



Aromatics in Hydrocarbons by Gas Chromatography

UOP Method 744-19

Scope

This method is for determining individual C₆ through C₁₀ aromatic compounds in petroleum distillates or aromatic concentrates having a final boiling point of 210°C or lower. C₁₁ and heavier aromatics are reported as a group. C₁₀ and heavier non-aromatics may interfere with the determination of benzene and toluene. When this occurs, benzene and toluene can be determined by ASTM Methods D 5443, D 5580, D 6729, or D 6839, or UOP Method 690. Other applications for this method include the assay of any C₁₀ or lower boiling aromatics, such as benzene, toluene, mixed xylenes, etc. This method may also be used to provide a distribution of C₈ aromatics and/or C₉ and heavier aromatics to a value determined by a different method. When used for any of the above applications, the limit of quantitation for a single aromatic component is 0.01 mass-%. The *Appendix* describes an extension to the method to analyze individual C₆ through C₁₀ aromatic compounds in petroleum distillates or aromatic concentrates having a final boiling point of less than 344°C (nC₂₀).

References

- ASTM Method D4307, "Preparation of Liquid Blends for Use as Analytical Standards," www.astm.org
- ASTM Method D5443, "Paraffin, Naphthene, and Aromatic Hydrocarbon Type Analysis in Petroleum Distillates Through 200°C by Multidimensional Gas Chromatography," www.astm.org
- ASTM Method D5580, "Determination of Benzene, Toluene, Ethylbenzene, p/m-Xylene, o-Xylene, C₉ and Heavier Aromatics, and Total Aromatics by Gas Chromatography," www.astm.org
- ASTM Method D6729, "Determination of Individual Components in Spark Ignition Engine Fuels by 100 Meter Capillary High Resolution Gas Chromatography," 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 690, "Octanes and Lower Boiling Hydrocarbons in Olefin-Free Gasolines by GC," www.astm.org
- UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

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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 polyethylene glycol. The mass-% composition of the sample is obtained by the normalization of peak areas after relative response factors are applied to correct for detector mass response differences. Alternatively, selected aromatic components, e.g., C₈ aromatics, may be normalized to their sum as determined by another technique.

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, 60 m of 0.32-mm ID fused silica capillary, internally coated to a film thickness of 0.5- μ m with cross-linked polyethylene glycol, Restek, Cat. No. 10642

Gas chromatograph, capable of multiple temperature ramping, 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 10 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 7890B.

Data System, for computerized instrument control of data acquisition and data reduction, ChemStation, Agilent Technologies.

Leak detector, gas, Thermo Scientific GLD Gas Leak Detector, Cat. No. 66002-001.

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 injecting a 0.5- μ L volume of sample. An automatic injection device is recommended. Agilent Technologies, Model 7693A.

Reagents and Materials

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%, Aldrich Chemical, Cat. No. 27070-9

Gas purifier, for hydrogen, to remove oxygen and moisture from carrier gas, VICI Metronics, Cat. No. P200-1

n-Heptane, 99+%, Aldrich Chemical, Cat. No. 27051-2

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

1-Methyl-2-ethylbenzene (2-ethyltoluene), >99%, TCI, Cat. No. E0184

Methylindane isomers, if needed for peak identification, AccuStandard, special order

Nitrogen or helium, zero-gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane, used for detector makeup gas

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

1,2,4,5-Tetramethylbenzene, 99.8%, TCI, Cat. No. T0140.

Toluene, 99.8%, Aldrich Chemical, Cat. No. 27037-7

Xylenes (C_8 aromatics), mixed, 98.5+%, Aldrich Chemical, Cat. No. 24764-2

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.
 - **CAUTION:** Hydrogen carrier 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 Chromatogram. Figures 1 through 3 constitute a single chromatogram.
4. Program the column oven temperature to 210°C and maintain this temperature until a stable baseline has been obtained at the required sensitivity.
5. Cool the column oven to a stabilized 50°C.
6. Thoroughly mix the sample.
7. Inject nominally 0.5 μ L of sample into the gas chromatograph and start the integrator and the column oven programming sequence.
 - The injection sequence of a GC is typically automated, performing the injection, and starting the integrator and column temperature program simultaneously.
8. Identify the components of interest by comparing the resultant chromatogram to the Typical Chromatogram, See Figure 1, part A, B and C.
 - All unidentified components eluting before *n*-butylbenzene are defined as non-aromatics.
 - All unidentified components eluting after *n*-butylbenzene are defined as C_{11+} aromatics. Olefinic C_9 and C_{10} aromatics, e.g., substituted styrenes, if present, elute after *n*-butylbenzene and may elute under other identified components or may be included in the C_{11+} aromatics. 2-Methylnaphthalene, 1-Methylnaphthalene, the ethylnaphthalene isomer, and three dimethylnaphthalene isomers are identified on the Typical Chromatogram, but are included in the C_{11+} aromatics for calculation and reporting purposes. They can be reported as individual isomers if they are clearly identifiable.
 - Methylindanes co-elute with other C_{10} and C_{11} aromatics. Identify and report these components only when they are known to be present in concentrations significantly higher than the interfering compounds. Use pure compounds or GC-MS to confirm identifications.

- Any unidentified component can be identified by experiment and reported as individual isomers, if required. Additional pure compounds can be obtained and analyzed, or other techniques such as GC-MS may be used.
- 1,3-Diethylbenzene and 1-methyl-2-isopropylbenzene co-elute at some concentrations.

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Column head pressure	68 kPa gauge (10 psig)
Mode	Constant flow^A
Equivalent flow @ 50°C	2.3 mL/min
Equivalent linear velocity @ 50°C	38 cm/sec
Split flow	200 mL/min
Injection port temperature	230°C
Column temperature program	
Initial temperature	50°C
Initial time	5 min
Programming rate A	8°C/min
Intermediate temperature A	100°C
Intermediate time A	0 min
Programming rate B	2°C/min
Intermediate temperature B	120°C
Intermediate time B	0 min
Programming rate C	20°C/min
Final temperature	240°C
Final time	17.75 min
Detector FID	
Temperature	240°C
Hydrogen flow rate^B	30 mL/min
Air flow rate^B	400 mL/min
Make up gas	nitrogen or helium
Makeup flow rate^B	30 mL/min
Sample size	0.5 µL

^AConstant pressure mode can also be used. Confirm separations and retention times.

^BConsult the manufacturer's instrument manual for suggested flow rates.

Calibration

Relative response factors are required to relate the peak areas of sample components to mass-% since all the components do not respond equally in a flame ionization detector.

- Prepare a calibration blend as described in ASTM Method D 4307 to contain 25 mass-% n-heptane, 15 mass-% benzene, 20 mass-% toluene, 20 mass-% mixed xylenes, 10 mass-% 1-methyl-2-ethylbenzene, and 10 mass-% 1,2,4,5-tetramethylbenzene.
 - The composition of the calibration blend is given based upon a broad spectrum of samples to be analyzed. If typical samples to be analyzed are of a similar composition, but different from the listed concentrations, prepare the calibration blend with component concentrations that more closely align with the typical sample.
- 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, again when changes are made to the equipment, and periodically thereafter to verify proper calibration.
- Identify the peaks and determine the average individual peak areas from the triplicate runs.

- 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.
4. Use the average peak areas to calculate the relative response factor for each component to three decimal places, using *n*-heptane as a reference, and Equation 1.

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

where:

- A** = concentration of the component or group of components in the calibration blend, mass-%
B = average peak area of *n*-heptane
C = concentration of *n*-heptane in the blend, mass-%
D = average peak area for the component or group of components
F = relative response factor for the component or group of components

Aromatic hydrocarbons have a greater response by weight than non-aromatics, with benzene having the highest relative response, and thus, the lowest (numerical) relative response factor. Therefore, the relative response factors determined will be proportional in the order: benzene < toluene < mixed xylenes < 1-methyl-2-ethylbenzene < 1,2,4,5-tetramethylbenzene < *n*-heptane. If the determined relative response factors are not proportional in that order, recheck the instrument hardware, particularly the inlet system, the operating conditions, the detector and integrator linearity, and the blend preparation.

Calculated relative response factors should be similar to the theoretical response factors shown in Table 2. The theoretical 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

<i>n</i> -Heptane	1.000
Benzene	0.909
Toluene	0.919
Xylenes	0.927
1-Methyl-2-ethylbenzene	0.933
1,2,4,5-Tetramethylbenzene	0.938

Use the relative response factor of *n*-heptane for all non-aromatics, the relative response factor of 1-methyl-2-ethylbenzene for the C₉ aromatics, and the relative response factor of 1,2,4,5-tetramethylbenzene for all C₁₀ and C₁₁+ aromatics.

Calculations

Total Sample

Calculate the concentration of each component or group of components using Equation 2.

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

where:

- F** = previously defined, Equation 1
G = peak area of individual component or group of components in the sample

N = sum of the products, **FG**, of all the components and groups of components in the sample; also expressed as $\sum_{i=1}^n F_i G_i$

100 = factor to convert to mass-%

Distribution of Selected Components

Normalize a selected group of aromatic components to a predetermined value using Equation 3.

$$\text{Component, mass - \%} = \frac{\text{FGM}}{Z} \quad (3)$$

where:

F = previously defined, Equation 1

G = previously defined, Equation 2

M = value to which the selected group is to be normalized, mass-%

Z = sum of the products, **FG**, of all the selected group of peaks; also expressed as $\sum_{i=1}^n F_i G_i$

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

Precision

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

Repeatability, Intermediate Precision and Reproducibility

A nested design was carried out for determining components in one aromatic hydrocarbon sample by two analysts on two separate days, performing two analyses each day in two separate laboratories for a total of 16 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means 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 repeatability allowable differences shown in Table 3 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 3 with 95% confidence. Two tests performed by different analysts in different laboratories on different days should not differ by more than the reproducibility allowable difference shown in Table 4 with 95% confidence.

Table 3
Repeatability and Intermediate Precision, mass-%

Component	Mean	Repeatability		Site Precision		Reproducibility	
		Within Day esd	Allowable Difference	Within Lab esd	Allowable Difference	Between Lab esd	Allowable Difference
Non-aromatics	1.78	0.005	0.01	0.005	0.02	0.006	0.02
Toluene	35.88	0.044	0.04	0.053	0.18	0.140	0.55
m-Xylene	9.16	0.005	0.01	0.006	0.02	0.059	0.23
1,2,4-trimethylbenzene	3.48	0.003	0.01	0.005	0.02	0.009	0.03
1,2,3,5-Tetramethylbenzene	2.41	0.003	0.01	0.003	0.01	0.035	0.14

The data in Table 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.

Time for Analysis

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

Suggested Suppliers

AccuStandard, 125 Market St., New Haven, CT 06513 (203-786-5290) www.accustandard.com

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

Aldrich Chemical Co., Inc., P.O. Box 355, Milwaukee, WI 53201 (414-273-3850) www.sial.com

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-648-4000)
www.mathesontrigas.com

Restek Corp., 110 Benner Circle, Bellefonte, PA 16823-8812 (814-353-1300) www.restekcorp.com

TCI America, 9211 North Harborage Street, Portland, OR 97203, (800-423-8616),
www.tcichemicals.com

VICI Metronics, 26295 Twelve Trees Poulsbo, Washington 98370 (360-697-9199) www.vici.com

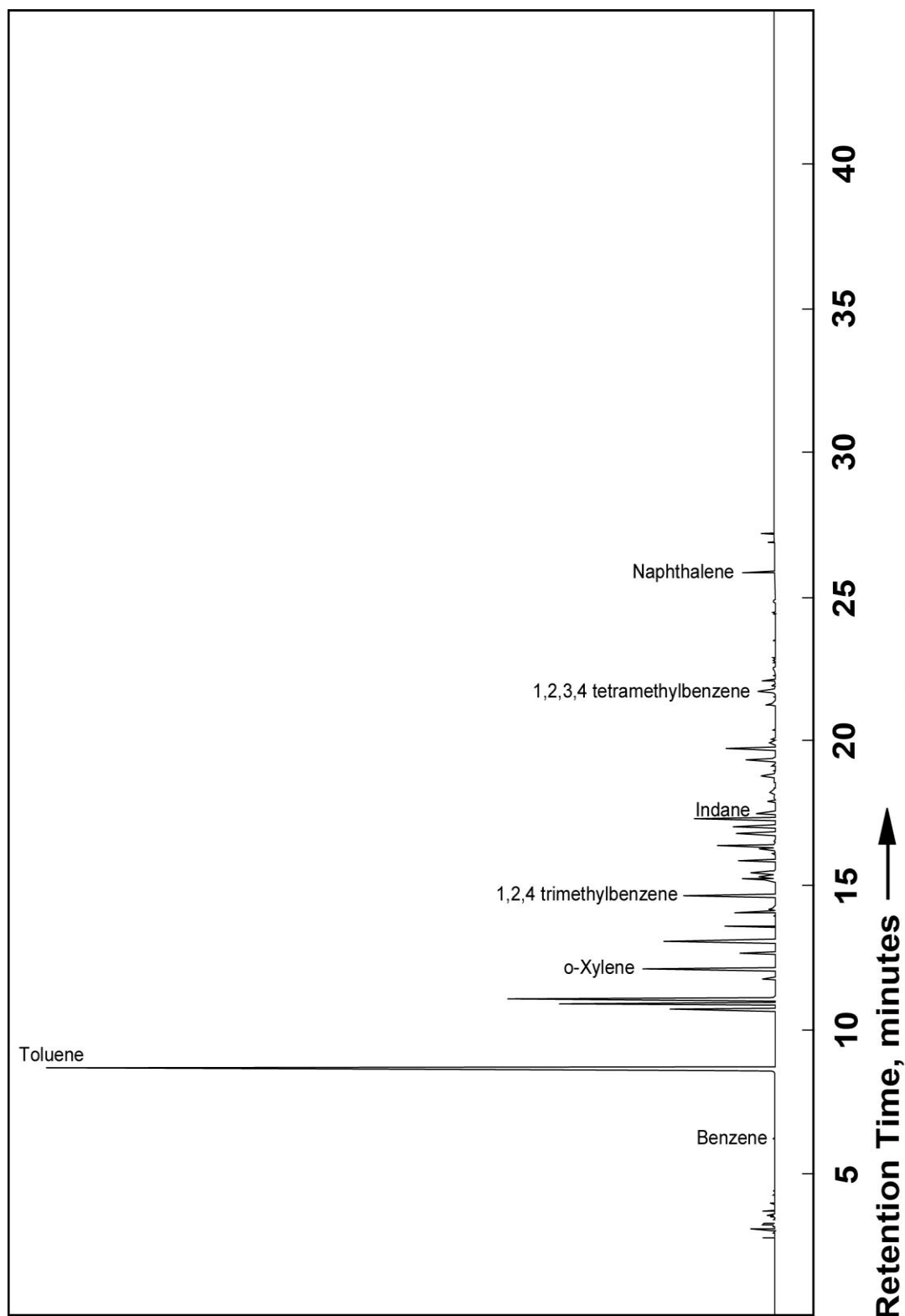


Figure 1
Typical Total Chromatogram, Parts A through C

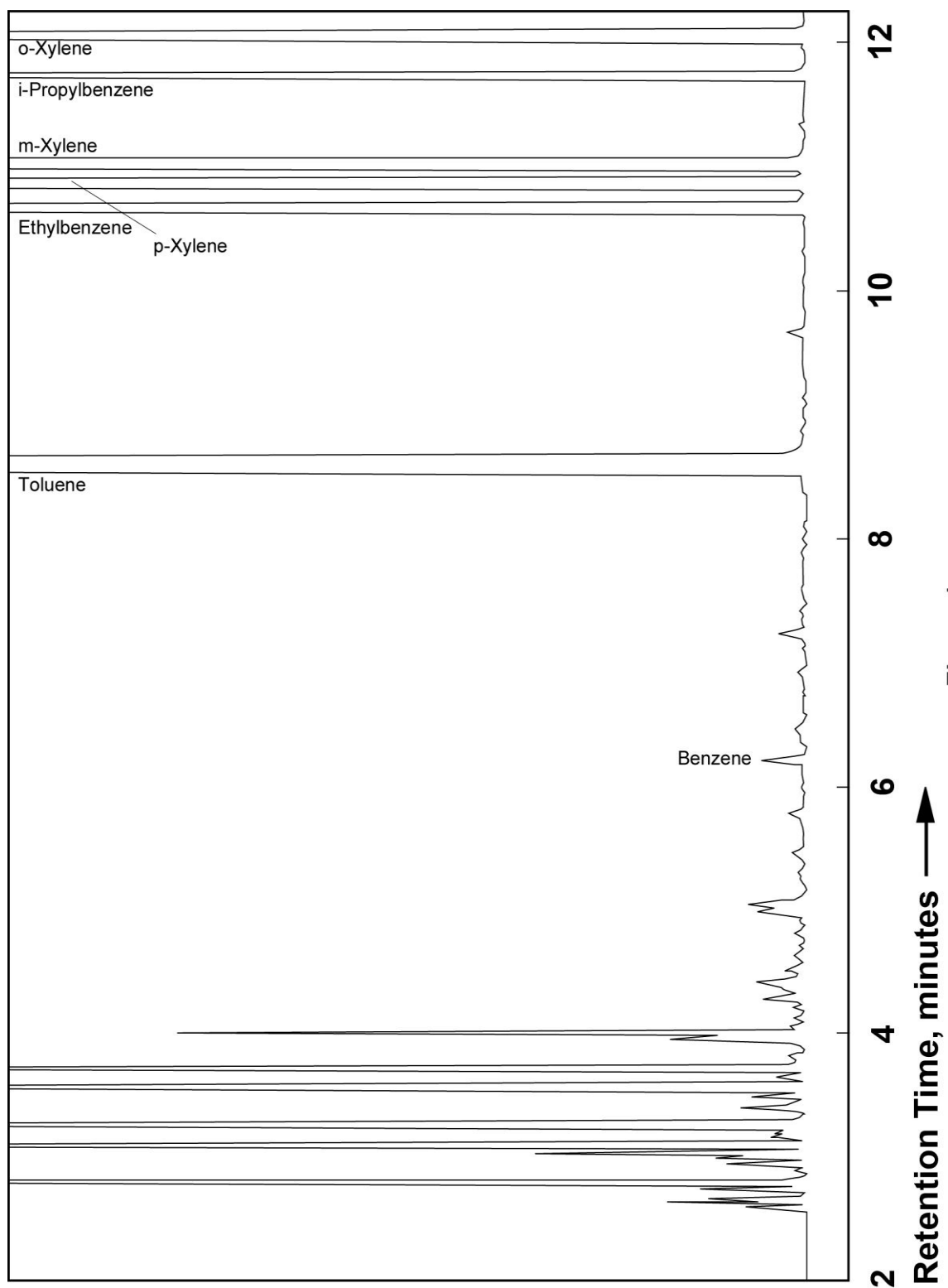
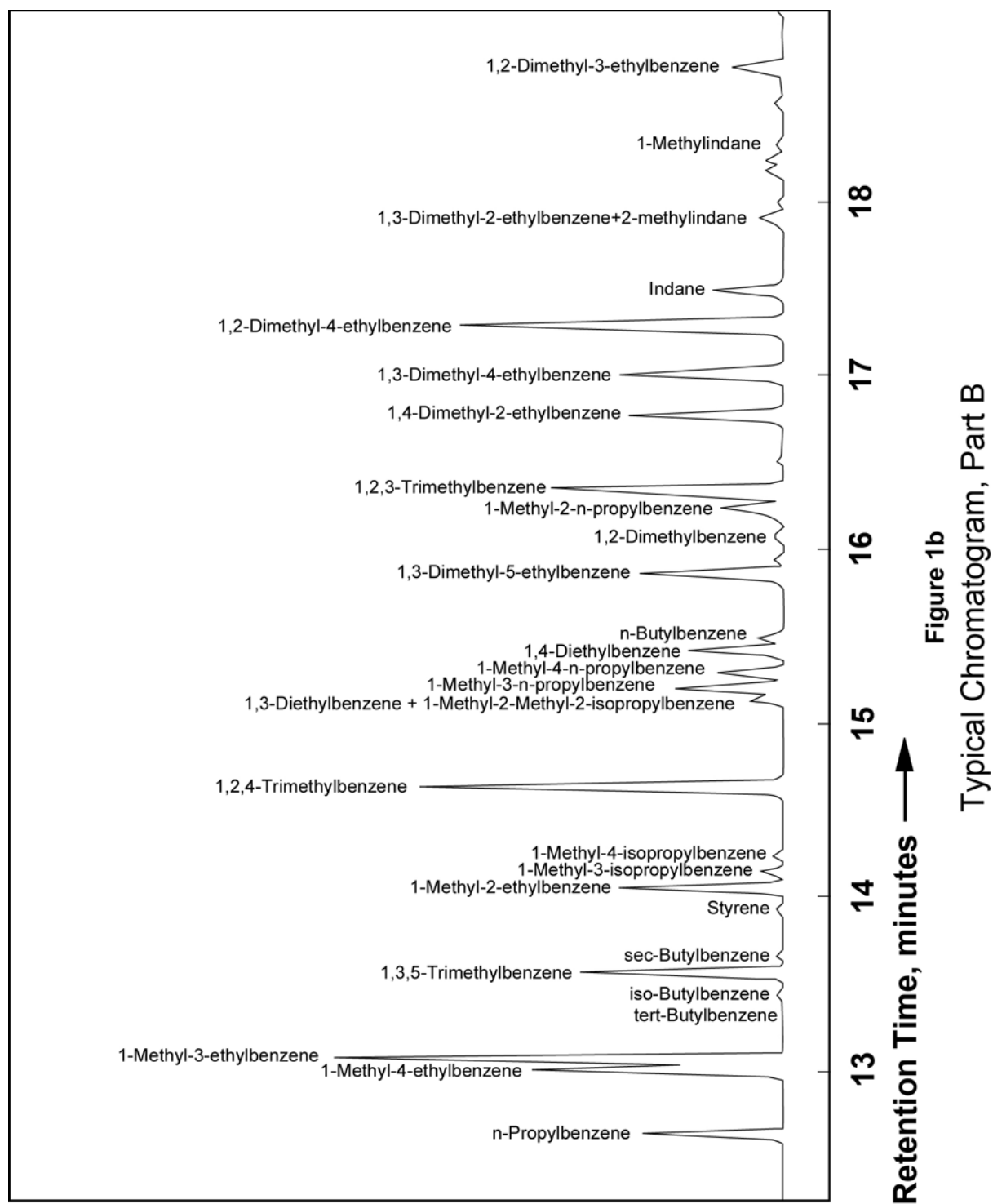


Figure 1a

Typical Chromatogram, Part A



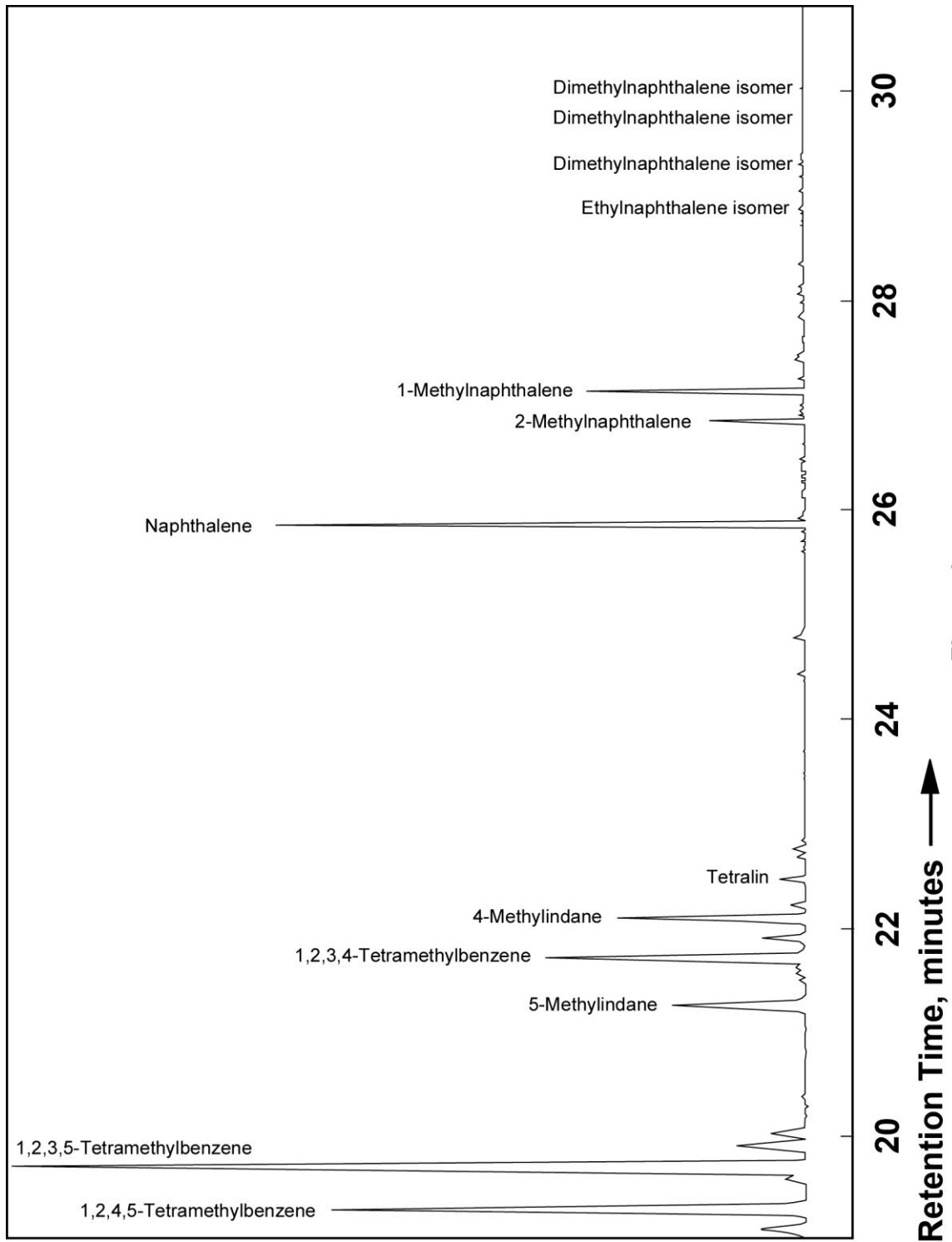


Figure 1c
Typical Chromatogram, Part C

Appendix

Analysis of Aromatics in Hydrocarbons by Gas Chromatography having a final boiling point less than 344°C

Scope

This appendix is for determining individual C₆ through C₁₀ aromatic compounds in petroleum distillates or aromatic concentrates having a final boiling point of less than 344°C (nC₂₀). Sample matrices, such as Diesel, Kerosene, and heavy Naphtha with high concentrations of non-aromatics and an increased final boiling point less than 344°C (nC₂₀) will not be applicable due to interference with aromatics. C₁₁ and heavier aromatics are reported as a group. C₁₀ and heavier non-aromatics may interfere with the determination of benzene and toluene. As the boiling point range of non-aromatics in the sample increases, there will be more interference with the determination of benzene, toluene, xylenes and some C₉ aromatics (Figure A1).

Outline of Method

The method is unchanged except for the Final time and Final Temperature in the operating conditions as given in Table A1. Steps above within Chromatographic Technique, Calibration and Calculations sections should be followed.

Procedure

Chromatographic Technique

- The final hold time in the recommended operating conditions is changed from 17.75 to 80 minutes as seen in Table A1.
 - Other conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram (Figures 1-3).

Table A1
Recommended Operation Conditions

Carrier gas	hydrogen
Column head pressure	68 kPa gauge (10 psig)
Mode	Constant flow ^A
Equivalent flow @ 50°C	2.3 mL/min
Equivalent linear velocity @ 50°C	38 cm/sec
Split flow	200 mL/min
Injection port temperature	230°C
Column temperature program	
Initial temperature	50°C
Initial time	5 min
Programming rate A	8°C/min
Intermediate temperature A	100°C
Intermediate time A	0 min
Programming rate B	2°C/min
Intermediate temperature B	120°C
Intermediate time B	0 min
Programming rate C	20°C/min
Final temperature	240°C
Final time	80 min

Detector FID	
Temperature	240°C
Hydrogen flow rate^B	30 mL/min
Air flow rate^B	400 mL/min
Make up gas	nitrogen or helium
Makeup flow rate^B	30 mL/min
Sample size	0.5 µL
^A Constant pressure mode can also be used. Confirm separations and retention times.	
^B Consult the manufacturer's instrument manual for suggested flow rates.	

- Identify the components of interest by comparing the resultant chromatogram to the Typical Chromatogram as shown in the attached Figure A1.

Precision

Precision statements were determined using UOP Method 999 from precision data obtained on two liquid samples using an auto sampler.

Repeatability and Site Precision

A nested design was carried out by two analysts, with each analyst performing analyses on two separate days, performing two analyses each day for a total of 8 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentrated means listed in Table A2. Two analyses performed in one laboratory 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 analyses performed in one laboratory by different analysts on different days should not differ by more than the intermediate precision allowable differences shown in Table 5 with 95% confidence.

Table A2
Repeatability and Intermediate Precision, mass-%

<u>Component</u>	<u>mean</u>	Repeatability		Site Precision	
		<u>Within Day esd</u>	<u>Allowable Difference</u>	<u>Within Lab esd</u>	<u>Allowable Difference</u>
Non-aromatics	17.11	0.061	0.24	0.063	0.25
Toluene	24.88	0.022	0.09	0.067	0.41
m-Xylene	12.34	0.017	0.07	0.018	0.07
1,2,4-trimethylbenzene	5.71	0.016	0.06	0.016	0.06
1,2,4,5-tetramethylbenzene	0.38	0.001	0.01	0.002	0.01

The data in Table A2 represent short-term estimates of repeatability of this appendix. 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.

Time for Analysis

The elapsed time for one analysis is 2.0 hours. The labor requirement is 0.5 hour.

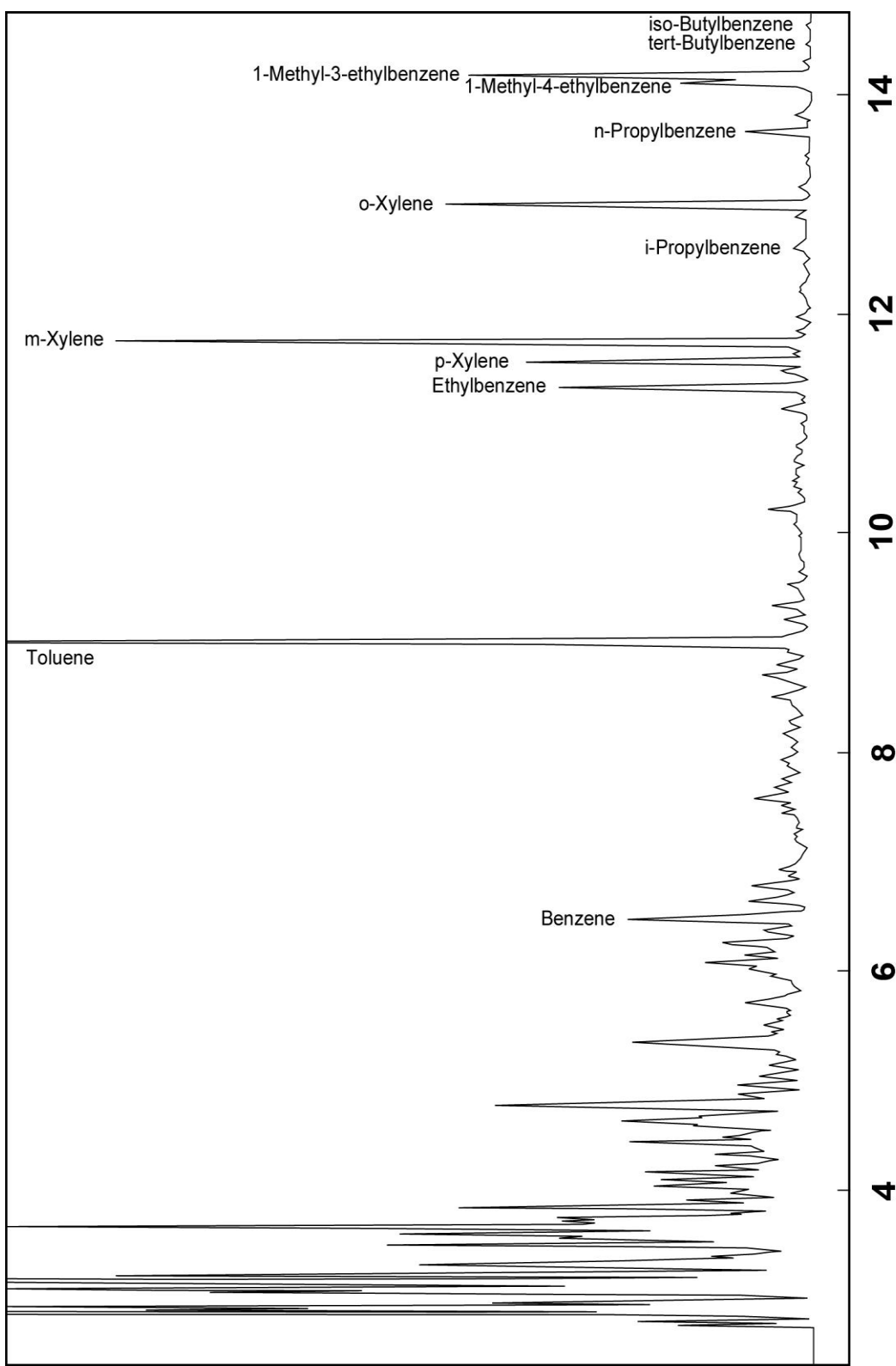


Figure A1

Example of Non-aromatic interference with the Aromatics