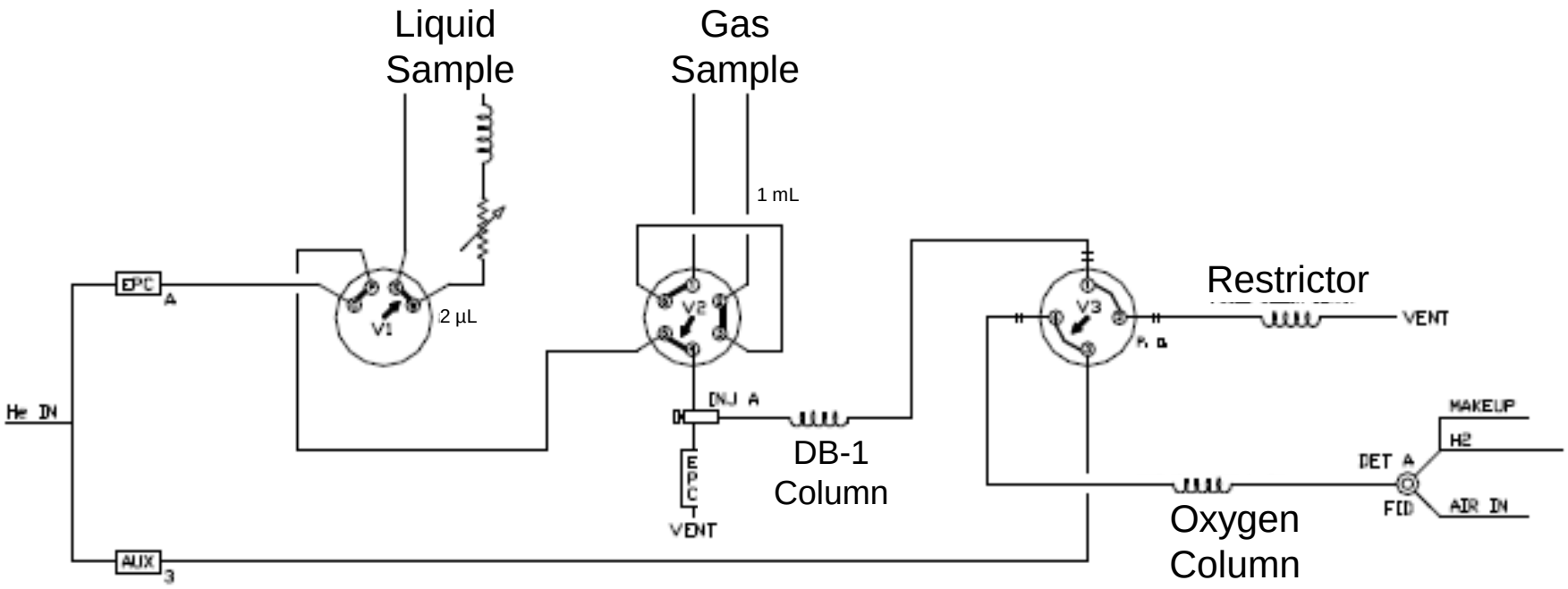
Note: GC analyzer conditions will vary depending on sample matrix type and type of Valve or Fluidic Switch configuration is being utilized.

Rotary Valve Configuration For ASTM Trace Oxygenate Analysis Methods



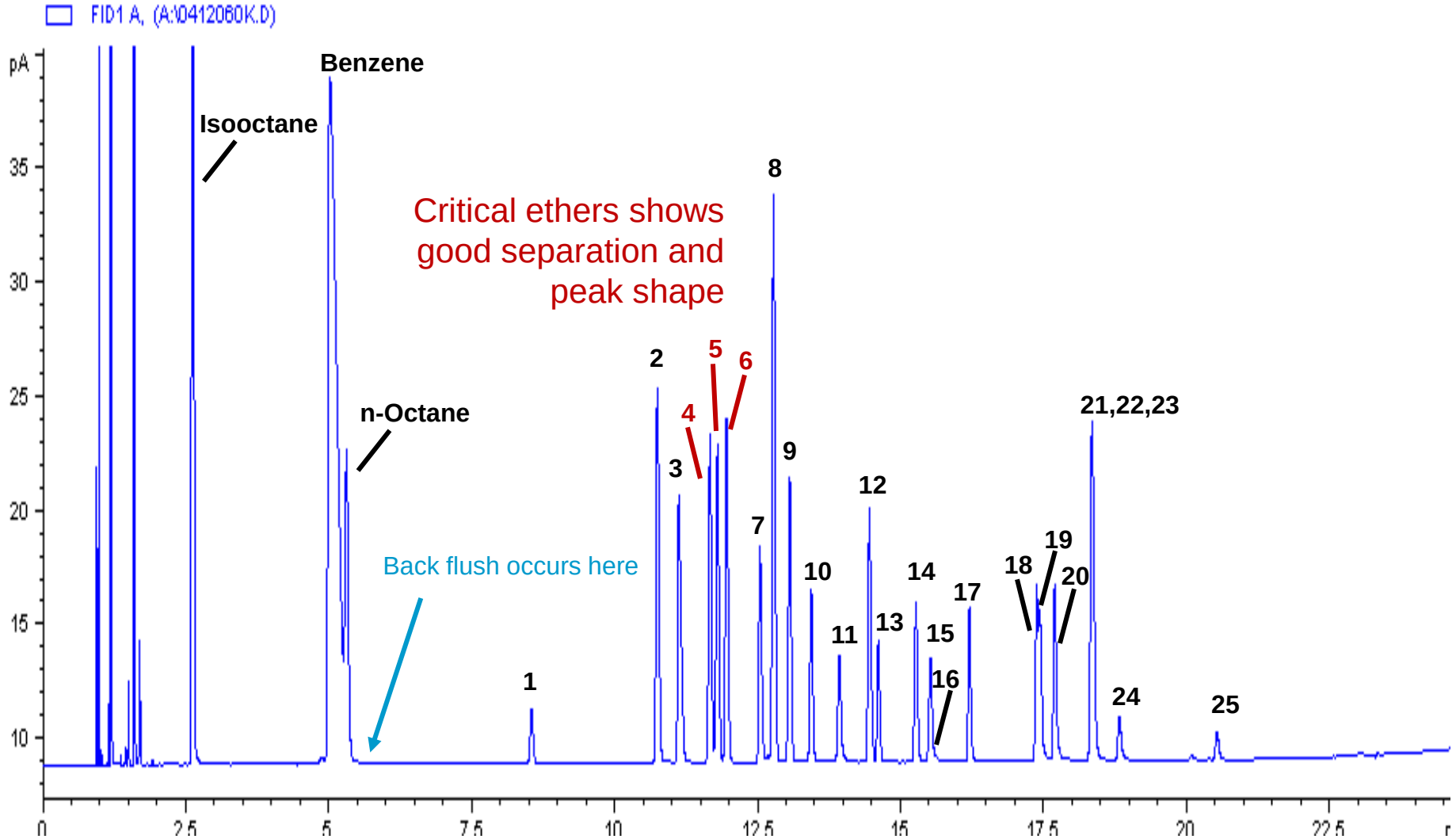


ASTM D7059 – Valve Configuration for Gas or Liquified Gas Sample Introduction



Agilent Technologies

Separation of Oxygenates in Light Hydrocarbon Stream Using Valve Configuration



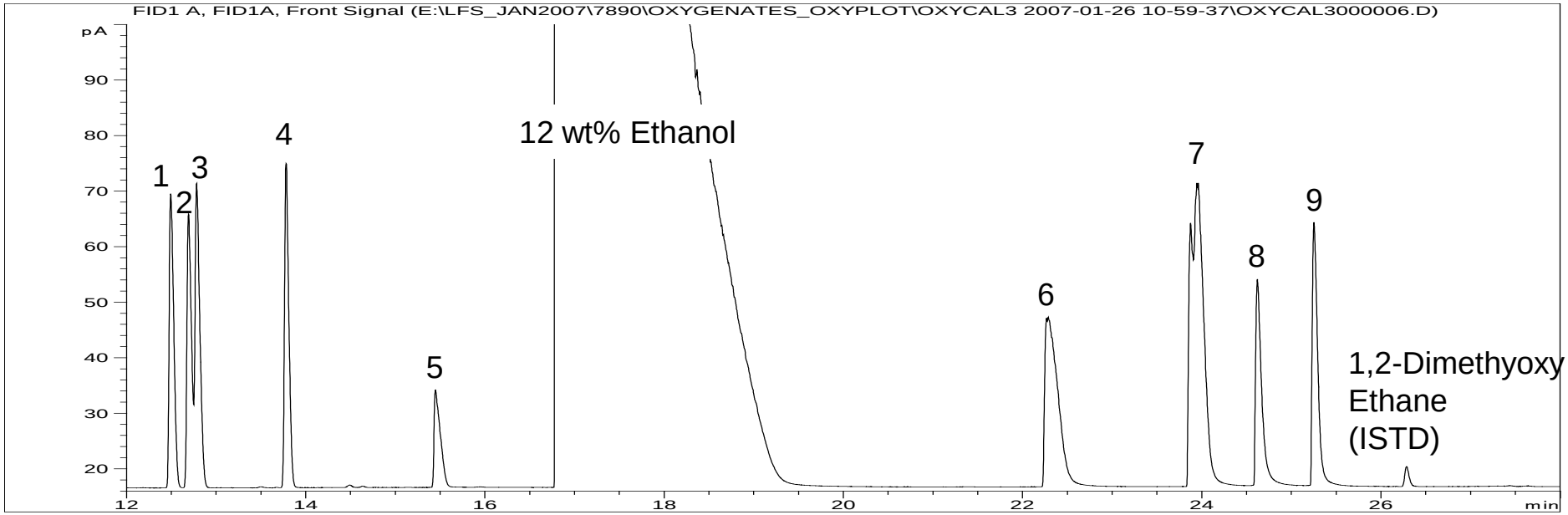
Agilent Technologies

Compound I.D.

1. Dimethyl ether
2. Diethyl ether
3. Acetaldehyde
4. Ethyl t-butyl ether
5. Methyl t-butyl ether
6. Diisopropyl ether
7. Propionaldehyde
8. Tert-amyl methyl ether
9. Propyl ether
10. Isobutylaldhyde
11. Butylaldehyde
12. Methanol
13. Acetone
14. Isovaleraldehyde
15. Valeradehyde
16. MEK
17. Ethanol
18. n-Propanol
19. Isopropyl Alcohol
20. Allyl Alcohol
21. Isobutyl Alcohol
22. t-Butyl Alcohol
23. s-Butyl Alcohol
24. n-Butyl Alcohol
25. 2-Methyl-2-pentanol

Analysis of Oxygenates in Reformulated Gasoline Using Valve Configuration

500 mg/kg oxygenates in reformulated gasoline

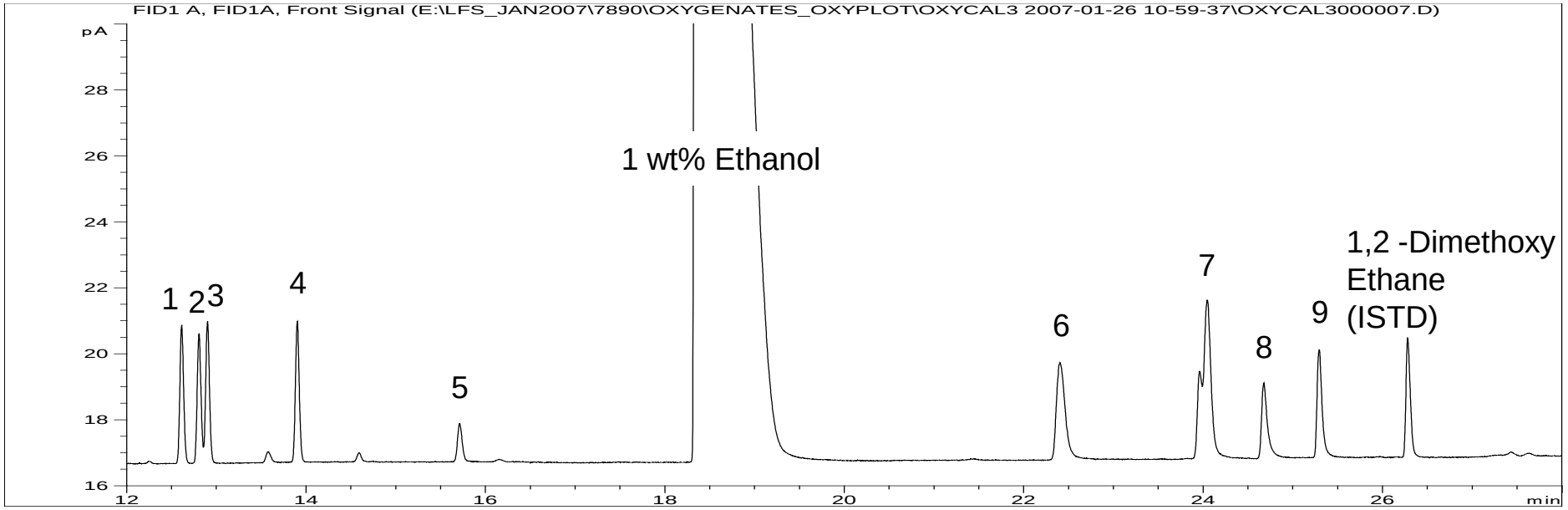


Ethers	Alcohols
1. EtBE	5. methanol
2. MtBE	6. i,n-propanols
3. DIPE	7. i,s,t-butanols
4. TAME	8. n-butanol
	9. tert-amyl alcohol

Agilent Technologies

Analysis of Oxygenates in Reformulated Gasoline Using Valve Configuration

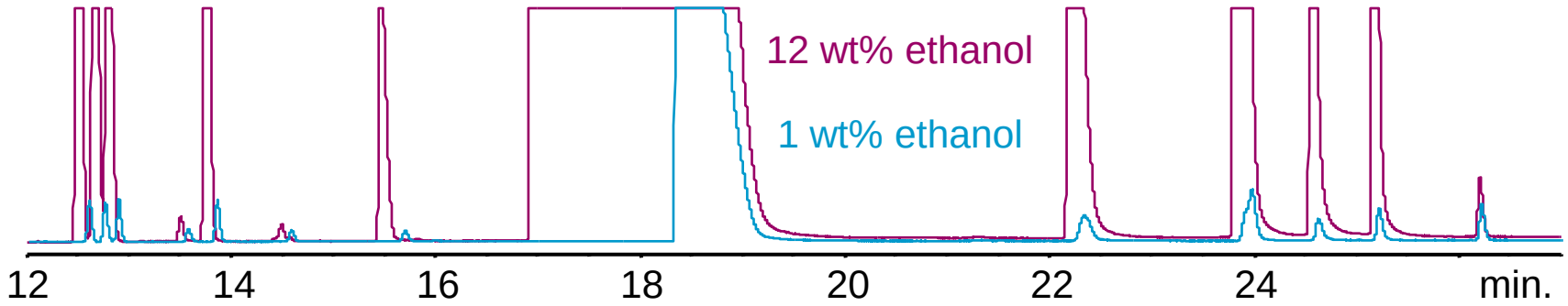
50 mg/kg oxygenates in reformulated gasoline

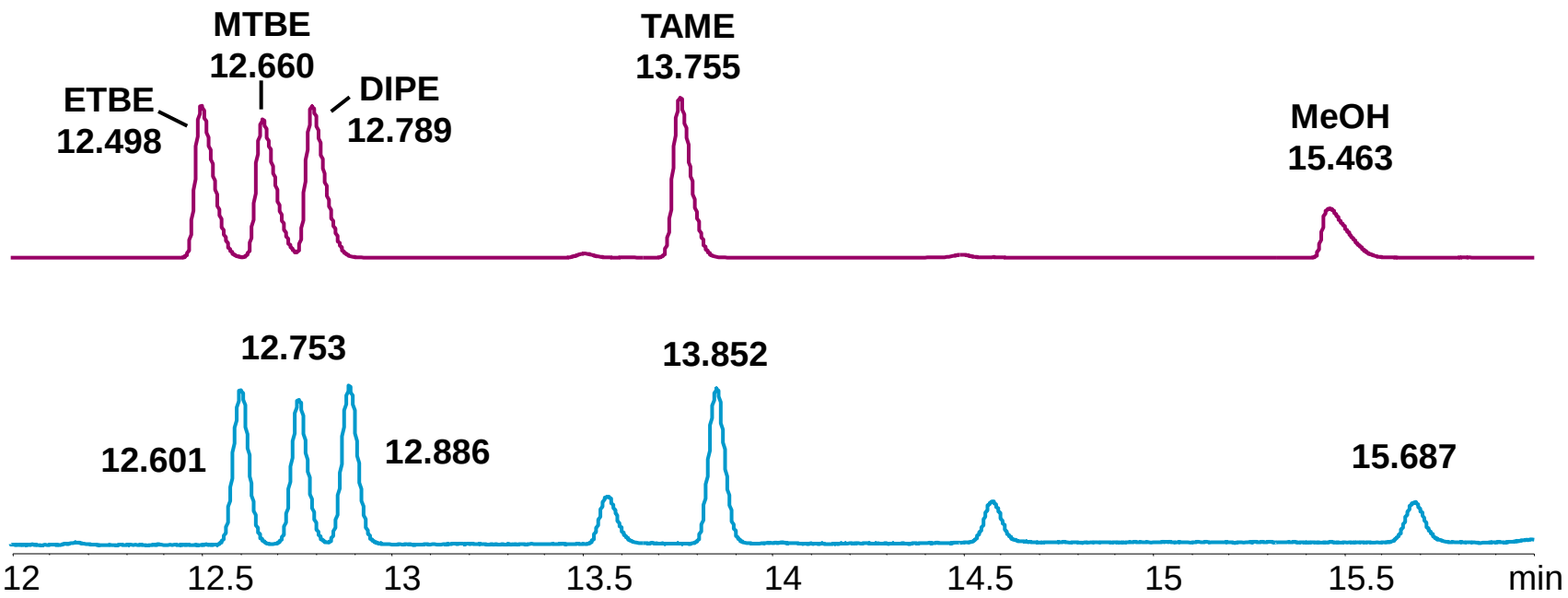


Ethers	Alcohols
1. EtBE	5. methanol
2. MtBE	6. i,n-propanols
3. DIPE	7. i,s,t-butanols
4. TAME	8. n-butanol
	9. tert-amyl alcohol

Agilent Technologies

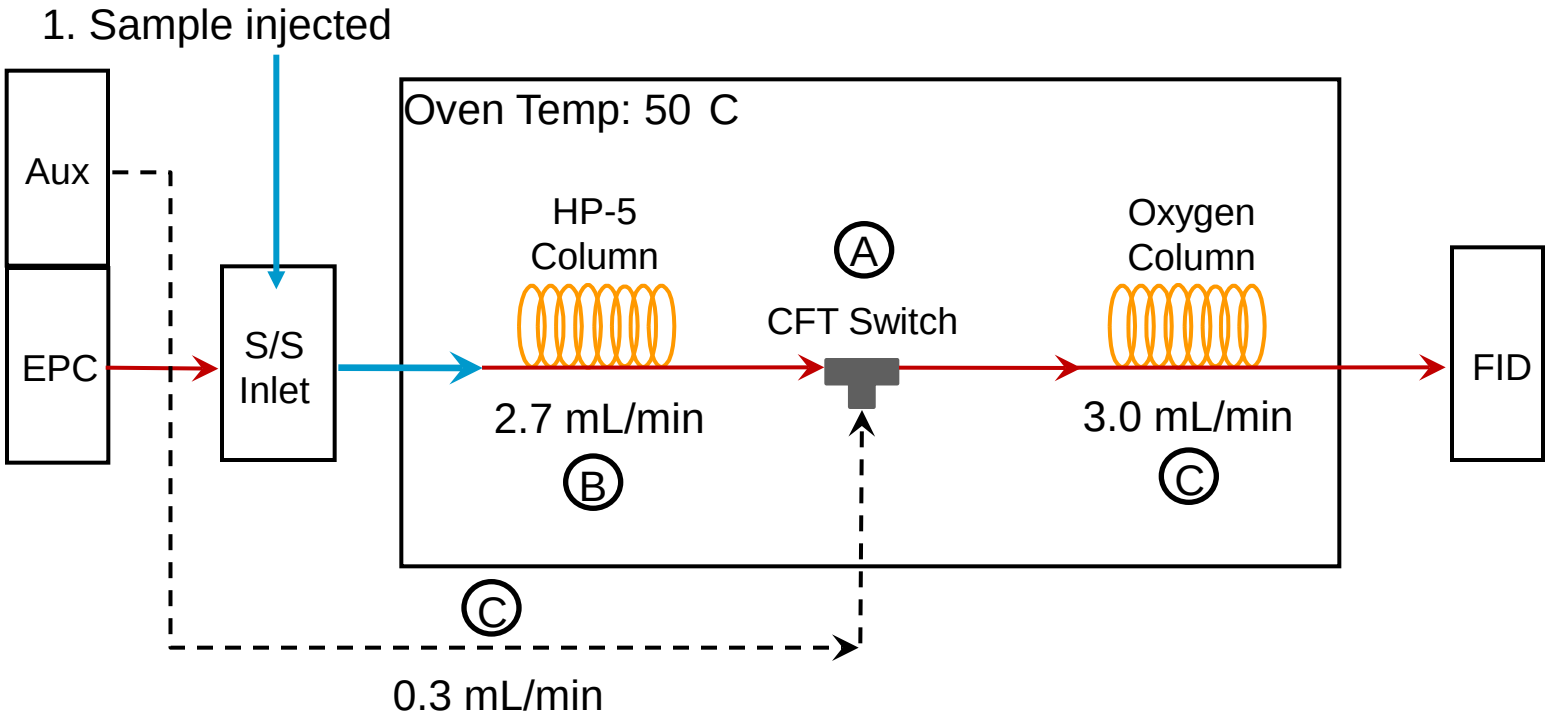
Ethanol Concentration Shifts Retention Time of Early Peaks





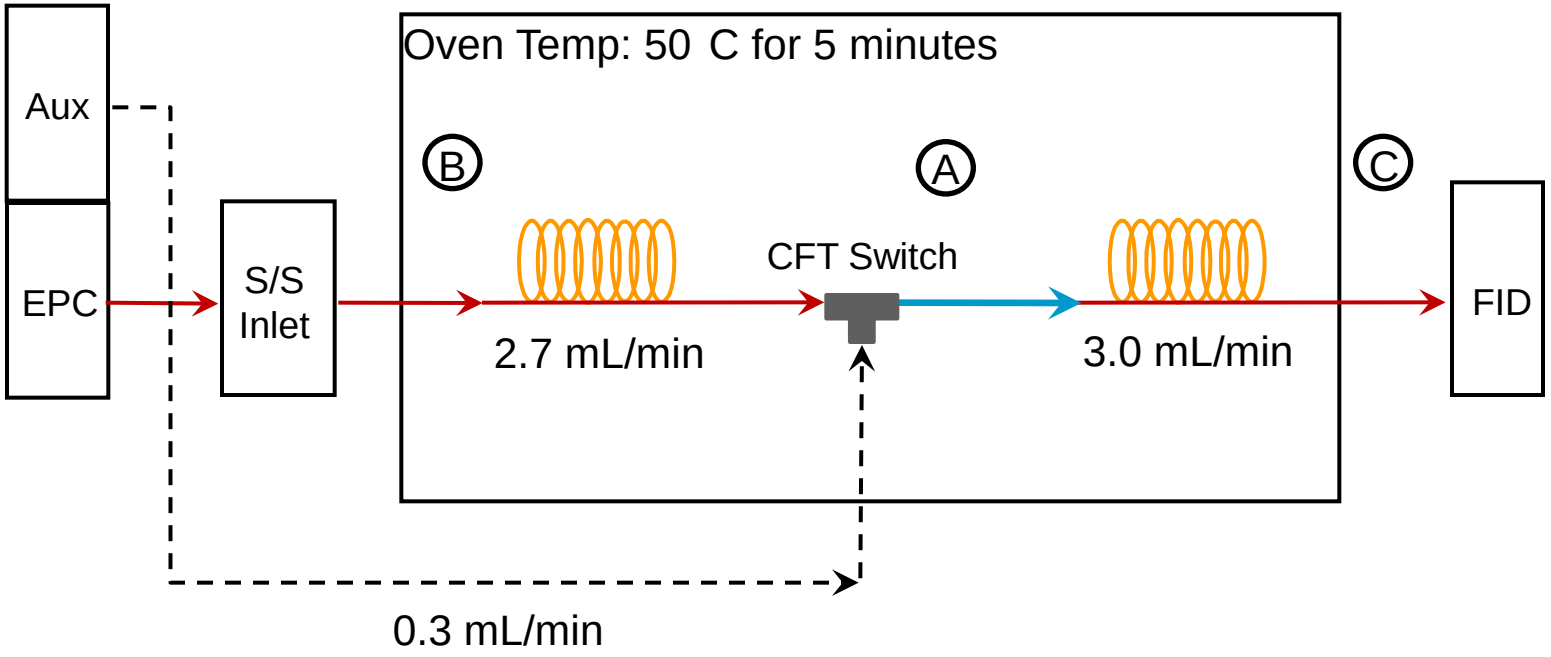
Fluidic Switch Configuration For ASTM Trace Oxygenate Analysis Methods

1. A. The HP-5 and the Oxygen columns are linked by Capillary Flow Technology (CFT)
   B. The Inlet EPC delivers 2.7 mL/min to both columns
   C. The Aux EPC delivers 0.3 mL/min to the Capillary Flow Technology Plate. This increases the flow to the Oxygen column to 3.0 mL/min.



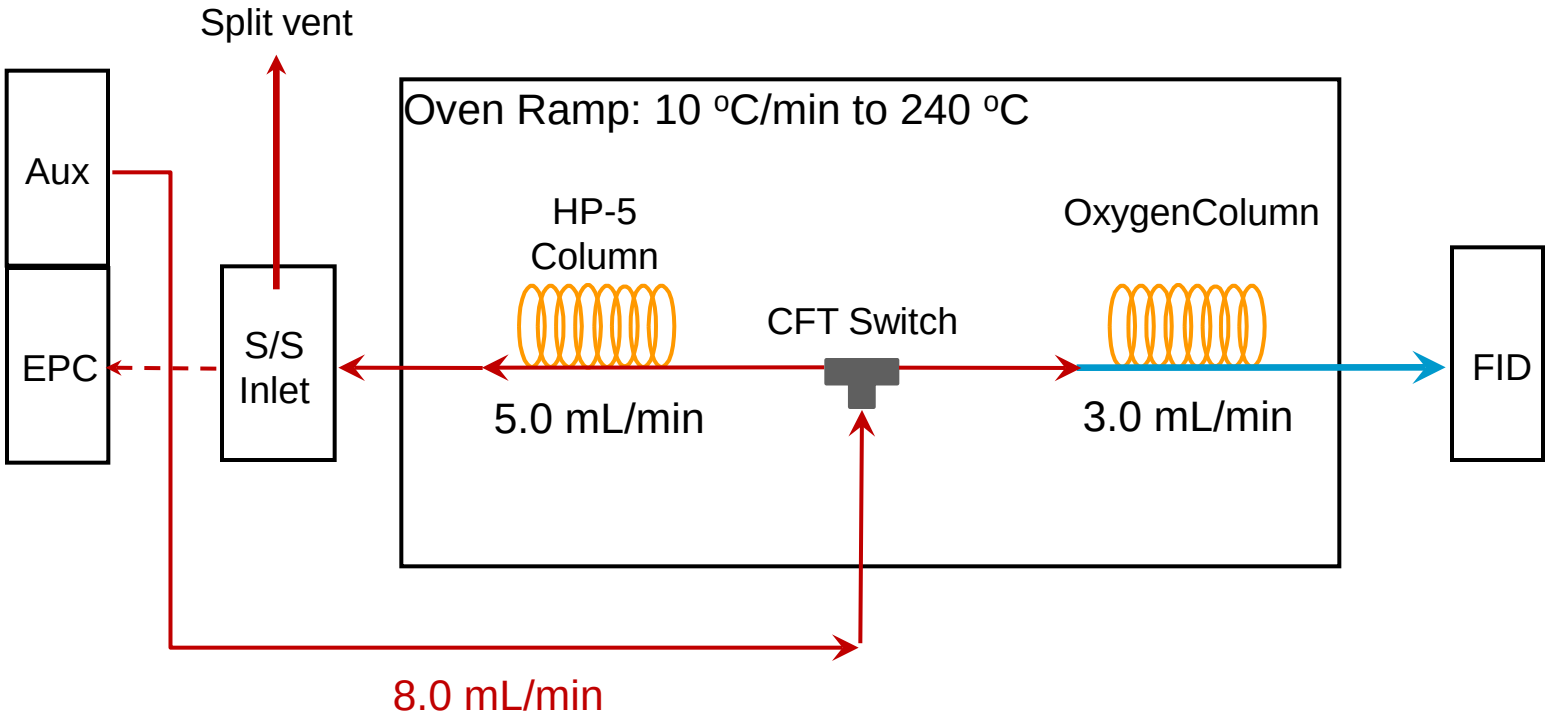
Fluidic Switch Operation For ASTM Trace Oxygenate Analysis Methods

2. A. Oxygenates and low boiling point hydrocarbons elute into Oxygen Column
   Oxygenates are trapped at the front of the GS-OxyPLOT
   B. High boiling point compounds are retained in HP-5
   C. Low boiling point hydrocarbons elute “unretained” through Oxygen to the FID

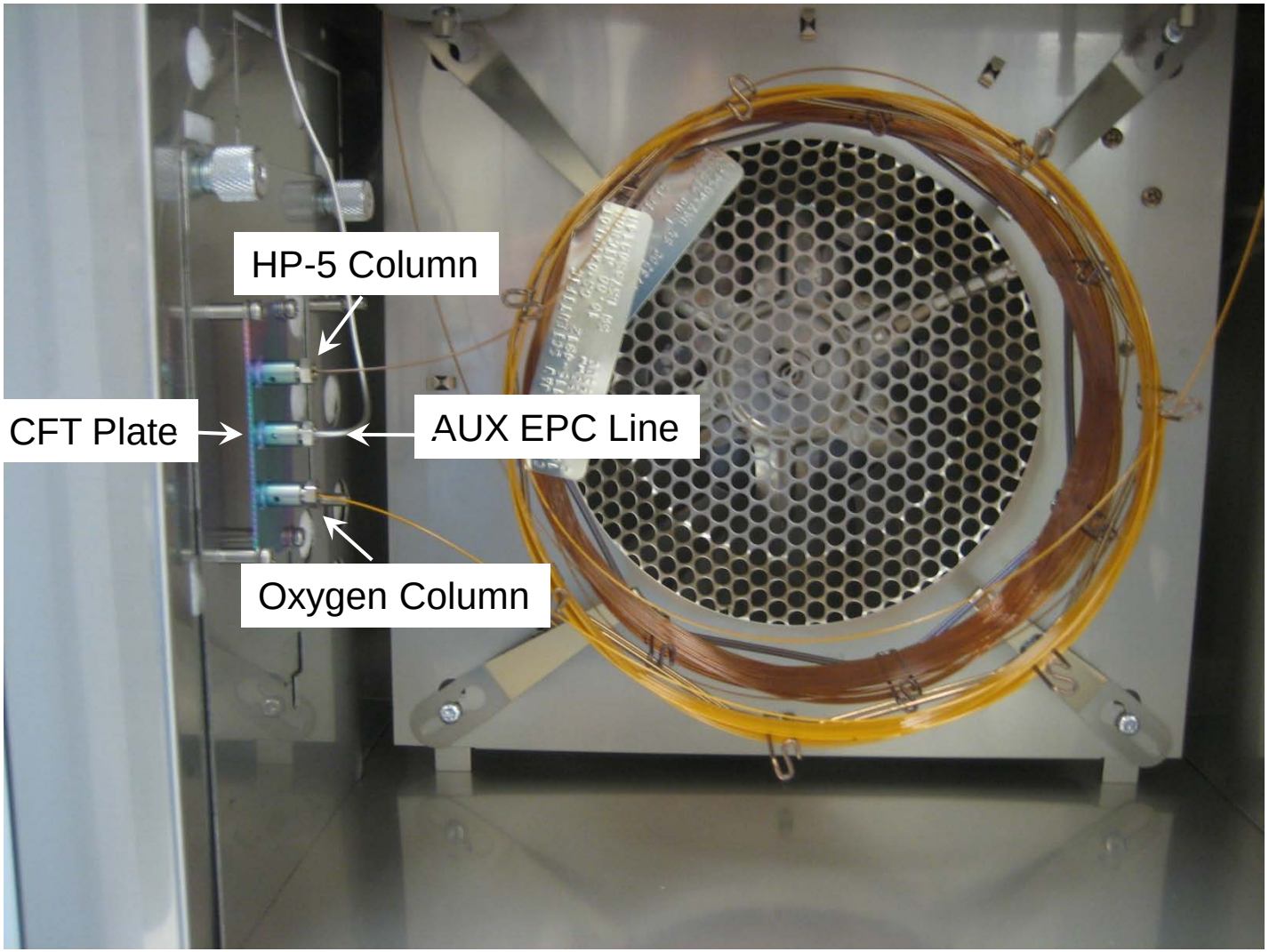


Fluidic Switch Operation For ASTM Trace Oxygenate Analysis Methods

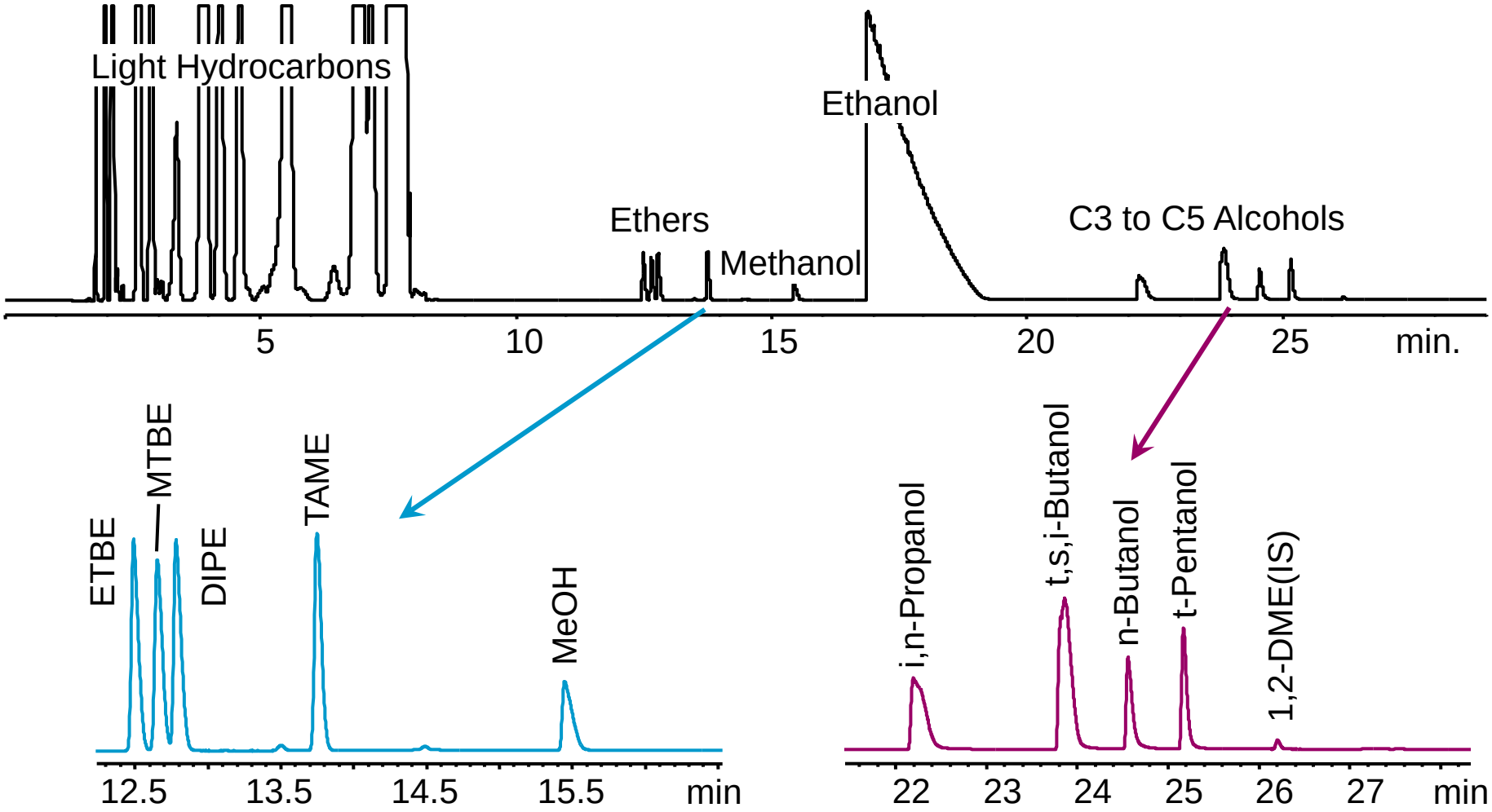
3. Inlet EPC flow reduced to 0.5 mL/min and AUX EPC flow increased to 8 mL/min
4. Gas flow through the Fluidic Switch back flushes the HP-5 to send high boiling compounds out the inlet split vent.
5. Oven temperature program begins and oxygenates are separated on the Oxygen Column to the FID.



Oxygenate Analysis in Hydrocarbons Using Capillary Flow Technology Fluidic Switch



Analysis of Oxygenates in Reformuated Gasoline Using CFT Fluidic Switch



Excellent Quantitative Precision

High Concentration QA/QC Check Sample

	Expected (ppm)*	Avg (ppm)*	Std Dev (ppm)*	RSD
ETBE	780	758	1.3	0.2%
MTBE	795	816	1.5	0.2%
DIPE	795	758	1.1	0.2%
TAME	779	779	1.4	0.2%
Methanol	802	759	1.6	0.2%
Ethanol*	12.0%	11.3%	0.0	0.4%
i,n-Propanol	1619	1566	14.7	0.9%
t,s,i-Butanol	2399	2372	4.4	0.2%
n-Butanol	798	791	1.7	0.2%
t-Pentanol	801	766	0.6	0.1%

Low Concentration QA/QC Check Sample

	Expected (ppm)*	Avg (ppm)*	Std Dev (ppm)*	RSD
ETBE	49	48	0.7	1.4%
MTBE	49	46	1.0	2.1%
DIPE	49	93	0.7	0.8%
TAME	48	48	0.3	0.6%
Methanol	50	67	0.6	0.8%
Ethanol*	1.0%	0.9%	0.0	2.2%
i,n-Propanol	101	95	1.3	1.4%
t,s,i-Butanol	150	152	2.4	1.6%
n-Butanol	50	47	0.8	1.6%
t-Pentanol	50	47	0.2	0.5%

*ethanol results are in wt%

Each QA/QC sample prepared in reformulated gasoline
Five consecutive runs of each sample

Feedstock and Ethanol Fuel Analysis
ASTM D5501-09

ASTM D4806 - Denatured Fuel Ethanol for Blending with Gasoline		
Property	**Specification**	**ASTM Test Method**
Minimum ethanol content	92.1 vol %	D5501-09
Maximum methanol content	0.5 vol%	D5501-09

ASTM D5798 Standard Specification for Fuel Ethanol (E75-E85)		
Property	**Specification**	**ASTM Test Method**
Minimum ethanol content	70 – 79 vol %	D5501
Maximum methanol content	0.5 vol%	None

ASTM Method D5501-09
Agilent 7890A GC Instrument Conditions

- Method Scope
  - 93 to 98 wt% ethanol
  - 0.01 to 0.6 wt% methanol

Column and Oven Temperature	
Column	PDMS, 150 m x 0.25mm x 1.0 um
Carrier gas	Helium at 2.3 mL/min
Initial Oven Temp	60 °C
Initial Hold Time	15 min.
Oven Ramp Rate	30 °C/min
Final Temp	250 °C
Final Hold Time	23 min.

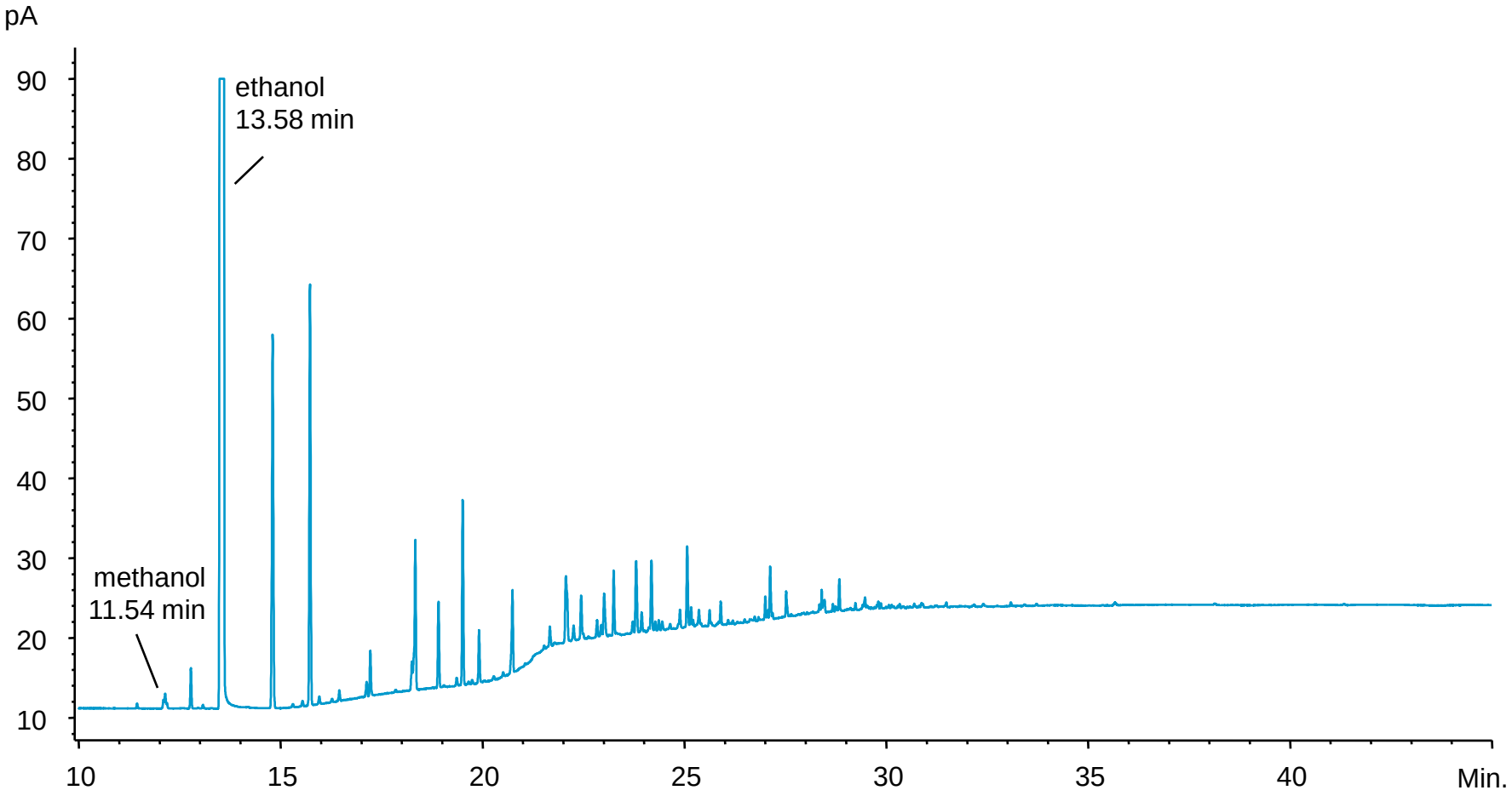
Split/Spltless Inlet	
Mode	Split Mode
Split ratio	200:1
Temp	300 °C
Injection Size	0.5 uL
Flame Ionization Detector	
Temp	300 °C

ASTM D5501-09 7890A GC Calibration

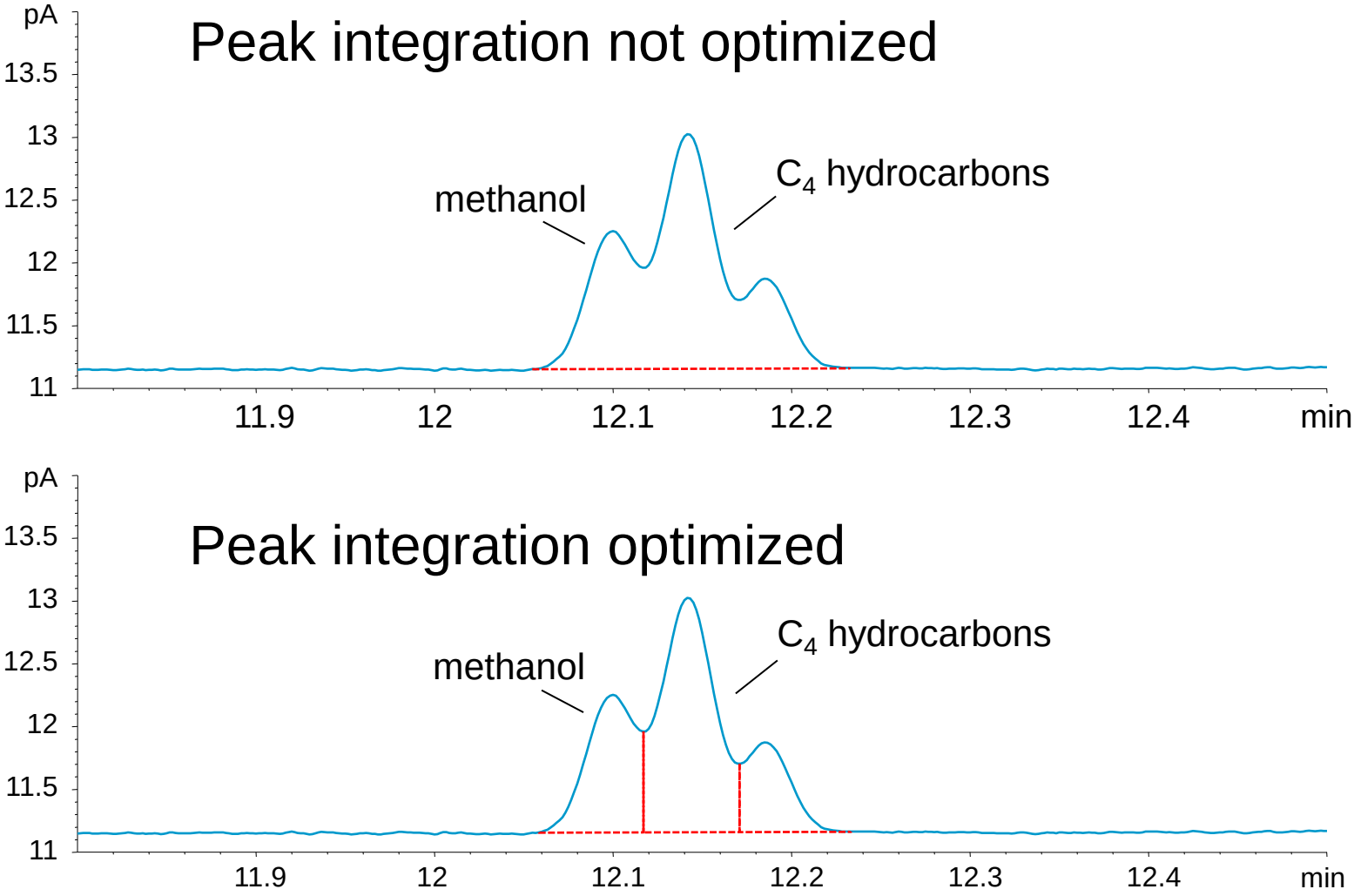
- 7 Levels of calibration
  - Heptane range: 1.95 to 7.4 wt%
  - Methanol range: 0.05 to 0.6 wt%
  - Ethanol range: 92 to 98 wt%
- **Use average RRF for sample quantification**

n-heptane	methanol	ethanol
Relative response factor	Relative response factor	Relative response factor
1.00	2.97	2.06

ASTM Method D5501-09
Commercial Denatured Fuel Ethanol Sample



D5501-09 Potential Methanol Interference



ASTM D5501-09
Agilent 7890A GC Analysis Precision
Commercially available denatured fuel ethanol sample

Run	methanol	ethanol
1	0.02	97.81
2	0.02	97.83
3	0.02	97.81
4	0.02	97.82
5	0.02	97.79
6	0.02	97.81
7	0.02	97.78
8	0.02	97.76
9	0.02	97.77
10	0.02	97.74
Avg	**0.02**	**97.79**
STDDEV	**2.18e-4**	**0.03**
RSD	**1.16%**	**0.03%**

Summary

Agilent Special Products for ASTM oxygenate analysis methods

- ASTM D7423 - 09 Standard Test Method for Determination of Oxygenates in C2, C3, C4, and C5 Hydrocarbon Matrices by GC and FID
- Proposed Gasoline Method - Standard Test Method for Determination of Trace Oxygenates in Finished Gasoline by Multidimensional GC
- ASTM D5501 - Standard Test Method for Determination of Ethanol Content of Denatured Fuel Ethanol by Gas Chromatography

- Preconfigured solutions based on Agilent 7890A GC platform
- Factory configured and tested to meet ASTM performance specifications