



A Honeywell Company

Residual Triglycerides in Deoxygenated Feedstocks by GC

UOP Method 733-10

Scope

This method is for process control to quickly determine by gas chromatography (GC) the presence of residual triglycerides and partially deoxygenated intermediates in deoxygenated feedstock derived from plant oils and animal fats including but not limited to canola, jatropha, soy, palm, or algal oils. An approximate carbon distribution of product naphtha, kerosene (jet fuel), and diesel derived from the deoxygenated feedstock is also determined through carbon number 24 (C₂₄) although there may be some interferences from partially deoxygenated feed components.

The lower limit of quantitation for any individual component or grouping is 0.01 mass-%. n-Paraffin values may be biased slightly high due to non-normals eluting at n-paraffin sites.

After it has been determined that there are no residual triglycerides, fatty acids, or partially deoxygenated intermediates in the sample a more detailed distribution can be determined by UOP Method 732, "Analysis of Distillate Fuels Derived from Oxygenated (Bio) Feedstocks by GC."

Reference

ASTM Practice D4307, "Preparation of Liquid Blends for Use as Analytical Standards," www.astm.org

UOP Method 732, "Analysis of Distillate Fuels Derived from Oxygenated (Bio) Feedstocks by GC," www.astm.org

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

A diluted sample is injected into a gas chromatograph (GC) that is equipped with a flame ionization detector (FID) and a high temperature stainless steel megabore column internally coated with 100% dimethylpolysiloxane. A quantitative blend is made from normal paraffins whose carbon number ranges extend beyond C₂₄ and un-reacted feed material is used to determine the n-paraffin and the triglyceride sites. By utilizing these sites, an approximate carbon number distribution of the sample components can be determined as well as identifying residual feed material. The mass-% composition of the sample is obtained by the internal normalization technique, wherein the peak areas for the entire samples are first corrected for differences in response and then normalized to 100%.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, readable to 0.1-mg

Chromatographic column, 15 m of 0.53-mm ID DB-ProSteel megabore capillary column, internally coated to a film thickness of 0.15 micron, DB-PS1, J&W Scientific, Cat. No. 145-1011, Agilent Technologies

Gas chromatograph, temperature programmable with cryogenic cooling, capable of constant flow, built for capillary column chromatography, utilizing a split injection system, equipped with a deactivated glass injection port, and a flame ionization detector that will give a minimum peak height response of five times the background noise for 0.01 mass-% n-decane when operated at the recommended conditions, Agilent Technologies, Model 7890

Data system, electronic, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that narrow peaks, typically obtained from a capillary column, can be accurately measured. The data system must have programmable parameters for controlling baseline events, and have graphics capabilities. The system must provide for integrating the detector signal and summing the peak areas between specific time intervals.

Leak detector, gas, Restek, Cat. No. 22451

Oven, laboratory, capable of operation at 45°C

Regulator, air, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-590

Regulator, hydrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-350

Regulator, nitrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Sample injector, syringe or injector capable of introducing a 0.5-μL volume of sample. An autosampler (or autoinjector) is recommended, Agilent Technologies, Model 7683.

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user, other suppliers may be used.

Acetone, 2-propanone, 99.9% purity, VWR, Cat. No. BJGC010-4

Air, zero gas, total hydrocarbons less than 2.0 ppm as methane

Carbon dioxide, commercial liquid, 99.5% minimum purity, with full-length eductor tube for liquid withdrawal, for cryogenic cooling

Carbon disulfide (CS₂), 99.9% purity, VWR, Cat. No. EM-CX0395-6

Gas purifier, for hydrogen, to remove oxygen and moisture from carrier gas, VICI Mat/Sen, Cat. No. P200-1

Hydrogen, zero gas, 99.95% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Injection port liner, split liner, 4.0 x 6.3 x 78.5mm for Agilent GCs, IP deactivated, with deactivated glass wool, Restek, Cat. No. 20782.

Nitrogen or helium, zero gas, total hydrocarbons less than 0.5 ppm as methane

n-Paraffins, 99% minimum purity, ChemSampCo. Obtain each individual carbon number that will be present in the sample. A mixture of n-paraffins, C₅-C₁₂, C₁₄-C₁₈, and C₂₀, is available from AccuStandard, Stock SIM DIS Paraffin Solution, Cat. No. ASTM-P-0050.

Septa, BTO (Bleed and Temperature Optimized), non-stick, 11mm, Agilent Technologies, Cat. No. 5183-4757

Syringe, for sample injector, 5-μL, Agilent Technologies, Cat. No. 5181-1273

Triglycerides, unreacted feed material, vegetable or tallow oil, as supplied to the deoxygenation process, local supply

Vials, with polyseal caps, 15-mL, VWR, Cat. No. 16087-062

Vials, for autosampler, if used, with caps, Agilent Technologies, Cat. No. 5182-0864

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, and the equipment being used.

Chromatographic Technique

1. Install the gas purifier in the supply line between the carrier gas source and the carrier gas inlet on the gas chromatograph.
 - Column life is significantly reduced if the gas purifier is not used.
2. Install the capillary column in the gas chromatograph, according to the column and gas chromatograph manufacturer's instructions.
 - CAUTION: Hydrogen gas leakage into the confined volume of the column oven can cause a violent explosion. It is, therefore, mandatory to check for leaks each time a connection is made and periodically thereafter.
3. Establish the recommended operating conditions as given in Table 1.
 - Other conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatograms (Figures).
4. Program the column oven to 345°C and maintain this temperature until a stable baseline has been obtained at the required sensitivity.
5. Cool the column oven to a stabilized 25°C.
6. Dilute process samples 2:1 by volume with CS₂ (2 parts CS₂, 1 part sample).
 - If needed, warm the sample in an oven at 45°C, then mix the sample thoroughly by shaking it vigorously.
 - For triglyceride feed samples, dilute 10:1 by volume with CS₂ (10 parts CS₂, 1 part sample).
 - CAUTION: CS₂ is highly flammable; do not expose to temperatures above 45°C; work in a fume hood.
7. Inject 0.1 μL of sample into the gas chromatograph and immediately start the integrator and the column oven programming sequence.

- When using an autosampler or autoinjector, the injection sequence of a GC is typically automated, performing the injection, and starting the data system and column temperature program simultaneously.
 - If an autosampler is used, make sure fresh solvents are used: first flush vial acetone, second flush vial CS₂.
8. Identify the n-paraffins and carbon number groupings by comparing the resultant chromatogram with the typical chromatogram (see Figures).
- A quantitative blend composed of n-paraffins and triglyceride within the boiling point range of the sample to be analyzed is to be run to determine the location of the n-paraffin and triglyceride sites. Reference paraffins used indicate a full sample range; actual paraffins used may be altered as long as n-C₅ through n-C₂₄ is present. These sites are then to be utilized in determining the approximate carbon distribution of samples and a relative response factor for the triglycerides. The typical major product peaks from triglyceride feeds will be n-C₁₅ through n-C₁₈ (See Figures), but will vary depending upon the source of the feed. See *Calibration* for further details on determining relative factors.
 - Other available n-paraffin reference materials may also be used to identify the n-paraffin sites. For example, a GC simulated distillation mixture is shown in Figure 6. This is just an example of another reference material that could be used, and is not required for the analysis.
 - Actual retention times of components can shift due to concentration or composition of the products vs. the reference blend but retention times can be confirmed by overlaying chromatograms or spiking the subsequent product sample with the reference blend.
 - The peaks assigned a carbon number grouping, tg (timed group), are those that elute between the valley immediately following the previous n-paraffin peak and the corresponding valley following the next n-paraffin peak. Quantification of carbon number groupings is approximate.
 - If identification of a n-paraffin peak is unclear, do not designate it as such. Exclude the name so that only the grouping will be called for the area in question.
 - The composition of the intermediates is largely unknown but could consist of hydrocarbons, fatty acids, partially hydrogenated fatty acids, hydrogenated sterols, monoglycerides, diglycerides, etc.

Table 1
Recommended Operating Conditions

Carrier Gas	hydrogen
Mode	constant flow
Column head pressure at 25 °C	1.8 psig
Linear velocity at 25°C	82 cm/sec
Equivalent flow at 25°C	11.2 mL/min
Split flow rate	60 mL/min
Injection port temperature	250°C
Column temperature program	
Initial temperature	25°C
Initial time	1.0 min
Programming rate	15° C/min
Final temperature	345°C
Final time	14 min
Detector	flame ionization
Detector temperature	360°C
Hydrogen flow rate*	20 mL/min
Air flow rate*	400 mL/min
Makeup gas	helium or nitrogen
Makeup gas flow rate*	30 mL/min
Sample size	0.1 µL

*Consult the manufacturer's instrument manual for suggested flow rates.

Calibration

This analysis uses internal normalization of the total sample, not including the CS₂ diluent, for quantitation. All components in the sample which elute from the column under the specified conditions are measured. Any components which do not elute from the column under the specified conditions are not measured. In order to accurately measure the total sample, triglycerides beyond the intermediate range must be calibrated. This is necessary because glycerides components that may be present in the sample do not have the same detector response as the hydrocarbon components. All expected paraffinic hydrocarbon components have essentially the same FID detector response.

Table 2
Typical Retention Times of n-Paraffin
and Timed Carbon Number Groupings

Typical Retention Time, Min	Component Identification	Typical Retention Time, Min	Component Identification
tg = Timed Group	tg = Timed Group	tg = Timed Group	tg = Timed Group
0.0 – 0.4_{tg}	Unknown C₅-_{tg} *	7.22	n-C₁₅
0.41	n-C₅	7.22 – 7.95_{tg}	i-C₁₆_{tg}
0.41 – 0.59_{tg}	i-C₆_{tg}	7.95	n-C₁₆
0.59	n-C₆	7.95 – 8.68_{tg}	i-C₁₇_{tg}
0.59 – 0.68_{tg}	i-C₇_{tg}	8.68	n-C₁₇
0.68	n-C₇	8.68 – 9.37_{tg}	i-C₁₈_{tg}
0.68 – 1.17_{tg}	i-C₈_{tg}	9.37	n-C₁₈
1.17	n-C₈	9.37 – 9.86_{tg}	i-C₁₉_{tg}
1.17 – 2.01_{tg}	i-C₉_{tg}	9.86	n-C₁₉
2.01	n-C₉	9.86 – 10.44_{tg}	i-C₂₀_{tg}
2.01 – 2.98_{tg}	i-C₁₀_{tg}	10.44	n-C₂₀
2.98	n-C₁₀	10.44 – 11.00_{tg}	i-C₂₁_{tg}
2.98 – 3.93_{tg}	i-C₁₁_{tg}	11.00	n-C₂₁
3.93	n-C₁₁	11.54	n-C₂₂
3.93 – 4.82_{tg}	i-C₁₂_{tg}	12.06	n-C₂₃
4.82	n-C₁₂	12.56	n-C₂₄
4.82 – 5.66_{tg}	i-C₁₃_{tg}	11.00 – 18.00_{tg}	Intermediates_{tg}
5.66	n-C₁₃	18.00 – 26.00_{tg}	Glycerides_{tg}
5.66 – 6.45_{tg}	i-C₁₄_{tg}	22.36	Triglycerides A
6.45	n-C₁₄	22.82	Triglycerides B
6.45 – 7.22_{tg}	i-C₁₅_{tg}	23.44	Triglycerides C
		26.00 – end of analysis_{tg}	Heavies_{tg}

*Not including the CS₂ peak

Since all paraffinic components have essentially the same detector response on a mass basis in a flame ionization detector, the same relative response factor calibration is used for the C₂₄ and lower hydrocarbon sites. Intermediates use the relative response factor of the hydrocarbons. Components in

the glycerides and heavies regions, other than the identified triglycerides, may include glycols, other glycerides, fatty acids or sterols. Use the response factor for triglycerides for any of these components remaining in the deoxygenated feedstock.

1. Prepare a quantitative blend, as described in ASTM Method D4307, containing 95% of the expected hydrocarbons, and 5% of the triglyceride feed being used in the process.
 - The hydrocarbons in the blend should be high in n-paraffins through C₂₄, but the hydrocarbons must not interfere with the triglyceride feed used in the process.
 - Use the blend to identify the expected n-paraffin peak retention times and the three largest triglyceride peaks, which are to be simply identified as A, B & C.
2. Analyze the blend in triplicate, diluting the blend in CS₂ and analyzing as described under *Chromatographic Technique*.
 - The peak areas from each of the three runs should not deviate from the average by more than 3% relative. If greater deviations occur, make certain that there are no problems with the equipment or technique, and then make additional runs until the required repeatability is obtained on three consecutive runs.
 - A calibration blend is run when the method is initially set up and thereafter when changes have been made to the equipment, or periodically, to verify proper calibration.
3. Based upon 3 replicate runs of the blend, determine the average response factor for triglycerides relative to hydrocarbons to four significant figures using Equation 1 and hydrocarbon-range peaks as reference:

$$\text{Relative response factor for triglycerides} = \frac{A B}{C D} \quad (1)$$

where:

- A** = feed triglycerides, mass-%
- B** = total peak area of hydrocarbon peaks
- C** = hydrocarbons, mass-%
- D** = total peak area of feed triglycerides

Calculations

Calculate the composition of samples, to the nearest 0.01 mass-% using Equation 2:

$$\text{Concentration of each specific component or group components, mass-\%} = \frac{100 E F}{G} \quad (2)$$

where:

- E** = relative response factor of the individual component or group of components, 1.0000 for all hydrocarbons, determined in Equation 1 for triglycerides
- F** = peak area of the individual component or group of components
- G** = sum of products, **EF**, of all the components and groups of components in the sample
- 100** = factor to convert to percent

Report each component or group of components to the nearest 0.01 mass-%.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods," from data obtained using an autosampler.

Repeatability

A nested design was carried out for determining components in one sample with four analysts in one laboratory. Each analyst carried out tests on two separate days, performing four tests each day. The total number of tests for each component was 32. The precision data are summarized in Table 4. Two tests performed by the same analyst on the same day should not differ by more than the repeatable allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

The data in Table 4 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of long-term precision.

Table 4
Repeatability and Site Precision, mass-%

<u>Sample Component or Region</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>
Total Hydrocarbons	97.13	0.037	0.15	0.045	0.22
Intermediates	0.81	0.014	0.05	0.017	0.08
Glycerides	0.09	0.004	0.01	0.006	0.02
Triglycerides A	0.07	0.001	0.01	0.001	0.01
Triglycerides B	0.57	0.010	0.04	0.012	0.05
Triglycerides C	1.34	0.028	0.11	0.035	0.13
Heavies	0.01	0.001	0.01	0.001	0.01

Reproducibility

There is insufficient data to calculate reproducibility at this time.

Time for Analysis

The elapsed time for one analysis is 1.0 hour. The labor requirement is 0.5 hour.

Suggested Suppliers

AccuStandard, 125 Market St., New Haven, CT 06513 USA (203-786-5290)

www.accustandard.com

Agilent, 2850 Centerville Road, Wilmington, DE 19808 USA (302-633-8000) www.agilent.com

ChemSampCo, 1880 Ryan Road, Dallas, TX 75220 USA (609-656-2440) www.chemsampco.com

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 USA (215-641-2700)

www.mathesontrigas.com

Restek, 110 Benner Circle, Bellefonte, PA 16823 USA (814-353-1300) www.restek.com

VICI Mat/Sen, 7806 Bobbitt, Houston, TX 77055 USA (713-688-9345) www.vicimatsen.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380 USA (610-431-1700)

www.vwr.com

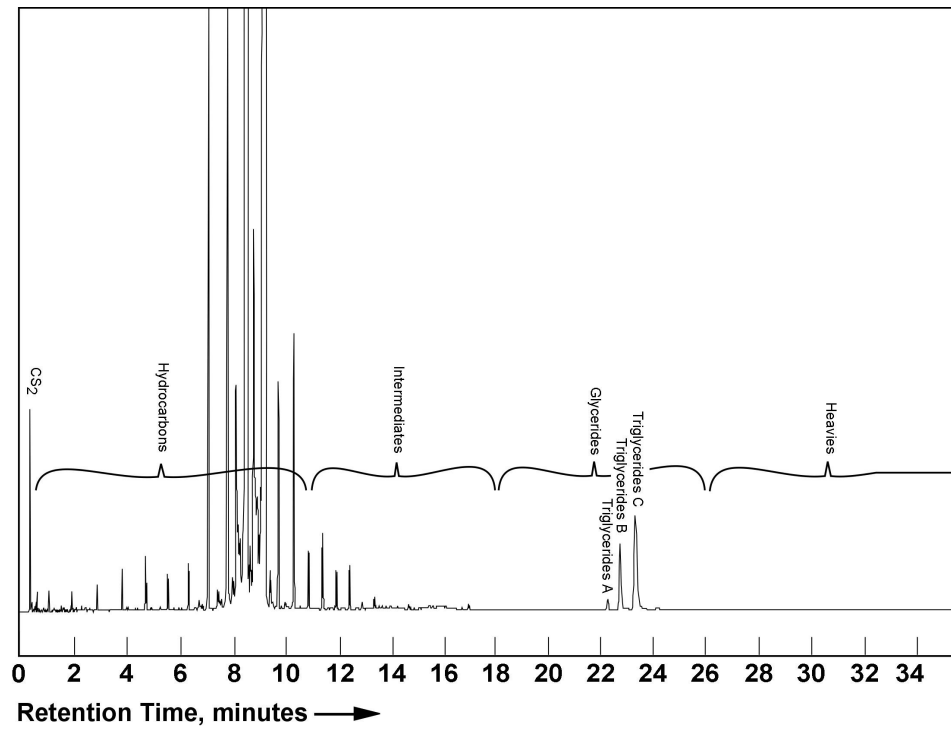


Figure 1
Example Chromatogram (Total)

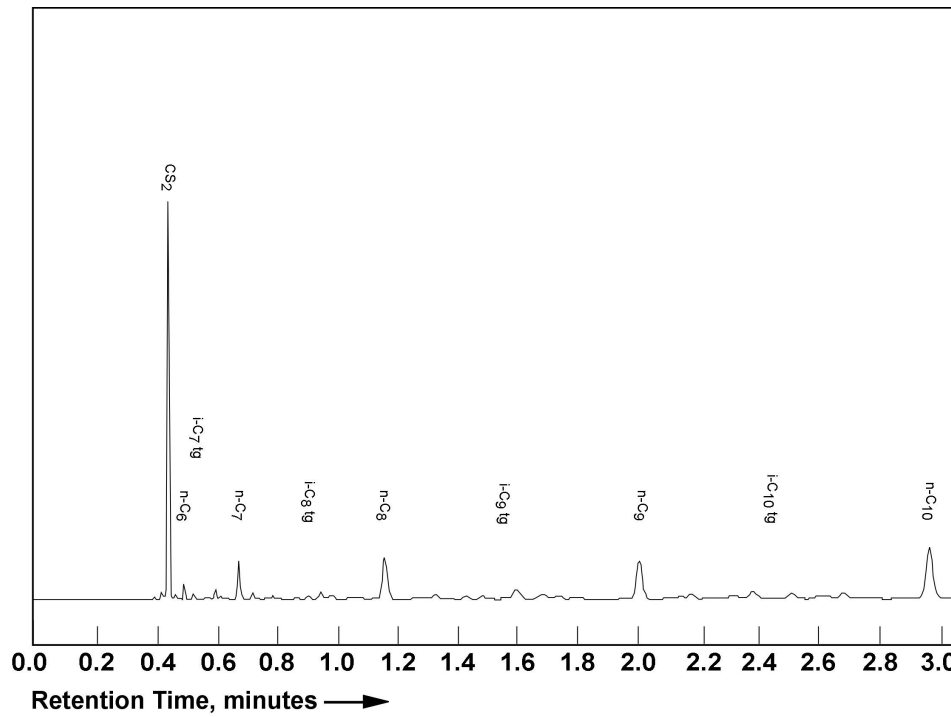


Figure 2
Example Chromatogram (0-C₁₀ region)

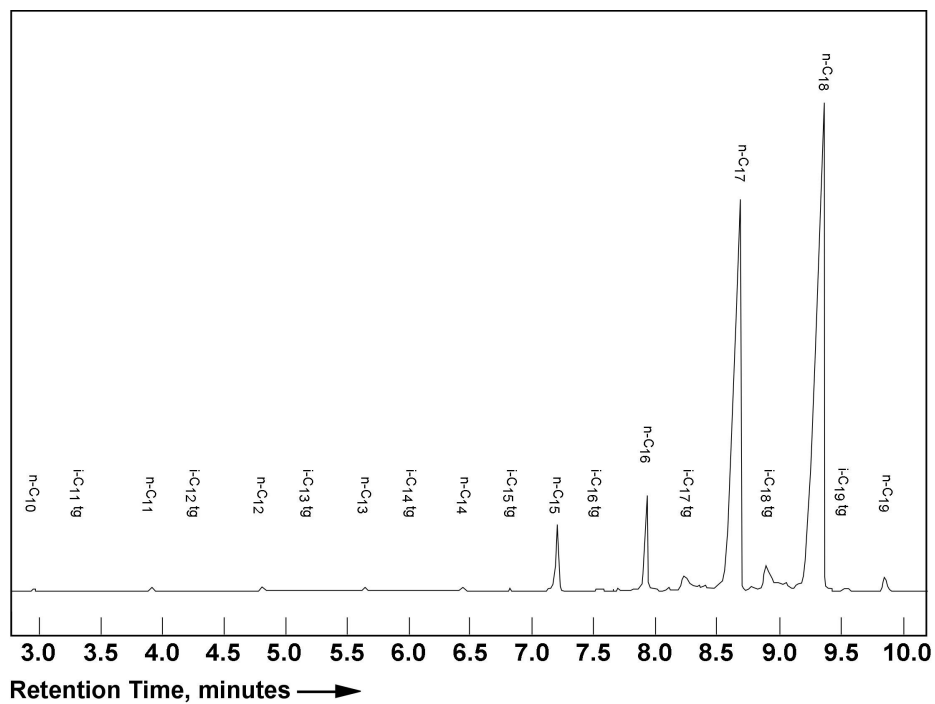


Figure 3
Example Chromatogram (C₁₀-C₁₉ region)

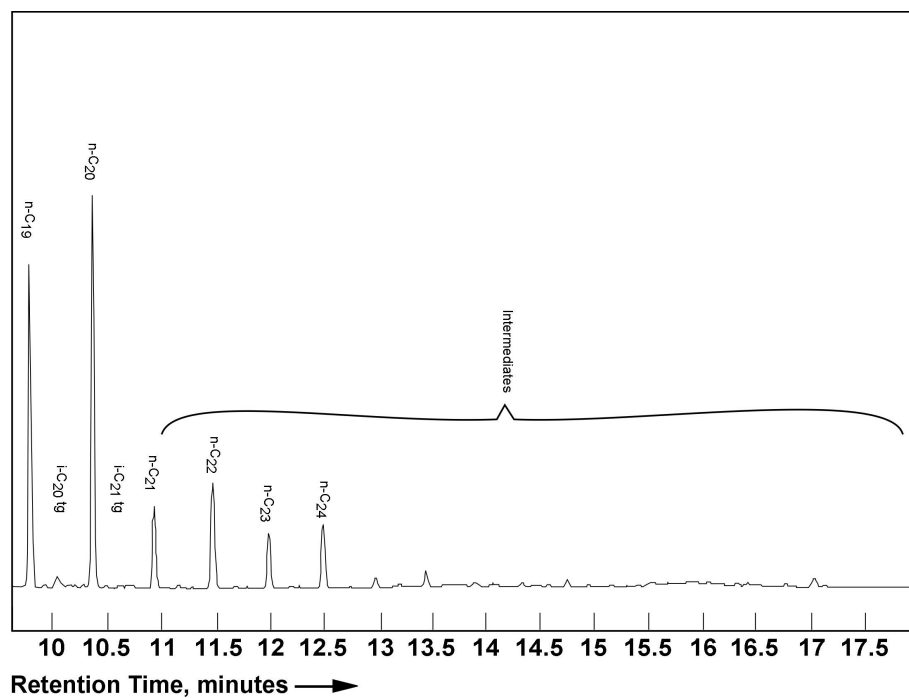


Figure 4
Example Chromatogram (C₂₀-end of intermediates region)

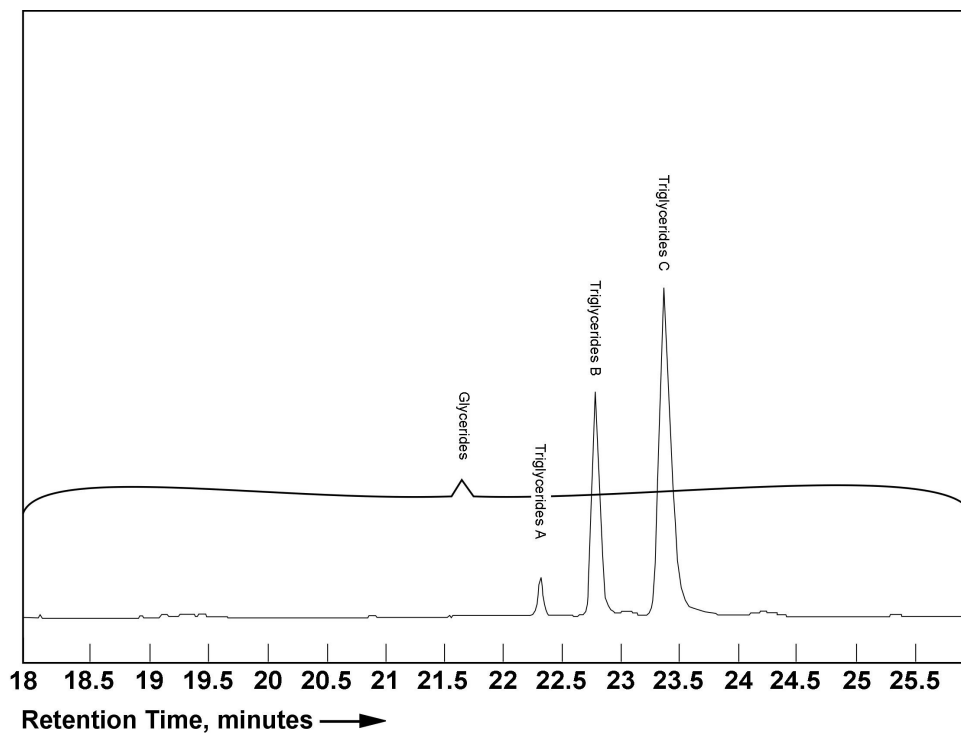


Figure 5
Example Chromatogram (Glycerides region
after intermediates region for 8 min)

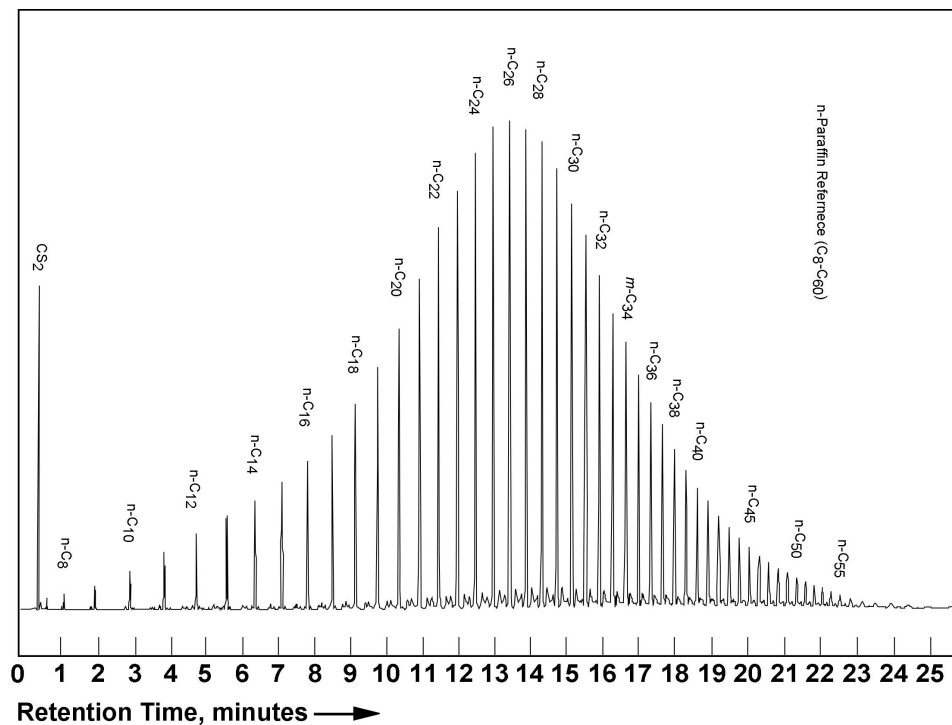


Figure 6
Example of n-paraffin reference (C₆-C₆₀)