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SEPARATION CHARACTERIZATION AND INSTRUMENTAL ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBON RING CLASSES IN PETROLEUM

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ABSTRACT

A high performance liquid chromatographic (HPLC) separation having selectivity for the number of fused aromatic rings up to four was used to separate polynuclear aromatic hydrocarbon (PAH) ring classes. Two crude oils: the heavy Lloydminster and the light Medicine River oils from the Alberta Basin were analyzed. Three- and four-ring structures dominated the aromatic concentrates of both oils. The abundance of five and larger fused ring contents, and higher degree of alkyl substitution distinguish the Lloydminster polyaromatic content.

The analytical potential of this approach was studied using refractive index and ultraviolet detectors, gas chromatography, mass spectrometry, ^{13}C nmr and spectrofluorometry. The procedure proved to be useful for characterization of the complex PAH mixtures in hydrocarbon materials.

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INTRODUCTION

To develop effective utilization technology for heavy streams from crude oils and unconventional resources such as heavy oils and oil-sand bitumens, detailed information on the chemical composition of the feedstocks is needed.

Attempts were made during the seventies to modify the API Project 60 scheme of analysis or to develop chemically more efficient, and less time consuming, separation and characterization methods (1-8). These attempts were aimed to improve characterization by separating the samples into concentrates of different structural types by type analysis (TA). The sample throughput of the TA was increased by using pressure, and the hydrocarbon types so isolated were further analyzed by high performance high pressure liquid chromatography (HPLC). Other valuable contributions have been made in the art of coal liquid characterization in terms of bringing about separations based on chemical functionalities (9,10).

The separation of aromatic ring classes and characterization or identification of their major components was our primary objective in this study. A silica-$R(NH_2)_2$-based HPLC system was used in our laboratory to study the analytical potential of this approach; the work was described in a previous publication (11). In the present study, the applicability of HPLC separation by this system and instrumental spectrometric characterization of 3- and 4-ring polynuclear aromatic hydrocarbons (PAHs) isolated from two Canadian oils were investigated. The oils used, Medicine River and Lloydminster, are examples of light and heavy crude oils, respectively.

EXPERIMENTAL

The separation-characterization schematic diagram is shown in Fig. 1.

Samples

The two crude oils were distilled up to 200°C and deasphaltened by precipitation in twenty volumes of pentane. The deasphaltened residues were vacuum distilled at 2 mm Hg up to 350°C, and the fraction boiling above 350°C was used in this investigation.

Reagents

HPLC-grade n-hexane, n-heptane, methylene chloride and acetonitrile. The following model compounds were used without further purification: benzo[b] fluorene, triphenylene, perylene, benzo[ghi]perylene, phenanthrene, dibenzo[a,h]anthracene, dibenzo[a,c]anthracene, pyrene, benzo[a]pyrene, benzo[b]-fluoranthene, benzo[k]fluoranthene, 3-methylphenanthrene, 3-methylpyrene, benzo[a]anthracene, anthanthrene, 1-methylpyrene, anthracene, n-decyl . phenanthrene and n-decyl pyrene were synthesized in our laboratory.

Liquid Chromatography

The deasphaltened distillation residues boiling above 350°C were separated into compound-type concentrates of saturates, monoaromatics, diaromatics, polyaromatics, polar materials, and basic compounds on a dual-packed silica-alumina gel chromatographic column (3) and the polyaromatic fraction was taken for further HPLC separation.

High Performance Liquid Chromatography (HPLC)

The silica-C_{18} (10 µm ; 314 x 4.6 mm) column and silica-$R(NH_2)_2$ (10 µm) bulk material were supplied by ES Industries, Marlton, New Jersey. The silica-$R(NH_2)_2$ column (250 x 4.6 mm) was slurry packed at 6000 p.s.i. using heptane with a Haskel DST-150A air-driven liquid pump. HPLC grade methylene chloride, acetonitrile and n-hexane solvents, dried by activated molecular sieves, were used. The HPLC system consisted of a Valco Sample injection valve, a Water's Model 6000 pump, Water's Model 401 RI Detector, and a Schoeffel SF 770 UV spectroflow monitor with 8 µL cell. Chromatographic separations were performed at a flow rate of 2 mL/min at 24°C. HPLC systems were studied using a 7-µL home made loop. A 100-µL loop was used for collecting the aromatic sub-fractions and for aromatic type quantitation. The refractive index detector was thermostated at 24°C to monitor the eluent from the $R(NH_2)_2$ column. Quantitation was accomplished by using model compounds (phenanthrene and chrysene), as well as standards isolated from fractions of both oils.

Collection of Aromatic Sub-fractions

Lloydminster and Medicine River polynuclear aromatic hydrocarbon fractions in hexane (10 mg/mL) were injected in 100-µL portions on the silica-$R(NH_2)_2$ column. Effluent cuts of 2 ml corresponding to the retention range of the standards of choice and their alkyl derivatives were collected and evaporated down to 10 µL with nitrogen. The cuts from four successive collections were combined and studied by means of gas chromatography and mass spectrometry to identify the main components.

Gas Chromatography and Gas Chromatography-Mass Spectrometry

A Tracor model MT-220 gas chromatograph fitted with a FID (350°C) was used for this work. Mixtures were separated on a stainless steel column (3 m x 3.1 mm) packed with 3% OV-1 on (100-120 mesh) Chromosorb W, A.W., DMCS, HP. The injector temperature was held at 240°C and hydrogen at 40 cm^3/min was used as the carrier gas. Temperature was programmed from 100° to 300°C at a rate of 10°/min.

A Finnegan Model 4000 GC-MS system employing electron impact at 70 eV (scan time 0.3 sec/1000 a.m.u.), direct inlet to mass spectrometer and a data acquisition Ingos Nova I computer was used for HPLC cut characterization. Concentrated aromatic sub-fractions were separated on a glass column (1.8 m x 6.3 mm o.d., 2 mm i.d.) packed with 2.5% Dexil 300 on (80-100 mesh) Chromosorb W, A.W. and helium was used as carrier gas (25 cm^3/min). Samples were injected at 220°C and a temperature program of 10°C/min was used from 100 to 300°C.

Nuclear Magnetic Resonance Spectrometry

Samples for ^{13}C nmr analyses were weighed directly into 5-mm nmr tubes. Deuterochloroform ($CDCL_3$) was added as solvent reference and internal lock. Chromium (tris) acetylacetonate ($Cr(ACAC)_3$) was added to the sample so that a rapid pulse repetition rate could be used without severe line broadening or shifting. The analysis was performed on a Varian CFT-20 Fourier transform spectrometer.

Spectrofluorimetry

Fluorescence excitation and emission spectra, uncorrected for variation of source and photomultiplier response, were recorded in HPLC grade hexane dried with activated molecular sieves. A Varian SF330 spectrofluorimeter was used. The spectra were recorded in dilute solutions to avoid excimer formation. Appropriate cut-off filters were used in the emission beam.

The fluorescence intensity of standard compounds was recorded as a function of the emission wavelength with the excitation wavelength held at a constant long wavelength of relatively high intensity. Similarly, the excitation spectra were recorded by varying the excitation wavelength at a constant emission wavelength.

Seven fractions representing different polyaromatic ring systems were collected from a HPLC separation on the diamine column. The retention times of model compounds were used as an aid in the selection of optimal excitation and emission wavelengths. Each sample was irradiated at several different wavelengths to obtain optimum emission spectra. Similarly, excitation spectra were recorded with the emission monochromator set at different wavelengths.

Elemental Analysis

Elemental analysis of the PAH fractions of both oils, obtained from the silica-alumina chromatographic separation, was performed on a Perkin Elmer 240 analyzer.

RESULTS AND DISCUSSION

The deasphaltened distillation residues boiling above 350°C, of both Medicine River and Lloydminster oils, were separated into chemical structural-type concentrates by the modified API method (3). The polynuclear aromatic content was higher in the Lloydminster sample than in the Medicine River (Table 1).

Our objective was to study the analytical potential of HPLC systems for characterizing sub-fractions of the polyaromatic concentrates. Commercially available sorbents and their selectivities for this purpose have been described elsewhere (11). A variety of instrumental methods were used in concert with HPLC systems for chemical characterization and to verify the effectiveness of separation according to ring number by HPLC.

HPLC Separation

The silica-$R(NH_2)_2$ based HPLC system has selectivity for the number of fused aromatic rings up to four with insignificant dependence on alkyl substitution (11). Retention indices of PAHs and increments in retention indices were calculated as in (12) and are presented in Table 2. In most cases studied alkyl substitution did not considerably affect the retention relative to the parent ring system. This system was developed to collect ring-class sub-fractions in sufficient amounts for GC-MS identification of major components. Various experimental factors and conditions had to be established. A separation of a mixture of model compounds was performed periodically to determine if there had been a change in retention indices because of temperature fluctuations, column deterioration or changes in mobile phase composition. Sample concentration affects separation reproducibility determined by a relation between column capacity and the linear sorption isotherm. Other experimental problems involve the sample recovery and its effect on the reproducibility of separation, as well as eluate monitoring when UV detector works beyond the linear response range.

In this work two HPLC systems, - silica-C_{18} and 80% acetonitrile in water as eluent, as well as silica-$R(NH_2)_2$ and non-polar eluent - were used for separation of Lloydminster and Medicine River PAH fractions.

The silica-C_{18} column yielded limited information. Although the chromatograms (Fig. 2) offered well-shaped peaks, the system had many drawbacks. Alkyl derivatives of PAHs overlap with PAHs of higher ring number. The solubilities of oil PAH fractions were lower in acetonitrile than in hexane used in the normal phase system. Furthermore, GC-MS characterization of collected cuts was complicated by the need to extract the organic material from the aqueous solvent.

The normal phase silica-diamine system with selectivity based on the number of aromatic rings (11), gave more compact chromatograms, i.e. less tailing and better recoveries of injected samples (Fig. 3).

The chromatographic profile obtained for the Lloydminster PAH sample in the reverse phase system indicates the presence of higher content of material strongly retained on the column than in the Medicine River sample. The chromatograms obtained in the normal phase system appeared to reflect selectivity centered on specific ring-classes. Monitoring both samples in the normal phase system by UV at 280 and 335 nm confirmed that shifting in the bulk of the chromatographic profile did not occur to any appreciable extent.

Evaluation of the elution profiles obtained from both systems shows that both samples are dominated by three- and four-ring classes and that the Lloydminster PAH fraction contains more alkyl-substituted structures.

Gas Chromatography-Mass Spectrometry

The separations achieved on the silica-$R(NH_2)_2$ column were studied in more detail. Cuts "X" and "Y" were collected from the Lloydminster and Medicine River aromatic concentrates respectively for further characterization (Fig. 3). These sub-fractions seemed to match meaningful portions of the eluted sample and correspond to the retention range of phenanthrene-anthracene and pyrene. The internal standards added increased detector responses in the chromatographic profile ranges that correspond to sharp peaks.

To collect X and Y sub-fractions containing sufficient amounts of hydrocarbon material for subsequent GS and GS-MS analysis, sample concentration was increased from 1.6 mg/mL up to 10 mg/mL. The loop size was also increased from 7 µL to 100 µL. Injections of larger samples resulted in deterioration of the elution profiles (overloading). However, the chromatogram gravity centers achieved on this analytical column were not shifted. Sample recoveries and separation reproducibility were satisfactory for sub-fraction collection, but the column required regeneration by equilibration with methylene chloride after a few injections. The 2-mL cuts from four successive runs were combined and evaporated to 10 µL with nitrogen. These sub-fractions were analyzed by gas chromatography and gas chromatography-mass spectrometry.

An examination of the gas chromatographic profiles obtained on the OV-1 column for cuts "X" and "Y" was performed by comparison with PAHs available in our laboratory. Major peaks of Lloydminster and Medicine River "X" and "Y" chromatographic profiles were found to correspond to phenanthrene, anthracene and their alkyl derivatives for the former and pyrene and methylpyrenes for the latter. These condensed ring structures and their alkyl-substituted derivatives have been identified as the predominant components of the PAH concentrates from both oils. Mass spectral evidence is presented in Table 3.

Spectrofluorometry, NMR and RI Quantitation

The high degree fluorescence specificity and selectivity for PAHs permits their determination in a multicomponent system even when resolution by HPLC is not achieved. Fluorescence does not always distinguish between members of homologous series, or parent aromatic nuclei from alkylated derivatives but the chromatographic retention time differences should spacially separate non discriminating fluorescence spectra sufficiently to avoid overlap. Similarly when differences in chromatographic retention times are negligible for two compounds their fluorescence spectra can allow this discrimination.

Alkyl substitution does not significantly alter the frequency of emission of substituted ring systems (Table 4) (13,14). Substitution effects decrease as ring size increases.

Peak maxima of both fluorescence emission and fluorescence excitation spectra of model polyaromatic compounds are listed in Table 5. These spectra are compared with spectra of oil sample PAH sub-fractions to aid in characterization. The peak maxima of excitation and emission spectra of ring systems in concentrate fractions are given in Table 6. The correspondence of the excitation and emission spectra of the concentrates to those of the model compounds (Tables 5 and 6) shows the general applicability of the fluorescence techniques for characterizing high-boiling petroleum fractions. The polyaromatic ring systems corresponded to anthracene, phenanthrene, pyrene, chrysene, benze[a]pyrene, perylene, and dibenzoanthracenes.

The retention times for anthracene and phenanthrene were close and the mass spectral analysis does not allow the differentiation of these two species. From experiments using mixtures of model compounds (13) it was found that the two compounds could be differentiated when present together in dilute solutions (less than 10^{-3} M). Similar experiments were performed on the sub-fractions of the "X" fraction after dilution with hexane. It was found that the first part of the "X" fraction contained only anthracene and the second part contained mainly phenanthrene. The relative intensities of the fluorescence measurements compared with the measurements of standard compounds indicate that the "X" fraction is dominated by phenanthrenes.

The results of the elemental analysis and the evaluation of aromatic and aliphatic carbon by ^{13}C nmr (15) indicated that there are more aliphatic alkyl substituents present in the Lloydminster polyaromatics fraction than in the Medicine River polyaromatics fraction (Table 7). The presence of these aliphatic substituents affects the reversed phase HPLC separation where substituted aromatic nuclei will elute with a higher-ring-number, unsubstituted structure. These results concur with the reversed phase HPLC separation which also indicated that the Lloydminster sample contained more alkyl substituted structures. The distribution of the three-, four- and poly ($\geq$ 5)-aromatic rings in the polynuclear aromatic sub-fractions was quantified by monitoring the eluate from the silica-$R(NH_2)_2$ column. The results (Table 8) indicated that the Lloydminster and Medicine River aromatic concentrates are dominated by three- and four-ring compounds. The Lloydminster sample contains more of the 5-ring and larger structure.

CONCLUSION

The silica-$R(NH_2)_2$ based HPLC system proved to be useful for the analysis of PAH mixtures in hydrocarbon materials. It permits the quantitation of meaningful aromatic sub-fractions on the basis of the number of rings. The scale of separation achieved on the analytical size column is sufficient for hydrocarbon material collection of the predominant aromatic components, and identification or more detailed characterization by gas chromatography-mass spectrometry and spectrofluorometry.

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TABLE 1

Compound-Type Distribution in Lloydminster and Medicine River Deasphaltened Residues > 350°C (API Procedure, wt %)

Sample	Saturates	Mono-Aromatics	Di-Aromatics	Poly-Aromatics	Polar Compounds	Basic Material
Medicine River	56.04	14.74	8.33	7.61	11.10	2.11
Lloydminster	20.30	6.90	9.55	13.41	37.65	8.20

Table 2: Retention indices of polynuclear aromatic hydrocarbons (PAH) and increments in retention indices due to PAH alkyl- and phenyl- substitution

Hydrocarbon	Silica-$R(NH_2)_2$ (n-heptane)			Silica-C_{18} (80% acetonitrile in water)		
	log I	Δ log I for alkyl	Δ log I for phenyl	log I	Δ log I for alkyl	Δ log I for phenyl
Benzene	1.000			1.000		
1,2,3,4,-tetrahydro-naphthelene	1.218			-		
Indene	1.782			-		
3-methylindene	1.757	0.015		-		
Naphthalene	2.000			2.000		
2-methylnaphthalene	2.076	0.076		2.670	0.670	
2-ethylnaphthalene	1.907	-0.093		3.128	1.128	
2,6-dimethylnaphthalene	2.208	0.208		3.211	1.211	
1,6-dimethylnaphthalene	2.179	0.179		3.211	1.211	
1,2-dimethylnaphthalene	2.109	0.109		2.951	0.951	
2,7-dimethylnaphthalene	1.907	-0.093		3.154	1.154	
1,4-dimethylnaphthalene	1.907	-0.093		3.086	1.086	
2,3,5-trimethylnaphthalene	2.171	0.171		3.355	1.355	
1,3,7-trimethylnaphthalene	2.055	0.055		3.591	1.591	
Acenaphthene	2.384	0.384		2.587	1.587	
Biphenyl	2.252		1.252	2.401		1.401
Biphenylene	2.300			-		
Azulene	2.424			-		
Fluorene	2.500			2.774		
2-methylfluorene	2.592	0.092		3.460	0.686	
1-phenylnaphthalene	2.484		0.484	3.237		1.237
1-benzylnaphthalene	2.587			3.128		
2-phenylnaphthalene	3.152		1.152	3.391		1.397
O-terphenyl	2.731		1.731	3.225		2.225
Anthracene	2.916			3.225		
9,10-dihydroanthracene	2.950			-		
2-methylanthracene	3.042	0.126		3.723	0.498	
9-methylanthracene	3.000	0.084		3.560	0.335	

Table 2: Retention indices of polynuclear aromatic hydrocarbons (PAH) and increments in retention indices due to PAH alkyl- and phenyl- substitution (continued)

Hydrocarbon	Silica-R(NH_2)2 (n-heptane)			Silica-C_{18} (80% acetonitrile in water)		
	log I	Δ log I for alkyl	Δ log I for phenyl	log I	Δ log I for alkyl	Δ log I for phenyl
2-phenylanthracene	3.225		0.309	4.299		1.074
9-phenylanthracene	3.290		0.374	4.038		0.813
9,10-diphenylanthracene	3.470		0.520	4.682		1.457
Phenanthrene	3.000			3.000		
3-methylphenanthrene	3.053	0.053		3.417	0.417	
3,6-dimethylphenanthrene	3.198	0.198		3.823	0.823	
9-n-dodecylphenanthrene	2.779	-0.221		> 5		
4,5-methylenephenanthrene	2.816	-0.184		3.517	1.517	
1,1 -dinaphthyl	3.167			3.860		
Acenaphthylene	3.199			2.230		
Triptycene	3.104			—		
m-terphenyl	3.330		2.330	3.474		2.474
p-terphenyl	3.488		2.488	3.851		2.851
pyrene	3.433			3.691		
1-methylpyrene	3.506	0.073		4.106	0.415	
3-methylpyrene	3.524	0.091		4.106	0.415	
4-methylpyrene	3.506	0.091		4.173	0.481	
3-n-decylpyrene	3.018	-0.414		> 5		
Fluoranthene	3.586			3.474		
benzo[a]fluorene	3.723			3.922		
benzo[b]fluorene	3.827			3.922		
benzo[c]fluorene	3.869			3.843		
benzo[a]anthracene	4.000			4.000		
benzo[b]chrysene	-			5.000		

Table 2: Retention indices of polynuclear aromatic hydrocarbons (PAH) and increments in retention indices due to PAH alkyl- and phenyl- substitution (concluded)

Hydrocarbon	Silica-$R(NH_2)_2$ (6% methylene chloride in n-heptane)			Silica-C_{18} (80% acetonitrile in water)		
	log I	Δ log I for alkyl	Δ log I for phenyl	log I	Δ log I for alkyl	Δ log I for phenyl
Phenanthrene	3.000			3.000		
Benzo[b]fluorene	3.469			3.922		
1,3,5,-triphenylbenzene	3.864		2.864	4.169		3.169
2,2'-dinaphthyl	3.879			4.169		
Benzo[a]anthracene	4.000			4.000		
7,12-dimethyl-benzo[a]anthracene	3.834	-0.164		4.376	0.376	
Chrysene	4.000			4.000		
Triphenylene	4.169			3.851		
3-methylcholanthrene	4.178			-		
20-methylcholanthrene	4.118			-		
22-methylcholanthrene	4.690			-		
1,2,3,4-tetraphenyl-naphthalene	4.402	2.402		4.571		2.571
Benzo[a]pyrene	4.425			4.591		
Benzo[b]fluoranthene	4.435			4.376		
Benzo[k]fluoranthene	4.435			4.461		
Perylene	4.559			4.404		
Difluorenyl	4.852			3.954		
Benzo[b]chrysene	5.000			5.000		
Anthanthrene	>5			-		
Rubicene	>5			-		
Benzo[ghi]perylene	>5			4.955		
Dibenzo[a,h]anthracene	>5			4.766		
Indeno[1,2,3-c,d]pyrene	>5			-		
Dibenzo[a,e]anthracene	>5			-		
Picene	>5			-		
Coronene	>5			-		
Dibenzo[e,h]pyrene	>5			-		
Dibenzo[a,h]pyrene	>5			-		

TABLE 3

Homologous Series of Polycyclic Aromatic Hydrocarbons in Aromatic Sub-fractions of Medicine River and Lloydminster Oils

Oil	Fraction	Series	First Mass	Last Mass	Major Assigned Structures*
Medicine River	X	-14	178	290	phenanthrenes/ anthracenes
	Y	-14	202	286	pyrenes
Lloydminster	X	-14	178	248	phenanthrenes/ anthracenes
	Y	-14	202	268	pyrenes

* Tentative Identifications that are most consistent with HPLC and GC retentions

TABLE 4

Effect of Alkyl Substituents on Wavelengths of Excitation and Emission Spectra
(Solvent: Hexane)

Compound	Excitation	Emission
Phenanthrene	241 252 275(S) 281(S) 307	335 362 377 414 439
3-methylphenanthrene	242 252 274 284 296	349 364 382(S) 406(S)
n-decylphenanthrene	251 267 276 285 299	351 367 386 412(S)
3,6-dimethylphenanthrene	251 272 276 286 299	327 353 368 388 416(S)
Pyrene	241 252 262 272 306 318 334	369 377 383 392
1-methyl pyrene	241 264 275 312 327 343	376 394 422 433(S)
3-methyl pyrene	241 266 276 311 326 342	376 393 414 433(S)
n-decyl pyrene	265 275 297 312 326 341	374 391 412

(*) S - shoulder

TABLE 5

Fluorescence Excitation and Emission Spectra of Model Compounds
(Solvent: Hexane, Temperature Thermostated at 25°C

Compound	Fluorescence Excitation Spectra wavelength, nm	Fluorescence Emission Spectra wavelength, nm
1. Anthracene	252* 311 325 339 356 375	378 398* 416 446(S)
2. Phenanthrene	241* 252 275(S) 281(S) 307 300(S)	335 362* 377 414 439 300(S)
3. Pyrene	241 252 262 272 306 318 334*	369* 377 383 392
Benzo[b]fluorene	263* 274(S) 285 307 317 326 340	340* 415 438 468
Benzo[a]anthracene	241 277 287* 297(S) 314 327 341	311 330 344 385* 405 457
4. Chrysene	260(S) 268* 294(S) 306 319(S)	362 369(S) 381* 402 426
Triphenylene	258* 268 274(S) 307 324 346	355* 362
5. Benzo[a]pyrene	266 285* 296 333 348 365 378(S) 386 396(S)	402* 407(S) 424 452
Benzo[b]fluoranthrene	241 252 257 276 291 301* 340 368	422* 444 457
Benzo[k]fluoranthrene	267 284 296 307* 323 340 360 369 380 403	400* 423 454 480
6. Perylene	368 387 408* 435	435* 465 496 536(S)
Anthanthrene	258 293 306* 381 399 404 406 422 429	428* 436(S) 458 487
Benzo[ghi]perylene	288 299* 346 363 383	397(S) 406(S) 418* 427(S) 443
7. Dibenzo[a,h]anthracene	276 286* 296 322 334 348	393* 412 440 460(S) 472(S)
Dibenzo[a,c]anthracene	248 267 276 286* 323 334(S)	378 395* 412

* most intense peak in each spectrum

(S) shoulder

TABLE 6

Fluorescence Excitation and Emission Spectra (wavelength, nm) of Lloydminster and Medicine River Fractions
(Solvent: Hexane, Temperature Thermostated at 25°C)

Fraction	Lloydminster		Medicine River	
	Excitation	Emission	Excitation	Emission
1. Anthracene	251* 310 324 336 354 370	375* 399 415(S) 446(S)	252* 310 325 340 356 375	377* 399 415(S) 447(S)
2. Phenanthrene	241* 252 280 300 304	335 360 370 426(S)	241* 252 282 302	335 360* 370 419(S)
3. Pyrene	241 252 262 270 306 318 354*	376 382 392*	241 252 261 272 318 334*	374 383 393*
4. Chrysene	260 268* 294 306	340 362 369(S) 381 399 426	260 277* 305 319	340 362 369(S) 380 402 426(S)
5. Benzo[a]pyrenes	240 251 266 284 294 345 360 384*	402* 407(S) 424 452(S)	251 262 285 295 330 348 364 386*	402* 407(S) 424 450
6. Perylene	406* 437 487	434* 469 533(S)	366 386 409* 435	435* 464 492 535(S)
7. Dibenzo[a,h] anthracene	276 286 296	393 410 440	275 286 296	395 412 440(S)

* most intense peak

(S) shoulder

TABLE 7

Elemental and ^{13}C nmr Analysis of PAH Concentrates

	Lloydminster	Medicine River
Elemental Analysis		
% C	82.52	87.31
% H	9.16	8.92
^{13}C nmr		
% Aromatic C	40.91	60.53
% Aliphatic C	59.09	39.47

TABLE 8

Quantitation (wt %) of Ring Classes in Lloydminster and Medicine River PAHs Using Refractive Index Detector

	Lloydminster	Medicine River
3-ring	48	49
4-ring	23	25
> 4-ring	19	15
retained on column	10	11

Model compounds used to determine calibration factors:

3-ring - phenanthrene, anthracene

4-ring - pyrene, chrysene

> 4-ring - dibenzo[a,c]anthracene

FIGURE CAPTIONS

FIGURE 1: Separation and Characterization Schematic

FIGURE 2: Chromatograms Obtained on the Silica-C_{18} Column with Mobile Phase of Water-Acetonitrile (20:80)

A. Lloydminster polynuclear aromatic hydrocarbon fraction

B. Medicine River polynuclear aromatic hydrocarbon fraction

C. Mixture of PAH standards

1: naphthalene; 2: diphenyl; 3: fluorene; 4: phenanthrene; 5: anthracene; 6: 2-phenylnaphthalene; 7: fluoranthene; 8: 9-methylanthracene; 9: pyrene; 10: triphenylene; 11: difluorenyl; 12: chrysene; 13: 1,3,5-triphenylbenzene; 14: 2,2'-dinaphthyl; 15: 2-phenylanthracene; 16: benzo[b]fluoranthene; 17: benzo[k]fluoranthene; 18: benzo[a]pyrene; 19: 9,10-diphenylanthracene; 20: dibenzo[a,h]anthracene; 21: benzo[ghi]perylene; 22: dibenzo[e,h]anthracene

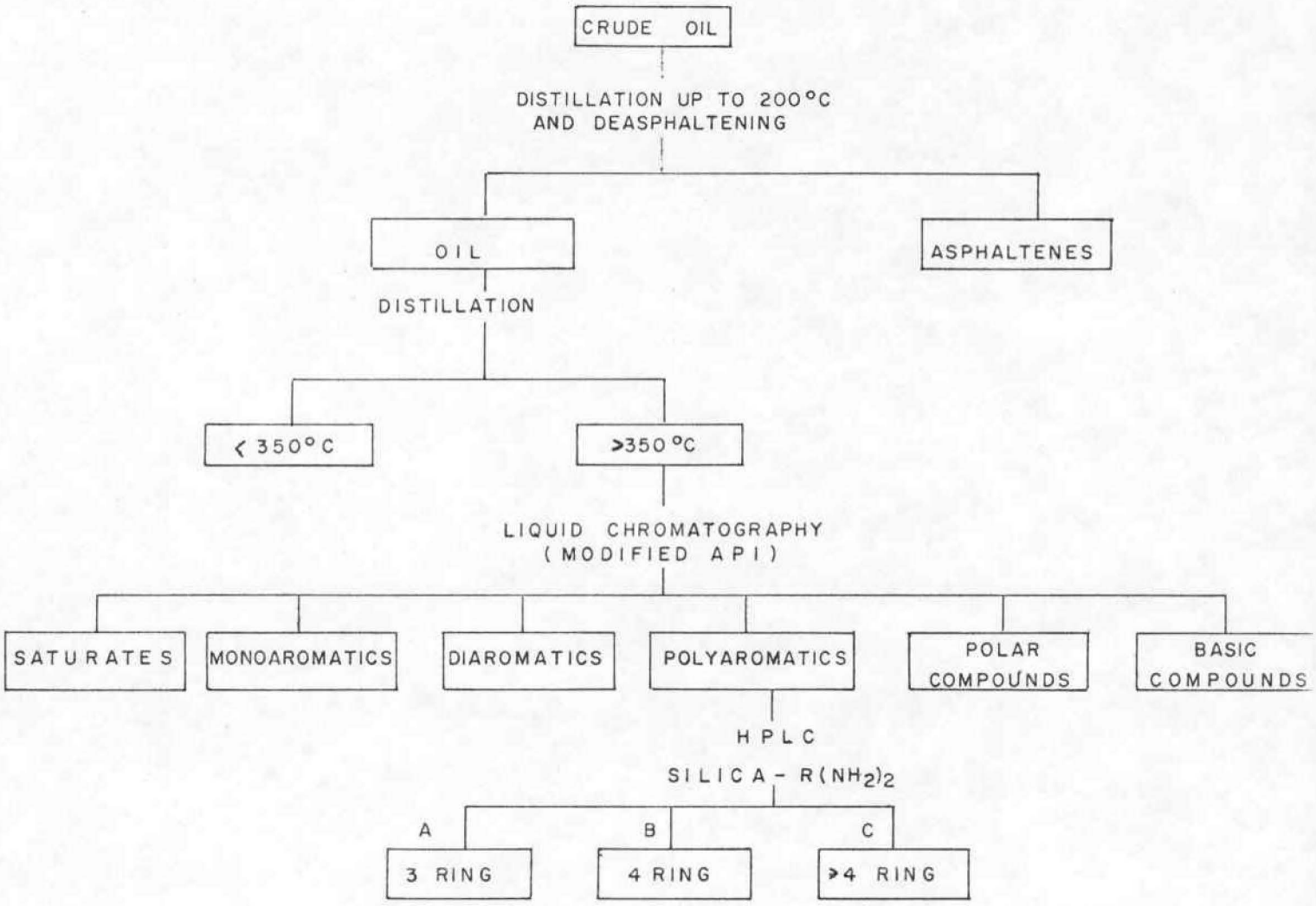
FIGURE 3: Chromatograms Obtained on the Silica-Diamine Column with Mobile Phase of Methylene Chloride-Hexane (4:96)

A. Lloydminster polynuclear aromatic hydrocarbon fraction

B. Medicine River polynuclear aromatic hydrocarbon fraction

C. Mixture of PAH standards

1: naphthalene; 2: anthracene; 3: phenanthrene; 4: pyrene; 5: benzo[b]fluorene; 6: benzo[a]anthracene; 7: chrysene; 8: benzo[a]pyrene; 9: perylene; 10: anthanthrene; 11: benzo[ghi]perylene



— SPECTROFLUORESCENCE CHARACTERIZATION OF A, B AND C.

— GC-MS IDENTIFICATION OF A, B.

FIG. 1

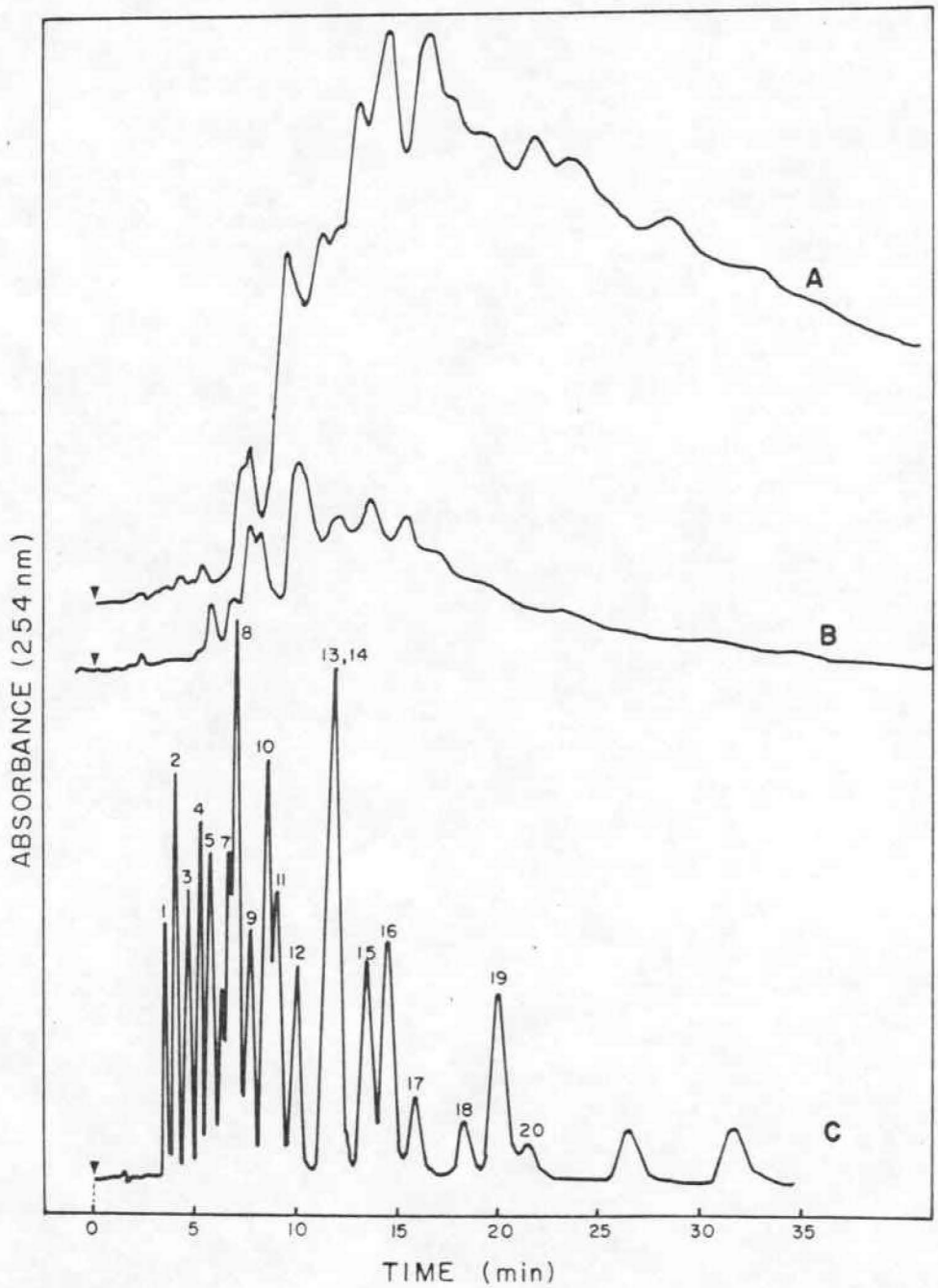

ABSORBANCE (254 nm)
A
B
C
1
2
3
4
5
7
8
9
10
11
12
13,14
15
16
17
18
19
20
0
5
10
15
20
25
30
35
TIME (min)

FIG 2

ABSORBANCE (254nm)
A
B
C
X
Y
TIME (min)

FIG 3

ABSORBANCE (254nm)
A
B
C
X
Y
TIME (min)

FIG 3