Rapid Method for the Chemical Analysis of Asphalt Cement: Quantitative Determination of the Naphthene Aromatic and Polar Aromatic Fractions Using High-Performance Liquid Chromatography

S. W. Bishara and Ernie Wilkins

An analytical method is described for the rapid quantitative determination of naphthene aromatics (aromatics) and polar aromatics (polars) in asphalt cement using high-performance liquid chromatography (HPLC). The hexane-insoluble asphaltenes are removed beforehand and the petrolene solution passed through an NH_2 energy analysis column. After elution of the naphthene aromatics, the solvent flow direction is reversed and the polar aromatics peak follows. Ultraviolet absorption at 254 nm is used for detection. A complete sample run consumes less than 3 hr. Results of analysis agree favorably with those obtained following the short procedure of ASTM D4124. Considering the ASTM D4124 results "correct," the average absolute error for 49 determinations on 22 samples from four different refineries amounted to ±0.66 and ±0.82 percentage point for the naphthene aromatics and polar aromatics fractions, respectively. The standard deviation for seven determinations on one sample is 0.89 and 0.45 percentage point for the naphthene aromatics and polar aromatics fractions, respectively.

Fourteen out of every 15 miles of surfaced roads in the United States are topped with asphalt. The United States spends more than $10 billion per year on asphalt pavements, about $3 billion of which is for asphalt itself (1).

Asphalt is, and will continue to be, a candidate for research investigations aimed at optimized field performance through physical as well as chemical testing. However, there is evidence that measurement of physical properties by itself is not sufficient to predict or assure pavement performance (2). Great interest is currently being expressed in probing the relationship between chemical composition and field performance.

Several approaches have been suggested for studying the chemical composition of asphalt cements. Elemental analysis (3,4), fractional separation analysis (5–11), and functional group analysis (12–14) are the most important. Molecular size distribution studies using high-performance gel-permeation chromatography (HP-GPC) are also receiving considerable attention (15–18). Vapor pressure osmometry (19) and field

ionization mass spectra (10) have been applied for determining the molecular weight of asphalt or asphalt fractions.

The literature reveals that almost all of the available analytical tools have been applied for the analysis of asphalt. Liquid chromatography (6–11), thin-layer chromatography (20), gas-liquid chromatography (14,21,22), size-exclusion chromatography (9,15–19), mass spectrometry (10,14,19,23), electrophotometric spectroscopy [IR and differential IR (12–14,22,24,25), UV (14,26)], nuclear magnetic resonance (16,26–28), electron spin resonance (26,29), spectrochemical analysis [X-ray fluorescence, neutron activation analysis, X-ray diffraction (30), atomic absorption (31)], distillation fractionation (10), and titrimetric/gravimetric analysis (32) have all been used (33).

For the past 30 years, separation of asphalt cement into fractions has been the basis of most asphalt chemical-analysis investigations. Such separations can, in effect, reduce the degree of chemical complexity of the analyte. They may also be useful for fingerprinting an asphalt or following up changes that may occur during manufacturing, hot-mix processing, or on-the-road use. Fractional separation may be performed by any of the following techniques.

1. Solvent-derived fractionation (34). The n-butanol-insoluble part (asphaltenes) is filtered out, and acetone is added to the butanol-solubles; the resulting solution is chilled to precipitate paraffins, leaving the cyclics in solution.
2. Chemical precipitation (5,35). After separation of the n-pentane insolubles, other fractions are consecutively precipitated with sulfuric acid of increasing concentration.
3. Liquid chromatography. In the clay-gel procedure (8), the n-pentane insolubles are separated followed by adsorption/desorption on clay and silica gel. Corbett procedure (36) depends on separating n-heptane insolubles, adsorption of the solubles on alumina, and desorption with solvents of increasing polarity.
4. Gel permeation chromatography (GPC). Fractional separation occurs according to molecular size (37) (see also ASTM D3593).

S. W. Bishara and E. Wilkins (retired), Materials and Research Center, Kansas Department of Transportation, 2300 Van Buren, Topeka, Kan. 66611.

A μ-BONDAPAK NH$_2$ column was first used by Dark and McGough (38) for the fractional analysis of whole asphalt after removing n-heptane insolubles by filtration. The authors (38) relied on response factors developed for crude oil to quantify the chromatographic envelopes obtained; they stated that because the average number of condensed aromatic rings in an asphalt is greater than in crude oil, the response factor will be in error. The procedure nevertheless provides a means of comparison between samples (relative values). Brule et al. (39,40) reported a correlation between HPLC data and the aromatic oil and resin contents of asphalt cement.

However, the potentialities of HPLC as a rapid analytical tool suggested its application for the quantitative determination of asphalt fractions. In the present method, after filtration of the n-hexane insolubles, the petrolenes are passed through an energy analysis column (μ-BONDAPAK NH$_2$). An ultraviolet detector measures the absorbance due to each of the naphthene aromatic and polar aromatics fractions as they elute from the column; the asphaltene figure is obtained gravimetrically and the saturates, by difference. The results agree favorably with those obtained using the ASTM method (7) after its "modification" to use n-hexane for dissolution. Initially, an asphalt cement sample (selected randomly to be the standard) is analyzed by the ASTM method, and the results obtained are logged as the standard values. A data handler calculates the results for subsequent sample runs based on these standard values. Because the molar absorptivity (extinction coefficient) of the standard and the sample material are not the same, however, a factor that will arbitrarily be called the absorptivity factor has to be determined for every sample. This factor accounts for variation in the molar absorptivity and is therefore included in the calculations.

EXPERIMENTAL

A Waters High Performance Liquid Chromatograph consisting of a Waters 600 Multisolvent Delivery System, U6K Injector, Temperature Control System (consisting of Temperature Control Module, TCM, and one column heater), and an ultraviolet/visible (UV/vis) LC Spectrophotometer (Lambda-Max, Model 481). The instrument is also equipped with a column backflush valve (model 7040, 5,000 psi—6 port, Rheodyne Co., Cotati, Calif.). A μ-BONDAPAK NH$_2$ Energy Analysis Column (3.9 mm i.d. by 30 cm long), Waters part #85173, was used. The data are received by a Waters 840 Data and Chromatography Control Station. This consists of a Digital Equipment Corporation Computer (Professional 380), a Digital Equipment Corporation LA Printer, and a Waters System Interface Module (SIM).

PROCEDURE

The Standard

Select any asphalt cement sample as the standard. Analyze using the ASTM method (7) to determine the percentage of the naphthene aromatics and polar aromatics fractions.

1. Removal of asphaltenes. Weigh 200–300 mg asphalt cement (to the nearest 0.1 mg) in a 125-mL Erlenmeyer flask fitted with a 24/40 ground glass stopper. Spread the sample on the bottom and lower sides of the flask. Add n-hexane in the ratio of 1 mL for every 10 mg of asphalt. To dissolve the sample, gently reflux for 20 min on a hot plate under a reflux condenser; maintain the solvent temperature near its boiling point, and stir using a magnetic stirrer at a moderate rate. Set aside for 1 hr to cool and allow the asphaltenes to settle down. Complete the asphaltene removal as described under sections 14.1.3 to 14.2.1 of the ASTM method (7). The asphaltene figure is obtained gravimetrically.

2. Determination of the molar absorptivity. The filtrate in the suction flask is transferred quantitatively to a 50-mL volumetric flask. Fill to the mark using n-hexane (this solution is referred to later as petrolene solution). Pipet out 5 mL of this solution into a 10-mL volumetric flask, and complete to volume with n-hexane (this solution is referred to later as dilute petrolene solution).

Remove the column from the HPLC system, and connect the two lines, originally joined to the column, to each other. Set the oven temperature to 35°C. Use n-hexane as the mobile phase at a flow rate of 0.2 mL/min. Inject 2 μL of the dilute petrolene solution. With the wavelength on the UV/vis LC Spectrophotometer set at 254 nm, watch the absorbance reading as it increases gradually, reaching a maximum before declining to the initial value (.001). Record the maximum absorbance reading (A).

Repeat the injection to get two concordant results (within about 3 percentage points of each other). From Beer's law:

$$A = abc \tag{1}$$

where

- A = absorbance;
- a = molar absorptivity (extinction coefficient);
- b = optical path length; and;
- c = concentration.

Because the eventual goal is the ratio of the molar absorptivity of the standard to that of the sample (rather than the absolute value of the constant a), and because the same sample cell is used in all the present work, b may be eliminated. The equation simplifies to:

$$A = ac \tag{2}$$

or

$$a = A/C \tag{3}$$

The concentration, c, may be calculated from

Wt. of petrolenes, mg

$$= \text{Sample wt., mg} - \text{wt. of asphaltenes, mg} = Y \tag{4}$$

Wt. of petrolenes, μg/2 μL = $Y \times 1000$

$$\times 5 \times 2/50 \times 10 \times 1000 = Y/50 = c \tag{5}$$

Thus,

$$a_{std} = A \times 50/Y \tag{6}$$

where 50 equals the volume of the petrolene solution.

3. Peaking of the naphthene aromatic (aromatics) and polar aromatic (polars). Insert the column in line. Maintain its temperature at 35°C. After sparging with helium, allow at least 30 mL of the mobile phase (n-hexane) to pass through the column before starting analysis. Set the flow rate at 3 mL/min. Inject 8 μL of the petrolene solution. The absorbance of the eluate is continuously monitored by the UV/vis LC Spectrophotometer at 254 nm. The naphthene aromatic peak appears 1.5 min from injection. Reverse the direction of solvent flow 5 min after injection. A peak for the polar aromatic fraction elutes 10 min from injection. The total run time is set at 12 min.

For the instrument to calibrate the standard run and calculate the response factors (RF), the weight of each of the aromatics and polars fractions (calculated from the sample weight and fraction percentages as determined by the standard method) is logged. RF equals the peak area divided by the amount of component, and it is used by the data handler to calculate the amount of component in unknown sample runs. Repeat injection of the standard, and program to average the two standard runs.

The Sample

Follow the foregoing procedure exactly but using an unknown asphalt cement sample. Determine the asphaltene content and the molar absorptivity (a_{spl}). Calculate the absorptivity factor from the ratio:

$$a_{std}/a_{spl} \tag{7}$$

Run the sample as already described for the standard. After the 12-min run time, the amount (mg) of each of the two fractions will be printed. Calculate the percentage from the equation:

$$\text{Fraction, percent} = T \times F \times 100/W \tag{8}$$

where

T = the fraction weight (mg);
F = the absorptivity factor; and
W = the sample weight (mg).

From the sum of the percentages of asphaltenes, aromatics, and polars, the percentage saturates may be determined.

RESULTS AND DISCUSSION

LC versus HPLC

The work of Dark and McGough (*38*) showed the possibility of using HPLC for the separation of asphalt cement into three fractions (saturates, aromatics, and polars) following removal of asphaltenes by filtration. Correct quantitation of the peaks was not feasible, however, because of the unavailability of some sort of a standard asphalt sample that can be run to establish the response factors.

The ASTM method D4124-86 (*7*) applies liquid chromatography for the separation of asphalt into four fractions. After filtration of the n-heptane insolubles, the petrolene solution is analyzed by adsorption on calcined F-20 alumina, then fractionated into saturate, naphthene aromatic, and polar aromatic fractions by downward elution, using a series of increasingly polar solvents. The apparent similarity in the number and functionality of the fractions obtained by the two approaches (*7, 38*) suggested the possibility of relying on the ASTM method (*7*) to establish quantitative results for a randomly selected asphalt sample that may then serve as the standard for an HPLC method. Sample 73286 gave the results shown in Table 1 after analysis using the LC method (*7*). The change of solvent from n-heptane to n-hexane caused the percentage of asphaltenes and naphthene aromatics to increase, and that of saturates and polar aromatics to decrease. This finding is in agreement with those of Puzinauskas (*2*) and others.

After the petrolenes were separated into three fractions by the ASTM method (*7*), each was dissolved in n-hexane, filtered, then run on the HPLC using the NH_2 energy analysis column. Figure 1 illustrates the chromatograms obtained.

TABLE 1 ANALYSIS OF ASPHALT CEMENT SAMPLE NUMBER 73286 BY ASTM METHOD

Fraction	Fraction, %	
	n-Heptane*	n-Hexane*
Asphaltenes	14.07	17.57
Saturates	12.97	12.82
Naphthene Aromatics	42.60	44.88
Polar Aromatics	32.34	25.41
Total, %	101.98	100.68

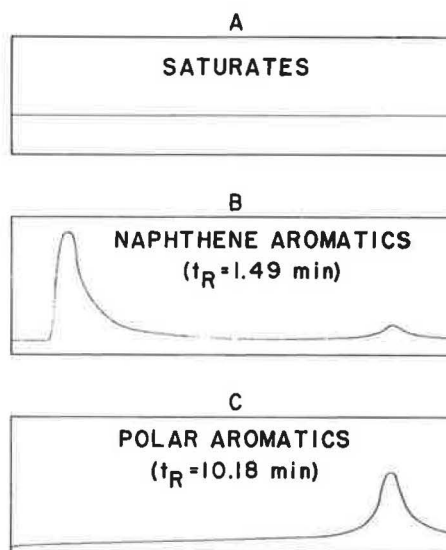* Solvent used for sample dissolution.

FIGURE 1 The HPLC chromatograms obtained for a 2.1820-g asphalt cement Sample 73286 after its separation into three fractions by Corbett's method (ASTM D4124-86, Method B).

Comparison of these with the chromatogram (Figure 2) obtained for a whole petrolene solution of the same sample, 73286, following the proposed procedure, may lead to the following conclusions:

1. The retention times (t_R) for the peaks obtained for aromatics (1.59 min) and polars (10.03 min), shown in Figure 2, correspond favorably to those obtained for naphthene aromatics (1.49 min) and polar aromatics (10.18 min), shown in Figure 1, respectively.

2. Each of the three fractions obtained after separation by LC, when tested by the proposed HPLC method, proved to contain but one fraction, as evidenced from the HPLC runs on each (Figure 1). Curve A for the saturates showed no peak for UV absorption, Curve B for the naphthene aromatics fraction exhibited a peak corresponding to the aromatics, and Curve C for the polar aromatics fraction showed a peak for the polars. The small hump observed for polars in Curve B is due to a minor quantity of polars being collected together with the middle fraction; the cut-point between middle (oranged-red) and last (brown-black) fractions is not always easy to locate, especially for some samples.

Absorptivity Factor

Having established qualitatively the similarity between fractions resulting from the LC and HPLC separation techniques,
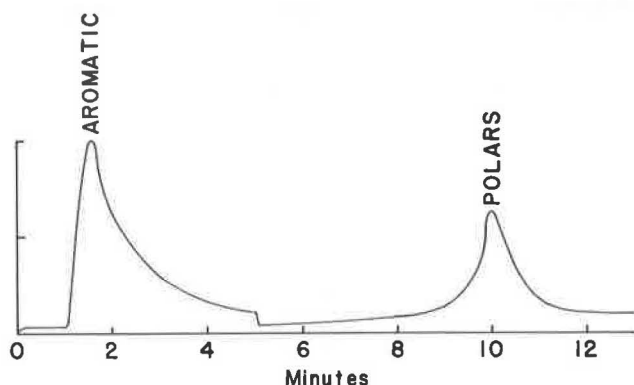

FIGURE 2 The HPLC chromatogram for Sample 73286, after separation of asphaltenes; t_R = 1.59 and 10.03 min.

the percentages of aromatics (naphthene aromatics) and polars (polar aromatics) calculated after the ASTM method (7) for Sample 73286 were logged as the standard values. A 200–300-mg weight of Sample 73286 (from Shell Oil Company, henceforth referred to as the standard) was analyzed following the present method. The data control station makes use of the values entered for the standard to calculate the response factors.

An asphalt Sample 14083 (Sinclair Oil Company), when analyzed by the two methods, gave the results shown in Table 2. The two fractions under investigation gave low, but consistent, recoveries. This is not surprising because the qualitative (and quantitative) chemical composition of any two asphalt cement samples is not the same, particularly if their sources are different. That the molar absorptivity of the standard would equal that of the sample is highly unlikely. To account for such differences, a factor (absorptivity factor) had to be introduced into the equation used for calculating the fraction percent.

One way of finding out the value of the absorptivity factor is by removing the column from the system, injecting a small sample volume (2 μL), and setting the solvent flow at a low rate (0.2 mL/min). As the initial fraction of the sample reaches the detector, the absorbance reading starts to increase. The reading then increases more rapidly as the sample/solvent ratio reaching the cell increases. The maximum absorbance reading is taken as A in Beer's law. Higher flow rates cause the absorbance readings to change very rapidly, making the maximum value difficult to observe. The low flow rate, in turn, requires small sample volumes to be injected; larger sample amounts cause the absorbance to exceed the acceptable range (i.e., beyond 1.8).

Inclusion of the absorptivity factor in the calculation of fractions percent for Sample 14083 gave results that agree favorably with those obtained by the LC method (Table 2). The absorptivity factor, F, equals $a73286/a14083$ (i.e., 0.407/0.308 = 1.321).

Beer's Law

The proposed method applies to a sample weight of 200–300 mg; the percentage of hexane-soluble petrolenes of the samples analyzed varied from 82.5 percent to 99.3 percent, with more than half the samples having 85 to 86 percent petrolenes.

TABLE 2 ANALYSIS OF ASPHALT CEMENT SAMPLE 14083 BY LC METHOD AND PROPOSED HPLC METHOD: EFFECT OF INCLUDING ABSORPTIVITY FACTOR, F, ON FRACTION PERCENT

Fraction	LC method	HPLC Method*				
		Without F	Recovery**	Including F	Recovery**
Asphaltene	6.74%	6.93%***	102.8%		
Saturates	20.99%				
Aromatics	40.13%	29.16%	72.7%	39.11%	97.46%
Polars	30.59%	22.77%	74.4%	30.08%	98.33%

*Sample 73286 served as the standard.

**Calculated on the basis of the LC results.

***This figure was obtained gravimetrically.

Sample 63525 (85.92 percent petrolene) has been selected for use in investigating the direct proportionality between petrolene concentration and the absorbance, A. A series of sample weights (180.6, 212.0, and 281.8 mg) was analyzed using the recommended procedure. The amount of petrolene present was then plotted against the absorbance. Figure 3 shows a
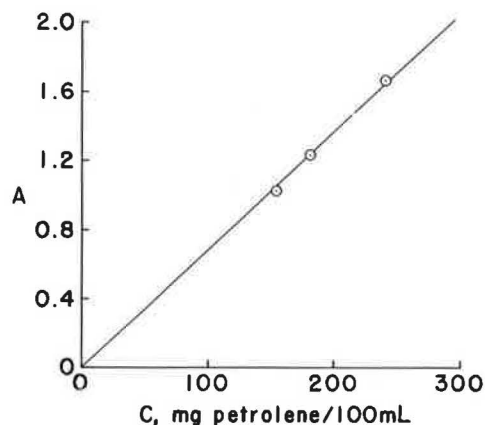
straight line passing by the origin, thus satisfying Beer's law over the concentration range tested.

Analysis of Samples

Twenty-two samples from four different refineries were analyzed following the proposed method. Table 3 shows the results obtained and compares them with those from the ASTM method (*7*). The naphthene aromatics percentage ranged between 36.04 and 46.77 and the polar aromatics percentage, between 22.27 and 37.94, thus covering a reasonably wide range of variation. Twenty of the 22 samples analyzed gave chromatograms similar to that obtained for Sample 73286, Figure 2. Samples 62574 and 63112, however, gave aromatic peaks that looked different (Figures 4 and 5). Like the rest of the samples, however, HPLC results for these two showed reasonable agreement with those obtained by LC (see Table 3).

The slight variation in retention time between individual samples can be attributed to (a) moisture uptake by the dry mobile phase (that is, hexane) (*41*) and (b) variation in the chemical constituents forming a particular fraction in the different samples. Because the chromatogram entails but two well-separated peaks, however, such variation should not constitute a problem and can readily be accommodated by

FIGURE 3   Variation of absorbance with petrolene concentration.

TABLE 3   ANALYSIS OF ASPHALT CEMENT SAMPLES BY LC AND HPLC METHODS

Sample No.*	Naphthene Aromatics LC,%	Aromatics HPLC,%	Error, Percentage Pts**	Polar Aromatics LC,%	Aromatics HPLC,%	Error, Percentage Pts**
62583	42.47	43.02	+0.55	30.48	30.25	-0.23
		43.15	+0.68		30.95	+0.47
14114	41.18	41.52	+0.34	32.16	32.82	+0.66
		41.08	-0.10		32.36	+0.20
62584	40.39	40.56	+0.17	27.49	28.88	+1.39
		39.92	-0.47		28.57	+1.08
14083	40.13	39.45	-0.68	30.59	30.19	-0.40
		39.62	-0.51		31.99	+1.40
62534	43.06	42.60	-0.46	29.85	28.58	-1.27
		42.93	-0.13		29.13	-0.72
62744	42.31	42.20	-0.11	30.34	31.22	+0.88
		41.46	-0.85		31.19	+0.85
62745	41.80	40.68	-1.12	31.68	32.24	+0.56
		41.58	-0.22		33.02	+1.34
62869	42.73	42.01	-0.72	29.95	29.52	-0.43
		42.25	-0.48		29.52	-0.43
62574	46.77	46.61	-0.16	37.94	39.84	+1.90
		47.81	+1.04		39.08	+1.14
63112	41.77	42.76	+0.99	36.22	35.82	-0.40
		42.86	+1.09		35.39	-0.83
62987	38.07	37.32	-0.75	22.27	21.03	-1.24
		38.20	+0.13		22.57	+0.30

TABLE 3 (*continued*)

Sample No.*	Naphthene LC,%	Aromatics HPLC,%	Error, Percentage Pts**	Polar LC,%	Aromatics HPLC,%	Error, Percentage Pts**
62989	39.06	39.10	+0.04	23.30	23.81	+0.51
		37.26	-1.80		22.08	-1.22
62575	46.76	47.66	+0.90	37.03	37.49	+0.46
		46.47	-0.29		35.55	-1.48
63527	38.56	37.82	-0.74	24.77	23.76	-1.01
		37.19	-1.37		23.25	-1.52
		37.71	-0.85		23.53	-1.24
63671	36.04	37.61	+1.57	24.80	24.67	-0.13
		35.29	-0.75		22.98	-1.82
63525	39.16	40.58	+1.42	26.06	26.60	+0.54
		40.31	+1.15		26.63	+0.57
		39.91	+0.75		25.06	-1.00
61589	41.16	42.27	+1.11	24.44	25.34	+0.90
		42.41	+1.25		25.26	+0.82
63897	37.69	37.60	-0.09	25.96	25.17	-0.79
		38.47	+0.78		25.16	-0.80
63528	37.58	37.52	-0.06	25.90	25.27	-0.63
		36.76	-0.82		24.89	-1.01
		36.56	-1.02		24.80	-1.10
62743	42.83	42.91	+0.08	30.31	31.38	+1.07
		42.25	-0.58		30.35	+0.04
		43.40	+0.57		30.57	+0.26
62248	39.95	39.62	-0.33	24.73	24.82	+0.09
		39.01	-0.94		25.52	+0.79
		39.47	-0.48		26.12	+1.39
73286	44.88	45.59	+0.71	25.41	25.05	-0.36
		44.74	-0.14		24.85	-0.56

* For all samples except the last one, 73286 was used as the standard. For the analysis of 73286, however, 73366 served as the standard.

** Calculated on the basis of the LC results.

increasing the calibration window to, say, 20 percent (i.e., by widening the retention-time range over which the data handler can "identify" a given peak as belonging to a previously entered name and retention time).

Accuracy and Precision

Insulating the tubing between the column and detector helps improve reproducibility of results. Precision of the method has been tested by calculating the standard deviation, s, for seven consecutive runs on Sample 63897 (Table 4). The formula

$$s = \{\Sigma(x - \bar{x})^2/n - 1\}^{1/2} \tag{9}$$

yielded standard deviations of 0.89 and 0.45 for the aromatics and polar fractions, respectively. Because a "correct" value for the fractions is unavailable, the percentage obtained by the ASTM method (7) has been considered a reference point to which HPLC data are compared for evaluating the accuracy of the proposed method. The average absolute error for 49
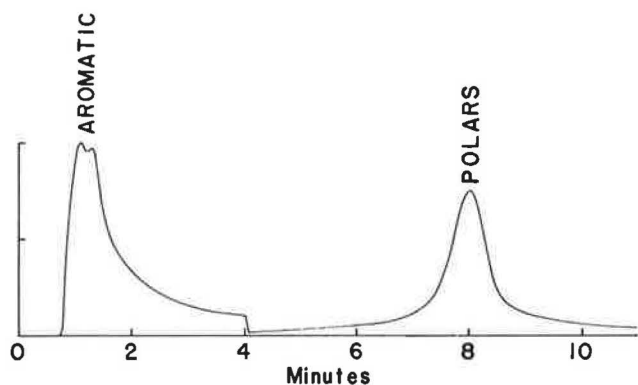
FIGURE 4 HPLC Chromatogram for Sample 62574; n-hexane, 3 mL/min across NH$_2$ energy analysis column backflushed 4 min after injection.
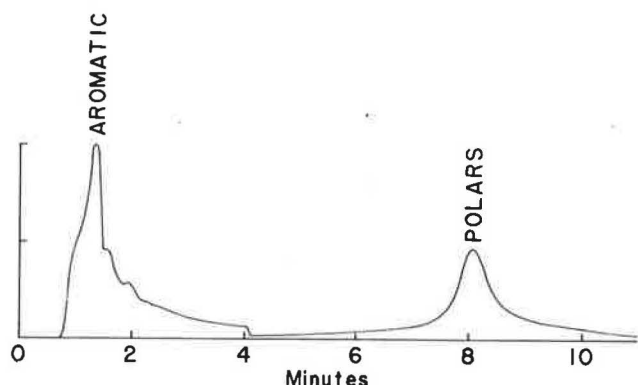

FIGURE 5 HPLC Chromatogram for Sample 63112; n-hexane, 3 mL/min across NH$_2$ energy analysis column backflushed 4 min after injection.

TABLE 4   REPRODUCIBILITY OF RESULTS OF ANALYSIS FOR SAMPLE 63897

Serial No.	Fraction, %	
	Aromatics	Polars
1	37.60	25.17
2	37.26	24.06
3	38.47	25.16
4	37.44	24.60
5	38.73	24.29
6	39.79	24.19
7	38.04	24.40
x̄	38.19	24.55
s	0.89	0.45

determinations amounted to ± 0.66 and ± 0.82 percentage point for the aromatics and polar fractions, respectively. The time required for analysis of one sample, including gravimetric determination of asphaltenes, is less than 3 hr.

CONCLUSION

Fractional analysis of asphalt cement using an alumina column and a series of progressively polar solvents yields four fractions that qualitatively and quantitatively match those obtained using a μ-BONDAPAK NH$_2$ column as part of an HPLC system. A factor that relates molar absorptivity of a standard to that of the analyzed sample should be included in calculation of fraction percent in order to account for variation in absorption properties of the materials involved.

ACKNOWLEDGMENT

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