Agilent Solutions for the Analysis of Ethanol-Based Fuels Derived From Biomass

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Senior Scientist
September 14, 2010

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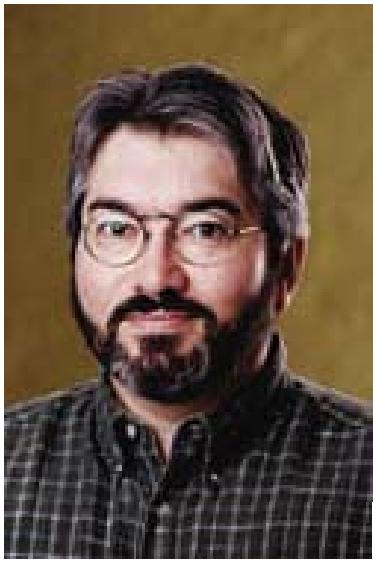

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Outline

- Overview of ethanol containing motor fuels
- Current ASTM fuel ethanol standards and methods
- New developments in ASTM for ethanol based fuel methods
- Agilent 7890A GC Analysis Using ASTM Method D5501
- Agilent 7890A GC Analysis Using New ASTM Method
- Improving Productivity and Resolution

Motor Fuels Containing Ethanol

- **Denatured fuel ethanol**
  - Anhydrous ethanol denatured with natural gasoline (natural gas condensates)
  - Used as a blending stock for oxygenated motor fuels (E85 and RFG)
  - Produced from renewable resources: sugars or biomass
- **Fuel ethanol (E75-E85) “Flex Fuel”**
  - A new fuel containing 75 to 85 vol% denatured fuel ethanol and 25 to 15 vol% gasoline hydrocarbons
  - High ethanol content encourages production using green, renewable sources
  - Requires special spark ignition engines
- **Reformulated gasoline (RFG)**
  - Contain up to 12 wt% ethanol
  - Additive used to reduce “smog” emitted from motor vehicles
  - Replaces methyl-*tert*-butyl ether (MtBE) and other oxygenated additives in many countries
  - Used in standard spark-ignition engines

ASTM Ethanol Fuel Standards Citing GC Methods

ASTM D4806 - Denatured Fuel Ethanol for Blending with Gasoline

Property	Specification	ASTM Test Method
Minimum ethanol content	92.1 vol %	D5501
Maximum methanol content	0.5 vol%	D5501

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
Agilent 7890A GC Instrument Conditions

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

Column and Oven Temperature	
Column	DB-1, 150 m x 0.25mm x 0.5 um
Carrier gas	Helium at 2.0 mL/min
Initial Oven Temp	60 ^{o}C
Initial Hold Time	15 min.
Oven Ramp Rate	30 ^{o}C/min
Final Temp	250 ^{o}C
Final Hold Time	23 min.

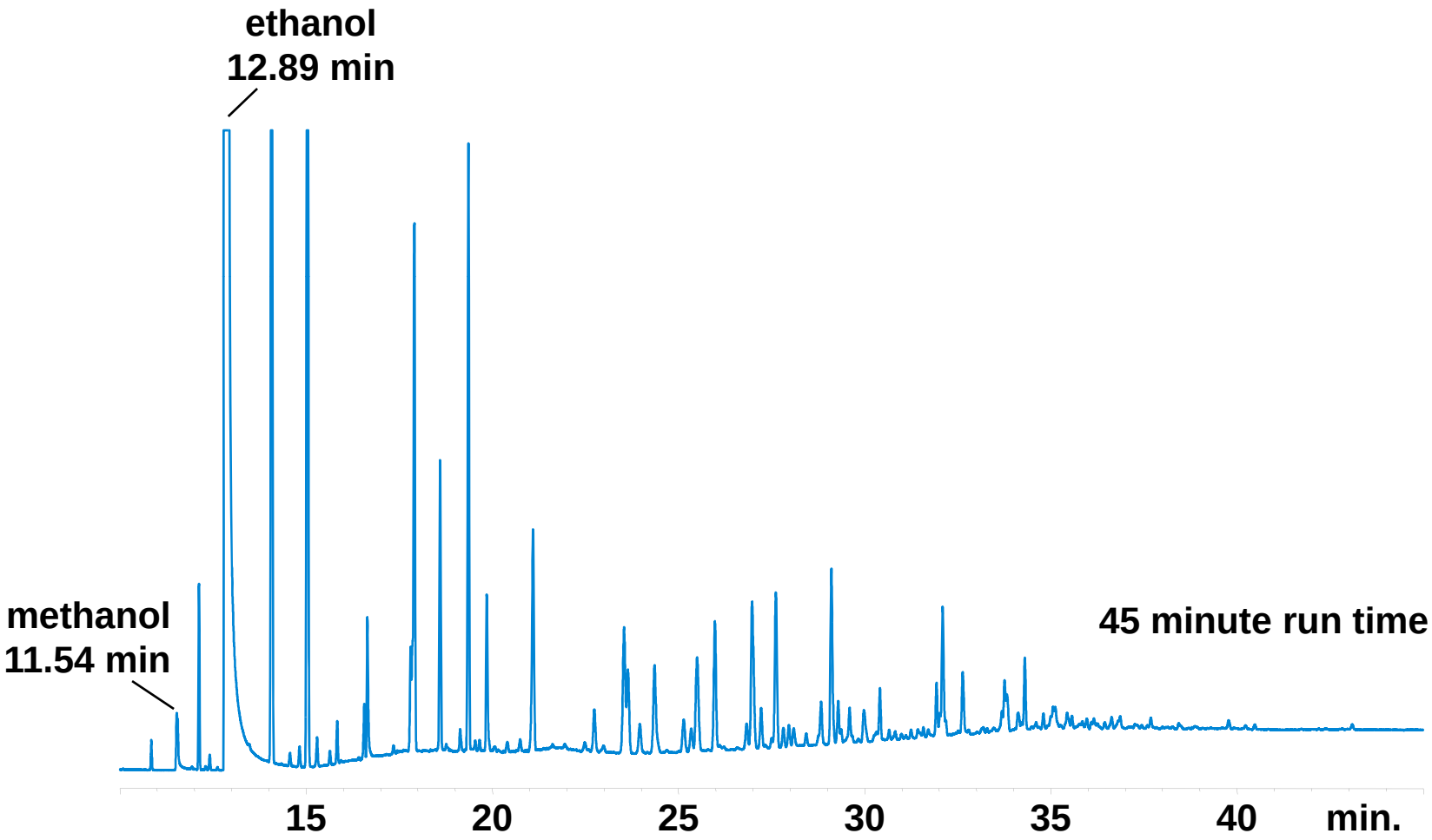
Split/Spltless Inlet	
Mode	Split Mode
Split ratio	200:1
Temp	300 ^{o}C
Injection Size	0.5 uL
Flame Ionization Detector	
Temp	300 ^{o}C

ASTM D5501 - Agilent 7890A GC Calibration

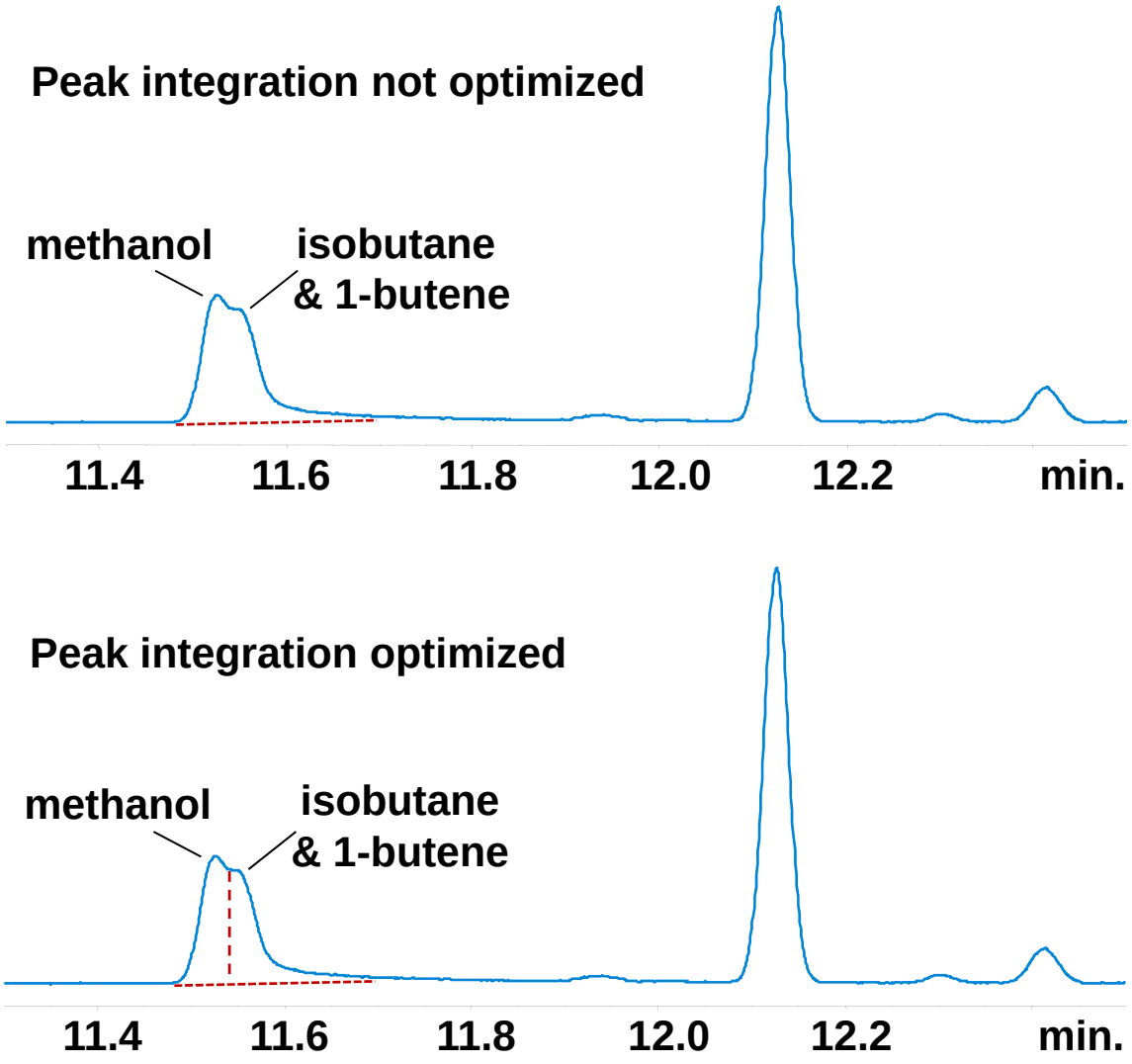
- 7 Levels of calibration
  - Heptane range: 1.95 to 7.4 wt%
  - Methanol range: 0.05 to 0.6 wt%
  - Ethanol range: 92 to 98 wt%
- **Use average RRF for sample quantification**

n-heptane			methanol			ethanol		
wt%	**RF (wt%/area)**	**RRF**	**wt%**	**RF (wt%/area)**	**RRF**	**wt%**	**RF (wt%/area)**	**RRF**
1.95	2.15E-03	1.00	0.05	6.06E-03	2.82	92	4.28E-03	1.99
2.9	2.14E-03	1.00	0.1	6.05E-03	2.82	93	4.24E-03	1.98
3.8	2.14E-03	1.00	0.2	5.86E-03	2.74	94	4.23E-03	1.98
4.7	3.55E-03	1.00	0.3	1.22E-02	3.43	95	4.13E-03	1.16
5.6	2.12E-03	1.00	0.4	7.66E-03	3.61	96	4.26E-03	2.01
6.5	2.14E-03	1.00	0.5	6.22E-03	2.90	97	4.25E-03	1.98
7.4	2.15E-03	1.00	0.6	6.43E-03	2.99	98	4.24E-03	1.97
Avg		**1.00**			**3.04**			**1.87**

ASTM Method D5501 – Commercial Denatured Fuel Ethanol Sample



D5501 – Interference of Methanol on 150-m Column



ASTM D5501 - Agilent 7890A GC Analysis Precision

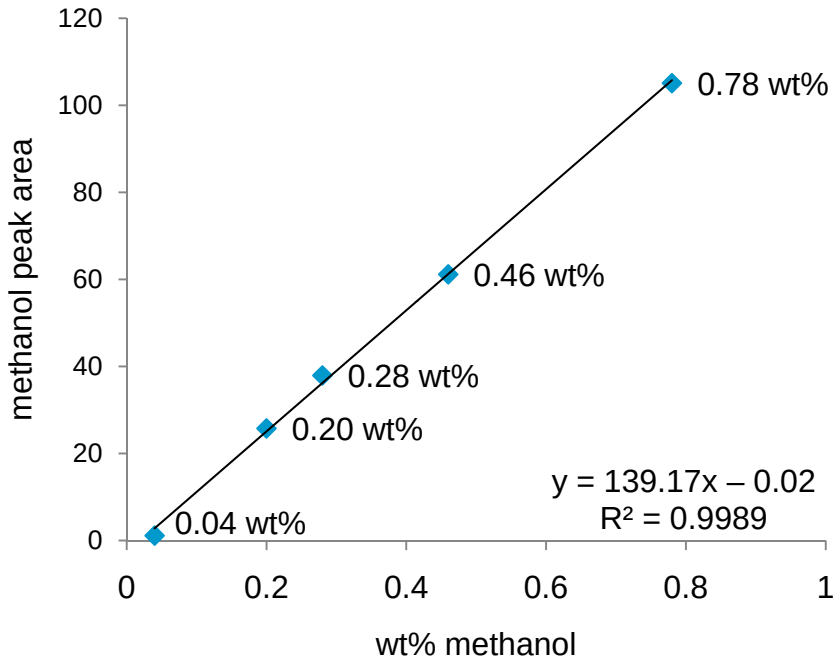
Commercially available denatured fuel ethanol sample

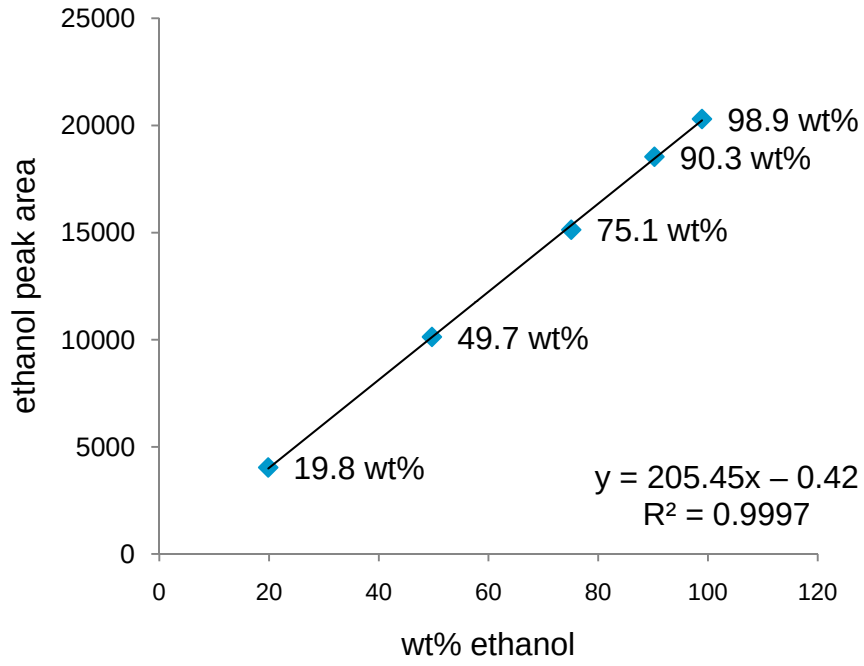
Run	methanol	ethanol	heptane
1	0.038	98.006	0.049
2	0.038	97.993	0.053
3	0.038	97.983	0.050
4	0.040	97.992	0.049
5	0.040	97.985	0.049
6	0.038	98.036	0.049
7	0.036	97.998	0.054
8	0.038	98.004	0.052
9	0.038	98.016	0.049
10	0.038	98.022	0.049
Avg	0.038	98.004	0.050
STDDEV	0.001	0.017	0.002
RSD	2.972%	0.017%	3.870%

Extended D5501 – A New ASTM Ethanol Fuel Method

- Needed for motor fuels containing > 10 vol% ethanol
- Identical GC configuration and conditions as existing D5501
- Method Scope
  - 10 to 100 wt% ethanol
  - 0.01 to 0.6 wt% methanol
- Method uses linear regression calibration instead of average RRF

Extended D5501 – Methanol and Ethanol Calibrations





Meets ASTM Calibration Specification:
$R^2 = 0.99$
y-int < 5

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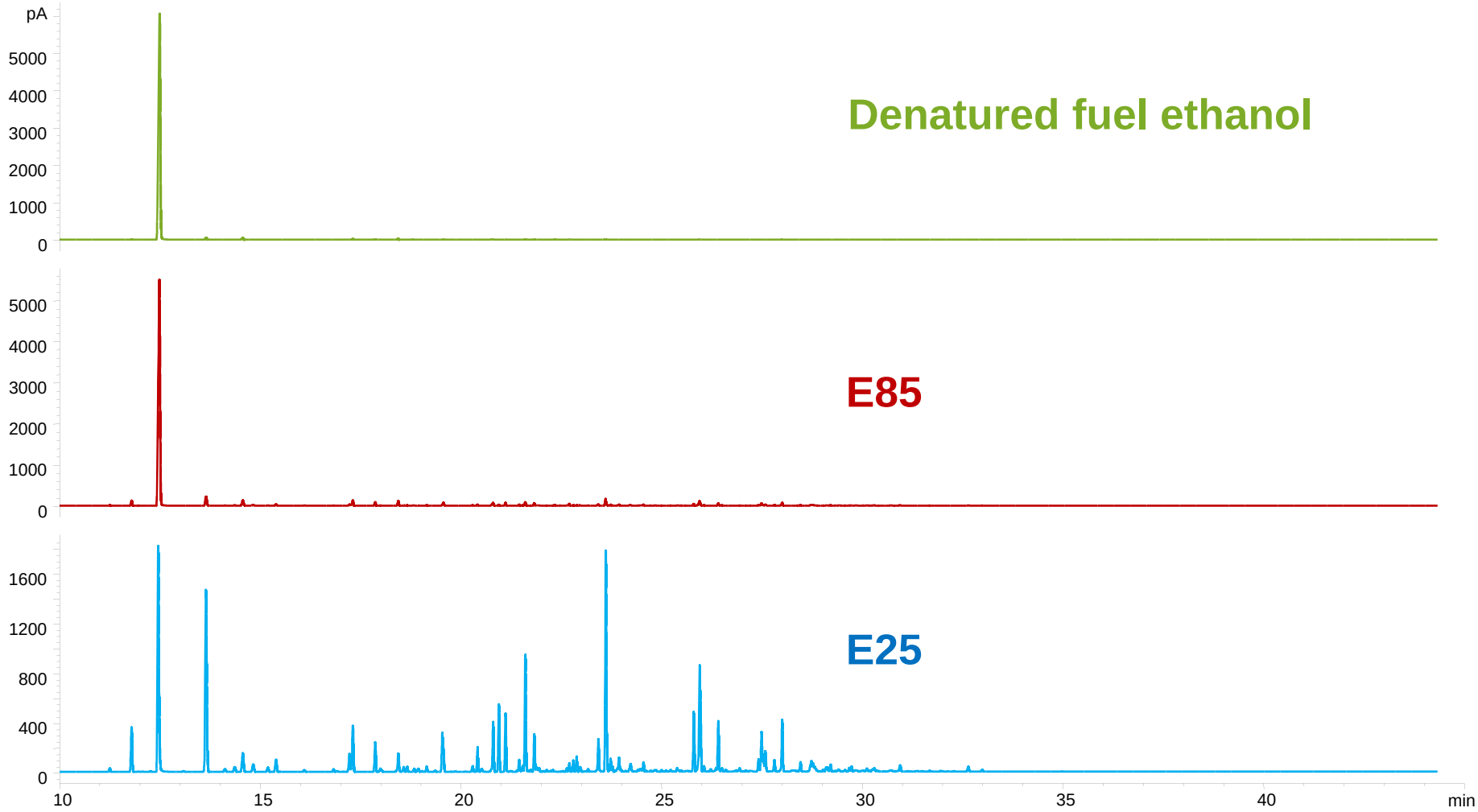
Extended D5501 – Analysis of Three Fuels



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Extended D5501 – Agilent 7890A Precision

Denatured Fuel Ethanol		
Run	**methanol**	**ethanol**
1	0.040	96.620
2	0.045	95.651
3	0.045	96.287
4	0.046	97.478
5	0.043	97.818
Avg	0.044	96.771
STDDEV	0.002	0.881
RSD	5.451%	0.911%

E85		
Run	**methanol**	**ethanol**
1	0.400	84.293
2	0.390	83.193
3	0.390	82.120
4	0.370	83.478
5	0.380	82.337
Avg	0.386	83.084
STDDEV	0.011	0.883
RSD	2.954%	1.062%

E25		
Run	**methanol**	**ethanol**
1	0.490	23.800
2	0.480	23.882
3	0.483	23.969
4	0.473	24.154
5	0.473	24.130
Avg	0.480	23.987
STDDEV	0.007	0.154
RSD	1.499%	0.641%

Results are precise but…

E85 and E25 has methanol errors

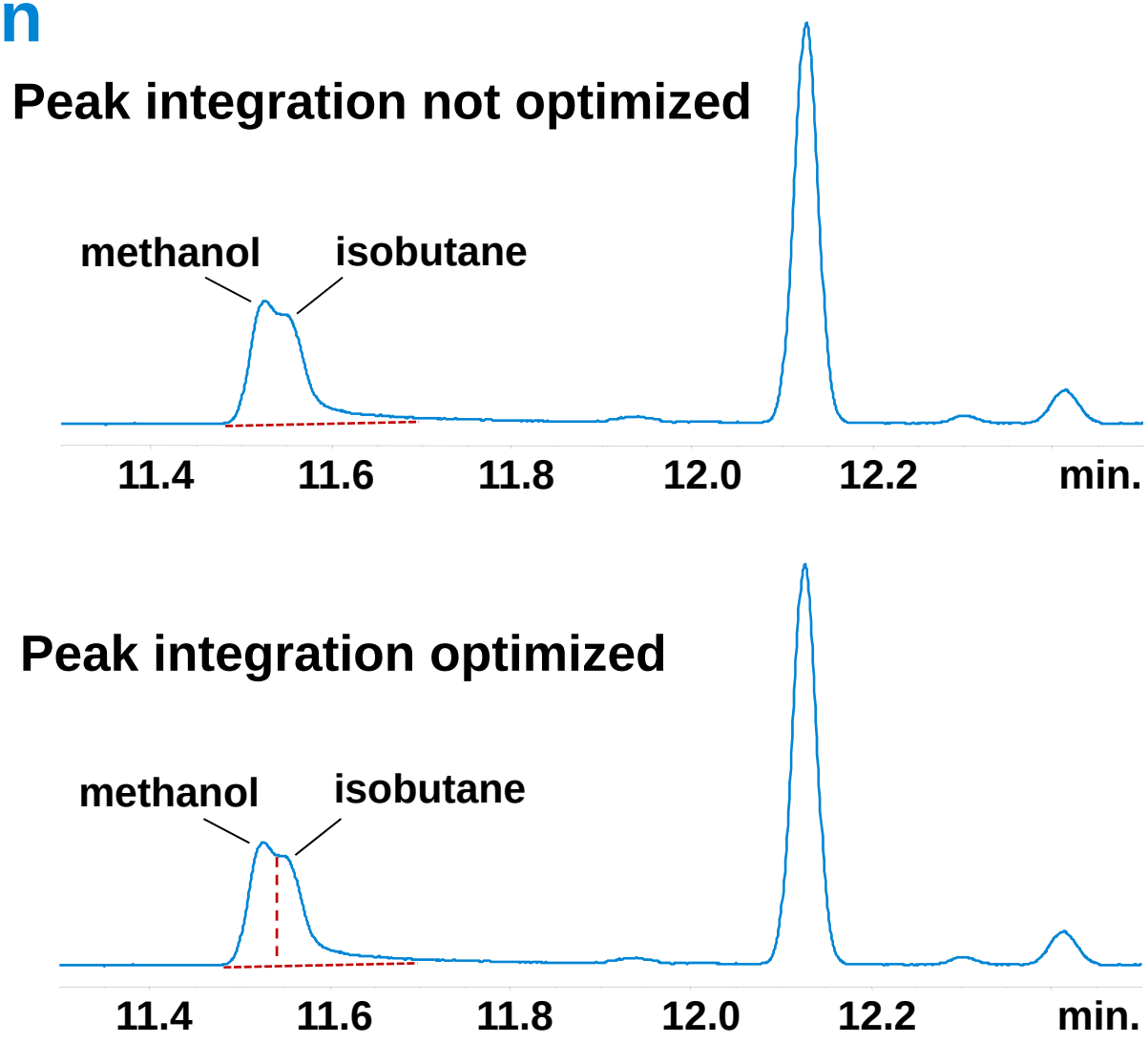
- Reported amounts too high
- Large isobutane interference in sample

Improving Speed and Resolution for Ethanol Fuel Analysis

- **D5501 and D5501 Extended methods run time > 50 minutes**
  - 150-meter column needed to resolve alcohols from hydrocarbons
    - Shorter column are faster, but have insufficient resolution
    - Higher selectivity columns (GS-OxyPLOT) have insufficient capacity
  - Long oven temperature program
    - Extra time needed to cool down between runs

- **Poor methanol/isobutane resolution**
  - Resolution only marginal with denatured fuel ethanol (92 – 99 wt% ethanol)
  - Accurate result requires fine tuning of column flow and peak integration
  - High hydrocarbon content fuel (E85 and E25) has higher isobutane content

D5501 – Interference of Methanol on 150-m Column



Extended D5501 – Agilent 7890A Precision

Denatured Fuel Ethanol		
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Avg	0.044	96.771
STDDEV	0.002	0.881
RSD	5.451%	0.911%

E85		
Run	**methanol**	**ethanol**
1	0.400	84.293
2	0.390	83.193
3	0.390	82.120
4	0.370	83.478
5	0.380	82.337
Avg	0.386	83.084
STDDEV	0.011	0.883
RSD	2.954%	1.062%

E25		
Run	**methanol**	**ethanol**
1	0.490	23.800
2	0.480	23.882
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Avg	0.480	23.987
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Results are precise but…

E85 and E25 has methanol errors

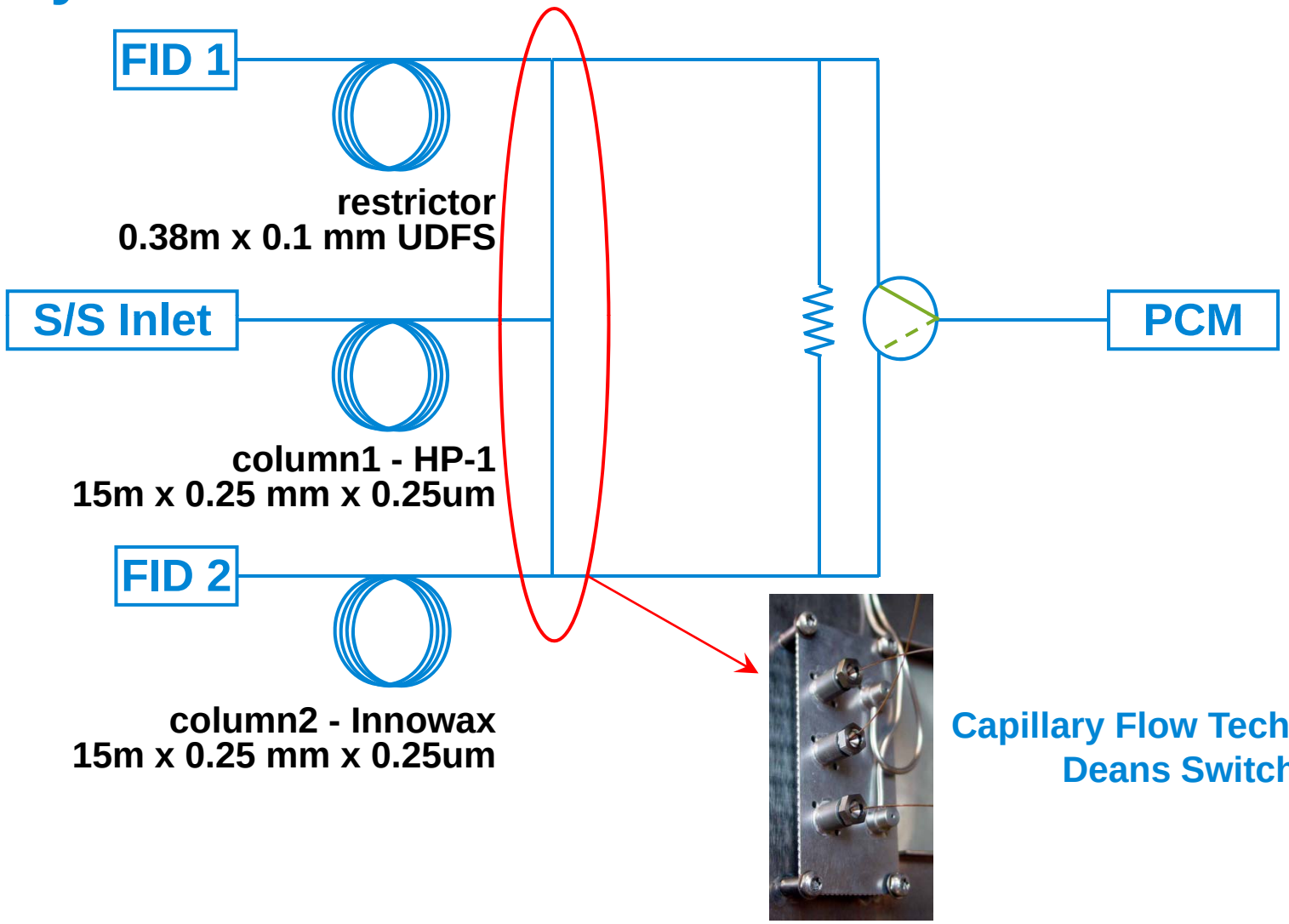
- Reported amounts too high
- Large isobutane interference in sample

Improving Speed and Resolution for Ethanol Fuel Analysis

- 2-D GC can improve both speed and resolution
  - Using shorter columns improves speed
  - Combining different column types improves resolution

- Use other techniques to improve speed
  - GC backflush can quickly remove unwanted peaks
  - Isothermal analysis have zero cycle time between runs

Deans Switch Configuration for Fuel Ethanol Analysis



Capillary Flow Technology
Deans Switch

Heart-Cutting 2-D GC Ethanol Fuel Analysis Agilent 7890A GC Instrument Conditions

Column and Oven Temperature

Column 1	HP-1, 15m x 0.25mm x 0.25 um
Column 1 flow	Helium at 1.0 mL/min
Column 2	HP-Innowax, 15m x 0.25mm x 0.25um
Column 2 flow	Helium at 2.0 mL/min
Oven Temp	45 ^{o}C **isothermal**
Backflush on	3 min.
Backflush off	3.5 min.

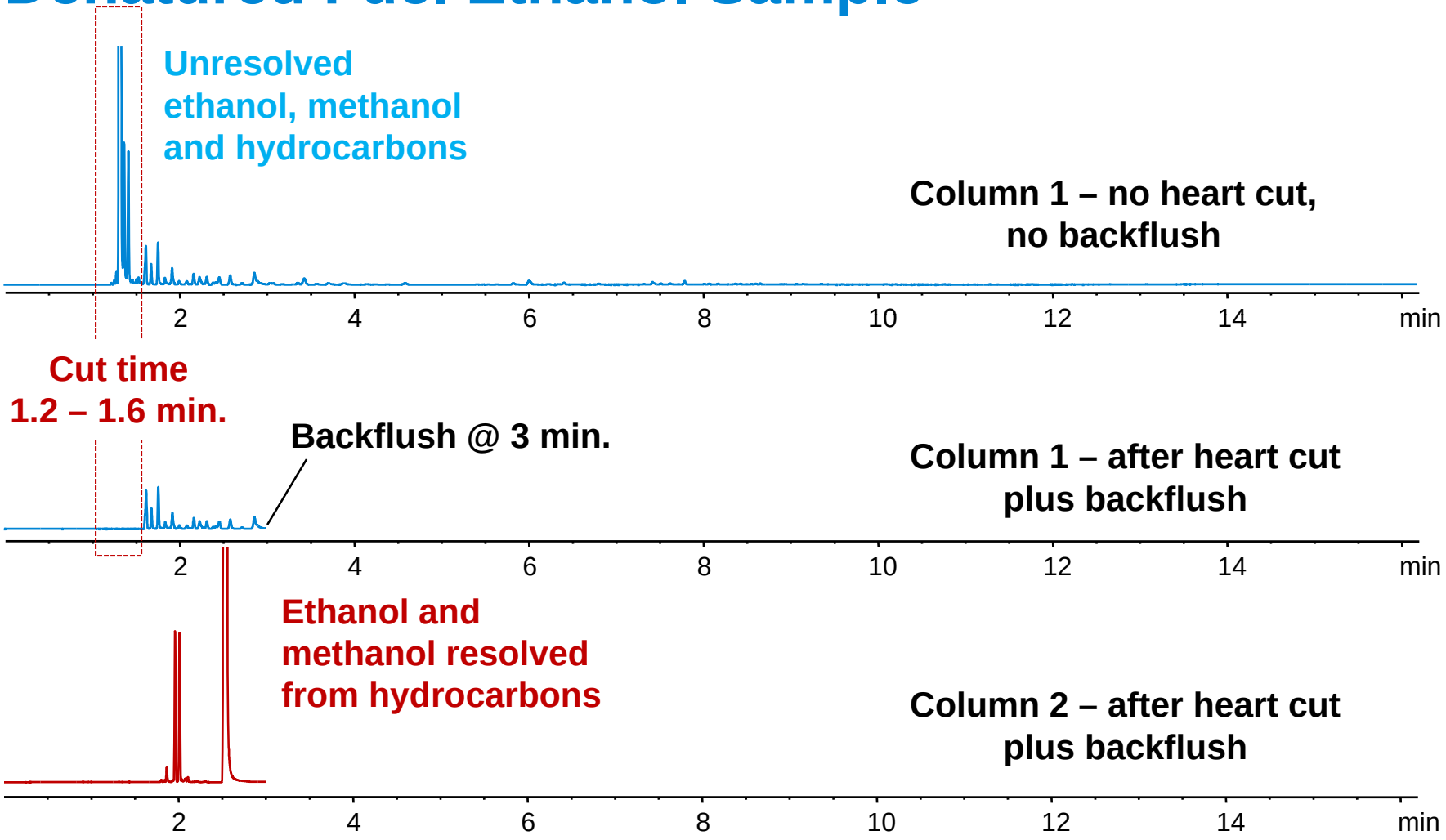
Split/Spltless Inlet

Mode	Split Mode
Split ratio	200:1
Temp	300 ^{o}C
Injection Size	0.5 uL

Flame Ionization Detector

Temp	300 ^{o}C

Heart-Cutting 2-D GC Ethanol Fuel Analysis
Denatured Fuel Ethanol Sample



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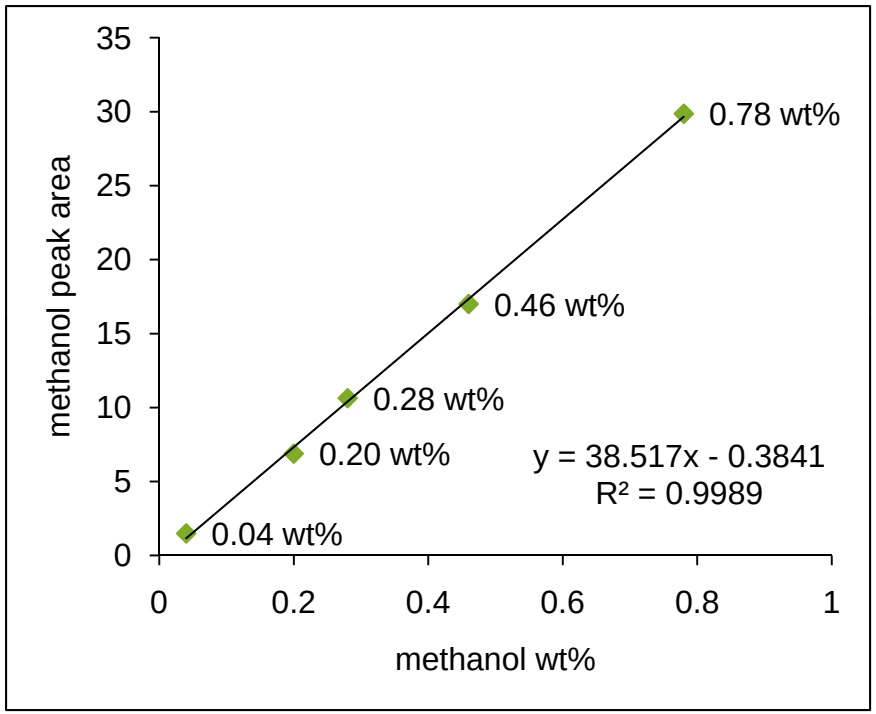
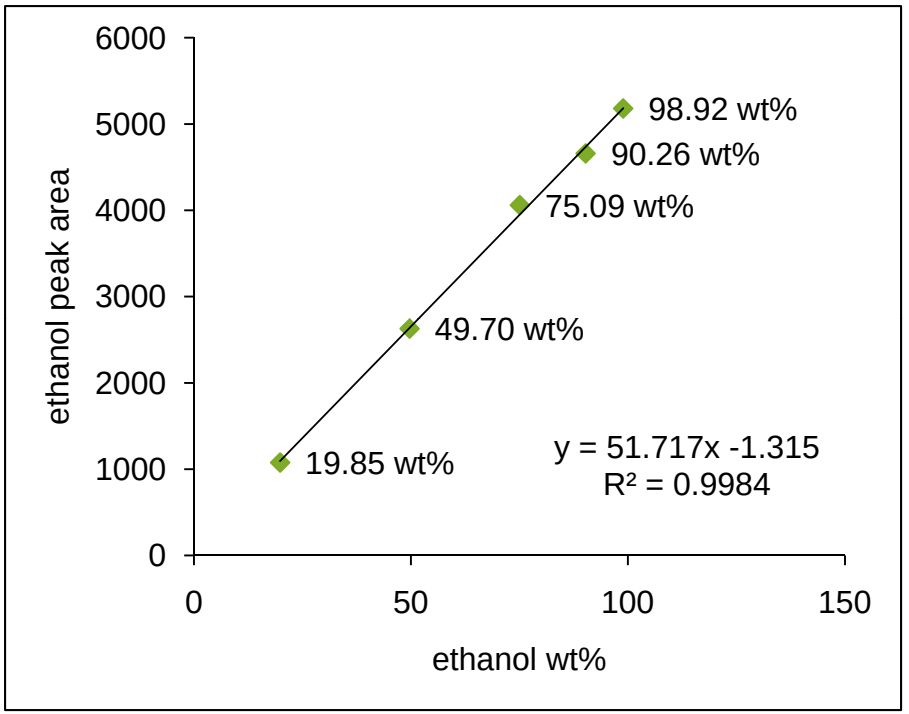
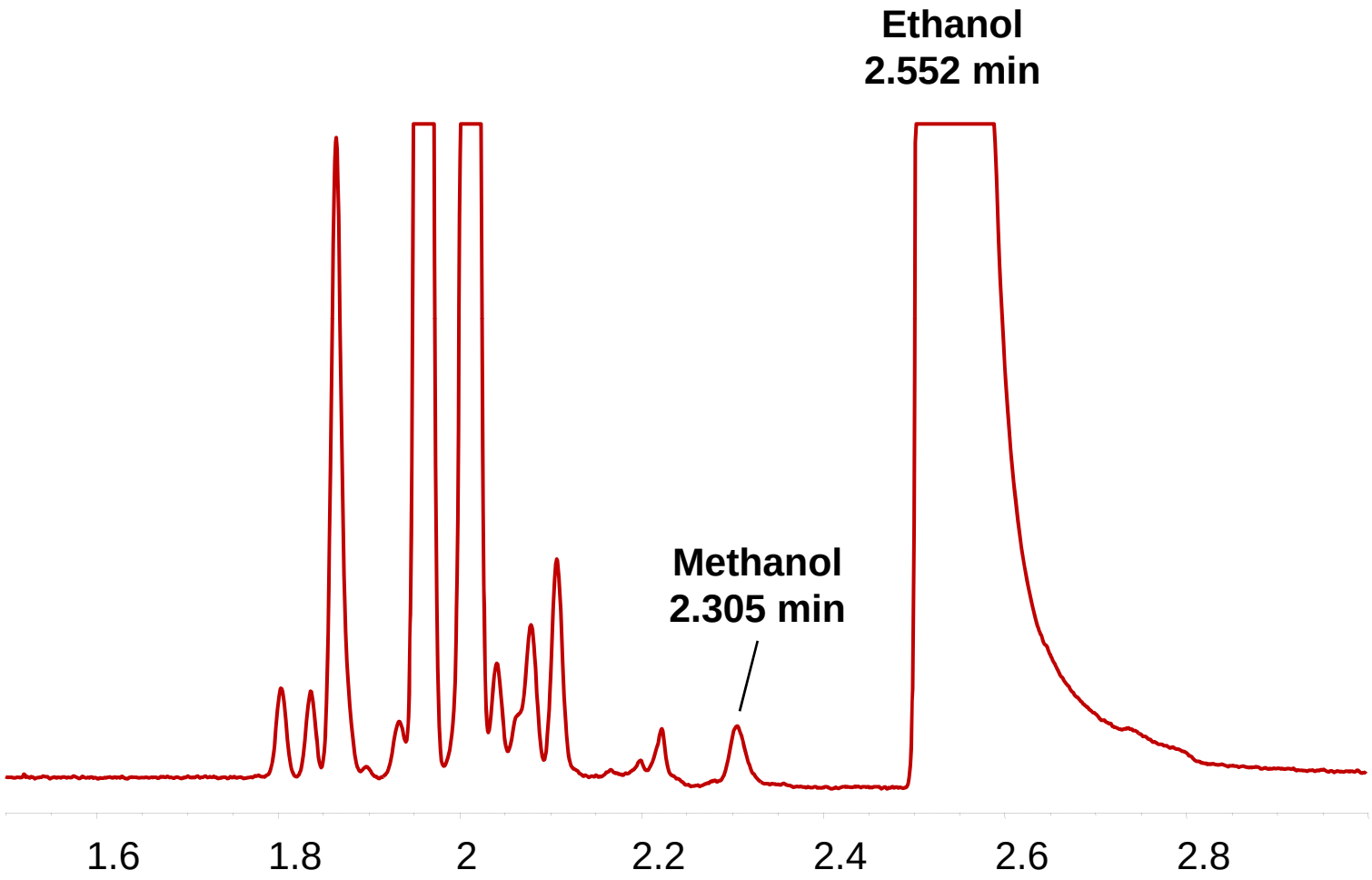
Heart-Cutting 2-D GC Ethanol Fuel Analysis
Methanol and Ethanol Calibrations





Meets ASTM Calibration Specification:
R^2 = 0.99
y-int < 5

Heart-Cutting 2-D GC Ethanol Fuel Analysis
Denatured Fuel Ethanol Sample



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Heart-Cutting 2-D GC Ethanol Fuel Analysis
Denatured Fuel Ethanol Sample Precision

Heart-Cutting 2-D GC

Run	methanol	ethanol
1	0.021	97.882
2	0.021	97.883
3	0.021	97.877
4	0.021	97.878
5	0.021	97.868
6	0.021	97.883
7	0.021	97.878
8	0.020	97.894
9	0.021	97.863
10	0.020	97.877
Avg	**0.021**	**97.878**
STDDEV	**0.000**	**0.008**
RSD	**2.027%**	**0.009%**

D5501 (150m column)

Run	methanol	ethanol
1	0.019	98.006
2	0.019	97.993
3	0.019	97.983
4	0.020	97.992
5	0.020	97.985
6	0.019	98.036
7	0.018	97.998
8	0.019	98.004
9	0.019	98.016
10	0.019	98.022
Avg	**0.019**	**98.004**
STDDEV	**0.001**	**0.017**
RSD	**2.972%**	**0.017%**

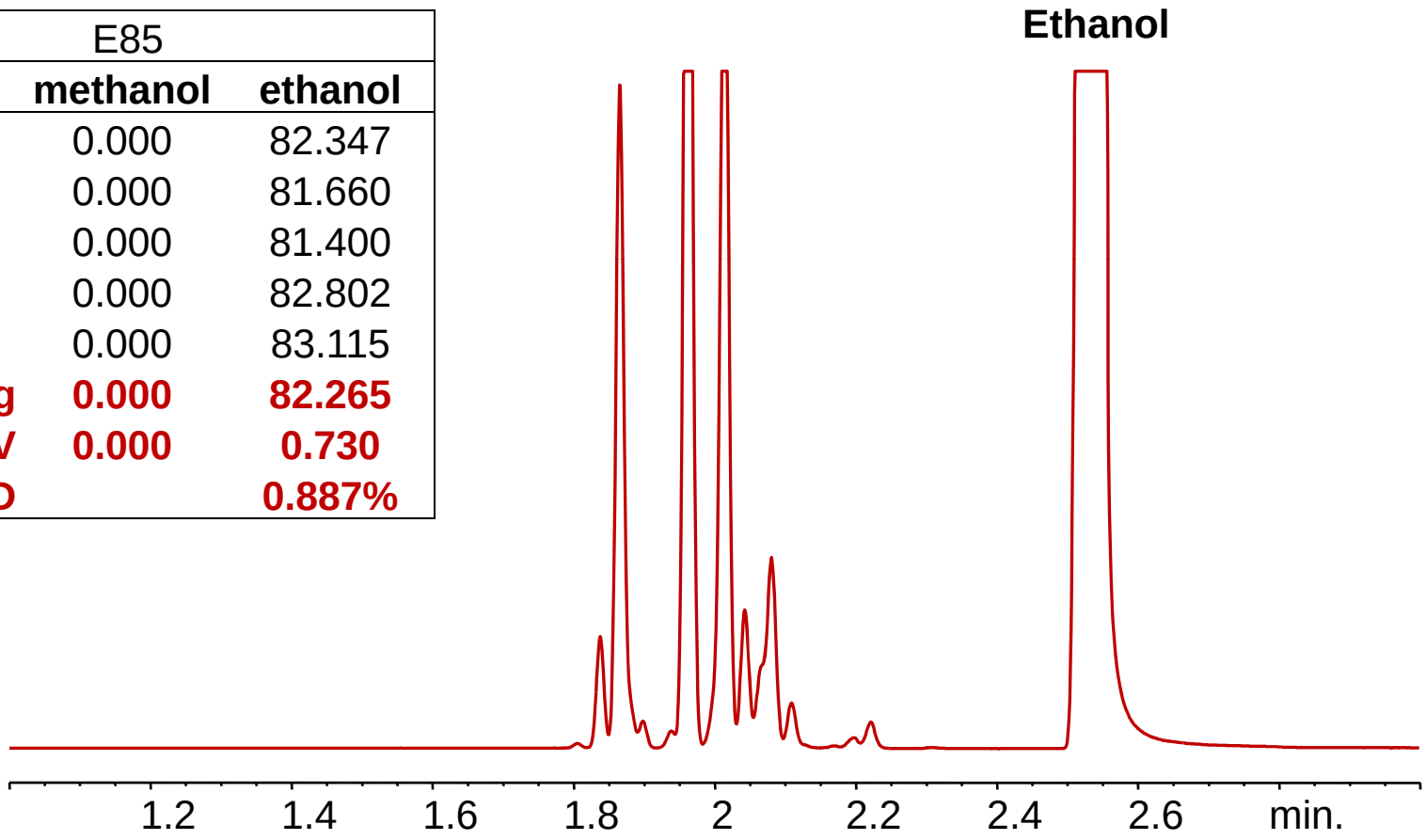
Heart-Cutting 2-D GC Ethanol Fuel Analysis Check Sample Results

Deans Switch

	methanol	**ethanol**	**heptane**
ref	0.3	95.0	4.7
1	0.3	95.1	4.6
2	0.3	95.1	4.6
3	0.3	95.1	4.5
4	0.3	95.1	4.6
5	0.3	95.1	4.6
Avg	0.3	95.1	4.6

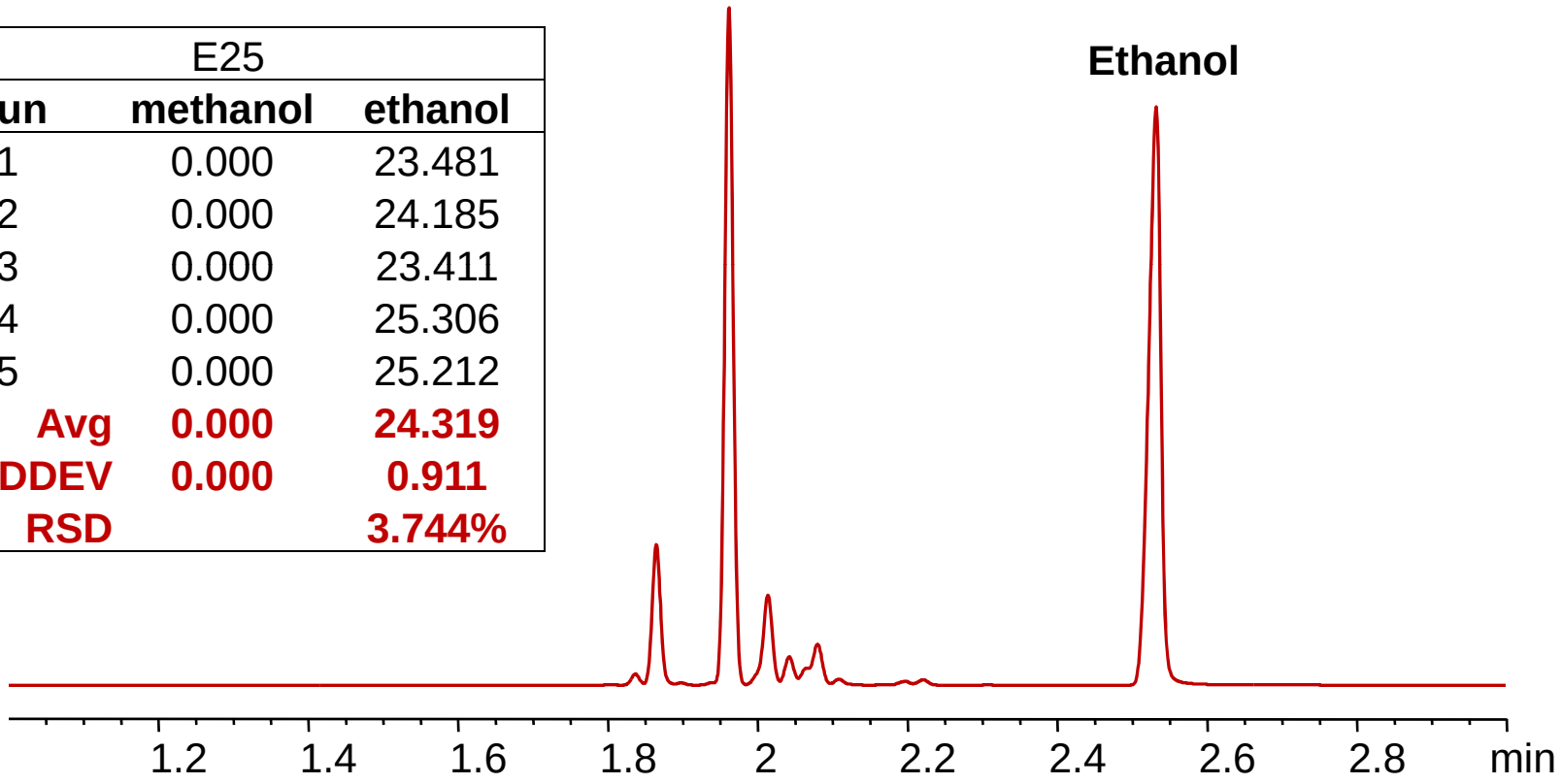
Heart-Cutting 2-D GC Ethanol Fuel Analysis
E85 Fuel Sample

E85		
Run	**methanol**	**ethanol**
1	0.000	82.347
2	0.000	81.660
3	0.000	81.400
4	0.000	82.802
5	0.000	83.115
Avg	**0.000**	**82.265**
STDDEV	**0.000**	**0.730**
RSD		**0.887%**

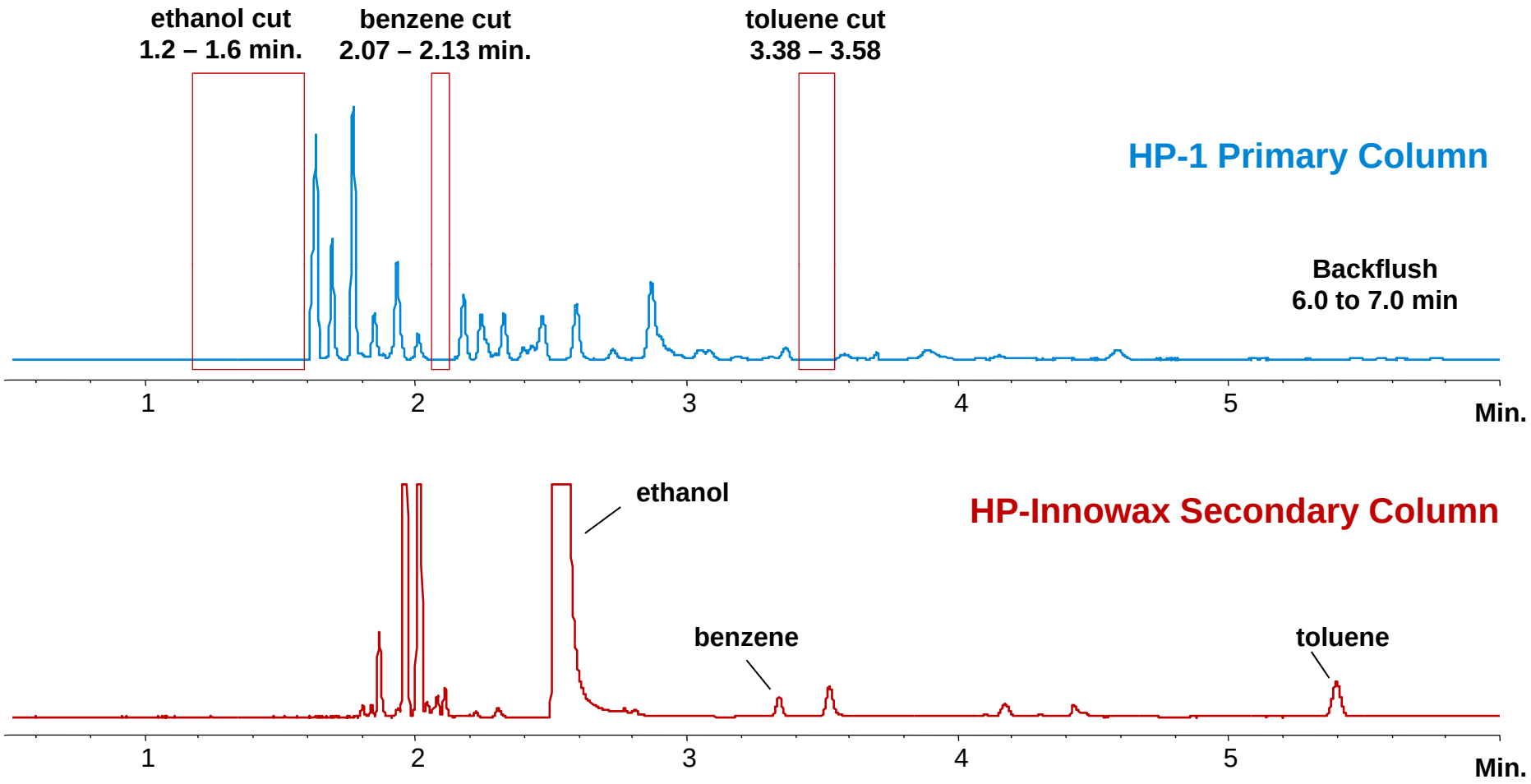


Heart-Cutting 2-D GC Ethanol Fuel Analysis
E25 Fuel Sample

E25		
Run	**methanol**	**ethanol**
1	0.000	23.481
2	0.000	24.185
3	0.000	23.411
4	0.000	25.306
5	0.000	25.212
Avg	**0.000**	**24.319**
STDDEV	**0.000**	**0.911**
RSD		**3.744%**



Expanding Analysis to Include Benzene and Toluene in a Single Run



Expanding Analysis to Include Benzene and Toluene in a Single Run

Denatured Fuel Ethanol				
	methanol	ethanol	benzene	toluene
avg wt%	0.021	97.881	0.006	0.016
RSD	2.794%	0.003%	3.892%	3.677%
E85 Flex Fuel				
	methanol	ethanol	benzene	toluene
avg wt%	<0.010	81.802	0.049	0.246
RSD		0.598%	3.876%	4.016%
E25 Fuel				
	methanol	ethanol	benzene	toluene
avg wt%	< 0.010	23.692	0.330	2.740
RSD		1.807%	2.020%	3.469%

Statistics calculated for 3 consecutive runs for each sample

Summary

- **Improving Speed and Accuracy of Ethanol Fuel Analysis with 2-D GC**
  - Initially developed by Agilent in 2003, now update for the 7890A GC
  - Greater Productivity
    - 7890A backflush capabilities to reduce run time to 3 minutes
  - Can be used to obtain same results as D5501 and the Extended D5501 methods
  - Higher resolution improves methanol accuracy
  - Easily expanded to include benzene and toluene analysis in ethanol fuels

Wrap-up e-Seminar Questions

Thank you for attending today's Agilent e-Seminar.

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