

TRACE AROMATIC HYDROCARBONS IN 90 TO 400°C BOILING RANGE PETROLEUM DISTILLATES BY HPLC

UOP Method 963-98

SCOPE

This method is for determining aromatics in petroleum distillates boiling in the range of 90 to 400°C by High Performance Liquid Chromatography (HPLC). The method determines aromatics from 0.001 to 4 mass-%. Above 4 mass-%, use IP Method 391. The aromatics should be predominantly mono-substituted, single-ring aromatics. Multiple-ring aromatic compounds and aromatic compounds containing two or more alkyl-substituents bias the results high. Significant levels of benzene bias the results low. Compounds containing sulfur, nitrogen, and oxygen may interfere. Mono-alkenes do not interfere, but conjugated di-alkenes and polyalkenes may interfere.

OUTLINE OF METHOD

A reproducible amount of sample is injected into an HPLC system consisting of an isocratic pump, sample injection valve, polar column and a refractive index detector. The separation is accomplished based on the polarity of the components. The aromatics portion of the sample is retained longer than the non-aromatic hydrocarbons. At a predetermined retention time, after the non-aromatic portion of the sample has eluted, the aromatics portion is back-flushed and detected as a single peak. The method is calibrated by an external standard procedure using calibration standards prepared from pure toluene.

APPARATUS

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

Back-flush valve, Rheodyne, Model 7010, Cat. No. 7010RV

Balance, readability 0.1-mg

Calculator, capable of performing least squares fit regression analyses

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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, 250 mm of 4.6-mm ID stainless steel tubing, packed with Partisil PAC, 5- μ m silica, Alltech, Cat. No. 228557

Column oven, capable of maintaining a constant temperature ($\pm 1^\circ\text{C}$) within the range of 20°C and 40°C , Hewlett Packard, Model G1316A

Differential refractometer, refractive index (RI) detector, capable of operation from 1.3 to 1.6 RI, yielding a minimum peak height response of 10 times the background noise for a 10 mass-ppm aromatic hydrocarbon when operated at the recommended conditions, Waters, Model 410

Flasks, volumetric, 100-mL, Class A, Fisher Scientific, Cat. No. 10-205C, several required

HPLC isocratic pump, Hewlett Packard, Model G1310A

Integrator, electronic, for obtaining peak areas

Manual HPLC injection valve, Rheodyne, Model 7125, Hewlett Packard, Cat. No. 0101-0607. An autosampler may be used.

Mobile phase reservoir, Erlenmeyer, glass, 4-L, Fisher Scientific, Cat. No. 10-039P

On-line mobile phase vacuum degasser, Alltech, Cat. No. 590100

Recorder, 10-mV full scale

Syringe, HPLC, 250- μ L, Fisher Scientific, Cat. No. 14-815-291. An autosampler 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.

Cyclohexane, 99+%, Aldrich Chemical, Cat. No. C10,030-7

n-Heptane, 99+%, HPLC grade, Aldrich Chemical, Cat. No. 27,051-2

Pasteur pipette, 146-mm length, disposable, borosilicate glass, Fisher Scientific, Cat. No. 13-678-20A

Sample vials and caps, 6-dram, Fisher Scientific, Cat. No. 03-339-10H

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

o-Xylene, 98%, HPLC grade, Aldrich Chemical, Cat. No. 29,588-4

PROCEDURE

Chromatographic Technique

1. Assemble and test all the HPLC system components as per the manufacturer's specifications.
 - Fig. 1 illustrates the instrument and valve configuration. Minimize tubing lengths connecting the various system components to minimize void volume and optimize temperature control.
2. Install the analytical column in the column oven and set the temperature control to 35°C.
3. Begin pumping *n*-heptane through the HPLC system at a flow rate of 0.6 mL/minute.
 - The column is the only system component in the column oven.
4. Set the parameters of the refractive index detector (see Table 1) to obtain the required sensitivity and an internal temperature of 35°C. Purge the reference side of the detector with mobile phase for approximately 15 minutes.
 - The system may take up to a couple hours to equilibrate as indicated by a stable baseline.

Operating Conditions

Table 1 summarizes the recommended chromatographic operating conditions. Other conditions may be used, provided they produce the required sensitivity and chromatographic separation equivalent to those shown in the Typical Chromatogram, Fig. 2.

Table 1
Recommended Chromatographic Conditions

Analytical column:	Alltech, Partisil PAC, 5 µm, 250- x 4.6-mm
Mobile phase:	<i>n</i>-Heptane, HPLC grade
Mobile phase flow rate:	0.6 mL/min
Injection volume:	10 µL
Column temperature:	35°C
Detector:	Refractive Index
Detector sensitivity:	8*
Detector scale factor:	20*
Detector temperature:	35°C

* Detector parameters are listed for a Waters Model 410 differential refractometer.

System Resolution Check

Perform a System Resolution Check at least once a week when samples are to be analyzed, or more frequently if deterioration in system resolution is suspected.

1. Prepare a System Resolution Standard by weighing 1.0 ± 0.1 g of cyclohexane and 0.5 ± 0.05 g of *o*-xylene into a 100-mL volumetric flask and dilute to volume with *n*-heptane. Mix the solution by capping the flask and shaking vigorously. Store the System Resolution Standard in a tightly capped bottle in a dark place between 5 and 25°C. Under these conditions, the standard is stable for one year.
2. When operating conditions are steady, inject 10 μ L of System Resolution Standard and immediately start the integrator to record the chromatogram.
 - Both cyclohexane and *o*-xylene should elute within 15 minutes.
3. Compare the resulting chromatogram with Fig. 3 to identify the peaks.
4. Calculate the resolution between cyclohexane and *o*-xylene by using Eq. 1 in *CALCULATIONS*.
 - If the resolution is less than 8.5, check that all system components are functioning correctly and that the chromatographic dead volume has been minimized. Adjust the flow rate to see if this improves the resolution and make sure the mobile phase is of sufficiently high quality. Finally, regenerate the column according to the manufacturer's recommendations or replace the column.

Back-flush Time Determination

The back-flush time is the point at which the back-flush valve is actuated to reverse the mobile phase flow on the HPLC system. This reverse of flow lumps the aromatics into one sharp peak, which can be easily integrated. In order to get the back-flush time for the analysis it is necessary to analyze a representative sample.

1. When operating conditions are steady, inject 10 μ L of a representative sample and immediately start the integrator. Allow the entire sample to elute off the column.
 - The entire sample should elute within 30 minutes.
2. Stop the integrator after the entire sample has eluted from the column and identify the paraffin peak by comparing the resulting chromatogram with Fig. 4. The back-flush time is the time at which the negative valley following the paraffin peak elutes (when estimating this time from the chromatogram, attempt to keep any error in the estimation in the positive direction and not more than 0.2 minutes; i.e., in Fig. 4, the negative valley is estimated at 6.7 minutes, therefore the back-flush time should be set between 6.7 and 6.9 minutes).

Calibration

Diesel and naphtha boiling range samples containing very low levels of aromatics are not likely to contain significant amounts of 2- and 3-ring aromatic hydrocarbons. Therefore toluene, a representative single-ring aromatic compound, is used in the calibration of this method. Significant levels of benzene in a sample will bias the results low. Conversely, significant amounts of 2- to 3-ring aromatics, or aromatics containing two or more alkyl constituents will bias the results high.

1. Prepare the calibration standards by weighing each component listed in Table 2 to the nearest 0.1-mg. Calculate the exact concentration of toluene in each standard based on the actual amounts of toluene, stock, calibration mix and/or *n*-heptane weighed using Eqs. 2 and 3 in *CALCULATIONS*.

Table 2
Calibration Standards
Quantities to Weigh, and Nominal Concentrations

Mass in g					
	<u>Toluene</u>	<u>Stock</u>	<u>Calibration 1</u>	<u>Calibration 2</u>	<u><i>n</i>-Heptane</u>
Stock	0.25	----	----	----	15.8
Calibration 1	----	1.0	----	----	9.4
Calibration 2	----	----	1.0	----	14.0
Calibration 3	----	----	----	1.0	9.0

<u>Nominal Toluene Concentration, mass-%</u>	
Stock	1.56
Calibration 1	0.150
Calibration 2	0.0100
Calibration 3	0.00100

2. Store the calibration standards in tightly capped bottles in a dark place between 5 and 25°C.
 - Under these conditions the solutions are stable for at least six months.
3. When operating conditions are steady, inject 10 µL of Calibration 1 and immediately start the integrator.
4. Actuate the back-flush at the appropriate time to elute the aromatics as one sharp peak. After the analysis is finished, again actuate the valve to return the flow to the forward direction.
 - Once the baseline has stabilized, proceed with the next injection.
5. Record the chromatogram and measure the peak areas for each toluene standard.
6. Repeat Steps 3 to 5 for Calibration 2 and 3.
7. Plot mass-% toluene concentration against area counts. Using the peak areas as the independent variable, and the calculated concentrations as the dependent variable, perform a linear regression including the origin to determine the coefficients of regression. See Eq. 4 in *CALCULATIONS*.
 - Calibration plots should be linear with a correlation coefficient greater than 0.999.
 - It is necessary to calibrate the refractive index detector daily when samples are being analyzed. It is recommended that a reference sample or one of the Calibration blends be run after every five samples to check the stability of the system.

Sample Analysis

1. Determine the density of the sample by ASTM D 4052 or another suitable technique and include this value in the calculation of the final concentration of aromatics in the sample (Eqs. 5 and 6).
2. When operating conditions are stable, inject 10 μL of sample into the HPLC system. Actuate the back-flush at the appropriate time to elute the aromatics as one sharp peak.
3. After the analysis is finished, again actuate the valve to return the flow to the forward direction.
 - Once the baseline has stabilized, the next injection can proceed.
4. Identify and integrate the aromatic peak by comparing the chromatogram obtained with the chromatogram in Fig. 2.

CALCULATIONS

Determine the resolution of the chromatographic system by using Eq. 1.

$$\text{Resolution} = \frac{A - C}{0.5(D + E)} \quad (1)$$

where:

- A** = retention time of *o*-xylene peak in seconds
- C** = retention time of cyclohexane peak in seconds
- D** = half-height peak width of cyclohexane in seconds
- E** = half-height peak width of *o*-xylene in seconds
- 0.5** = factor to average the peak widths at half-height

Calculate the actual concentration of toluene in the stock solution to three significant figures using Eq. 2.

$$G = \frac{100T}{T + H} \quad (2)$$

where:

- G** = toluene concentration in stock solution, mass-%
- H** = actual mass of *n*-heptane weighed, g
- T** = actual mass of toluene weighed, g
- 100** = factor to convert to mass-%

Calculate the actual concentrations of toluene in the three calibration solutions to three significant figures using Eq. 3.

$$N = \frac{PR}{R + H} \quad (3)$$

where:

- H** = *n*-heptane mass actually weighed for each respective calibration solution, g
N = actual concentration of toluene in each respective calibration solution, mass-%
P = concentration of toluene in each respective stock or calibration solution used to produce the next calibration solution, mass-%
R = actual mass of stock or calibration solution weighed for each respective calibration solution, g

Calculate the detector response for toluene by performing a linear regression of the data based upon the analysis of the toluene calibration blends. Use the different toluene calibration standard peak areas as the independent variable, and the corresponding toluene concentrations as the dependant variable. Include the origin as a data point. Eq. 4 is the model that describes a straight line.

$$Y = MX + B \quad (4)$$

where:

- B** = zero-order regression coefficient for toluene (y-intercept), mass-%
M = first-order regression coefficient for toluene (slope of line), mass-%/area counts
X = detector response of toluene, area counts
Y = concentration of toluene, mass-%
- Linear regression (also called linear estimation) is a statistical method for finding a straight line that best fits a set of x,y-data. This is a standard calculation common to many integrators, data systems or scientific calculators.

Calculate the density correction factor to three significant figures using Eq. 5.

$$J = \frac{0.684}{K} \quad (5)$$

where:

- J** = density correction factor
K = density of sample (determined by ASTM D 4052), g/mL
0.684 = density of heptane at 25°C, g/mL

Calculate the concentration of aromatics in the injected sample to two significant figures at or above 0.01 mass-% or to one significant figure below 0.01 mass-% using Eq. 6.

$$L = (MZ + B)J \quad (6)$$

where:

B = previously defined, Eq. 4

J = previously defined, Eq. 5

L = concentration of aromatics in sample, mass-%

M = previously defined, Eq. 4

Z = peak area of aromatics in sample, area counts

PRECISION

ASTM Repeatability

A nested design was carried out for low aromatics analysis with two analysts. Each analyst carried out tests on two separate days, performing two tests each day at each of five concentrations. The total number of tests performed was 40. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentrations listed in Table 3. Two tests performed by the same analyst on the same day should not differ by more than the ASTM allowable differences shown in Table 3 with 95% confidence.

UOP Repeatability

A nested design was carried out for low aromatics analysis with two analysts. Each analyst carried out tests on two separate days, performing four tests each day at each of five concentrations. The total number of tests performed was 40. Using a stepwise analysis of variance procedure, the within-lab standard deviations (esd) were calculated at the concentrations listed in Table 3. Two tests performed in one laboratory by different analysts on different days should not differ by more than the UOP allowable differences shown in Table 3 with 95% confidence.

Table 3
ASTM and UOP Repeatability, mass-%

Aromatics Concentration	ASTM Repeatability		UOP Repeatability	
	Within- Day esd	Allowable Difference	Within- Lab esd	Allowable Difference
0.11	0.004	0.01	0.004	0.01
0.066	0.0026	0.006	0.0026	0.006
0.045	0.0019	0.004	0.0019	0.004
0.022	0.0015	0.004	0.0015	0.004
0.001	0.0001	0.001	0.0001	0.001

The data in Table 3 are short-term estimates 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.

TIME FOR ANALYSIS

The elapsed time for calibration and analysis of one sample is three hours. The labor requirement is one hour.

REFERENCES

ASTM Method D 4052, www.astm.org

IP Method 391, *Standard Methods for Analysis and Testing of Petroleum and Related Products and British Standard 2000 Parts 1997*, **Vol. 2**, Institute of Petroleum, 61 New Cavendish St., London, UK, W1M 8AR

SUGGESTED SUPPLIERS

Aldrich Chemical Co., 1001 W. St. Paul Ave., Milwaukee, WI 53233 (414-273-3850)
Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015 (847-948-8600)
Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-562-8300)
Hewlett Packard, 2850 Centerville Rd., Wilmington, DE 19808-1610 (302-633-8000)
Rheodyne, Inc., P.O. Box 996, Cotati, CA 94931 (707-664-9050)
Waters Co., 34 Maple St., Milford, MA 01757-3696 (508-478-2000)

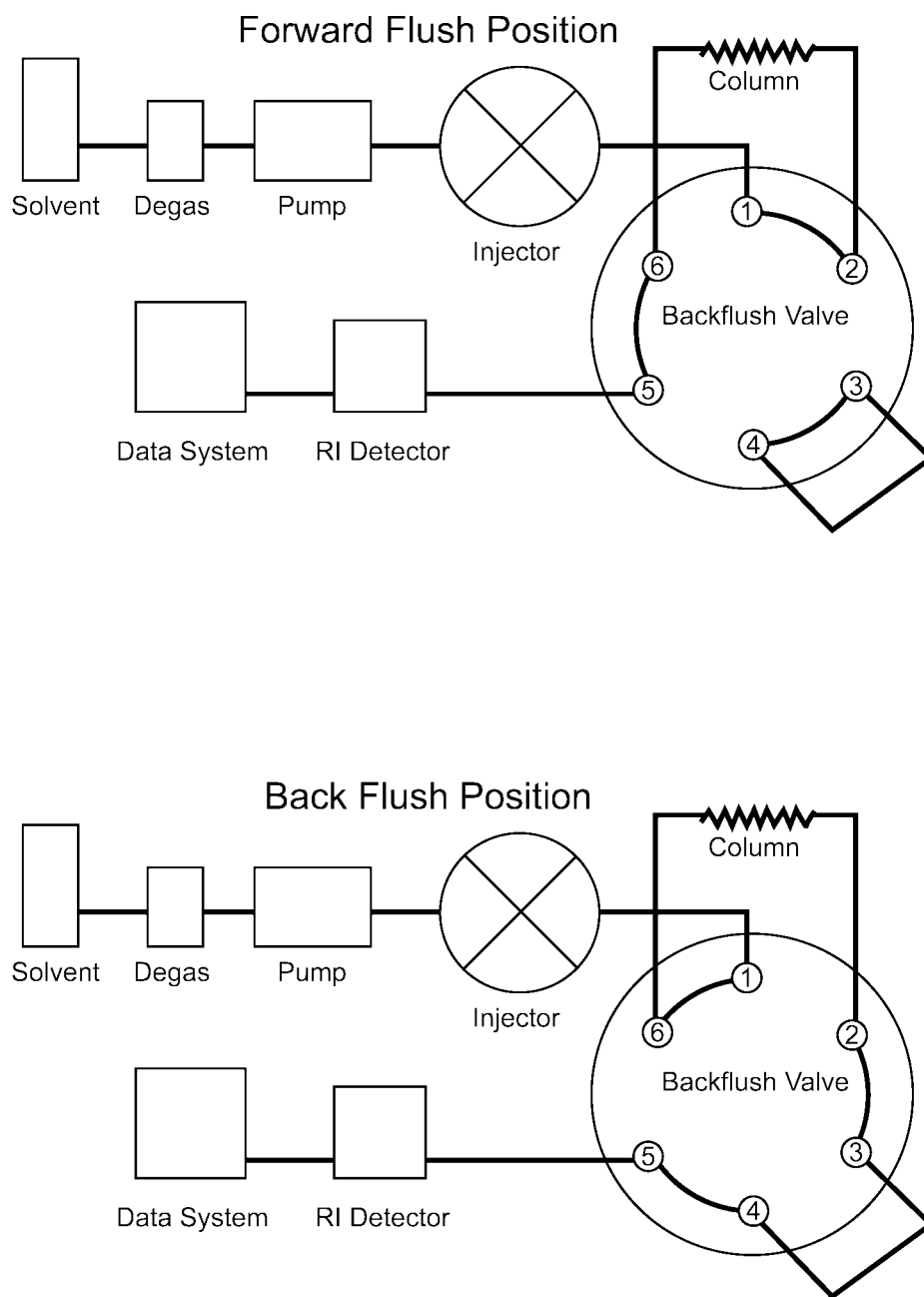


Figure 1
Instrument Configuration

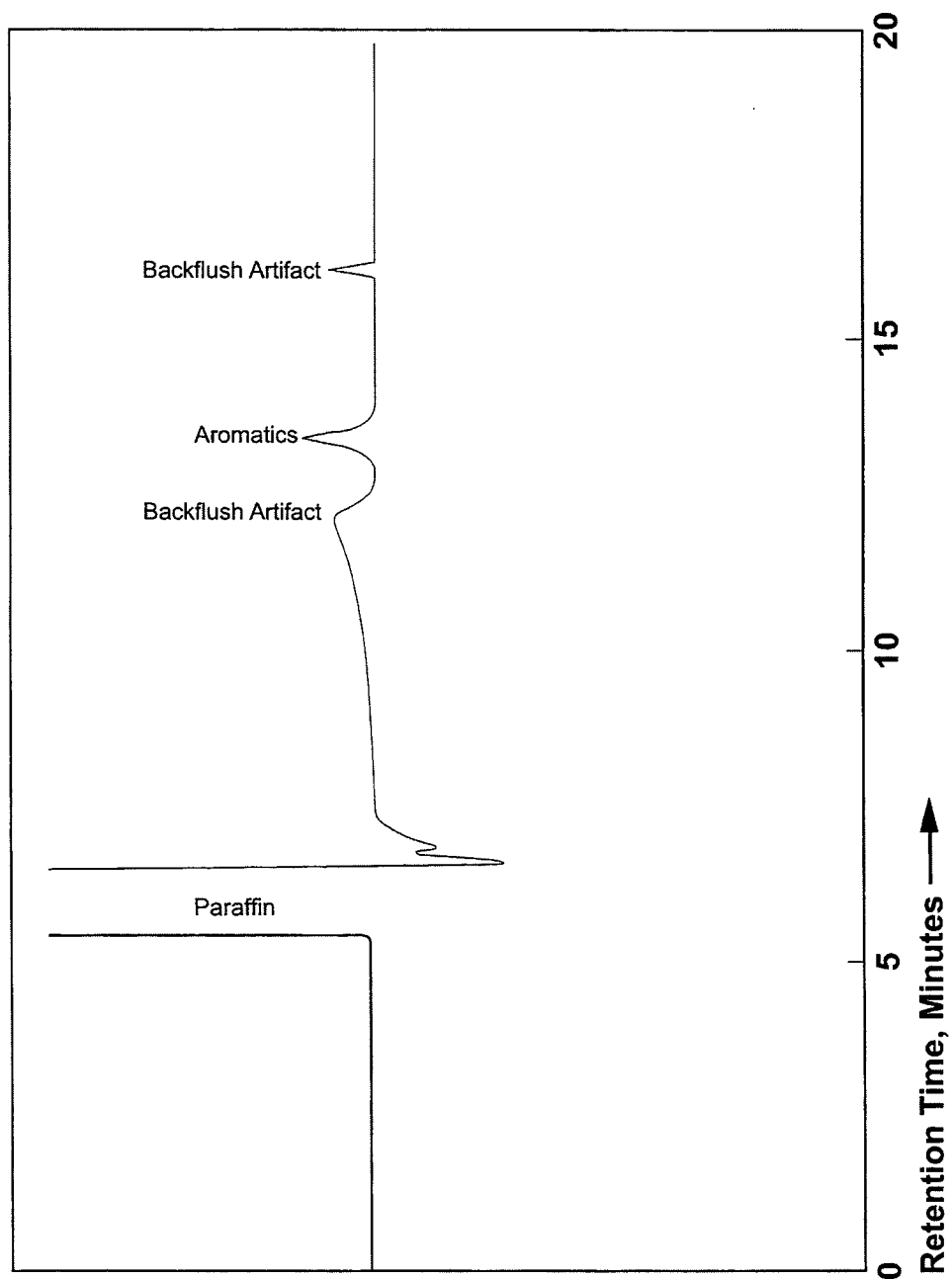


Figure 2
Typical Chromatogram

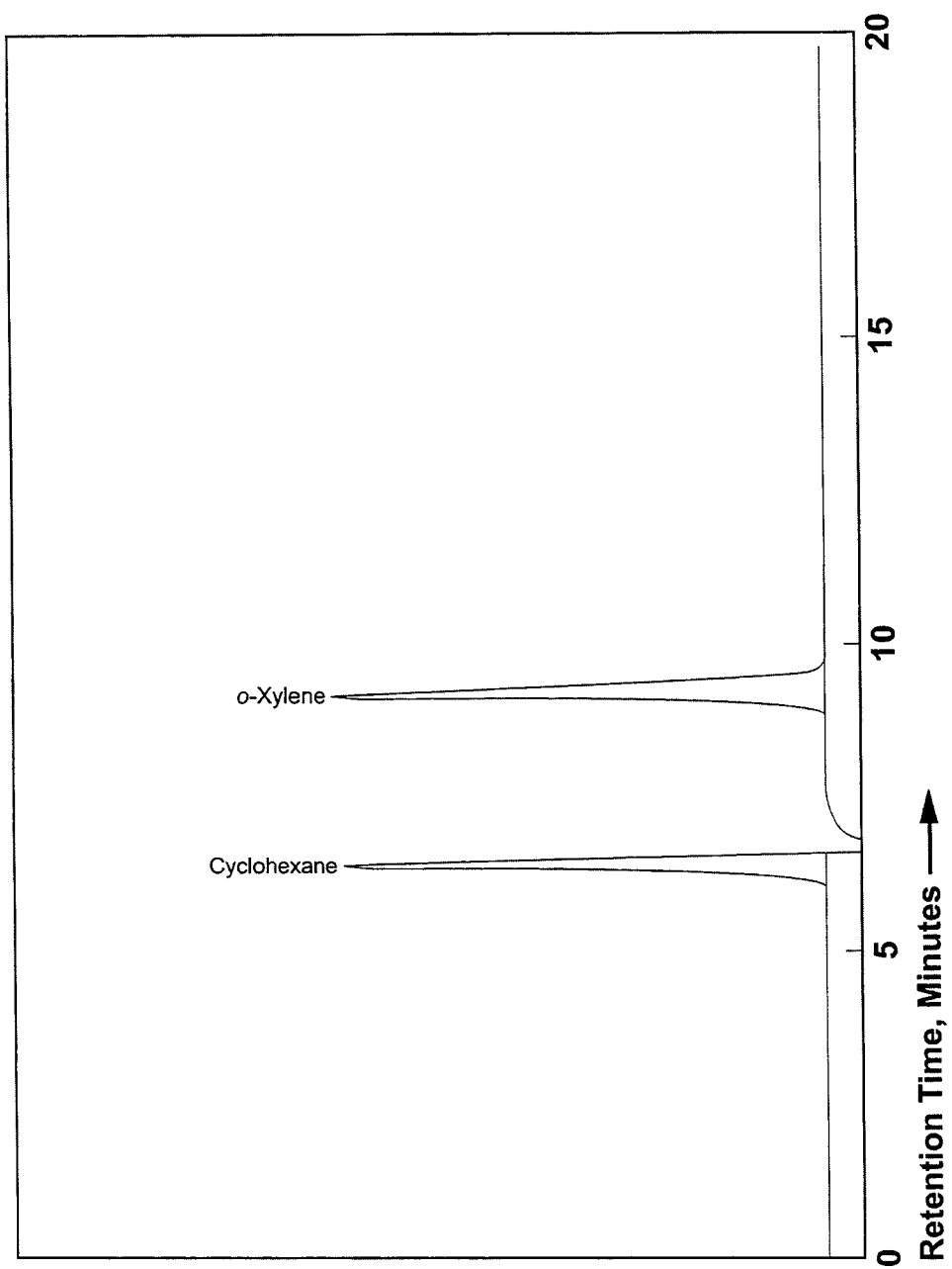


Figure 3
Resolution Check

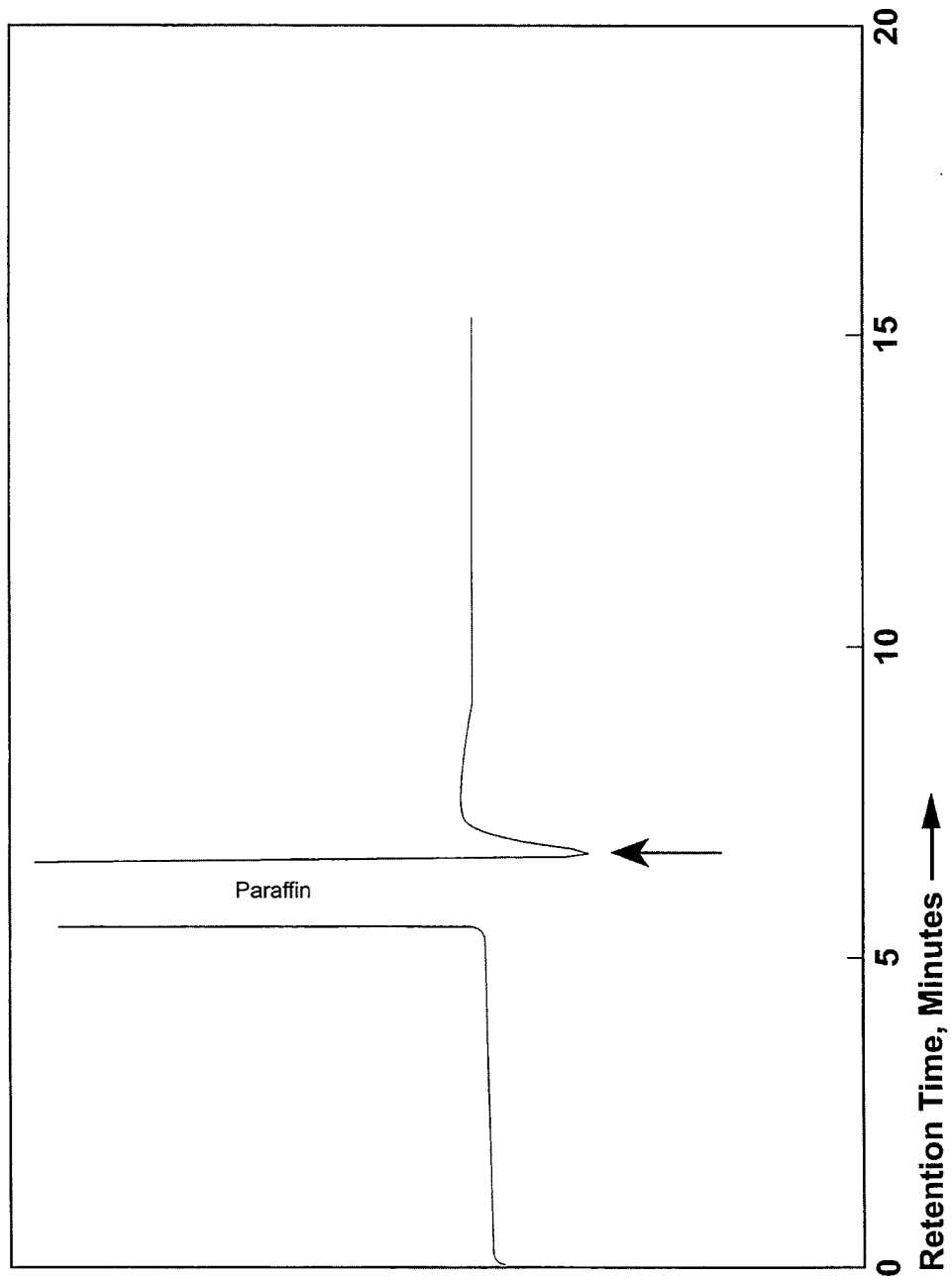


Figure 4
Back-Flush Time Determination