



A Honeywell Company

C₈ and Lower Boiling Paraffins and Naphthenes in Low-Olefin Hydrocarbons by GC

UOP Method 690-13

Scope

This gas chromatographic method is for determining C₈ and lower boiling paraffins and naphthenes in hydrocarbons containing less than 2 mass-% olefins (see *Note 1*) having a maximum final boiling point of 260°C. Benzene and toluene are also determined. Certain non-aromatic components of interest are reported as composites and C₈ aromatics are not determined (see *Note 2*). The quantitation limit for any reported component is 0.01 mass-%.

References

ASTM Method D4307, "Preparation of Liquid Blends for Use as Analytical Standards," www.astm.org

ASTM Method D6839, "Hydrocarbon Types, Oxygenated Compounds, and Benzene in Spark Ignition Engine Fuels by Gas Chromatography," www.astm.org

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

UOP Method 304, "Bromine Number and Bromine Index of Hydrocarbons by Potentiometric Titration," www.astm.org

UOP Method 744, "Aromatics in Hydrocarbons by GC," www.astm.org

Outline of Method

Two gas chromatographic analyses using the same column are required to determine the greatest number of resolved non-aromatic components. Based on the degree of resolution required, either Analysis A alone, or both Analyses A and B may be used. In both analyses, a sample is injected into a gas chromatograph that is equipped with a fused silica capillary column and a flame ionization detector (FID). A separate set of operating conditions is used for each analysis. The mass-% composition of the sample is obtained by the internal normalization technique of quantitation, wherein component peak areas for the entire sample are first corrected for differences in response and then normalized to 100%. Some unresolved non-aromatic components from Analysis A can then be resolved and calculated using data obtained from Analysis B (see *Note 3*).

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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, readable to 0.0001 g

Chromatographic column, 50 m of 0.20-mm ID fused silica capillary, internally coated to a film thickness of 0.5- μ m with cross-linked methyl silicone, Agilent Technologies, Cat. No. 19091S-001. Use of this specific column is recommended. The same column is used for Analysis A and Analysis B.

Data system, or electronic integrator, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that narrow peaks typically resulting from use of a capillary column can be accurately measured. Agilent Technologies, ChemStation

Gas chromatograph, capable of multiple temperature ramping and capable of cryogenic operation at 32°C, 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 5 times the background noise for 0.01 mass-% of benzene when operated at the recommended conditions. Electronic pressure control (EPC) is recommended. Agilent Technologies, Model 7890

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

Leak detector, gas, Grace Davison, Cat. No. 21-250

Refrigerator, explosion-proof or flammable storage, VWR, Cat. No. 55700-340

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, 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 injecting a 0.5- μ L volume of sample. An automatic injection device 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

Benzene, 99.9% minimum purity, Sigma-Aldrich, Cat. No. 270709

Carbon dioxide, liquid, if necessary for cryogenic cooling of the GC column oven to 32°C

n-Hexane, 99% minimum purity, Sigma-Aldrich Chemical, Cat. No. 139386

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

Syringe, for sample injector, 10- μ L, Agilent Technologies, Cat. No. 5181-1273

Toluene, 99% minimum purity, Sigma-Aldrich, Cat. No. 179965

p-Xylene, 99% minimum purity, Sigma-Aldrich, Cat. No. 134449

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

Chromatographic Technique

1. Install the gas purifiers in the supply lines between the gas sources and the gas inlets on the gas chromatograph.
 - Column and FID life may be significantly reduced if the gas purifiers are not used.
2. Install the fused silica capillary column in the gas chromatograph.
 - CAUTION: Hydrogen carrier gas leakage into a confined volume of the column oven can cause a violent explosion. It is, therefore, mandatory to test for leaks each time a connection is made and periodically thereafter.
3. Establish the recommended operating conditions as given in Table 1, Analysis A.
 - Other conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram (Figures 1 and 2).

Table 1
Recommended Operating Conditions

	<u>Analysis A</u>	<u>Analysis B</u>
Carrier gas	hydrogen	hydrogen
Column head pressure @ 32°C	140 kPa (20 psig)	140 kPa (20 psig)
Equivalent flow	1.1 mL/min	1.1 mL/min
Equivalent linear velocity	33 cm/sec	33 cm/sec
Split flow	215 mL/min	215 mL/min
Injection port temperature	230°C	230°C
Column temperature program		
Initial temperature	32°C	60°C
Initial time	6 min	8 min
Programming rate 1	5°C/min	5°C/min
Intermediate temperature	52°C	90°C
Intermediate time	14 min	0 min
Programming rate 2	20°C/min	20°C/min
Final temperature	250°C	250°C
Final time	9 min	10 min
Detector	FID	FID
Temperature	250°C	250°C
Hydrogen flow rate*	30 mL/min	30 mL/min
Air flow rate*	400 mL/min	400 mL/min
Makeup nitrogen flow rate*	30 mL/min	30 mL/min
Sample size	0.5 µL	0.5 µL

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

4. Program the column oven to 250°C and maintain this temperature until a stable baseline has been obtained at the required sensitivity.
5. Cool the column oven to 32°C.

6. Inject 0.5 μL of sample and start the integrator and the column temperature programming sequence.
 - The use of an autoinjector or autosampler automates the injection of the sample into the GC, starts the data system, and the GC oven program simultaneously.
7. Identify the components by comparing the resultant chromatogram to the Typical Chromatogram shown in Figures 1 and 2. If necessary, confirm the sites of the aromatic components by comparison with the calibration blend (see *Calibration*).
8. Establish the recommended operating conditions as given in Table 1, Analysis B, if resolution of the co-eluting components in Analysis A is required, and proceed to Steps 9 and 10.
 - Other conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram (Figures 3 and 4).
9. Inject 0.5 μL of sample and start the integrator and the column temperature programming sequence.
10. Identify the components by comparing the chromatogram obtained to the Typical Chromatogram shown in Figures 3 and 4. If necessary, confirm the sites of the aromatic components by comparison with the calibration blend (see *Calibration*).

Calibration

This analysis uses internal normalization of the entire sample to quantitate the C_8 minus components. In order to accurately analyze the entire sample, C_6 through C_8 aromatic components must be identified and response factors determined for them. This is necessary because C_6 through C_8 aromatic components do not have the same detector response as the non-aromatic components. The non-aromatic components all have essentially the same detector response. Calibrate whenever chromatographic conditions have changed and periodically thereafter.

1. Prepare a calibration blend as described in ASTM Method D 4307, "Preparation of Liquid Blends for Use as Analytical Standards," to contain approximately equal masses of n-hexane, benzene, toluene and p-xylene.
 - This blend is stable for six months if refrigerated.
2. Analyze the blend in triplicate as described under *Chromatographic Technique*, Analysis A.
3. Identify the peaks and obtain the peak areas for each component from the triplicate runs.
4. Determine the relative response factor for each component in each run to three decimal places, using n-hexane as reference and Equation 1.

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

where:

- A** = component in the blend, mass-%
- B** = peak area of n-hexane
- C** = n-hexane, mass-%
- D** = peak area of component
- F** = relative response factor for each component

Relative response factors from each of the triplicate runs should not deviate from the average by more than 2% of the value. If greater deviations occur, make certain that there are no problems with the equipment, then make additional runs until the required repeatability is obtained on three consecutive runs.

5. Average the relative response factors for each component from the three runs. Use these averages as **J** in Equation 2.

Use the relative response factor for n-hexane for all the non-aromatic (see Table 3) and C₉+ (the unidentified peaks eluting after methylcyclohexane in Figure 1) components in the sample. Use the relative response factor of p-xylene for ethylbenzene, m-xylene, p-xylene and o-xylene.

Calculated relative response factors should be similar to the theoretical relative response factors shown in Table 2. 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 5% from those shown in Table 2, recheck the apparatus, operating conditions, and blend preparation procedures.

Table 2
Theoretical Relative Response Factors

n-Hexane	1.000
Benzene	0.906
Toluene	0.916
p-Xylene	0.924

If the C₉+ components are known to be primarily aromatics, use the response factor for p-xylene instead of the response factor for n-hexane for the C₉+ components.

Calculations

Calculate the concentration of each C₈ and lighter component in the sample for Analysis A, and, if applicable, Analysis B, to the nearest 0.01 mass-% using Eq. 2.

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

where:

J = average relative response factor of individual component

P = peak area of individual component

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

100 = factor to convert to mass-%

When Analysis B is used, peaks 30A, 31A, 40A, 40B, 56A, 56B, 56C, 60A, 60B, 62A and 62B (see Tables 3 and 4) are resolved and the concentrations calculated directly from Analysis B, using Equations 1 and 2.

Composite peaks 40, 56 and 60, Analysis A, are fully resolved in Analysis B. The Analysis B individual concentrations require re-normalization to conform to the composite concentration totals in Analysis A. This is accomplished by use of Equation 3.

$$\text{Individual component, mass - \%} = \frac{WX}{Y} \quad (3)$$

where:

W = component amount, Analysis B

X = composite amount, Analysis A

Y = sum of component concentrations from Analysis B, in Analysis A composite

Additionally, determine the concentrations for 1-cis-2-dimethylcyclopentane, 2,2-dimethylhexane and 3-ethylhexane, which are unresolved in Analysis A, from the Analysis A and B data Equations 4, 5, and 6.

$$\text{1-cis-2-Dimethylcyclopentane, mass-\%} = L-G \quad (4)$$

where:

G = methylcyclohexane, from Analysis B

L = methylcyclohexane + 1-cis-2-dimethylcyclopentane, from Analysis A

$$\text{2,2-Dimethylhexane, mass-\%} = \text{N-H} \quad (5)$$

where:

H = 1,1,3-trimethylcyclopentane, from Analysis B

N = 1,1,3-trimethylcyclopentane + 2,2-dimethylhexane, from Analysis A

$$\text{3-Ethylhexane, mass-\%} = \text{R-S} \quad (6)$$

where:

R = 3-ethylhexane + 1-cis-3-dimethylcyclohexane + 1-cis-2-trans-3-trimethylcyclopentane, from Analysis A

S = 1-cis-3-dimethylcyclohexane + 1-cis-2-trans-3-trimethylcyclopentane, from Analysis B

If, after all the calculations above, the sum of all components (resolved and unresolved) does not total 100 mass-%, renormalize the data to 100 mass-%.

Report each component to the nearest 0.01 mass-% below one mass-%, and to three significant figures at or above one mass-%.

Table 3
Retention Times of
Identified Components, Analysis A

Peak numbers with letter designations refer to co-eluting peaks, i.e.; 30A and 30B co-elute. If some separation of these peaks does occur, it should not be inferred that A elutes before B.

Typical Retention Time, Min	Peak No.	Component Identification
2.10	*	Ethane site
2.35	1	Propane
2.54	2	Isobutane
2.71	3	n-Butane
2.79	4	2,2-Dimethylpropane
3.33	5	Isopentane
3.67	6	n-Pentane
4.32	7	2,2-Dimethylbutane
5.00	8	Cyclopentane
5.04	9	2,3-Dimethylbutane
5.16	10	2-Methylpentane
5.60	11	3-Methylpentane
6.23	12	n-Hexane
7.19	13	2,2-Dimethylpentane
7.28	14	Methylcyclopentane
7.45	15	2,4-Dimethylpentane
7.67	16	2,2,3-Trimethylbutane
8.29	17	Benzene
8.56	18	3,3-Dimethylpentane
8.72	19	Cyclohexane
9.16	20	2-Methylhexane
9.23	21	2,3-Dimethylpentane
9.35	22	1,1-Dimethylcyclopentane
9.58	23	3-Methylhexane
9.86	24	1-cis-3-Dimethylcyclopentane
9.99	25	1-trans-3-Dimethylcyclopentane
10.06	26	3-Ethylpentane

<u>Typical Retention Time, Min</u>	<u>Peak No.</u>	<u>Component Identification</u>
10.13	27	1-trans-2-Dimethylcyclopentane
10.46	28	2,2,4-Trimethylpentane
10.82	29	n-Heptane
11.93	30A	Methylcyclohexane
	30B	1-cis-2-Dimethylcyclopentane
12.08	31A	1,1,3-Trimethylcyclopentane
	31B	2,2-Dimethylhexane
12.61	32	Ethylcyclopentane
12.70	33	2,5-Dimethylhexane
12.82	34A	2,2,3-Trimethylpentane
	34B	2,4-Dimethylhexane
13.20	35	1-trans-2-cis-4-Trimethylcyclopentane
13.30	36	3,3-Dimethylhexane
13.71	37	1-trans-2-cis-3-Trimethylcyclopentane
13.93	38	2,3,4-Trimethylpentane
14.22	39A	2,3,3-Trimethylpentane
	39B	Toluene
14.78	40A	2,3-Dimethylhexane
	40B	1,1,2-Trimethylcyclopentane
14.86	41	2-Methyl-3-ethylpentane
15.29	42	2-Methylheptane
15.41	43	4-Methylheptane
15.53	44A	3,4-Dimethylhexane
	44B	3-Methyl-3-ethylpentane
15.74	45A	1-cis-2-trans-4-Trimethylcyclopentane
	45B	1-cis-2-cis-4-Trimethylcyclopentane
15.94	46	3-Methylheptane
16.03	47A	3-Ethylhexane
	47B	1-cis-3-Dimethylcyclohexane
	47C	1-cis-2-trans-3-Trimethylcyclopentane
16.20	48	1-trans-4-Dimethylcyclohexane
16.68	49	1,1-Dimethylcyclohexane
17.03	50	1-Methyl-trans-3-ethylcyclopentane
17.23	51	1-Methyl-cis-3-ethylcyclopentane
17.35	52	1-Methyl-trans-2-ethylcyclopentane
17.56	53	1-Methyl-1-ethylcyclopentane
17.83	54	1-trans-2-Dimethylcyclohexane
18.38	55	1-cis-2-cis-3-Trimethylcyclopentane
18.59	56A	n-Octane
	56B	1-cis-4-Dimethylcyclohexane
	56C	1-trans-3-Dimethylcyclohexane
19.37	57	Isopropylcyclopentane
20.35	58	1-Methyl-cis-2-ethylcyclopentane
21.33	59	1-cis-2-Dimethylcyclohexane
21.92	60A	n-Propylcyclopentane
	60B	Ethylcyclohexane
23.90	61	Ethylbenzene
24.40	62A	m-Xylene
	62B	p-Xylene
25.70	63	o-Xylene

Table 4
Components Determined by Analysis B

Peak numbers with letter designations refer to co-eluting peaks; i.e., 4A and 4B co-elute. If some separation of these peaks does occur, it should not be inferred that A elutes before B.

Typical Retention Time, Min	Peak No., Analysis B	Peak No., Analysis A	Component Identification
7.05	1A	30B	1-cis-2-Dimethylcyclopentane
	1B	31B	2,2-Dimethylhexane
7.12	2	30A	Methylcyclohexane
7.17	3	31A	1,1,3-Trimethylcyclopentane
7.51	4A	32	Ethylcyclopentane
	4B	34B	2,4-Dimethylhexane
7.66	5	34A	2,2,3-Trimethylpentane
8.74	6	40A	2,3-Dimethylhexane
8.91	7	40B	1,1,2-Trimethylcyclopentane
9.42	8A	47A	3-Ethylhexane
	8B	45B	1-cis-2-cis-4-Trimethylcyclopentane
9.59	9A	47B	1-cis-3-Dimethylcyclohexane
	9B	47C	1-cis-2-trans-3-Trimethylcyclopentane
10.66	10	56A	n-Octane
10.77	11	56B	1-cis-4-Dimethylcyclohexane
10.87	12	56C	1-trans-3-Dimethylcyclohexane
12.02	13	60A	n-Propylcyclopentane
12.25	14	60B	Ethylcyclohexane

Notes

1. Low concentrations of total olefins may be estimated by summing the unidentified peaks eluting before methylcyclohexane. Unidentified peaks eluting after methylcyclohexane may include C₉ saturates and thus may not be summed for olefin quantitation. If the olefin content so determined is greater than 2%, interferences will make the paraffin and naphthene results invalid. An alternative estimate of total olefins may be obtained by analyzing the sample by UOP Method 304, "Bromine Number and Bromine Index of Hydrocarbons by Potentiometric Titration." Olefins greater than 2% may also be determined by ASTM Method D 6839, "Hydrocarbon Types, Oxygenated Compounds, and Benzene in Spark Ignition Engine Fuels by Gas Chromatography."
2. Although C₈ aromatics are identified and response factors developed, these values may not be as accurate as other methods specific for aromatics determination due to non-aromatic interference. Therefore, C₈ aromatic values should not be reported from this method. An alternative method for C₈ aromatics is UOP Method 744, "Aromatics in Hydrocarbons by GC."
3. Analysis A alone is typically sufficient for reformat samples or gasolines having low naphthene content. For naphthas and gasolines with high naphthene content, both Analyses A and B must be used.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods," from precision data obtained using an autosampler.

Repeatability and Site Precision

A nested design was carried out for component analysis with two analysts. Each analyst carried out tests on two separate days, performing two tests each day using two samples. The total number of tests performed was 16 for each component. Using a stepwise analysis of variance procedure, the within-day and within-lab estimated standard deviations (esd) were calculated for the components at the concentration levels listed in Table 5. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 5 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 differences shown in Table 5 with 95% confidence.

The data in Table 5 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 the reproducibility of the test at this time.

Table 5
Repeatability and Site Precision, mass-%

<u>Component</u>	<u>Mean</u>	<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>
Methylcyclopentane	0.22	0.001	0.01	0.001	0.01
Methylcyclopentane	5.64	0.003	0.01	0.019	0.12
Benzene	0.24	0.001	0.01	0.001	0.01
Benzene	9.93	0.005	0.02	0.011	0.07
n-Heptane	1.23	0.001	0.01	0.001	0.01
n-Heptane	7.46	0.003	0.01	0.023	0.14
Methylcyclohexane	0.27	0.001	0.01	0.001	0.01
Methylcyclohexane	7.21	0.004	0.01	0.022	0.04
Toluene	1.38	0.001	0.01	0.001	0.01
Toluene	24.64	0.008	0.03	0.010	0.05

Time for Analysis

The elapsed time for Analysis A only is 0.8 hour with a labor requirement of 0.7 hour. The elapsed time for both Analyses A and B is 1.6 hours with a labor requirement of 1.3 hours.

Suggested Suppliers

Agilent Technologies, 2850 Centerville Rd., Wilmington, DE 19808-1610, USA, 1-302-633-8000, www.agilent.com

Grace Davison Discovery Sciences, 2051 Waukegan Rd., Deerfield, IL 60015, USA, 1-847-948-8600, www.discoverysciences.com

Matheson Tri-Gas, 166 Keystone Dr., Montgomeryville, PA 18936, USA, 1-215-641-2700, www.mathesontrigas.com

SGE Incorporated, 2007 Kramer Lane, Austin, TX 78758, USA, 1-512-837-7190, www.sge.com

Sigma-Aldrich Co., 1000 West Saint Paul Ave., Milwaukee, WI 53201, USA, 1-414-438-3850, www.sigma-aldrich.com

VICI Mat/Sen, 7806 Bobbitt, Houston, TX 77055, USA, 1-713-688-9345, www.vicimatsen.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA, 1-610-431-1700,
www.vwr.com

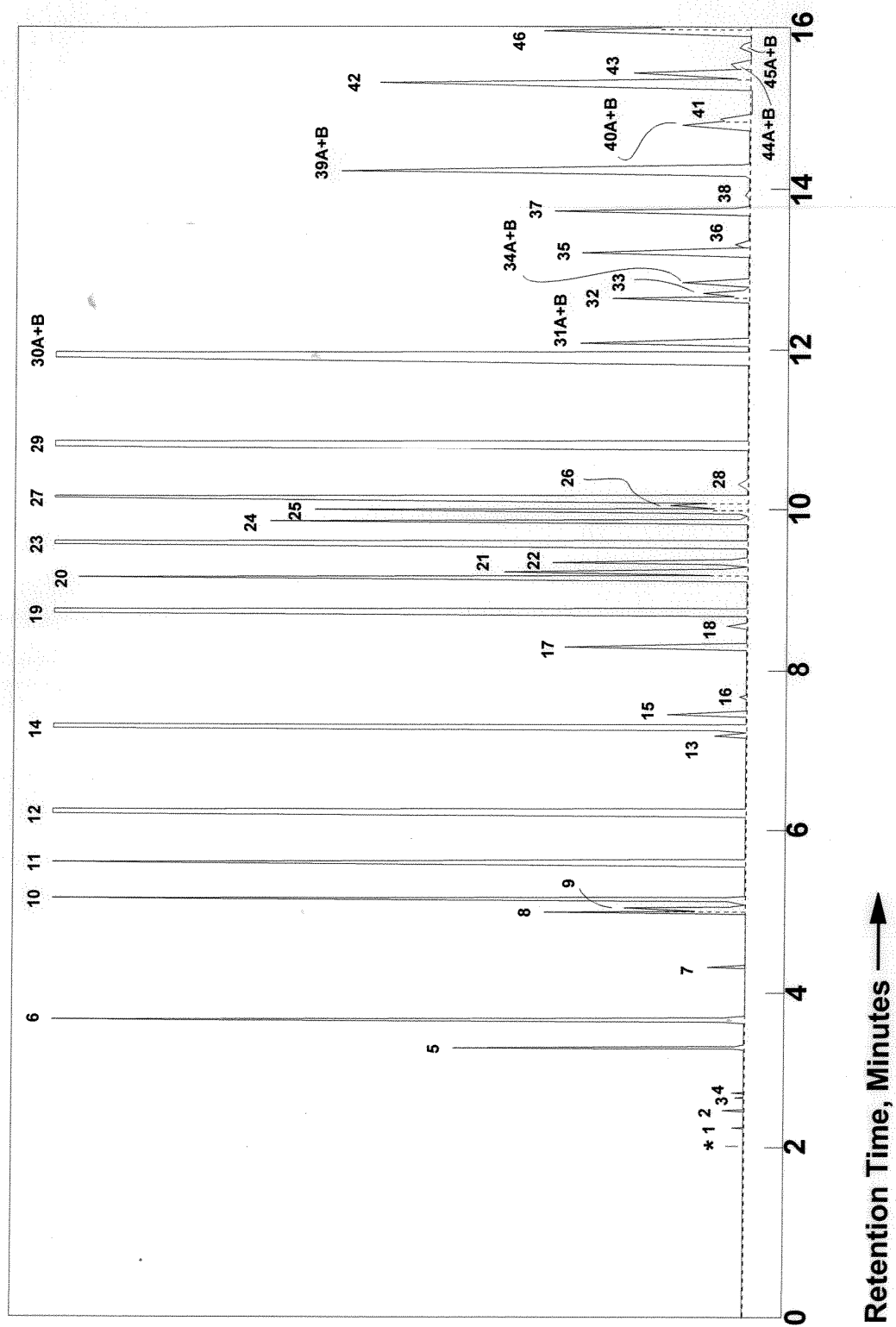


Figure 1

Typical Chromatogram, Analysis A, Part 1

UOP Method 690

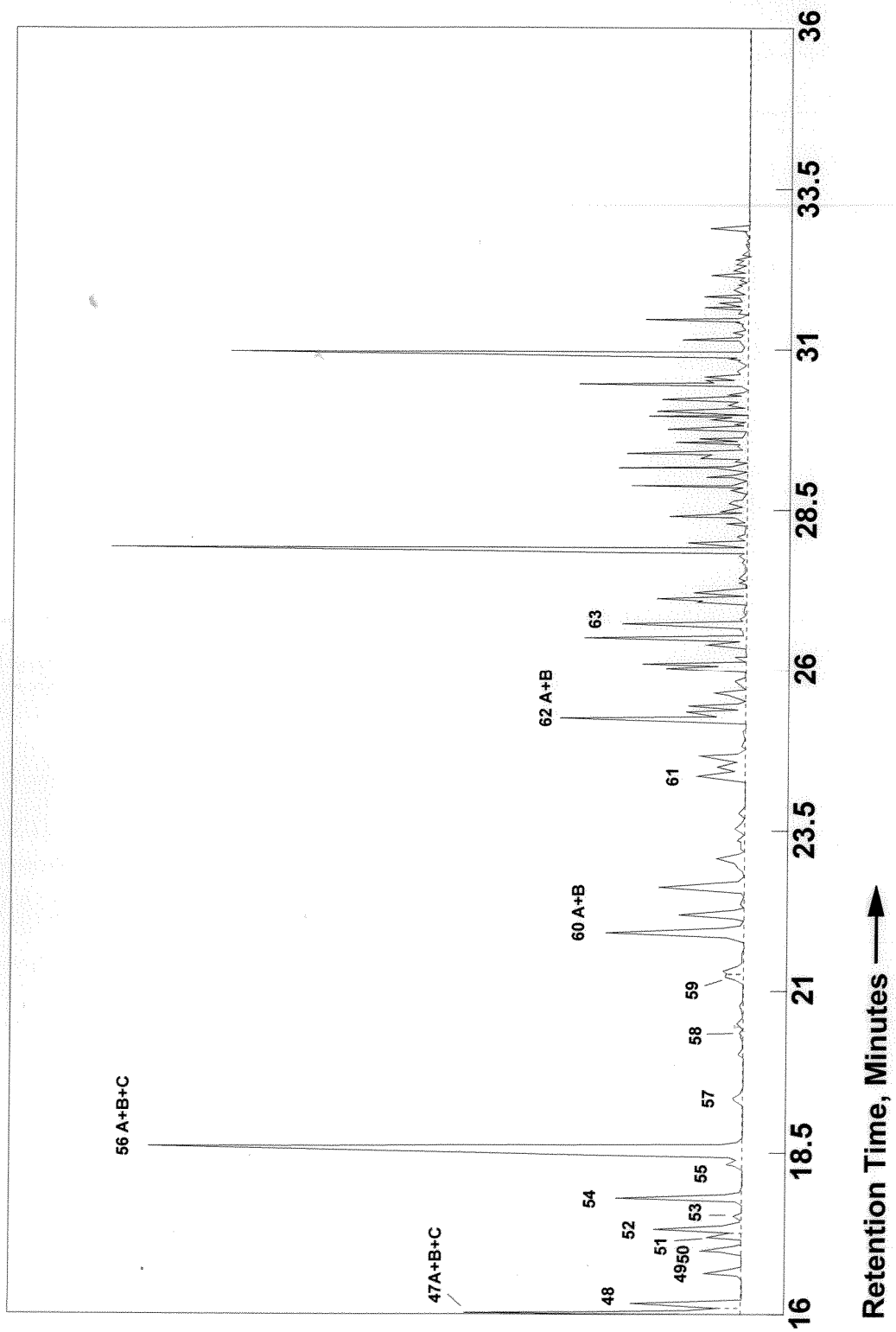
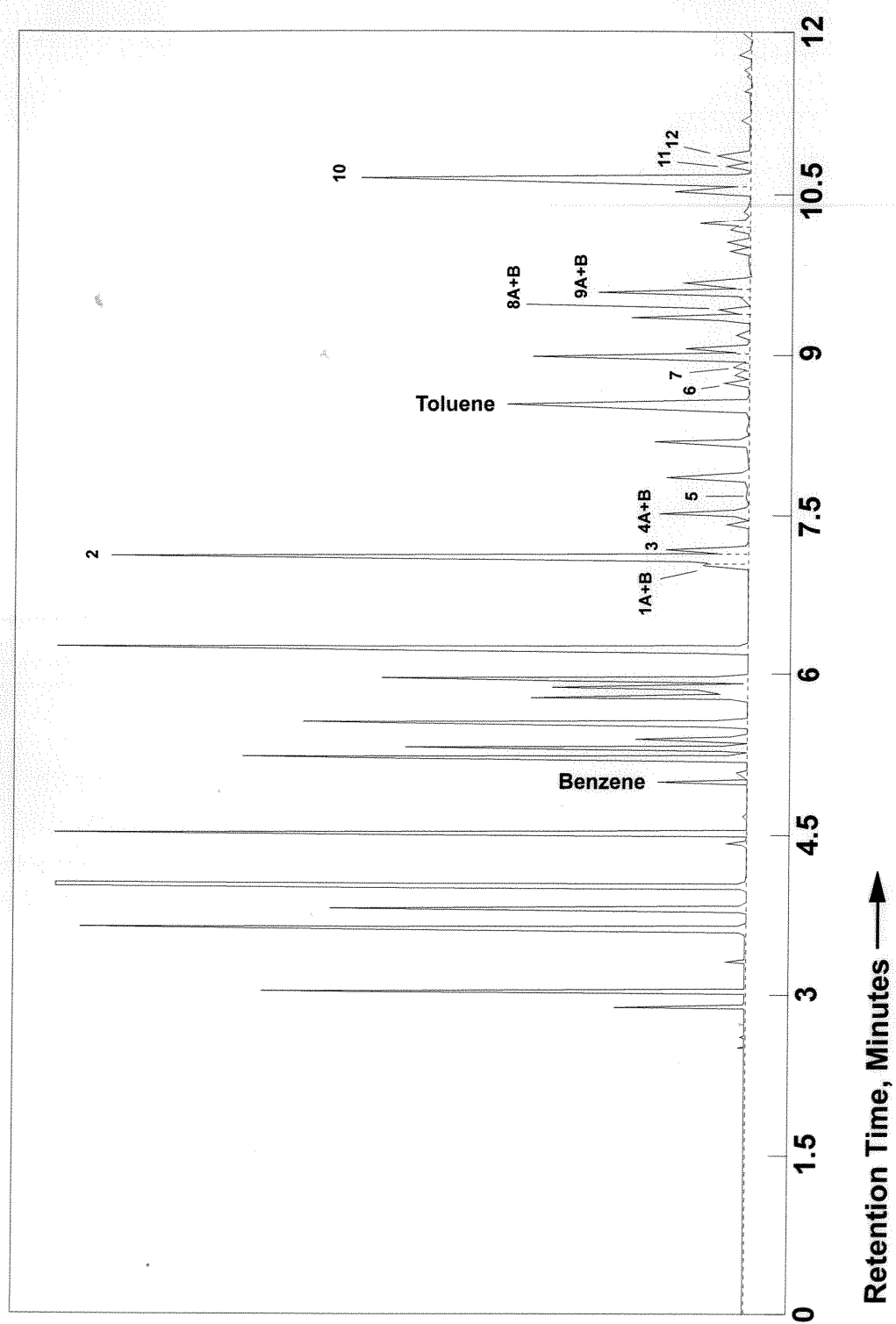


Figure 2
Typical Chromatogram, Analysis A, Part 2

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Retention Time, Minutes →

Figure 3
Typical Chromatogram, Analysis B, Part 1

UOP Method 690

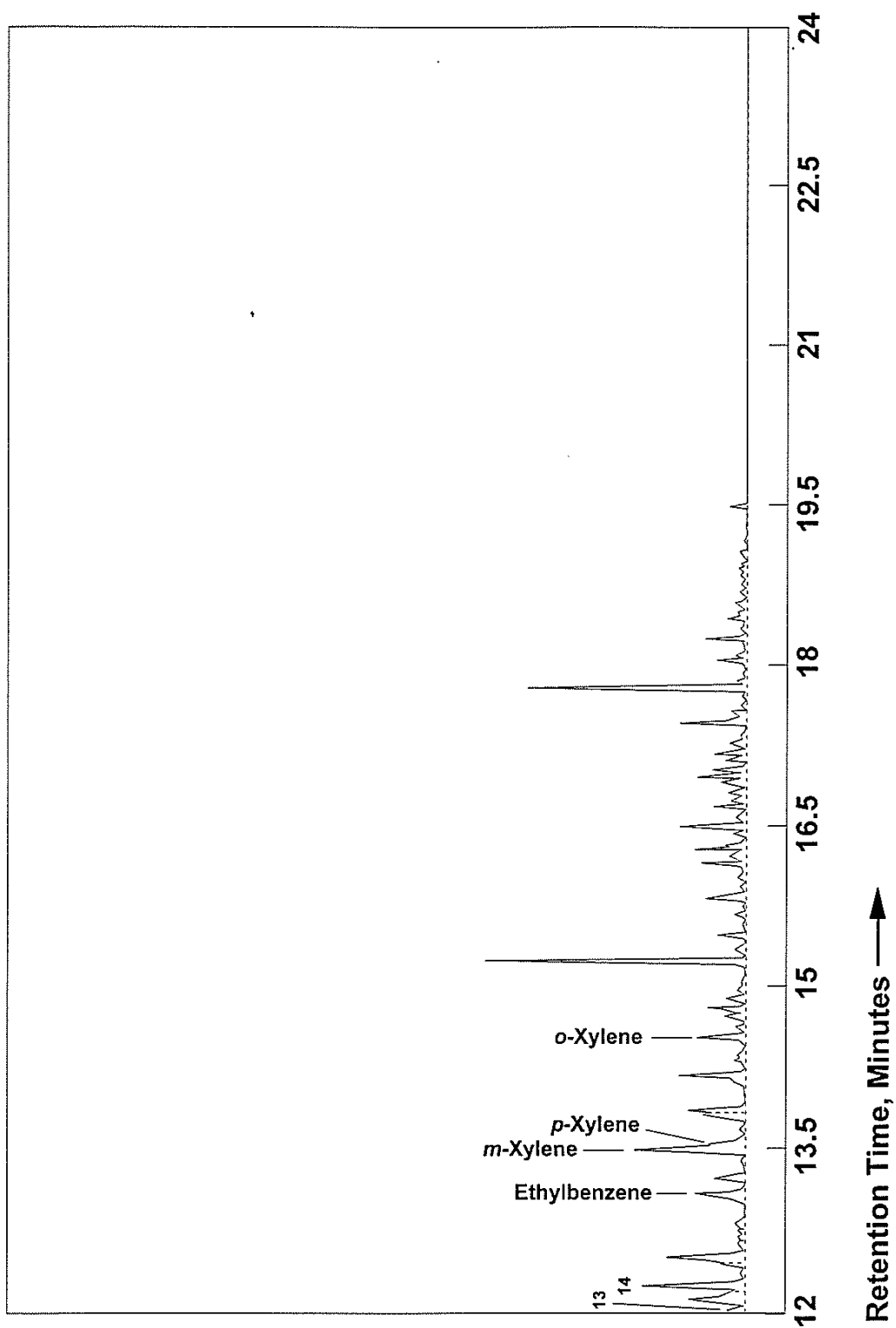


Figure 4
Typical Chromatogram, Analysis B, Part 2

Test Method 960