Analysis of Biodiesel and Biodiesel Blends using Capillary Flow Technology

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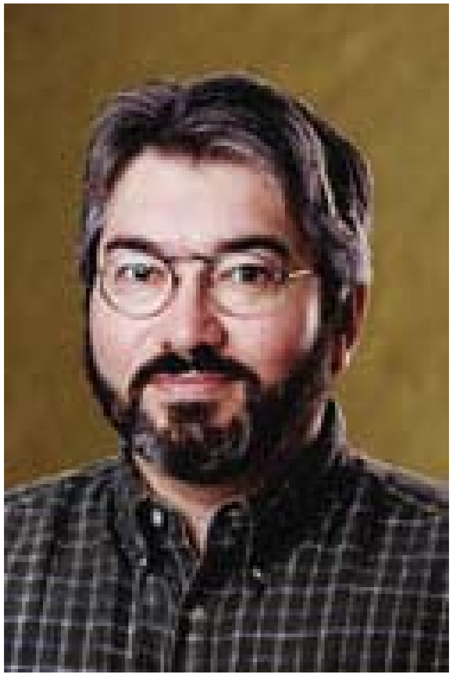
Today's Presenter….



James D. McCurry holds a B.S. in Biochemistry from the University of Scranton and an M.S. and Ph.D. in Chemistry from Lehigh University. In 1980 Jim joined AT&T Bell Laboratories as an organic analytical chemist working in environmental chemistry and process analysis for semiconductor manufacturing. He left Bell Laboratories in 1989 and joined Agilent Technologies as a field applications specialist in gas chromatography and mass spectrometry. In 1997, Jim accepted a position at the Agilent Technologies Little Falls Site as a senior applications chemist specializing in analytical chemistry measurements for the chemical and refining industries. His current work is in multidimensional GC, trace analysis in complex matrices, LC/MS and fast GC and GC/MS. He is a member of the American Chemical Society, the American Society of Mass Spectrometry, and the American Society of Testing and Materials (ASTM)

Biodiesel – What is It?

Biodiesel is a replacement fuel for compression ignition engines.

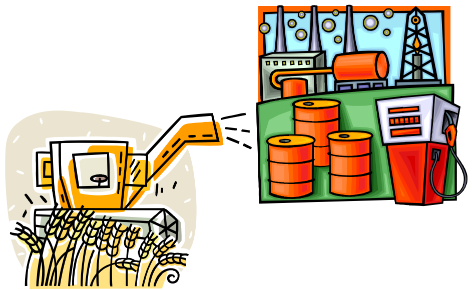
It is GREEN fuel made from renewable, locally sourced plant oils

- **Agricultural: soybean, rapeseed, sunflower seed, palm**

- **Plant oils are chemically processed with methanol**
  - **Fatty acids in oils are converted to fatty acid methyl esters (FAME)**
  - **FAME is pure biodiesel also called B100**

Biodiesel Reduces Emissions

- **Reduced or near zero-net gain in CO_2 emissions**
- **Reduced tailpipe particulate matter (PM), hydrocarbons (HC) and CO**
  - **Biodiesel is a naturally oxygenated fuel**
- **Reduced sulfur gas emissions**



Biodiesel – How is it Made?

Transesterification reaction

Vegetable Oil	Methanol		Biodiesel (FAME)		Glycerin
$CH_2\text{-}OCOR_1$			R_1COOCH_3		$CH_2\text{-}OH$
$CH\text{-}OCOR_2$	$+ 3\ CH_3OH$	$\overset{\text{Basic catalyst}}{\rightleftharpoons}$	R_2COOCH_3	$+$	$CH\text{-}OH$
$CH_2\text{-}OCOR_3$			R_3COOCH_3		$CH_2\text{-}OH$
			<u>Mono-alkyl esters</u>		
			100 parts		11 parts

Biodiesel – Chemical Composition

- Usually contains 6 to 10 major FAME compounds depending on feedstock
- Most common feedstock are geographically sourced
  - The major three feedstocks are:
    - Rapeseed oil (canola) - Europe & North America
    - Soybean oil - North America & China
    - Palm oil – Southeast Asia
  - Other “tropical oils”
    - Palm kernal and coconut oils are abundant
    - Complexity makes it difficult to measure product quality

	Weight Percent Fatty Acid											
Oil Type	**C8:0**	**C10:0**	**C12:0**	**C14:0**	**C16:0**	**C16:1**	**C18:0**	**C18:1**	**C18:2**	**C18:3**	**C20:0 C22:0**	**C20:1 C22:1**
Rapeseed					2-5	0.2	1-2	10-15	10-20	5-10	0.9	50-60
Soybean				0.3	7-11	0-1	3-6	22-34	50-60	2-10	5-10	
Palm				1-6	32-47		1-6	40-52	2-11			
Palm Kernal	2-4	3-7	44-51	14-19	6-9	0-1	1-3	10-18	1-2		1-2	
Coconut	5-9	4-10	45-52	13-18	7-10		1-4	5-8	1-3			

*K. Shaine Tyson, ”Biodiesel Handling and Use Guidelines”,National Renewable Energy Laboratory, NREL/TP-580-30004, September 2001

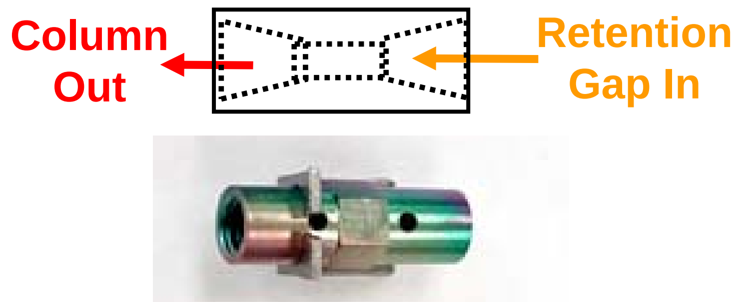
Challenges for Analysis of Biodiesel and Biodiesel Blends

- **ASTM D6584/ EN 14105 – Free and Total Glycerins**
  - High amounts of glycerins cause engine fouling
  - Difficult analysis to run
    - challenging sample and standard preparation
    - on-column injection
    - many interferences from large FAMEs peaks in samples
      - not suitable for B100 from tropical oils (coconut, palm kernel)
- **Analysis of Biodiesel Blends**
  - biodiesel blended into petroleum diesel from 2 to 20 vol% (B2 to B20)

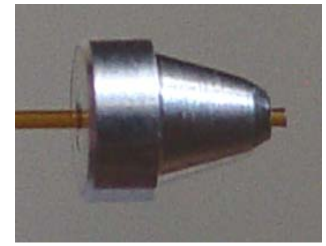
EN14105/ASTM D6584 - Retention Gap Advantages Using Capillary Flow Technology

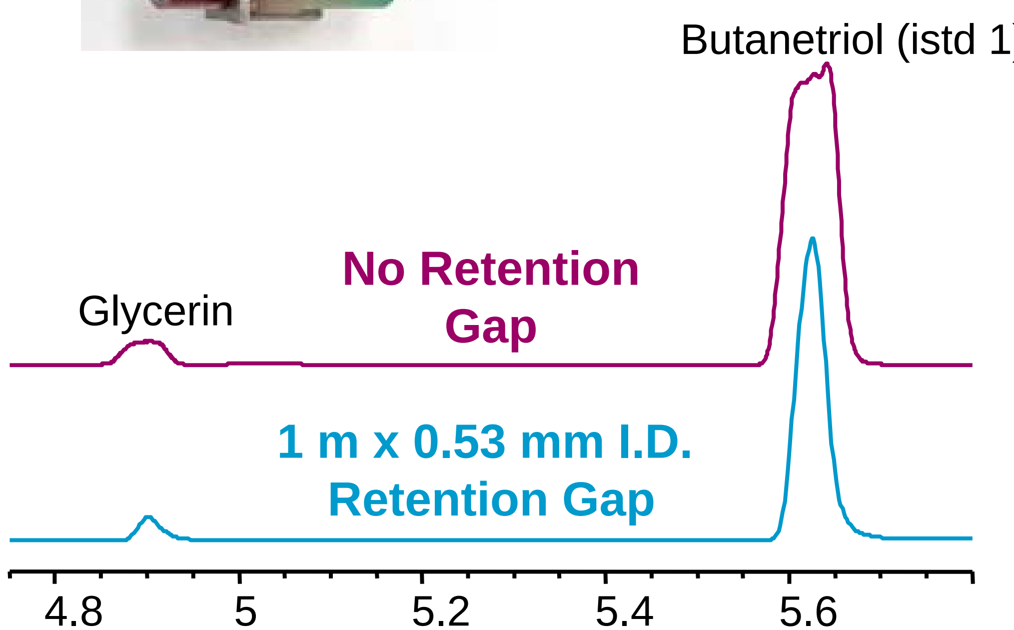
- Use 1 to 5 m, 0.53 mm ID deactivated fused silica tubing
- Improves peak shape
- Ultimate Union
  - easy, robust connection
  - deactivated
  - no-leak metal ferrule
  - optimized for high temperatures

Capillary Flow Technology Ultimate Union

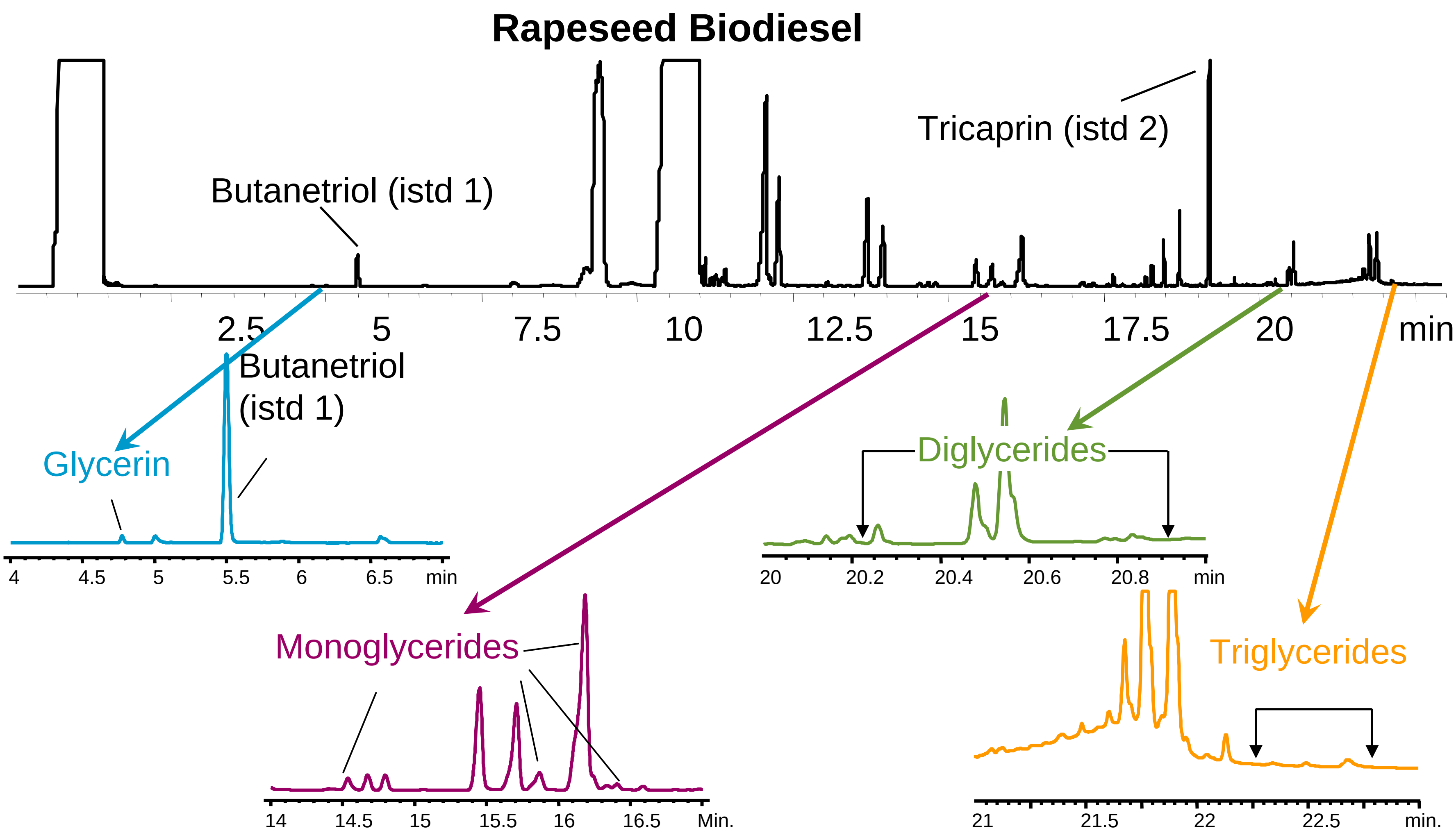


Inert, High Temp Metal Ferrule





ASTM D6584/EN 14015
Free and Total Glycerin Analysis of Biodiesel



ASTM D6584/EN 14105 – Repeatability Results

Exceeds Standard Method's Specification

	EN14105 Spec %(m/m)	Observed %(m/m)			
		Day 1	Day 2	Day 3	Day 4
Free glycerin	0.0015	0.0000	0.0000	0.0000	0.0000
Monoglycerides	0.048	0.007	0.000	0.006	0.000
Diglycerides	0.019	0.003	0.002	0.000	0.001
Triglycerides	0.0069	0.0002	0.0003	0.0001	0.0001
Totol glycerin	0.0135	0.0016	0.0002	0.0014	0.0002

	Amount Found %(m/m) in Rapeseed Oil Biodiesel						
	Day 1 (avg)*	Day 2 (avg)*	Day 3 (avg)*	Day 4 (avg)*	Total Avg	Stdev	RSD%
Free glycerin	0.002	0.002	0.002	0.002	0.002	0.000	2.428
Monoglycerides	0.365	0.375	0.370	0.371	0.370	0.004	1.091
Diglycerides	0.256	0.262	0.256	0.256	0.257	0.003	1.110
Triglycerides	0.021	0.019	0.018	0.016	0.019	0.002	11.218
Total glycerin	0.137	0.140	0.137	0.137	0.138	0.001	1.024

EN14331- Separation & Characterization of FAME from Middle Distillate Fuels

Difficult method to run because:

- The biodiesel blend is first physically separated on a silica column
- Petroleum diesel fraction is eluted with hexane and discharged
- Biodiesel fraction is eluted with diethyl ether and analyzed by GC
- Can only be used with B5 (5%) or lower blends

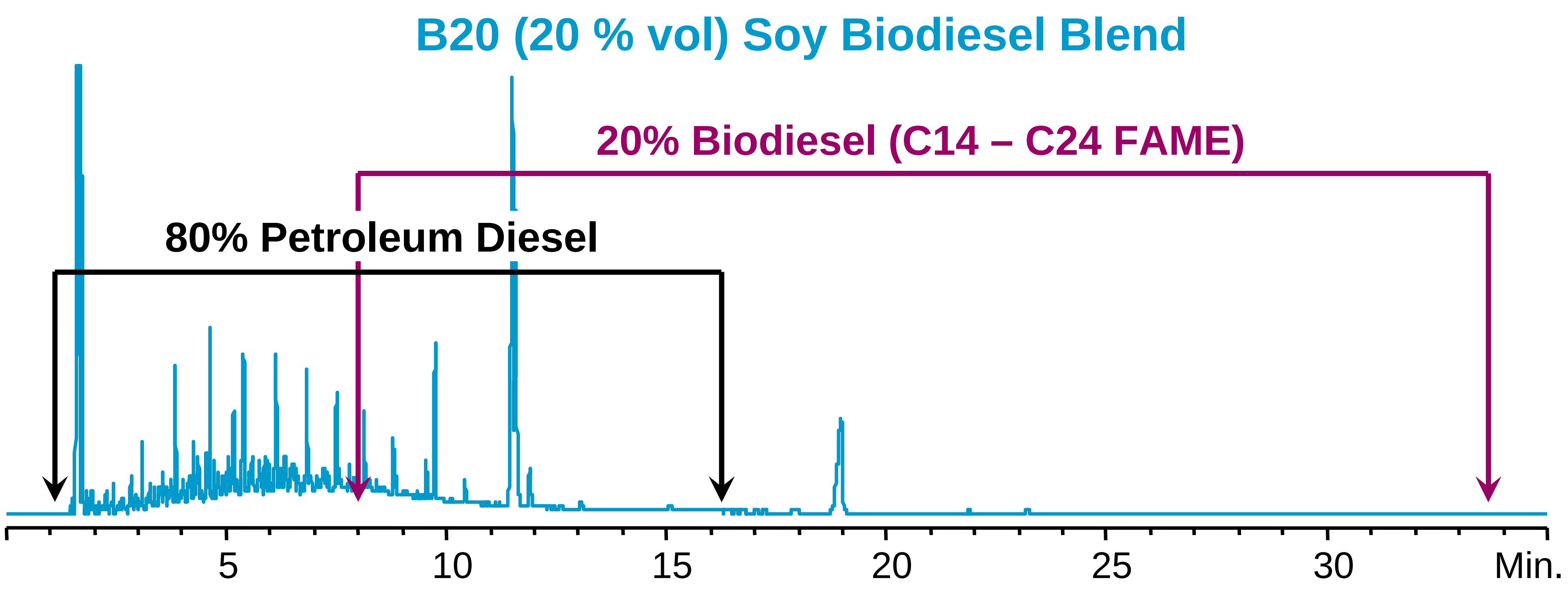
Increasing demand for higher level biodiesel blends (B20, etc) calls for a faster, easier analysis solution

The Problem with GC Analysis of Biodiesel Blends

Customers need to know:

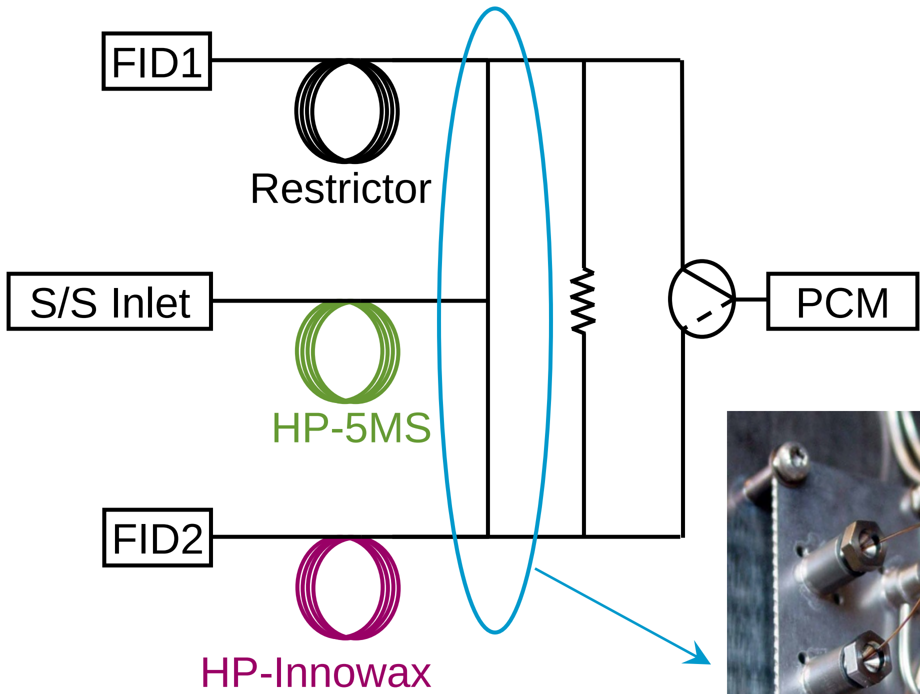
1. How much biodiesel is in the blend
2. What FAME compounds are in the blend

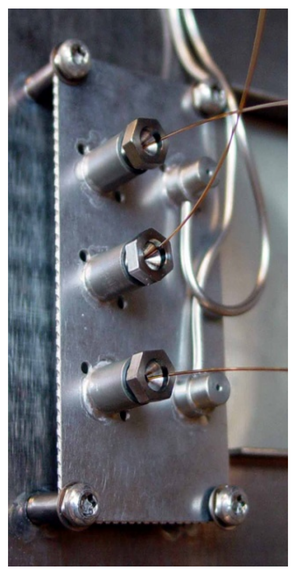
But no single column can separated the biodiesel from the petroleum diesel



Deans Switch for 2-D Heart Cutting GC

Capillary Flow Technology
Deans Switch





Eliminated complicated and costly sample prep

- no silica column preparation
- fewer consumable costs – silica columns, solvents

Faster, easier analysis

- 10 mg/mL ISTD solution of C21:0 in heptane
- add 5 ml ISTD to 250 mg sample
- B2 to B25 cal. stds prepared in No.2 diesel fuel

Employs the latest developments in GC

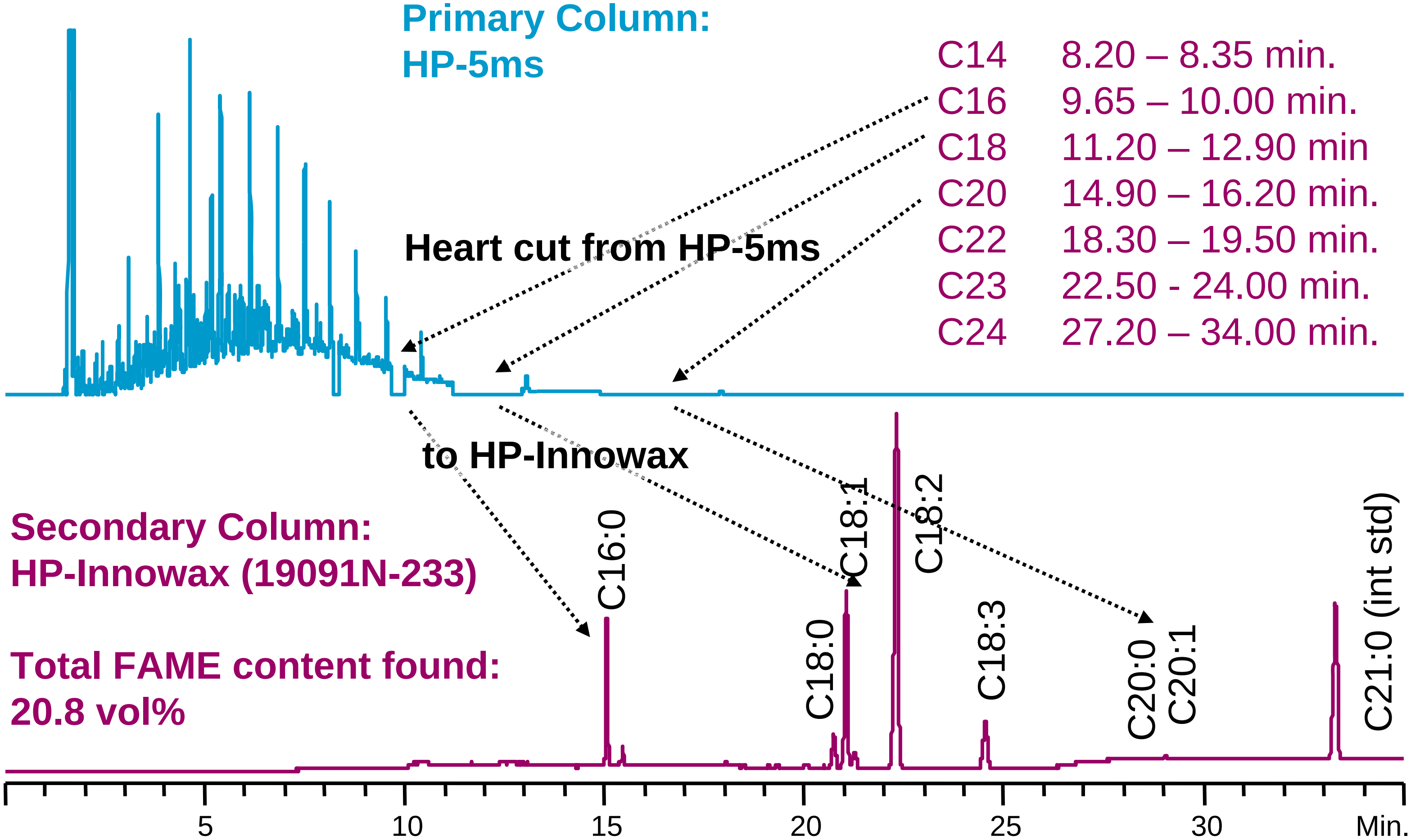
- heart-cutting 2-D GC becoming a widely used tool

Biodiesel Blend Analysis Using Heart-Cutting 2-D GC

Instrument Conditions:

- Inlet: split/splitless at 250 °C; 200:1 split ratio
- Injection: 0.5 uL
- Column 1: HP-5ms, 15m x 0.25mm ID x 0.1um (19091S-331)
  - Col1 Flow: 1.5 mL/min helium
- Column 2: HP-Innowax, 30m x 0.25mm ID x 0.5um (19091N-233)
  - Col2 Flow: 3.5 mL/min helium
- Oven temperature program: 50 °C for 0 min
  20 °C /min to 210 °C, 210 °C for 18 min
  20 °C /min to 230 °C, 230 °C for 13 min|
- Detectors: dual flame ionization at 300 °C

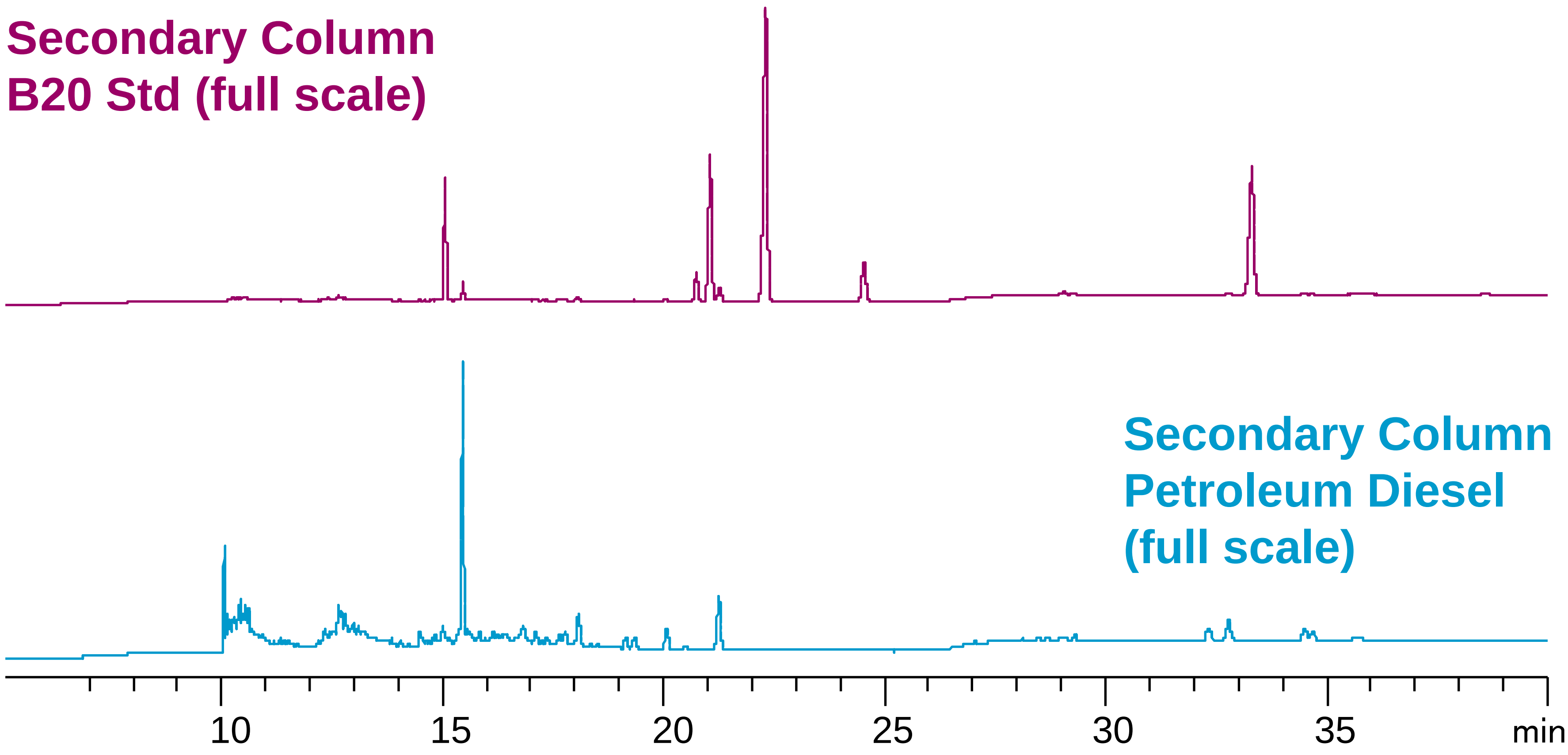
Analysis of a Commercial B20 Biodiesel Blend Using Heart-Cutting 2-D GC



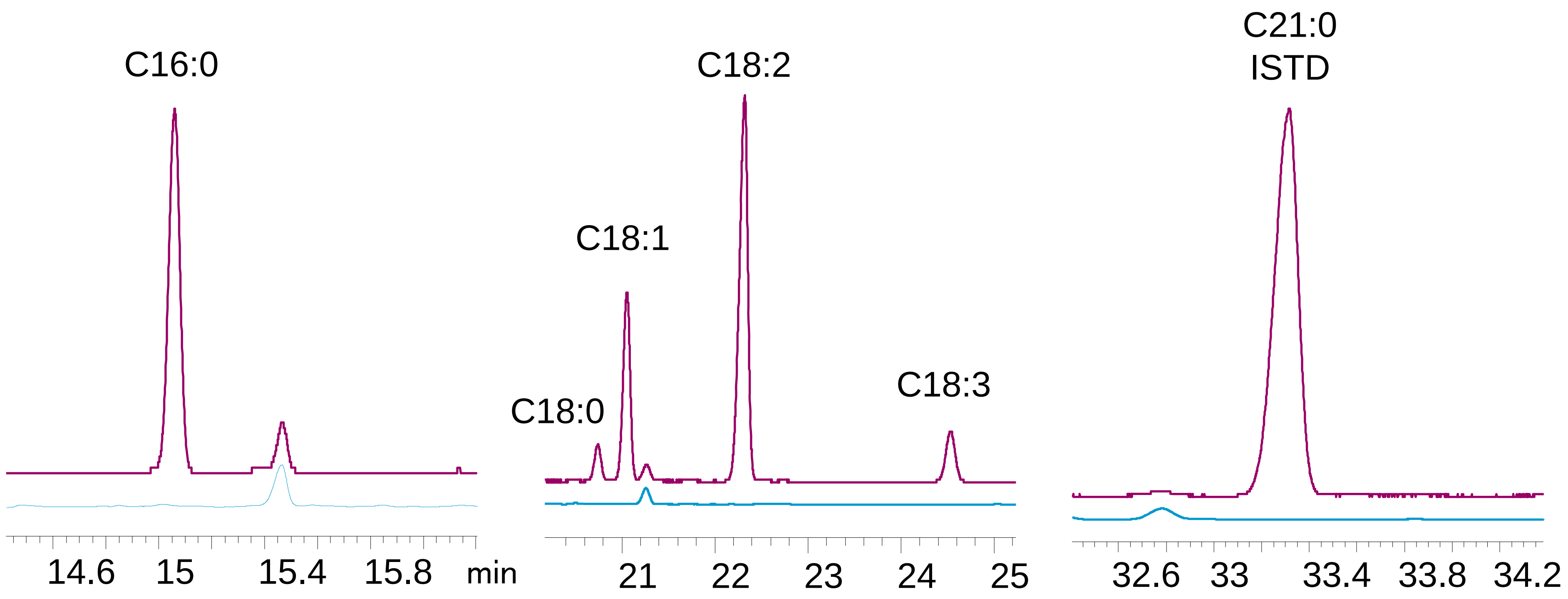
Cut times for FAMES

C14	8.20 – 8.35 min.
C16	9.65 – 10.00 min.
C18	11.20 – 12.90 min
C20	14.90 – 16.20 min.
C22	18.30 – 19.50 min.
C23	22.50 - 24.00 min.
C24	27.20 – 34.00 min.

Evaluation of Matrix (hydrocarbon) Interference

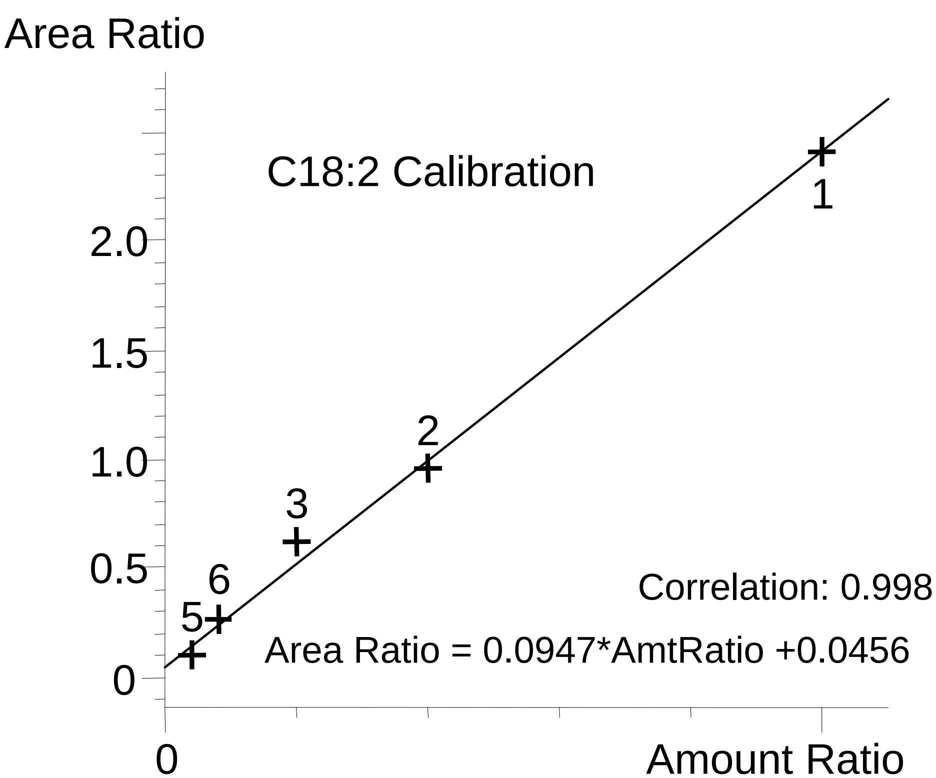


No Matrix Interference for C16 and C18 FAMES



2-D Deans Switch GC for Biodiesel Blends

Calibration Performance and Quantitiative Precision



	Vol %	
Run	**ESTD**	**ISTD**
1	20.3	21.1
2	20.8	21.1
3	21.0	21.2
4	21.6	21.1
5	21.6	21.1
Avg	21.1	21.1
Stdev	0.55	0.04
% RSD	2.63%	0.21%

2-D Deans Switch GC for Biodiesel Blends

Provides Detailed Information on FAME Distribution in Biodiesel Blends

	Mass Fraction of FAME in B20 Biodiesel Blend						
Run	**C16:0**	**C18:0**	**C18:1**	**C18:2**	**C18:3**	**C20:0**	**C20:1**
Avg	**11.16**	**4.02**	**21.79**	**53.32**	**7.61**	**1.48**	**0.64**
Stdev	0.02	0.01	0.01	0.04	0.01	0.04	0.01
% RSD	0.16%	0.18%	0.06%	0.07%	0.13%	2.69%	2.12%
% in Soy	**7-11**	**3-6**	**22-34**	**50-60**	**2-10**	**5-10**	

Exceeds EN14331 Specification for Repeatability

	Repeatability (% m/m)	
FAME	**EN14331 spec**	**2-D GC**
C16:0	0.50	0.03
C18:1	0.60	0.06
C18:3	0.40	0.02

Summary

Heart-cutting 2-D GC Can Separate and Quantify FAMES in Biodiesel Blends

- **Capillary Flow Technology Deans switch system heart cuts C16 to C22 FAMES from HP-5MS to HP-Innowax column**
- **Secondary Innowax column separates hydrocarbon matrix from FAME**
- **Combination of HP-5MS and Innowax column separates individual FAME to identify biodiesel source (soybean oil)**
- **More work needed for other types of biodiesel blends (rapeseed, palm, etc)**

Eliminate Complex and Costly Sample Preparation

- **Addition of ISTD is the only sample preparation**
- **B2 to B25 calibration standards prepared in No. 2 diesel**