INTEGRATING MULTIPLE GC METHODS WITH AUTOMATED SAMPLE PREPARATION FOR COMPREHENSIVE BIODIESEL ANALYSIS

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Introduction

Producers and users of biodiesel use several industry standard GC methods to ensure product quality. Several of these methods employ columns that are not compatible on a single instrument due to upper temperature limitations. Today's GCs have sufficient hardware capacity (such as heated zones, pressure/flow controls, inlets, and detectors) to enable the co-residence of multiple methods. However, separate ovens for incompatible columns are often lacking. This poster shows a small external, isothermal capillary column oven used to isolate a polar wax column from a high temperature column. This allows five different biodiesel methods to reside on the same GC. Design criteria of this external oven are discussed to assure each method's performance and column compatibility. Three isothermal biodiesel methods are used to test the external column oven performance and demonstrate the ability to combine these methods on a single GC.

An approach to automating the biodiesel standard and sample preparation prior to GC analysis is also presented using the enhanced capabilities of an automated liquid sampler (ALS). An automated derivatization protocol for the silylation of glycerol, mono-, and di-glycerides was derived from the ASTM D6584 method. The resulting calibrations and GC sample runs of these methods shows excellent comparison to manual preparation methods.

Five GC Methods For Biodiesel QC

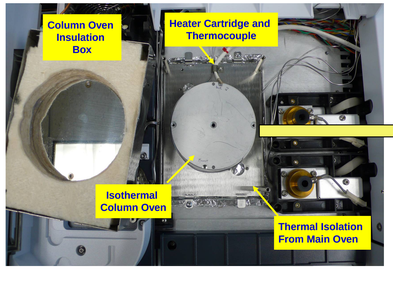
Method	Scope	GC Column	Column Temperature	Inlet/Detector
ASTM D6584	Analysis of Free and Total Glycerin	High Temp 5% DB-5 15 m x 0.32 mm x 0.1 um	Temperature programmed 50 °C to 380 °C	Cool-on-column/FID
EN14105	Analysis of Free and Total Glycerin	High Temp 5% DB-5 10 m x 0.32 mm x 0.1 um	Temperature programmed 50 °C to 380 °C	Cool-on-column/FID
EN14103	Ester and Linoleic Acid Methyl Ester Content	HP-Innowax 30 m x 0.25 mm x 0.25 um	Isothermal 200 °C or 210 °C	Split-splitless/FID
EN14110	Residual Methanol Content by Headspace	HP-Innowax 30 m x 0.25 mm x 0.25 um	Isothermal 50 °C	Split-splitless/FID
EN14106	Determination of Free Glycerol	HP-Innowax 30 m x 0.25 mm x 0.25 um	Isothermal 200 °C	Split-splitless/FID

There are five industry standard methods designed to measure some aspect of biodiesel quality. Most labs run 2 or 3 of these methods. This table shows the methods grouped according to the column and upper temperature used by the method. As you can see, two methods use a high temperature column ramped to 380 °C. Three other methods use a an HP-Innowax column run isothermally at 60 ° C or 210 °C.

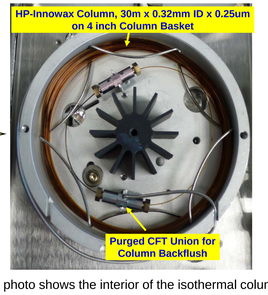
Bioidiesel labs have two choices if they wish to run the high temperature column and the wax column methods. They could buy two instruments to accommodate the temperature limitations of the columns. While this offers the greatest flexibility, many labs, especially in emerging economies cannot afford this option. Additionally, some production labs do not have the space or resources to support two GCs. The other alternative is to buy one GC and change the columns when changing methods. While economical, this is time consuming and requires technical skills not always found in many QC labs. Most labs prefer to keep a GC configured for a set of methods with minimal changes.

7890A External Isothermal Capillary Column Oven

A solution for biodiesel analysis is to have an two column ovens on a single GC. The high temperature column methods require precise oven programming performance, therefore that column should reside in the high performance main column oven. Since the methods using the HP-Innowax column are isothermal, the performance criteria for a second oven are less stringent. The 7890A GC has a separate heated region on the top of the GC between the inlets and detectors. Normally, this heated zone is used for valves. Fortunately it is large enough to accommodate a properly designed external column oven provided the column can be wound on a smaller cage.



This photo shows the isothermal oven mounted on the 7890A. The oven insulation box is removed and shown on the left. The external oven is thermally isolated from the main column oven using specially designed insulation. A heater cartridge and thermocouple automatically controls the external oven temperature.



This photo shows the interior of the isothermal column oven. A 4-inch cage contains the 30 m x 0.25 mm ID x 0.25 um capillary column. A Capillary Flow Technology (CFT) union connects the column to the split/splitless inlet via deactivated stainless steel tubing. The column outlet is connected to the FID using a purged CFT inlet. The purged inlet enables the use of backflushing to improve column performance and extend column life.

Isothermal Biodiesel Analysis Using External Oven

High Temperature (210 °C) Isothermal Precision

EN14103 – Determination of Ester and Linolenic Acid Methyl Ester Content

Thermal isolation from main column oven

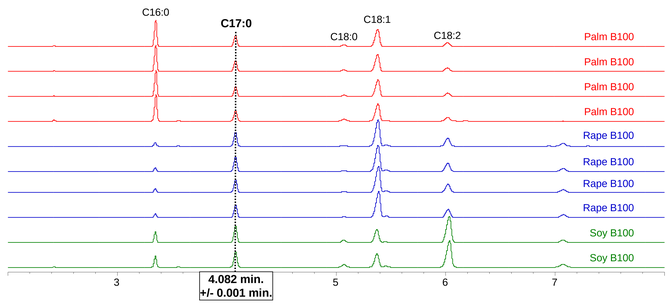
– Run ASTM D6584 temperature program for 24 hours:

- 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

Measuring high temperature oven precision

– Biodiesel samples using EN14103 (210 °C)

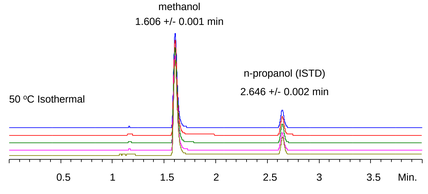
- Measured internal air temperature over 24 hours: 210 °C +/- 0.1 °C
- Measure C17:0 (ISTD) retention time over ten runs
  – C17:0 retention time; 4.082 min., +/- 0.001 min.



Low Temperature (50 °C) Isothermal Precision

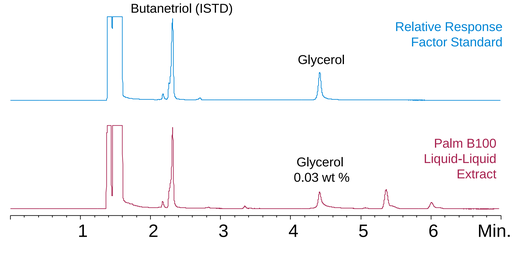
EN14110 – Determination of Methanol Content (50 °C)

Measured oven temperature precision: 50 °C, +/- 0.1 °C
Observed retention time precision:



System Inertness for Isothermal Column

EN14106 – Determination of Free Glycerol Content (210 °C)



Deactivated stainless steel tubing and Capillary Flow Technology unions are used to connect the external column to the system's split/splitless inlet and FID. This provides an inert flow path for the analysis of polar compounds. This is demonstrated by the analysis of free glycerol extracted from biodiesel.

Automated Sample Preparation with 7693 ALS

The 7693A Automated Liquid Sampler (ALS) offers enhance capabilities for automatic standard and sample preparation at the GC. Both ASTM D6584 and EN14105 methods require the derivatization of non-volatile glycerides in B100 prior to GC analyses. The preparation procedures described by these methods result in a final volume of 15 mL for each sample. The maximum vial size used by the 7693A ALS is 2 mL. Therefore the standard and sample preparation procedures were scaled by 10% for the final volume to fit into the 2 mL vials. For this analysis, two injection towers were used. The front injector was equipped with a 100 uL gas tight syringe and was used exclusively for sample preparation. The rear tower was equipped with a 10 uL syringe and positioned over the cool-on-column inlet and was only used for sample injection after sample preparation. Listed below are the steps used to prepare the calibration standards and biodiesel samples respectively:

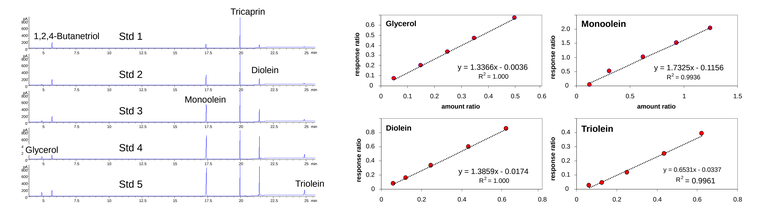
10% Scaled Calibration Standard Derivatization Procedure for 7693A ALS

1. Move an empty 2 mL vial from the sample tray to front tower.
2. Add 10 uL calibration standard mixture #1 to vial (100 uL syringe).
3. Add 10 uL ISTD1 solution (butanetriol) to vial using front tower.
4. Add 10 uL ISTD2 solution (tricaprin) to vial using front tower.
5. Add 100 uL derivatization reagent (MSTFA) to vial using front tower.
6. Transfer vial to mixer and mix for 1 minute.
7. Transfer vial to heater and react for 30 minutes at room temperature.
8. Transfer vial to front tower.
9. Add 800 uL n-heptane to vial using front tower.
10. Transfer vial to mixer and mix for 1 minute.
11. Transfer vial to rear tower (10 uL syringe).
12. Inject 1 µL on-column using rear tower.

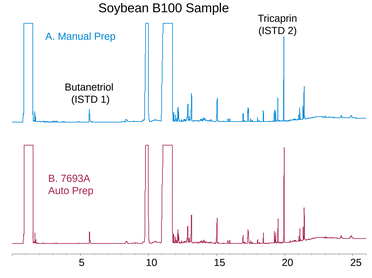
10% Scaled B100 Biodiesel Sample Derivatization Procedure for 7693A ALS

1. Move vial containing 10 mg B100 sample from sample tray to front tower.
2. Add 10 uL ISTD1 solution (butanetriol) to vial using front tower.
3. Add 10 uL ISTD2 solution (tricaprin) to vial using front tower.
4. Add 100 uL derivatization reagent (MSTFA) to vial using front tower.
5. Transfer to vial mixer and mix for 1 minute.
6. Transfer to vial heater and react for 30 minutes at room temperature.
7. Transfer vial to front tower.
8. Add 800 uL n-heptane to vial using front tower.
9. Transfer vial to mixer and mix for 1 minute.
10. Transfer vial to rear tower (10 uL syringe).
11. Inject 1 uL on-column using rear tower.
12. Repeat for other B100 samples

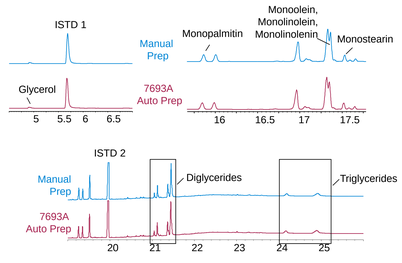
ASTM D6584 – GC Analysis of Free and Total Glycerin After Silylation Comparison of Manual and Automated Calibration Standard Preparation



ASTM D6584 – GC Analysis of Free and Total Glycerin After Silylation Comparison of Manual and Automated Sample Preparation



Comparison of a soybean B100 sample prepared (A) manually according to the ASTM D6584 protocol and (B) the 10% scaled automatic protocol using the 7693A ALS.



Details of the glycerol, mono-, di- and tri-glycerides contained in a soybean B100 sample. The automated sample preparation yields the same chromatographic result as the manual sample preparation.

Summary

- New external capillary column oven for isothermal chromatography
- New Liquid Sampler Automates 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