

C₅ AND LOWER BOILING DIENES, OLEFINS, AND PARAFFINS IN NAPHTHAS BY GC

UOP™ METHOD 980-03

SCOPE

This method is for determining C₅ and lighter diolefins, mono-olefins, and paraffins in olefinic naphthas. Resolved acetylenes, and resolved C₆ hydrocarbons, including resolved dienes, are also identified. The method is applicable to selective hydrogenation process feeds, products, and other process streams with similar matrixes having a final boiling point of 260°C or lower. Components that do not elute from the chromatographic system under the specified conditions are not determined. The lower limit of detection for any compound is 0.01 mass-%.

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) poly-dimethyl siloxane, and a flame ionization detector (FID). The mass-% composition of the sample is obtained by the internal normalization technique, wherein the peak areas are first corrected for differences in response and then normalized to 100%.

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, 100 m of 0.25-mm ID fused silica capillary, internally coated to a film thickness 0.5 micron (bonded) with poly-dimethyl siloxane, Petrocol DH, Supelco, Cat. No. 24160-U

Gas chromatograph, temperature programmable with cryogenic cooling, 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 five

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times the background noise for 0.01 mass-% *n*-heptane when operated at the recommended conditions, Agilent Technologies, Model 6890. The inclusion of an autosampler (or autoinjector) is recommended but not required.

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

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

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

Refrigerator, flammable-materials storage, Fisher Scientific, Cat. No. 97-938-1

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 or helium, two-stage, high purity, Matheson Gas Products, Model 3122-580

Sample injector, any syringe or injector capable of introducing a 0.5- μ L 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.

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

Autosampler vials, glass, 12 x 32 mm, for Agilent autosampler, Fisher Scientific, Cat. No. 03-391-8

Caps, for autosampler vials, open hole with septum, screw, 9 mm, with Tef/Sil/Tef liner, Fisher Scientific, Cat. No. 03-377-2A

Benzene, 99.9% purity, Aldrich, Cat. No. 27,070-9

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

n-Heptane, 99.9⁺% purity, Aldrich, Cat. No. 27,051-2

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

Pipet bulbs, Fisher Scientific, Cat. No. 13-678-9B

Pipets, disposable, Pasteur, Fisher Scientific, Cat. No. 13-678-20A

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

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

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

p-Xylene, 99⁺% purity, Aldrich, Cat. No. 31,719-5

Vials, 15-mL, with screw cap, Fisher Scientific, Cat. No. 03-339-21J

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.
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, 2, and 3).

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Mode	constant pressure
Head pressure	207 kPa gauge (30 psig)
Linear velocity @ 15°C	38 cm/sec
Equivalent flow @ 15°C	2.6 mL/min
Split flow	200 mL/min
Injection port temperature	215°C
Column temperature program	
Initial temperature	15°C
Initial hold time	15 min
Programming rate A	8°C/min
Intermediate temperature	75°C
Intermediate hold time	14 min
Programming rate B	20°C/min
Final hold temperature	250°C
Final hold time	27.5 min
Detector	flame ionization
Detector temperature	250°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.

4. Program the column oven to 250°C. Maintain this temperature until a stable baseline has been obtained at the required sensitivity.
5. Cool the column oven to a stabilized 15°C.
6. If an autosampler is used, transfer a portion of the sample into an autosampler vial and place it in 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.
 - Better precision is obtained when an autosampler is used.
 - If samples are not to be run immediately, they should be refrigerated until time for analysis. Samples should be removed from refrigerator and well mixed prior to injection.
8. Identify the components by comparing the resultant chromatogram with the Typical Chromatograms (see Figures 1, 2, and 3) and Table 2. The Peak No. in Table 1 refers to the identifications in the Chromatograms, Figures 1, 2, and 3. If necessary, confirm the sites of the aromatic compounds by comparison with the calibration blend (see *Calibration*). Group all unidentified components as Unknowns.
 - Any individual peak or peaks can be identified and reported separately.

Table 2
Retention Times of Identified Components

Typical Retention Time, Min	Peak No.	<u>Component Identification</u>
5.19		Ethylene
5.23		Ethane
5.75	1	Propylene
5.79	2	Propane
6.33	3	Isobutane
6.68	4	1-Butene & Isobutylene
6.73	5	1,3-Butadiene
6.83	6	<i>n</i> -Butane
6.91	7	Vinylacetylene
7.02	8	<i>trans</i> -2-Butene
7.11	9	Ethylacetylene & 2,2-Dimethylpropane
7.31	10	<i>cis</i> -2-Butene
7.85	11	1,2-Butadiene
8.19	12	3-Methyl-1-butene
8.80	13	Isopentane
8.93	14	1,4-Pentadiene
9.42	15	1-Pentene
9.73	16	2-Methyl-1-butene
9.96	17	<i>n</i> -Pentane
10.19	18	2-Methyl-1,3-butadiene
10.37	19	<i>trans</i> -2-Pentene

Typical Retention Time, Min	Peak No.	Component Identification
10.72	20	3,3-Dimethyl-1 butene
10.81	21	<i>cis</i> -2-Pentene
11.09	22	2-Methyl-2-butene
11.26	23	1- <i>trans</i> -3-Pentadiene
11.90	24	3-Methyl-1,2-butadiene & Cyclopentadiene
12.07	25	1- <i>cis</i> -3-Pentadiene
12.14	26	2,2-Dimethylbutane
12.86	27	3-Methyl-1,4-pentadiene
13.41	28	Cyclopentene
13.88	29	4-Methyl-1-pentene
13.97	30	3-Methyl-1-pentene
14.38	31	Cyclopentane
14.66	32	2,3-Dimethylbutane
14.84	33	2,3-Dimethylbutene
15.05	34	<i>cis</i> -4-Methyl-2-pentene
15.17	35	2-Methylpentane
15.37	36	<i>trans</i> -4-Methyl-2-pentene
15.42	37	2-Methyl-1,4-pentadiene
15.96	38	1,5-Hexadiene
16.48	39	3-Methylpentane
16.98	40	2-Methyl-1-pentene
17.08	41	1-Hexene
17.62		1,4-Hexadiene
17.97	42	2-Ethyl-1-butene
18.03	43	<i>n</i> -Hexane
18.25	44	<i>cis</i> -3-Hexene
18.31	45	<i>trans</i> -3-Hexene
18.44	46	<i>trans</i> -2-Hexene
18.63	47	2-Methyl-2-pentene
18.83	48	<i>cis</i> -3-Methyl-2-pentene
19.15	49	<i>cis</i> -2-Hexene
19.33	50	2,3-Dimethyl-1,3-butadiene
19.62	51	3-Methyl- <i>trans</i> -2-pentene
19.72	52	<i>trans</i> -1,3-Hexadiene
19.89	53	<i>cis</i> -1,3-Hexadiene
19.94	54	Methylcyclopentane
20.38	55	2,3-Dimethyl-2-butene
21.50	56	Methylcyclopentene
21.59	57	Benzene
28.88	58	Toluene
37.29	59	Ethylbenzene
37.93	60	<i>m</i> -Xylene
38.00	61	<i>p</i> -Xylene
39.27	62	<i>o</i> -Xylene

Calibration

This analysis uses internal normalization of the entire sample to be quantitative, and requires that all components in the sample elute from the column under the specified conditions and are measured.

In order to accurately measure the entire sample, certain components beyond the C₅ range must be identified and calibrated. This is necessary because C₆ through C₈ aromatic components that may be present in the sample do not have the same detector response as the non-aromatic components. All non-aromatic components have essentially the same detector response.

1. Prepare a blend as described in ASTMTM Method D4307 to contain approximately equal quantities of *n*-heptane, benzene, toluene, and *p*-xylene.
2. Analyze the blend in triplicate as described under *Chromatographic Technique*.
 - The peak areas from each of the three runs should not deviate from the average by more than 3% of the value. If greater deviations occur, make certain that there are no problems with the equipment or technique, and then make further 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 relative response factors for each component using Equation 1 and *n*-heptane as reference:

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

where:

- A** = component of interest, mass-%
- B** = area of *n*-heptane peak
- C** = *n*-heptane, mass-%
- D** = area of component of interest
- F** = relative response factor

Calculated relative response factors should be similar to the theoretical relative response factors shown in Table 3. The theoretical relative response factors were calculated using the effective carbon number (ECN) concept as described by Scanlon and Willis. If the determined relative response factors differ by more than 10% from those shown in Table 3, recheck the apparatus, operating conditions, and blend preparation procedures.

Table 3
Theoretical Relative Response Factors

<i>n</i>-Heptane	1.000
Benzene	0.909
Toluene	0.919
<i>p</i>-Xylene	0.927

All C₈ aromatics will use the same factor as *p*-xylene. Due to the volatility of C₆ and lighter material, and the similarity of response factors, *n*-heptane can represent all paraffins, olefins, and diolefins, and unknowns.

CALCULATIONS

Obtain peak areas for each individual component or group of components and calculate the concentration of each identified peak in the sample to the nearest 0.01 mass-% using Equation 2:

$$\text{Component, mass-\%} = 100 \frac{PF}{T} \quad (2)$$

where:

F = relative response factor, from Equation 1

P = area of individual component or group of components

T = the sum of the products, **PF**, of all the recorded peaks

NOTE

If desired, the same equipment and conditions may be used for UOP Method 725, which identifies paraffins and olefins only through C₅.

PRECISION

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

ASTM and UOP Repeatability

A nested design was carried out for determining components in one olefinic hydrocarbon 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 ASTM allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the UOP 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 the long-term repeatability.

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time for one analysis is 1.5 hours. The labor requirement is 0.5 hour.

Table 4
ASTM and UOP Repeatability, mass-%

<u>Component</u>	<u>Mean Conc.</u>	<u>ASTM Repeatability</u>		<u>UOP Repeatability</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
<i>trans</i> -2 butene	0.49	0.004	0.02	0.008	0.03
Isopentane	19.08	0.04	0.15	0.06	0.18
1-Pentene	2.28	0.004	0.01	0.006	0.02
<i>trans</i> -2-Pentene	5.53	0.006	0.02	0.011	0.04
<i>n</i> -Pentane	3.04	0.002	0.009	0.003	0.01
2-Methyl-1,3-butadiene	0.23	0.0004	0.002	0.0009	0.003
2-Methyl-2-butene	8.15	0.008	0.03	0.013	0.04
1- <i>trans</i> -3-Pentadiene	0.22	0.0005	0.002	0.0009	0.003
3-Methyl-1,2-pentadiene	0.08	0.0003	0.001	0.0007	0.002
1- <i>cis</i> -3-Pentadiene	0.10	0.0004	0.001	0.0006	0.002
2-Methylpentane	8.84	0.011	0.04	0.029	0.10
1,4-Hexadiene	0.09	0.0006	0.002	0.0004	0.001

REFERENCES

ASTM Method D4307, "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 Methods 725, "Pentenes and Lower Boiling Hydrocarbons in Olefinic Gasolines by GC," and
 999, "Precision Statements in UOP Methods," www.astm.org

SUGGESTED SUPPLIERS

Agilent Technologies, 2850 Centerville Rd., Wilmington, DE 19808-1610 (302-633-8000)
www.agilent.com
 Aldrich Chemical Co., P.O. Box 355, Milwaukee, WI 53201 (414-273-3850) www.sigma-aldrich.com
 Alltech Associates Inc., 2051 Waukegan Rd., Deerfield, IL 60015 (847-948-8600)
www.alltechweb.com
 Matheson Gas Products Inc., 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700)
www.mathesontrigas.com
 Mat/Sen, 26272 Twelve Trees #C, Poulsbo, WA 98370 (360-697-9199) www.vici.com
 Supelco, 595 North Harrison Road, Bellefonte, PA 16823-0048 (814-359-3441) www.sial.com

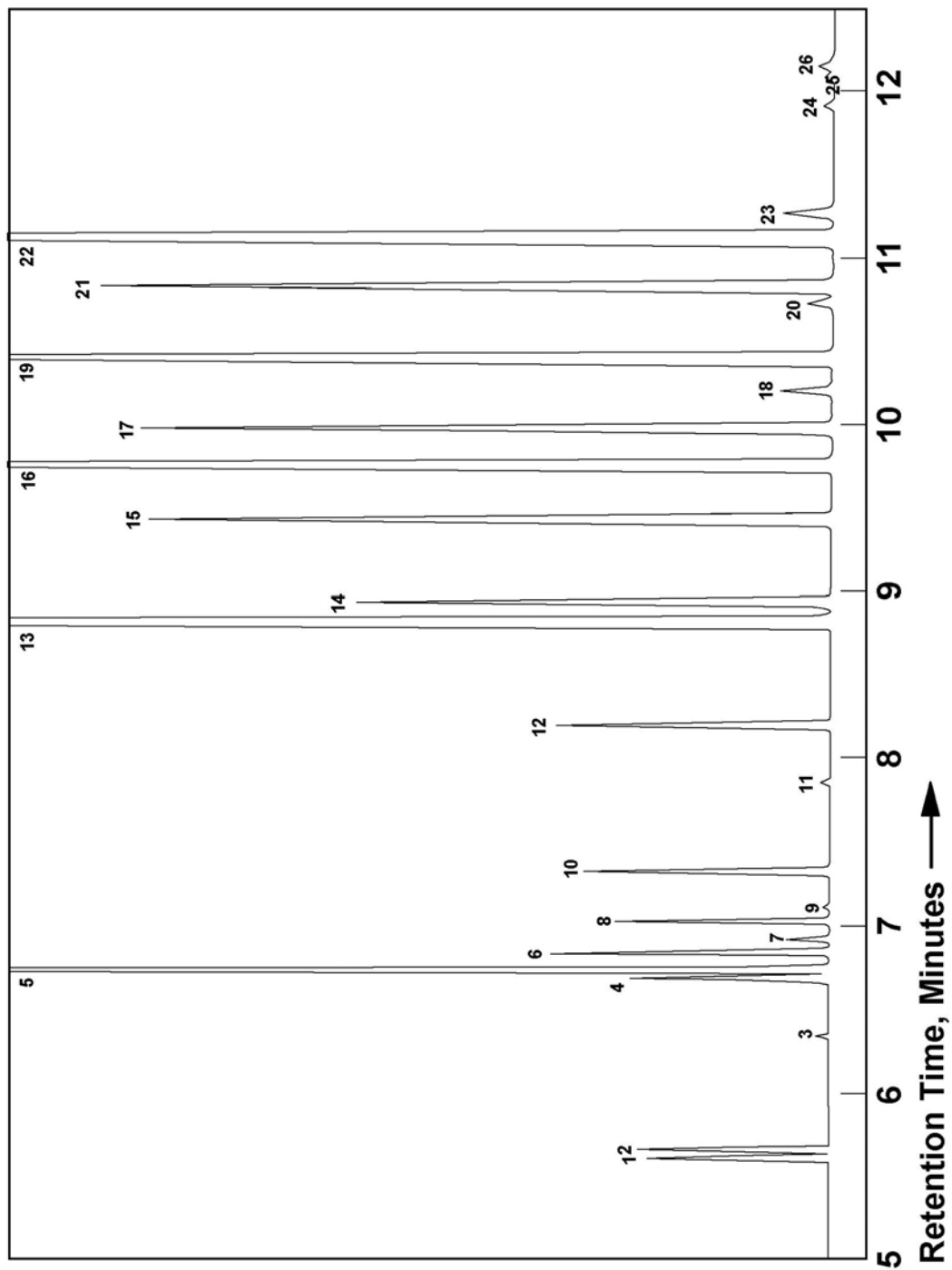


Figure 1

Typical Chromatogram (5-12.5 Minutes)

UOP Method 980-03

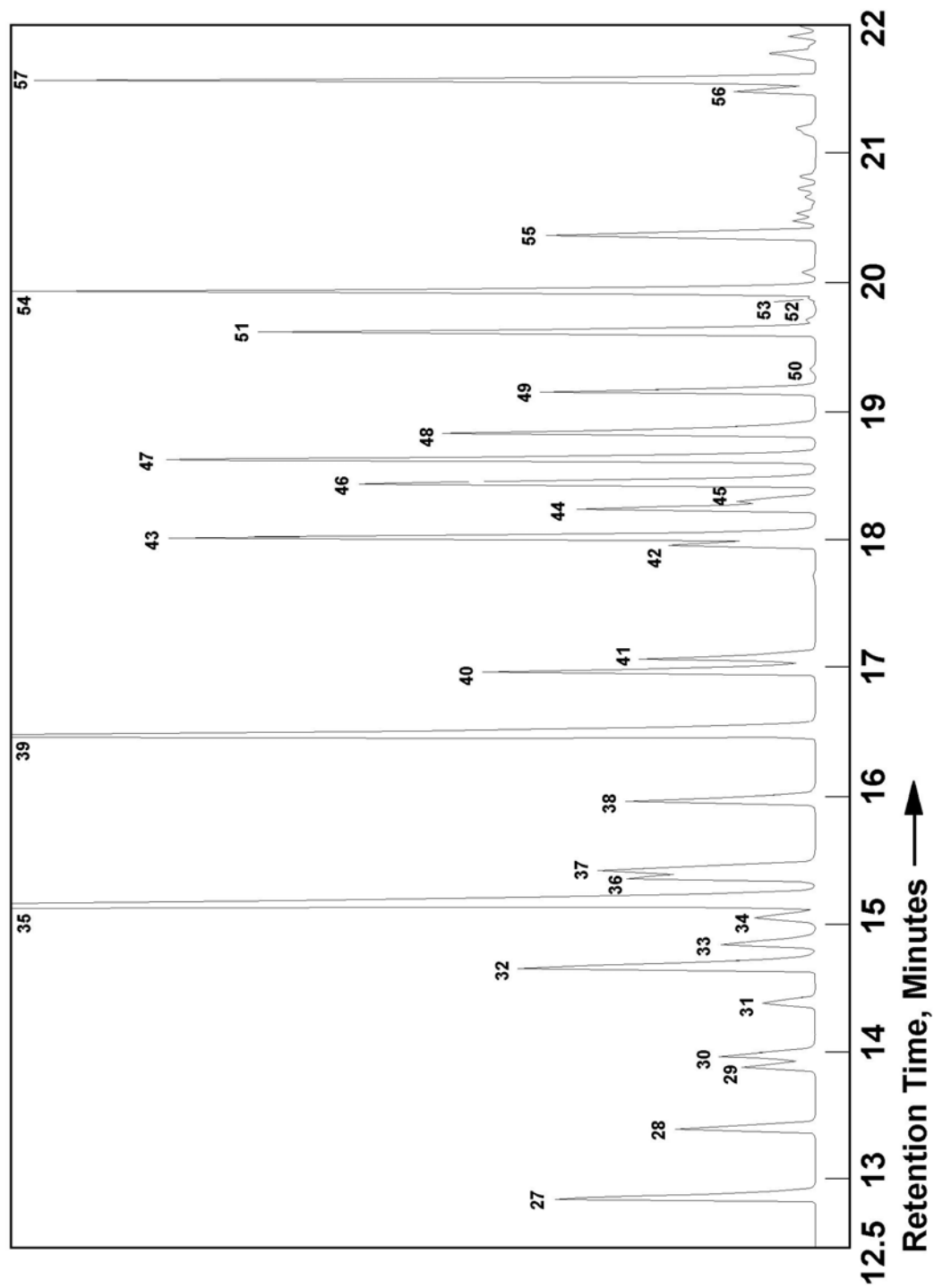


Figure 2

Typical Chromatogram (12.5-22 Minutes)

UOP Method 980-03

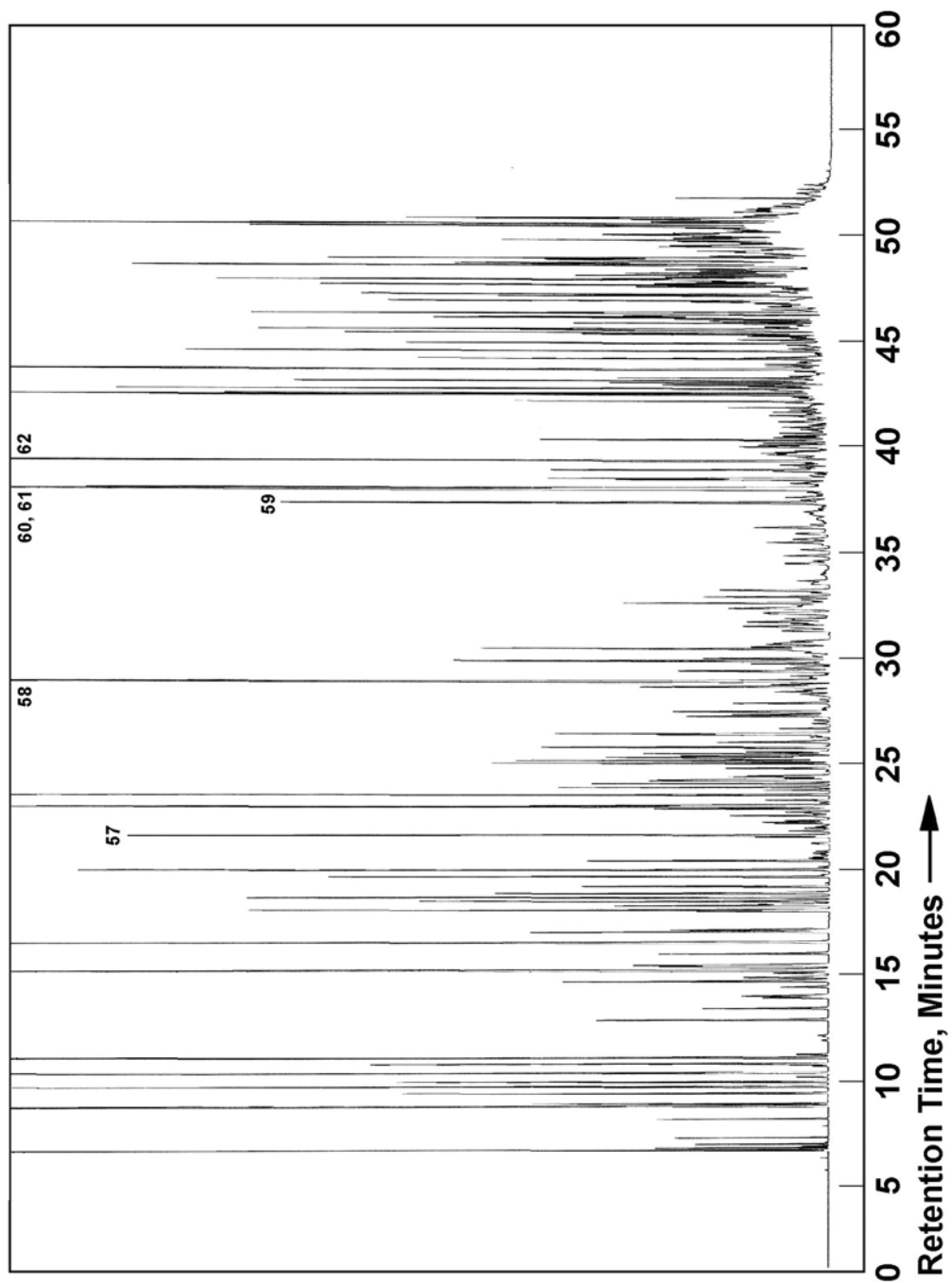


Figure 3

Typical Chromatogram (1-60 Minutes)

UOP Method 980-03