



A Honeywell Company

Normal Olefins and Normal Paraffins by GC

UOP Method 688-09

Scope

This method is for determining total normal olefins (TNO), individual carbon number normal olefins, total normal paraffins (TNP), and individual normal paraffins in the UOP Pacol[®], UOP Define[®], and UOP Olex[®] process feed and product streams. Samples can be in the C₉ to C₁₈ carbon number range, consisting of light ends (cracked by-products), normal paraffins, normal olefins, and associated non-normals compounds. Normal olefins include diolefins, if present. Small amounts of non-normals elute with the normal paraffins and normal olefins resulting in an approximate value for the total non-normals (TNN). A more accurate TNN value can be determined separately by UOP Method 411 (see Note 1). The lower limit of quantitation for any compound is 0.01 mass-%. The lower limit of quantitation for any carbon number group is approximately 0.05 mass-%.

References

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

Scanlon, J. T. and Willis, D. E., *Journal of Chromatographic Science*, **23**, 333-340 (1985)

UOP Method 411, "Normal Paraffins by Subtractive Gas Chromatography," www.astm.org

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

Outline of Method

The sample to be analyzed is injected into a gas chromatograph that is equipped with a fused silica capillary column, internally coated with (bonded) methyl phenyl polysiloxane, and a flame ionization detector (FID). The mass-% composition of the sample is obtained by the internal normalization technique. The UOP Pacol process feed (high-purity *n*-paraffins) and the Olex process extract (high purity *n*-olefins) samples are reported without further calculations. The composition of other stream samples requires correction for low concentrations of non-normal compounds eluting at the normal olefin sites. The amount of correction is determined from the analysis of the olefin-free UOP Pacol process feed under the same chromatographic conditions (see Note 1).

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, readability 0.1-mg

Chromatographic column, 30 m of 0.25-mm ID fused silica capillary, internally coated to a film thickness of 1.0 μ with RTX[®]-50 (bonded) methyl phenyl polysiloxane, Restek, Cat. No. 10553

Gas chromatograph, temperature programmable, built for capillary column chromatography, utilizing a split injection system, having a glass injection port insert, and equipped with a flame ionization detector that will give a minimum peak height response of ten times the background noise for 0.01 mass-% *n*-tetradecane when operated at the recommended conditions, Agilent Technologies, Model 7890. The inclusion of an autosampler (or autoinjector) is recommended but not required.

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 system must have programmable parameters for controlling baseline events, and have graphics capabilities. Agilent Technologies, ChemStation.

Leak detector, gas, Alltech Associates, Cat. No. 21-250

Pipet bulbs, VWR, Cat. No. 82024-552

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, any syringe or injector capable of introducing a 0.5- μ L volume of sample. An auto sampler (or auto injector) 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.

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

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

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 represented in the feed, typically C₉ to C₁₈, to identify peak sites.

Pipets, disposable, Pasteur, VWR, Cat. No. 14673-043

Syringe, replacement, for sample injector, 5- μ L, Agilent Technologies, Cat. No. 5181-1273

Vials, autosampler, for recommended sample injector, Agilent Technologies, Cat. No. 5182-0864

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

Procedure

Chromatographic Technique

The analyst is expected to be familiar with 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 inlets 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 leakage into the confined volume of the column oven can cause a violent explosion. Therefore, it is mandatory to check for leaks each time a connection is made and periodically thereafter.

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Mode	constant pressure
Head pressure	83 kPa gauge (12 psig)
Linear velocity @ 100°C	46.6 cm/sec
Equivalent flow @ 100°C	1.6 mL/min
Split flow	200 mL/min
Injection port temperature	250°C
Column temperature program	
Initial temperature	100°C
Initial hold time	5 min
Programming rate A	5°C/min
Intermediate temperature	175°C
Intermediate hold time	15 min
Programming rate B	5°C/min
Final hold temperature	275°C
Final hold time	5 min
Detector	flame ionization
Detector temperature	280°C
Hydrogen flow rate*	30 mL/min
Air flow rate*	400 mL/min
Makeup gas	nitrogen or helium
Makeup gas flow rate*	30 mL/min
Sample size	0.5 µL

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

3. Establish the recommended operating conditions as given in Table 1.
 - Different conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatograms (Figures 1, 2, and 3).
4. Program the column oven to 275°C. Maintain this temperature until a stable baseline has been obtained at the required sensitivity.
5. Cool the column oven to a stabilized 100°C.
6. If using an autosampler, multiple samples may be transferred into autosampler vials and preloaded into the tray.
7. Inject 0.5 µL of the sample to be analyzed into the gas chromatograph and start the integrator and column temperature programming sequence.
 - When using an autosampler or injector, 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 components by comparing the resultant chromatogram with the Typical Chromatograms (see Figures 1, 2, and 3).
 - Any individual peak or peaks can be identified and reported separately.
 - To avoid understating the amount of TNN, a common baseline with perpendicular drops to baseline are typically required. One should avoid using valley to valley baseline for unresolved peaks.

Calibration

Since all the sample components have essentially the same detector response on the mass basis, no relative response factor calibration is required (area-% is equivalent to mass-%). The mass-% composition of the sample is obtained by the internal normalization technique of quantitation wherein the peak areas are normalized to 100%.

- A quantitative blend prepared as described in ASTM Method D4307 composing of equal portions of the expected n-paraffins within the carbon number range of the sample is analyzed to check for instrument linearity.
- The quantitative n-paraffin blend is run when the method is initially set up and thereafter when changes have been made to the equipment or periodically to verify instrument linearity.

Calculations

Calculate the uncorrected composition of any sample to the nearest 0.01 mass-% using Equation 1:

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

where:

A = peak area of the individual component or group of components

B = sum of all the peak areas

D = uncorrected concentration of a specific component or group of components, mass-%

100 = factor to convert to mass%

Calculate the corrected mass-% normal olefins for each carbon number to the nearest 0.01 mass-% using Equation 2:

$$E = F - G \quad (2)$$

where:

E = corrected normal olefin concentration for each carbon number, mass-%

F = uncorrected concentration of normal olefins eluting in a specific normal olefin region (Equation 1), mass-%

G = concentration of non-normals eluting in a specific normal olefin region of the UOP Pacol process feed (Equation 1), mass-%

Calculate the corrected non-normals to the nearest 0.01 mass-% for each carbon number using Equation 3:

$$H = G + K \quad (3)$$

where:

G = previously defined, Equation 2

H = corrected non-normals, mass-%

K = non-normals determined for a specific carbon number region (Equation 1), mass-%

Sum the n-paraffins, n-olefins and non-normals previously calculated for each carbon number to obtain totals.

- If Method U411 is used to obtain the mass-% TNN, see Note 2.

Notes

1. UOP Method 411 is the more accurate procedure for determining TNN. If the equipment for performing UOP Method 411 is not available, determining the amount of correction for the non-normals eluting in the specific olefin regions can be obtained from the analysis of the olefin free UOP Pacol Process Feed.
2. Using the mass-% TNN, obtained by UOP Method 411, requires renormalization of TNO (after correction) and TNP to equal 100 minus the mass-% TNN from UOP Method 411. The data report should stipulate TNN obtained by UOP Method 411.

Precision

Precision statements were determined using UOP Method 999 from precision data obtained using an autosampler.

Repeatability and Intermediate Precision

A nested design was carried out for determining components in one olefinic hydrocarbon sample at two levels with two 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 eight. The precision data are summarized in Tables 2 and 3. 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 Tables 2 and 3 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 the long-term repeatability.

Table 2
Repeatability and Site Precision, mass-%

C9-C14 Pacolate Composite Component	Mean Conc.	<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>
Light Ends	0.20	0.01	0.04	0.02	0.07
n-Nonane	0.04	0.01	0.01	0.01	0.01
n-Decane	9.70	0.02	0.08	0.03	0.15
n-C10 Olefins	1.28	0.01	0.01	0.01	0.06
n-Undecane	29.14	0.04	0.16	0.09	0.40
n-C11 Olefins	4.33	0.01	0.02	0.02	0.15
n-Dodecane	28.48	0.04	0.15	0.08	0.34
n-C12 Olefins	5.00	0.01	0.06	0.03	0.14
n-Tridecane	16.23	0.03	0.12	0.03	0.12
n-C13 Olefins	3.42	0.01	0.01	0.01	0.02
n-Tetradecane	0.29	0.01	0.01	0.01	0.02
n-C14 Olefins	0.14	0.01	0.02	0.01	0.04
Non-Normals	1.74	0.10	0.39	0.15	0.60
Total Normal Paraffins	83.88	0.12	0.45	0.22	0.99
Total Normal Olefins	14.18	0.03	0.13	0.09	0.58

Table 3
Repeatability and Site Precision, mass-%

C14-18 Olex Feed Component	Mean Conc.	<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>
Light Ends	0.05	0.01	0.01	0.01	0.02
n-Tetradecane	0.48	0.01	0.01	0.01	0.01
n-C14 Olefins	0.03	0.01	0.02	0.01	0.02
n-Pentadecane	57.81	0.03	0.13	0.06	0.27
n-C15 Olefins	5.29	0.01	0.01	0.01	0.09
n-Hexadecane	28.86	0.01	0.04	0.01	0.03
n-C16 Olefins	3.06	0.01	0.02	0.01	0.09
n-Heptadecane	2.85	0.01	0.02	0.01	0.07
n-C17 Olefins	0.34	0.01	0.02	0.01	0.02
n-Octadecane	0.06	0.01	0.01	0.01	0.01
Non-Normals	1.16	0.03	0.13	0.03	0.11
Total Normal Paraffins	90.07	0.04	0.15	0.05	0.20
Total Normal Olefins	8.72	0.01	0.05	0.03	0.21

Reproducibility

There is insufficient data to calculate reproducibility of the test at this time.

Time for Analysis

The elapsed time for one analysis is 1.2 hours. The labor requirement is 0.5 hour.

Suggested Suppliers

Agilent Technologies, 2850 Centerville Rd., Wilmington, DE 19808-1610 (302-633-8000)
www.agilent.com

Alltech Associates Inc., 2051 Waukegan Rd., Deerfield, IL 60015 (847-948-8600)
www.alltechweb.com

Chemsampco, 40 Enterprise Ave., Trenton, NJ 08638 (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

VWR International, 1310 Goshen Parkway, West Chester, PA 19380 (610-431-1700)
www.vwr.com

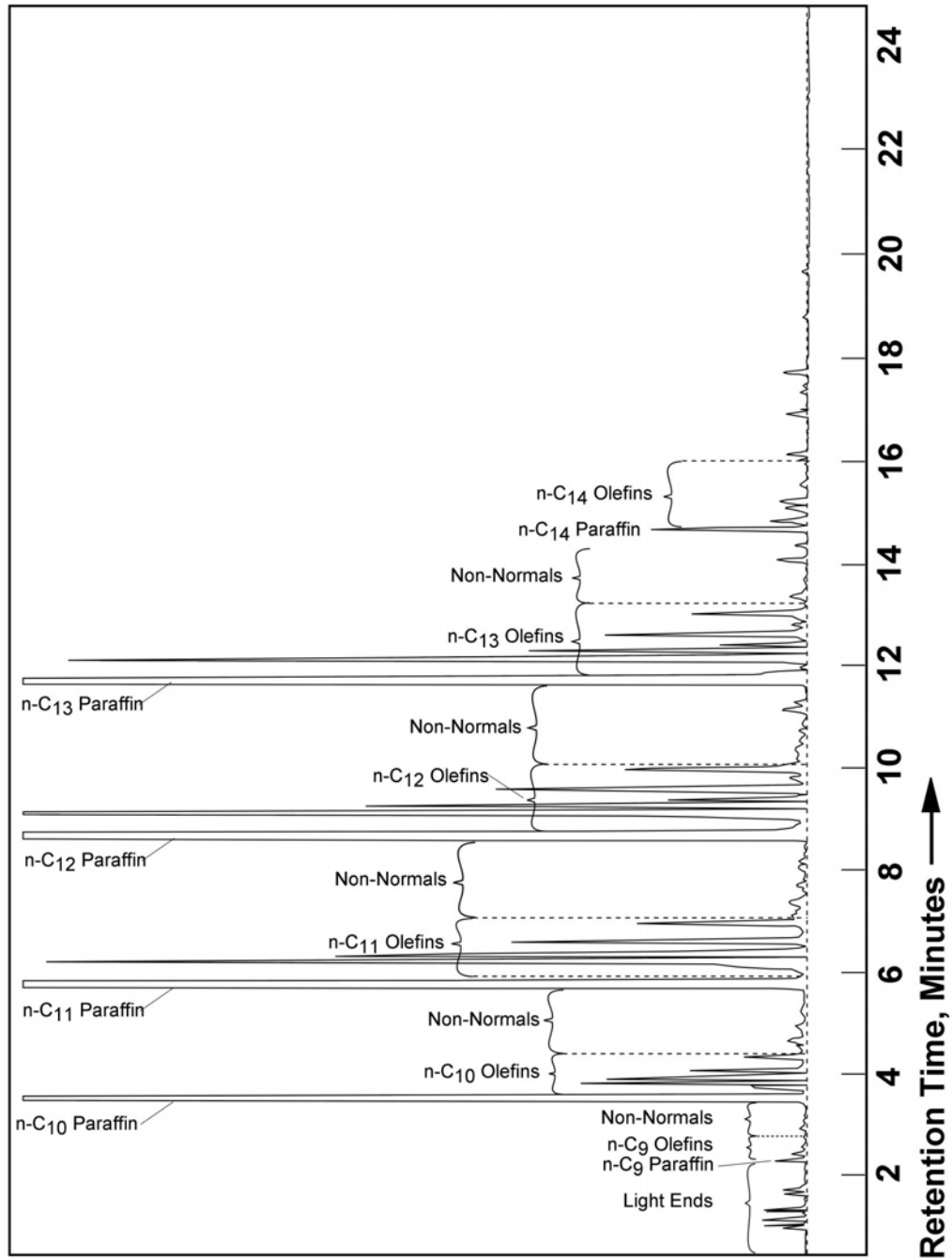


Figure 1
Typical Chromatogram
Stream Sample (C₉-C₁₄ Range)

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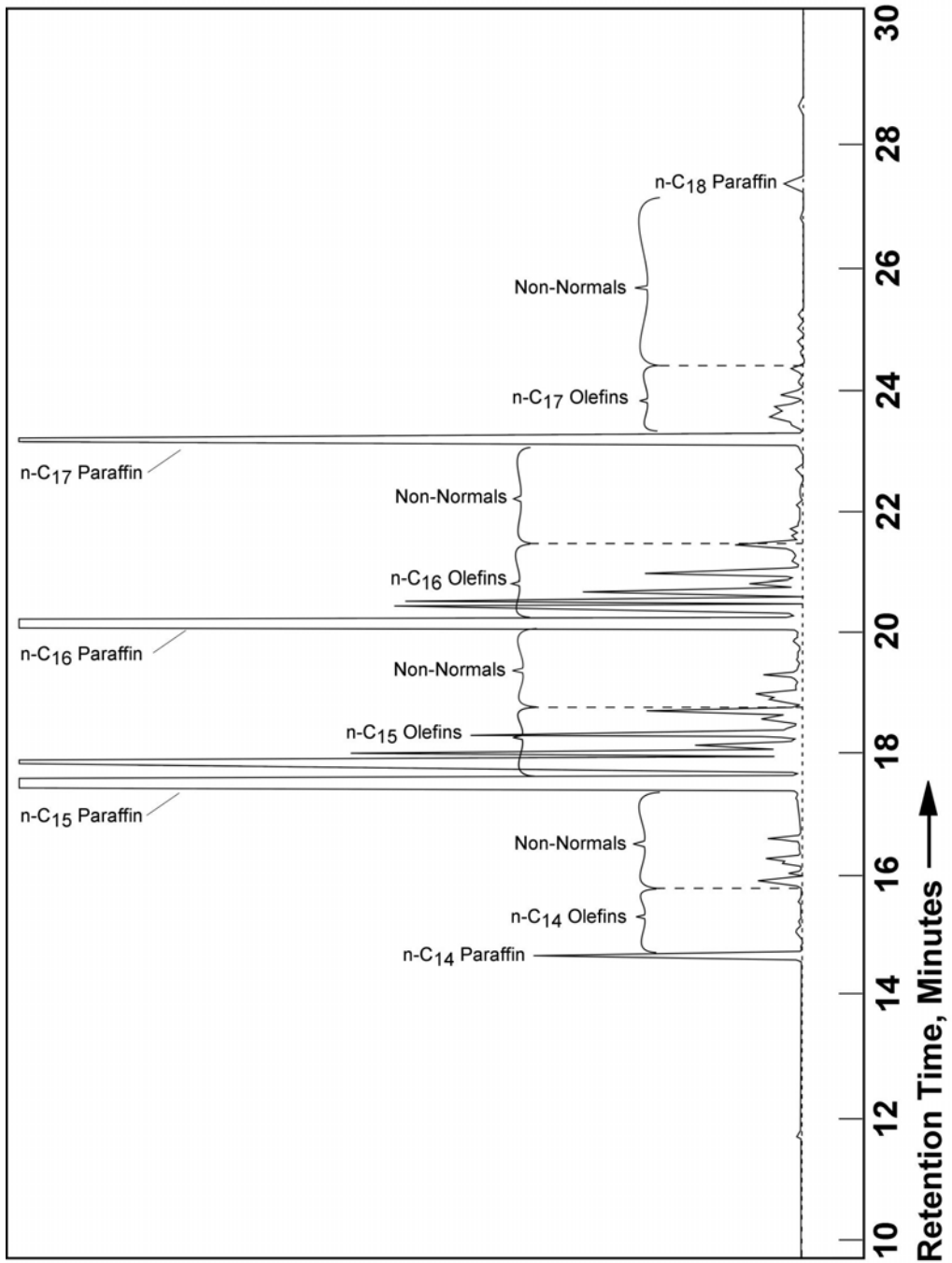


Figure 2
 Typical Chromatogram
 Stream Sample (C₁₄-C₁₈ Range)

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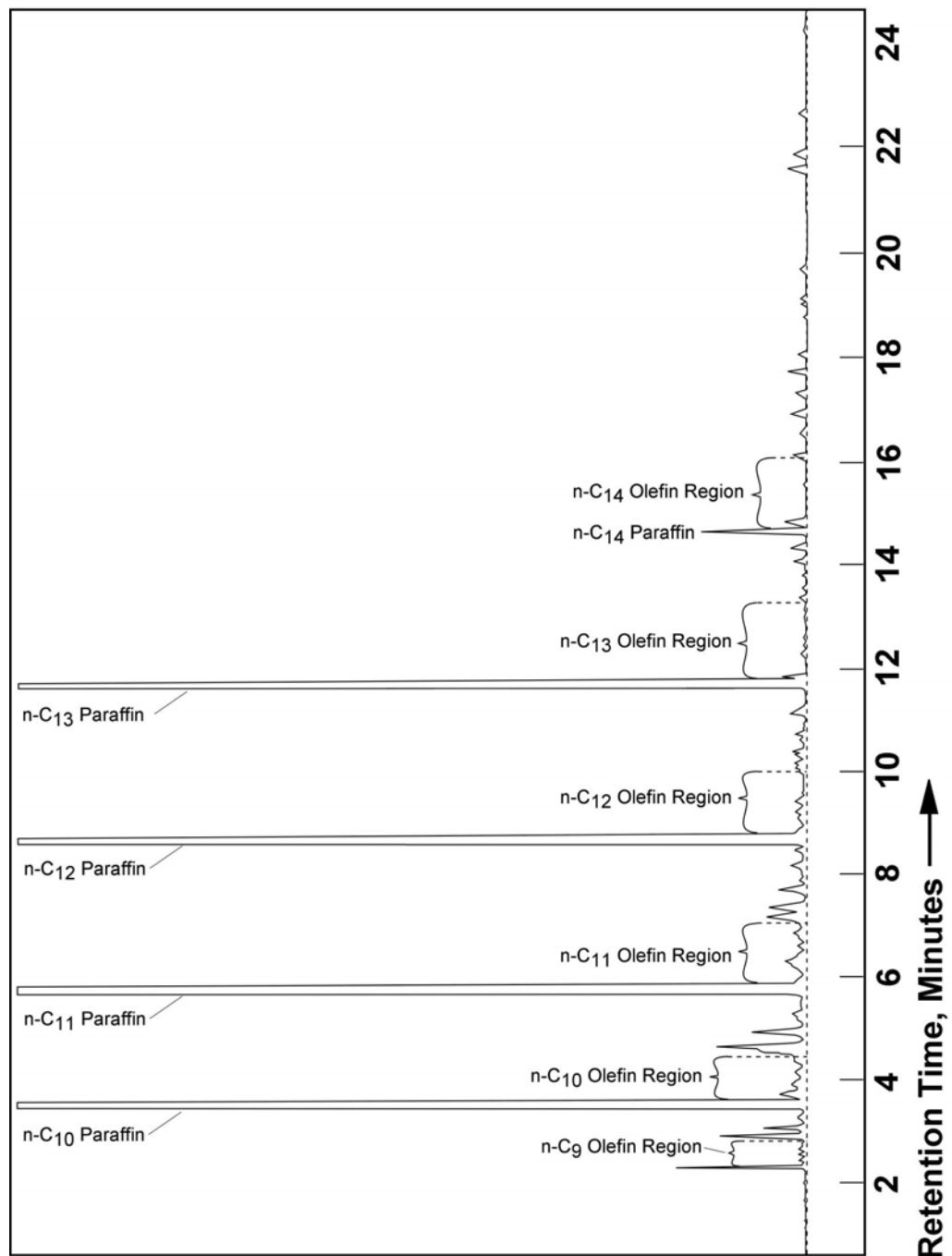


Figure 3
Typical Chromatogram
Olefin-Free Feed

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