



A Honeywell Company

Analysis of Distillate Fuels Derived from Oxygenated (Bio) Feedstocks by GC

UOP Method 732-09

Scope

This method is for determining hydrocarbon distribution in petroleum naphtha, kerosene (jet fuel), and diesel derived from oxygenated feedstocks such as vegetable or tallow oils in the range of C₃ to C₃₉. Specific components of a boiling point of 85°C (C₆) and less are identified individually. Higher boiling normal paraffins are identified individually, while the non-normals are grouped according to approximate carbon number distribution. The lower limit of quantitation for any compound or grouping is 0.01 mass-%. Due to non-normals eluting at n-paraffin sites, the lower limit of quantitation for n-paraffins may not be as low. Components of C₃ and lower molecular weight should not be considered quantitative due to their volatility, see *Note*.

This procedure is not appropriate for analyzing oxygenated feed-stocks prior to the deoxygenation stage in the EcoFining® process. Residual oxygenates in feedstocks may not elute from the instrument and are not quantified by this analysis.

Reference

ASTM Practice D 4307, "Preparation of Liquid Blends for Use as Analytical Standards," www.astm.org

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

Outline of Method

The sample is injected into a gas chromatograph (GC) that is equipped with a flame ionization detector (FID) and a fused silica capillary column internally coated with 100% dimethylpolysiloxane. A quantitative blend composed of petroleum hydrocarbons, whose boiling points extend throughout the boiling range of the sample, is to be used to determine the n-paraffin sites. By utilizing these sites, an approximate carbon number distribution of the sample components can be determined. The mass-% composition of the sample is obtained by the internal normalization technique, wherein the peak areas are 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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Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Apparatus

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

Balance, readable to 0.1-mg.

Chromatographic column, 30 m of 0.25 mm ID fused silica capillary, internally coated to a film thickness of 0.25 μm with 100% dimethylpolysiloxane, Restek, Cat. No. 10123

Gas chromatograph, temperature programmable, 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

Gas purifier, used to remove oxygen from the hydrogen carrier gas, Mat/Sen, Cat. No. P-200-1

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. Agilent Technologies, ChemStation

Leak detector, gas, Restek Cat. No. 22451

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 or helium, 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 user. Other suppliers may be used.

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

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

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.

Procedure

Chromatographic Technique

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

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 fused silica 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 1-6).
 - For samples with high concentrations of a specific component, care must be taken that sample size does not allow for the major peaks to overload the column capacity or the linear range of the detector.

Table 1
Recommended Operating Conditions

Carrier Gas	hydrogen
Mode	constant flow
Column head pressure at 40°C	44 kPa (6.4 psig)
Linear velocity at 40°C	28 cm/sec
Equivalent flow at 40°C	1.0 mL/min
Split flow rate	250 mL/min
Injection port temperature	285°C
Column temperature program	
Initial temperature	40°C
Initial time	8.0° min
Programming rate	3°C/min
Final temperature	300°C
Final time	65 min
Detector	flame ionization
Detector temperature	320°C
Hydrogen flow rate*	40 mL/min
Air flow rate*	400 mL/min
Makeup gas	Nitrogen or Helium
Makeup gas flow rate*	35 mL/min
Sample size	0.5 µL

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

4. Program the column oven to 300°C and maintain this temperature until a stable baseline has been obtained at the required sensitivity.
5. Cool the column oven to a stabilized 40°C.
6. Mix the sample thoroughly by shaking it vigorously.
7. Inject 0.5 µL of sample into the gas chromatograph and immediately start the recorder, 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.
8. Identify the n-paraffins and carbon number groupings by comparing the resultant chromatogram with the typical chromatograms, Figures 1-6, and Tables 2 and 3. Actual retention times will vary depending on the installation. Use the Figures and Tables as examples, not for absolute retention times.
- A quantitative blend composed of equal portions of expected n-paraffins within the boiling point range of the sample to be analyzed is to be run to determine the location of the n-paraffin sites. Reference paraffins used indicate a full sample range, actual paraffins used may be altered depending on the expected carbon range of the sample. These sites are then to be utilized in determining the approximate carbon distribution of samples (see Figure 7). The quantitative blend can also be used to check for system linearity. See *Calibration* for further details on linearity and satisfactory performance.
 - The peaks assigned a carbon number grouping are those that elute between the valley immediately following the previous n-paraffin peak and the valley immediately before the n-paraffin peak of the carbon number group (see Figure 7). Quantification of carbon number groupings are approximate.
 - At sites with co-elution where the n-paraffin can be clearly identified (see Figure 8), a tangent line is drawn from one peak valley to another. All of the area above the tangent line is to be considered the n-paraffin peak; all of the area below the tangent line is to be placed into the appropriate grouping (see Figure 8). At all other areas of the chromatogram, other than n-paraffin sites where co-elution exists, a common baseline must be established through the chromatogram and perpendiculars from valleys dropped to the common baseline to insure all peak areas are summed. To aid in determining a common baseline, a blank run can be run and the baseline noted. Some rise in the baseline is normal at the end of the chromatogram due to column bleed and is acceptable as long as it is repeatable and not integrated as peak area.
 - If a specific n-paraffin site cannot be determined from the initial chromatogram, it may be necessary to add a few drops (spike) of the paraffin in question to 10 to 15 mL of the sample. Rerun the sample with the added paraffin and compare the two chromatograms to find the location of the n-paraffin site in question.
 - 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 used for the area in question (see Figure 9).

Table 2
Typical Retention Times of Identified Components

<u>Typical Retention Time, Min</u>	<u>Component Identification</u>
1.81	Ethane
1.84	Propane
1.89	Isobutane
1.93	n-Butane
2.07	Isopentane
2.14	n-Pentane
2.29	2,2-Dimethylbutane
2.47	Cyclopentane
	+2,3-Dimethylbutane
	+2-Methylpentane
2.56	3-Methylpentane
2.69	n-Hexane
2.96	Methylcyclopentane
3.25	Benzene
3.37	Cyclohexane

Table 3**Typical Retention Times of n-Paraffins
and Timed Carbon Number Groupings**

Typical Retention Time, Min	Component Identification	Typical Retention Time, Min	Component Identification
0-2.69	Unknown C ₆ -	67.61	n-C ₂₃
2.69-4.07	C ₇ group	67.61-70.22	C ₂₄ group
4.07	n-C ₇	70.22	n-C ₂₄
4.07-7.49	C ₈ group	70.22-72.71	C ₂₅ group
7.49	n-C ₈	72.71	n-C ₂₅
7.49-13.42	C ₉ group	72.71-75.13	C ₂₆ group
13.42	n-C ₉	75.13	n-C ₂₆
13.42-19.28	C ₁₀ group	75.13-77.46	C ₂₇ group
19.28	n-C ₁₀	77.46	n-C ₂₇
19.28-24.61	C ₁₁ group	77.46-79.71	C ₂₈ group
24.61	n-C ₁₁	79.71	n-C ₂₈
24.61-29.48	C ₁₂ group	79.71-81.88	C ₂₉ group
29.48	n-C ₁₂	81.88	n-C ₂₉
29.48-33.98	C ₁₃ group	81.88-83.95	C ₃₀ group
33.98	n-C ₁₃	83.95	n-C ₃₀
33.98-38.19	C ₁₄ group	83.95-86.03	C ₃₁ group
38.19	n-C ₁₄	86.03	n-C ₃₁
38.19-42.55	C ₁₅ group	86.03-87.81	C ₃₂ group
42.55	n-C ₁₅	87.81	n-C ₃₂
42.55-45.99	C ₁₆ group	87.81-89.92	C ₃₃ group
45.99	n-C ₁₆	89.92	n-C ₃₃
45.99-49.68	C ₁₇ group	89.92-92.32	C ₃₄ group
49.68	n-C ₁₇	92.32	n-C ₃₄
49.68-53.04	C ₁₈ group	92.32-94.93	C ₃₅ group
53.04	n-C ₁₈	94.93	n-C ₃₅
53.04-56.10	C ₁₉ group	94.93-97.39	C ₃₆ group
56.10	n-C ₁₉	97.39	n-C ₃₆
56.10-59.18	C ₂₀ group	97.39-100.06	C ₃₇ group
59.18	n-C ₂₀	100.06	n-C ₃₇
59.18-62.08	C ₂₁ group	100.06-117.23	C ₃₈ group
62.08	n-C ₂₁	117.23	n-C ₃₈
62.08-64.91	C ₂₂ group	117.23-123.71	C ₃₉ group
64.91	n-C ₂₂	123.71	n-C ₃₉
64.91-67.61	C ₂₃ group		

Calibration

Since all paraffinic components have essentially the same detector response on a mass basis in a flame ionization detector, no relative response factor calibration is required (area-% is equivalent to mass-%).

- Prepare a quantitative blend as described in ASTM Method D4307 to obtain the target values of the following n-paraffin blend.
- A quantitative blend composed of equal portions of expected n-paraffins within the boiling point range of the sample is then analyzed to check for instrument linearity.

- o Use the blend to identify the expected n-paraffin peak retention times
- o Each n-paraffin within the blend should be within 3% of the expected value not to exceed +/- 0.3 mass-%.

Calculations

Calculate the composition of samples, to the nearest 0.01% mass-% using Equation 1:

$$C = \frac{100A}{B} \quad (1)$$

where:

A = peak area of the individual component or group of components. The area included in each group does not include the area of the individual component.

B = sum of all the peak areas

C = concentration of all specific component or group components, mass-%

100 = factor to convert to percent

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

Note

Components of C₃ and lower molecular weight may be partially lost before analysis due to their volatility. Due to the nature of the internal normalization technique, a reduction of one group of components will result in the increase of the other components, thereby keeping the sum of all the components at 100%. However, for practical purposes, the loss of a portion of the light components, when spread across the balance of the sample, results in a negligible difference in the quantitation of the heavier components.

Precision

Precision statements were determined using UOP Method 999 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 two tests each day. The total number of tests for each component was 16. 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.

Reproducibility

There is insufficient data to calculate reproducibility at this time.

Time for Analysis

The elapsed time for one analysis is 3 hours. The labor requirement is 1.0 hour.

Table 4
Repeatability and Site Precision, mass-%

Sample Component or Region	Mean	<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>
n-Butane	0.09	0.001	0.01	0.006	0.03
Isopentane	0.07	0.001	0.01	0.001	0.01
n-Pentane	0.30	0.003	0.01	0.004	0.01
n-Hexane	0.09	0.002	0.01	0.003	0.01
C₆-C₇ Group	0.88	0.009	0.03	0.010	0.03
n-Heptane	0.41	0.002	0.01	0.003	0.01
C₇-C₈ Group	0.04	0.004	0.02	0.005	0.02
n-C₉	0.24	0.004	0.01	0.004	0.01
C₁₀-C₁₁ Group	2.73	0.023	0.08	0.031	0.10
n-C₁₂	0.44	0.002	0.01	0.003	0.01
C₁₃-C₁₄ Group	2.45	0.059	0.19	0.063	0.21
n-C₁₅	0.99	0.009	0.03	0.010	0.03
C₁₆-C₁₇ Group	32.83	0.055	0.18	0.080	0.29
n-C₁₇	4.33	0.035	0.11	0.036	0.12
C₁₇-C₁₈ Group	10.67	0.040	0.13	0.049	0.16
n-C₁₈	5.71	0.011	0.03	0.019	0.07
C₁₈-C₁₉ group	0.19	0.016	0.05	0.053	0.24
C₂₀-C₂₁ Group	0.03	0.005	0.01	0.009	0.04

Suggested Suppliers

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

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

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700)
www.mathesontrigas.com

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

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

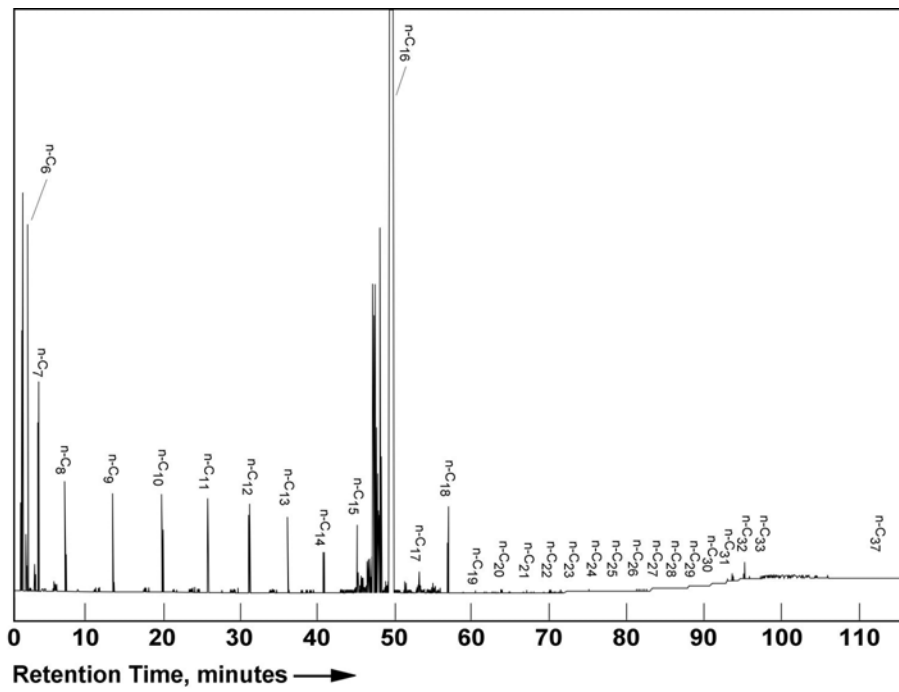


Figure 1
Example Chromatogram (Total)

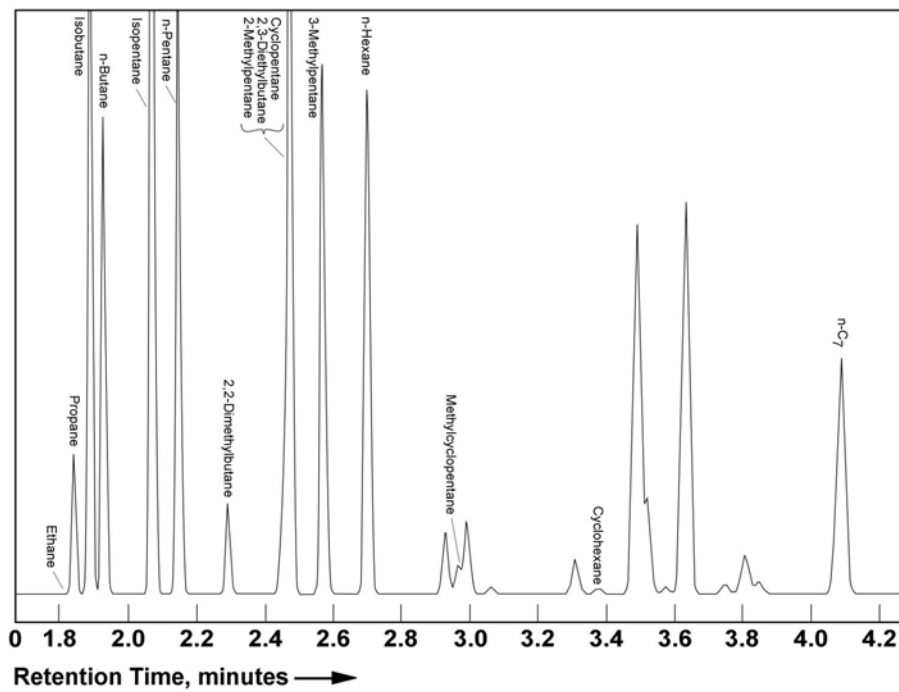


Figure 2
Example Chromatogram (C₃-C₇ region)

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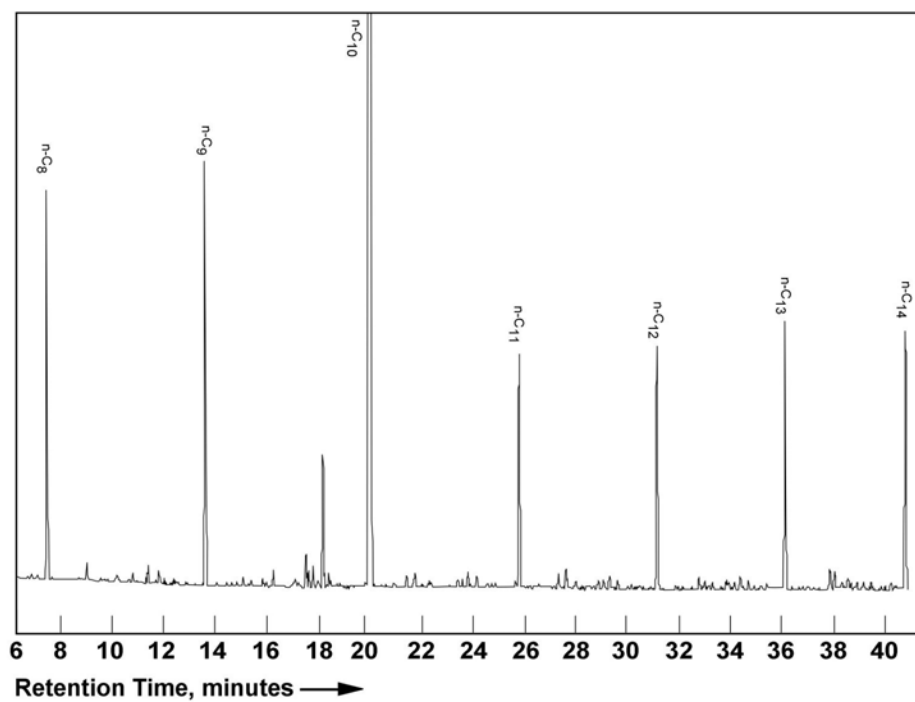


Figure 3
Example Chromatogram (C₈-C₁₄ region)

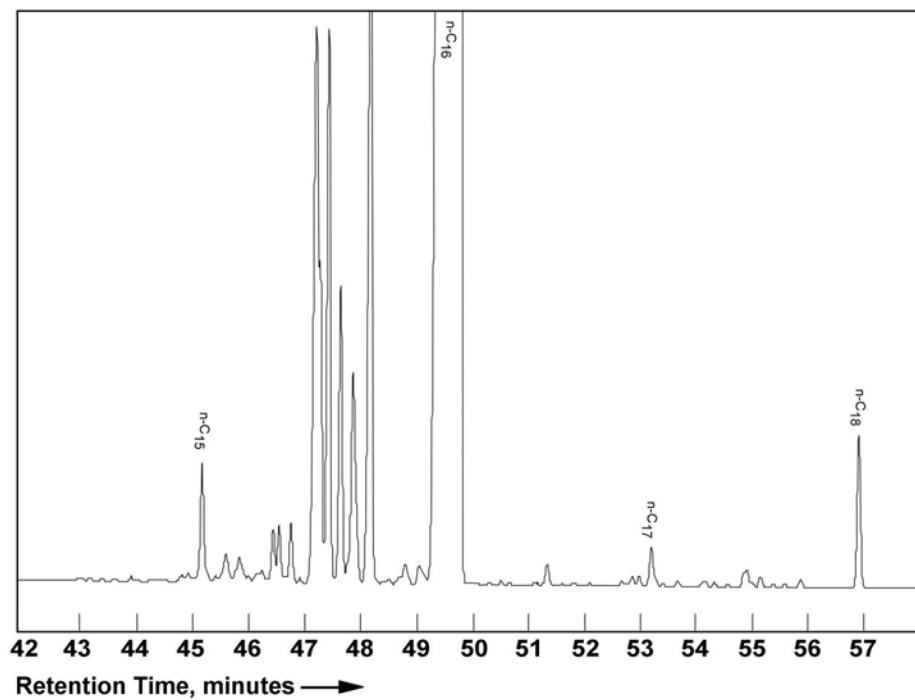


Figure 4
Example Chromatogram (C₁₅-C₁₈)

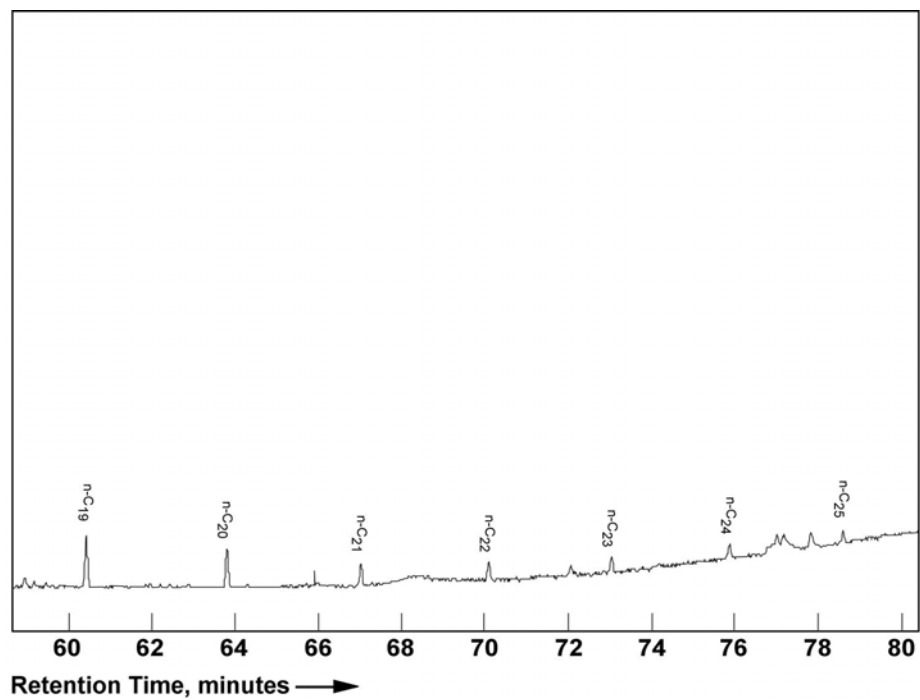


Figure 5
Example Chromatogram (C₁₉-C₂₅ region)

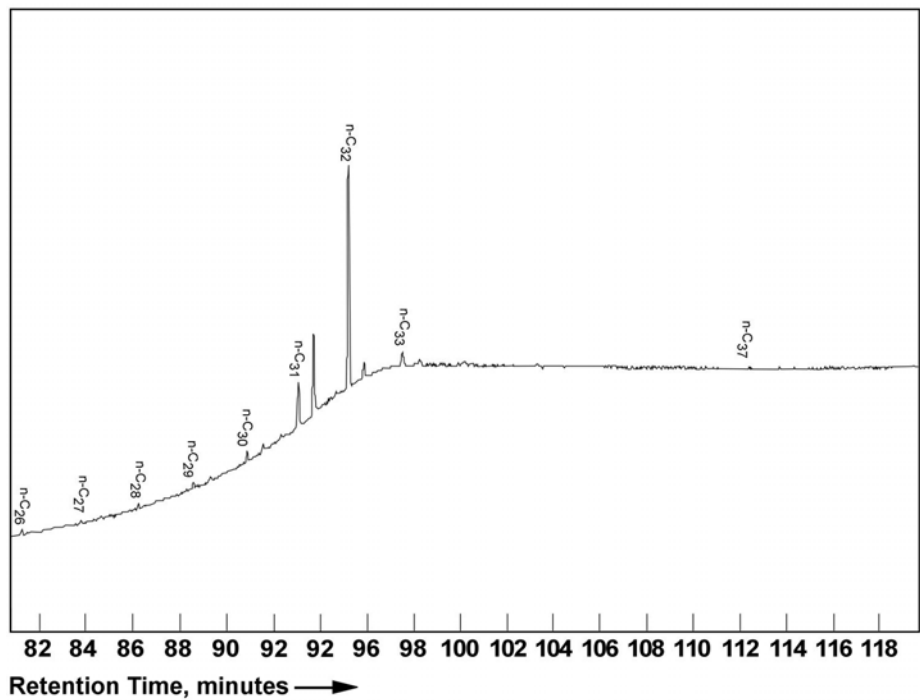


Figure 6
Example Chromatogram (C₂₆-C₃₉ region)

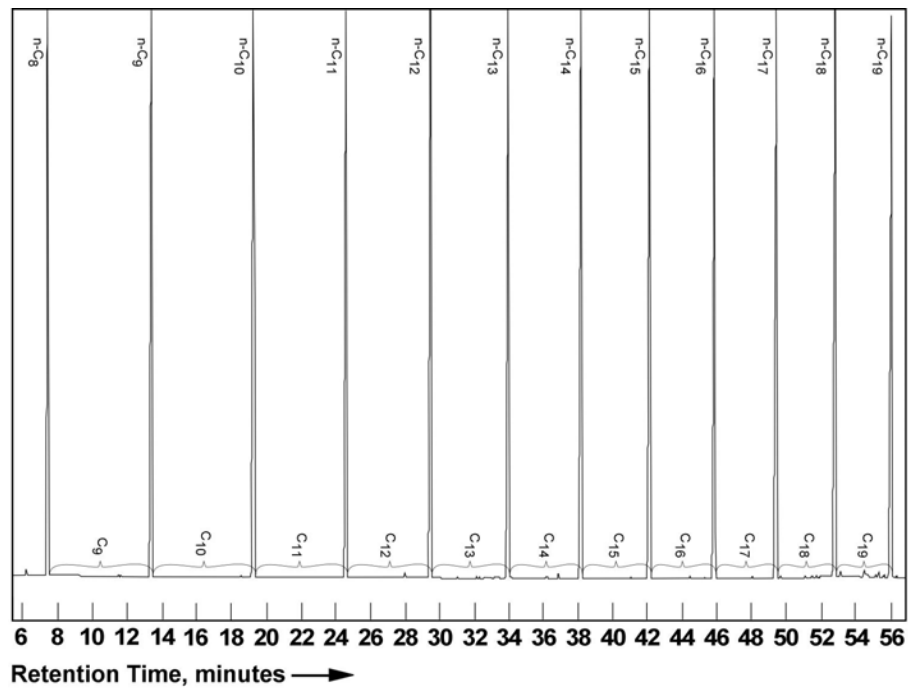


Figure 7
Example of n-Paraffin Blend

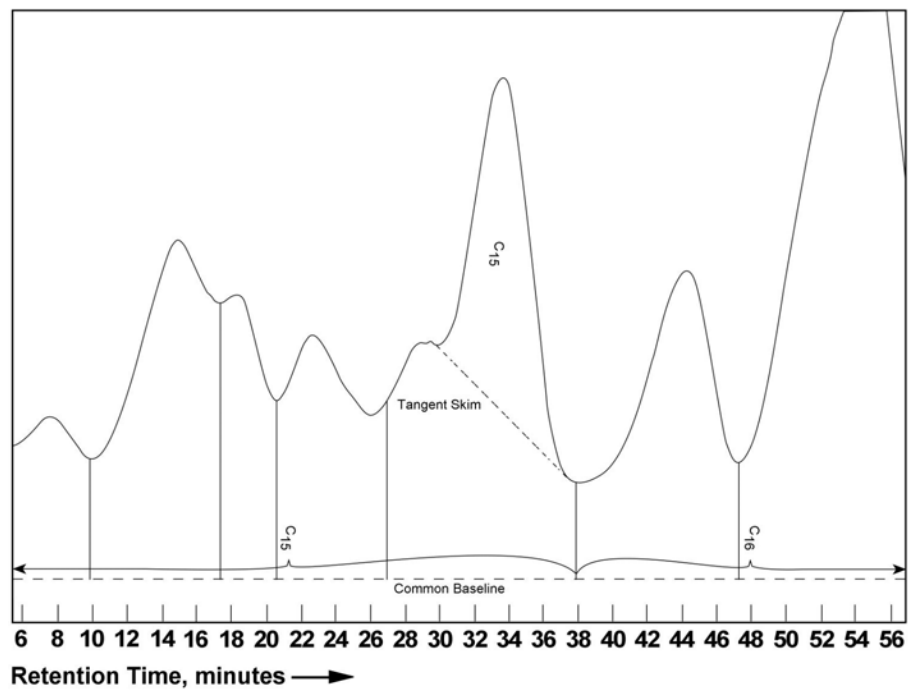


Figure 8
Example of Tangent Skimming Threshold (n-C15)

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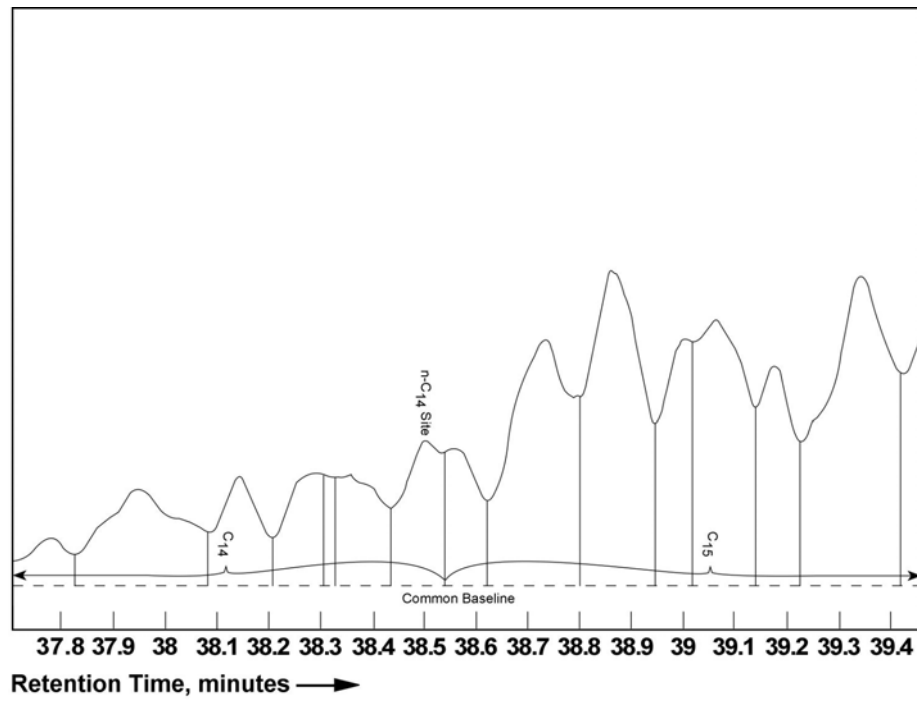


Figure 9
Example of Unclear n-Paraffin Site

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