

NORMAL PARAFFINS BY CAPILLARY GAS CHROMATOGRAPHY

UOP Method 915-92

SCOPE

This method is for determining total normal paraffins (TNP) and individual normal paraffins in hydrocarbons, such as the UOP Molex[®] process streams, including samples containing the Molex process desorbent. Samples are typically in the C₈ to C₂₀ carbon number range. By preheating the sample and adding a suitable solvent, the range can be extended up to C₄₀. The mass-% TNP at the high and low concentrations tend to be biased slightly high because of incomplete compensation for non-normals at the normal paraffin sites. A slightly more accurate TNP value would be expected using UOP Method 411 (see *NOTE*). The lower limit of detection is 0.01 mass-% for any compound.

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 DB-17 (bonded) methylphenyl-polysiloxane, and with a flame ionization detector (FID). To determine the total normal paraffins at all concentrations requires analysis by two different procedures, designated Method A and Method B.

In *Method A*, samples containing less than 75 mass-% TNP are injected using the appropriate operating conditions. The integrator events are programmed to force a baseline at the valley point before and after each normal paraffin to compensate for the underlying non-normals at the normal paraffin site (Figs. 1 and 2). The mass-% of each normal paraffin is obtained by the internal standard method of quantitation, wherein peak areas are compared to the peak area of a known amount of an internal standard. The individual normal paraffins are summed to obtain TNP.

In *Method B*, samples containing 75 mass-% or greater concentrations of total normal paraffins are injected using the appropriate operating conditions. The mass-% composition of the sample is obtained by the internal normalization technique. The individual normal paraffins are summed to obtain TNP.

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

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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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The 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.

Chromatographic column, 30 m of 0.32-mm ID fused silica capillary, internally coated to a film thickness of 0.25 μm with DB-17 (bonded) 50% methyl-50% phenyl-polysiloxane, J & W Scientific, Cat. No. 123-1732

Gas chromatograph, temperature programmable, built for capillary column chromatography, utilizing a split injection system, having a packed glass injection port insert, and equipped with a flame ionization detector that will give a minimum peak height response of 10 times the background noise for 0.01 mass-% normal decane when operated at the recommended conditions.

Integrator, 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 integrator must have programmable parameters for controlling baseline events.

Oxygen remover, Oxy-Trap, Alltech Associates, Cat. No. 4001

Recorder, 1-mv full scale, 1-sec or less full-scale response

Regulator, air, two-stage, high purity, Matheson Gas Products, Model 3104-590

Regulator, nitrogen, two-stage, high purity, Matheson Gas Products, Model 3104-580

Regulator, hydrogen, two-stage, high purity, Matheson Gas Products, Model 3104-350

Sample injector, an autoinjector is recommended but any syringe or injector capable of introducing a 1.0- μL volume of sample, such as a Hamilton 7105 syringe, Alltech Associates, Cat. No. 88000, is satisfactory.

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

Glass wool, DMCS treated, Alltech Associates, Cat. No. 4037, to pack the glass injection port liner

n-Hexane, 99.9% minimum purity, Wiley Organics, Cat. No. 3442.00, to be used as a solvent to dilute heavy samples

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

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

n-Paraffins, 99% minimum purity, Wiley Organics. Obtain each individual carbon number that will be present in the sample, typically C_7 to C_{20} , to identify peak sites and to be used as an internal standard

PROCEDURE

Chromatographic Technique

1. Install the oxygen remover in the supply line between the carrier gas source and the carrier gas inlets on the gas chromatograph.
 - Column life is significantly reduced if an oxygen remover is not used.
2. Install the fused silica capillary column in the gas chromatograph.
 - **CAUTION:** Hydrogen carrier gas 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.
3. Establish the operating conditions listed in Table 1; except, set the column oven to 260°C until the baseline is stable.
 - Other conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatograms.
 - If the carbon number range is significantly different from that shown in the Typical Chromatograms, the starting temperature, final temperature or programming rate (Table 1) can be adjusted to optimize component elution.
4. Cool the column oven to a stabilized 32°C.

Method A: Normal Paraffins by Internal Standard — Less Than 75 Mass-% TNP

1. Inject 0.5 μL of the sample to be analyzed into the gas chromatograph and start the recorder, integrator and column temperature programming sequence. Typical chromatograms are shown in Figs. 1 and 2.
 - Better precision is obtained when an autoinjector is used.
 - This experimental run determines the carbon number distribution of the sample, the internal standard to be used, and the approximate TNP composition.
 - For samples containing equal to or greater than 75 mass-% TNP, use Method B.
2. Choose an internal standard having one less or one more carbon number than the lowest or highest contained in the sample.
3. Add approximately 0.5 g of the internal standard, weighed to the nearest 0.1 mg, to approximately 5 g of the weighed liquefied sample.
 - Samples containing solids at ambient temperature are heated in an oven at 85°C until the entire sample is liquefied.
 - A solvent such as *n*-hexane can be added to the weighed sample—internal standard solution, if necessary, to maintain a liquefied state at ambient temperature.
4. Set the integrator events to force a baseline at the valley points before and after each normal paraffin (see Figs. 1 and 3).
 - The baseline *must* be set in this way to compensate for the underlying non-normals at the *n*-paraffin sites.
5. Inject 0.5 μL of the sample with the internal standard added and start the recorder, integrator and column temperature programming sequence.

- If the sample has been diluted, inject a proportionately larger sample volume.
6. Identify the normal paraffins from the resultant chromatogram by comparing the chromatogram obtained to the Typical Chromatograms (Figs. 1 or 2), or to a known blend of normal paraffins analyzed under identical conditions.

Method B: Normal Paraffins by Normalized Composition — Equal To or Greater Than 75 Mass-% TNP

1. Set the integrator events to ensure that a true baseline, from the beginning to the end of the chromatogram, is maintained (see Fig. 3).
 - A horizontal forward or equivalent baseline event must be used to prevent the integrator from establishing a new baseline during data processing of unresolved groups of non-normals.
2. Inject 1.0 μL of the sample to be analyzed and start the recorder, integrator and column temperature programming sequence.
 - Heat the sample and add solvent, if necessary, to maintain a liquefied state at ambient temperature.
 - Set the integrator events to inhibit peak detection while the solvent peak is eluting.
3. From the resultant chromatogram, identify the normal paraffins by comparing the chromatogram to the Typical Chromatogram (Fig. 3) or to a known blend of normal paraffins analyzed under identical conditions.

Table 1

Carrier gas	hydrogen
Carrier gas velocity	40 cm/sec (1.5 mL/min at 50°C)
Column head pressure	32 kPa gauge (5 psig)
Split flow rate	150 mL/min
Injection port temperature	275°C
Column temperature program	
Initial temperature	32°C
Initial time	8 min
Programming rate ^a	2°C/min
Final temperature ^b	260°C
Final Time ^b	Hold
Detector	flame ionization
Detector temperature	300°C
Hydrogen flow rate ^c	30 mL/min
Air flow rate ^c	275 mL/min
Makeup gas	nitrogen
Makeup gas flow rate ^c	30 mL/min
Chart speed	10 mm/min
Sample size, Method A	0.5 μL
 Method B	1.0 μL

^a Program rate should be increased to 3°C/min for carbon number ranges exceeding C₂₄.

^b Hold until all peaks have eluted or abort program ramp early when all peaks have eluted.

^c Consult the manufacturer's instrument manual for suggested flow rates to ensure detector linearity between small and large peaks.

Calibration

Since all the sample components have essentially the same detector response on a mass basis, no relative response factor calibration is required (area-% is equivalent to mass-%). The internal standard method of quantitation is used for Method A, wherein the *n*-paraffin peak areas are compared to the peak area of a known amount of internal standard. The internal standard technique is required because the non-normals that underlie the normal paraffins are not measured. The internal normalization technique is used for Method B where area contribution from non-normals is minimal.

CALCULATIONS

Using the peak areas for each sample component or group of components, calculate the composition of each sample using the appropriate formula.

Method A

Normal Paraffins by Internal Standard

Calculate the mass-% of each normal paraffin in the sample to the nearest 0.01 mass-% using the following formula:

$$C = \frac{100 AB}{DE} \quad (1)$$

where:

A = peak area of the specific normal paraffin

B = mass of the internal standard added, g

C = concentration of the specific normal paraffin, mass-%

D = peak area of the internal standard

E = mass of the sample to which the internal standard was added, g

100 = factor to convert to mass-%

Calculate the total normal paraffin (TNP) content of the sample to the nearest 0.1 mass-% by summing the individual normal paraffins. The total non-normals are calculated by difference, 100—TNP.

Method B

Normal Paraffins by Normalized Composition

Calculate the mass-% of each normal paraffin in the sample to the nearest 0.01 mass-% using the following formula:

$$C = \frac{100 A}{F} \quad (2)$$

where:

A = previously defined, Eq. 1

C = previously defined, Eq. 1

F = sum of all peak areas including *n*-paraffins and non-normals

100 = previously defined, Eq. 1

Calculate the total normal paraffin (TNP) content of the sample to the nearest 0.1 mass-% by summing the individual normal paraffins. Total non-normals are calculated by difference, 100–TNP.

NOTE

UOP Method 411 is limited to samples having a carbon number range ending at C₃₀. Also, the method requires a customized arrangement of two gas chromatographs, connected in series, utilizing molecular sieve extraction of normal paraffins, and extensive calibrations.

PRECISION

Repeatability

Based on 2 tests performed by each of 2 analysts on each of 2 different days (8 tests), the within-laboratory estimated standard deviations (esd) were calculated for components at specific concentrations in typical process streams and are listed in Table 2. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable differences in Table 2 at the concentrations listed (95% probability).

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time for one analysis is 1.0 hour for carbon numbers to C₁₆ and 2.5 hours for carbon numbers to C₄₀. The labor requirement is 0.5 hour and 1.0 hour, respectively.

REFERENCE

UOP Method 411, "Normal Paraffins by Subtractive Gas Chromatography"

SUGGESTED SUPPLIERS

Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015 (708-948-8600)
 J & W Scientific, Inc., 91 Blue Ravine Rd., Folsom, CA 95630 (961-351-0387)
 Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)
 Wiley Organics, 1245 South 6th St., Coshocton, OH 43812 (614-622-0755)

Table 2

Process Stream	Component	Concentration, mass-%	Within-Lab esd, mass-%	Allowable Difference, mass-%
Extract	TNP	98.4	0.07	0.2
	TNN	1.6	0.07	0.2
	<i>n</i> -C ₁₀	5.10	0.094	0.31
	<i>n</i> -C ₁₁	10.00	0.122	0.41
	<i>n</i> -C ₁₂	14.87	0.093	0.31
	<i>n</i> -C ₁₃	24.53	0.037	0.12
	<i>n</i> -C ₁₄	24.40	0.116	0.39
	<i>n</i> -C ₁₅	14.60	0.130	0.44
	<i>n</i> -C ₁₆	4.95	0.060	0.20
Feed	TNP	26.3	0.37	1.2
	TNN	73.7	0.37	1.2
	<i>n</i> -C ₁₀	1.43	0.013	0.04
	<i>n</i> -C ₁₁	2.63	0.024	0.08
	<i>n</i> -C ₁₂	3.75	0.074	0.25
	<i>n</i> -C ₁₃	6.84	0.116	0.39
	<i>n</i> -C ₁₄	6.41	0.108	0.36
	<i>n</i> -C ₁₅	3.88	0.083	0.28
	<i>n</i> -C ₁₆	1.34	0.037	0.12
Raffinate	TNP	7.3	0.17	0.7
	TNN	92.7	0.17	0.7
	<i>n</i> -C ₁₀	0.46	0.005	0.02
	<i>n</i> -C ₁₁	0.88	0.010	0.03
	<i>n</i> -C ₁₂	1.27	0.050	0.20
	<i>n</i> -C ₁₃	1.61	0.077	0.30
	<i>n</i> -C ₁₄	1.78	0.037	0.15
	<i>n</i> -C ₁₅	0.97	0.021	0.08
	<i>n</i> -C ₁₆	0.32	0.008	0.03

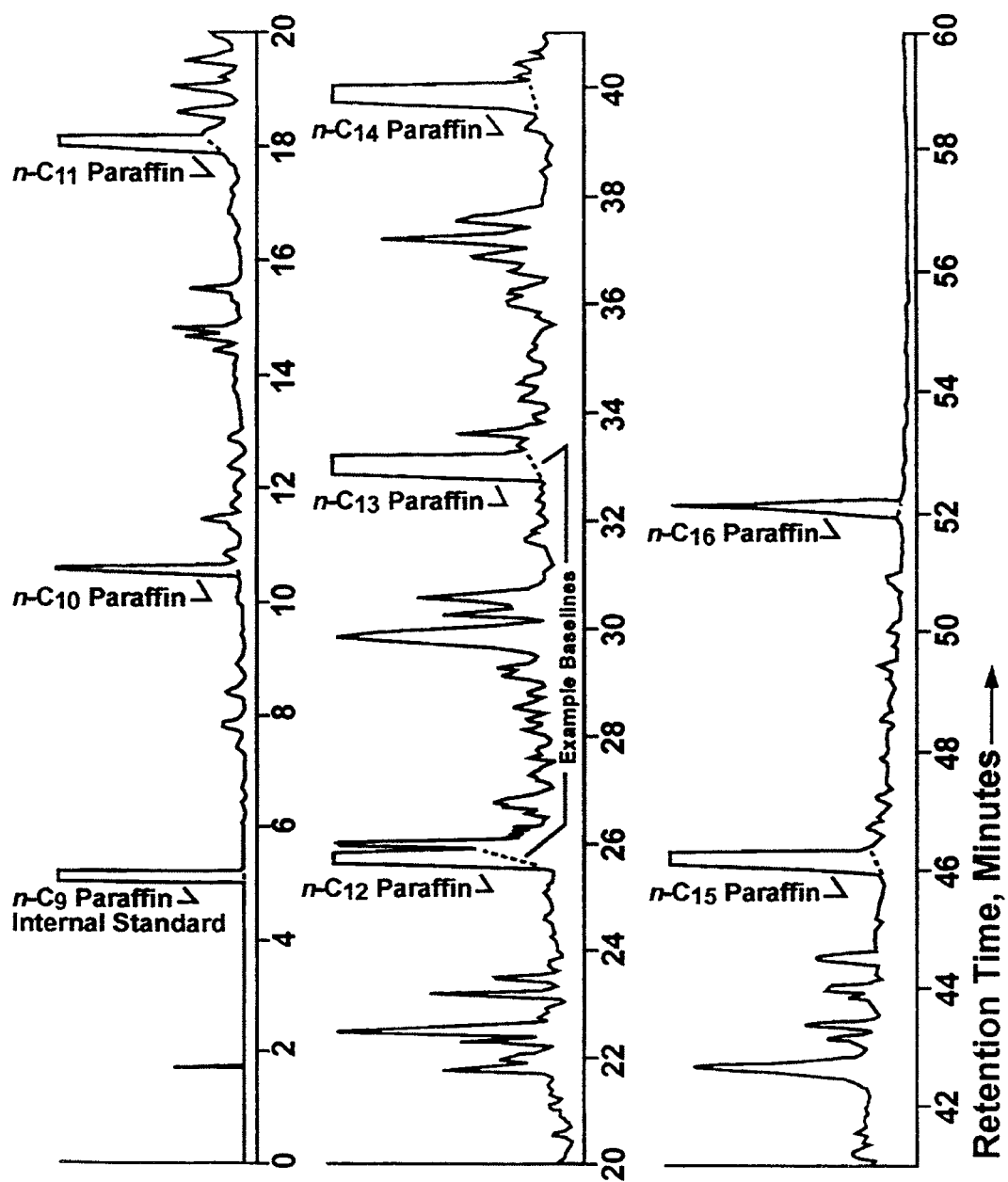


Figure 1

Typical Chromatogram, Molex Process Feed

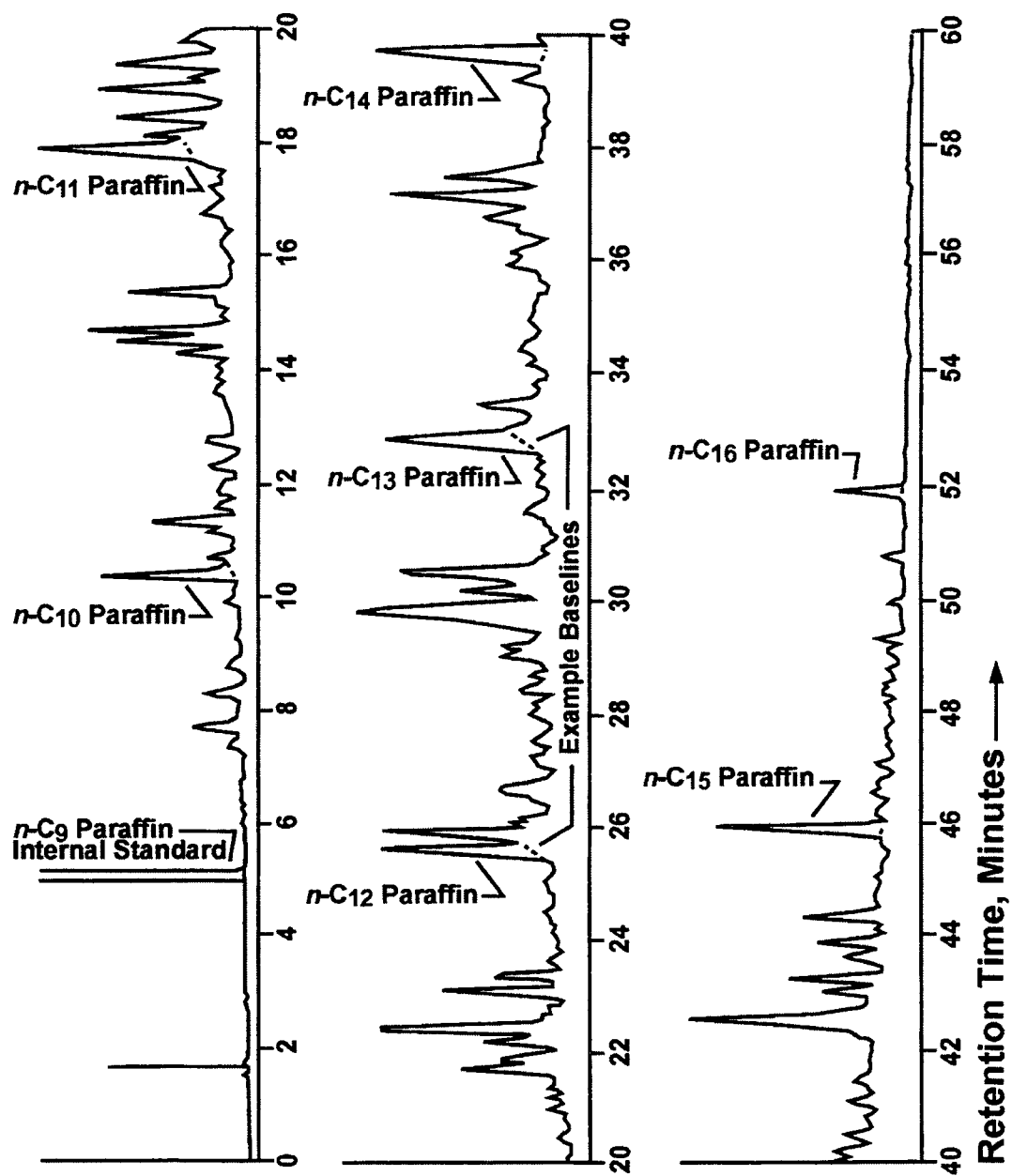


Figure 2
Typical Chromatogram, Molex Process Raffinate

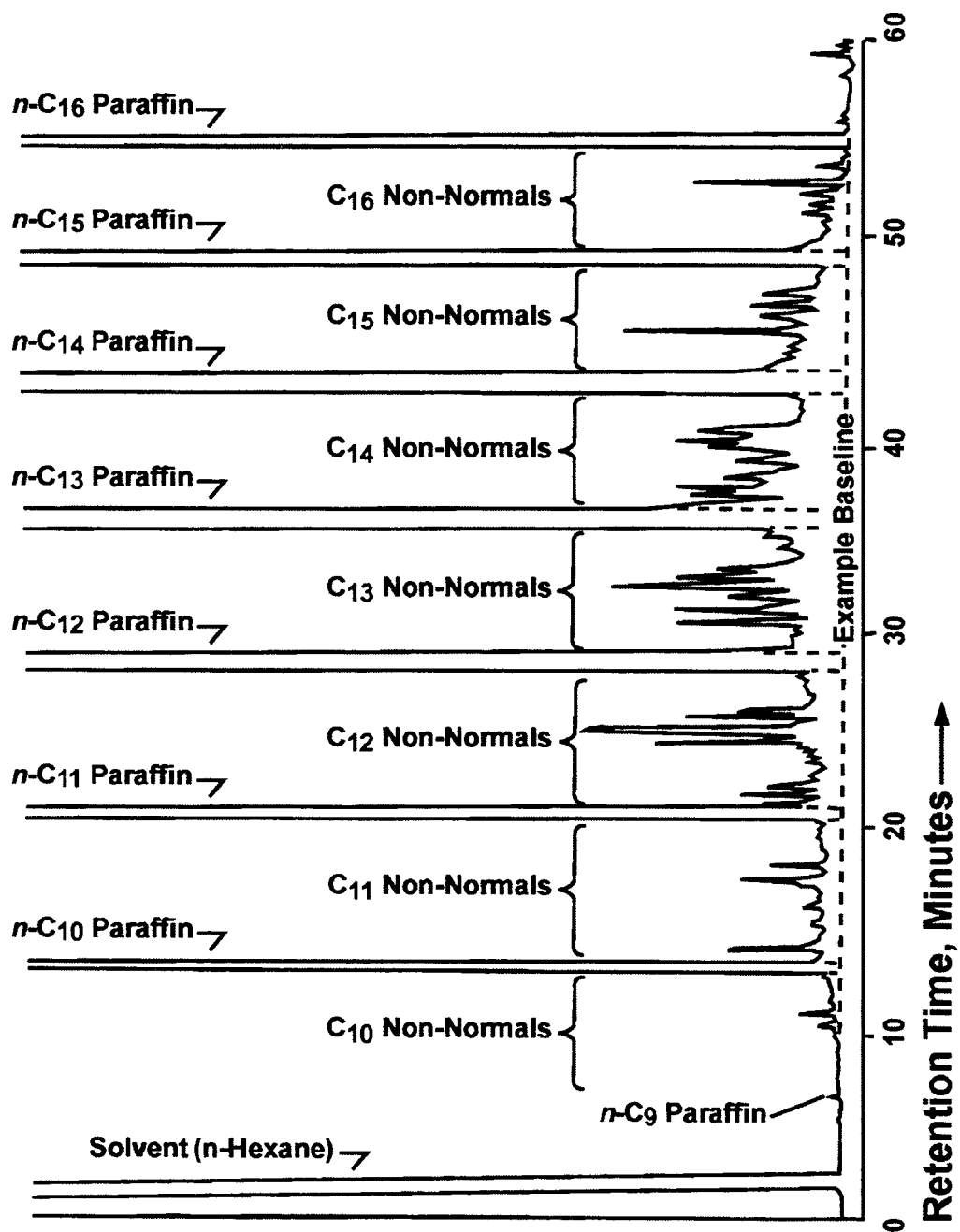


Figure 3
Typical Chromatogram, Molex Process Extract