

DETERMINATION OF TETRALIN AND NAPHTHALENE IN A COAL-DERIVED SOLVENT

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Introduction

There are a variety of methods currently in use for the separation and characterization of components in coal liquids. Most involve fractionation into various classes of compounds which are subjected to further analysis. Sternberg *et al.* (1,2) divided coal conversion products into asphaltenes and oils. These main constituents were further subdivided by column chromatography and precipitation. Slightly modified separation and characterization methods developed by the Bureau of Mines - API Research Project 60 for characterizing heavy ends of petroleum were used successfully in analyzing coal liquid distillates within the boiling range 200° to 540°C (3). Farcasiu (4) developed an alternative scheme based on separation of fractions of different chemical functionality using sequential elution of the fractions from silica gel. Process solvents and liquefaction products were separated into saturates, aromatics, and various polar materials with neutral alumina by Schiller (5) and then subjected to GC/MS analyses. After preparative separation using gel permeation chromatography various coal liquid fractions were studied by quantitative ¹H and ¹³C Fourier transform nuclear magnetic resonance techniques by Dorn *et al.* (6,7). Raw anthracene oil was separated using cation, anion, and complexation chromatography by Scheppelle *et al.* (8,9). They studied some of the fractions with low- and high-resolution field ionization mass spectrometry. Prather *et al.* (10) used high-performance liquid chromatography (HPLC) to characterize creosote oil during hydrogenation/hydrodesulfurization of the oil.

Tetralin is important in the study of the hydrogen donor capacity of recycle solvents (11, 12-14). A measure of tetralin in recycle solvents can be obtained by gas-liquid chromatography using a Dexil 300 liquid phase to obtain simulated boiling-point distributions (11). This type of approach is useful but can result in complex chromatograms and is subject to interferences (15).

In this study an analytical method was developed to determine specifically tetralin and naphthalene in a Wyodak coal-derived solvent from the Southern Services Inc. SRC plant located at Wilsonville, Alabama. Several other hydro-aromatic and polycyclic aromatic hydrocarbons were also separated from the solvent and identified. Aluminum oxide open-column chromatography, μ -Bondapak

C₁₈ high-performance liquid chromatography and fluorescence spectroscopy were combined to give qualitative and quantitative information on tetralin and naphthalene in the coal-derived solvent which was hydrogenated under different conditions.

Experimental

Apparatus. The high-performance liquid chromatograph used was a Waters model ALC/GPC 244 equipped with a model 6000-A pump, a U6K injector, and a free standing ultraviolet detector set at 254 nm. A stainless steel tube 11 cm x 0.23 mm I.D. attached to the exit port of the detector cell was used in sample collection. A μ -bondapak C₁₈ column with methanol:water (65:35) at a flow rate of 1 ml/min was employed, and a 10 mv recorder completed the system.

The columns used in open column chromatography were 50 cm x 11 mm I.D. Pyrex (Corning #2145) and were dry packed to a height of 35 cm with aluminum oxide activity II-III according to Brockmann (aluminum oxide from I.C.N. Life Sciences, Cleveland, Ohio and Brinkmann, Westbury, N.Y. were used interchangeably). Columns packed with silica gel (Brinkmann) were prepared in the same manner. Brinkmann ALOX N/UV 254 thin-layer chromatoplates were used in the thin-layer chromatography (TLC) work with n-hexane as the mobile phase.

Reagents. Pure grade (99% min) n-hexane was obtained from Phillips Chemical. Glass distilled methanol from Burdick and Jackson, and glass distilled water were filtered prior to mixing.

Naphthalene (99+%) and Tetralin (99%) were obtained from Aldrich and used as received. All other chemicals were obtained from commercially available sources and were purified when necessary.

Recycle Solvents. Recycle solvent from the liquefaction of Wyodak Coal at Wilsonville, Alabama (designated F-1) was hydrogenated at 2000 psi initial hydrogen pressure at 700°F for 1 hr over a Co-Mo on Al₂O₃ catalyst (Nalcoma 471). The product was designated F-2. Hydrogenation of the original solvent at 3000 psi initial hydrogen pressure at 800°F for 1 hr over the same catalyst resulted in a product designated F-3. The nominal boiling range of the three solvents was from 177-427°C (350-800°F).

Procedures.

Preparation of samples with no hexane insolubles (F-3). 20 g of sample was brought to volume with n-hexane in a 100 ml volumetric flask. Aliquots of 25 ml were added to each of three 50 ml volumetric flasks. Standard additions of 50 mg and 100 mg each of tetralin and naphthalene were added volumetrically to two of the flasks, respectively. All three flasks were diluted to volume with n-hexane. Aliquots of 1 ml of each of the solutions were pipetted onto the top of each of three aluminum oxide columns. Elution was performed with n-hexane. Work with standards showed that the tetralin was eluted totally in the first 15 ml (Fraction 1) and the naphthalene in 15-55 ml (Fraction 2). Fraction 1 was collected in a 25 ml volumetric flask and Fraction 2 in a 50 ml volumetric flask, each flask diluted to the appropriate

volume with n-hexane.

Preparation of samples with hexane insolubles (F-1 and F-2). Hexane insolubles coat the volumetric glassware when the sample solution is less than about 25% w/v in n-hexane. The volume displacement was found to be approximately 0.5 ml for a 20 g sample. To minimize this source of error, a solution of 20 g sample in approximately 120 ml n-hexane was made and swirled in a sealed flask. After at least two hours, most of the solid material coated the flask, and the remaining solution was rinsed into a 250 ml volumetric flask, then made up to volume. Three aliquots of 25 ml each were prepared as before, but the standard addition quantities were 20 mg and 50 mg for both tetralin and naphthalene. Aliquots of 2 ml were pipetted onto the aluminum oxide columns and Fraction 1 and Fraction 2 collected.

Determination of tetralin and naphthalene. Determination of tetralin in F-1, F-2 and F-3 was accomplished by an injection of 10 μ l of each of the unknown and two standard addition solutions onto the μ -bondapak C₁₈ column with the detector at 0.01 absorbance units. The heights of the tetralin peaks were all measured and were "normalized" to the peak height of the only other predominant chromatographic peak in Fraction 1 which was identified as indan. This internal reference peak represented a constant amount of indan present in the unknown and two standard addition solutions for a given sample. Normalization of all the tetralin peak heights to a constant indan peak height compensated for the non-reproducible injections inherent in the HPLC system. A standard addition curve was prepared by plotting peak height vs mg tetralin added. The line intersecting the peak height axis was extrapolated to zero peak height to obtain the tetralin concentration in the prepared solution. From this value the percentage tetralin was calculated (Figure 1).

Injections of 10 μ l at 0.1 absorbance units were used for the determination of naphthalene. Peak heights were normalized to the predominant peak at 18.4 ml elution volume, which was believed to be composed mainly of biphenyl and 2-methylnaphthalene. The percentage naphthalene was calculated in the same manner as tetralin.

Peak identification. An appropriate amount of sample or standard solution was injected onto the μ -bondapak C₁₈ column, and peaks collected directly into a 1x1 cm quartz cuvette. Final volume was made up to 3-4 ml, and fluorescence excitation and emission spectra taken. Spectra were then compared with standard spectra taken from standards run through the aluminum oxide-HPLC system.

Results and Discussion

Initial Experiments. Initial exploratory work was performed with one or two μ -bondapak C₁₈ columns used singly or connected in series with methanol:water (70:30) as a mobile phase at 1 ml/min. Fluorescence spectra were employed for chromatographic peak identification, as very dilute samples can be analyzed without any preconcentration steps. Samples thought to contain tetralin were separated on the μ -bondapak C₁₈ columns and were collected from 20 μ l injections of the first 50 ml of n-hexane eluted from both silica gel and aluminum oxide columns charged with approximately 100 mg of F-1. Fluorescence spectra showed two components present in the chromatographic sample

collected at the elution volume for tetralin. Tetralin was one component with an emission maximum at 286 nm, and an unknown, with emission maxima at 324 and 339 nm. An excitation spectrum of the interferent was taken by setting the emission monochromator at 360 nm. Comparing the unknown's excitation maxima with the maxima of several published ultraviolet absorption spectra (16) led to the assumption that the unknown was an alkyl-substituted naphthalene. It was later identified as acenaphthene by fluorescence spectroscopy. In order to remove this interferent, two separate fractions had to be collected, one containing tetralin and the other acenaphthene. Both silica gel and aluminum oxide columns, prepared as before, were investigated. It was assumed that in both systems tetralin would elute first and naphthalene would elute slightly before acenaphthene. The desired separation would, therefore, provide a fraction containing all the tetralin (Fraction 1), and a second fraction containing naphthalene and acenaphthene (Fraction 2).

Approximately 10 mg each of tetralin and naphthalene were placed on top of individual columns packed with each adsorbant. Samples were collected every 5 ml, diluted to an appropriate volume, and absorbance data obtained. Results were plotted as percentage of the total absorbance of all samples at 273 nm for each sample vs ml eluted (Figures 2 and 3). 98.5% of the tetralin eluted from the aluminum oxide column before the naphthalene started to elute, while only 44.2% eluted from silica gel before naphthalene started to elute. Thus, aluminum oxide provided a relatively clean separation of tetralin and naphthalene, whereas silica gel did not. To check if tetralin was separated from acenaphthene with the aluminum oxide system, samples corresponding to the chromatographic peaks at the elution volume of tetralin from a μ -bondapak C₁₈ column were collected for both Fractions 1 and 2 from F-1. Fluorescence excitation and emission spectra were obtained for each sample. The fluorescence spectra indicated the chromatographic peak from Fraction 1 was tetralin, and the chromatographic peak from Fraction 2 gave a fluorescence excitation and emission spectra identical to acenaphthene (Figures 4-7). These results indicated that tetralin was separated from acenaphthene.

Sample size studies were performed with aluminum oxide columns with F-1. Sample sizes of 1000, 500, and 200 mg overloaded the column to the extent that naphthalene was present in Fraction 1. Acenaphthene was also present in Fraction 1 with sample sizes of 1000 and 500 mg, but not 200 mg. Sample sizes of 100 and 50 mg resulted in a clean separation of tetralin and naphthalene with no interference from acenaphthene.

Precision and Accuracy of the Method. The precision of the method for five replicate determinations of tetralin and naphthalene on F-3 was quite good, yielding results at the 95% confidence level of $6.11 \pm 0.030\%$ for tetralin and $6.36 \pm 0.043\%$ for naphthalene (Table I).

Results of analysis of F-1, F-2, and F-3 at two different sample size levels illustrate the absence of any significant constant error (Table II). The average results for naphthalene in F-1 and F-2 were identical for two different sample sizes, and the other tetralin and naphthalene results showed no significant deviation. Spiking experiments for each sample at two levels of tetralin and naphthalene indicated good percentage recovery (Tables III and IV). The pretreatment for removal of hexane-insolubles from F-1 and F-2

described in Experimental did not appear to cause any significant loss of tetralin and naphthalene.

Identification of Tetralin, Indan and Naphthalene. Chromatographic peaks corresponding to tetralin, indan, and naphthalene each from F-1, F-2 and F-3 were all collected from the μ -bondapak C_{18} column after separation on aluminum oxide columns. The fluorescence excitation and emission spectra were obtained and were compared with excitation and emission spectra of standards treated chromatographically in an identical manner (Figures 8-11). Comparison of the sample excitation and emission spectra with the corresponding standard excitation and emission spectra shows very good comparison for the respective compounds. The fluorescence excitation and emission spectra of tetralin (Figure 4) and indan (Figure 8) are identical. However, because of the chromatographic systems used these compounds are separated completely. These results show how fluorescence spectroscopy can be used in combination with chromatographic techniques in the analysis of complex samples like coal-derived solvents.

Internal Reference Standard. A basic assumption in using an internal reference peak from the sample chromatogram for the standard addition method is the reference peak represents the same amount of internal reference compound in all solutions used in a determination and thus the same chromatographic peak heights. At one point a new batch of aluminum oxide was used and erratic reference peak heights in the naphthalene fraction were noticed. The collection of Fraction 2 was made from 15-50 ml, and a change to 15-55 ml rectified the problem indicating that all the internal reference compound was not obtained in the first collection. As a precaution against nonuniformity within a given standard addition series, the amount of aluminum oxide placed in the glass column was weighed, and was kept uniform for a given batch of adsorbant. Chromatograms of both Fractions 1 and 2 from F-1 show the positions of the internal reference peaks, tetralin peak and naphthalene peak (Figures 12 and 13). The peak corresponding to indan was the internal reference for Fraction 1, and the peak for biphenyl and 2-methylnaphthalene was the internal reference for Fraction 2.

Limits of detection were calculated at maximum detector absorbance settings of 0.01 for tetralin and 0.1 for naphthalene. Since baseline noise at these settings is minimal, the smallest practical measurable peak height was chosen arbitrarily to be 2 mm. Typically observed standard addition curve slopes of 10 mm/mg for tetralin and 17 mm/mg for naphthalene were used. For a 100 mg sample, this would correspond to limits of detection for the method as described of 0.2 mg tetralin, or 0.2% tetralin, and 0.1 mg naphthalene, or 0.1% naphthalene. These limits could be lowered by increasing the detector sensitivity or concentrating the hexane fractions. All anticipated samples fall well above these limits.

R_f Values and Retention Volumes of Several Hydroaromatic and Polycyclic Aromatic Hydrocarbons. R_f values from thin-layer chromatography and retention volumes from HPLC for the compounds studied are given in Table V. Aluminum oxide separations with the appropriate mobile phase occur mainly by aromatic ring number (17). Compounds with the greater number of aromatic rings are retained more strongly. The separation mechanism on a μ -bondapak C_{18} column is not as clear (18). It has been shown that the retention volumes of aromatic hydrocarbons generally increase with increasing carbon number on columns of Zipax Permaphase

ODS in water-methanol mixed solvents (19). The retention volumes of substituted alkyl derivatives of aromatic compounds indicated that these compounds separated with increasing aliphatic carbon number. However, without prior information as to the parent compound type, approximate capacity factors are difficult to estimate (19).

The R_f values and retention volumes obtained in this work (Table V) suggest the possibility of developing an overall characterization scheme for aromatic and hydroaromatic hydrocarbons in coal liquid samples. This is presently under investigation. Also the data in Table V indicate the importance of initial separation with aluminum oxide. For example, with the compounds in Table V, four main fractions could be initially separated with aluminum oxide. These fractions would contain compounds 1-6, 7-19, 20-22, 23-25 respectively. Further separation of each fraction with μ -bondapak C_{18} would give almost complete separation of each compound in a given fraction. Phenanthrene and fluorene would have nearly the same retention volumes and 2-methylnaphthalene and biphenyl would have nearly the same retention volumes. However, with refinements in the chromatographic systems, it should be possible to achieve complete separation of these compounds.

The results in Table V show that it was necessary to obtain two fractions from the coal-derived solvents to determine tetralin and naphthalene. Acenaphthene and tetralin have identical retention volumes on μ -bondapak C_{18} , thus necessitating the initial separation step with aluminum oxide.

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Table I

Precision of the Method with F-3

<u>Sample weight, mg</u>	<u>Tetralin, %w/w</u>	<u>Naphthalene, %w/w</u>
97.92	6.08	6.36
97.92	6.13	6.40
97.92	6.10	6.38
96.67	6.10	6.31
96.67	6.14	6.34
	$\bar{x} = 6.11$	$\bar{x} = 6.36$
	$s = 0.024$	$s = 0.035$

95% confidence level

tetralin: $6.11 \pm 0.030\%$

naphthalene: $6.36 \pm 0.043\%$

Table II

Variation of Sample Size

Sample	Weight, mg	Tetralin, %w/w	Average	Naphthalene, %w/w	Average
F-3	96.67	6.10		6.31	
	96.67	6.14	6.12	6.34	6.32
	48.93	6.13		6.40	
	48.93	6.15	6.14	6.36	6.38
F-2	81.20	2.71		7.09	
	81.20	2.73	2.72	7.03	7.06
	43.61	2.77		7.08	
	43.61	2.73	2.75	7.04	7.06
F-1	85.29	2.24		7.27	
	85.29	2.32	2.28	7.33	7.30
	44.24	2.24		7.28	
	44.24	2.28	2.26	7.32	7.30

Table III

Percentage Tetralin Recovery in Spiked Samples

Sample	Weight, mg	Tetralin ^a Present, mg	Tetralin Added, mg	Tetralin ^b Found, mg	Recovery, %
F-3	95.79	5.86	0.96	0.96	100
	95.79	5.86	0.96	1.01	105
	96.67	5.92	2.41	2.33	97
	96.67	5.92	2.41	2.46	102
					<hr/> x̄ = 101
F-2	86.32	2.36	0.77	0.77	100
	86.32	2.36	0.77	0.74	96
	84.60	2.32	1.93	1.98	102
	84.60	2.32	1.93	1.91	99
					<hr/> x̄ = 99
F-1	84.98	1.93	0.78	0.72	92
	84.98	1.93	0.78	0.73	94
	81.02	1.84	1.95	1.92	98
	81.02	1.84	1.95	1.89	97
					<hr/> x̄ = 95

^aResults obtained from the standard addition method.

^bResults corrected for original tetralin content present in the sample.

Table IV

Percentage Naphthalene Recovery in Spiked Samples

Sample	Weight, mg	Naphthalene ^a Present, mg	Naphthalene Added, mg	Naphthalene ^b Found, mg	Recovery, %
F-3	95.79	6.09	0.87	0.85	98
	95.79	6.09	0.87	0.83	95
	96.67	6.15	2.18	1.98	91
	96.67	6.15	2.18	2.02	93
				average	94
F-2	86.32	6.09	0.70	0.65	93
	86.32	6.09	0.70	0.71	101
	84.60	5.97	1.75	1.81	103
	84.60	5.97	1.75	1.80	103
				average	100
F-1	84.98	6.20	0.69	0.68	99
	84.98	6.20	0.69	0.66	96
	81.02	5.91	1.73	1.66	96
	81.02	5.91	1.73	1.69	98
				average	97

^aResults obtained from standard addition method.

^bResults corrected for original naphthalene content present in the sample.

Table V

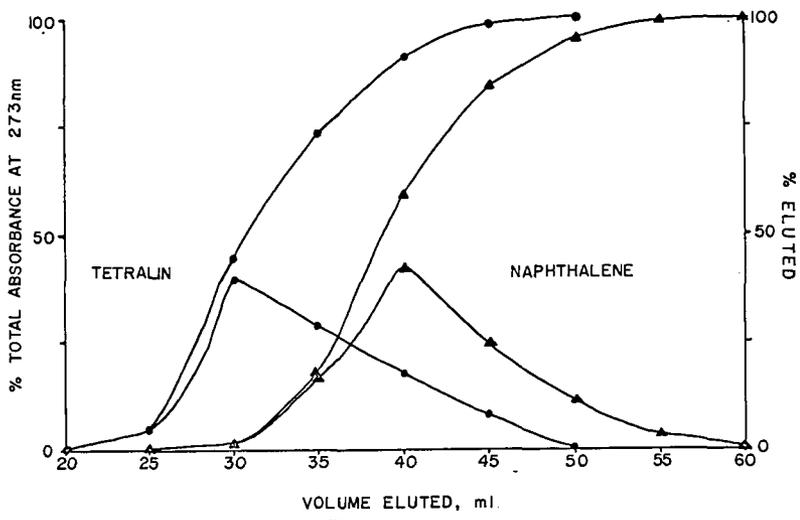
R_f Values and Retention Volumes^a of Hydroaromatic
and Polycyclic Aromatic Hydrocarbons

Compound	R_f Value	Retention Volume, ml
1) benzene	--	6.3
2) 1,2,4-trimethylbenzene	--	19.5
3) 1-phenyldodecane	--	No indication of elution
4) tetralin	0.74	21.5
5) indan	--	14.8
6) 5-methyltetralin	--	33.0
7) indene	0.55	10.5
8) naphthalene	0.50	11.7
9) acenaphthene	0.44	21.5
10) 1,5-dimethylnaphthalene	0.43	26.8
11) 1-methylnaphthalene	0.43	17.6
12) biphenyl	0.43	18.3
13) 2-methylnaphthalene	0.42	18.4
14) 2,3-dimethylnaphthalene	0.40	27.3
15) 1-phenyl-3,4-dihydronaphthalene	0.38	55.2
16) 9,10-dihydroanthracene	0.34	26.1
17) acenaphthylene	0.32	14.6
18) 9,10-dihydrophenanthrene	0.27	30.3
19) [2.2] paracyclophane	0.24	32.8
20) fluorene	0.20	25.2
21) anthracene	0.14	28.0
22) phenanthrene	0.13	25.0
23) pyrene	0.069	39.6
24) fluoranthene	0.056	36.9
25) chrysene	0.054	62.1

^aOne μ -bondapak C₁₈ column with methanol:water (65:35) at 1 ml/min.

FIGURES

- Figure 1 Standard addition curve for determination of tetralin.
- Figure 2 Elution of tetralin and naphthalene from silica gel.
- Figure 3 Elution of tetralin and naphthalene from aluminum oxide.
- Figure 4 Fluorescence excitation and emission spectra of standard tetralin.
- Figure 5 Fluorescence excitation and emission spectra of tetralin peak collected from Fraction 1 of F-1.
- Figure 6 Fluorescence excitation and emission spectra standard acenaphthene.
- Figure 7 Fluorescence excitation and emission spectra of acenaphthene peak collected from Fraction 2 of F-1.
- Figure 8 Fluorescence excitation and emission spectra of standard indan.
- Figure 9 Fluorescence excitation and emission spectra of indan peak collected from Fraction 1 of F-1.
- Figure 10 Fluorescence excitation and emission spectra of standard naphthalene.
- Figure 11 Fluorescence excitation and emission spectra of naphthalene peak collected from Fraction 2 of F-1.
- Figure 12 HPLC chromatograms of Fraction 1 from F-1 and F-3.
- Figure 13 HPLC chromatogram of Fraction 2 from F-1.



VOLUME ELUTED, ml.
Figure 2

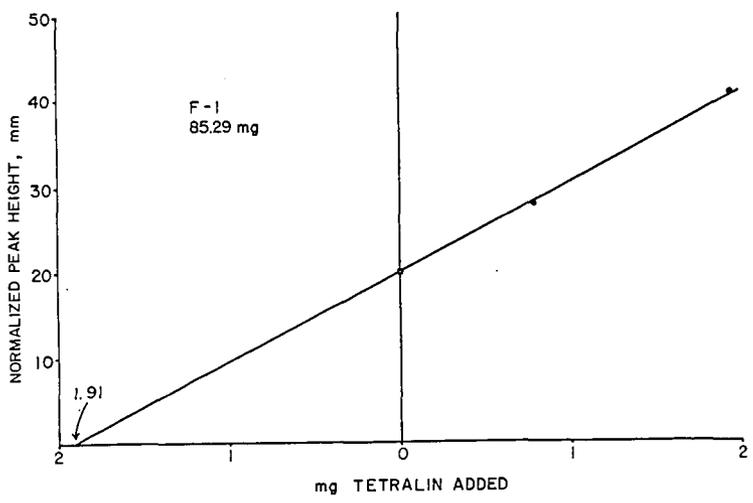
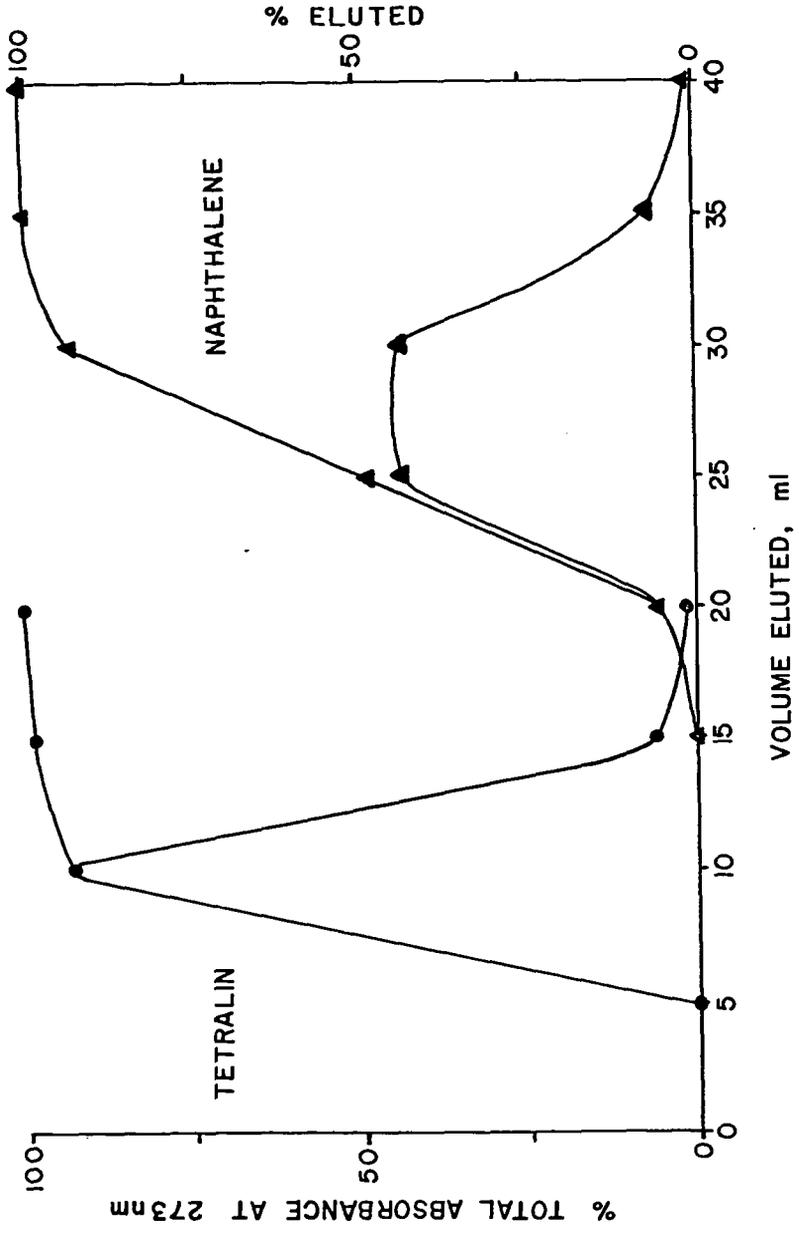
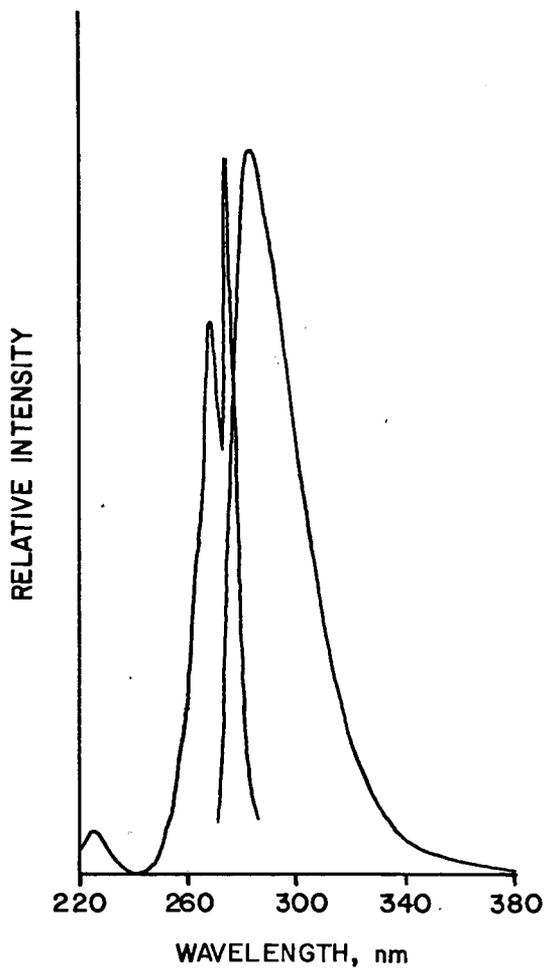
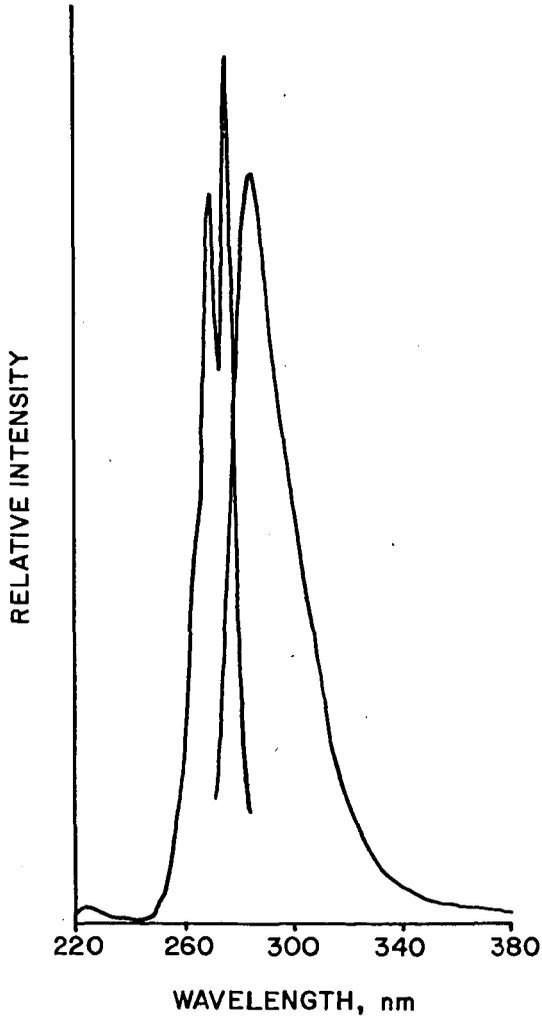
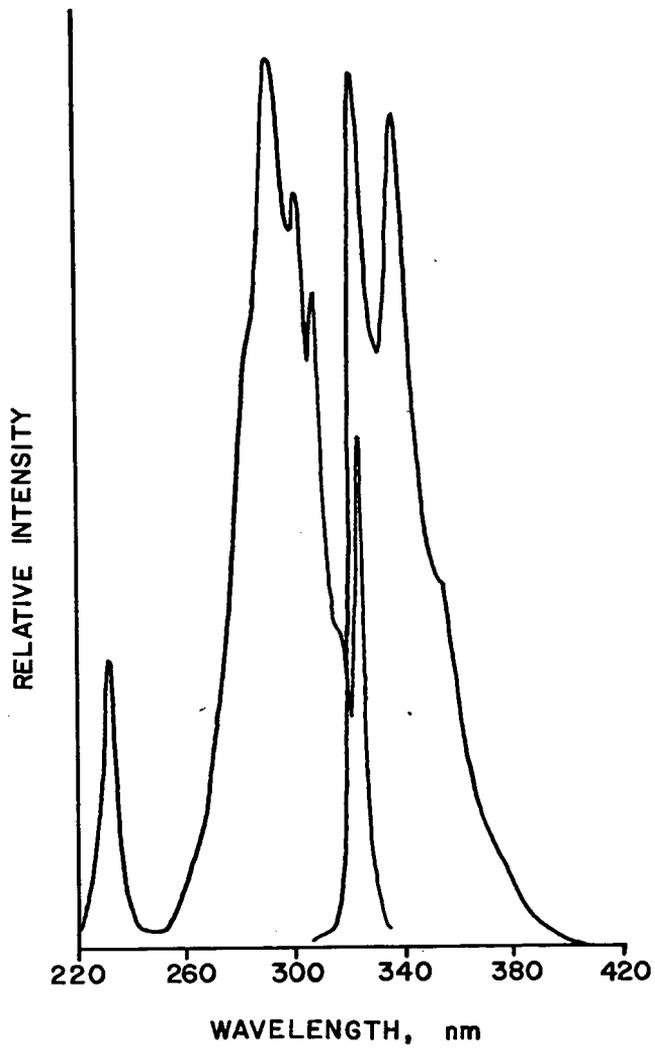


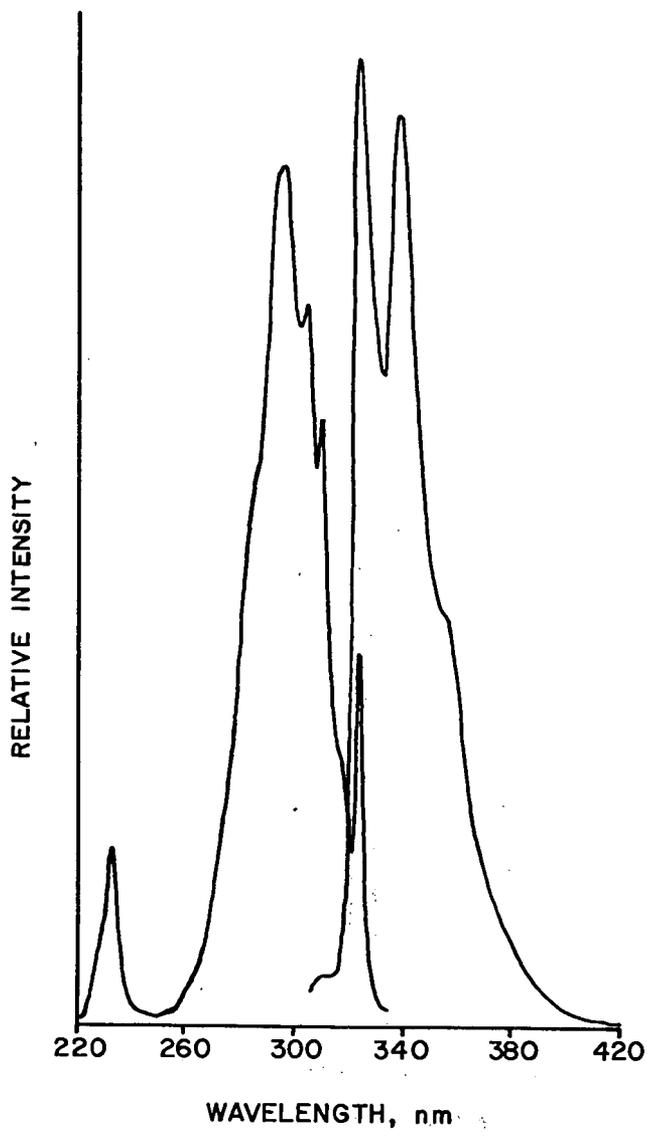
Figure 1

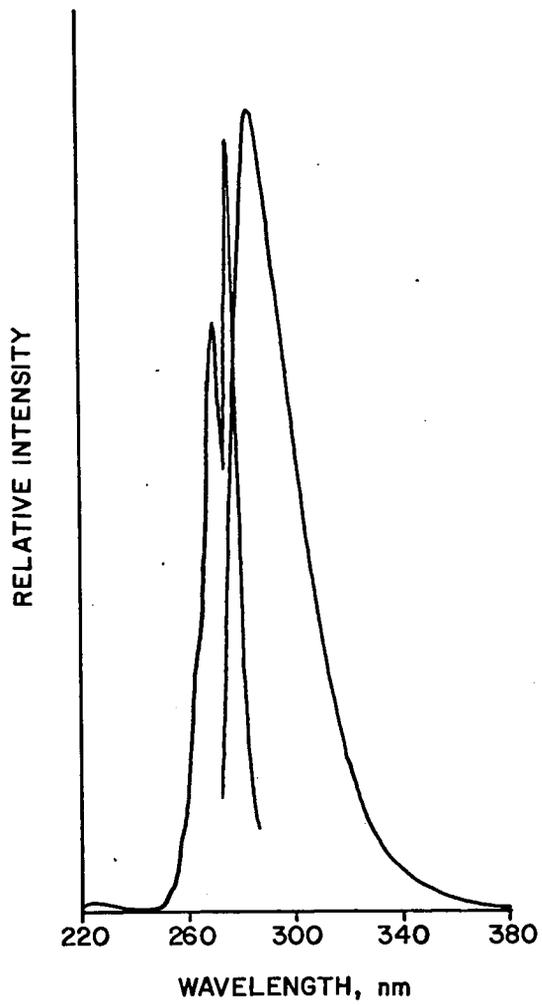


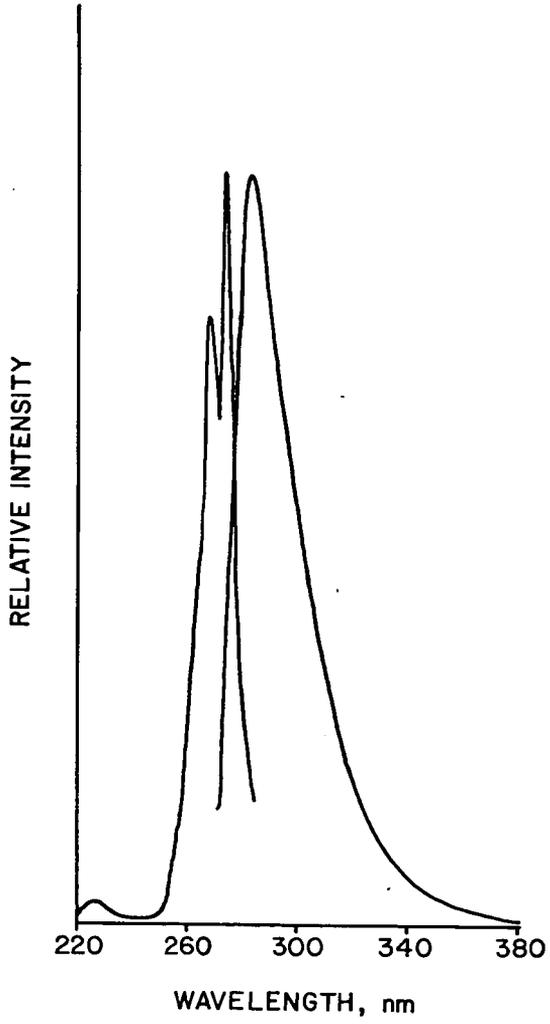


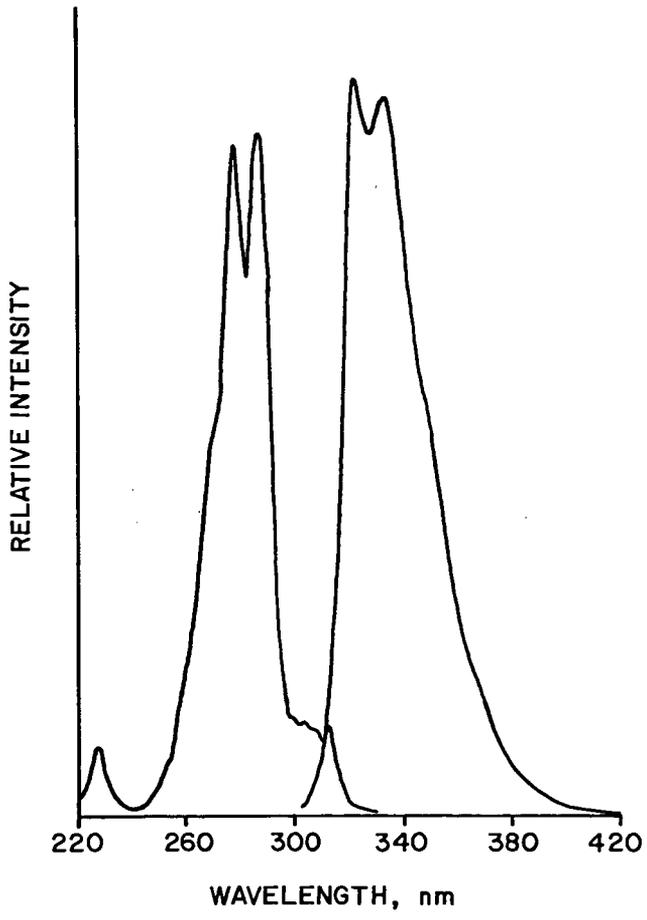


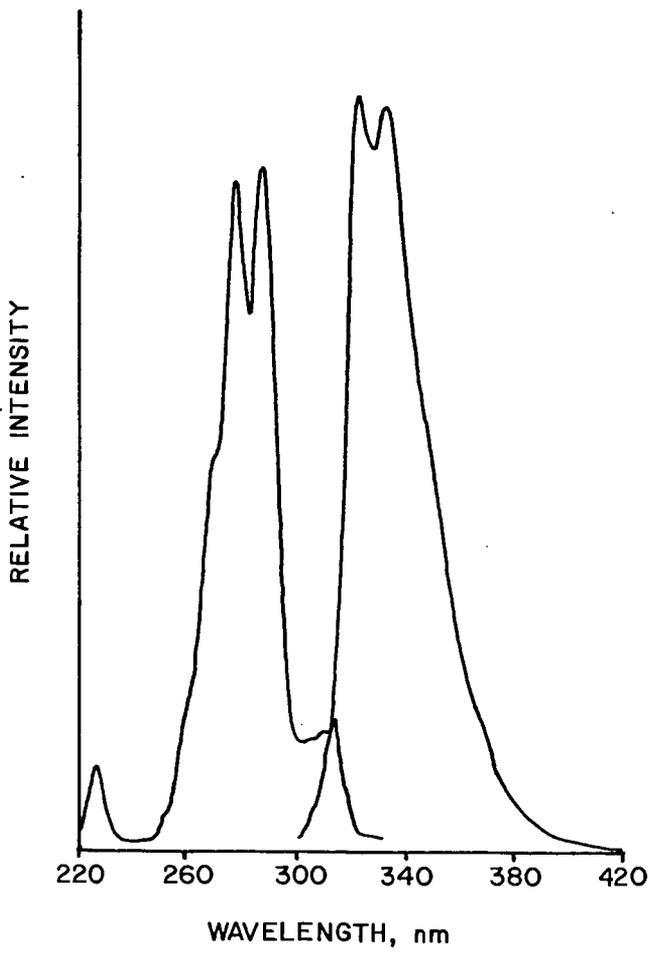


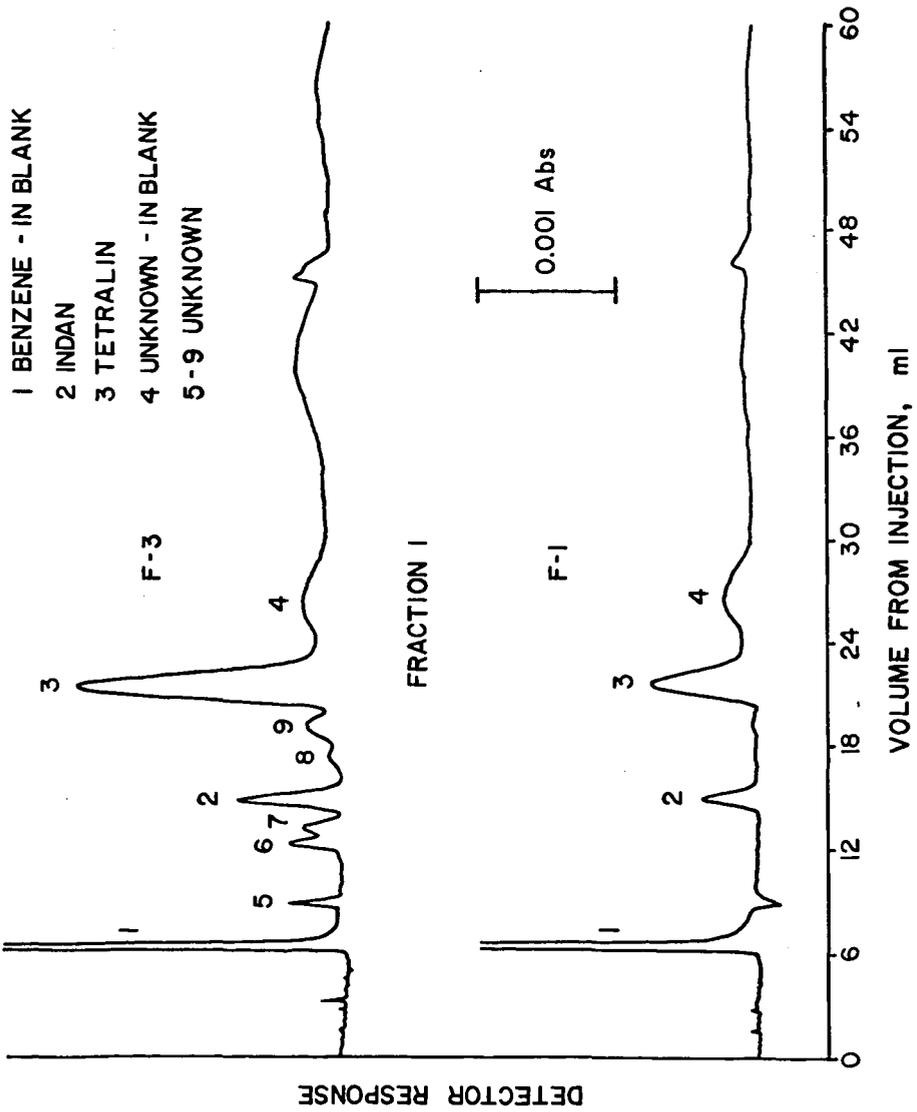












F-1 FRACTION 2

- 1 BENZENE - IN BLANK
- 2 NAPHTHALENE
- 3 BIPHENYL, 2-METHYLNAPHTHALENE,
OTHER COMPONENT(S)
- 4-6 UNKNOWN
- 7 ACENAPHTHENE

