

BOILING POINT DISTRIBUTION OF HYDROCARBONS BY GAS CHROMATOGRAPHY

UOP Method 621-98

SCOPE

This method is for analyzing by gas chromatography mixtures of liquid hydrocarbons in the range of C₅ through C₂₀, using a column that separates components by boiling points. Procedures are provided for several applications, depending on the calibration used. These include, but are not limited to, (a) component distribution as defined by boiling points and corresponding carbon numbers, (b) determination of individual components resolved from a mixture of other components, and (c) analysis of a total sample wherein the identities of the major components or groups of components are known. Variations may be made as required, such as grouping of specific components by boiling ranges or extending the application to other ranges. The range of quantitation for a single component (or group of components) is 0.05 to 99.9 mass-%.

OUTLINE OF METHOD

The sample is injected into a gas chromatograph that is equipped with a flame ionization detector (FID) and a fused silica capillary column internally coated with cross-linked methyl silicone. One of the following is analyzed under identical conditions:

- a) A quantitative blend composed of *n*-paraffins whose boiling points extend throughout the boiling range of the sample to be analyzed. The “calibration chromatogram” obtained is used to determine the various boiling points or ranges by comparing the retention times of the *n*-paraffins to the observed retention times of the sample components.
- b) A quantitative blend containing the individual components of interest in a mixture similar in composition to the sample.
- c) A quantitative blend of a wide boiling range mixture wherein all the major components are known.

The mass-% composition of the sample is obtained by the internal normalization technique of quantitation wherein component areas are first corrected for response differences and then normalized to 100%. Since hydrocarbon components have essentially the same detector response on a mass basis in an FID, a relative response factor of 1.000 may be used for all components or groups, except when greater accuracy is desired or the samples contain a significant amount of benzene, toluene or mixed xylenes.

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, 50 m of 0.2-mm ID fused silica capillary, internally coated to a film thickness of 0.5- μ m with cross-linked methyl silicone, Hewlett Packard, Cat. No. 19091S-001

Gas chromatograph, capable of constant pressure mode and multiple temperature ramping, built for capillary column chromatography, utilizing a split injection system, having a glass injection port insert, and equipped with a FID that will give a minimum peak height response of 10 times the background noise for 0.05 mass-% of *n*-decane, when operated at the recommended conditions, Hewlett Packard, Model 6890

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

Integrator, electronic, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that the narrow peaks typically resulting from use of a capillary column can be accurately measured.

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

Recorder (optional), used to supplement integrator plot

Regulator, air, two-stage, high purity, Matheson Gas Products, Model 3122-590

Regulator, hydrogen, two-stage, high purity, Matheson Gas Products, Model 3122-350

Regulator, nitrogen, two-stage, high purity, Matheson Gas Products, Model 3122-580

Sample injector, syringe or injector capable of introducing a 1.0- μ L volume of sample, such as a SGE Universal Syringe, Fisher Scientific, Cat. No. SG-001105. An autoinjector may be used.

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified.

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

Air, total hydrocarbons less than 2 ppm as methane

Benzene, 99.9% purity, Aldrich Chemical, Cat. No. 27,070-9. *CAUTION: Benzene is a known carcinogen. All operations involving its use must be performed in a properly ventilated area, while wearing appropriate personal protective equipment.*

Ethylbenzene, 99.8% purity, Aldrich Chemical, Cat. No. 29,684-8

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

Nitrogen, zero-gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane

n-Paraffins, carbon nos. 5 through 20, for blending purposes, 99% minimum purity, Aldrich Chemical.
Additional hydrocarbons may be required for calibration purposes.

<i>n-Paraffin</i>	Cat. No.	<i>n-Paraffin</i>	Cat. No.
<i>C</i> ₅	27,041-5	<i>C</i> ₁₃	T5,740-1
<i>C</i> ₆	13,938-6	<i>C</i> ₁₄	17,245-6
<i>C</i> ₇	27,051-2	<i>C</i> ₁₅	P340-6
<i>C</i> ₈	41,223-6	<i>C</i> ₁₆	H670-3
<i>C</i> ₉	N2,940-6	<i>C</i> ₁₇	12,850-3
<i>C</i> ₁₀	D90-1	<i>C</i> ₁₈	O-65-2
<i>C</i> ₁₁	U40-7	<i>C</i> ₁₉	N2,890-6
<i>C</i> ₁₂	D22,110-4	<i>C</i> ₂₀	21,927-4

Toluene, 99.8% purity, Aldrich Chemical, Cat. No. 27,037-7

m-Xylene, 99% minimum purity, Aldrich Chemical, Cat. 18-556-6

o-Xylene, 97% minimum purity, Aldrich Chemical, Cat. No. X104-0

p-Xylene, 99% minimum purity, Aldrich Chemical, Cat. No. 13,444-9

PROCEDURE

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 fused silica capillary column in the gas chromatograph, according to the column and gas chromatograph manufacturers 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 (Figs. 1, 2, and 3).
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 100°C.
6. Mix the sample thoroughly by shaking it vigorously.

7. Inject 1.0 μL of sample into the gas chromatograph and immediately start the recorder, the integrator and the column oven programming sequence.
8. Identify the components of interest by comparing the resultant chromatogram to the corresponding Typical Chromatogram, Fig. 1, Fig. 2 or Fig. 3. In determining the composite area of the components within a given carbon number boiling point value (Fig. 1), start area measurements immediately after the *n*-paraffin peak of the previous carbon number; that is, one carbon less, and continue up to the end of the *n*-paraffin peak of the boiling point value under consideration. In this manner, a distribution by boiling point, or by approximate carbon number, is determined. All material thus measured should be considered as the higher of the two *n*-paraffin carbon numbers for approximate carbon number identification.
 - Single ring aromatics elute one carbon number later than *n*-paraffins of the same carbon number (Fig. 3).
 - Two ring aromatics elute approximately two carbon numbers later than *n*-paraffins of the same carbon number (Fig. 3).

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Column head pressure @ 100°C, constant pressure mode	105 kPa gauge (15 psig)
Equivalent flow	0.6 mL/min
Equivalent linear velocity	24 cm/sec
Split flow	150 mL/min
Injection port temperature	250°C
Column temperature program	
Initial temperature	100°C
Initial time	1.5 min
Programming rate	6°C/min
Final temperature	300°C
Final time	10.5 min
Detector	FID
Temperature	275°C
Hydrogen flow rate*	30 mL/min
Air flow rate*	400 mL/min
Makeup nitrogen flow rate*	30 mL/min
Sample size	1.0 μL

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

Calibration

This analysis uses internal normalization of the entire sample to quantitate the desired components in any given mixture. Since hydrocarbons, except C₆ to C₈ aromatics, respond almost equally in the FID on a mass basis, a relative response factor of 1.000 may be used for all components unless the sample contains a significant amount of identified C₆ to C₈ aromatics, or when greater accuracy is desired.

1. Prepare a calibration blend as described in ASTM Method D 4307 to contain a representative composition of the sample to be analyzed.
2. Run the calibration blend three times as described in Steps 7 through 8 under Chromatographic Technique.
 - 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 or peak identification.
3. Identify the peaks and average the individual peak areas from the triplicate runs.
4. Use the average peak areas to calculate the relative response factor for each component of interest to three decimal places, using one of the components as a reference (1.000), and Eq. 1.

$$F = \frac{AB}{CD} \quad (1)$$

where:

- A** = concentration of the component of interest (or group) in the blend, mass-%
- B** = average peak area of the reference component
- C** = concentration of the reference component in the blend, mass-%
- D** = average peak area for the component of interest
- F** = relative response factor for component of interest

A blend of *n*-paraffins, in about equal proportions, is used for designating specific boiling points over a wide range. The boiling points of *n*-paraffins, from C₅ through C₂₀, are listed in Table 2.

Table 2
Boiling Points of Normal Paraffins

<u><i>n</i>-Paraffin</u>	<u>Boiling Point, °C</u>	<u><i>n</i>-Paraffin</u>	<u>Boiling Point, °C</u>
C ₅	36.1	C ₁₃	235.4
C ₆	68.7	C ₁₄	253.6
C ₇	98.4	C ₁₅	270.6
C ₈	125.7	C ₁₆	286.8
C ₉	150.8	C ₁₇	301.8
C ₁₀	174.1	C ₁₈	316.1
C ₁₁	195.9	C ₁₉	329.7
C ₁₂	216.3	C ₂₀	342.7

CALCULATIONS

Calculate the concentration of each component (or group) using Eq. 2.

$$\text{Component (or group), mass - \%} = 100 \left(\frac{GF}{N} \right) \quad (2)$$

where:

F = relative response factor for component (or group), Eq. 1 or 1.000, if appropriate

G = peak area of individual component (or group) in the sample

N = sum of the products **GF** of all the components in the sample

100 = factor to convert to mass-%

Report to one significant digit below 0.1 mass-%, two significant digits from 0.1 to 1 mass-%, and three significant digits above 1 mass-%.

PRECISION

ASTM Repeatability

A nested design was carried out for boiling point distribution of hydrocarbons analysis with four analysts. Each analyst carried out tests on two separate days, performing two tests each day. The total number of tests performed was 16. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esds) were calculated for the components listed in Table 3. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the ASTM allowable differences shown in Table 3 at the concentrations listed with 95% confidence.

UOP Repeatability

A nested design was carried out for boiling point distribution of hydrocarbons analysis by four analysts, with each analyst carrying out tests on two separate days and performing two tests each day. The number of analyses performed was 16. Using a stepwise analysis of variance procedure, the within-lab estimated standard deviations (esds) were calculated for the components listed in Table 3. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the UOP allowable differences shown in Table 3 at the concentrations listed with 95% confidence.

Table 3
ASTM and UOP Repeatability, mass-%

Component	Concentration	ASTM Repeatability		UOP Repeatability	
		Within-Day esd	Allowable Difference	Within-Lab esd	Allowable Difference
C₅ Non-aromatics	0.23	0.004	0.01	0.01	0.03
Benzene	26.5	0.03	0.1	0.05	0.2
Toluene	40.7	0.06	0.2	0.10	0.3
C₈ Aromatics	14.9	0.03	0.1	0.05	0.2
C₁₀ Aromatics	1.05	0.006	0.02	0.005	0.02
Naphthalene	3.13	0.013	0.04	0.015	0.05
C₁₂ Aromatics	0.05	0.003	0.01	0.003	0.01

The data in Table 3 were obtained using an autoinjector and are a short-term estimate of repeatability. When the test is run routinely in the field, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time for one analysis is one hour. The labor requirement is 0.25 hour.

REFERENCE

ASTM Method D 4307, www.astm.org

SUGGESTED SUPPLIERS

Aldrich Chemical Co., Inc., P.O. Box 355, Milwaukee, WI 53201 (414-273-3850)
 Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015 (847-948-8600)
 Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300)
 Hewlett Packard Co., 2850 Centerville Rd., Wilmington, DE 19808-1610 (302-633-8000)
 Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)
 UOP Mat/Sen, 4509 Golden Foothill Pkwy., El Dorado Hills, CA 95762 (916-939-8800)

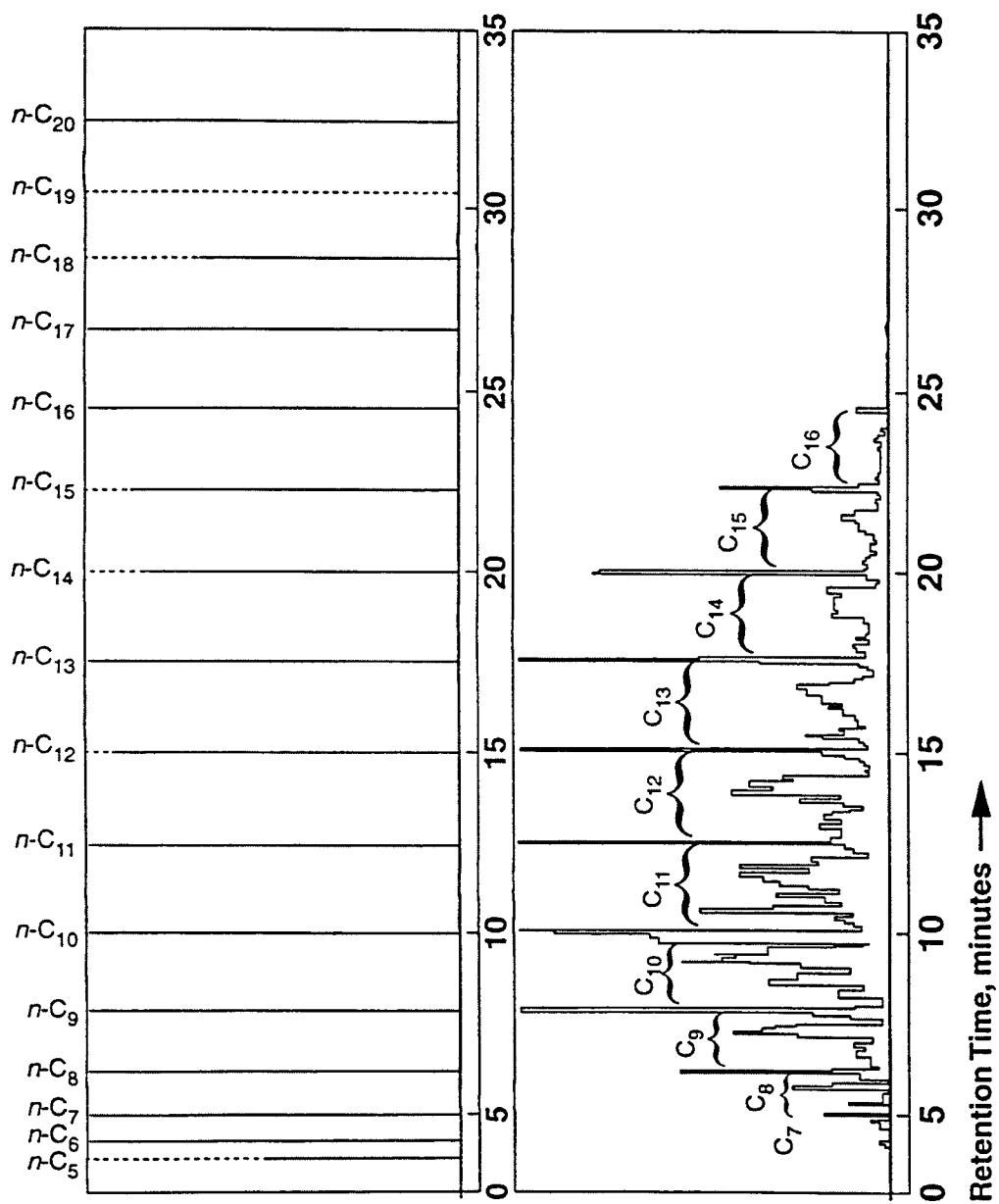


Figure 1
 Typical Chromatogram
n-Paraffins and Components by Carbon Number

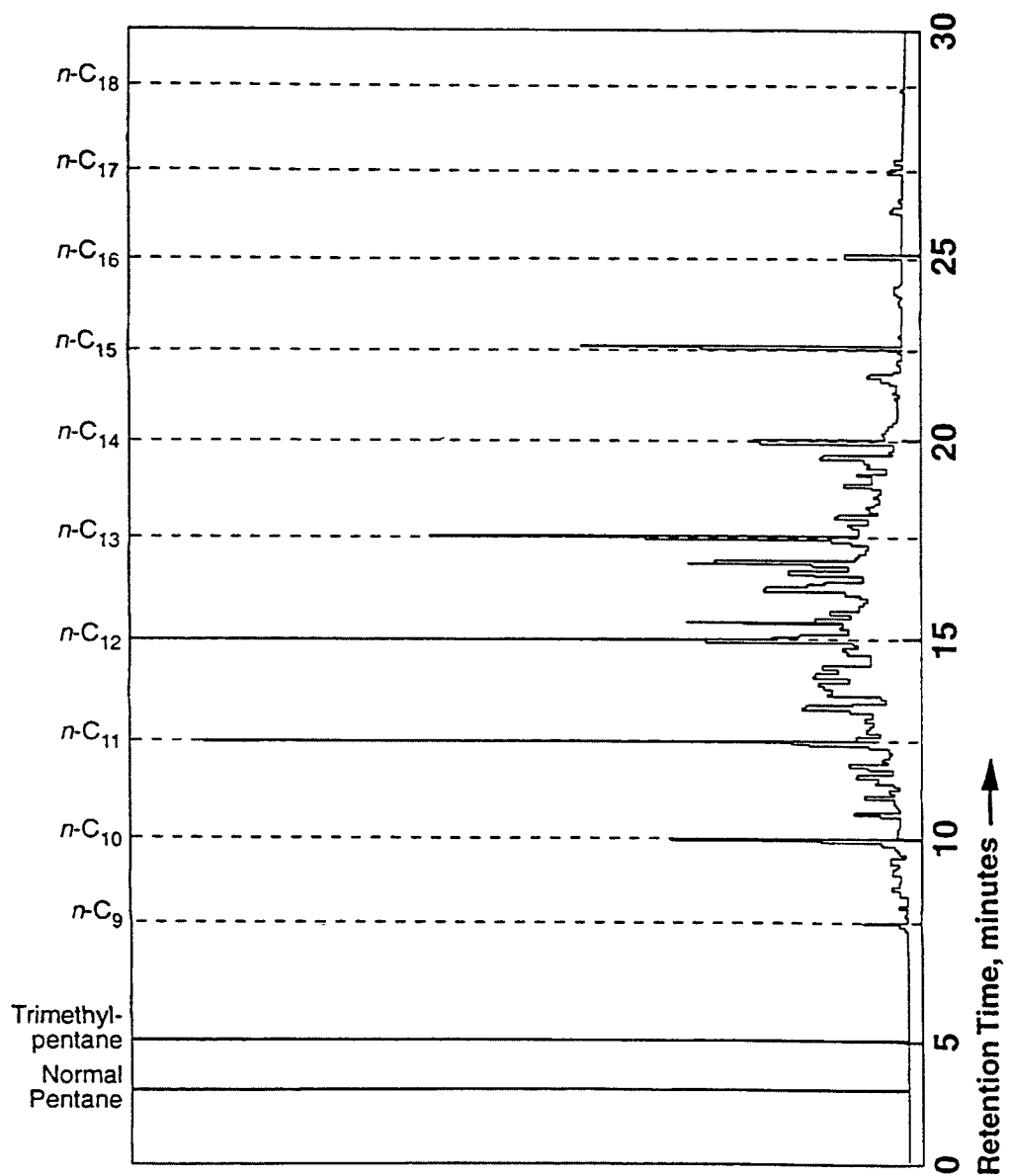


Figure 2
Typical Chromatogram
Molex Sample with Desorbent

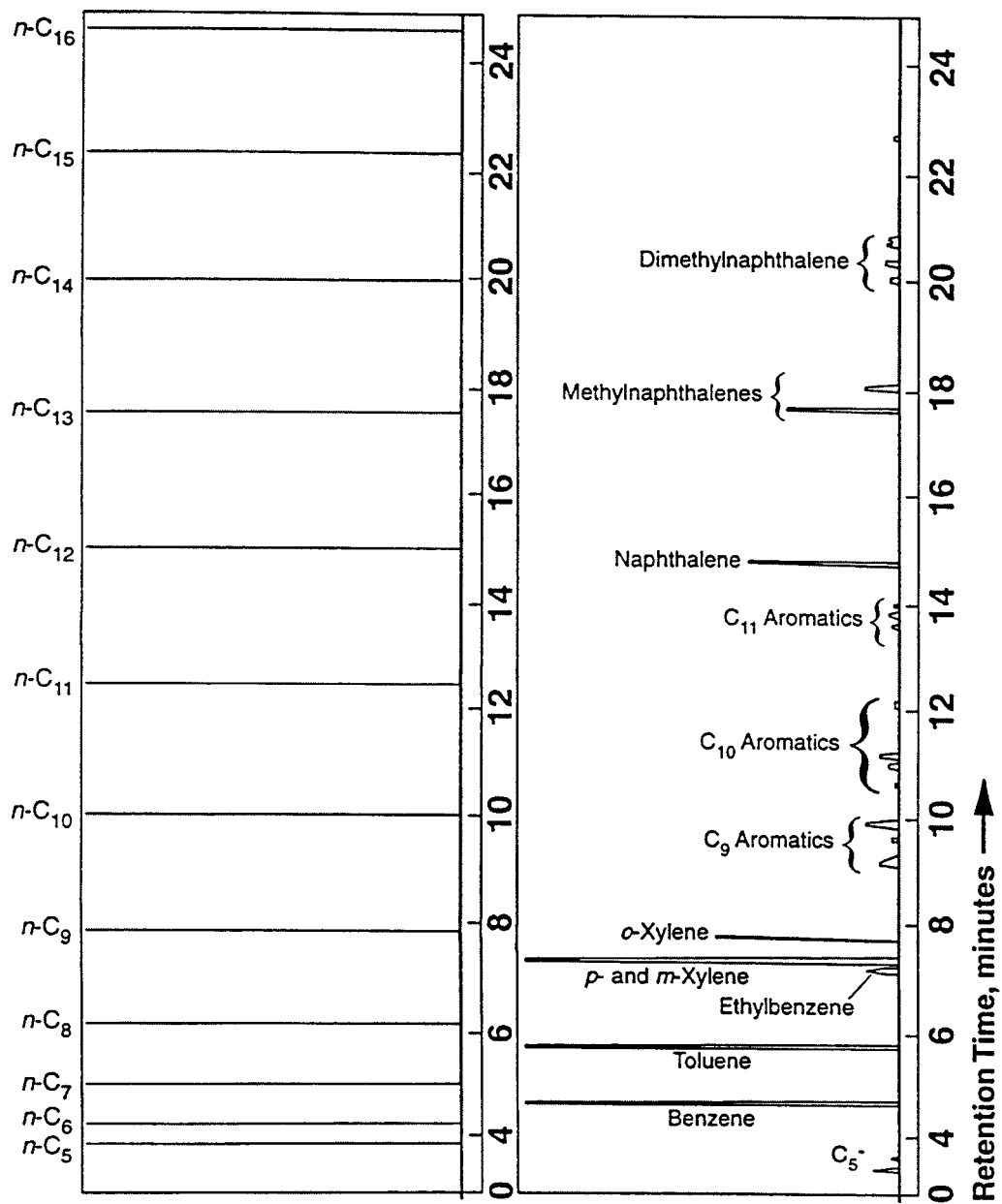


Figure 3
Typical Chromatogram
 n -Paraffins and Aromatics