Improving Productivity for the GC Analysis of Biodiesel

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

5-in-1 Biodiesel Analyzer and Automated Sample Preparation

- Biodiesel GC Analysis Overview
- Problems faced by biodiesel QA/QC labs
- Unique 7890A 2-column oven solution
- Design criteria
- Performance of 5-in-1 Biodiesel Analyzer
- Automated biodiesel sample prep with the Agilent 7693A ALS

Improving Productivity for the GC Analysis of Biodiesel

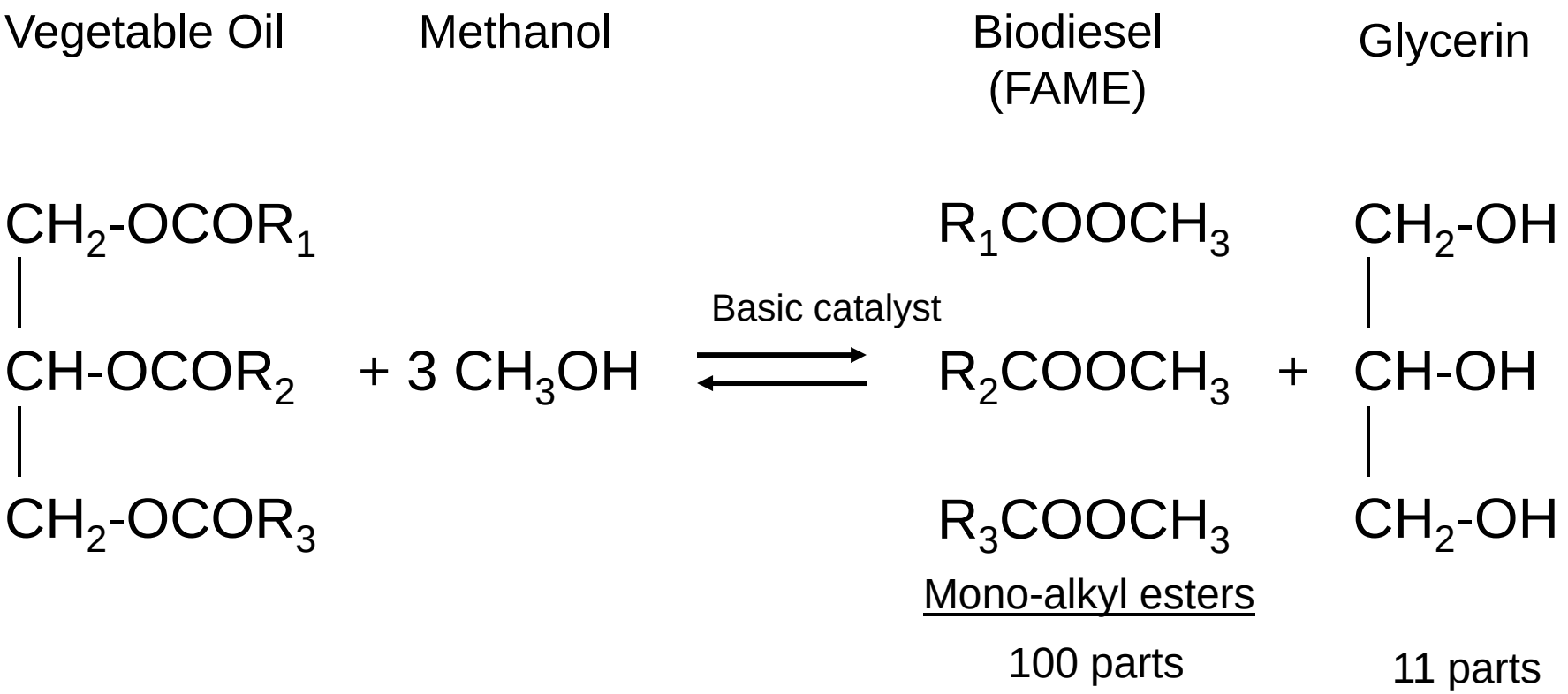
GC Analysis of B100 Quality

- Expand the capabilities of the GC instrument
  - combining multiple methods onto a single platform
- Automation of sample preparation
  - reduce time and effort required for manual techniques

GC Analysis of Biodiesel Blends

- Use MDGC techniques to reduce hydrocarbon interference
  - capillary flow technology Deans switch
- Use less complex sample preparation
  - eliminate time consuming sample clean-up prior to GC analysis

Biodiesel Production
3 Step Trans-Esterification Reaction



Common Trans-Esterification By-products and Contaminates Found in Biodiodiesel

- Glycerols
  - Unseparated glycerin
  - Intermediate glycerols (mono-, diacyl-)
    - Partially reacted vegetable oils
  - Unreacted triacylglycerols (vegetable oil)
- Residual Methanol
- Fatty Acids
- Catalysts

GC Methods Used to Measure B100 Quality

- **Methods Developed for Biodiesel from Rapeseed, Soybean, Palm and Sunflower Oils**
  - will not work for palm kernel and coconut oil biodiesel
- **EN14105 and ASTM D6584** Determination of Free and Total Glycerin and Mono-, Di-, Triglyceride Content
  - high glycerin content can cause engine fouling
  - low glycerin levels indicates
- **EN14103** Determination of Ester and Linolenic Acid Methyl Ester Content
  - determine minimum total FAME content and maximum linolenic FAME (C18:3) content
- **EN14110** Determination of Methanol Content
  - high methanol content can raise vapor pressure
  - high methanol content can cause higher flammability
- **EN14106** Determination of Free Glycerol
  - not a commonly used method
  - EN14105/ASTM D6584 provides more complete result
  - May be written into some contracts for product specifications

GC Methods Used to Measure B100 Quality

Method	Scope	GC Column	Column Temperature	Inlet/Detector
ASTM D6584	Analysis of Free and Total Glycerin	High Temp 5% Phenyl/methyl Siloxane	Temperature progammed 50 °C to 380 °C	Cool-on-column/FID
EN14105	Analysis of Free and Total Glycerin	High Temp 5% Phenyl/methyl Siloxane	Temperature progammed 50 °C to 380 °C	Cool-on-column/FID
EN14103	Ester and Linoleic Acid Methyl Ester Content	PEG	Isothermal 200 °C or 210 °C	Split-splitless/FID
EN14110	Residual Methanol Content by Headspace	PEG	Isothermal 60 °C	Split-splitless/FID
EN14106	Determination of Free Glycerol	PEG	Isothermal 200 °C	Split-splitless/FID

Problems with Running Multiple GC Analyses of Biodiesel

High temperature methods not compatible with other methods

- ASTM D6584 and EN14105 requires high temperature column (380 deg C)
- EN14103, EN14106, EN14110 use PEG column (260 deg C max)
  - PEG column cannot be in the same oven as high temp column

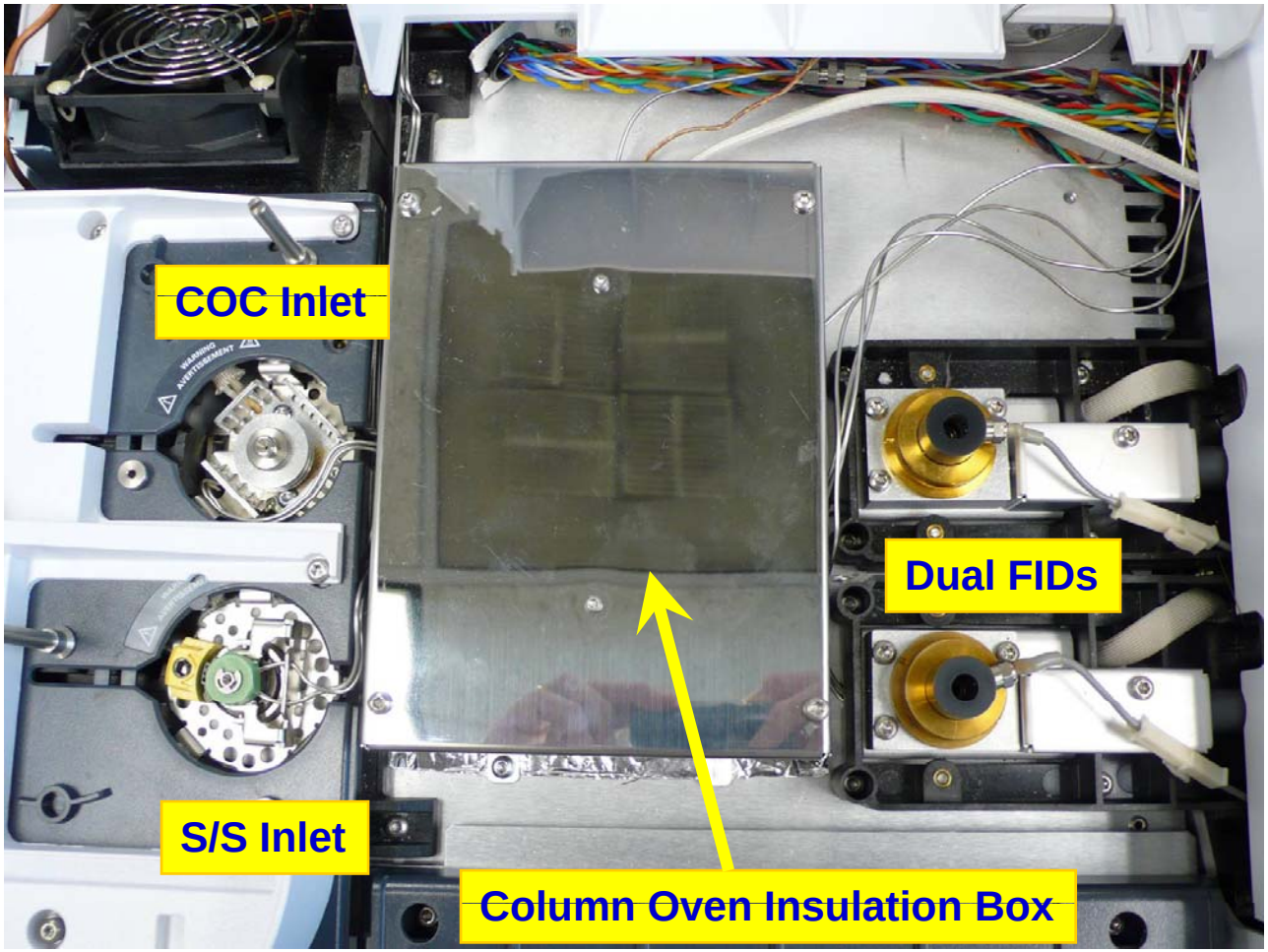
- Running multiple methods can be expensive:
  - customers must buy 2 GCs
- Running multiple methods can be less efficient:
  - reconfigure a single GC when changing methods

Thermally Isolate PEG Column From High Temperature Column Oven

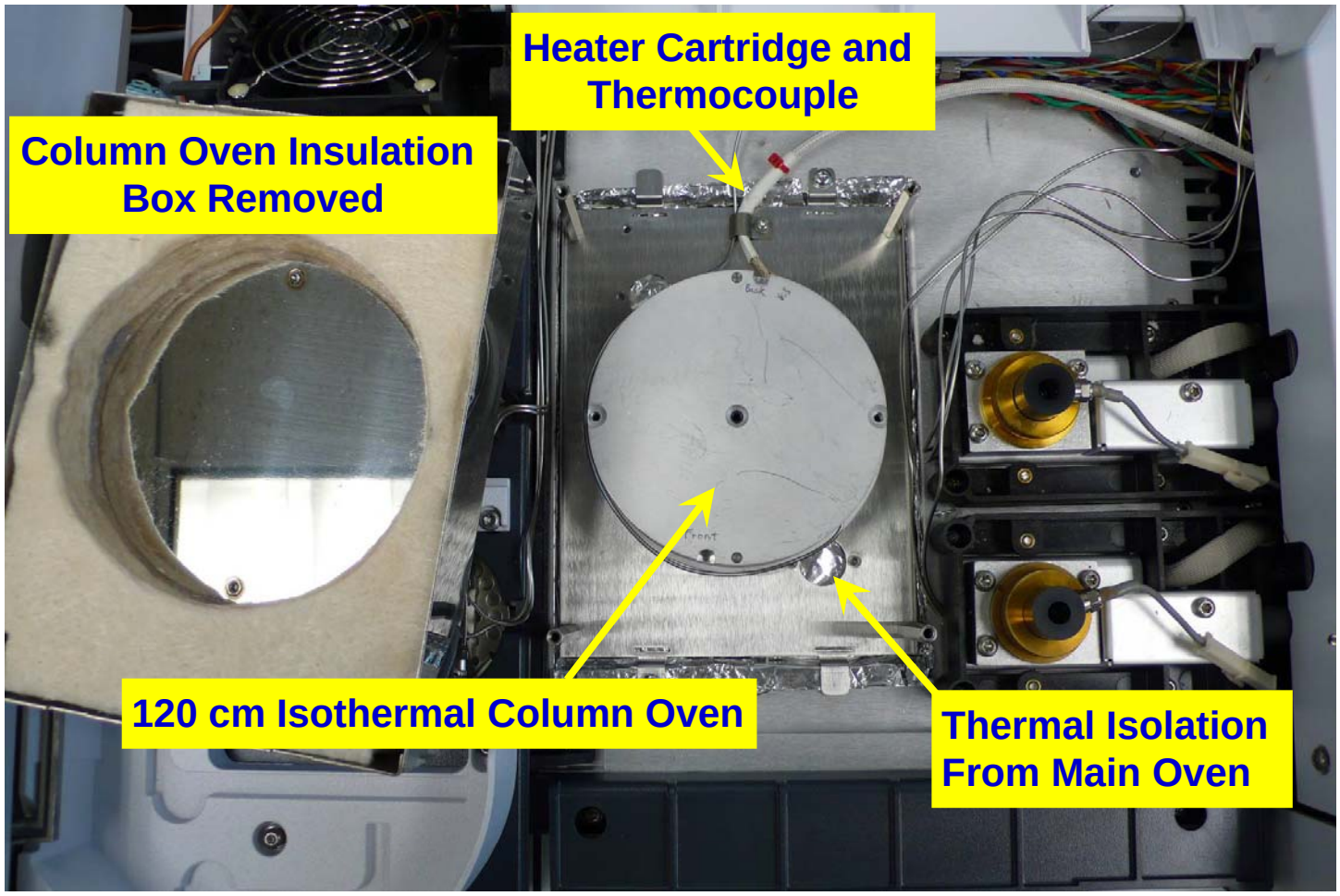
Design Criteria:

- PEG column methods are all isothermal
  - FAME Content (EN14103): 210 deg C for 30 minutes
  - Residual Methanol (EN14110): 60 deg C for 10 minutes
  - Free Glycerol (EN14106): 210 deg C for 10 minutes
- External, isothermal column oven mounted on top of 7890A
  - must accommodate 30 m x 0.32 mm column on 120 mm diameter
  - Need new column cage design
  - must not exceed 260 deg C when main oven is >380 deg C
  - Use Capillary Flow Technology:
    - Join column to stainless steel tubing from inlet and detector
    - Provide backflush capability to PEG column

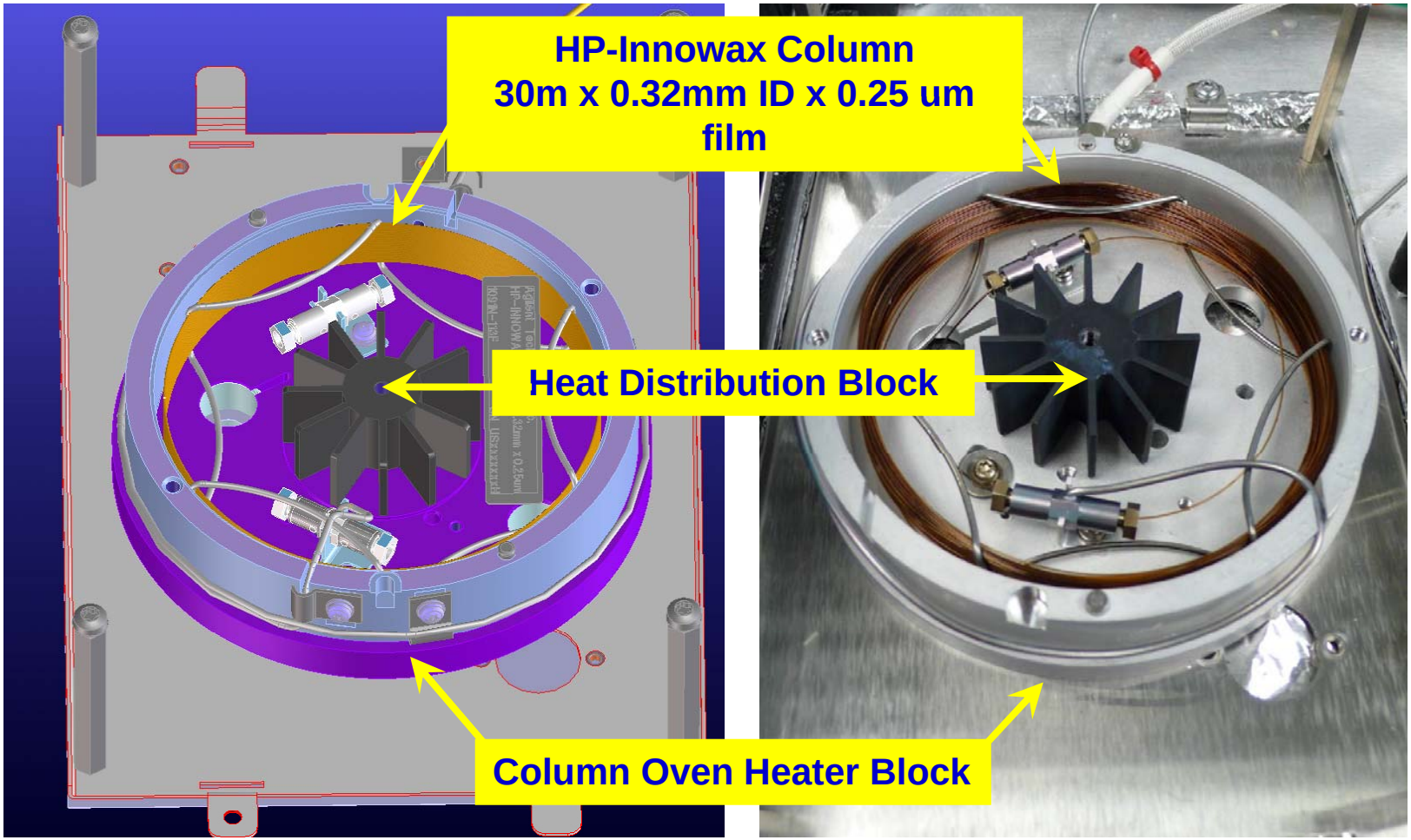
7890A External Capillary Column Oven
Mounted on valve cut-out



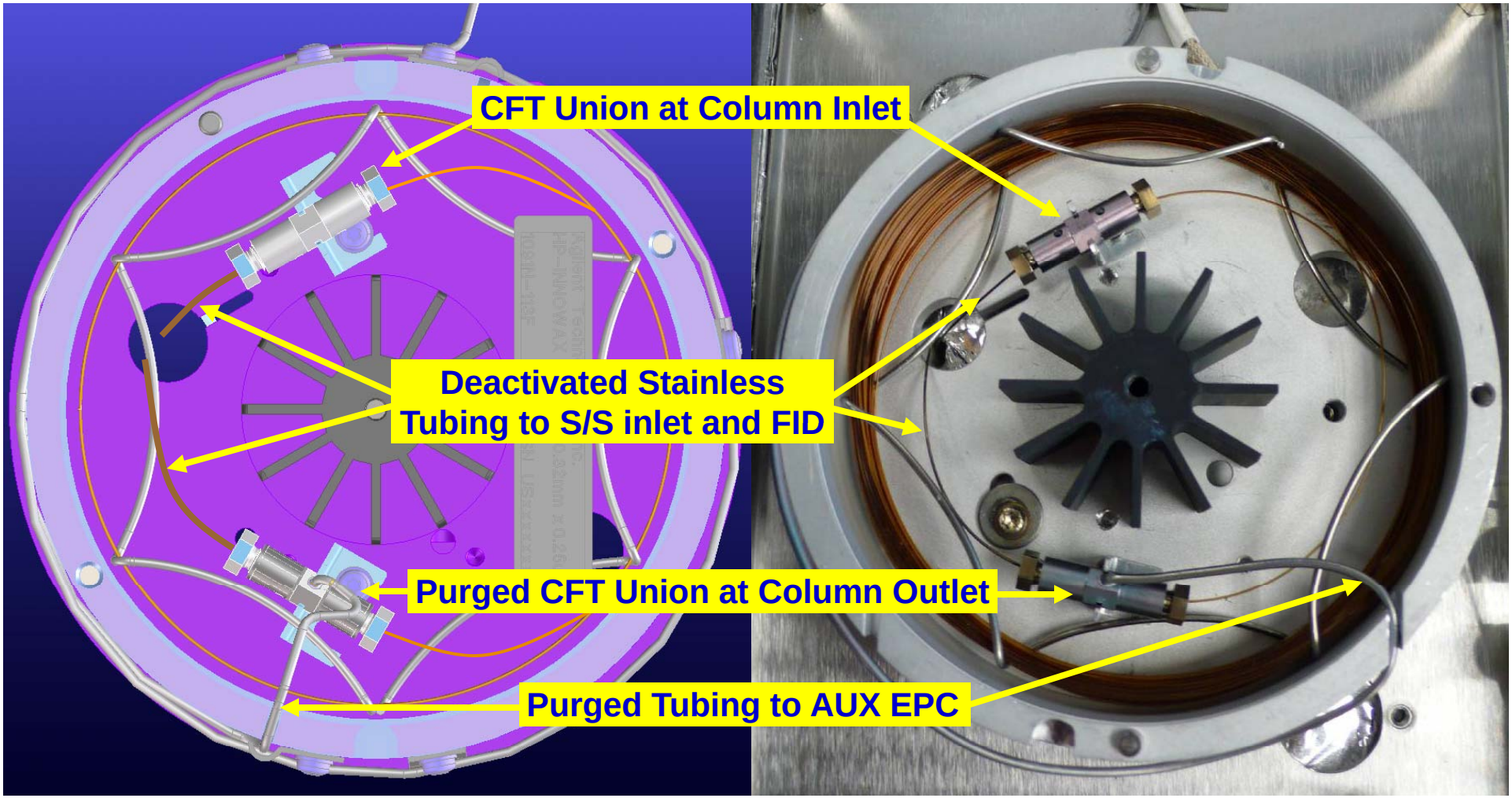
7890A External Capillary Column Oven



7890A External Capillary Column Oven Cover Removed



7890A External Capillary Column Oven Detailed View



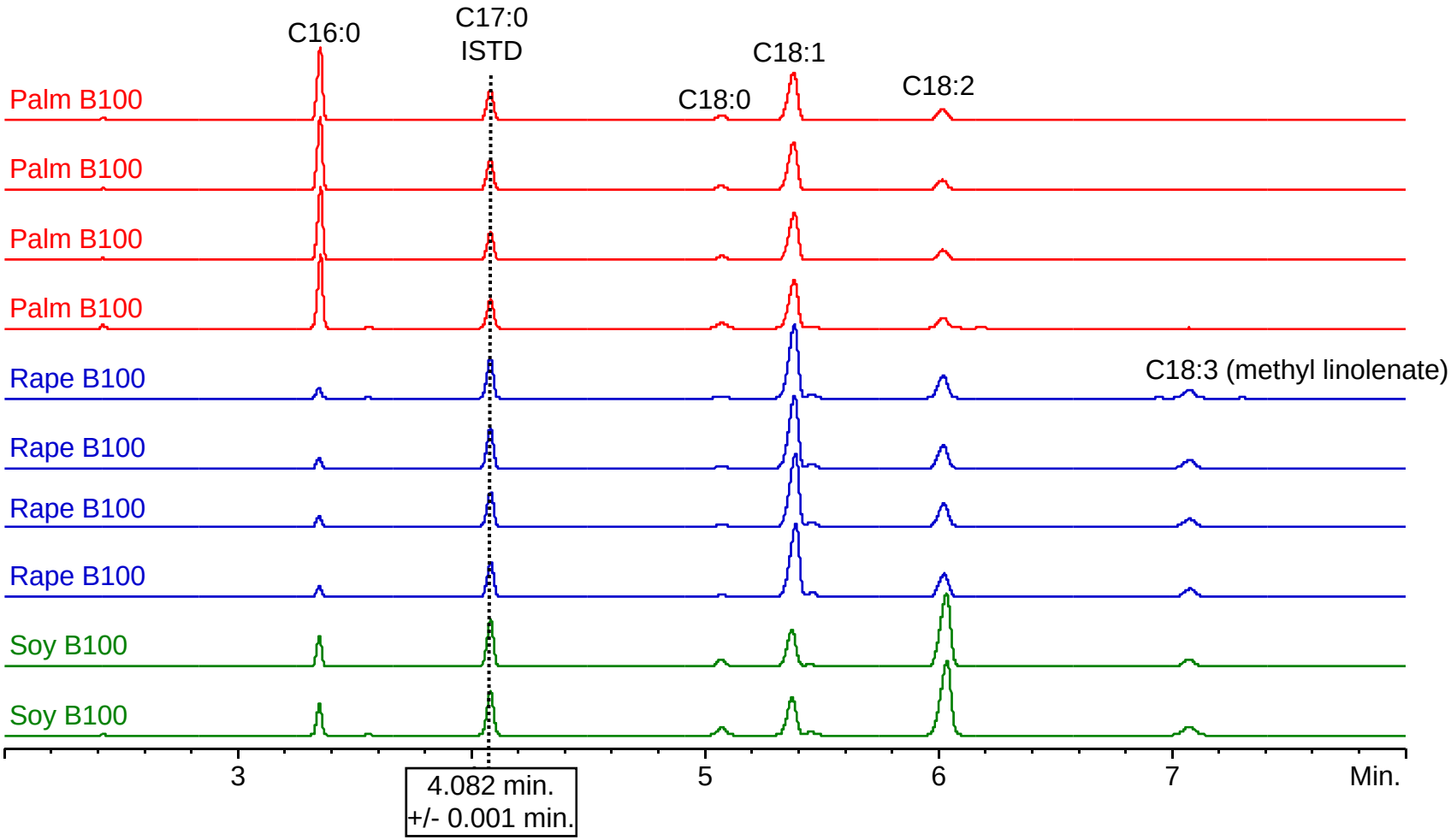
7890A External Capillary Column Oven

Evaluating external column oven performance

- Thermal isolation from main column oven
  - Run ASTM D6584 temperature program for 24 hours:
    - 50 °C 1 min, 15 °C /min to 180 °C, 7 °C/min to 230 °C, 30 °C/min to 380 °C, hold 10 min.
    - External capillary column oven temperature never exceeds 190 °C
- Oven temperature precision
  - Run ten B100 samples using EN14103
  - Measured internal air temperature over 24 hours: 210 °C +/- 0.1 °C
  - Measure C17:0 (ISTD) retention time over ten runs
  - C17:0 retention time; 4.082 min., +/- 0.001 min.

7890A External Capillary Column Oven

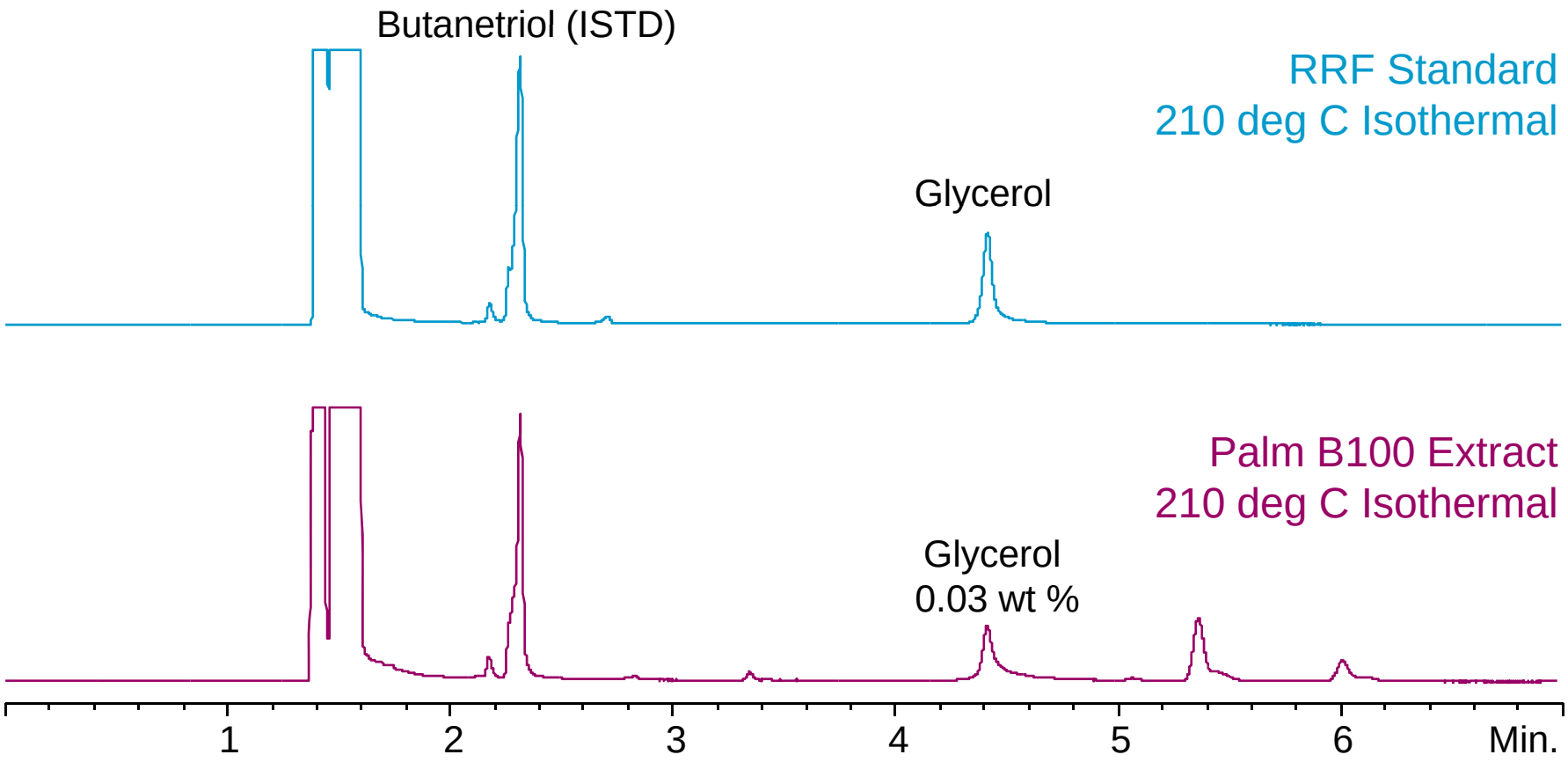
EN14103 – Ester and Linolenic Acid Methyl Ester



Precise Oven Temperature Control Provides Precise Retention Times

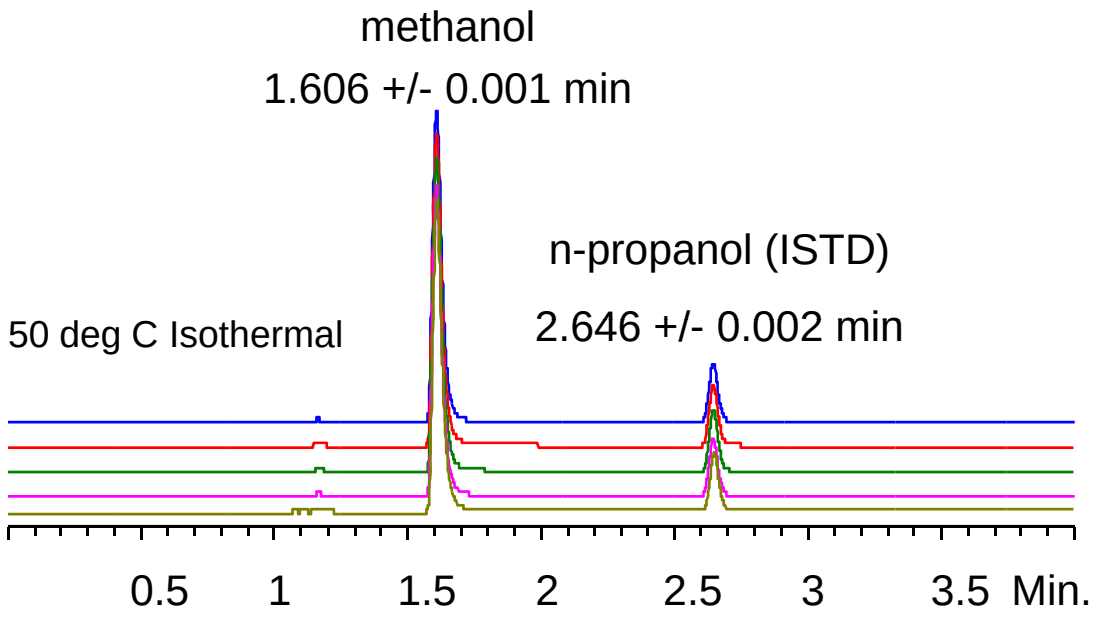
7890A External Capillary Column Oven

EN14106 – Analysis of Free Glycerol



7890A External Capillary Column Oven

EN14110 – Determination of Methanol Content



Methanol retention time standard using
10 uL ambient headspace injection

Break for Questions

7693ALS/7890A GC
Automating Biodiesel Sample Preparation

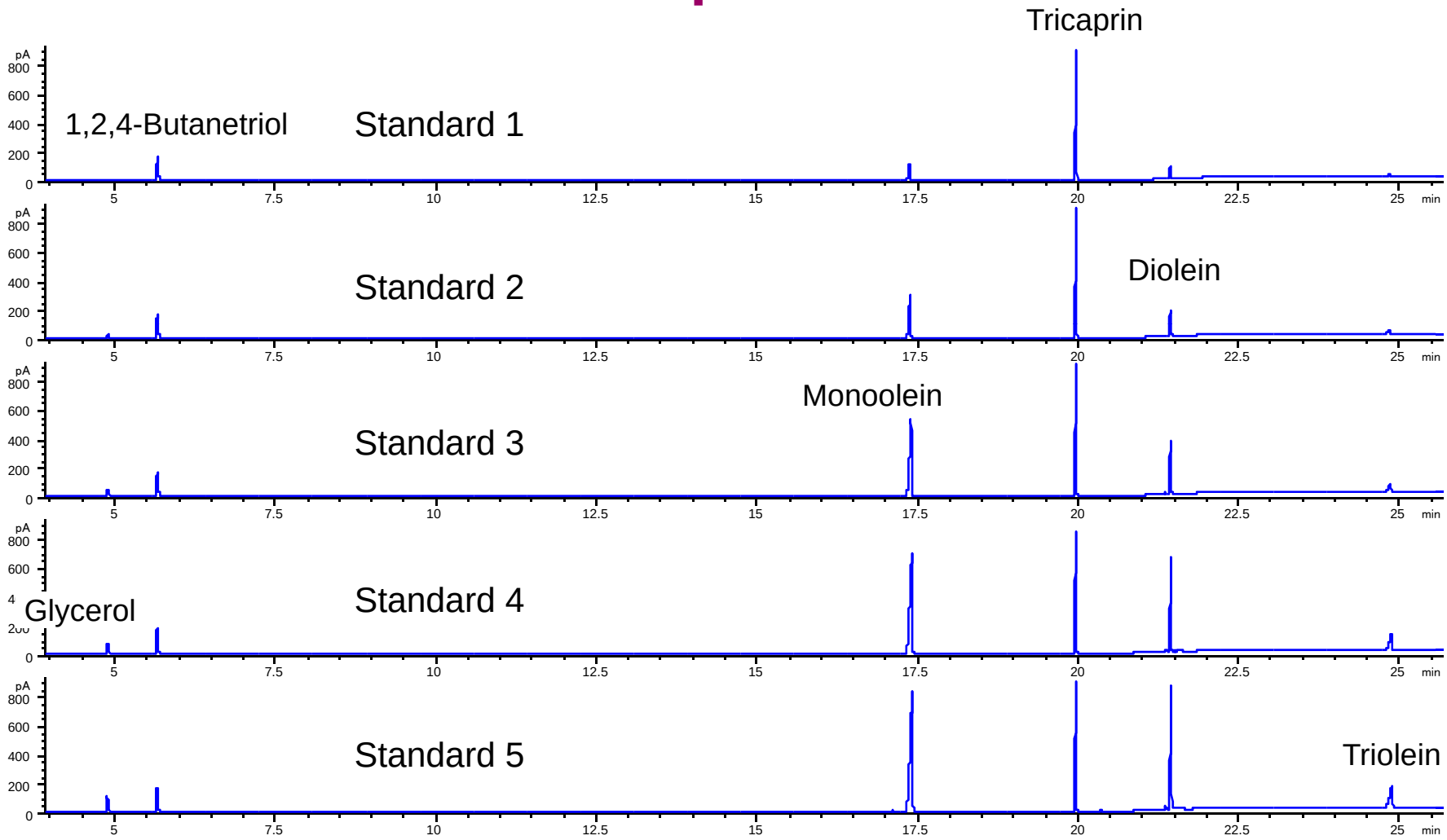
7693A ALS Provides Automated Sample Preparation

- Productivity tool for complex and time consuming Biodiesel GC methods
- Reduces the amount of expensive standards
- Reduce exposure to toxic reagents
- Create “transportable” GC methods with sample and standard preparation

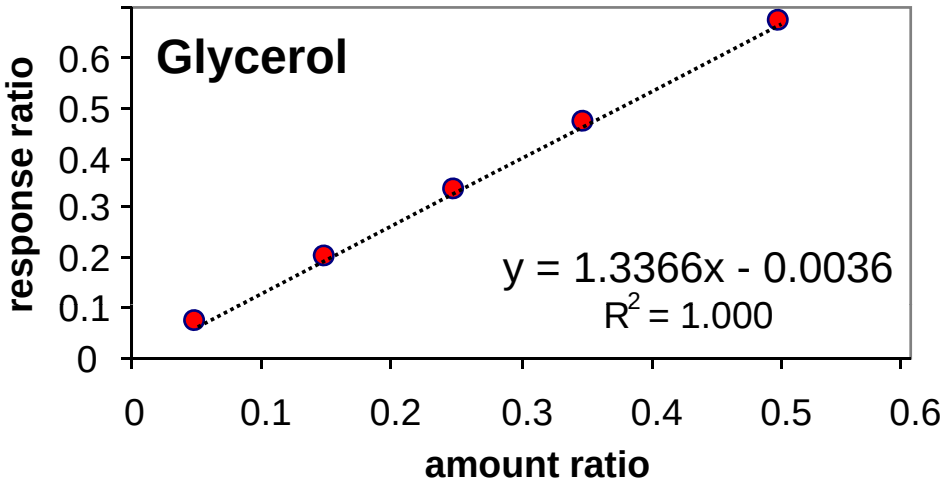
D6584 Analysis of Total Glycerin in Biodiesel
10% Scaled Automated Standard Preparation Steps

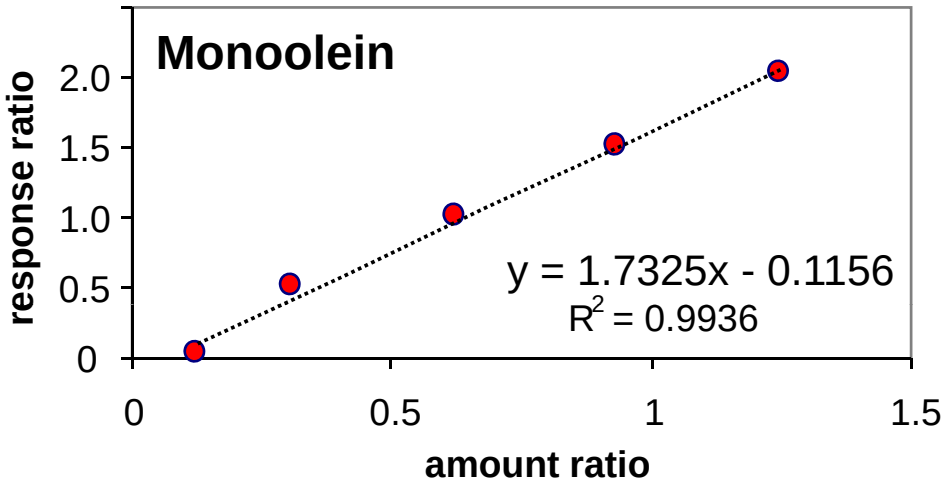
- Move an empty 2 mL vial from tray to front tower
- Add 10 uL calibration standard mix #1
- Add 10 uL ISTD1 solution (butanetriol) using front tower (100 uL syringe)
- Add 10 uL ISTD2 solution (tricaprin) using front tower
- Add 100 uL derivatization reagent (MSTFA) using front tower
- Transfer to mixer and mix for 1 minute
- Transfer to heater and react for 30 minutes
- Add 800 uL n-heptane to quench reaction and dilute using front tower
- Transfer to mixer and mix for 1 minute
- Transfer to rear tower
- Inject 1 uL on-column using rear tower
- Repeat for calibration standard mixes numbers 2 - 5

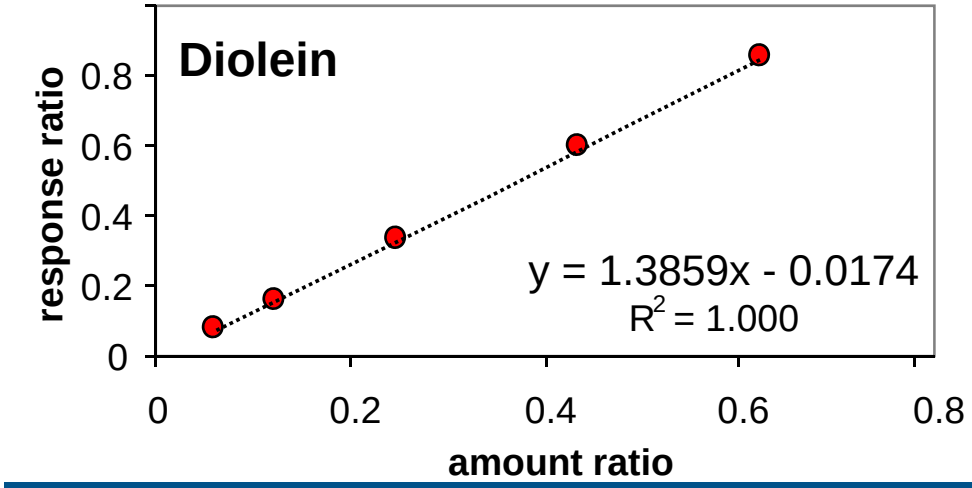
D6584 Analysis of Total Glycerin
Automated Standard Preparation

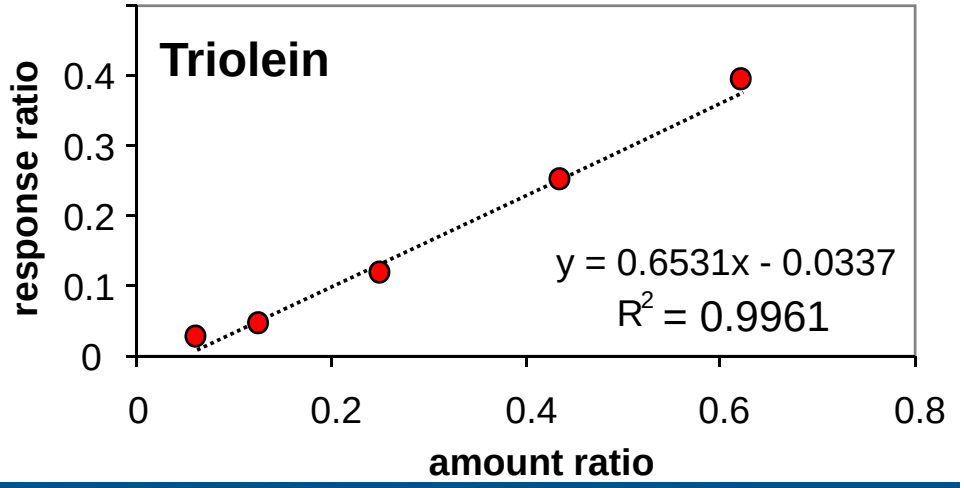


D6584 Analysis of Total Glycerin
Automated Standard Preparation









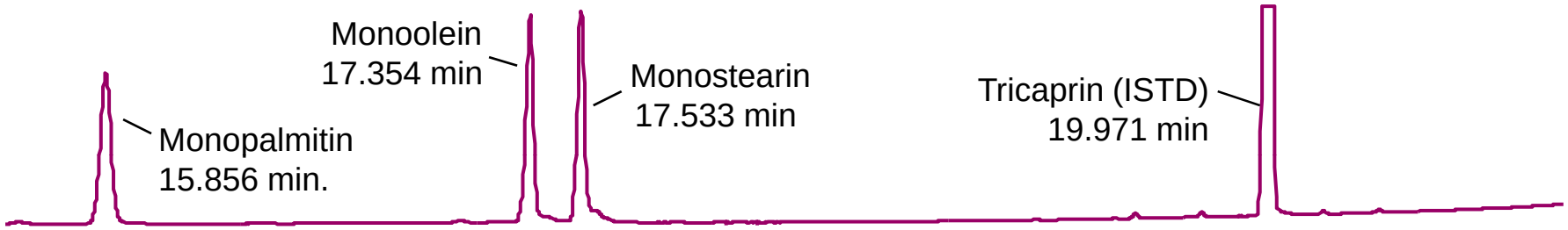
D6584 Analysis of Total Glycerin

10% Scaled Automated Sample Preparation Steps

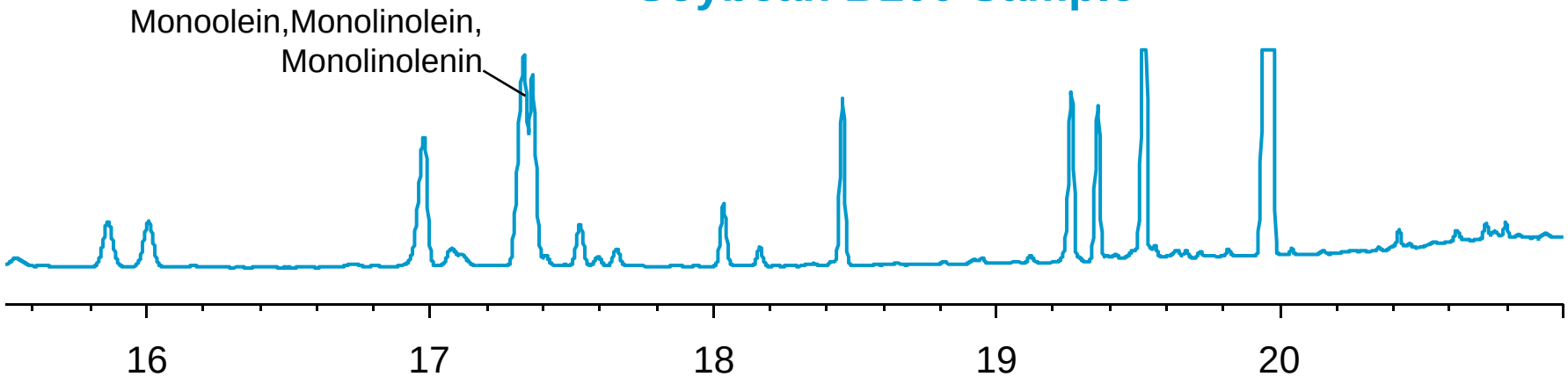
- Manually Weigh 10 mg B100 biodiesel sample into 2 mL ALS vial
- Add 10 uL ISTD1 solution (butanetriol) using tower 1 (100 uL Syringe)
- Add 10 uL ISTD2 solution (tricaprin) using tower 1
- Add 100 uL derivatization reagent (MSTFA) using tower 1
- Transfer to mixer and mix for 1 minute
- React for 30 minutes
- Add 800 uL n-heptane to quench reaction and dilute using tower 1
- Transfer to mixer and mix for 1 minute
- Inject 1 uL on-column using rear tower
- Repeat for other B100 samples

Monoglyceride Retention Time Standard
Recommended to Assure ID of Monoglycerides

Monoglyceride Retention Time Standard

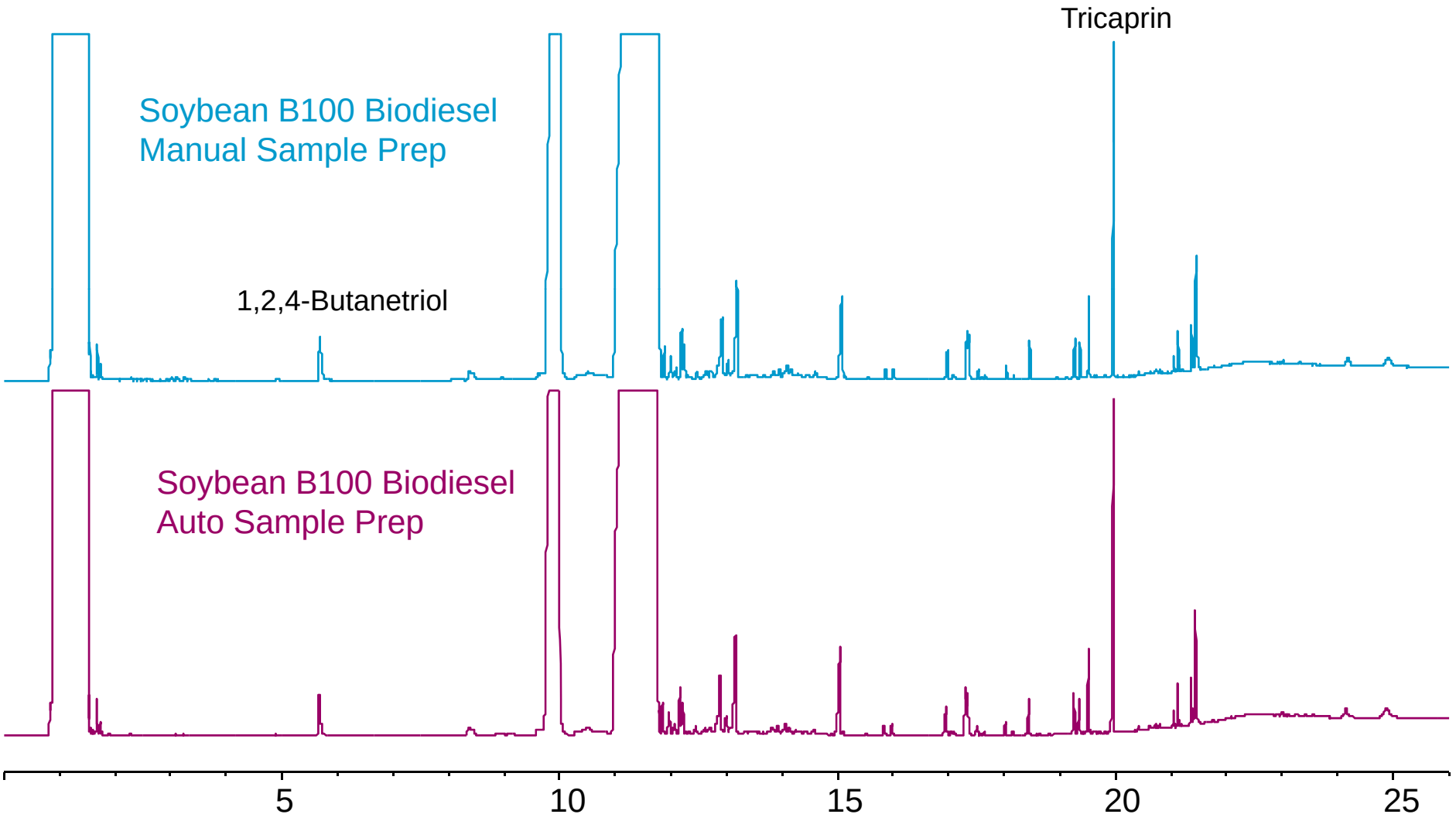


Soybean B100 Sample



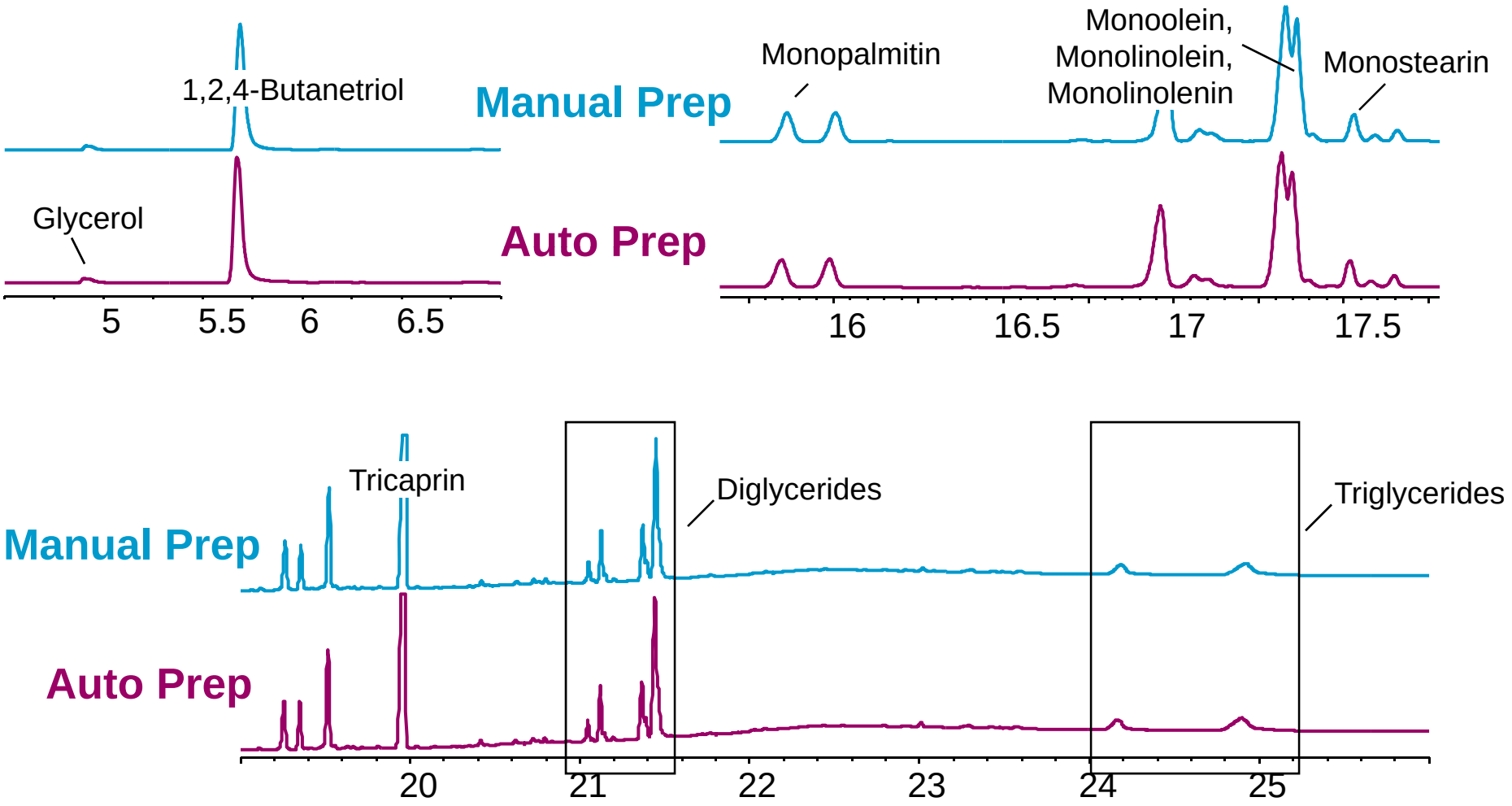
D6584 Analysis of Total Glycerin

Comparison of Manual and Automated Sample Preparation

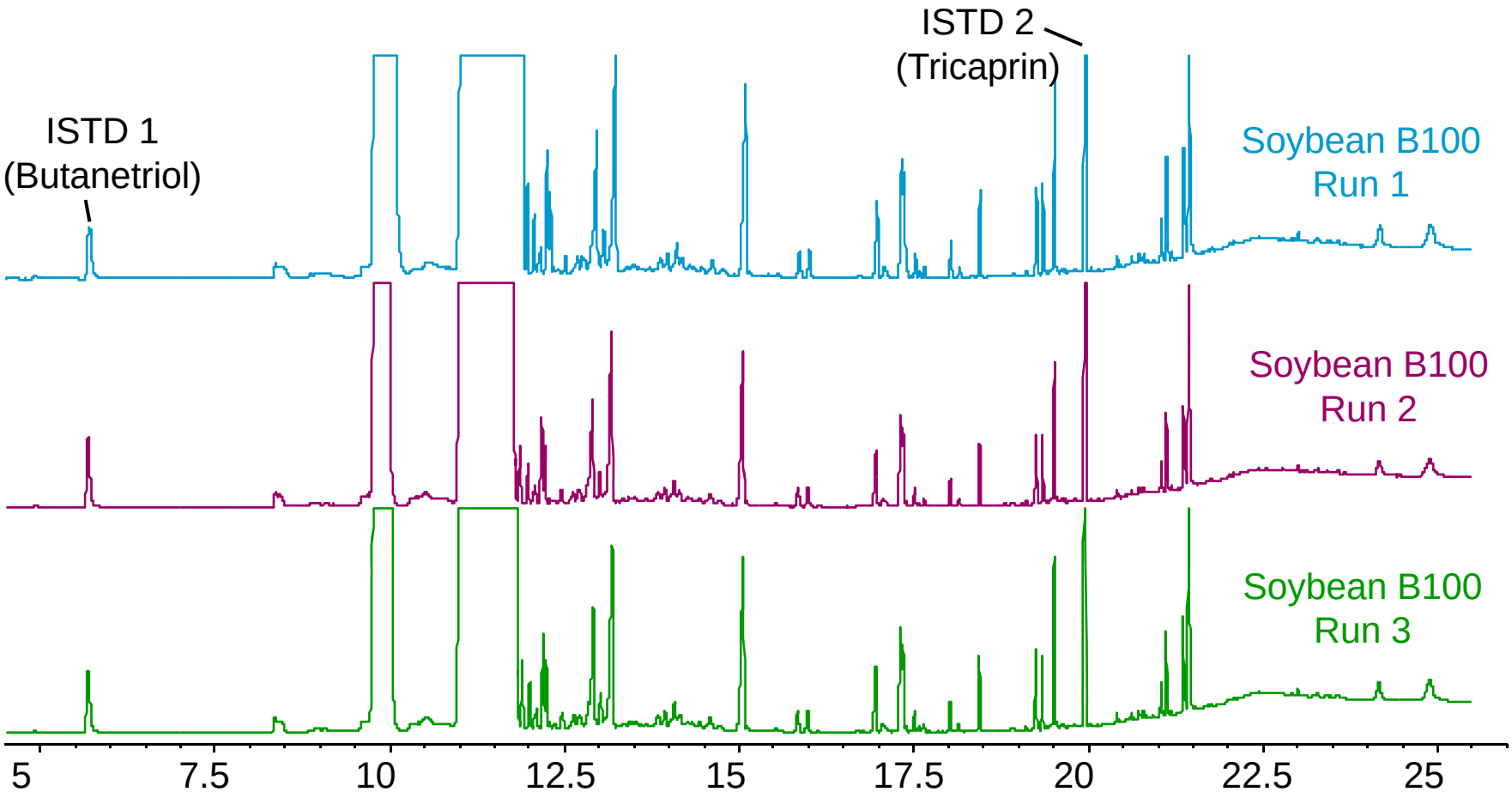


D6584 Analysis of Total Glycerin in Biodiesel

Comparison of Manual and Automated Sample Preparation



D6584 Analysis of Total Glycerin
Automated Sample Preparation Precision

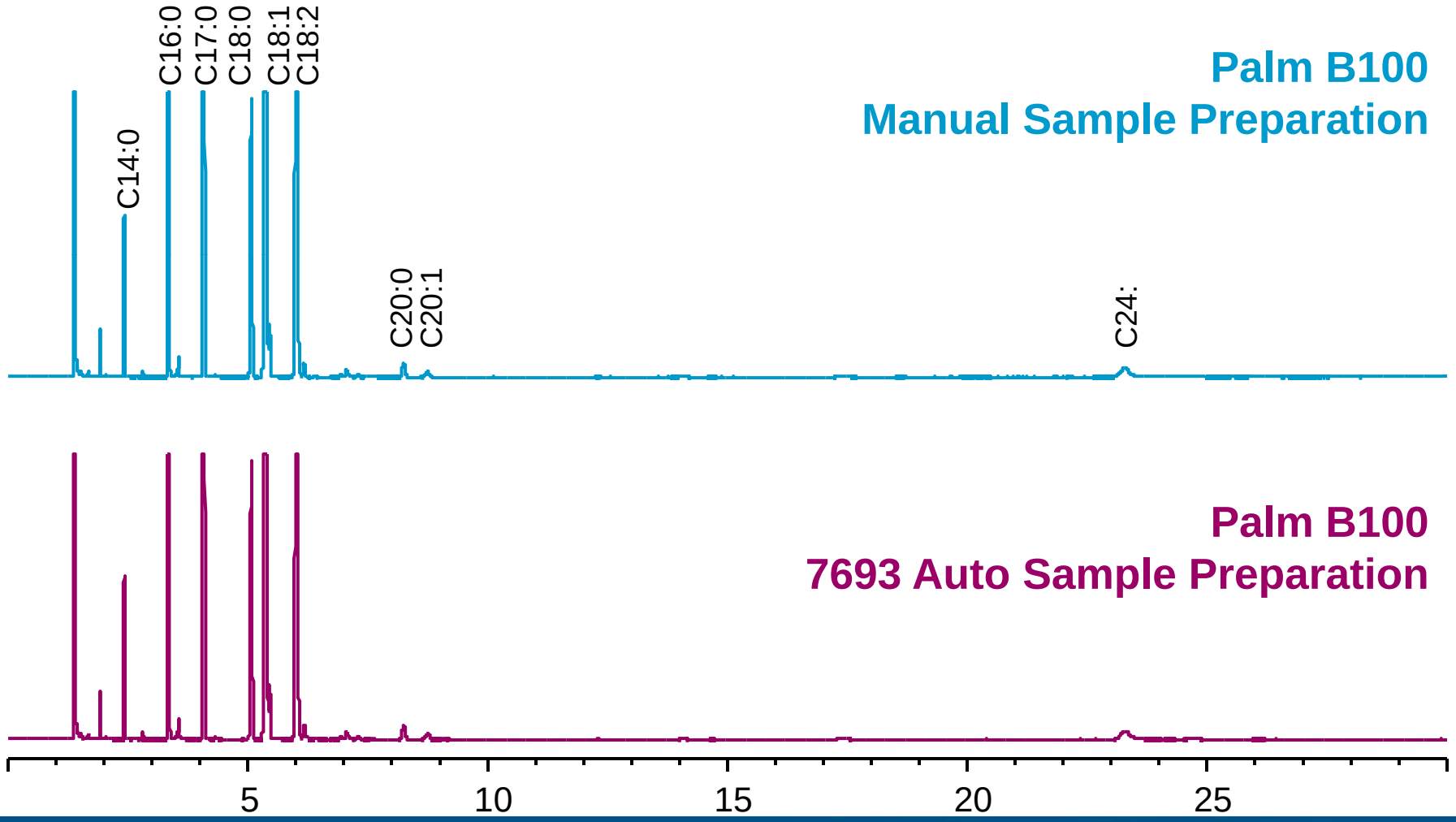


EN14103 – B100 FAME Analysis
Automated Sample Preparation

- Manually weigh 10 mg of B100 biodiesel sample into 2 mL ALS vial
- Add 500 uL ISTD Solution (10 mg/mL C17:0 in n-heptane) using rear tower (100 uL Syringe)
- Transfer to mixed and mix for 1 minute
- Inject 1 uL onto split inlet using front tower
- Repeat for other B100 Samples

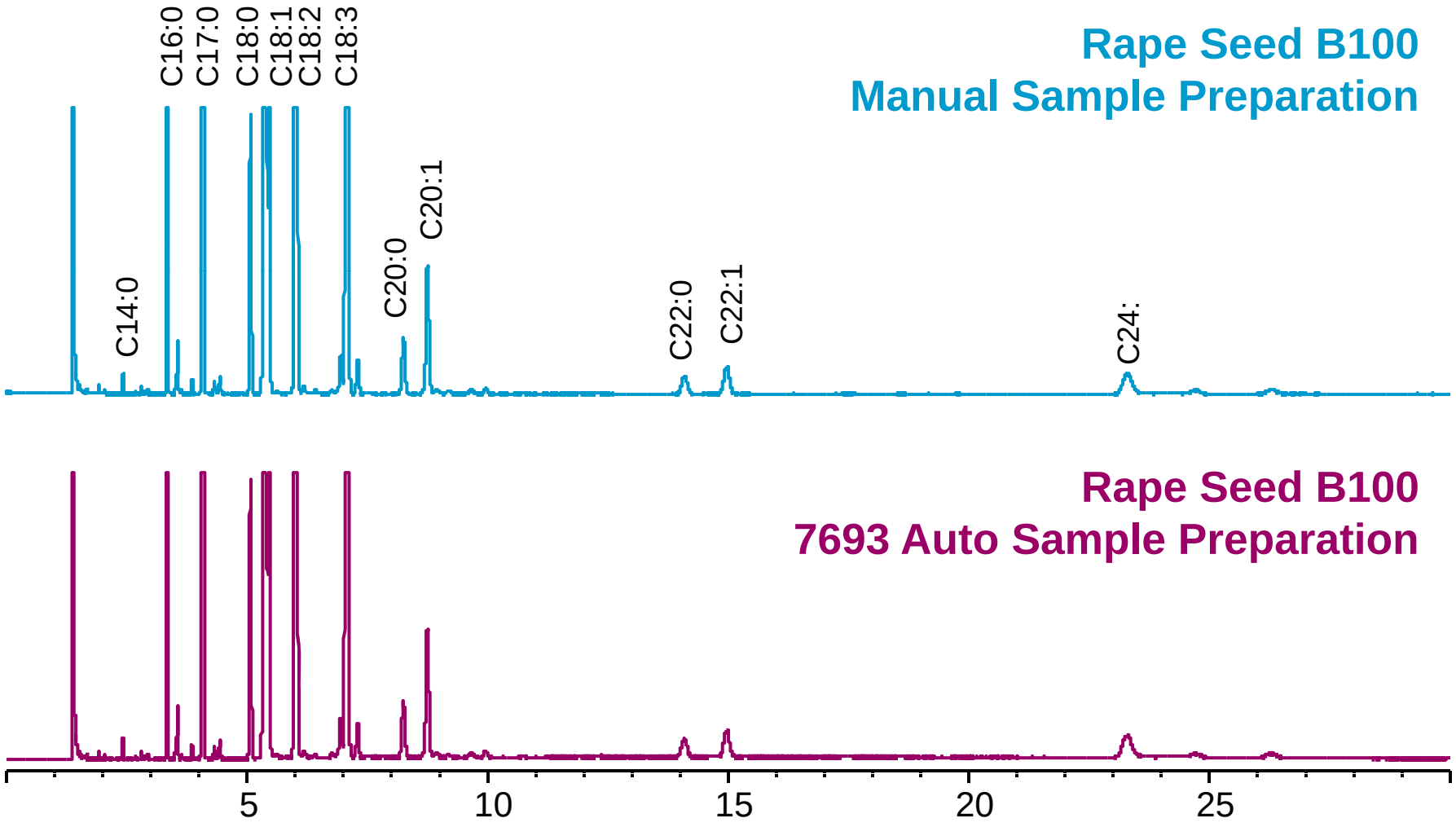
EN14103 – B100 FAME Analysis

Comparison of Manual and Automated Sample Preparation



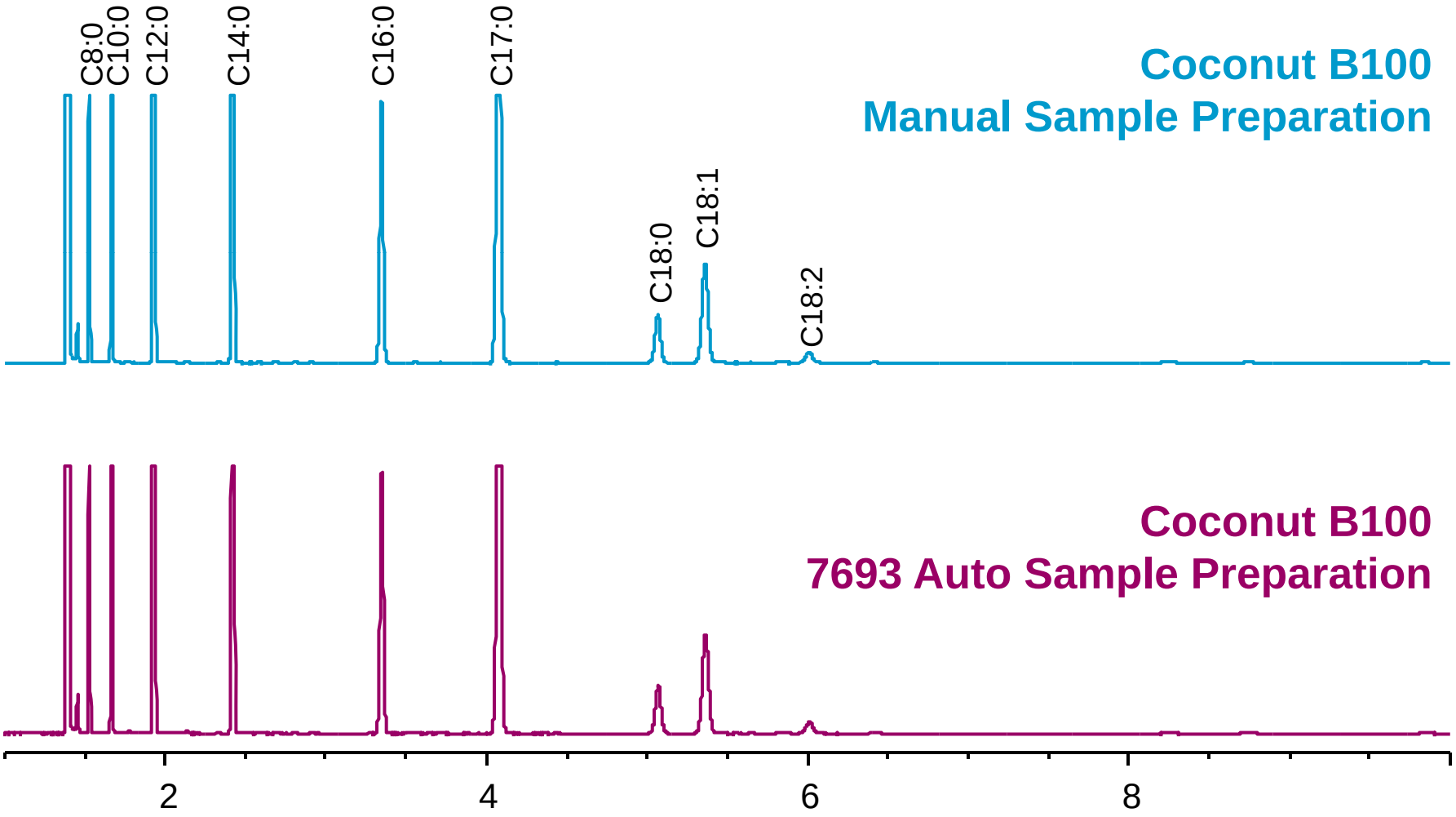
EN14103 – B100 FAME Analysis

Comparison of Manual and Automated Sample Preparation



EN14103 – B100 FAME Analysis

Comparison of Manual and Automated Sample Preparation



Summary

- New external capillary column oven for isothermal chromatography
- Thermally isolate low temperature column form high temperatures in main column oven
- New 7693 ALS Automate Complex Standard and Sample Preparation
- A single GC for complete analysis of biodiesel using 5 different methods:
  - ASTM D6584: Free and Total Glycerin
    - Automated derivatization of samples and standards
  - EN14105: Free and Total Glycerin
    - Automated derivatization of samples and standards
  - EN14103: FAME Content
    - Automated addition of internal standard to samples
  - EN14110: Residual Methanol Content
  - EN14106: Free Glycerol Content

Recent Publications

- “5-in-1 Biodiesel: An Approach to combining Five Biodiesel Gas Chromatographic Methods on a Single Instrument”, James D. McCurry, *Biofuels, Bioprod. Bioref*. 3:296–298 (2009).
- “Automated Standard and Sample Preparation for Multiple Gas Chromatographic Analyses of Biodiesel”, James D. McCurry, *Agilent Technologies Application Note No. 5990-3781EN*, April, 2009.
- “Analysis of Fatty Acid Methyl Ester (FAME) Content and Distribution in Biodiesel Blends Using Heart-Cutting 2D Gas Chromatography”, James D. McCurry and Cunxiao Wang, *Agilent Technologies Application Note No. 5989-8107EN*, March, 2008.
- “Analysis of Glycerin and Glycerides in Biodiesel (B100) Using ASTM D6584 and EN14105”, James D. McCurry and Chunxiao Wang, *Agilent Technologies Application Note No. 5989-7269EN*, November, 2007.
- “Determining the Ester and Linoleic Acid Methyl Ester Content to Comply with EN14103, Chunxiao Wang and James McCurry, *Agilent Technologies Application Note No. 5989-5924EN*, December, 2006.