

THE DETERMINATION OF
NITROGEN-CONTAINING COMPOUNDS
IN HEAVY SYNCRUDE OILS

By

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ABSTRACT

A two stage chromatographic separation method was adapted to the separation of nitrogen-containing compounds from heavy syncrude oils. Crude oil samples were first chromatographed on alumina to obtain an aliphatic fraction A1 (70 wt% of oil, <1% of total nitrogen), a polycyclic aromatic hydrocarbon fraction A2 (20%, 16%N) and a nitrogenous fraction A3 (3%, 80%N). The nitrogenous fraction was further separated on silicic acid into three fractions: a secondary-PANH fraction S1 (61% total N), an amino-PAH and tertiary-PANH fraction S2 (4%N) and a tertiary-PANH fraction S3 (9%N). One Tar Sand and two oil residue samples, provided by Shell Canada Ltd, were taken through this procedure.

The nitrogen-containing fractions were analyzed by mass spectrometry (electron impact, methane chemical ionization and ammonia chemical ionization) and by two chromatographic methods (gas and reverse phase liquid chromatography). Further analyses were performed using gas chromatography/mass spectrometry, liquid chromatography/mass spectrometry and nuclear magnetic resonance (^1H and ^{13}C) spectroscopy.

The nitrogenous components in the S1 fractions were shown to be alkylated carbazoles, containing from one to twenty carbons attached to the carbazole nucleus, in varying degrees of unsaturation ranging from zero to five degrees of unsaturation. The distribution of carbon substitution

maximized in the C₅ to C₈ range for the different series of alkylcarbazoles. The distribution of the degrees of unsaturation in the Tar Sand oil sample was: saturated carbazoles, 32%, 1-degree unsaturates, 23%, 2-degree, 9%, 3-degree, 16%, 4-degree, 12% and 5-degree, 8%. In the processed Peace River residue, the ratio between the saturated, 1-, 2-, 3-, 4- and 5-degree unsaturated carbazoles was 28%:39%:18%:6%:6%:3%. From the ¹H NMR spectrum the ratio of benzylic to aliphatic resonances was 1:1.25 which was interpreted to mean that the alkyl chains attached to the carbazole nucleus were short on average. A complete lack of vinyl proton absorption indicated that few alkene bonds if any were present; thus, the degrees of unsaturations must be accommodated by rings or benzo-annulations.

Of all the analytical methods used, ammonia chemical ionization mass spectrometry (NH₃ CIMS) was found to be a most useful and selective method and was used in probe MS, GC/MS and LC/MS experiments. Reverse phase liquid chromatography (RPLC) was more useful in this work than capillary column gas chromatography (CCGC). A combination of nuclear magnetic resonance (NMR) experiments (¹H, ¹³C, ¹³C spectral editing, ¹H-¹³C shift correlation and ¹³C T₁) was found to be extremely useful for these samples because of the unique information these experiments provided.

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TABLE OF CONTENTS

	<u>PAGE</u>
ABSTRACT	III
ACKNOWLEDGEMENTS	V
LIST OF TABLES	X
LIST OF FIGURES	XI
I. <u>INTRODUCTION</u>	1
I.1 NITROGEN COMPOUNDS IN CRUDE OILS AND TAR SANDS	1
I.2 TYPES OF CRUDE OILS STUDIED IN THE LITERATURE	1
I.3 TYPES OF ORGANIC NITROGEN COMPOUNDS IN OILS	3
I.4 SEPARATION METHODS	4
I.5 ANALYTICAL METHODS	5
I.6 RESEARCH OBJECTIVES	6
II. <u>EXPERIMENTAL</u>	9
II.1 SOLVENTS	9
II.2 OIL SAMPLES	9
II.3 CHROMATOGRAPHIC SEPARATION METHODS	10
II.4 MODIFIED SEPARATION METHOD	13
II.4.1 MEDIUM PRESSURE ALUMINA SEPARATION	13
II.4.2 MEDIUM PRESSURE SILICIC ACID SEPARATION	15

II.5 ASPHALTENE SEPARATION	16
II.6 SCALED-UP ALUMINA SEPARATION	17
II.7 ANALYTICAL METHODS	19
II.7.1 MASS SPECTROMETRY	19
II.7.1.a LOW RESOLUTION MASS SPECTROMETRY	19
II.7.1.b HIGH RESOLUTION MASS SPECTROMETRY	19
II.7.2 REVERSE PHASE LIQUID CHROMATOGRAPHY	21
II.7.3 LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY	22
II.7.4 GAS CHROMATOGRAPHY	23
II.7.5 GAS CHROMATOGRAPHY-MASS SPECTROMETRY	23
II.7.6 PROTON AND CARBON-13 NMR	24
II.7.7 NITROGEN DETERMINATION PROCEDURE	25
III. <u>RESULTS AND DISCUSSION</u>	26
III.1 SEPARATION METHODS	26
III.1.1 SELECTION OF A SEPARATION METHOD	26
III.1.2 APPLICATION OF THE SEPARATION METHOD TO HEAVY OILS	27
III.1.3 SUMMARY	35
III.1.4 MODIFIED SEPARATION METHODS	38
III.1.4.a MODIFIED ALUMINA SEPARATION	38
III.1.4.b MODIFIED SILICIC ACID SEPARATION	43

III.1.5 SCALED-UP ALUMINA SEPARATION	51
III.1.6 ASPHALTENE SEPARATION	54
III.1.7 SUMMARY OF THE SEPARATION SCHEME	55
III.2 ANALYTICAL FINISHES	56
III.2.1 LOW RESOLUTION MASS SPECTROMETRY	56
III.2.1.a PROBE ELECTRON IMPACT MASS SPECTROMETRY	56
III.2.1.b COMPARISON OF SPECTRA FROM DIFFERENT IONIZATION MODES	58
III.2.2 HIGH RESOLUTION MASS SPECTROMETRY	71
III.2.3 SUMMARY	73
III.2.4 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY	73
III.2.5 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY (HPLC-MS)	82
III.2.6 SUMMARY	89
III.2.7 GAS CHROMATOGRAPHY (GC)	91
III.2.8 GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC/MS)	94
III.2.9 SUMMARY	103
III.2.10 COMPARISON OF AREAS DETERMINED FROM THE PROBE AMMONIA CIMS ANALYSIS AND THE LC/MS ANALYSIS	105
III.2.11 NUCLEAR MAGNETIC RESONANCE (NMR)	107
III.2.12 SUMMARY	115
III.2.13 COMPOUND INTERPRETATION	115

IV.	<u>CONCLUSIONS</u>	117
V.	<u>APPENDICES</u>	119
	APPENDIX I	A literature review: oil samples, nitrogenous compounds, separation and analytical methods that have been studied. 119
	APPENDIX II	Mass chromatograms of sat, 1-, 2-, 3-, 4- and 5-degree unsaturated carbazoles from the LC/MS (NH ₃ CI) analysis of Tar Sand A3 fraction. 127
	APPENDIX III	Area of peaks from the LC/MS mass chromatograms of the six different carbazole series from Tar Sand A3 fraction. 133
	APPENDIX IV	Area of carbazole peaks from the GC/MS (NH ₃ CI) mass chromatograms of processed residue S1 fraction. 134
	APPENDIX V	Relative intensities of carbazole ions from the averaged NH ₃ CI mass spectrum Tar Sand A3 fraction. 135
	APPENDIX VI	¹³ C spectra of carbazole and benzolalcarbazole. 136
	APPENDIX VII	Expansion plot of the ¹³ C- ¹ H 2-D shift correlation spectrum. 137
	APPENDIX VIII	UV spectra of six nitrogen-containing aromatics. 139
VI.	<u>REFERENCES</u>	140

LIST OF TABLES

<u>Table Number</u>	<u>Title of Table</u>	<u>Page</u>
1	Types of Oil Samples Studied for Organic Nitrogenous Compounds.	119
2	Types of Nitrogen Compounds Found in Different Oil Samples.	120
3	Separation Methods Used.	122
4	Analytical Finishes.	124
5	Experimental Conditions used in Probe Mass Spectrometry.	20
6	Nitrogen Distribution using Different Separation Methods.	33
7	Volumes of Solvents and Times used in Separations.	39
8	High Resolution EIMS Analyses.	72
9	Carbon T ₁ Values from Tar Sand A3 Fraction.	114

LIST OF FIGURES

<u>Figure Number</u>	<u>Figure Title</u>	<u>Page</u>
1	Schematic diagram of Later's separation method.	11
2	Schematic diagram of modified separation method.	14
3	Gas chromatogram and reverse phase liquid chromatogram of Tar Sand A3 fraction.	30
4	Reverse phase liquid chromatogram of Tar Sand S1, S2 and S3 fractions.	31
5	Reverse phase liquid chromatogram of processed residue A3 fraction separated by Later's alumina separation.	34
6	Probe electron impact mass spectra of Tar Sand S1, S2 and S3 fractions.	36
7	Chromatogram of processed residue A1, A2 and A3 fractions from a modified alumina separation.	41
8	Reverse phase liquid chromatogram of processed residue A3 fraction separated by modified alumina separation.	42
9	Chromatogram of standard mixture from a modified silica separation: S1 eluted with 1:1 hexane:benzene and S2, benzene.	45
10	Chromatogram of standard mixture from a modified silica separation: S1 eluted with 1:1 hexane:benzene and S2, benzene.	46
11	Chromatograms of Tar Sand and processed residue A3 fractions from a modified silica separation.	49

12	Reverse phase liquid chromatograms of Tar Sand S1, S2 and S3 fractions separated by modified silica separation.	50
13	Chromatograms of Tar Sand A3 fractions separated by Later's method and by scaled-up method.	53
14	Probe EIMS total ion current chromatogram and mass spectra of Tar Sand S1 fraction.	57
15	Methane and ammonia CI mass spectra of naphthalene, xanthene and dibenzothiophene.	61
16	Methane and ammonia CI mass spectra of carbazole, aminopyrene and dibenzocarbazole.	62
17	EI, CH ₄ CI and NH ₃ CI mass spectra of Tar Sand S1 fraction.	64
18	Ammonia CI mass spectra of Tar Sand S1, S2 and S3 fractions.	66
19	Ammonia CI mass spectra of processed residue S1, S2 and S3 fractions.	68
20	Ammonia CI mass spectrum of unprocessed residue A3 fraction.	70
21	Comparison of chromatograms detected from different wavelengths in the HPLC analyses.	75
22	UV spectra from Tar Sand S1 RPLC chromatogram.	77
23	Reverse phase liquid chromatograms of processed residue S1, S2 and S3 fractions.	78
24	UV spectra from processed residue S1 HPLC chromatogram.	80
25	Comparison of Peace River residue A3 fraction before and after processing.	82
26	Total ion current and mass spectra from LC/MS (NH ₃ CI) analysis of Tar Sand A3 fraction.	83

27	Mass chromatograms of the saturated carbazole series.	85
28	Example of area measurement of elution peak from mass chromatograms.	87
29	Distribution of carbazoles in each series from the LC/MS (NH ₃ CI) analysis of Tar Sand A3 fraction.	88
30	Capillary gas chromatograms of Tar Sand S1, S2 and S3 fractions.	92
31	Capillary gas chromatograms of processed residue S1, S2 and S3 fractions.	94
32	Total ion current chromatogram and mass chromatograms from the GC/MS (NH ₃ CI) analysis of Tar Sand A3 fraction.	95
33	Total ion current chromatogram and mass spectra from the GC/MS (NH ₃) analysis of Tar Sand A3 fraction.	97
34	Mass chromatograms of C ₅ - and C ₁₀ -carbazoles from different degree of unsaturation.	98
35	Comparison of GC/MS and LC/MS mass chromatograms from C ₉ to C ₂₀ -carbazoles.	99
36	Comparison of the detection range in the GC/MS and LC/MS analyses.	101
37	Total ion current chromatogram and mass spectra of the GC/MS (NH ₃ CI) analysis of processed residue S1 fraction.	102
38	Relative area distribution of carbazole group in the Tar Sand A3 fraction and processed residue S1 fraction from GC/MS (NH ₃ CI) analysis.	104
39	Relative area distribution of carbazoles data from the averaged NH ₃ CI mass spectrum.	106

40	500 MHz ^1H NMR spectrum of Tar Sand A3 fraction.	108
41	125 MHz ^{13}C NMR spectrum of Tar Sand A3 fraction.	111
42	^{13}C - ^1H 2-D shift correlation spectrum of Tar Sand A3 fraction.	113

I. Introduction

I.1 Nitrogen compounds in Crude oils and Tar Sands

All fossil fuels contain nitrogen which exists primarily in the form of organic compounds at levels varying from 0.5 to 2% by weight. While these nitrogen compounds are not the major components in crude oils, the presence of these compounds in refinery feedstocks is detrimental for several reasons: (a) they are associated with the colour, odour and corrosive properties of the oils; (b) they are responsible for the formation of gums and deposits during storage (F1139); (c) they are believed to deactivate and poison some of the catalysts during the refining processes (F1139) and (d) they are associated with most of the mutagens and carcinogens in the crude oils. For these reasons, the nitrogen content of feedstocks must be reduced to ppm or sub-ppm levels before the reforming process in order to prevent catalyst poisoning; in addition, their removal is essential for environmental and health reasons (F1136, F1139).

I.2 Types of Crude Oils Studied in the Literature

Many oil samples have been studied with a view to the characterization of the nitrogenous components. These

studies can be divided into several types (Table 1 of Appendix I): (a) coal liquids including solvent refined coal (SRC II), coal oils, gasifier oils, anthracene oils, coal tars, tar base concentrates and coal liquifaction products; (b) shale oils; (c) petroleum liquids including gasolines, petroleum, asphaltenes, crude oils and kerosene; (d) syncrude oils; and (e) tar sand oils. In most cases, these oils went through a series of refining treatments before they were analyzed. Processes such as the hydrotreatment, distillation and solvent refining have been the most common methods used to refine these oils.

Depending on the sources and the refining methods, the nitrogen contents of different oils vary; the boiling ranges of these oils also vary from less than 200°C to above 500°C. Amongst these oils, shale oils have been studied in greatest detail while heavy distillates as those from such as the tar sands have been rarely examined. There are two principal reasons why the heavy distillates have not been studied in detail. First, heavy oil distillates that have a wider and higher boiling range were not interesting to the petroleum industry previously because they are more difficult and more costly to refine than the light oils. Second, the components of these heavy distillates were so complex that standard analytical techniques such as gas chromatography were unable to give any conclusive information as to the composition of these oils. Recently, more and more interest has been shown

in heavy distillates, particularly in Canada.

I.3 Types of Organic Nitrogen Compounds in Oils

Table 2 in Appendix I gives a list of different nitrogen compounds and representative structures that have been found in a variety of crude oil samples. Most of the nitrogen-containing compounds exist as polycyclic aromatic nitrogen derivatives (PANH). The three main PANH types are the secondary-PANH (e.g., carbazoles), tertiary-PANH (e.g., quinolines) and the amino-PAH (e.g., amino-naphthalene). In all of these PANHs studies, the tertiary-PANHs especially aniline and quinoline derivatives were found to be the most common and abundant nitrogenous compounds in the oil samples. On the other hand, carbazoles and its alkylated derivatives were another major nitrogenous group found in different oil samples (F1186). These carbazoles compounds were reported to be very resistant to the catalytic hydrodenitrogenation, more resistant than other nitrogenous compounds such as the indoles and the quinolines. Hence, the carbazoles were expected to be the major nitrogen components that would persist after oil samples were subjected to severe processing conditions. Amino-compounds, another major nitrogenous group in the oil samples, were less abundant than the secondary- and the tertiary-PANHs. Minor components such as the N-ethylaniline, N,N-dimethylaniline (F0236, F1122), cyano-PAH

(F1124), amides (F1168) and nitro-PAH (F0214) have also been found in low concentrations in some oils. Some nitrogen-containing compounds that contain more than one hetero-atom have also been reported by Burchill and his group. These compounds were found to contain two nitrogen atoms or a nitrogen together with a sulphur or oxygen heteroatoms (F1112, F1125).

I.4 Separation Methods

Since nitrogenous compounds are minor components in the oils, separation procedure are essential to isolate these compounds before analysis. Table 3 in Appendix I shows some of the methods that have been used to isolate PANH from different oil samples. Among these methods, the classical method was liquid-liquid extraction with pH control (F0007, F0029, F1145 etc). However, this approach suffers from disadvantages such as poor resolution, low selectivity, poor reproducibility and the possibility of decomposition of labile compounds. More recent papers have used liquid chromatographic methods in the separation of nitrogen compounds. Silica and alumina have been the most popular normal phase supports while other packings such as amino- and cyano-bonded silica gels have also been used (F0001, F1114). In the past decade, liquid chromatographic methods have attracting increasing attention due to their superior

reproducibility and suitability for labile compounds. In many cases, comprehensive isolation procedures usually employ a combination of several separation steps (e.g. F0210, F0025).

I.5 Analytical Methods

Some of the common analytical technique used for the separation and detection of nitrogen compounds are shown in Table 4 in Appendix I and the most popular method has been capillary column gas chromatography (CCGC). In last decade, almost all work has been done using fused silica wall-coated open tubular capillary columns (WCOT); glass capillary (SCOT) columns are too fragile while packed GC columns do not provide sufficient resolution for these complex mixtures. The two most important general detectors used for GC, the flame ionization detector (FID) and the mass spectrometer (MS) have been used extensively in these studies whereas the nitrogen-selective detector (TSD) has been used to a much lesser extent (F1124-26).

The analysis of nitrogenous compounds by high performance liquid chromatography (HPLC) has not been as common as GC analyses. The ultraviolet absorption detector (UVD), the most commonly used detector for LC, provides sensitive detection of UV-absorbing compounds. Recently, UV/Visible diode-array detectors have become available for LC use; this detector allows the collection of UV/Visible

spectra of eluting components during a LC run. It is unfortunate that an easy-to-use and universal detector (such as the FID in GC) is not available as yet for LC. The mass spectrometer is a universal detector but combined LC/MS is much more difficult experiment to perform than GC/MS, making the mass spectral identification of peaks in LC chromatograms more difficult than in the case of GC.

Probe electron ionization mass spectrometry (EIMS) is another very useful technique in identifying the nitrogen compounds. For example, a LC peak can be collected, evaporated and then analyzed by EIMS. Other ionization modes such as chemical ionization mass spectrometry (CIMS) have been less commonly used; only a few papers have reported the use of CIMS for the detection of the PANHs.

Other spectrometric techniques like the ultra-violet visible or infrared spectroscopy are also important for the characterization of these nitrogen compounds. Nuclear magnetic resonance (NMR) is an analysis not feasible in most cases (F1101, F1102, F1117, F1131) since the amounts of these compounds are far too low to afford usable spectra. In most papers, the structural elucidation of compounds is usually accomplished using a combination of spectroscopic techniques.

I.6 Research Objectives

Shell Canada has encountered problems in processing

heavy oils from sources such as the tar sands. Some components of these oils appear to be refractory to the hydrocracking operations. Such oils are called refractory because their nitrogen content cannot be reduced to ppm levels without extensive hydrotreating, suggesting that the refractory components may be nitrogen-containing compounds. While these refractory oils may contain up to 5000 ppm nitrogen, the identities of the nitrogenous organic compounds in tar sand oils are largely unknown. The principal objective of this thesis was to develop methods for the isolation, analysis and structure determination of the nitrogenous compounds in heavy oils.

To accomplish this objective the research was directed to the following five specific goals:

- (a) to evaluate literature methods for the isolation and analytical detection of nitrogenous organics in order to find the best method(s) for the problem at hand,
- (b) to apply the separation method selected above to two or three heavy oil samples and to prepare subfractions for further analyses,
- (c) to examine these subfractions by both gas and liquid chromatographic techniques,
- (d) to examine the above subfractions by mass spectrometry, alone and in conjunction with gas and/or liquid chromatographic methods,

(e) to identify as many of the nitrogenous components as possible with the specific goal of identifying the refractory components.

II. Experimental

II.1 Solvents

HPLC grade hexane was obtained from BDH Chemicals (Toronto, Ontario); acetonitrile, dichloromethane and acetone were purchased from Caledon Laboratories (Georgetown, Ontario). Benzene, chloroform (stabilized by 0.75% ethanol, from Caledon, Georgetown, Ont.) and absolute ethanol (Fisher Scientific, Toronto, Ont) were distilled before use. Anhydrous diethyl ether was used as supplied (Fisher Scientific, Toronto, Ontario). Distilled water was passed through a Milli-Q water purification system (Millipore Corp., Bedford, MA) which contained one ion-exchange, two carbon and one 0.22 μm particulate filters. All solvent mixtures are specified as volume/volume ratios.

II.2 Oil Samples

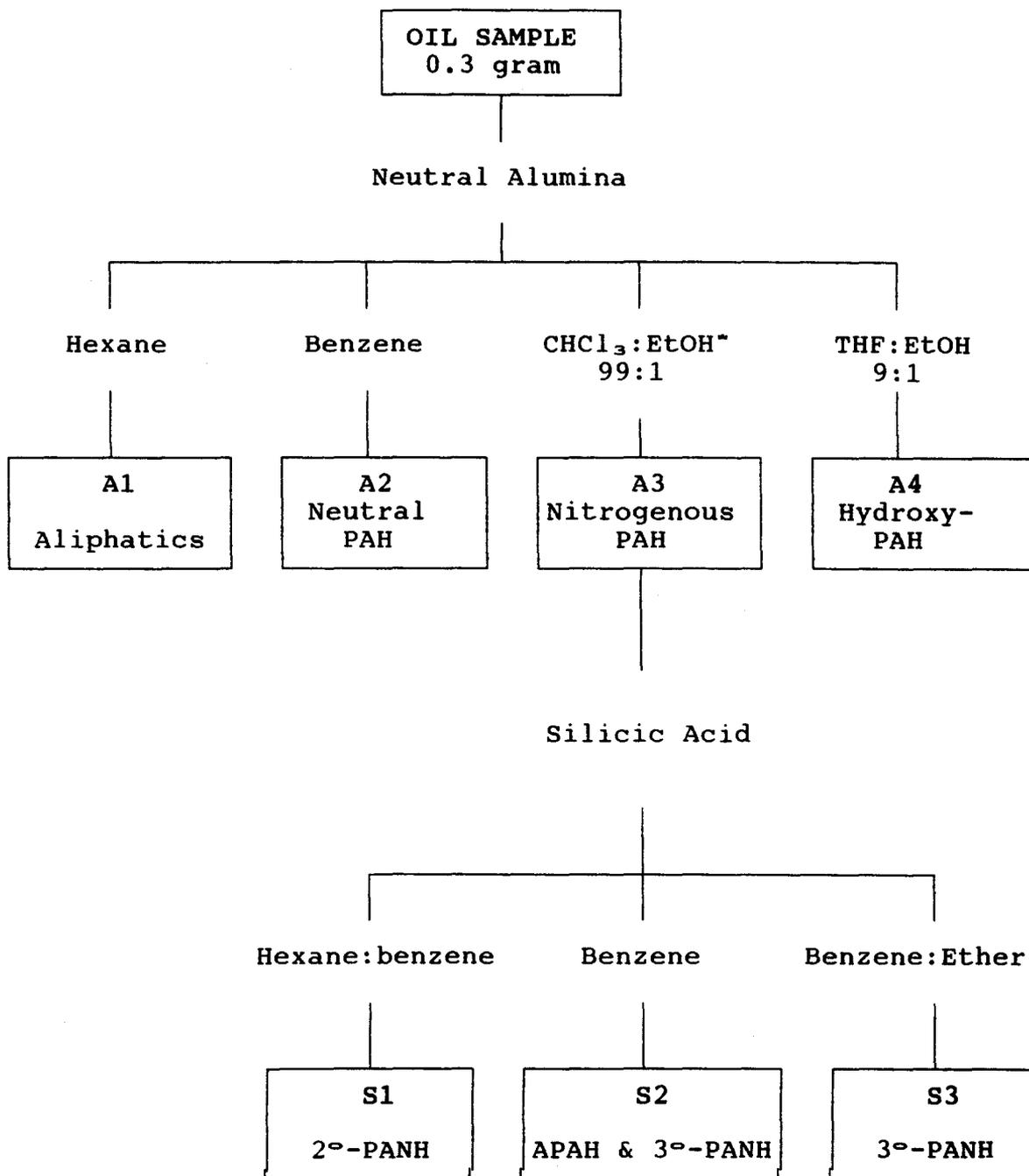
Three heavy oil samples were kindly supplied by Shell Canada Ltd. The first sample was a brownish processed Athabasca Tar Sand syncrude oil with a boiling range of 200 to 540°C and a nitrogen content in the 700 ppm range. The second sample was a black, gummy unprocessed Peace River residue sample which contained about 4000 ppm of nitrogen. The third sample, prepared by processing the second sample

(Shell Canada), was distilled over a boiling range of 111 to 535°C. The nitrogen content of the third sample had been decreased about 20-fold to 200 ppm as a result of the processing. The appearance of the unprocessed Peace River residue changed from a black gummy solid to a golden brown liquid after processing.

II.3 Chromatographic Separation Methods

After reviewing about twenty separation methods, the fractionation procedure described by Lee, Later and coworkers (F0024) was selected for the isolation of nitrogen compounds from the oil samples. A schematic diagram of this separation method is shown in Fig 1. Neutral alumina (Brockman, Activity I, 80-200 mesh, Fisher No. A950) was dried in an oven at 150-170°C for at least 5 hours before use. To about 0.1 - 0.3 gram of oil dissolved in a few milliliters of chloroform was added 3 grams of neutral alumina. After removal of the chloroform on a rotary evaporator under reduced pressure, the sample-coated alumina was packed into an 11-mm i.d. glass chromatography column fitted with a glass frit which had been previously dry-packed with 6 grams of oven-dried neutral alumina. This packing procedure was used in all alumina separations; any changes to this procedure will be mentioned specifically. The alumina column was then eluted with the following solvents in order to afford a

Fig.1: Schematic diagram of the procedure used for the isolation of nitrogen heterocycles.



EtOH*: absolute ethanol

series of fractions: the aliphatic hydrocarbon fraction (A1), 20 mL of hexane; the neutral PAH fraction (A2), 50 mL of benzene; the basic nitrogenous fraction (A3), 70 mL of chloroform: absolute ethanol (99:1); and the hydroxy-PAH fraction (A4), 50 mL tetrahydrofuran: absolute ethanol (9:1). The nitrogen-containing fraction (A3) was evaporated at reduced pressure to afford a golden yellow oil.

For the silicic acid separation, silicic acid (Mallinckrodt No. 2847, 100 mesh powder) was used as received. The A3 fraction from an alumina separation of 0.1 to 0.3 gram crude oil was dissolved in a few milliliters of chloroform. To this solution was added 0.5 gram of silicic acid and the mixture evaporated to dryness at reduced pressure. Meanwhile, silicic acid (2 grams) was dry packed in a glass chromatographic column (11 mm i.d.) fitted with a glass frit and then wetted with 10 mL of hexane. The sample-coated silica was then added to the top of these silicic acid. The column was then eluted with the following series of solvents in order to give three fractions: the secondary-PANH fraction (S1), 50 mL of hexane:benzene (1:1); the amino and tertiary PANH fraction (S2), 30 mL of benzene; and the tertiary PANH fraction (S3), 50 mL of benzene:anhydrous diethyl ether (1:1).

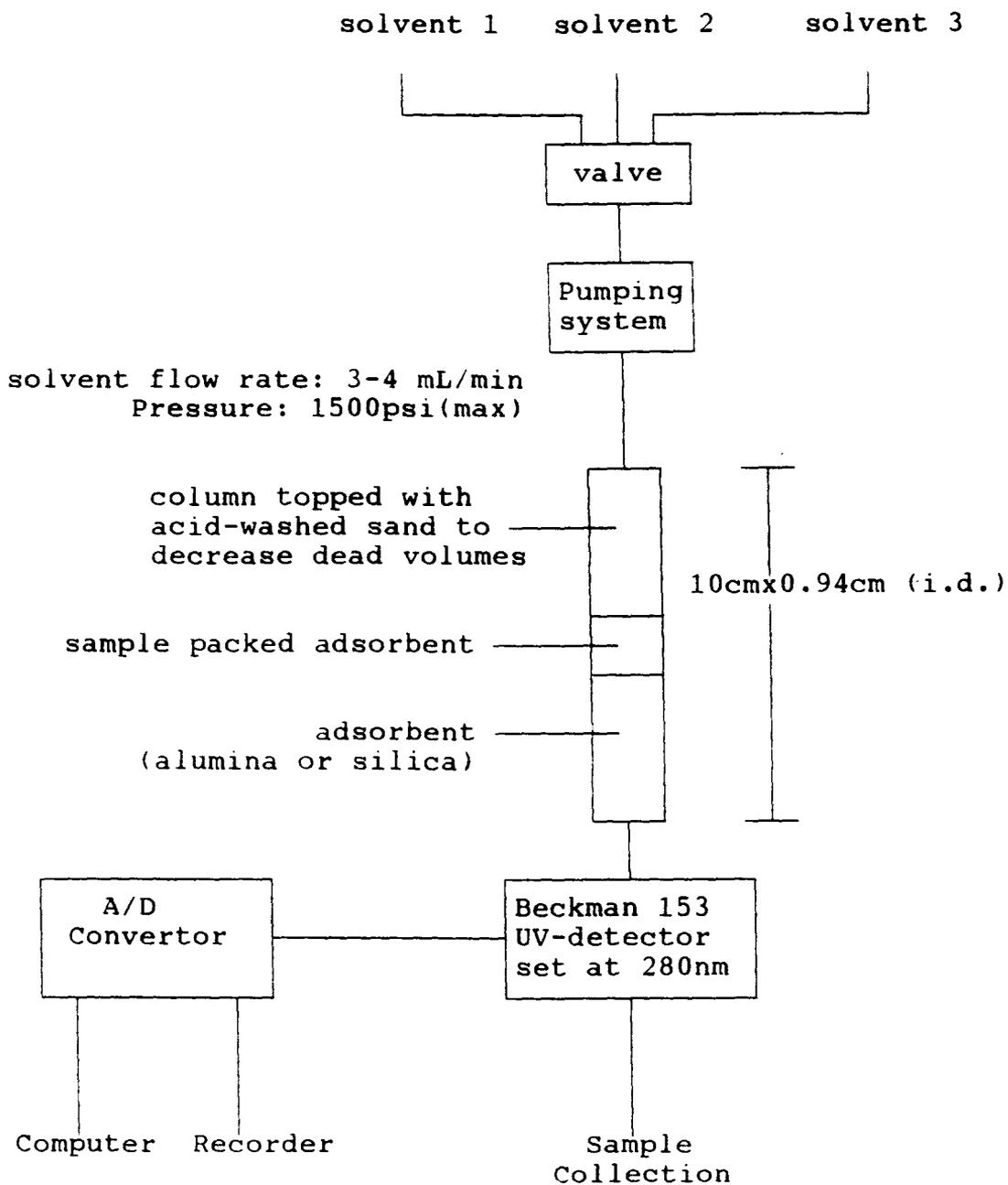
II.4 Modified Separation Method

A modification of Later's method was developed because of carry over of compounds from one fraction to another and because of the long time (12 hours) required to complete a silica column chromatography. A general schematic diagram of the modified separation method is shown in Fig 2. A medium pressure LC system was assembled which consisted of a single piston pump (Analab, Model No. B-94) pumping at a flow rate of 3-4 mL/min through a stainless steel column with the eluent passing through a Beckman analytical UV detector (Beckman Instruments Inc., Model 153, Berkeley, Calif.). The columns were made using a length of stainless steel tubing (10 cm x 0.94 cm i.d., SPE, Rexdale, Ont.) fitted with 1/2" to 1/16" reducing unions and 2 micron stainless steel frits (Niagara Valve and Fitting Ltd, Hamilton, Ontario). The wavelength of the UV detector was set at 280 nm to minimize the absorbance due to benzene. An Apple II+ microcomputer (Apple Computer Inc., Cupertino, Calif.) equipped with 12-bit analog to digital convertor and autoranging amplifier (Interactive Microwave Inc., State College, Philadelphia) was used to acquire all the chromatographic data.

II.4.1 Medium Pressure Alumina Separation

In the case of the alumina separation, two 10 cm

Fig.2: Schematic diagram of modified separation scheme.



stainless steel columns were connected in series in order to accommodate all of the required alumina adsorbent. A 0.3 gram sample of oil was adsorbed into 3 g of oven-dried alumina as described in section II.3 and packed dry into one of the columns while the other column was dry packed with 6 g of oven-dried alumina. The columns were tapped gently during packing to afford a uniform bed. Acid-washed sea sand was used to top both of the columns to ensure minimal dead volume. Hexane was used to elute the fraction A1 (the aliphatic hydrocarbon fraction), benzene to elute fraction A2 (the neutral PAH fraction) and chloroform: absolute ethanol (99:1) to elute the fraction A3 (the nitrogenous fraction). The criterion for changing from one solvent to the next eluting solvent was a tailing off of the UV-absorbing components, i.e., when the detector response had plateaued. Typical elution volumes were: A1, 20 mL, A2, 200-250 mL and A3, 130-220 mL. The solvents were removed as soon as possible at reduced pressure.

II.4.2 Medium Pressure Silicic Acid Separation

The medium pressure A3 fraction was dissolved in chloroform and evaporated onto 0.5 g of silicic acid as described above and then packed on the top of a column which contained 2 g of dry-packed silicic acid. All of the silicic acid used could be packed into one 10 cm stainless steel

column and acid-washed sea sand was used to top the column to minimize any dead volume. The column was eluted with a series of solvents in order: fraction S1, benzene:hexane (1:3), fraction S2, benzene and fraction S3, benzene:anhydrous diethyl ether (1:1). The S1 solvent (hexane:benzene, 3:1) is a slight modification to that employed by Later et al (hexane:benzene, 1:1). Typical elution volumes for the modified silicic acid chromatography were: S1, 100-160 mL; S2, 90-100 mL; S3, 70-85 mL.

In both separations, each column was freshly packed and none of the alumina or the silicic acid was reused. Each fraction was concentrated in vacuo on a rotary evaporator to approximately 4 mL and then evaporated to dryness under a stream of nitrogen gas and weighed. For sample storage and LC analyses, the residue was dissolved in a 1:4 (v:v) dichloromethane:acetonitrile solution. For GC analyses, the residues were redissolved in acetone to a concentration of approximately several mg/mL. Some fractions were also sent to Shell Research Laboratory for nitrogen determination analysis. Fractions derived from the unprocessed oil sample were dissolved in pure dichloromethane since they were insoluble in acetonitrile.

II.5 Asphaltene Separation

This asphaltene separation was only used on the

unprocessed oil sample from Peace River. The following method was kindly provided by Dr. D. MacLean, Shell Canada Ltd, Oakville. To the black gummy oil (5.5 grams) was added about 160 mL pentane to achieve a 1:30 residue:pentane ratio. This mixture was heated to the boil for 30 min with constant stirring then filtered through a coarse sintered glass frit. The filtrate was evaporated at reduced pressure to give a dark brown oil, 3.4 grams (63% mass recovery).

A 0.3 g sample of this asphaltene-depleted oil was subsequently chromatographed on 3 g of alumina using the method of Later et al.

II.6 Scaled-Up Alumina Separation

In order to obtain sufficient fraction A3 material for a ^1H - and ^{13}C -NMR spectroscopic examinations, it was necessary to scale up the alumina separation procedure about 100-fold. The height of the column was held approximately constant (5 cm) while the diameter was increased about 10-fold. (i.e., about a 100-fold increase in cross-sectional area of the column). In Later's method, one weight of oil adsorbed onto 10 weights of alumina was packed atop 20 weights of alumina. This ratio was scaled up directly in two separate experiments wherein 35 g and 50 g of Athabasca Tar Sand oil were adsorbed onto 350 g of neutral alumina; this material was then added to the top of 700 g alumina contained

in a 2000 mL Buchner funnel (13.5 cm i.d.). The height of this "column" was approximately the same as the columns used for separations on 0.3 g of oil while the area was 90 times greater. A layer of acid-washed sea sand was added to the top of the "Buchner" column to prevent any disturbance of the alumina bed.

The volumes of solvents passed through the "Buchner column" were increased by 90 times compared to the volumes used in 0.3 g oil experiments. Fraction A1 was eluted with 2.5 L of hexane, fraction A2 with 6 L of benzene and fraction A3 with 8 L chloroform: absolute ethanol (99:1). In the 35 g separation of Tar Sand, 0.67 g of fraction A3 (1.9 wt%) was collected while in the 50 g separation the yield was 1.36 g (2.7 wt%).

II.7 Analytical Methods

II.7.1 Mass Spectrometry

II.7.1.a Low Resolution Mass Spectrometry

Direct inlet probe electron impact (EI) and chemical ionization (CI) mass spectrometry were performed using a VG 7070-F mass spectrometer (VG Analytical, Altrincham, U.K.). Methane and ammonia gases (Matheson, Whitby, Ontario) were used as reactant gases in the CIMS experiments. In each analysis, approximately 20 mg weight equivalent of oil sample was analyzed. Details of various parameters for the operation of the mass spectrometer in each ionization mode are listed in Table 5. A PDP 11/24 data system (Digital Equipment Co.) was used for data acquisition and analysis.

II.7.1.b High Resolution Mass Spectrometry

A VG ZAB-E mass spectrometer (VG Analytical, Altrincham, U.K.) was used to performed the high resolution mass spectrometric measurements. Perfluorokerosene-H (PCR Inc., Gainesville, Florida) was used as the reference compound for peak matching experiments and as the standard for the

TABLE 5: Experimental Conditions used in Probe Mass Spectrometry

Operating Parameter	Electron Ionization	Chemical Ionization
Electron energy	70 eV	50 eV
Emission	100 μ A	100 μ A
Source Temperature	200°C	200°C
Probe Temperature:		
Initial Temperature	30°C	30°C
Temperature Programming	+4°C/sec	+4°C/sec
Final Temperature	300°C	300°C ¹
Accelerating voltage	4 KV	2.5 KV
Source Pressure	10 ⁻⁶ torr	CH ₄ CIMS: ² CH ₅ ⁺ :C ₂ H ₅ ⁺ =1:1 NH ₃ CIMS: NH ₄ ⁺ :(NH ₄ •NH ₃) ⁺ =1:20
Resolution (10% valley definition)	1000	1000

- 1: for the Unprocessed Peace River Reisdue oil sample, the final temperature of the probe was increased to 400°C.
- 2: the ratio of the ions was measured by the intensity of each ion in the ion source.

high resolution MS experiments. The resolution of the instrument was set at 6250 to give a 3 decimal point range of accuracy. Data were stored and processed on a Digital Equipment PDP 11/73 data system.

II.7.2 Reverse Phase Liquid Chromatography (RPLC)

A Hewlett-Packard 1090 liquid chromatograph equipped with diode-array detector and tertiary solvent capability was used in conjunction with a HP 85B computer and a HP 7470A plotter. All analyses were performed on a Vydac 201-TP column (25 cm x 4.6 mm i.d. 5 μ m, Mandel Scientific Co., Rockwood, Ont.) at 45°C and approximately 3 mg (weight equivalence) of oil sample was injected in each analysis. A standard gradient elution program was used for all RPLC work (except where noted): 60% acetonitrile/water increasing to 100% acetonitrile over 30 min then a hold at 100% acetonitrile at a flow rate of 1.0 mL/min. For fractions derived from the unprocessed Peace River oil, a double sequential gradient was applied: following the 30 min acetonitrile-water gradient, 100% acetonitrile was maintained for 20 min before a 20 min 0% to 100% dichloromethane in acetonitrile gradient, followed by 100% dichloromethane. Chromatographic information was acquired with two wavelength programs: the first wavelength program was 254 nm with a bandwidth of 4 nm and the second program was 300 nm with a

bandwidth of 200 nm. A UV/visible spectrum was collected and stored every 640 msec; this is the shortest time between spectral acquisitions due to limitations in the memory available on the computer diskettes. UV spectra were plotted from 210 to 400 nm in all LC runs. Data processing was done on a Hewlett-Packard ChemStation equipped with a HP ColorPro plotter.

II.7.3 Liquid Chromatography-Mass Spectrometry (LC-MS)

The LC-MS experiment was performed by Dr. M.A. Quilliam at the NRC Atlantic Research Laboratory, Halifax. A HP 1090 liquid chromatograph was interfaced to a VG ZAB-EQ mass spectrometer with a VG belt-transport LC-MS interface (VG Analytical, Altrincham, U.K.). The eluent from a 25 cm Vydac 201-TP reverse phase column (identical to that described in section II.7.2) was split 1:1 between a UV-visible diode array detector and the LC-MS interface. The same gradient elution used in section II.7.2 was used. The temperature of the ion source was maintained at 220°C with an ammonia gas pressure of 3×10^{-5} Torr. Mass spectra were acquired using the full scan mode with a scan range of 600 to 100 amu at 2 sec/dec with an exponential downscan and an interscan delay of 0.5 sec. UV-visible spectral data were stored in a HP ChemStation and the mass spectrometric data were stored in a Digital Equipment PDP 11/73 data system.

II.7.4 Gas Chromatography

Capillary column gas chromatography was performed with a Varian model 3700 gas chromatograph (Varian Canada Inc., Georgetown, Ont.) equipped with a flame ionization detector. A 30 m narrow bore (0.25 mm) DB-5 fused silica column (polymethyl +5% phenyl siloxane, 0.25 μ film thickness, J&W Scientific, Orangevale, Calif.) was used for the GC analyses. The column used was calibrated with n-alkane standards from C₈ to C₃₄. All samples were dissolved in acetone before the analysis. Sample introduction, approximately 6 mg (wt. eq.) of oil/analysis, was by cold, on-column injection with a temperature program from 60 to 300°C at +8°C min⁻¹ and hold at 300°C to 50 min. The head pressure of helium gas was 5 psi and the FID attenuation was set at 10⁻¹¹ AMP/mV. An Apple II+ microcomputer (Apple Computer Inc., Cupertino, Calif.) equipped with a 12-bit analog to digital convertor and autoranging amplifier (Interactive Microware Inc., State College, Phil.) was used to handle data acquisition and storage.

II.7.5 Gas Chromatography-Mass Spectrometry (GC/MS)

Combined gas chromatography-chemical ionization (ammonia) mass spectrometry (GC/CIMS(NH₃)) was performed with

a Varian Model 3700 gas chromatograph attached to a VG-7070F mass spectrometer. The 30 m narrow bore DB5 column described in the above section was introduced directly into the ion source of the mass spectrometer. The head pressure of the He carrier gas at the on-column injector was 5 psi. The pressure of the ammonia gas in the ion source was adjusted so that the ratio between the NH_4^+ and the $(\text{NH}_4 \cdot \text{NH}_3)^+$ ions was 20 to 1. The temperature program was identical to that in section II.7.5; the ion source was maintained at 300°C during the run. Acquisition was performed in the full scan mode from 550 to 100 amu at 2 sec/dec with a interscan delay of 1 sec. Data was acquired and stored on the Digital Equipment PDP 11/24 data system.

II.7.6 Proton and Carbon-13 NMR

A 1.2 g sample of the combined A3 sample obtained from the scaled-up alumina separations of 35 and 50 grams of Athabasca Tar Sand oil was dissolved in a minimum (about 1.8 mL) of deuteriated benzene and then filtered into a clean 10 mm o.d. NMR tube. A Bruker AM500 NMR spectrometer operated at ambient temperature was used for the analysis and data processing. The NMR spectrometer frequency was 500 MHz for the proton NMR analyses and 125 MHz for the ^{13}C NMR analyses. For the ^1H spectrum, a total of 8 scans were acquired and 144 scans for the ^{13}C spectrum.

An T_1 inversion-recovery experiment was performed in order to obtain the carbon T_1 values. A π pulse was first applied to the sample and the peak intensities were measured at different variable delay time after the application of another $\pi/2$ pulse. The relaxation delay time was set at 3 sec.

The ^{13}C spectrum was also edited by the distortionless enhancement by polarization transfer (DEPT) to provide identification of methyl (CH_3), methylene (CH_2), methine (CH) and quaternary carbons. A proton-carbon coupling constant of $^1J_{\text{CH}}=138$ Hz was assumed and the DEPT spectra were acquired at $\theta=3\pi/4$ and $\theta=\pi/2$.

II.7.7 Nitrogen Determination Procedure

The nitrogen determinations were performed under the supervision of Mr. D. Crosby at the Shell Canada's Oakville Research Centre. Crude oils and chromatographic fractions for analysis were redissolved in Cyclosol 63, a nitrogen-free solvent with a boiling range from 184 to 206°C. The samples were introduced through a 10 ul syringe into a boat injector in an Antek chemiluminescence analyzer.

III. RESULTS AND DISCUSSION

III.1 Separation Methods

III.1.1 Selection of the Separation Method

The first goal of the thesis work was to find a good separation method for the analysis of nitrogenous compounds in heavy oil samples. The criteria for the selection of such a separation method should include good reproducibility, ease of use, rapid turnover time and low cost. In addition, this method should be compound class selective and applicable to heavy oils.

Of the twenty or so methods examined approximately one-half of them used liquid-liquid extractions followed by one or more high resolution chromatographic steps. These methods were discounted primarily because they exhibit poor compound class selectivity, low capacity and poor reproducibility. Most of the remaining methods used low resolution silica gel and/or alumina chromatographic separations as the basis for their approach. These latter methods were examined in detail to see if they met our criteria; our attention was focused on those methods that had been applied to heavy oils since we did not want to get involved in extensive method development in adapting a light oil method to tar sand products.

The method of Later et al (F0023) used for the isolation of the nitrogenous compounds from Solvent Refined

Coal heavy oils (SRC II, boiling range from 260 to 450°C) was selected as the best method for the isolation of the nitrogenous compounds from heavy syncrude distillates.

In the Later method, a neutral alumina column was used to separate the oil sample into three fractions: an aliphatic fraction, a PAH fraction and a nitrogen-containing fraction. The nitrogenous fraction was then further separated on a silica gel column into three subfractions containing different compound classes, i.e., secondary-PANH, tertiary-PANH and amino-PAH.

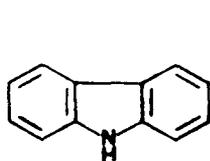
The reasons for the selection of this method over the others are three-fold. First, this method had been applied successfully to the heavy SRC II oil samples and had proven to give very good results (F0012, F0023, F0025, F0107, F1041, F1183). Second, this method was able to separate the nitrogen compounds into major compound classes better than other methods examined. Third, this method appeared to be a rapid, inexpensive procedure with good capacity. Also, it appeared likely that the separations could be scaled up from the 300 mg levels used by Later.

III.1.2 Application of the Separation Method to Heavy Oils

Three oil samples were kindly provided by Shell Canada Ltd. The first oil sample was an Athabasca Tar Sand syncrude distillate (called "Tar Sand") with a boiling range of 200 to

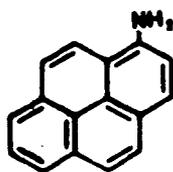
540°C and a nitrogen content in the 700 ppm range. The second sample was an unprocessed Peace River residue sample (hereafter called "unprocessed residue") with a nitrogen content in the 4000 ppm range. The last sample was the above Peace River residue after the oil had been processed (hereafter called "processed residue") with a boiling range from 111 to 535°C and a nitrogen content about 200 ppm.

In a typical separation in the present work, an oil sample (300 mg) was first subjected to alumina chromatography to afford three fractions: designated A1, the aliphatic hydrocarbon fraction, A2, the PAH fraction and A3, the nitrogenous PAH (PANH) fraction. The A3 fractions from 300 mg samples of the different oils weighed only a few milligrams. The A3 fraction was further separated on a silicic acid column; a sequence of three eluting solvents gave three fractions designated S1, S2 and S3. Secondary PANH such as carbazole eluted in fraction S1, followed by amino and tertiary PANH such as aminopyrene and quinoline, respectively, in fraction S2 and finally tertiary PANH in fraction S3.



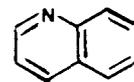
Carbazole

(M.W.=167)



Aminopyrene

(M.W.=217)



Quinoline

(M.W.=139)

Quantitatively, about 210 mg of the original 300 mg Tar

Sand oil sample (68 wt %) was found in the aliphatic A1 fraction, another 50 mg (18%) in the PAH A2 fraction, and only about 8 mg (3%) in the A3 fraction. In the silica separation, about 5 out of 8 mg of the original A3 fraction was found in the S1 fraction (63 wt%), 0.8 mg in S2 (10%) and 1.6 mg (20%) in S3.

In the typical residue separation, approximately 210-240 mg (70-80 wt%) of the original 300 mg were collected in fraction A1, 35 mg (10%) in fraction A2, and only about 1.2 mg (0.4%) in the nitrogenous A3 fraction. After the silica gel separation, almost 1 mg of the A3 fraction was found in fraction S1, 0.4 mg in fraction S2 and 0.2 mg in fraction S3.

The A3, S1, S2 and S3 fractions were analyzed by GC and RPLC. The gas chromatographic profiles of the A3 and S1 fractions were always very complex with many unresolved components, giving rise to a broad hump of peaks (see Fig. 3). The RPLC chromatograms of the A3 and S1 fractions were also very complex but showed greater promise for further analysis; the chromatograms resulting from RPLC analysis of A3, S1, S2, S3 fractions from the Tar Sand oil sample are shown in Figs. 3b and 4. A direct comparison of the chromatograms of the silica gel fractions S1, S2 and S3 (Fig. 4) with the A3 fraction chromatogram (Fig. 3b) showed the S1 chromatogram to be almost identical to the A3 chromatogram suggesting that most of the nitrogenous compounds in the A3 fraction eluted in the S1 secondary-PANH fraction.

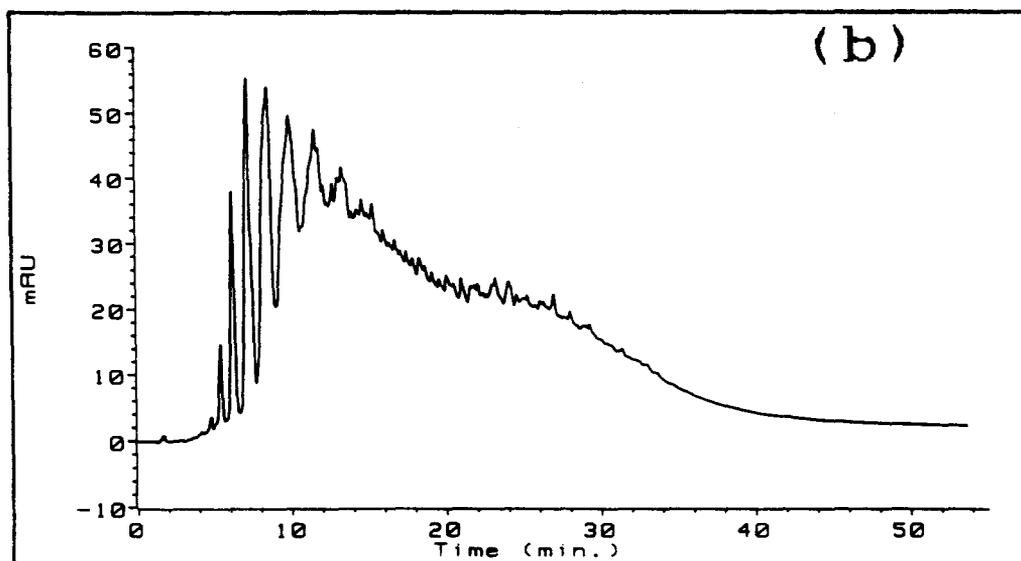
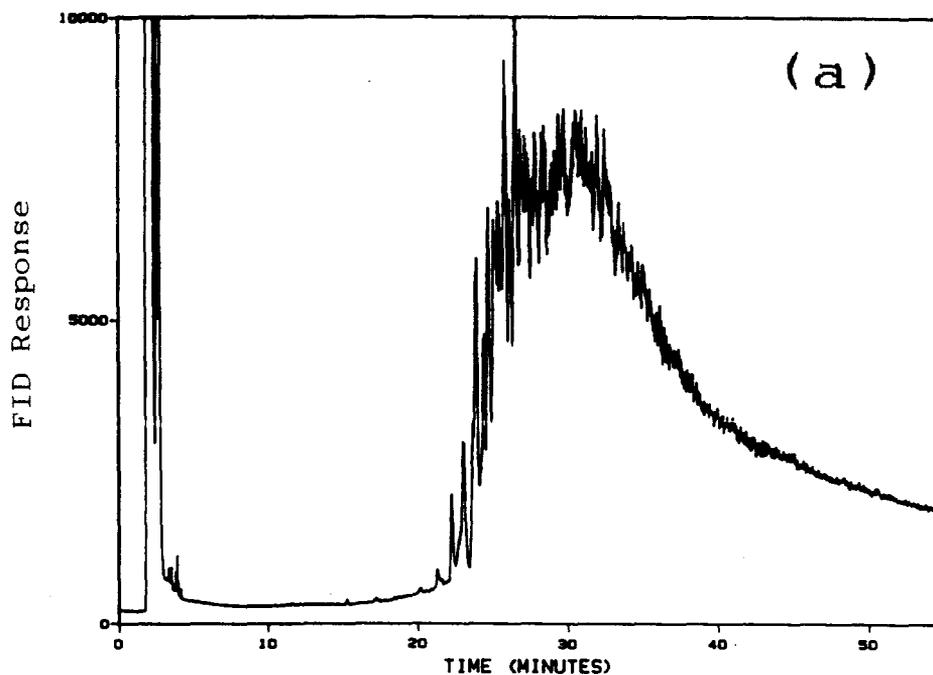


Fig.3 (a) Capillary column gas chromatogram of Tar Sand A3 fraction. Conditions: 30 m x 0.25 mm DB-5 narrow bore fused-silica capillary column; temperature programmed from 60°C to 300°C at 8°C/min, then hold at 300°C to 55 minutes. (b) Reverse phase liquid chromatogram of Tar Sand A3 fraction. Standard RPLC conditions: 25 cm x 4.6 mm Vydac 201-TP C-18 column, column temperature, 45°C; flow rate, 1 mL/min; solvent gradient from 60% acetonitrile/water to 100% acetonitrile over 30 minutes and hold at 100% acetonitrile for a further 30 minutes. Detector: diode array detector at 300 nm with a 200 nm bandwidth.

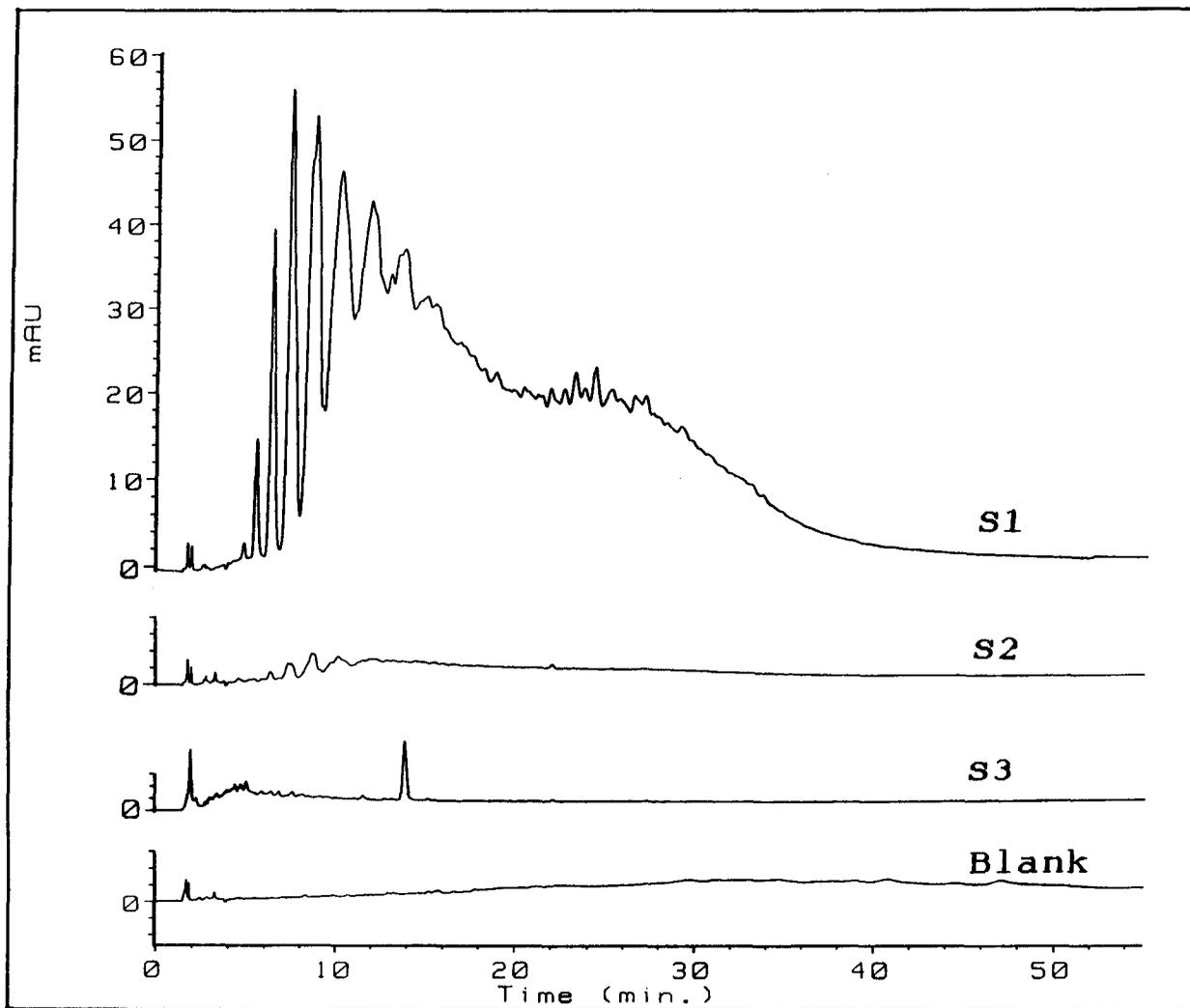


Fig.4 Reverse phase liquid chromatograms of Tar Sand S1, S2 and S3 fractions. Conditions same as Fig.3b except detection at 254 nm.

Samples of these fractions were kindly analyzed for their nitrogen content by Shell Canada Ltd and the results for the Tar Sand fractions are shown in Table 6. The data in the second column of number in Table 6 is typical. About 16% of the total nitrogen was found in the A2 fraction and 80% in the A3 fraction. The silica gel chromatography, further separated the nitrogen components in fraction A3 into fractions S1 (>60% of the total nitrogen in the original oil sample), S2 (4%) and S3 (9%).

The RPLC chromatogram of the A3 fraction derived from the processed residue (Fig. 5) is very similar to the chromatogram of the Tar Sand A3 fraction. While the chromatogram is very complex with many unresolved compounds, several distinct peaks were observed at retention times of 41, 46, 53, 58 and 62 min. Some of these peaks were collected, evaporated to dryness and analyzed by probe mass spectrometry.

The EI mass spectra of the 41 and 46 minute peaks are shown as inserts in Fig. 5. The 41 minute peak showed very clean spectrum with a major peak at $m/z=276$ and its doubly charged counterpart at $m/z=138$. The presence of a doubly charged ion in the spectrum strongly suggested that this component was a polycyclic aromatic compound with a molecular weight of 276 amu. It was unlikely that this compound was a nitrogen-containing species because with an even number of

Table 6: Nitrogen Distribution of the Athabasca Tar Sand Oil Using Different Separation Methods

Fraction	<u>Nitrogen Distribution</u>		Scaled Up	
	<u>Later Method</u>	<u>Modified Method</u>		
	(1)	(2)		
	L.P. Al ₂ O ₃ L.P. SiO ₂	L.P. Al ₂ O ₃ M.P. SiO ₂	M.P. Al ₂ O ₃ M.P. SiO ₂	
Crude Oil	685 ppm	754 ppm	737 ppm	-
<u>Alumina Separation:</u>				
A1	-	-	> 1 ppm (>0.1%)	-
A2	-	120 ppm (1st 100mL) (16%)	212 ppm (29%) 64 ppm (9%) (2nd 100mL)	91 ppm (13%)
A3	616 ppm (90%)	602 ppm (80%)	438 ppm (59%)	540 ppm (75%)
<u>Silicic Acid Separation:</u>				
S1	425 ppm (62%)	457 ppm (61%)	333 ppm (45%)	
S2	41 ppm (6%)	28 ppm (4%)	14 ppm (2%)	
S3	59 ppm (9%)	69 ppm (9%)	19 ppm (3%)	

Note: The above value are all within a standard deviation of 10%.

L.P.= Low Pressure Open Column system

M.P.= Medium Pressure system

% = Percentage of total nitrogen from crude oil

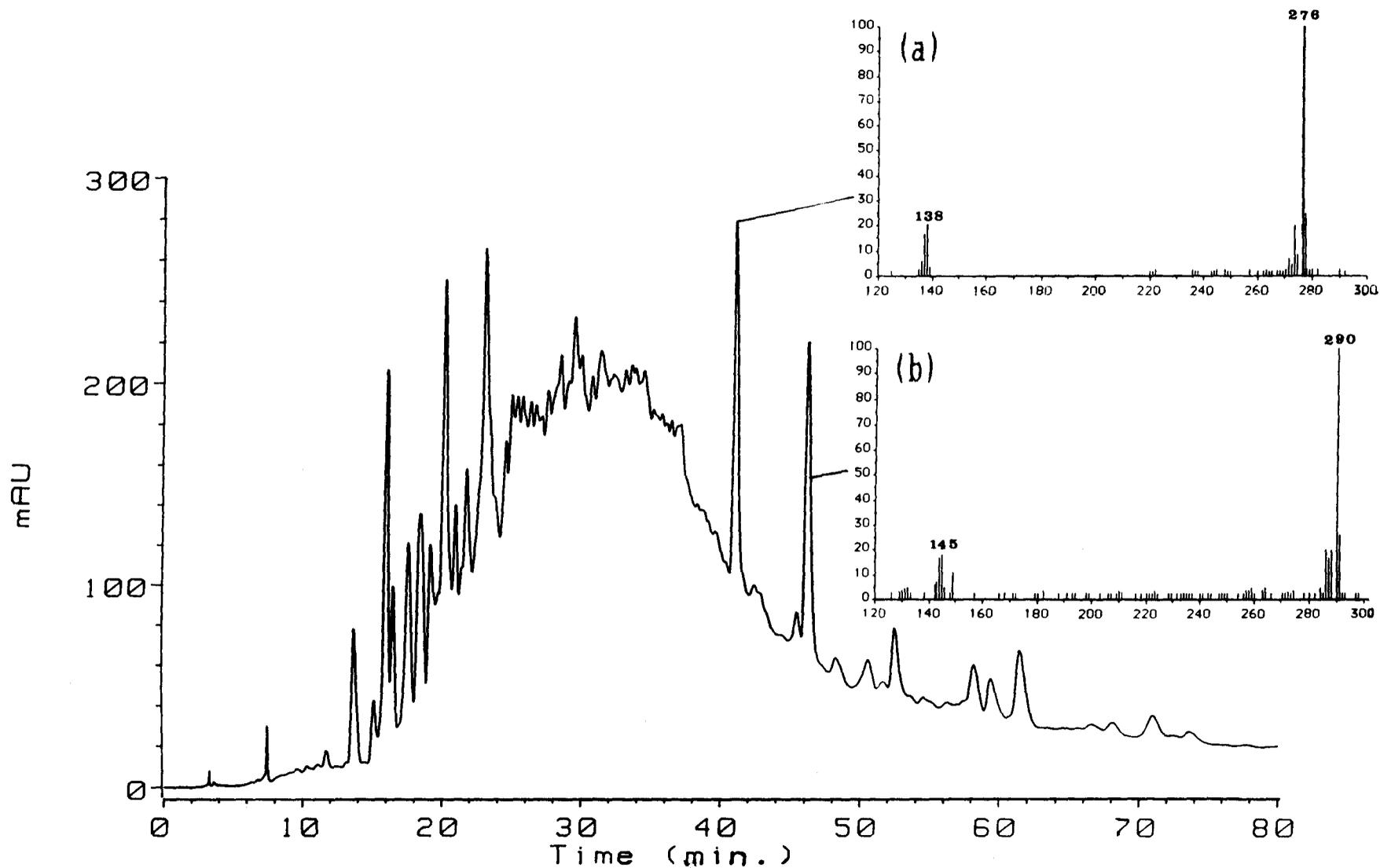


Fig.5 Reverse phase liquid chromatogram of processed residue A3 fraction separated by Later's scheme. Conditions same as in Fig.3b except a dual column system was used, column temperature, 25°C and detection at 254 nm. Inset (a): probe EI mass spectrum of 41 minute peak. Inset (b): probe EI mass spectrum of 46 minute peak.

nitrogen atoms would be required in the molecule. The 46 minute peak showed ions at $m/z=290$ and $m/z=145$ again suggesting the presence of a polycyclic aromatic compound of molecular weight 290. These mass spectrometric results together with the nitrogen determination data indicated that the alumina chromatography of Later et al was not cleanly fractionating the PAH from the nitrogen-containing compounds; some nitrogen compounds ($\approx 16\%$) were eluting in the A2 fraction while some PAH were being carried over into A3 fraction.

Turning to the silica gel chromatography, the RPLC chromatograms of fractions S1 and S2 (Fig. 4) showed some similarities even though fraction S2 contained less UV-absorbing material than S1. The major peaks in fraction S2 seemed to be the same as those in S1 although present to a much lesser amount. The probe EIMS spectra of these Tar Sand silica gel fractions (Fig. 6) showed that peaks in the spectrum of fraction S1 were also found, with lesser intensities, in the spectrum of fraction S2. Both the RPLC and the mass spectrometric results indicated that some S1 components had spilled over into the S2 fraction.

III.1.3 Summary

Overall, Later's method had some good features and some not-so-good features; but basically, the method worked. With

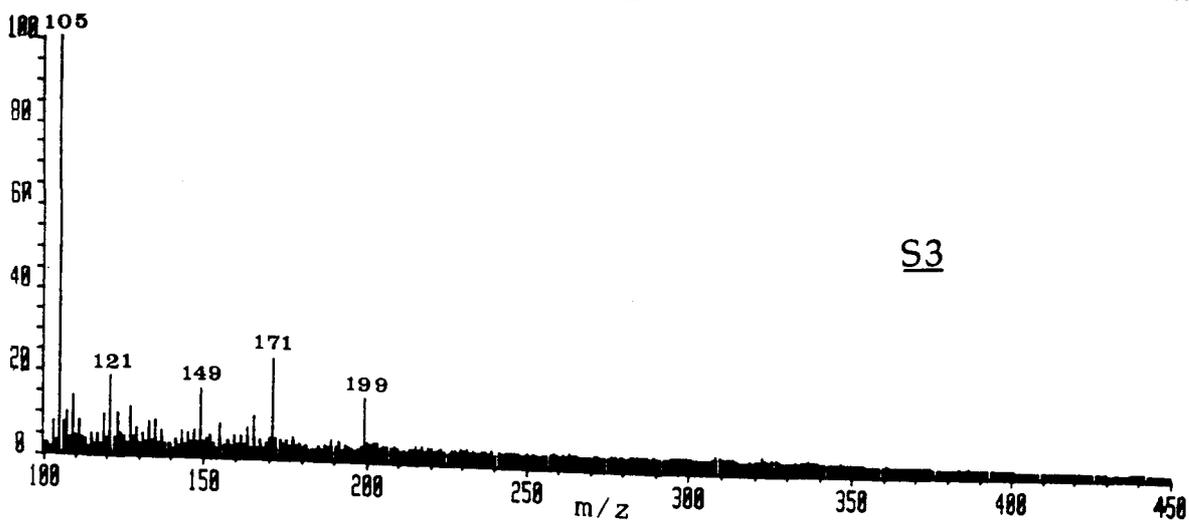
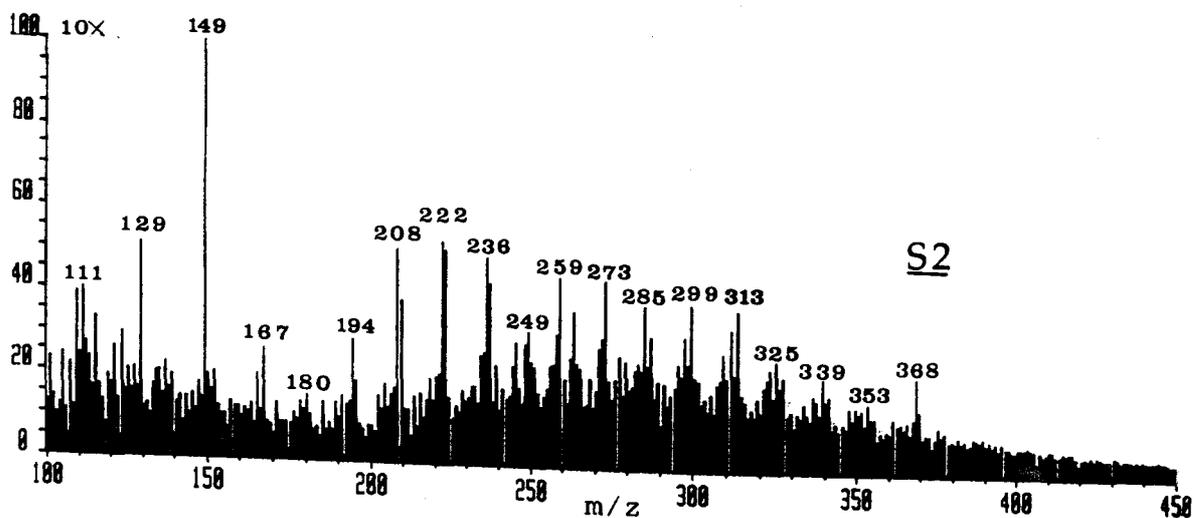
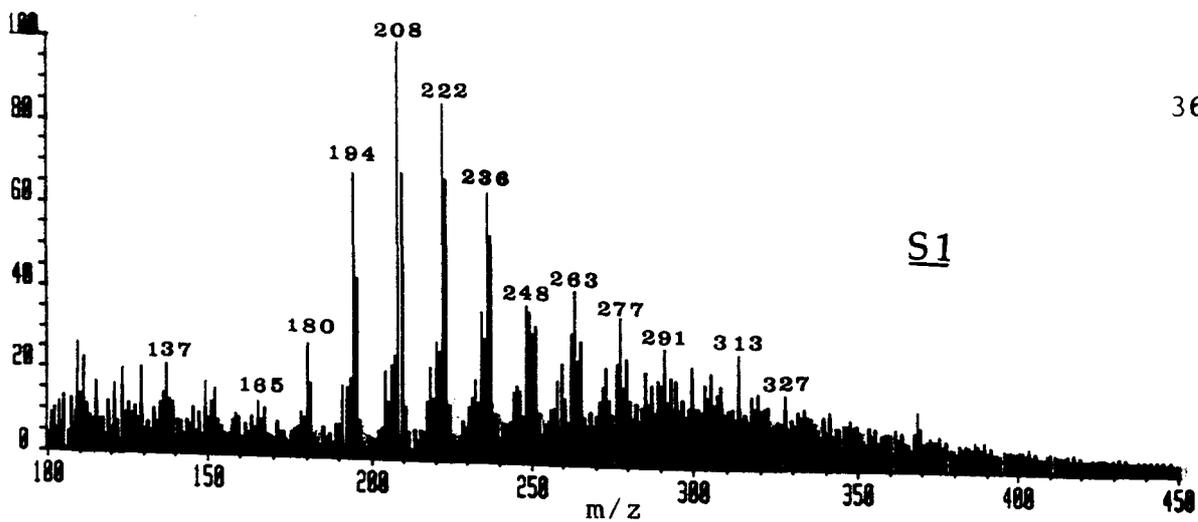


Fig.6 Averaged EI mass spectrum of the Tar Sand S1 fraction (1 wt eq.), S2 fraction (10 wt eq.) and S3 fraction (1 wt eq.). Mass spectral conditions as listed in Table 5.

this procedure we were able to chromatograph heavy oil samples such that roughly 80% of the total nitrogen was found in a fraction which accounted for only a couple of percent of the total mass of the original sample. The aliphatics and almost all of the aromatics were removed by the alumina column. Quantitatively, more aliphatics (about +10 wt%) were found in the processed residue A1 fraction than in the Tar Sand A1 fraction while more PAH and PANH were found in the Tar Sand A2 and A3 fractions than in the corresponding processed residue fractions. In the silica gel separations of both oil samples, the S1 fractions contained most of the nitrogenous material while the components in the S2 fractions seemed to be primarily spillover from S1 fractions.

On the other side of the ledger, it was unfortunate that neither the alumina nor the silicic acid separations afforded the clean fractionations we had hoped for. Carry-overs of materials from one fraction to another led to the incomplete isolation of one compound class from another. In addition, the silicic acid specified by Later et al was very fine-meshed, thus, the silica columns were extremely tedious to elute, requiring a total of 12 hours. It was decided that we would attempt to improve the separation scheme with the goals of cleaner fractionation by compound class and faster sample throughput.

III.1.4 Modified Method

For both the alumina and silica separations our approach was the same. First, pack the chromatographic supports into stainless steel columns and use a medium pressure pump to pump the solvent so as to reduce the elution times. Second, place a UV detector in the effluent stream to determine when to change eluting solvents.

III.1.4.a Modified Alumina Separation

A medium pressure LC system was constructed using two 10cm x 0.9cm (i.d.) stainless steel columns placed in series connected to an inexpensive UV detector (280 nm). The termination of any fraction collection was determined by the return of the absorption peak back to its baseline.

In Table 7, the volumes of solvents and the times of elution of Later's method and of the modified scheme needed to separate two identical oil samples are listed. The most significant difference between the original and the modified methods was the volumes of solvents used to elute each fraction: in Later's method 50 mL of benzene was used to elute fraction A2 followed by 70 mL of chloroform: absolute ethanol (99:1) for A3; in the modified scheme 200 mL of benzene was needed for the A2 collection followed by either 130 mL (processed residue) or 220 mL (Tar Sand) of

TABLE 7: Elution Times and Volumes of Solvents Used in the Separation Methods

<u>Volumes of Solvents and Total Elution Time</u>			
<u>Fraction:eluent</u> s	<u>Later's method</u>	<u>Modified method</u>	
		<u>Tar Sand</u>	<u>Processed Residue</u>
<u>Alumina Separation:</u>			
A1: hexane	20 mL	20 mL	20 mL
A2: benzene	50 mL	250 mL	200 mL
A3: chloroform:EtOH (99:1)	70 mL	220 mL	130 mL
Total Time Required (average)	2 hours	2.5 hours	2.5 hours
<u>Silicic Acid Separation:</u>			
S1: hexane:benzene (v:v)	50 mL (1:1)	100 mL (3:1)	160 mL (3:1)
S2: benzene	30 mL	90 mL	100 mL
S3: benzene:ether (1:1)	50 mL	70 mL	85 mL
Total Time Required (average)	12 hours	2 hours	2 hours

chloroform: absolute ethanol (99:1).

The chromatogram obtained from the modified alumina separation of the processed residue sample shown in Fig. 7 was typical of these separations. The chromatogram shows that 50 mL of benzene (the volume suggested by Later) was insufficient to elute all the UV-absorbing A2 components; in Later's scheme those components requiring more than 50 mL of benzene would be collected in the A3 fraction. This increase in the A2 fraction elution volume should reduce the PAH spill-over into the A3 fraction. However, a determination of the nitrogen content in A2 would be needed to assess the impact of this additional solvent.

The nitrogen determination results of Tar Sand fractions separated by the modified alumina method (third column in Table 6) showed that the percentage of the nitrogenous components that eluted in the A2 fraction had increased dramatically. While only 16% of the total nitrogen had eluted in the A2 fraction in Later's separation, 38% was collected in the same fraction in the modified method. Consequently, only about 60% of the total nitrogen eluted in the A3 fraction whereas 80% of the nitrogen had eluted in the A3 fraction obtained by Later's method.

The RPLC chromatogram of the processed residue A3 fraction separated by the modified alumina method is shown in Fig. 8. On comparing this chromatogram with Fig. 5, the two chromatograms were quite similar in the low molecular weight

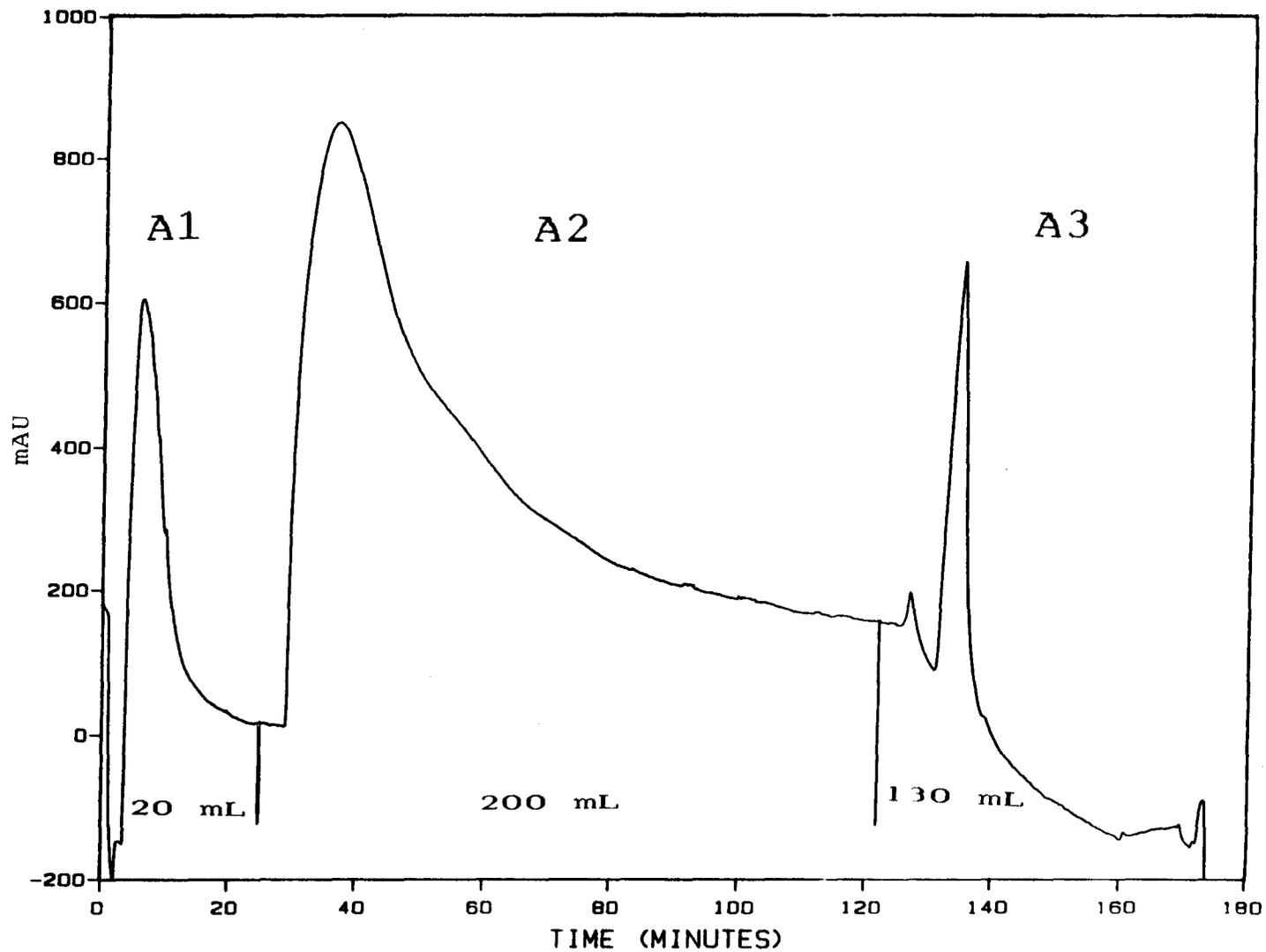


Fig.7 Chromatogram of the modified alumina separation of the processed residue. Fraction A1 eluted with 20 ml hexane, fraction A2 with 200 ml benzene and fraction A3 with 130 ml chloroform:ethanol (99:1). Detection at 280 nm.

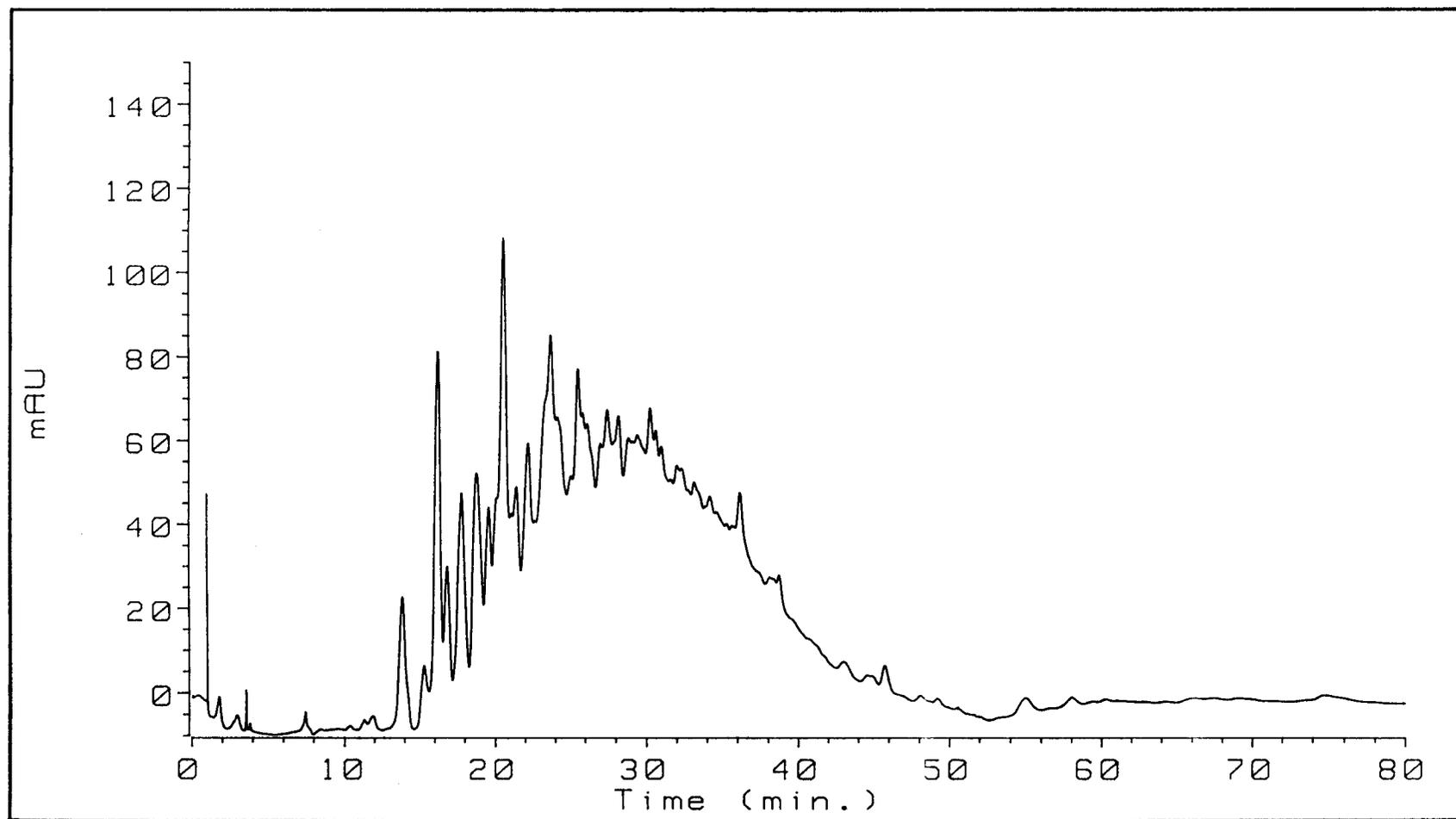


Fig.8 Reverse phase liquid chromatogram of processed residue A3 fraction separated by modified alumina chromatography. Conditions same as Fig.5.

(short retention time) region but somewhat different in the long retention time region. Most important of all, the PAH peaks that were found in Fig. 5 were not observed in the modified A3 fraction chromatogram. The chromatographic and nitrogen determination results indicate that while the PAH contamination had been reduced dramatically, a substantial portion of the nitrogenous components were lost from the "nitrogen fraction". The elution procedure of Later et al was clearly the better procedure to follow.

III.1.4.b Modified Silicic Acid Separation

Preliminary results on the silica separation of an Athabasca Tar Sand A3 sample showed that some components from fraction S1 tended to spill over into fraction S2. This carry-over might be explained in two ways. First, the volume of 1:1 hexane:benzene (50 mL) was insufficient to elute all the S1 components. Second, the solvent strength of the S1 solvent was not strong enough to elute all the S1 components. Thus, a mixture containing two standard compounds, carbazole (a 2°-PANH) and 1-aminopyrene (an amino-PAH), was chromatographed on silicic acid in order to determine the solvent strength to minimize this spill-over. Carbazole was selected because it should be one of the last eluting compounds in fraction S1; aminopyrene was chosen because it should elute quite early in the S2 fraction. These two

compounds were chromatographed on silicic acid with different solvents in order to optimize the solvent strength so that only carbazole would be collected in fraction S1 and aminopyrene in fraction S2.

To accomplish this, the same amounts of a mixture of carbazole and aminopyrene were chromatographed on two identical silica gel columns. In each case, the silica gel was packed into a 10 cm x 0.96cm i.d. stainless steel column and the eluent passed through a 280 nm UV detector. Column one was eluted with 100 mL of a 1:1 benzene:hexane solution for S1 collection while column two was eluted with a 1:3 benzene:hexane solution; then both columns were eluted with 75 mL of benzene for S2 collection. The chromatograms of these separations are shown in Fig. 9 and Fig. 10, respectively.

A simple comparison between the two chromatograms in Figs.9 and 10 shows some major differences. First, the peak area of the S1 fraction in Fig. 9 was greater than the corresponding fraction in Fig. 10, suggesting that more material has been eluted with 1:1 benzene:hexane. Second, in Fig. 9 the UV absorbance toward the end of the S1 collection did not return to a level baseline; by contrast, a level baseline was obtained with the 1:3 benzene:hexane solvent. Third, the areas under the S2 peaks also differed, indicating that more material had eluted in the S2 fraction from the column which had been eluted with the less polar solvent

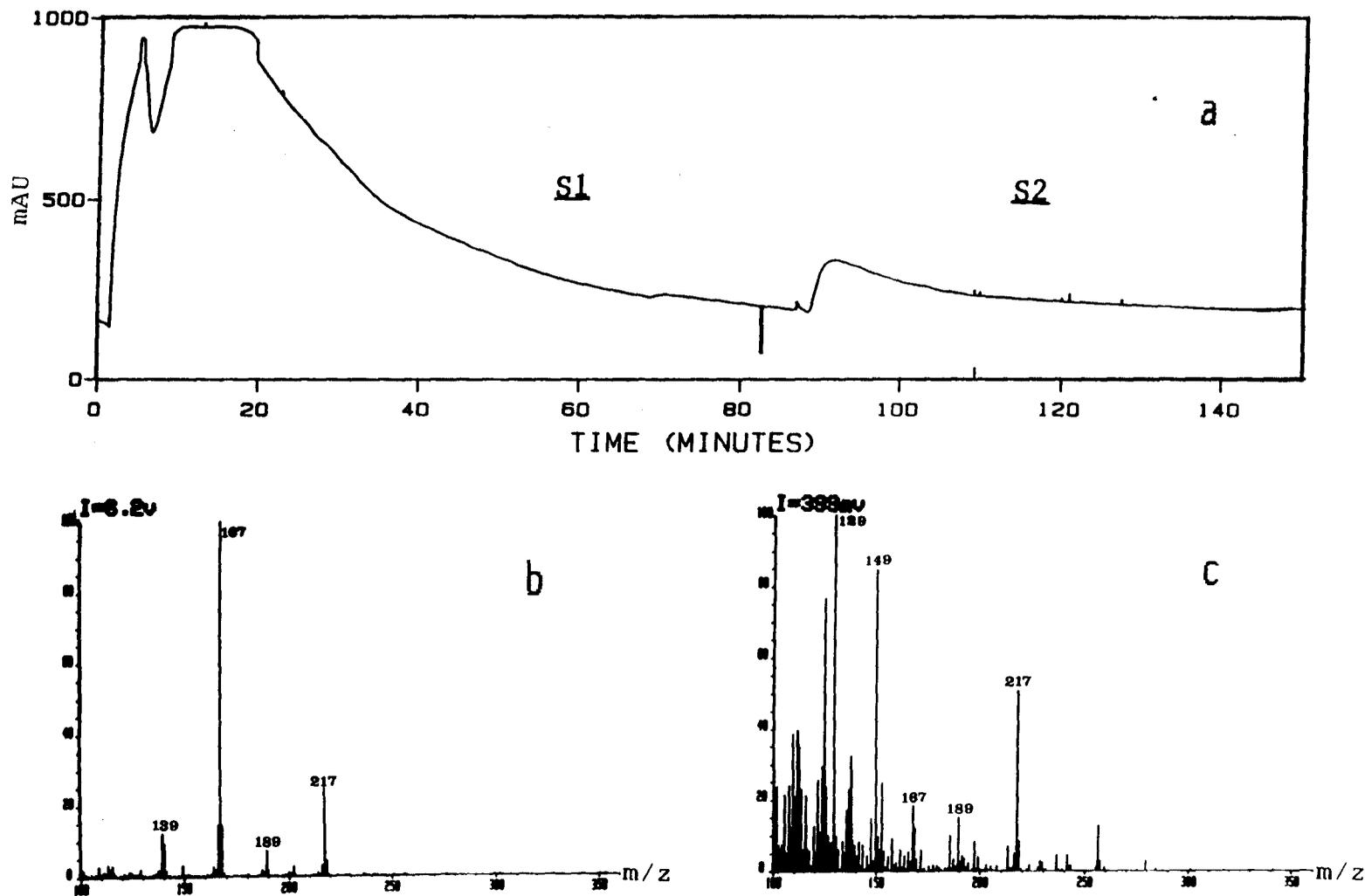


Fig.9 (a) Modified silicic acid separation of standard compounds, carbazole and aminopyrene. S1 fraction: 100 ml benzene:hexane (1:1); S2 fraction: 70 ml benzene. Detection at 280 nm. (b) Probe EI mass spectrum of combined S1 eluent. (c) Probe EI mass spectrum of combined S2 eluent. (I: voltage at detector of base peak in mass spectrum. For display base peak set at 100% relative intensity.)

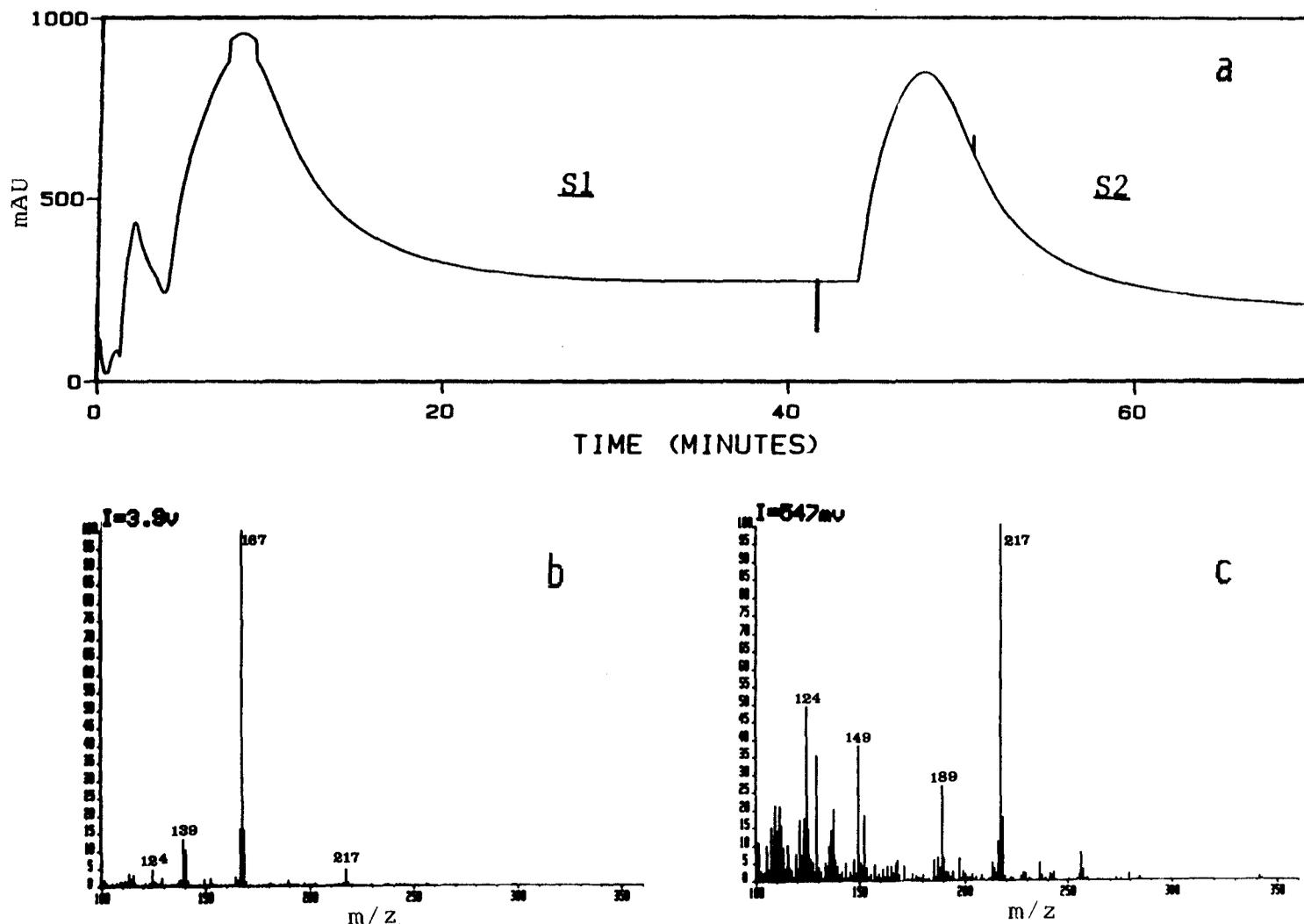


Fig.10 (a) Modified silicic acid separation of standard compounds, carbazole and aminopyrene. S1 fraction: 100 ml benzene:hexane (1:3); S2 fraction: 70 ml benzene. Detection at 280 nm. (b) Probe EI mass spectrum of combined S1 eluent. (c) Probe EI mass spectrum of combined S2 eluent. (I: voltage at detector of base peak in mass spectrum. For display base peak set at 100% relative intensity.)

(Fig. 10).

The S1 and S2 fractions from both columns were collected, evaporated to dryness and analyzed by probe EIMS. The EI mass spectrum of each fraction is inserted at the bottom of Figs.9 and 10, respectively. The mass spectrum of S1 material eluted by the 1:1 benzene:hexane solvent shows a base peak at $m/z=167$ (carbazole) and a smaller peak (25%) at $m/z=217$ (aminopyrene); the mass spectrum of fraction S2 shows a small aminopyrene peak and an even smaller carbazole peak. By contrast, the mass spectrum of the S1 fraction collected from the 1:3 benzene:hexane solvent shows a base peak at $m/z=167$ due to carbazole and a small (5%) peak at $m/z=217$ due to aminopyrene whereas the spectrum of the S2 fraction shows a base aminopyrene peak and very little carbazole. These results clearly indicated that the 1:3 benzene:hexane solvent was the more suitable eluent for medium pressure silica chromatography; this solvent should minimize the elution of amino-aromatics into the S1 fraction and the tailing of carbazoles into the S2 fraction.

A typical silica gel separation of a heavy oil A3 fraction was performed as follows. First, a chloroform solution of the A3 fraction was evaporated to dryness in the presence of 0.5 gram of silicic acid; this coated material was then dry-packed into a stainless steel column on top of 2 grams of silicic acid that had been previously dry-packed into the column. A sequence of 3 solvents was pumped through

the column to afford 3 fractions: S1, benzene:hexane (1:3), S2, benzene, and S3, benzene:anhydrous diethyl ether (1:1). Both Tar Sand A3 and processed residue A3 fractions were chromatographed in this fashion, the resulting chromatograms are shown in Fig. 11. Both chromatograms show large S1 peaks compared to the small S2 and S3 peaks, indicating that most of the UV-absorbing material had eluted in the S1 fraction. The solvent volumes used to elute each fraction are given in Table 7. Much larger solvent volumes were used in these separations than those specified by Later. Although the solvent elution volumes had been increased, the time for the separation was reduced from 12 to 2 hours, allowing a more rapid turnover of samples and, most important of all, decreasing the chance of losing any labile components to oxidation.

The RPLC chromatograms of the above S1, S2 and S3 fractions derived from the Tar Sand oil are shown in Fig. 12; the RPLC chromatograms of the corresponding silica fractions obtained by Later's method were presented previously in Fig. 4. The chromatographic profiles of the S1 fractions in Fig. 4 and 12 appear identical whereas the S2 fractions are quite different. The spill-over of S1 components into fraction S2 noted previously in Fig. 4 has been diminished markedly in Fig. 12. The nitrogen-determination results confirm these observations (column 1 and 2 in Table 6). In the original separation 62% of the total nitrogenous material

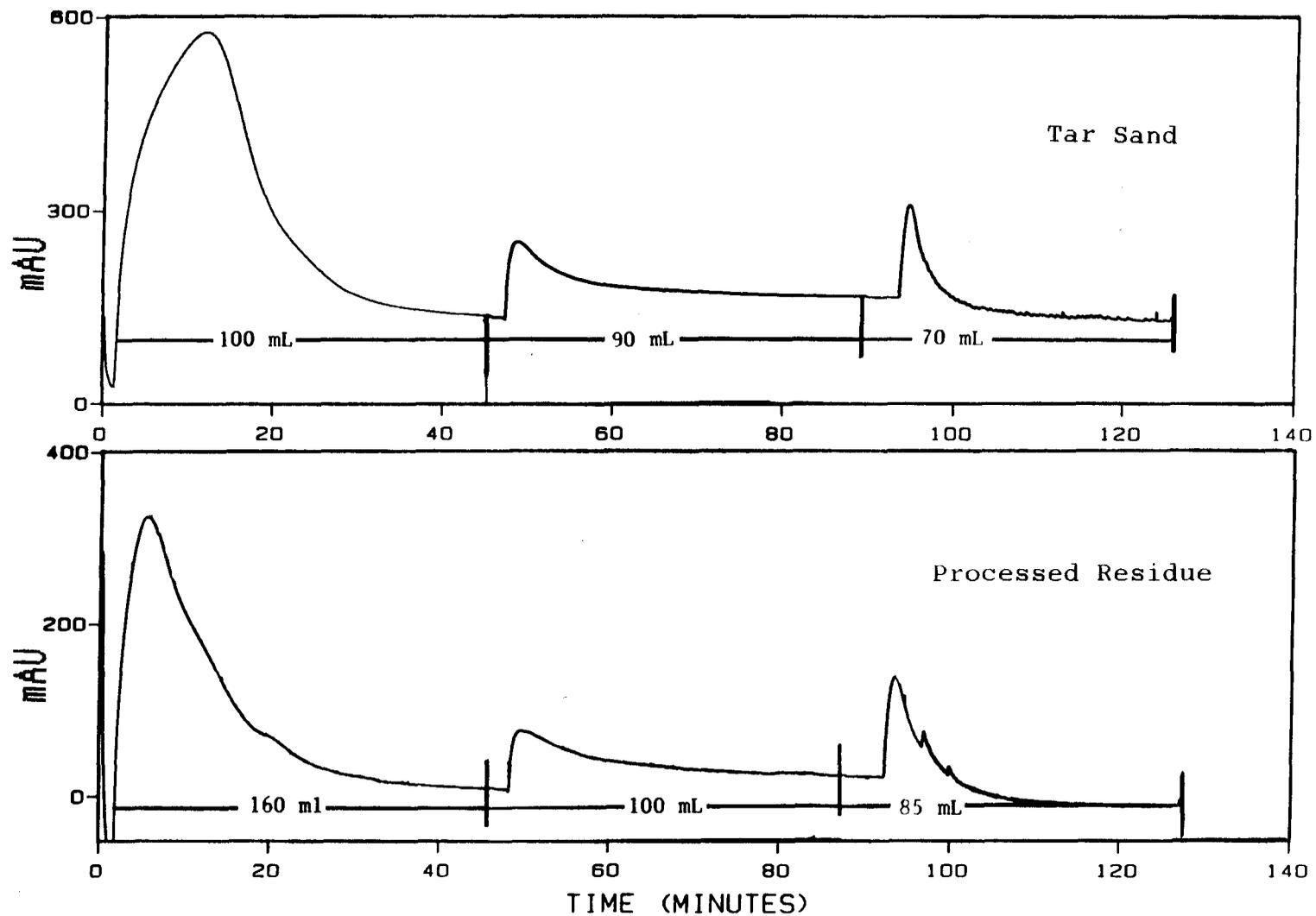


Fig.11 Liquid chromatogram of modified silicic acid separations. (a) Tar Sand oil sample: S1(100 ml), S2(90 ml) and S3(70 ml). (b) Processed residue oil sample: S1(160 ml), S2(100 ml) and S3(85 ml). Detection at 280 nm.

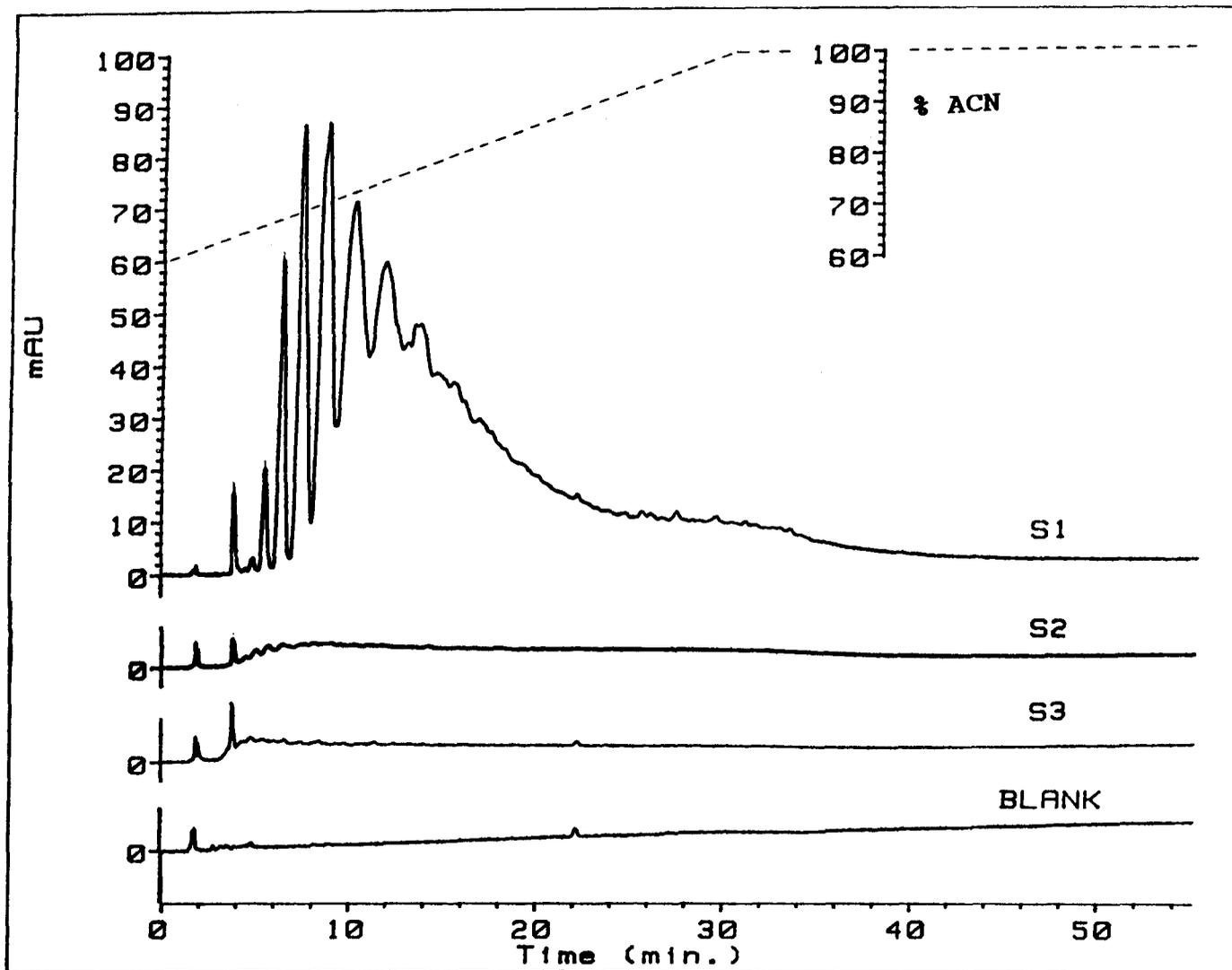


Fig.12 Reverse phase liquid chromatograms of Tar Sand fractions S1, S2 and S3 following separation by the modified silicic acid column. Conditions same as Fig.3b.

eluted in fraction S1 and another 6% in fraction S2 (column 1). In the case of the modified silica separation (column 2) 61% of the total nitrogen eluted in S1 and only 3.7% eluted in S2. The chromatographic and nitrogen-determination results are consistent with the interpretation that the tailing of S1 components into S2 had been decreased dramatically by the use of modified silica gel chromatography. Mass spectral data to be presented later confirm this conclusion.

III.1.5 Scaled-Up Alumina Separation

Nuclear magnetic resonance spectroscopy (NMR) is widely used in organic structure determination. Compared to most analytical methods NMR spectroscopy is a very insensitive technique, requiring milligram amounts of pure compounds for ^1H spectra and tens of milligrams for ^{13}C spectra. However, NMR spectra provide structural information about the sample that most other analytical methods cannot ever provide. For example, the numbers and types of protons and/or carbons in a molecule can be inferred from the chemical shifts of peaks and their relative areas. Given the complex nature of these samples, a substantial amount of sample would be required in order to obtain useful NMR ^{13}C spectrum, i.e., hundreds of milligrams.

The idea of applying NMR spectroscopy to the

investigation of these nitrogenous fractions necessitated the design of a scaled-up alumina separation such that hundreds of milligrams of an A3 fraction could be collected. In this scaled-up experiment, a 2 litre Buchner funnel (13.2 cm i.d.) was used as a column. The height of the alumina packing in the funnel was maintained at about 5 cm, the same height that was used in the 300 mg scale separations. However, the "Buchner column" cross-sectional area was about 100 times greater than the analytical scale column; thus, the weight of crude oil packed on the alumina and the volumes of solvents used were all increased proportionally. In practice, a 35 g or 50 g Tar Sand oil sample was evaporated onto 350 g of alumina and then placed on the top of another 700 g of alumina. The "Buchner column" was eluted with 2.5 L of hexane for the fraction A1, 6 L of benzene for fraction A2 and lastly 8 L of chloroform: absolute ethanol (99:1) for the nitrogenous A3 fraction. With application of mild suction the "Buchner column" had a flow rate of about 200 mL/min and the separation required about 1.5 hours. Portions of the A2 and A3 fractions from this scaled-up separation were evaporated to dryness and then submitted for nitrogen analysis (see Table 6). About 13% of the total nitrogen was collected in fraction A2 and 71% in fraction A3. The RPLC chromatograms of the Tar Sand A3 fractions collected from Later's and the scaled-up separations are compared in Fig. 13; the two chromatograms look very similar.

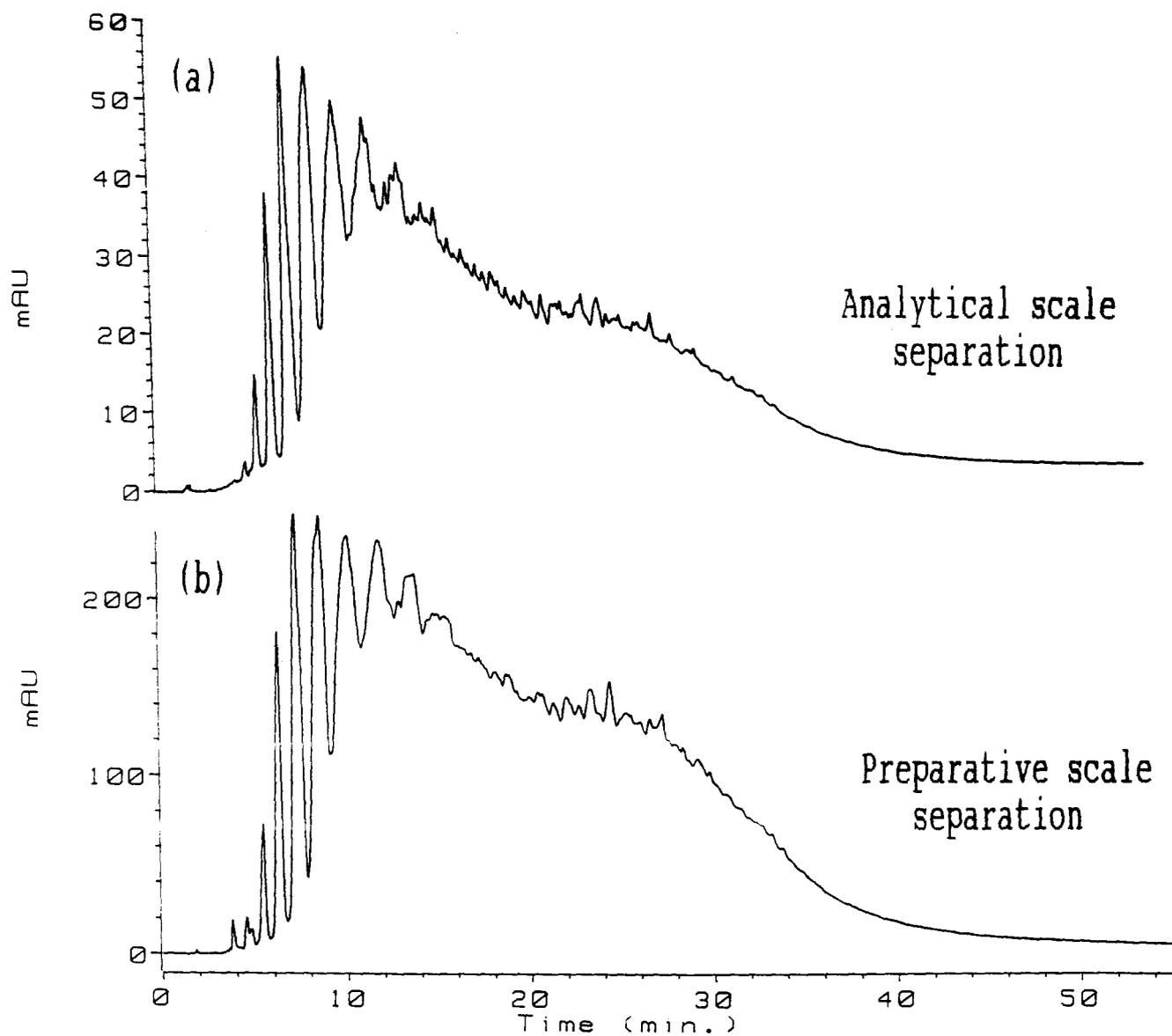


Fig.13 Reverse phase liquid chromatogram of Tar Sand A3 fractions: (a) analytical scale (0.3 g oil); (b) preparative scale (35 g oil). Conditions same as Fig.3b.

Both the nitrogen analysis and HPLC results showed that the scaled-up separation gave the same separation results as the analytical separation. By keeping the height of the alumina column constant, the elution pattern of materials was similar in both separations. A total of 1.2 grams of A3 material was afforded by combining the products of the 35 and 50 g separations; this 1.2 g sample was examined by NMR spectroscopy.

III.1.6 Asphaltene Separation

Asphaltenes are high molecular weight polycyclic aromatic/aliphatic compounds that are found in many crude oils. Preliminary HPLC analyses of the unprocessed Peace River residue indicated the presence of some very non-polar substances which were suspected to be asphaltenes. Thus it was decided to remove these materials from the unprocessed residue sample. The black gummy unprocessed Peace River residue was boiled in 30 volumes of pentane for 30 minutes. The solubility of the asphaltenes in pentane is very low such that they separated from the pentane-soluble materials and were removed by filtration. After this treatment, approximately 40 wt% of the residue sample had been removed, leaving a dark brownish liquid. The asphaltene-removed residue oil was then packed on an alumina column and separated by Later's method into A1, A2 and A3 fractions

only. The result of this separation will be discussed in the analytical sections.

III.1.7 Summary of the Separation Scheme

The separating of nitrogenous components from heavy oil samples using Later's method was reasonably successful but was accompanied by a substantial spillover of material from one fraction to another. Modification of the alumina separation, on one hand, minimized the carry over of the A2 components into the A3 fraction but also increased the elution of nitrogenous A3 materials in the A2 fraction. On the other hand, by altering the silica separation, the spillover of S1 components into the S2 fraction as well as the separation time were both reduced. When the alumina separation was scaled up over 100-fold, the relative separation of the components was unaffected, compared to the analytical scale (300 mg) separation.

III.2 Analytical Finishes

III.2.1 Low Resolution Mass Spectrometry

III.2.1.a Probe Electron Impact Mass Spectrometry

Once the nitrogenous fractions (S1, S2, S3) had been isolated from the three oil samples, they were examined first using probe electron impact mass spectrometry. The distillation profile, i.e., the plot of the total ion current versus scan number, of the Athabasca Tar Sand S1 fraction is presented in Fig. 14a, together with three selected mass spectra. All three spectra are very complex and are clearly the sum of the mass spectra of a large number of components. In the low mass range ($m/z < 170$), a number of doubly charged ions were observed, indicative of polycyclic aromatic systems. In the high mass range ($m/z > 170$) many of the major peaks were separated by a difference of 14 mass units suggesting homologous series of compounds. Examples include the ion series 180, 194, 208, 222, 236 and 250 in Fig. 14b and the series 305, 319, 333, 347 and 361 in Fig. 14c.

The m/z value of the most intense ion in the spectrum increased as the probe temperature increased. For example, in scan 45, the most intense ion was $m/z=222$ (Fig. 14b), in

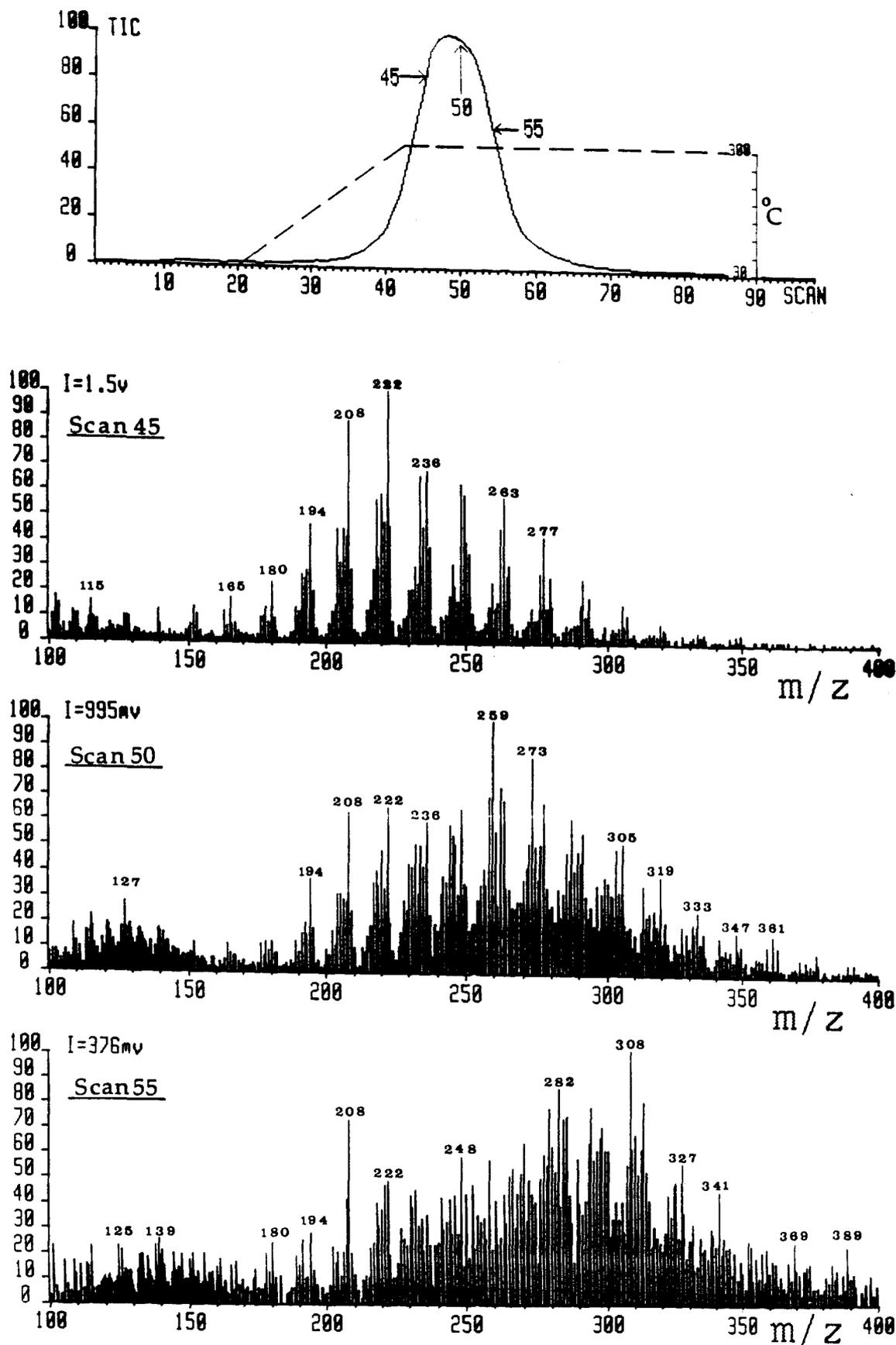


Fig.14 (a) Probe EIMS total ion current chromatogram of Tar Sand S1 fraction. Conditions as described in Table 5. (b) Mass spectrum 45, (c) mass spectrum 50 and (d) mass spectrum 55. (I : voltage at detector of base peak in mass spectrum. For display base peak set at 100% relative intensity.)

scan 50, $m/z=259$ (Fig. 14c), and in scan 55, $m/z=308$ (Fig. 14d). These results indicate that in a temperature-programmed probe mass spectrometry experiment, lower molecular weight components were volatilized earlier than higher molecular weight species and also that each spectrum only contained part of the total mass spectral information of the entire sample. In order to obtain the "total" mass spectrum, all the mass spectral data from such an experiment can be averaged into a single spectrum. In this averaged spectrum (Fig. 17a) all the spectrometric information from scans 15 to 90 of Fig. 14a were added together and then divided by the total number of scans.

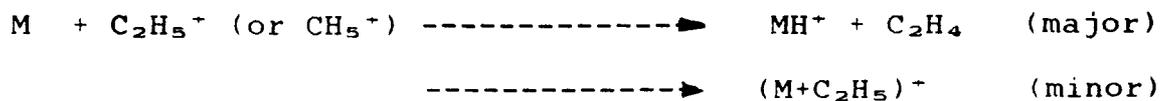
III.2.1.b Comparison of Spectra Obtained Using Different Ionization Modes

In order to get a better understanding of the nitrogenous components, especially the molecular weights of the compounds, methane and ammonia chemical ionization mass spectrometry (CH_4 and NH_3 CIMS) were applied to the nitrogenous fractions.

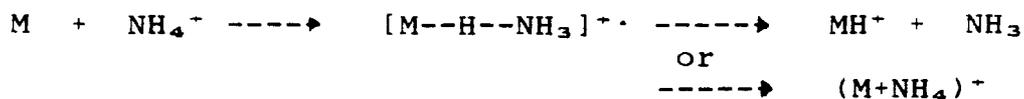
Methane and ammonia have very different proton affinities which makes them behave very differently in chemical ionization mass spectrometry. The proton affinity (PA) of methane is 536 kJ/mole and for ammonia, 847 kJ/mole (F1187). The low PA value of methane enables it to function

as a "universal" CI reagent gas, that is, the methane plasma can protonate many compounds. In contrast the high PA value of ammonia makes it a much more "selective" CI gas, only able to protonate those compounds with PA values higher than that of ammonia.

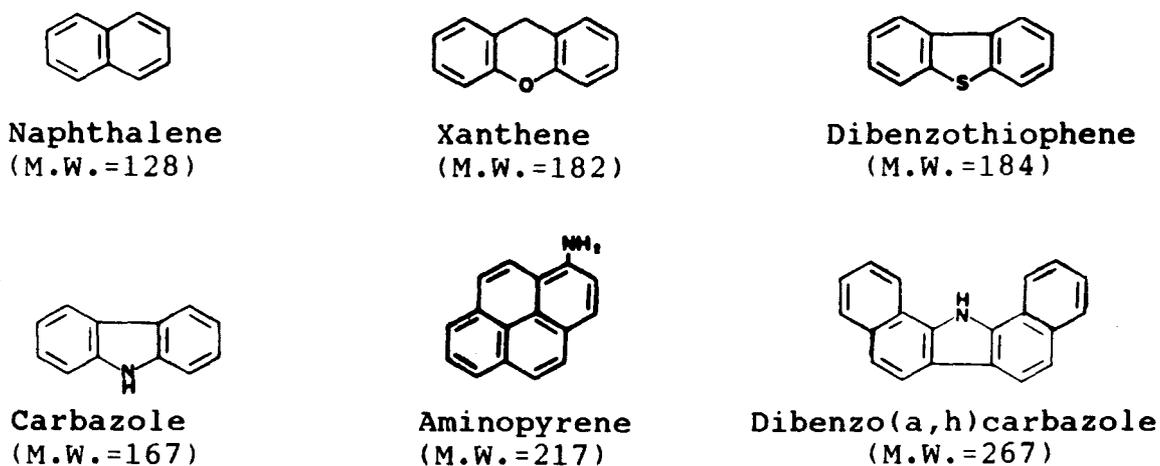
In the methane CIMS mode, the electron beam from the ion source first ionizes methane gas to produce CH_4^+ ions which react with methane molecules to form two major ions, CH_5^+ and C_2H_5^+ . The gas pressure in the ion source was adjusted to obtain a 1:1 ratio between the two ions, These two ions can react with and ionize sample molecules M, principally by proton transfer, to afford a species MH^+ ; in addition, some electrophilic addition ions (e.g., $(\text{M}+\text{C}_2\text{H}_5)^+$) may be formed in small amounts.



In an ammonia CIMS experiment, ammonia gas is first ionized by the electron beam to form the NH_3^+ ion which can then react with other ammonia molecules to form the NH_4^+ and the $(\text{NH}_4 \cdot \text{NH}_3)^+$ ions. The gas pressure can be adjusted so as to obtain a 20:1 ratio between the two ions. The NH_4^+ ions can then donate a proton to a sample molecule to form MH^+ ions or the electrophilic addition ion $(\text{M}+\text{NH}_4)^+$.



Before these two chemical ionization modes were applied to the complex oil fractions, the mass spectral responses of six standards were determined. These six standards included: a PAH standard, naphthalene ($\text{C}_{12}\text{H}_{10}$, 128 AMU); a PAOH standard, xanthene ($\text{C}_{13}\text{H}_{10}\text{O}$, 182 AMU); a PASH standard, dibenzothiophene ($\text{C}_{13}\text{H}_{10}\text{S}$, 184 AMU); and three nitrogen-containing PAHs: carbazole ($\text{C}_{12}\text{H}_9\text{N}$, 167 AMU), aminopyrene ($\text{C}_{16}\text{H}_{11}\text{N}$, 217 AMU) and dibenzocarbazole ($\text{C}_{20}\text{H}_{13}\text{N}$, 267 AMU). The CH_4 and NH_3 CI mass spectra of these six compounds are shown in Fig. 15 and 16.



In the naphthalene spectra (Fig. 15a and 15d) the $m/z=129$ $(M+H)^+$ ion was found in both mass spectra but the peak intensity of this ion in the NH_3 CI spectrum was ten times less than in the CH_4 CI spectrum. Similar results were obtained for xanthene and dibenzothiophene (Fig. 15b, c, e

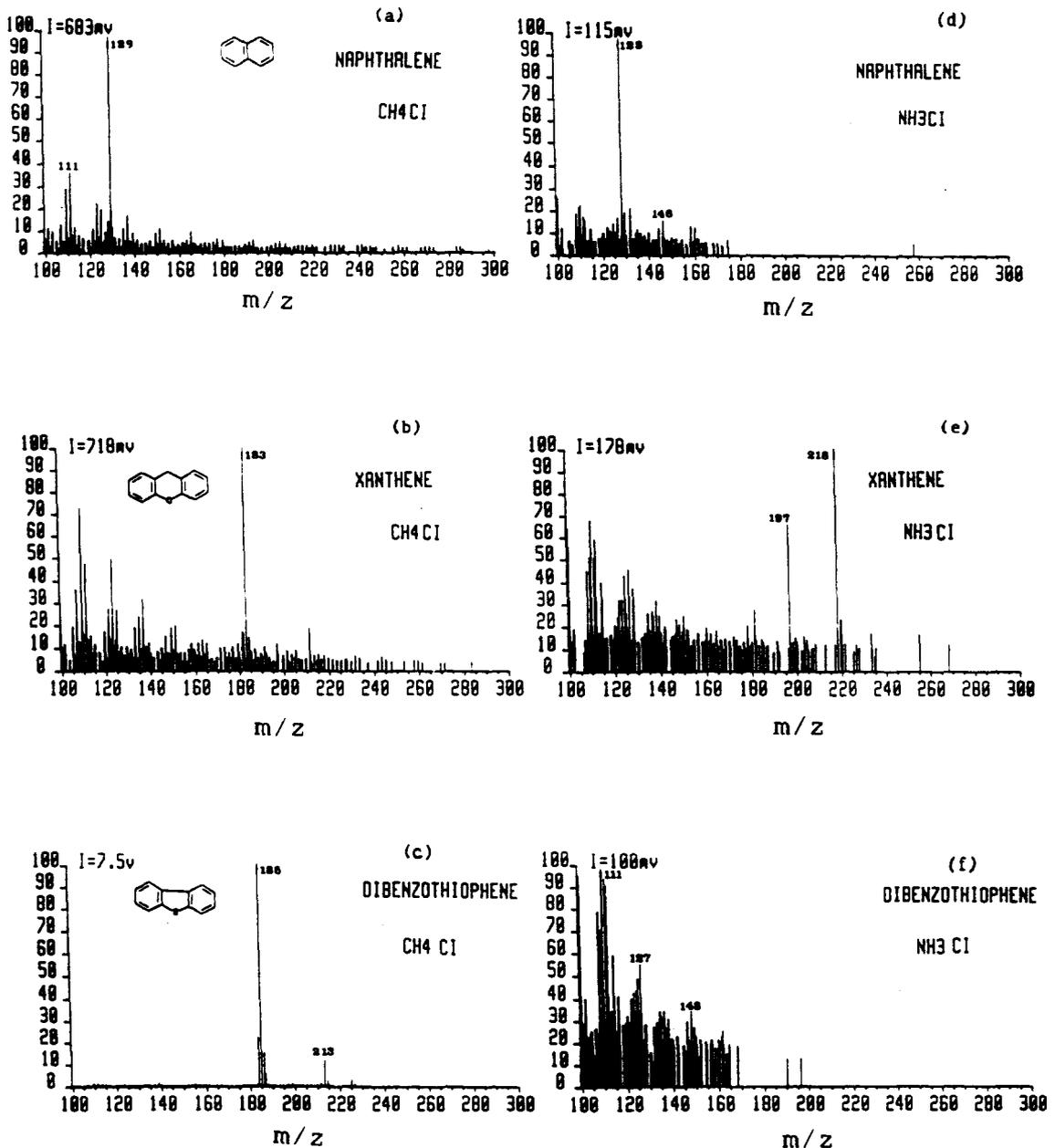


Fig.15 Methane CI mass spectra of (a) naphthalene, (b) xanthene and (c) dibenzothiophene; ammonia CI mass spectra of (d) naphthalene, (e) xanthene and (f) dibenzothiophene. (I : voltage at detector of base peak in mass spectrum. For display base peak set at 100% relative intensity.)

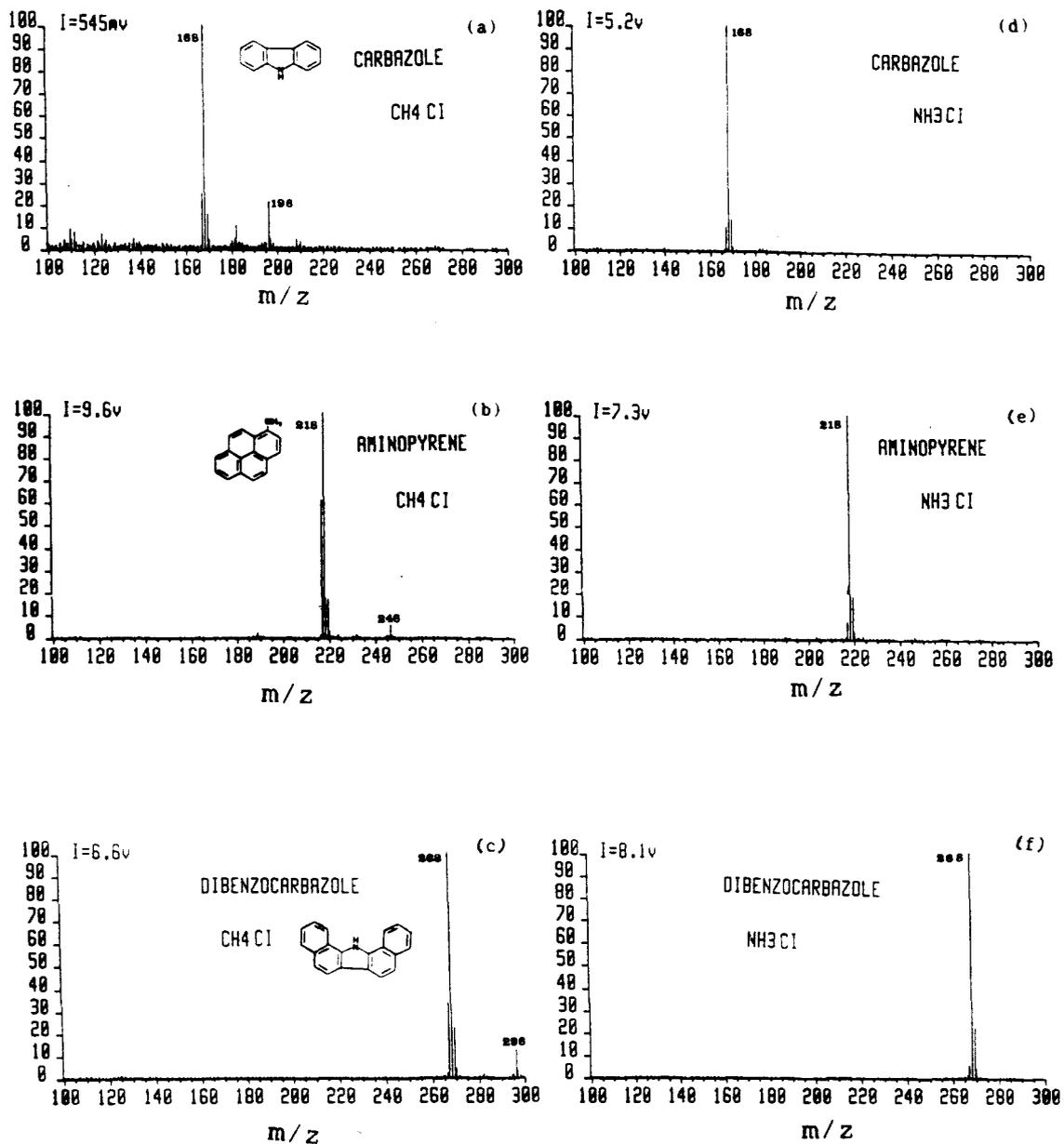


Fig.16 Methane CI mass spectra of (a) carbazole, (b) aminopyrene and (c) dibenzo(a,h)carbazole; ammonia CI mass spectra of (d) carbazole, (e) aminopyrene and (f) dibenzo(a,h)carbazole. (I: voltage at detector of base peak in mass spectrum. For display base peak set at 100% relative intensity.)

and f). For these compounds proton transfer from the methane plasma was much more efficient than from the ammonia plasma.

The CI spectra of three nitrogenous standards are shown in Fig. 16. Their responses in the methane CI analysis were very similar to the responses of the above non-nitrogenous compounds, i.e., a major $(M+1)^+$ ion with a minor $(M+C_2H_5)^+$ ion. However, in the ammonia CI spectra, their responses were very different from the non-nitrogenous standards. All three nitrogen standards gave very strong $(M+1)^+$ ions, indicating they were protonated very easily by the ammonium ions in the ion source.

All six standards were protonated in the methane plasma to form major $(M+H)^+$ ions and small addition ions, $(M+29)^+$. In the ammonia plasma, the ammonia reagent gas readily protonated the nitrogen-containing standards to produce intense $(M+H)^+$ ions but did not easily protonate the non-nitrogenous standards.

The EI, methane CI and ammonia CI mass spectra of the Tar Sand S1 fraction are shown in Fig. 17. The EI spectrum, the most complex of the three, was the only spectrum to exhibit doubly charged ions. The methane CI spectrum was cleaner than the EI spectrum, showing fewer low intensity peaks, especially in the low mass range ($m/z=150$ to 275). The series of peaks in the EI spectrum ($180, 194, 208, 222...$ etc) was replaced in the methane spectrum by the series $182, 196, 210, 224...$ etc. These ions suggested the presence

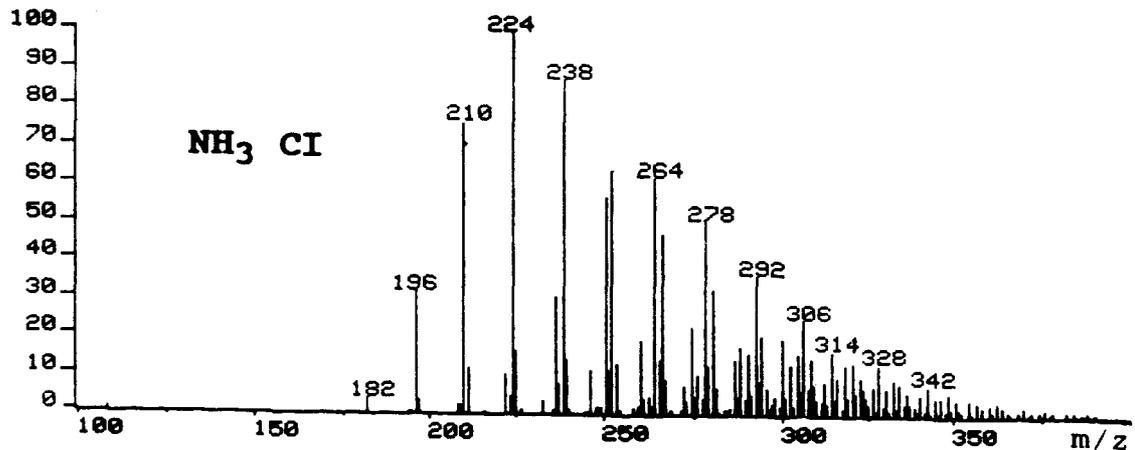
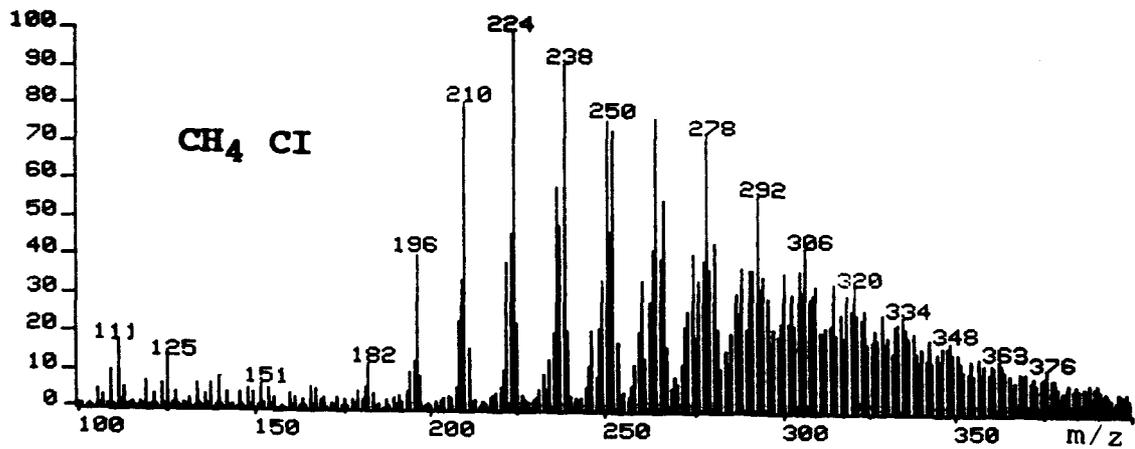
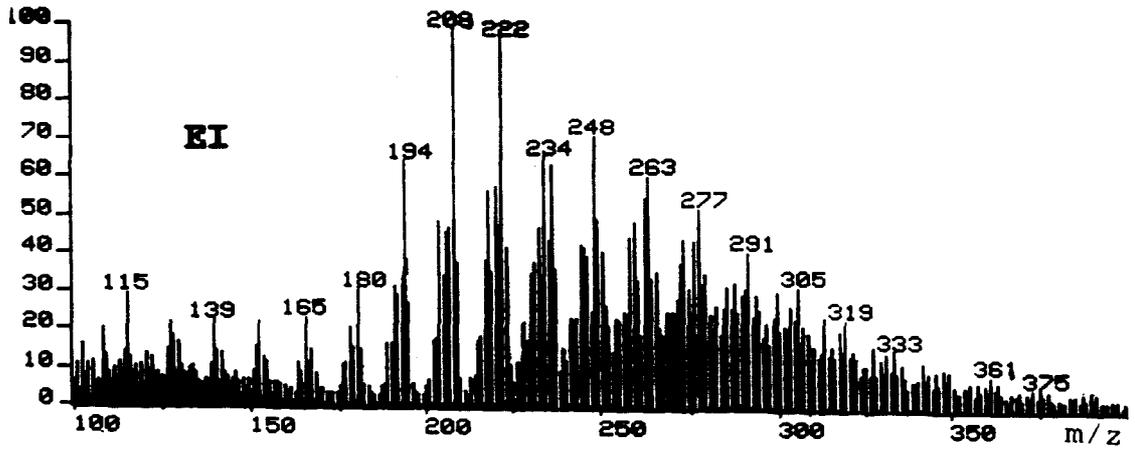


Fig.17 Averaged mass spectrum of Tar Sand S1 fraction:
 (a) EI, (b) methane CI and (c) ammonia CI. Conditions as in Table 1.

of compounds of molecular weights 181, 195, 209, 223... etc. since the predominant peaks of many N-H containing molecules are $(M-H)^+$ ions in EI spectra and $(M+H)^+$ ion in CI spectra. In the higher mass range ($m/z > 300$) the methane CI spectrum was still very complicated. The NH_3 CI spectrum of Tar Sand S1 fraction was the simplest of all three spectra (Fig. 17). There are few peaks below $m/z=170$; the $m/z=182, 196, 210...$ etc. ion series was consistent with the presence of nitrogen-containing compounds of molecular weights 181, 195, 209...etc. Clearly, ammonia CIMS was the most suitable ionization method for the analysis of these complex oil samples due to the selective ionization of the nitrogenous compounds.

These mass spectral results suggested that these nitrogen-containing compounds were probably polycyclic in nature with an odd number of nitrogen atoms. UV spectra of many components in the S1 fractions (to be discussed in the next section) were very similar to each other and were very similar to carbazole. Taken together, these results indicated that the nitrogen-containing compounds in the Tar Sand S1 fraction were probably carbazole derivatives.

The ammonia CI spectra of the Tar Sand S1, S2 and S3 fractions are shown in Fig. 18. Most of the nitrogenous compounds in fraction S1 are present in trace amounts in the amino (S2) and tertiary PANH (S3) fractions. In fraction S1, the ion series 182, 196, 210, 224...etc. was attributed to an

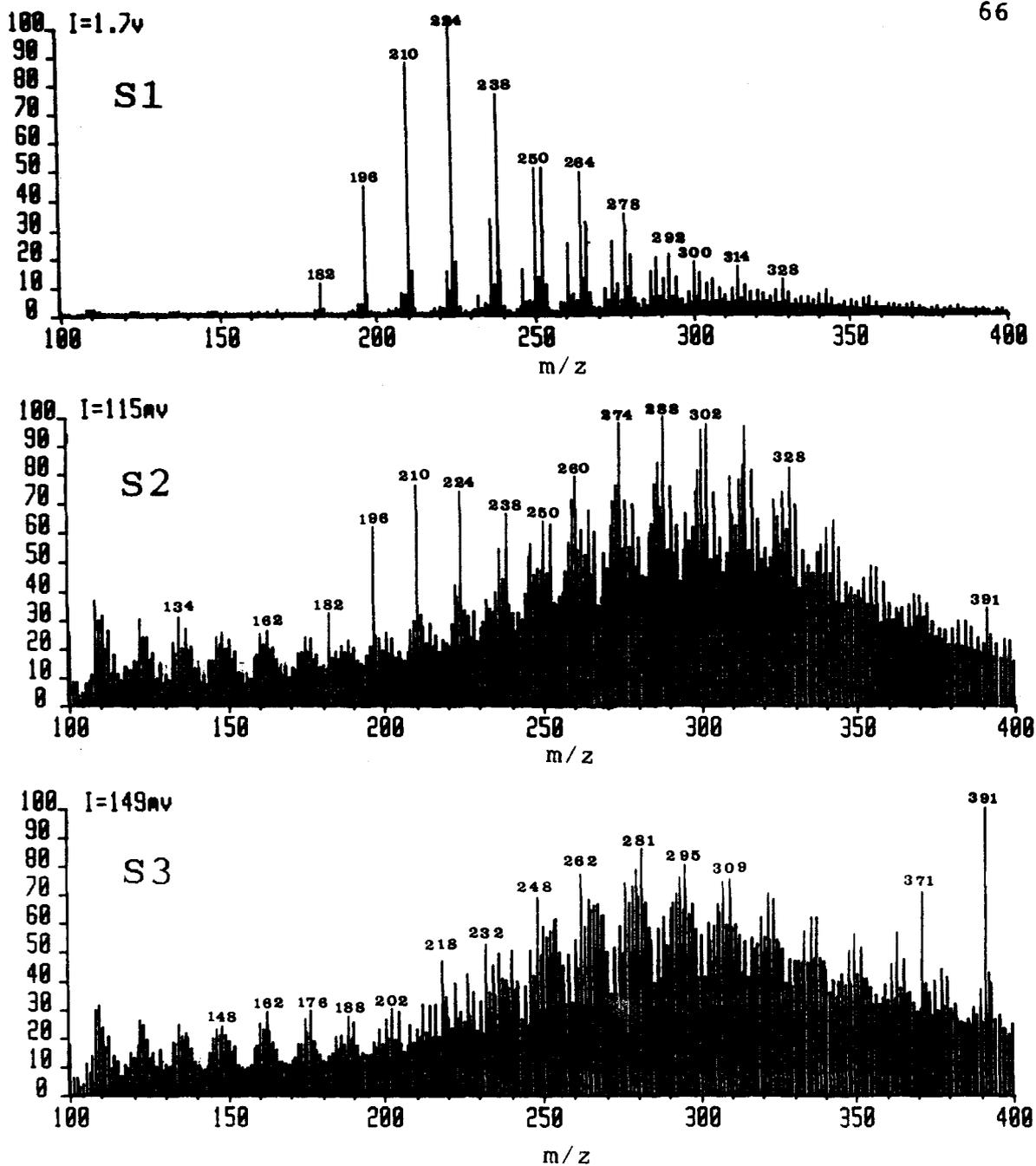


Fig.18 Ammonia CI mass spectra of Tar Sand silica-separated fractions: S1 (1 wt eq.), S2 (3 wt eq.) and S3 (3 wt eq.). Conditions as in Table 5. (I: voltage at detector of base peak in mass spectrum. For display base peak set at 100% relative intensity.)

homologous series of alkylated carbazoles. However, other ion series were also apparent in the S1 spectrum; these series have m/z values that are 2, 4 and 6 mass units less than the above series. These ion series were attributed to carbazoles containing one degree, two degrees and three degrees of unsaturation, respectively. The 1-degree unsaturates constitute the series 250, 264, 278 and 292, the 3-degree unsaturates, the series 274, 288, 302, 316 and 330. These ion series suggested that the S1 fraction consisted of a complex mixture of alkylated carbazoles present in various degrees of unsaturation.

The NH_3 CI spectrum of fraction S2 spectrum also showed two major series of ions with $m/z=182, 196, 210, 224$ and 238 and $m/z=260, 274, 288$ and 302 . The intensities of these ions were 40 times less than the corresponding ions in the S1 fraction. It was concluded that these ions were probably due to S1 components which had been carried over into the S2 fraction. The ion intensities in the NH_3 CI spectrum of fraction S3 were very weak and no pattern of peaks was discerned; thus, the amounts of nitrogenous materials in this fraction were very low.

The ammonia CI mass spectra of the processed residue S1, S2 and S3 fractions are shown in Fig. 19. As in the Tar Sand sample, most of the nitrogenous compounds were found in fraction S1. Series of peaks separated by 14 mass units were again observed, suggesting homologous series of alkylated

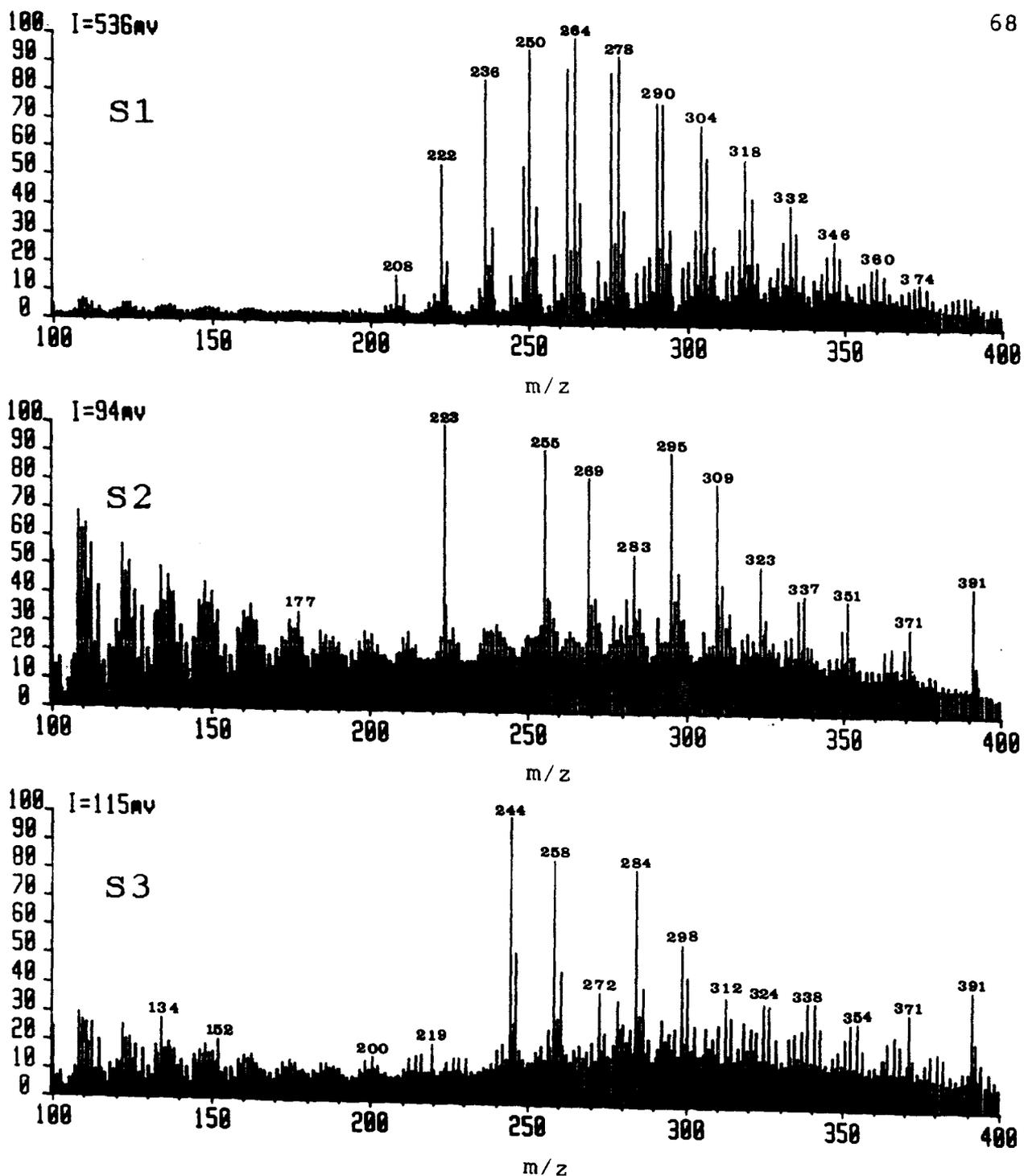


Fig.19 Ammonia CI mass spectra of Processed residue silica-separated fractions: (a) S1, (b) S2 and (c) S3 fraction. Conditions as given in Table 5. (I: voltage at detector of base peak in mass spectrum. For display base peak set at 100% relative intensity.)

carbazoles in different degrees of unsaturation.

However, two differences were found between the averaged spectra from Tar Sand and the processed residue S1 fractions. First, the most intense ion in the Tar Sand S1 spectrum was the $m/z=224$ peak, in the processed residue, the $m/z=250$ peak. Second, the most intense ion series found in the Tar Sand S1 spectra was in the saturated alkylated carbazole series ($m/z=182, 196, 210, 224, 238$) while in the processed residue sample it was in the 1-degree unsaturated alkylcarbazole series, ($m/z=206, 222, 236, 250$).

The ammonia CI spectra of the S2 and S3 fractions (Fig. 19b and c) showed ion intensities far lower than for the S1 fractions. Two series of ions separated by 14 amu were observed: $m/z=255, 269, 283, 297, 311\dots$ and $m/z=295, 309, 323, 337$ and 351. Ion intensities in fraction S3 spectrum (Fig. 19c) were also very low. The most significant ion series were $m/z=244, 258, 272, 286\dots$ etc. and $m/z=284, 298, 312, 326,\dots$ etc. Nevertheless, the low intensities of the peaks in the S2 and S3 fractions indicated that the amounts of amino-PAH and tertiary-PANH components were very low.

The ammonia CI spectrum of the unprocessed asphaltene-removed residue A3 fraction (Fig. 20) is complex with an envelope of peaks reminiscent of the EI spectrum of the Tar Sand A3 sample. The only peak series that could be identified was the $m/z=196, 210, 224, 238$ and 252 series which corresponds to the saturated carbazoles. This A3

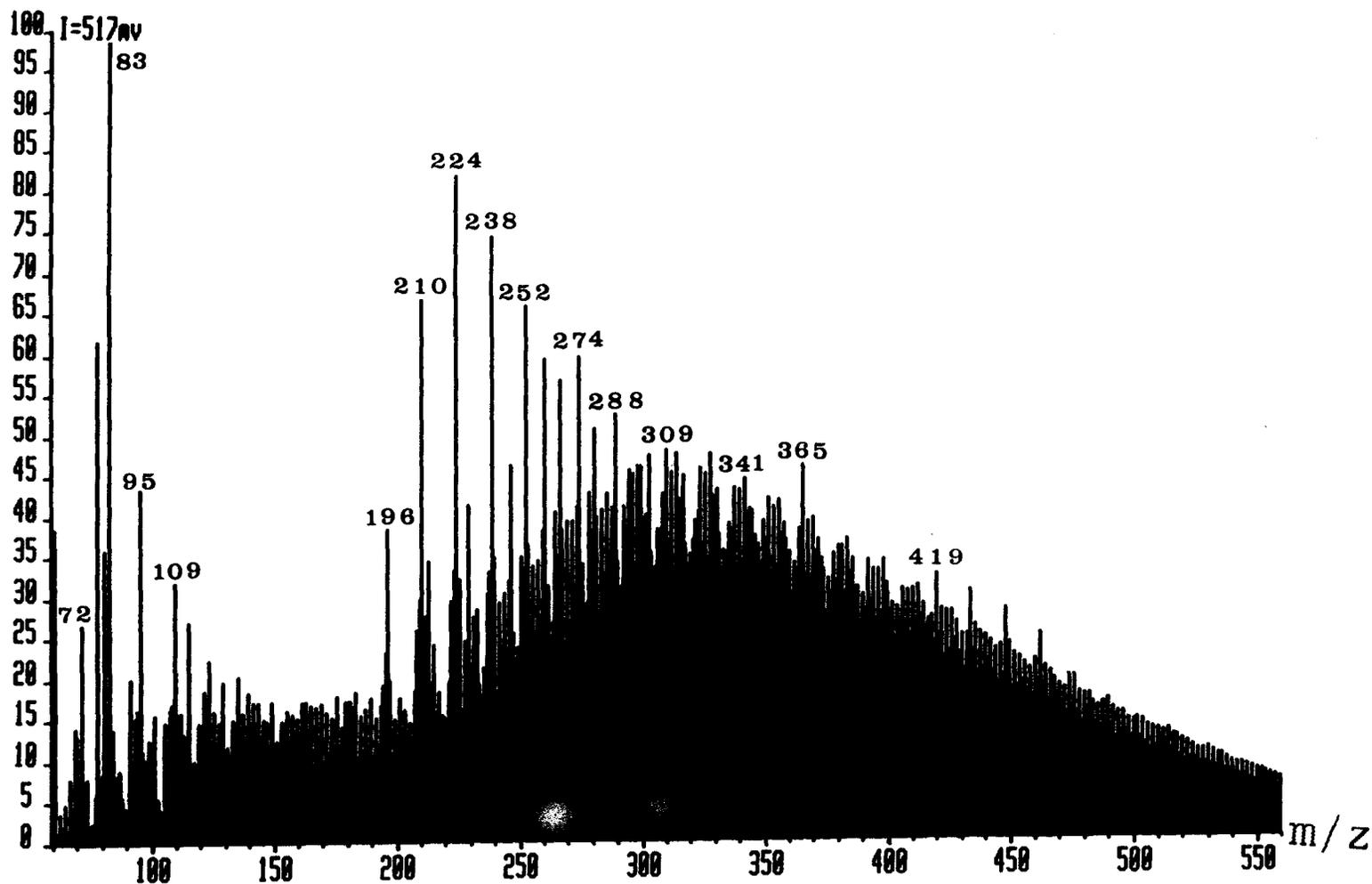


Fig.20 Probe ammonia CI mass spectrum of asphaltene-removed unprocessed residue A3 fraction. Conditions in Table 5. (I: voltage at detector of base peak in mass spectrum. For display base peak set at 100% relative intensity.)

fraction was sufficiently complex that no further separations were attempted.

III.2.2 High Resolution Mass Spectrometry (HRMS)

Low resolution mass spectrometry had shown that carbazoles were the major PANH components in both the Tar Sand and the processed residue samples. High resolution electron impact mass spectrometry (HRMS using the peak-matching method) was used to obtain the exact masses of some of the major S1 components at a nominal resolution of 6250. The five ions ($m/z=208, 209, 222, 223$ and 249) chosen for high resolution analysis were derived from two saturated carbazoles and one 1-degree unsaturated carbazole; these data are listed in Table 8. The first column gives the nominal m/z values, the second column, the experimentally determined mass values (EDM) from the HRMS analysis, the third column, a list of molecular formulas whose mass values were close to the EDM value. In the high resolution mass spectrometric analysis, the accuracy of the EDM values can be reached to the third decimal. In the fourth column, the milli mass unit (MMU) difference between the suggested formula (column 3) and the EDM value (column 2). Of the suggested molecular formulas for each exact mass value some are extremely unlikely elemental compositions in these circumstances. From all the suggested molecular formulas, the most probable are the

TABLE 8: High Resolution Mass Spectrometric Analysis of Five Ions in the Electron Impact Spectrum of Athabasca Tar Sand Sl Oil Sample

m/z value	EDM*	Molecular Formula	MMU*
208	208.1134	$C_9H_{20}O_3S$	-0.1
		$C_{15}H_{14}N$	-0.8
		$C_{12}H_{18}NS$	+2.6
		$C_7H_{18}N_3O_2S$	-1.4
209	209.1205	$C_{12}H_{17}O_3$	-2.7
		$C_9H_{21}O_3S$	+0.6
		$C_{15}H_{15}N$	-0.1
		$C_{12}H_{19}NS$	+2.6
		$C_7H_{19}N_3O_2S$	-0.7
222	222.1284	$C_{13}H_{18}O_3$	-2.8
		$C_{10}H_{22}O_3S$	+0.6
		$C_{16}H_{16}N$	-0.1
		$C_6H_{26}N_2S_3$	-2.6
		$C_8H_{20}N_3O_2S$	-0.8
223	223.1359	$C_{13}H_{19}O_3$	-2.5
		$C_{10}H_{23}O_3S$	+0.9
		$C_{16}H_{17}N$	+0.2
		$C_6H_{27}N_2S_3$	-2.3
		$C_8H_{21}N_3O_2S$	-0.5
249	249.1513	$C_{15}H_{21}O_3$	-2.2
		$C_{12}H_{25}O_3S$	+1.1
		$C_{18}H_{19}N$	+0.4
		$C_{10}H_{23}N_3O_2S$	-0.2
		$C_8H_{29}N_2S_3$	-2.0

*EDM: Experimentally Determined Mass

*MMU: Milli Mass Unit difference between observed mass value and exact mass of that molecular formula.

following: $C_{15}H_{14}N$ ($m/z=208$), $C_{15}H_{15}N$ ($m/z=209$), $C_{16}H_{16}N$ ($m/z=222$), $C_{16}H_{17}N$ ($m/z=223$) and $C_{18}H_{19}N$ ($m/z=249$).

III.2.3 Summary

Of the three ionization modes (electron impact, methane CI and ammonia CI), ammonia chemical ionization was found to be most suitable for the analysis of heavy oil nitrogenous compounds. The high proton affinity of ammonia results in selective protonation of nitrogenous compounds, affording very clean mass spectra of rather complex mixtures. Moreover, the lower ionization energy of the ammonia, as compared to methane, resulted to give less ion fragmentation and no adduct (such as the $M+C_2H_5^+$ in the methane spectra) were found in the ammonia plasma.

Interpretation of the ammonia CI mass spectra and the HRMS analyses indicated that carbazoles, in different degrees of unsaturation, were the predominant nitrogenous compounds in the Tar Sand and the processed residue samples. The ammonia CIMS analysis of the unprocessed asphaltene-removed residue indicated that the A3 fraction was even more complex and contained a lot of additional material compared to the two above samples.

III.2.4 High Performance Liquid Chromatography (HPLC)

All HPLC analyses were performed in the reverse phase mode using a Vydac reverse phase C-18 column with a solvent gradient from 60% acetonitrile:water to 100% acetonitrile over 30 minutes and hold at 100% acetonitrile. A UV-visible diode-array detector was set to collect data in two modes simultaneously: (1) narrow band: 254 nm detection with a bandwidth of 4 nm, i.e., from 252-256 nm only and (2) wide band: 300 nm with a bandwidth of 200 nm, i.e., from 200-400 nm.

Two chromatograms of the Tar Sand A3 fraction using these two wavelength modes are shown in Fig. 21. The peak intensities in the narrow band mode (254 nm detection) were almost three times greater than those in the broad band mode. This difference in peak intensities resulted from averaging the absorption data over the range of wavelengths. During a spectral acquisition, the UV-absorbance at each photodiode in the selected wavelength range was measured, summed and then divided by the number of photodiodes in that wavelength range to give an averaged value. The larger signals in the 254 nm chromatogram means that components in this fraction have strong UV absorptions near 254 nm. Although 254 nm detection gave better signal-to-noise ratios, diode-array detection was still applied routinely to all the HPLC analyses in order that compounds with strong absorptions at wavelengths other

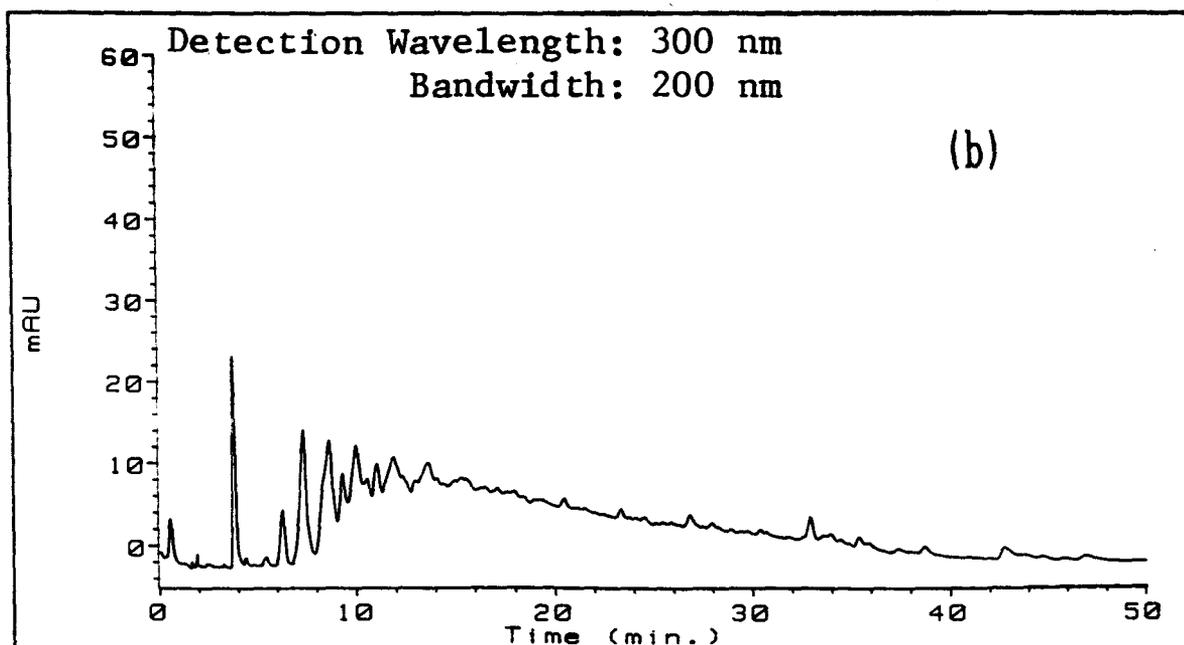
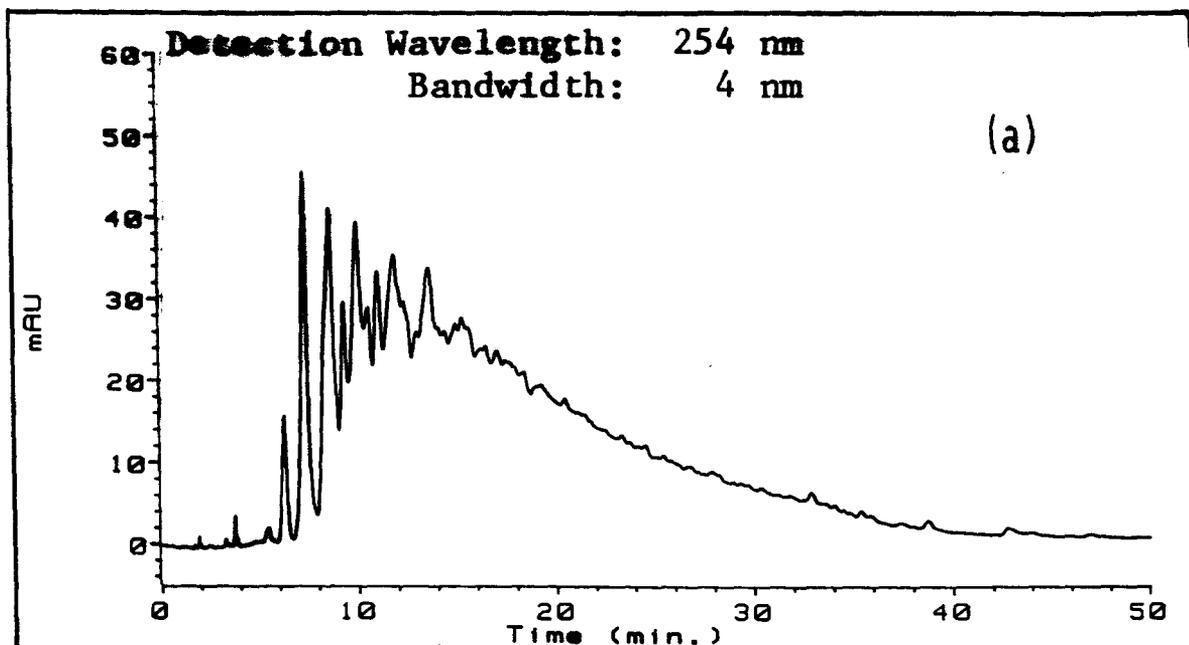


Fig.21 Reverse phase liquid chromatograms of Tar Sand A3 fraction. Detected at (a) 254 nm and (b) 200-400 nm. Conditions as in Fig.3b.

than 254 nm, such as quinoline ($\epsilon_{\max} > 270$ nm) and many benzo homologs, would be detected with similar sensitivities.

The LC-DAD chromatograms of the Tar Sand silica fractions S1, S2, S3 were previously shown in Fig. 12. Most of the nitrogenous components eluted in fraction S1, while the low intensities in the S2 and S3 fraction chromatograms indicated that little material had eluted in these two fractions. From the S1 fraction chromatogram, four peaks were selected and their UV spectra (210 to 400 nm) are shown in Fig. 22. These spectra are surprisingly similar to each other and to the spectrum of carbazole itself, suggesting that most of the S1 components contained the carbazole nucleus. This observation was consistent with the mass spectrometric evidence presented above which indicated that the major nitrogenous components in the Tar Sand and the processed residue samples were alkylated carbazoles existing in different degrees of unsaturation. As the retention time of the peaks increased, the absorption maxima shifted to a longer wavelength. For example, the 5.3 min peak has its absorption maximum at 235 nm, the 7.3 min peak, at 240 nm and the 11.9 and 15.7 min peaks, at 243 nm. Simple alkyl substitution on the carbazole nucleus would result in small spectral shifts such as these.

The LC chromatograms of the processed residue S1, S2, S3 fractions (Fig. 23) are very similar to the corresponding Tar Sand samples. As in the Tar Sand S1 case, early eluting

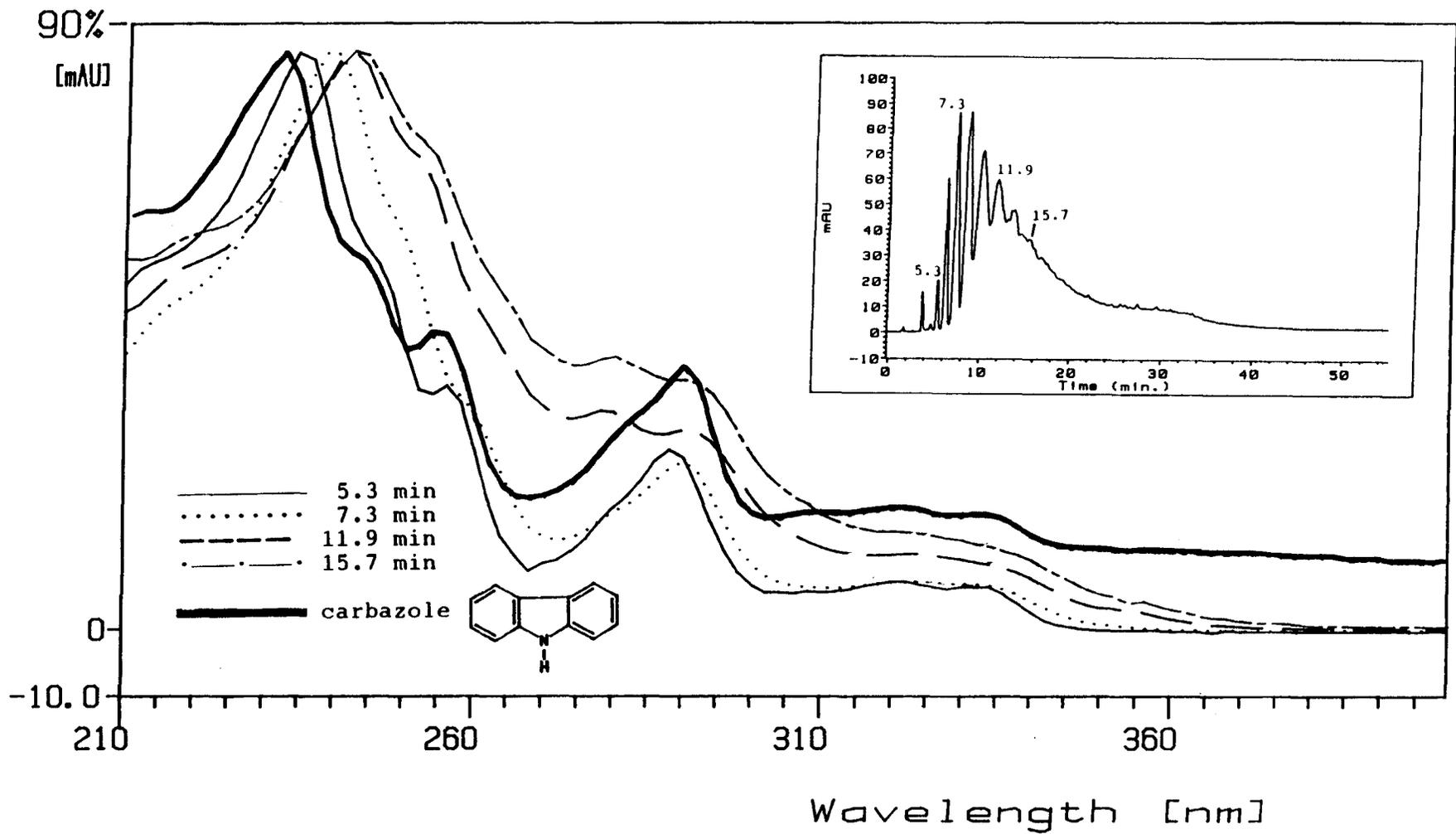


Fig.22 UV spectra of carbazole and four selected peaks from RPLC chromatogram (inset) of Tar Sand S1 fraction.

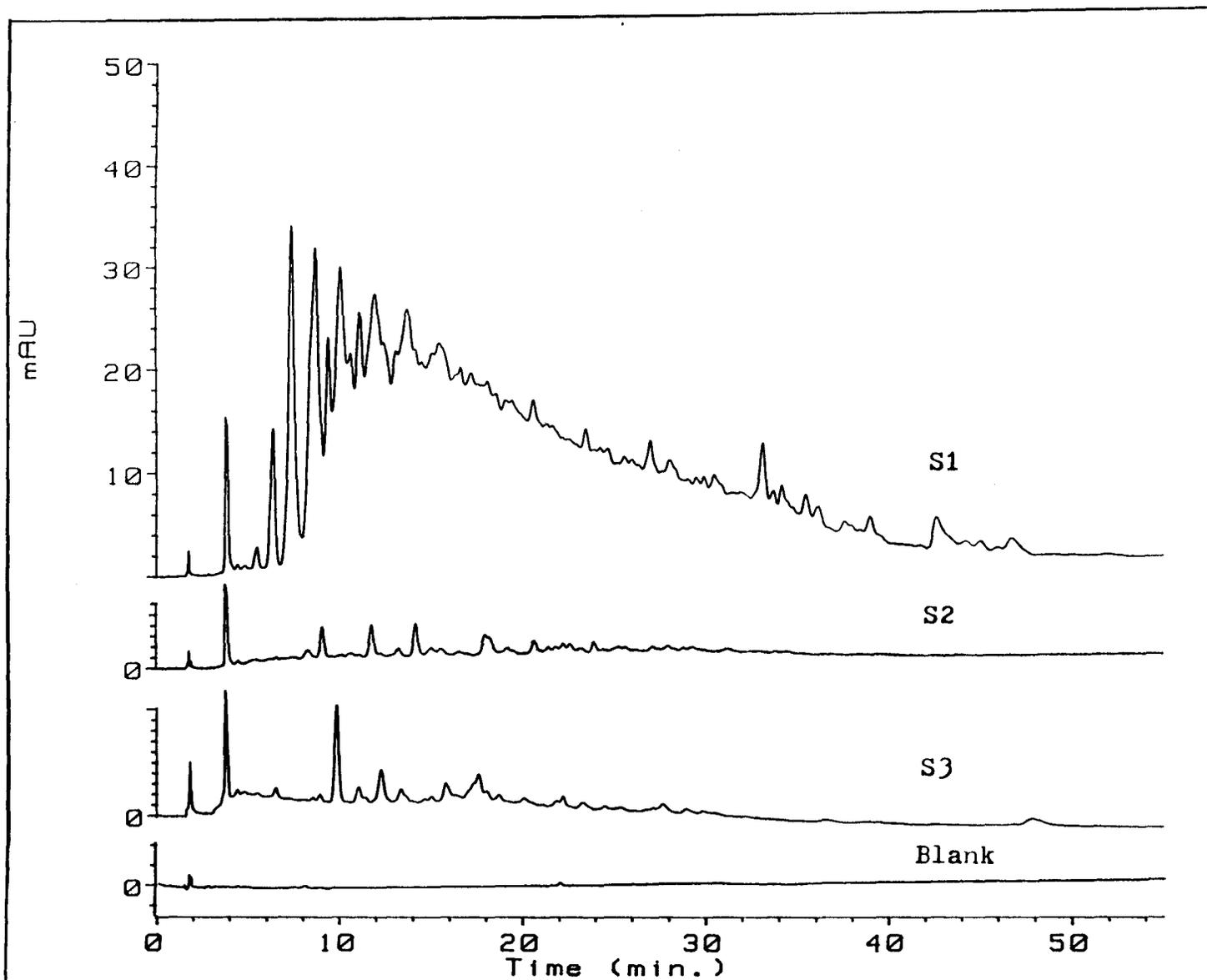


Fig.23 Reverse phase liquid chromatogram of processed residue S1, S2 and S3 fractions. Conditions same as Fig.3b.

peaks were better resolved than later eluting peaks. Several representative UV spectra (Fig. 24) from the processed residue S1 chromatogram show chromophores similar to carbazole and to the components observed in the Tar Sand S1 fraction. Unlike the Tar Sand spectra, the absorption maxima were all close to 245 nm and showed no trend to shift to longer wavelengths.

One minor difference between the two S1 chromatograms was the total elution time of the two analyses. The Tar Sand S1 fraction eluted in 40 minutes, the processed residue in 50 min suggesting the presence of longer eluting compounds in the processed residue, undoubtedly higher molecular compounds.

The chromatograms of the processed residue S2 and S3 fractions (Fig. 23) were very weak in intensity, meaning that very few components had eluted in these fractions. The focus of the discussion from hereon will be concentrated on the S1 fraction.

Two chromatograms from the RPLC analyses of the Peace River residue A3 fractions are shown in Fig. 25: one of the oil before processing, the other, after processing. A double solvent gradient elution program was used for these LC analyses: a linear 60% acetonitrile:water to 100% acetonitrile gradient over 30 minutes was followed by a 20 minutes hold at 100% acetonitrile then a linear 0-100% dichloromethane gradient was applied over 20 minutes. A 254 nm wavelength setting was used for detection in order to

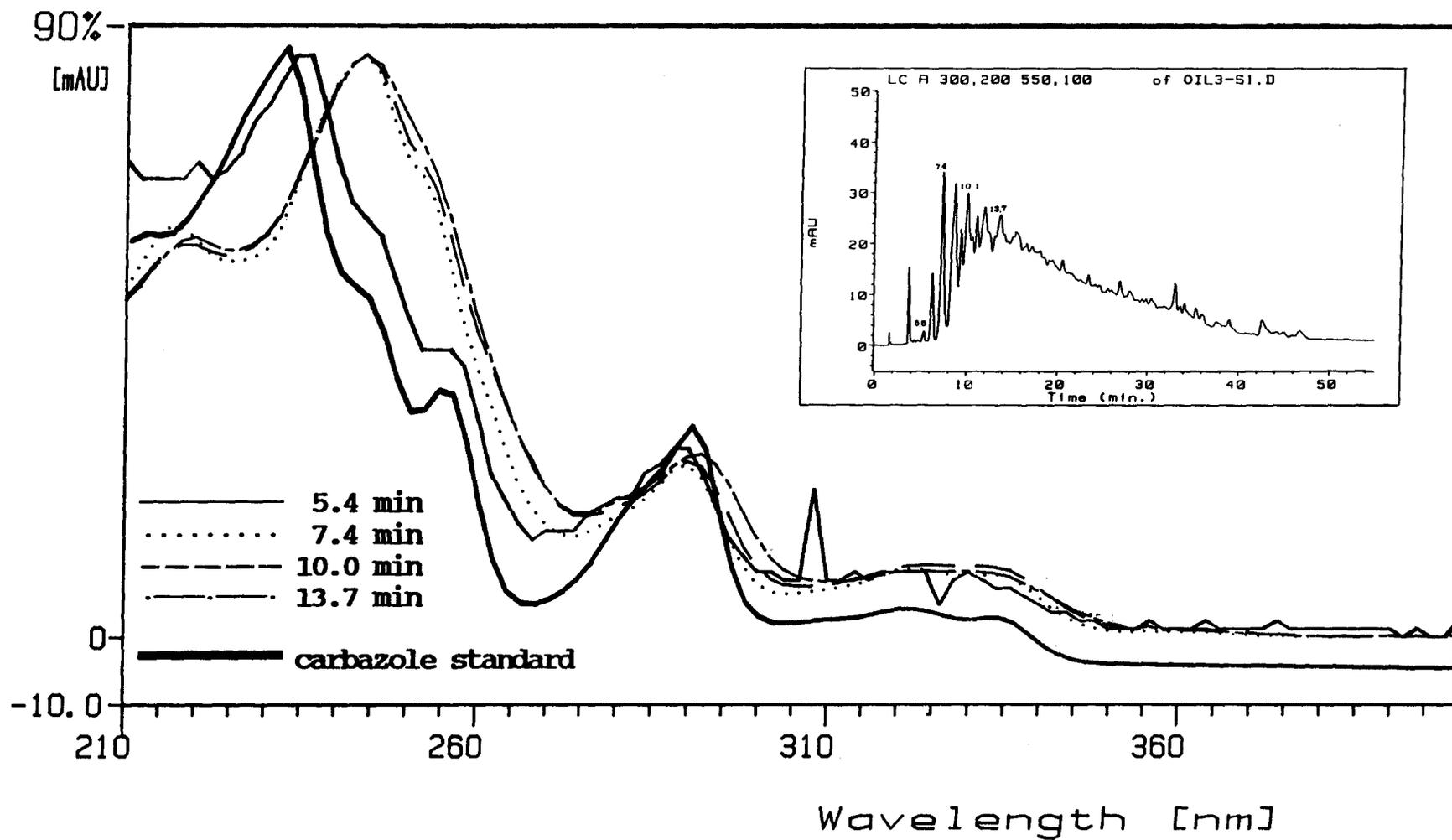


Fig.24 UV spectra of carbazole and four selected peaks from RPLC chromatogram (inset) of processed residue S1 fraction.

minimize the strong dichloromethane absorption below 240 nm.

The chromatogram from the unprocessed residue A3 fraction was extremely complex. No individual peaks were observed and most important of all, a very large peak eluted in the dichloromethane gradient, indicating that these nitrogen components were highly nonpolar. In contrast, the chromatogram of the processed residue A3 fraction was much cleaner (Fig. 25). Very little material eluted in the dichloromethane gradient showing that these components had been removed, presumably by conversion to smaller and more polar components during processing.

III.2.5 High Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS)

Since probe MS results, especially in the ammonia chemical ionization mode, had indicated that the components in the two S1 fractions were homologous series of carbazoles in different degrees of unsaturation, it seemed logical at this stage to use combined high performance liquid chromatography/mass spectrometry in either the EI or CI modes to examine these complex samples.

The LC/MS total ion current chromatogram (TIC) of the Tar Sand A3 fraction is shown at the top of Fig. 26. The same chromatography column packing and gradient elution conditions used previously in LC-DAD analyses were employed

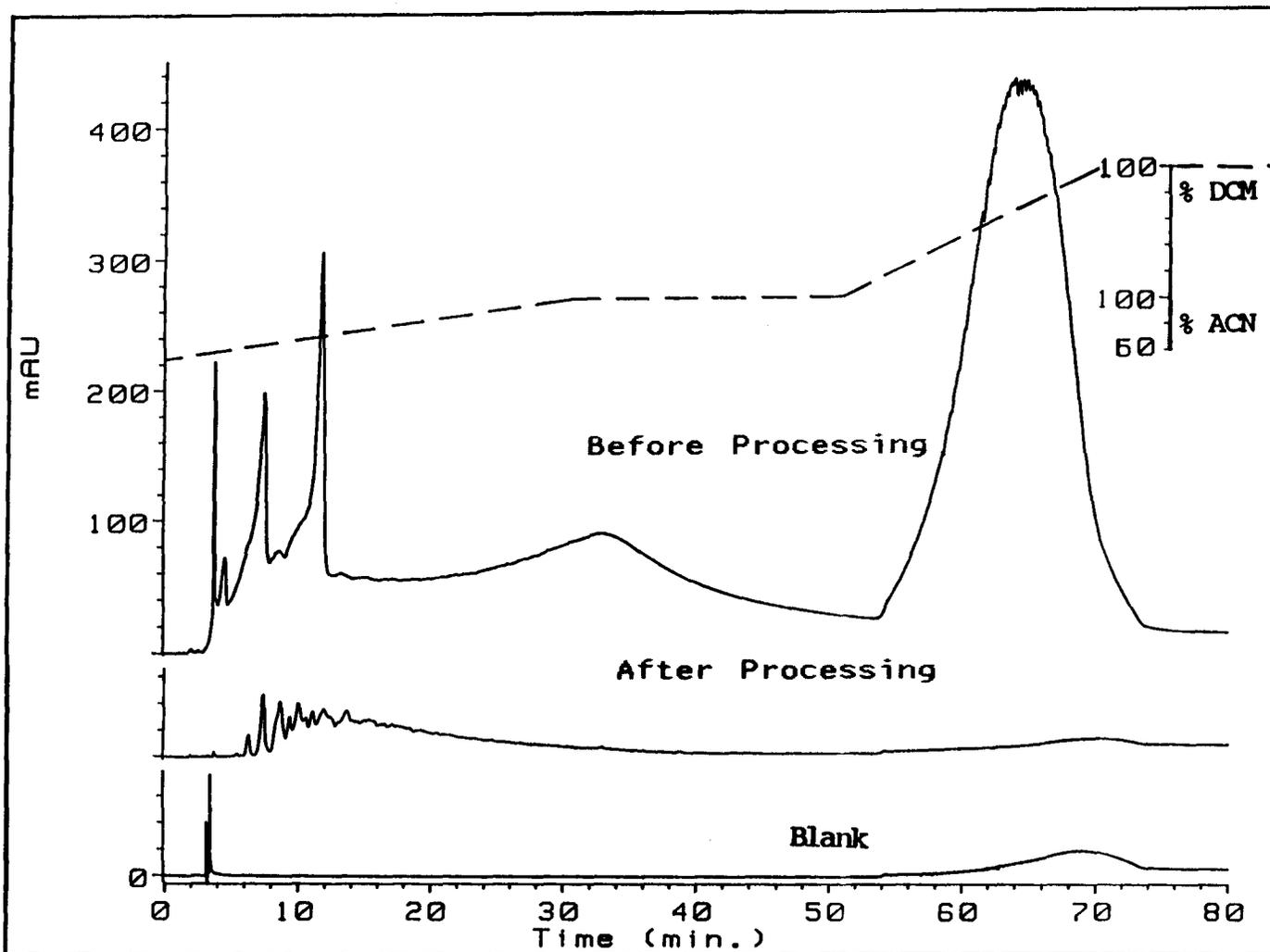


Fig.25 Reverse phase liquid chromatogram of Peace River residue A3 fractions before and after processing. Conditions same as Fig.3b except that a double sequential gradient was employed with detection at 254 nm. See top of figure for gradient profile.

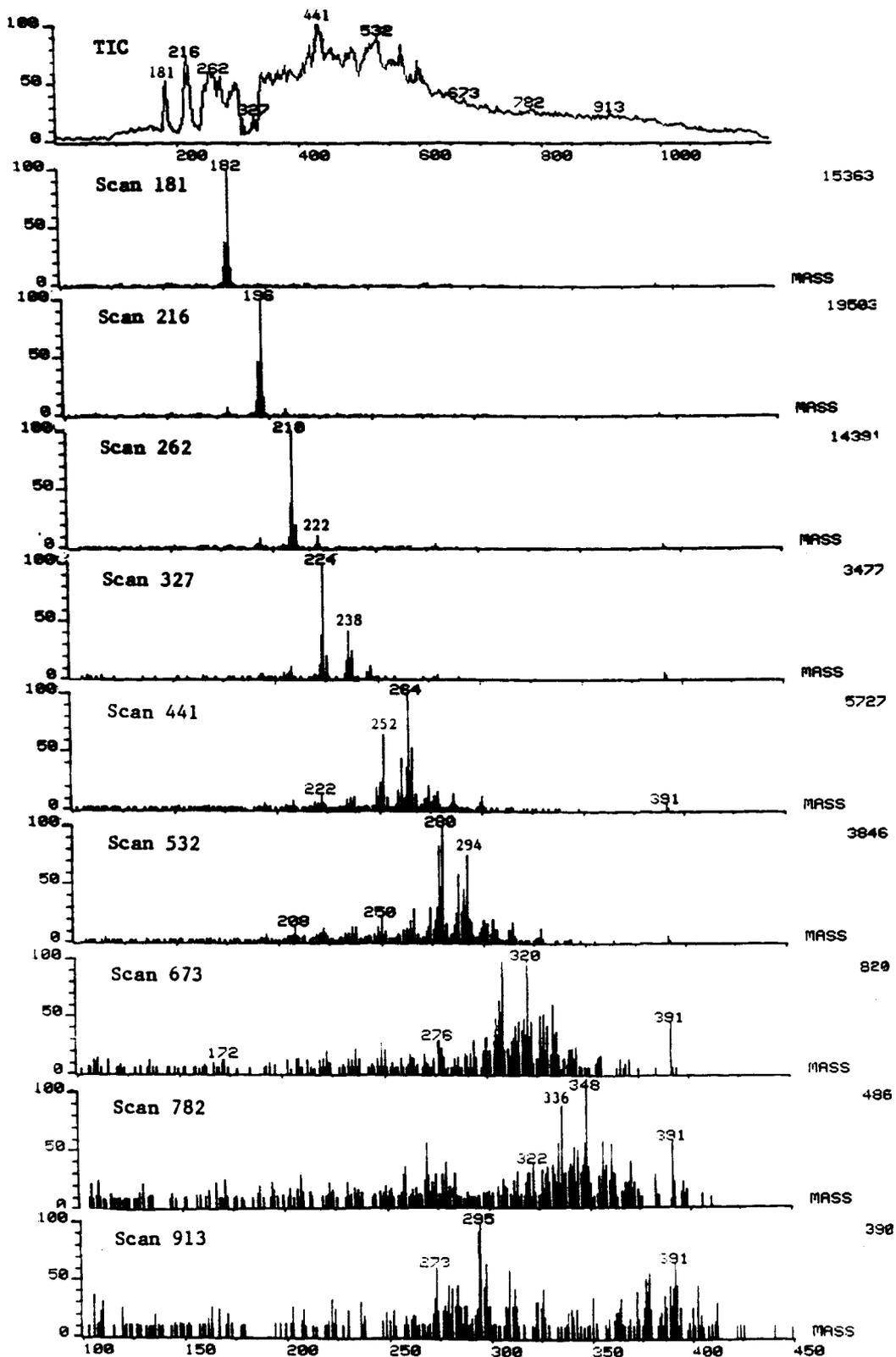


Fig.26 Total ion current chromatogram and selected mass spectra from the LC/MS (NH_3 CI) analysis of the Tar Sand A3 fraction.

in this experiment. A selection of ammonia CI mass spectra obtained during this analysis are also shown in Fig. 26. Lower molecular weight compounds eluted from the column earlier while later eluting components gave rise to higher mass ions. Moreover, the spectra of early eluting components were very simple; the spectra of later eluting components became increasingly complex. For example, only one major ion ($m/z=182$) was found in spectrum 181 whereas spectra 532 and 673 contained many ions of modest intensity. In addition, the masses of the major ions in spectra 181, 216, 262 and 327 differ by 14 mass units, indicative of an homologous series.

Mass spectral data presented in a previous section was interpreted in term of series of alkylated carbazoles of increasing numbers of degrees of unsaturation. Thus, the series of saturated alkyl carbazoles containing 1, 2, 3... 10 carbons would exhibit a series of $(M+H)^+$ ions with m/z values of 182, 196, 210... 308; the mass chromatograms of this series of ions are displayed in Fig. 27. As expected, as the number of carbon atom substituents increased, the retention times of those components increased; also, the number of possible structural isomers increases with increasing carbon number, resulting in broader chromatographic peaks. Similar series of mass chromatograms have been reconstructed from the mass spectral data for the unsaturated alkyl carbazoles containing 1, 2, 3, 4 and 5 degrees of unsaturation; these data are included in Appendix II. Interestingly, no 6 or 7

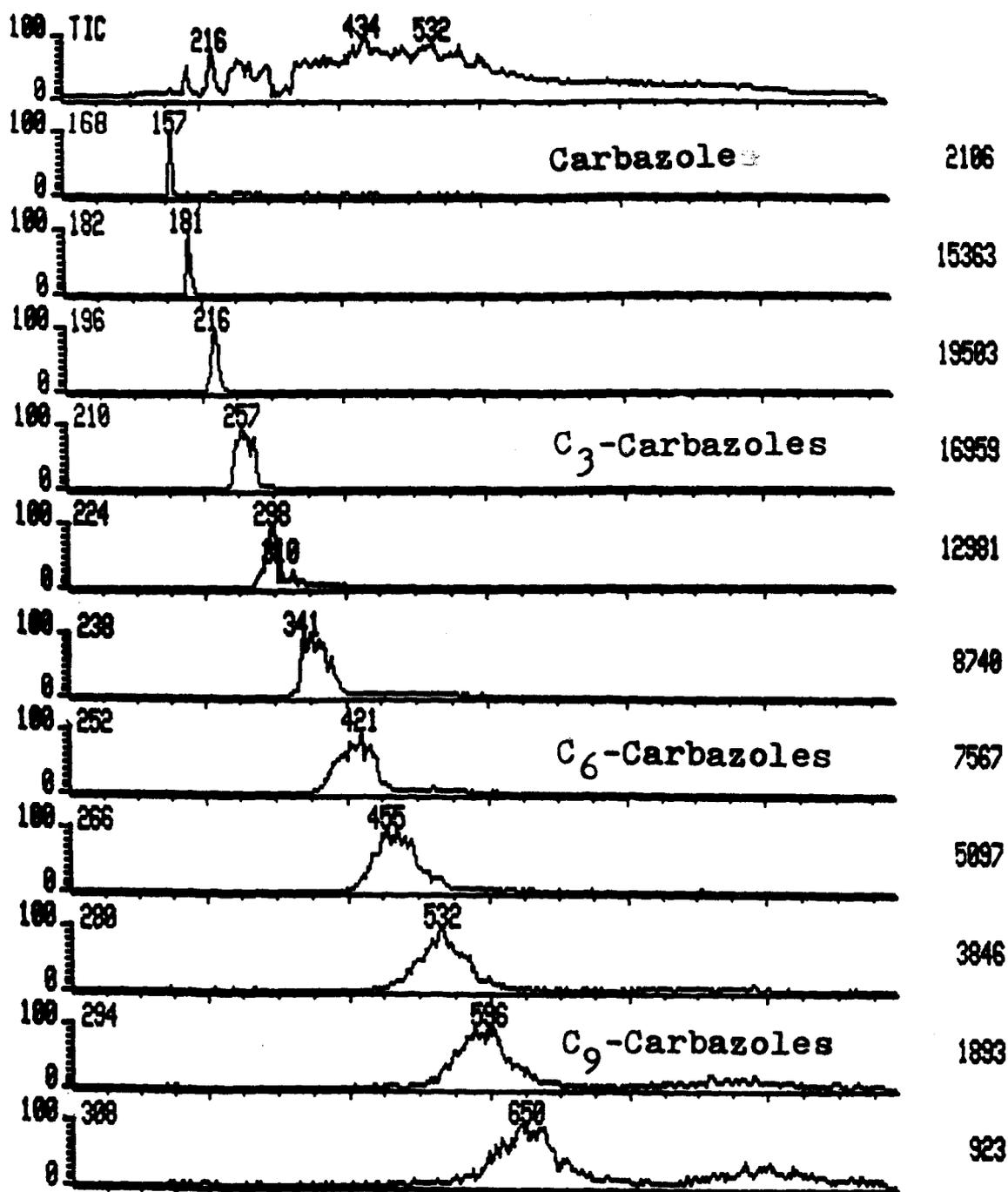


Fig.27 Mass chromatograms of the saturated carbazole series obtained from the LC/MS (NH₃ CI) analysis of the Tar Sand A3 fraction.

degree unsaturates were detected.

In order to compare the relative abundances of each m/z value in these alkyl carbazoles, the area under the peaks in each mass chromatogram was determined. The relative heights of these peaks is shown in the top right hand corner of each mass chromatogram; in each mass spectral display the top of the peak is automatically normalized to 100 intensity. Since the peak widths vary quite markedly in different peaks (especially in the four- and five-degree unsaturated carbazoles) the use of peak heights alone was precluded.

The best way to compare the relative areas due to each carbazole was to determine the area under the peak of each mass chromatogram. Unfortunately, this peak area information is not automatically calculated by the Digital PDP 11/24 data system. To make these area measurements the operator had to chose two points in each mass chromatogram (Fig. 28), an initial point and a final point, well to either side of the eluting peak. The computer would then draw a line joining these two points and calculate the area (ion intensities) for the enclosed region. This value can then be compared directly to similarly derived numbers. The error in these calculated areas was $\pm 10\%$ at the most.

Peak areas were determined in this manner for the six carbazole series and the results are listed in Appendix III; these data are plotted in Fig. 29 to show the distribution of peak areas as a function of the number of carbon atoms

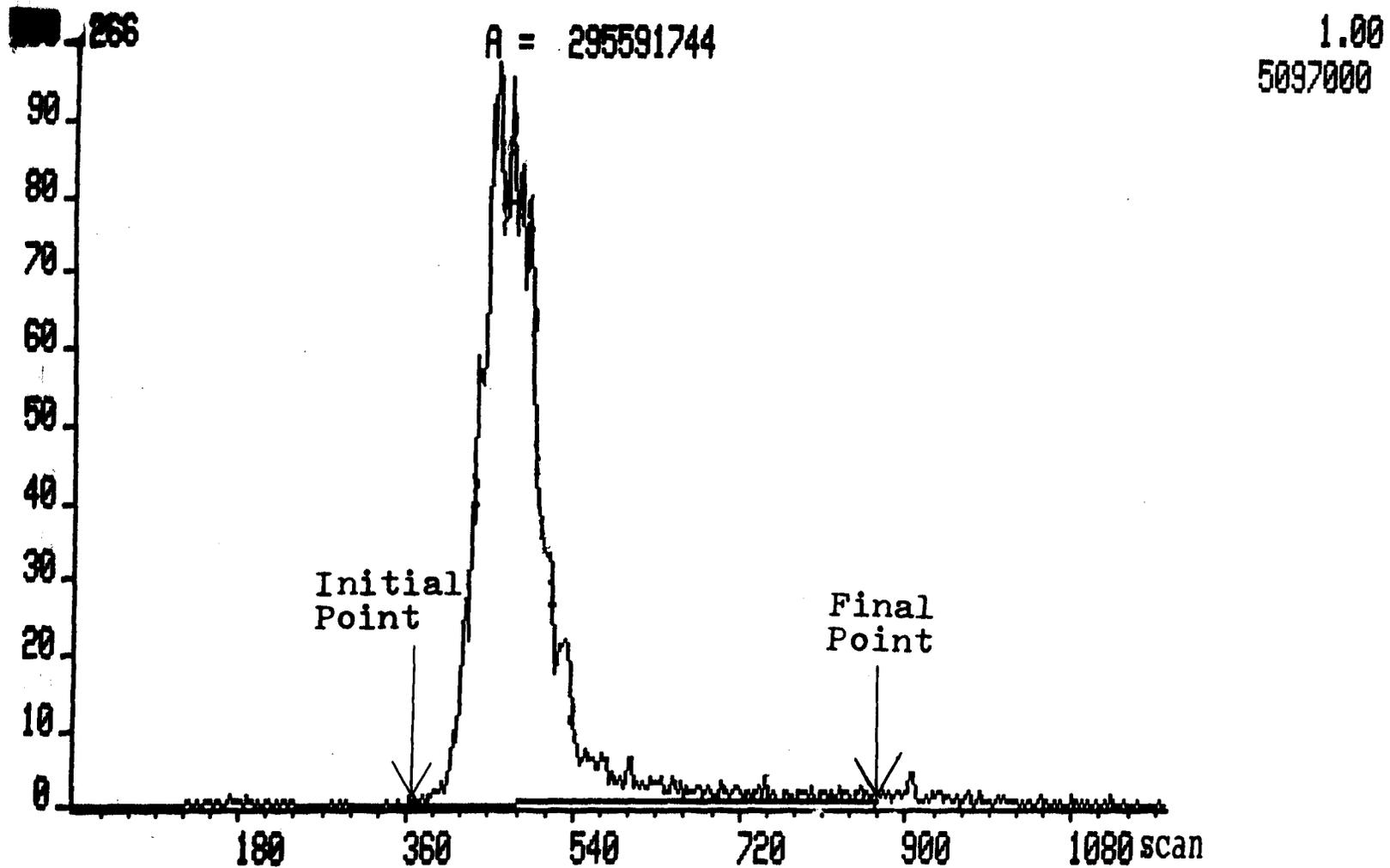


Fig-28 Example of method used to determine area under a peak in a mass chromatogram.

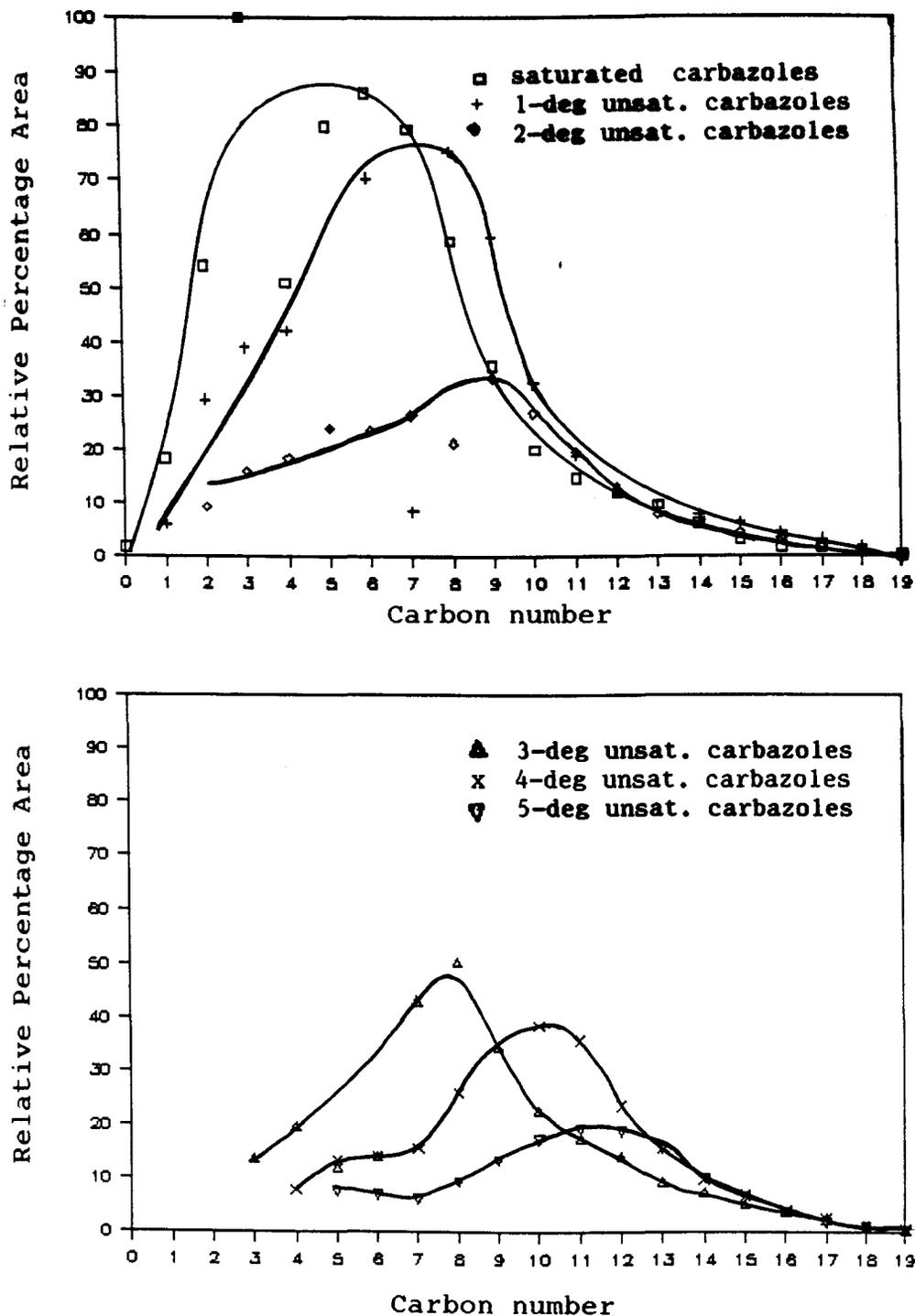


Fig.29 Relative areas under mass chromatogram peaks from the NH_3 CI LC/MS analysis of Tar Sand A3 fraction. Areas plotted as a function of number of carbons attached to carbazole nucleus for six carbazole series of differing degrees of unsaturation: saturated, one, two, three, four and five degree of unsaturation.

attached to the carbazole nucleus for each series. The summation of the areas from each carbazole series is tabulated at the bottom of each column in Appendix III. The results of the area determination indicated that saturated carbazoles constituted the major carbazole group in the Tar Sand A3 fraction followed by the one-degree unsaturates, then the three-degree unsaturates (possibly benzocarbazole derivatives) while the least abundant groups were the four and five-degree unsaturated carbazoles (Fig.29).

As the degree of unsaturation increased the maximum in the distribution shifted to larger numbers of carbons attached to the carbazoles. C₃-carbazoles (m/z=210) were the most abundant compounds in the saturated carbazole series, the C₈-carbazoles (m/z=278) the maximum in the one-degree unsaturates, the C₉-carbazoles (m/z=290) the maximum in the two-degree unsaturates, The three degree unsaturates maximized as C₈-carbazoles (m/z=274) the four degree unsaturates as C₁₀-carbazoles (m/z=300) and the five degree unsaturates as C₁₁-carbazoles (m/z=312). Fig. 29 also showed that the intensities of ions for compounds with carbon numbers above 19 (i.e., compounds with molecular masses above 400 amu were very small. The HPLC/MS data was kindly collected by Dr. M.A. Quilliam at the Atlantic Research Laboratory in Halifax. All data analyses were performed at McMaster University.

III.2.6 Summary

Results from the high performance liquid chromatography analyses showed that most of the nitrogenous components in the Tar Sand and the processed residue oil sample eluted in the S1 fraction in complex chromatographic patterns with many unresolved peaks. UV spectra indicated that most compounds in the S1 fractions had a carbazole nucleus. On the other hand, the difference of the elution time and chromatographic patterns in the two S1 chromatograms and their UV-spectra suggested that the carbazole components in these two samples were slightly different. Compared to the S1 fractions, only very few amino-PAH and tertiary-PANH were eluted into the S2 and S3 fractions.

For the unprocessed residue oil sample, a sequential double gradient LC analysis indicated that the components of this sample were extremely poorly resolved and that the sample contained a substantial amount of nonpolar compounds even after the removal of the asphaltenes. Hence, no further separations or analyses were done in this sample.

Combined LC/MS in the NH_3 CI mode was very useful for elucidating the complexity of the Tar Sand A3 fractions; six homologous series of alkylated carbazoles of different degrees of unsaturation were identified. Amongst these carbazole groups, the saturated carbazole series was found to be the major carbazole group and, in general, as the degree

of unsaturation increased, the amounts of carbazoles in that series decreased. The lower molecular weight compounds eluted earlier in the reverse phase chromatogram and had relatively simple mass spectra while the higher molecular weight compounds eluted at a longer retention time and exhibited more complex spectra.

III.2.7 Gas Chromatography (GC)

Capillary gas chromatography was performed on a 30 m x 0.25 mm narrow-bore DB-5 column with temperature programming from 60° to 300°C over 30 min (8°C per min) and a hold at 300°C. Capillary GC chromatograms obtained from the Tar Sand fractions S1, S2 and S3 are shown in Fig. 30. Not surprisingly, most of the nitrogenous compounds were found in fraction S1 and with traces in the other two fractions. In the S1 fraction chromatogram, compounds began to elute from the capillary column at an oven temperature of 220°C (22 min). Early eluting components were better resolved than those that eluted later; peaks eluting after 30 min were poorly resolved resulting in a broad tailing peak. The S2 fraction chromatogram and the blank chromatogram was very similar; thus negligible amounts of amino components had been collected in this fraction. A comparison of the S2 and S3 chromatogram shows that slightly more material was found in the S3 fraction but in comparison to fraction S1, the S3

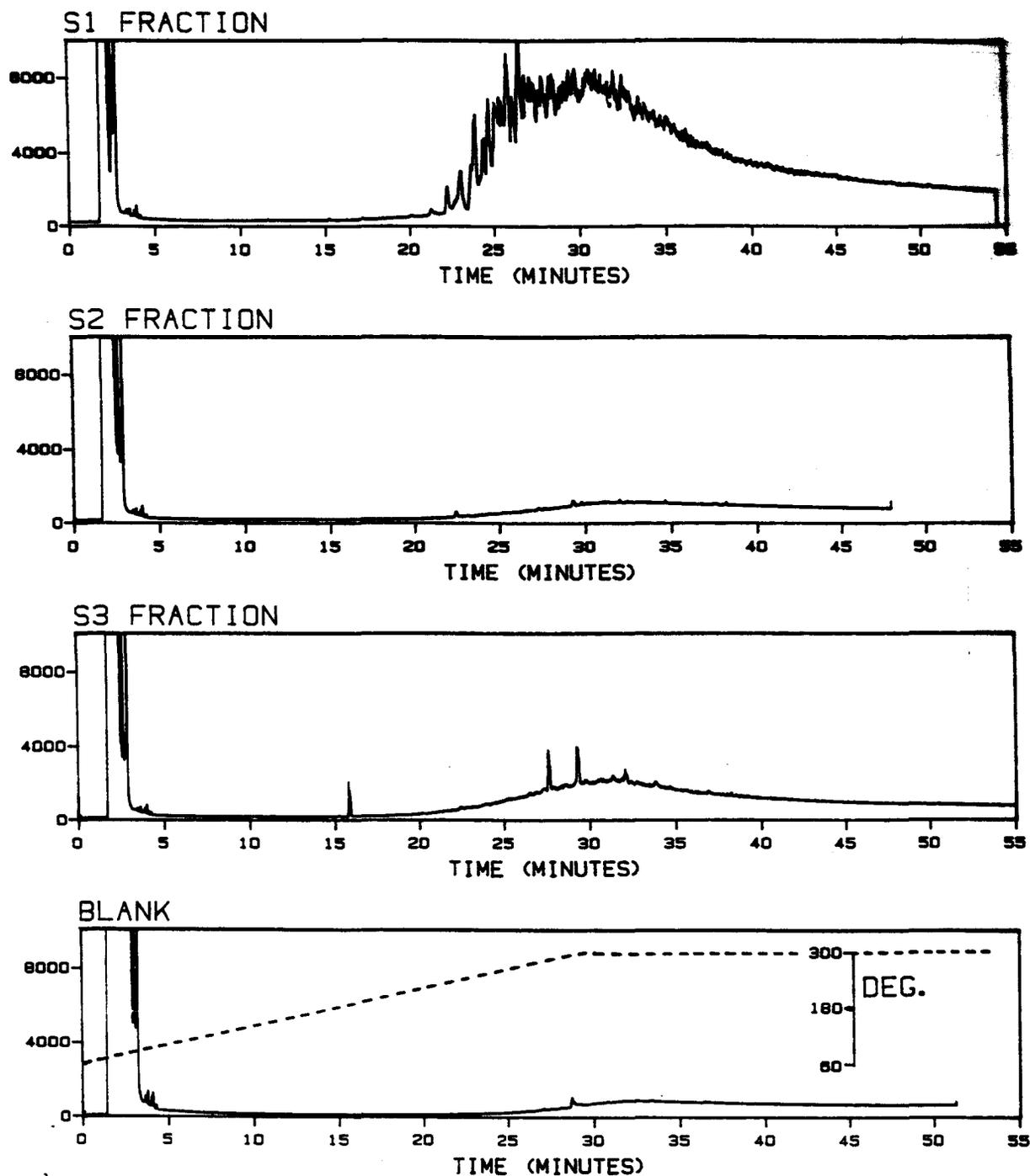


Fig.30 Capillary column GC analysis with FID detection of Tar Sand fractions: S1, S2, S3 and blank. Conditions: 30 m x 0.25 mm DB-5 narrow bore fused-silica capillary column; temperature programmed from 60°C to 300°C at 8°C/min then hold at 300°C to 55 minutes (shown on blank chromatogram).

fraction contained relatively little material.

The gas chromatograms of the processed residue fractions (S1, S2 and S3) are shown in Fig. 31. Most of the components were found in fraction S1 with only a few in fractions S2 and S3. Compounds started to emerge from the column at an oven temperature of 195°C and eluted as a broad featureless peak. A major difference between the Tar Sand and the processed residue S1 chromatograms was profile of the broad peak. The chromatogram of fraction S2 differed little from the blank chromatogram. Few peaks were found in the S3 fraction chromatogram and the elution pattern was similar that of the Tar Sand S3 fraction. The peaks at 16, 27 and 29 min found in both S3 GC chromatograms were probably phthalate contaminants since none of these peaks were observed in the NH₃ CI GC/MS analysis.

III.2.8 Gas Chromatography-Mass Spectrometry (GC-MS)

The GC/MS analyses in the NH₃ CI mode were performed by Mr. F. Ramalen. The GC/MS total ion current (TIC) chromatogram of Tar Sand A3 fraction and a series of mass chromatograms of the saturated carbazole group are shown in Fig. 32. The broad, featureless elution peak of the TIC chromatogram is similar to the FID chromatogram. The mass chromatograms of the saturated carbazole series again indicated that lower molecular compounds eluted earlier than

fraction contained relatively little material.

The gas chromatograms of the processed residue fractions (S1, S2 and S3) are shown in Fig. 31. Most of the components were found in fraction S1 with only a few in fractions S2 and S3. Compounds started to emerge from the column at an oven temperature of 195°C and eluted as a broad featureless peak. A major difference between the Tar Sand and the processed residue S1 chromatograms was profile of the broad peak. The chromatogram of fraction S2 differed little from the blank chromatogram. Few peaks were found in the S3 fraction chromatogram and the elution pattern was similar that of the Tar Sand S3 fraction. The peaks at 16, 27 and 29 min found in both S3 GC chromatograms were probably phthalate contaminants since none of these peaks were observed in the NH₃ CI GC/MS analysis.

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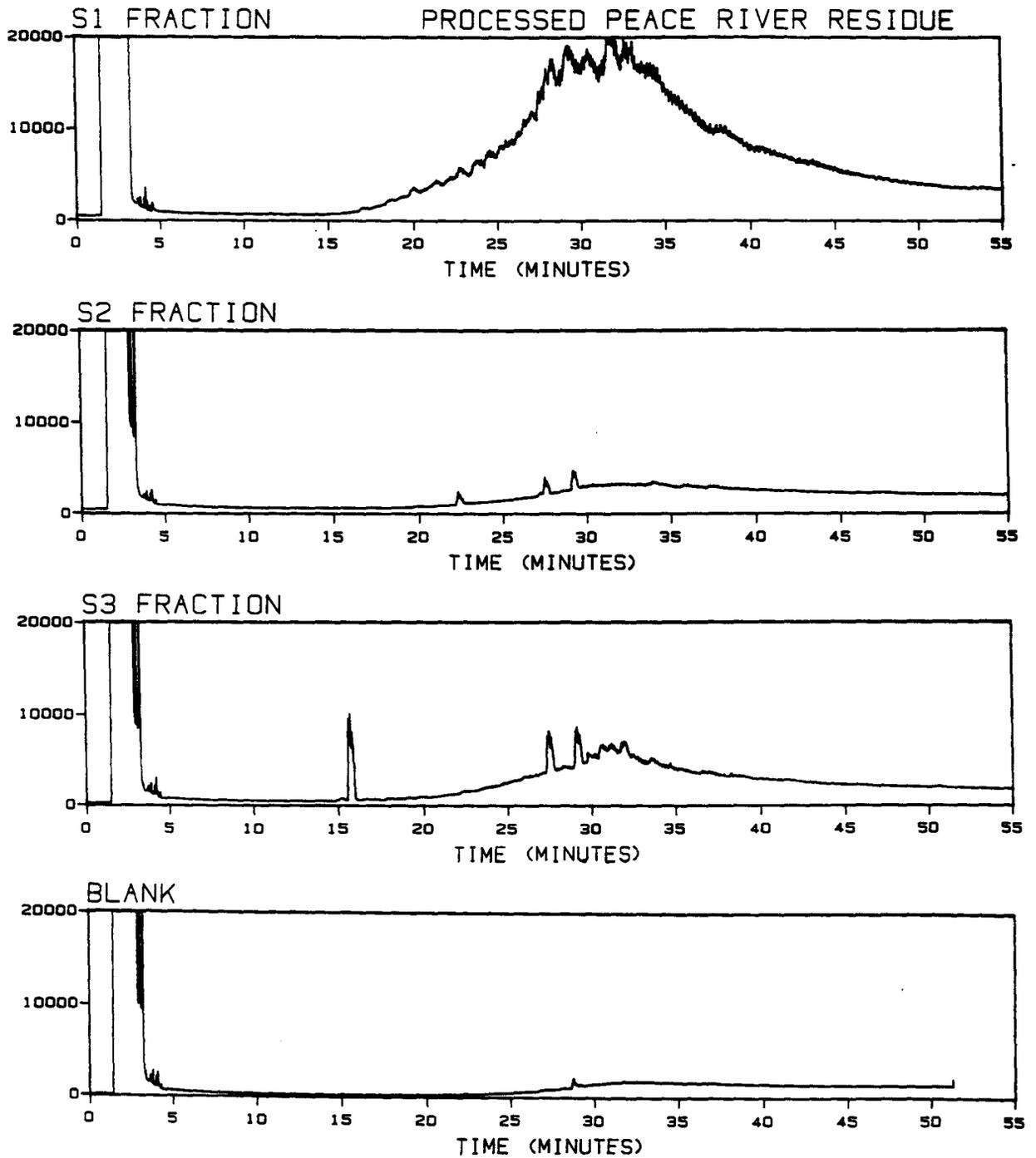


Fig.31 Capillary column GC analysis with FID detection of processed residue fractions S1, S2, S3 and blank. Conditions same as in Fig.30.

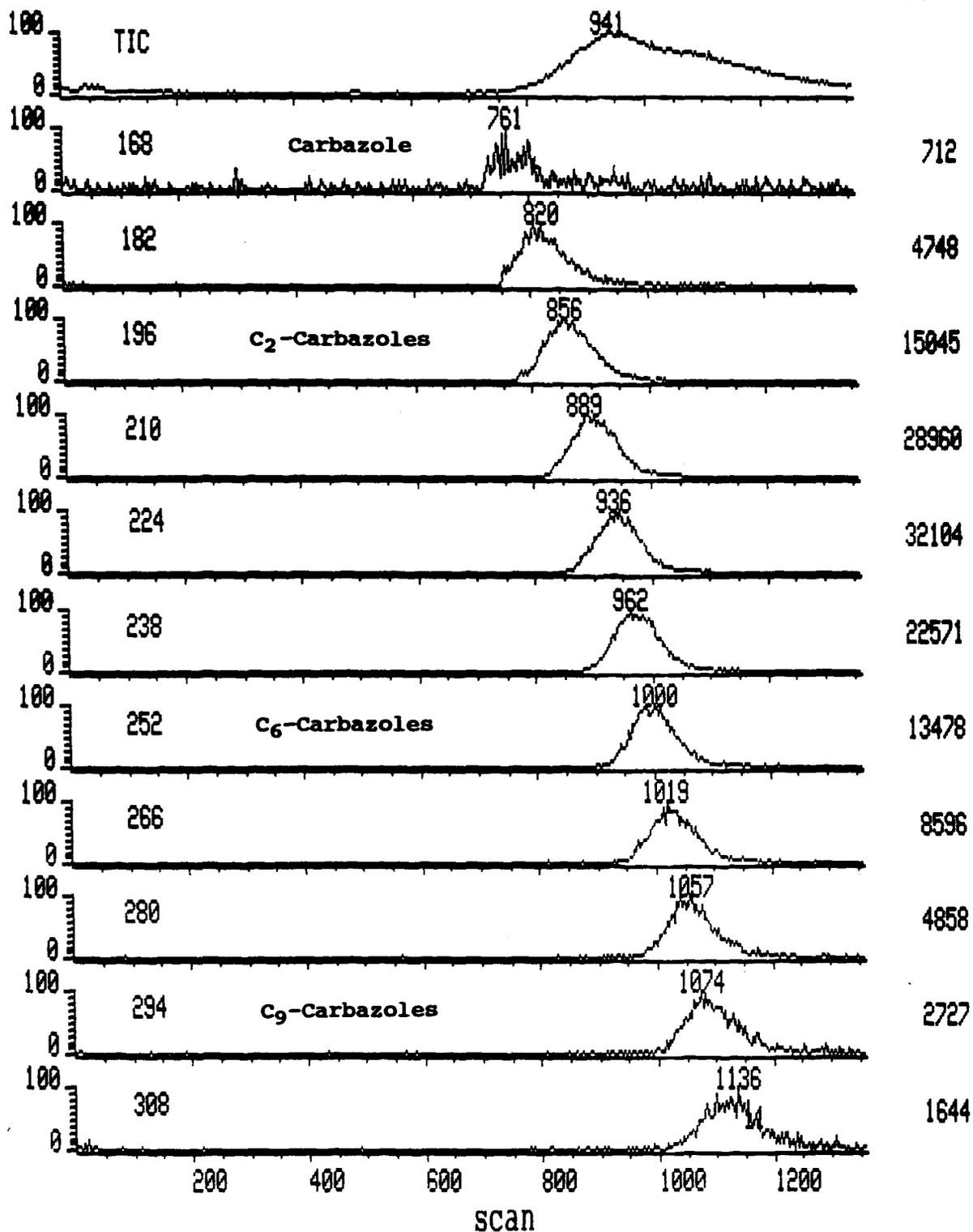


Fig.32 Total ion current chromatogram and the mass chromatograms of the saturated carbazole series of the Tar Sand A3 fraction GC/MS (NH_3) analysis.

the higher molecular weight compounds.

A selection of mass spectra obtained during the GC/MS analysis (Fig. 33) are very similar to the spectra obtained in the LC/MS experiment (Fig. 26). The spectra of early eluting components had fewer peaks than spectra of later eluting compounds. Moreover, the total ion intensities in the spectra of early eluting components were greater than those of later eluting components. Mass chromatograms of the saturated, one-, two- and three-degree unsaturated C₅- and C₁₀-carbazoles are shown in Fig. 34. In both series the saturated compounds were the first eluting components and as the degree of unsaturation increased, the retention time increased.

In comparing the results obtained from the GC/MS and the LC/MS experiments, some differences were noted. First, the peak widths of peaks in the GC/MS mass chromatograms (Fig. 32) were more constant than the LC/MS peak widths; the peak widths in the LC/MS analysis increased as the molecular weights of the eluting components increased (see the LC/MS mass chromatograms in Appendix II). Second, the intensities of higher molecular weight ions were greater in the LC/MS experiment; Fig. 35 shows several mass chromatograms of the C₉- to C₂₀- saturated carbazoles from both the GC/MS and LC/MS analyses. In the GC/MS mass chromatograms, as the masses of the ions increased from m/z=294 (C₉-carbazoles) to m/z=336 (C₁₂-carbazoles) to m/z=378 (C₁₅-carbazoles), the ion

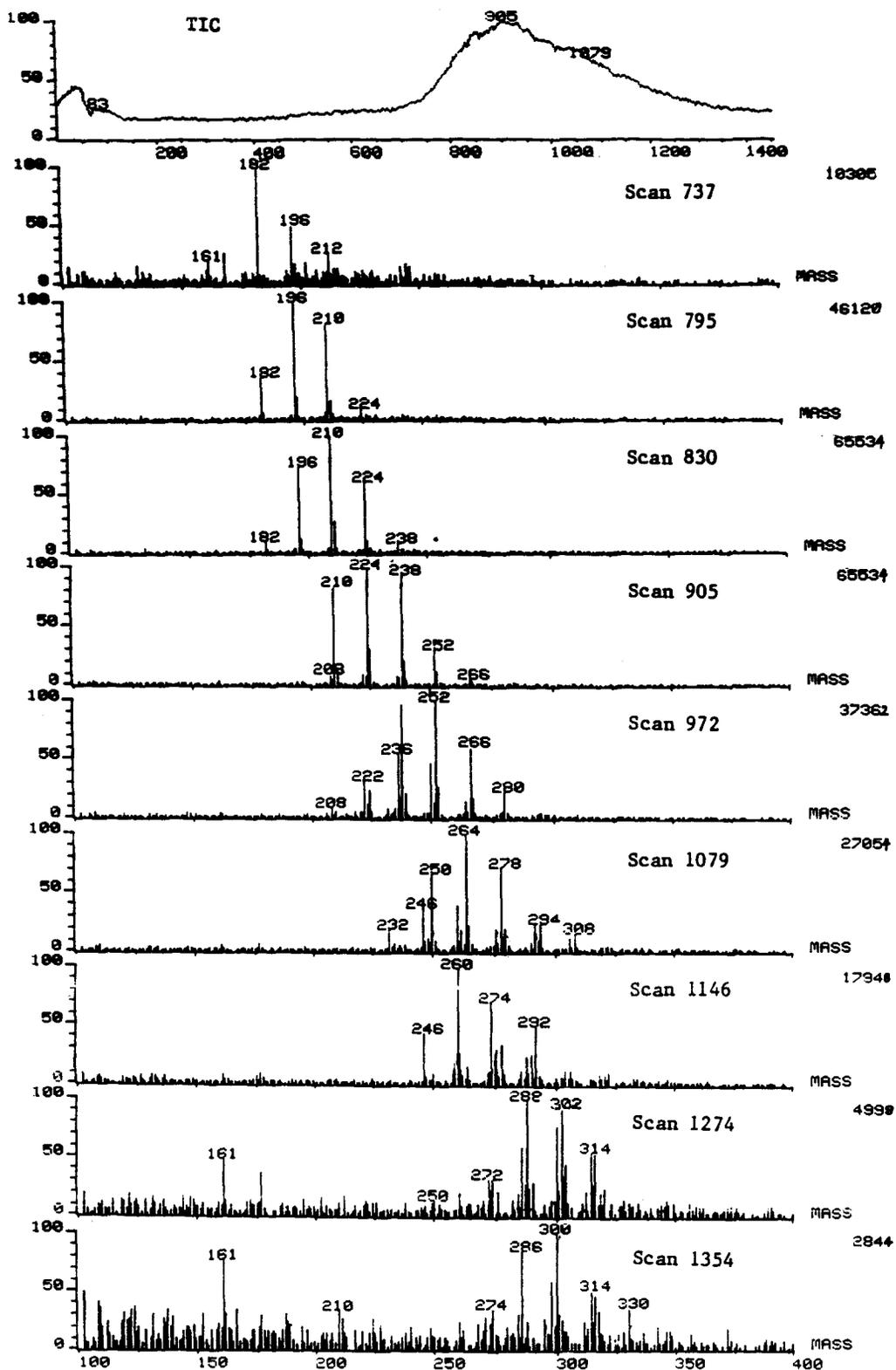


Fig.33 Total ion current chromatogram and selected mass spectra from the GC/MS (NH_3 CI) analysis of the Tar Sand A3 fraction.

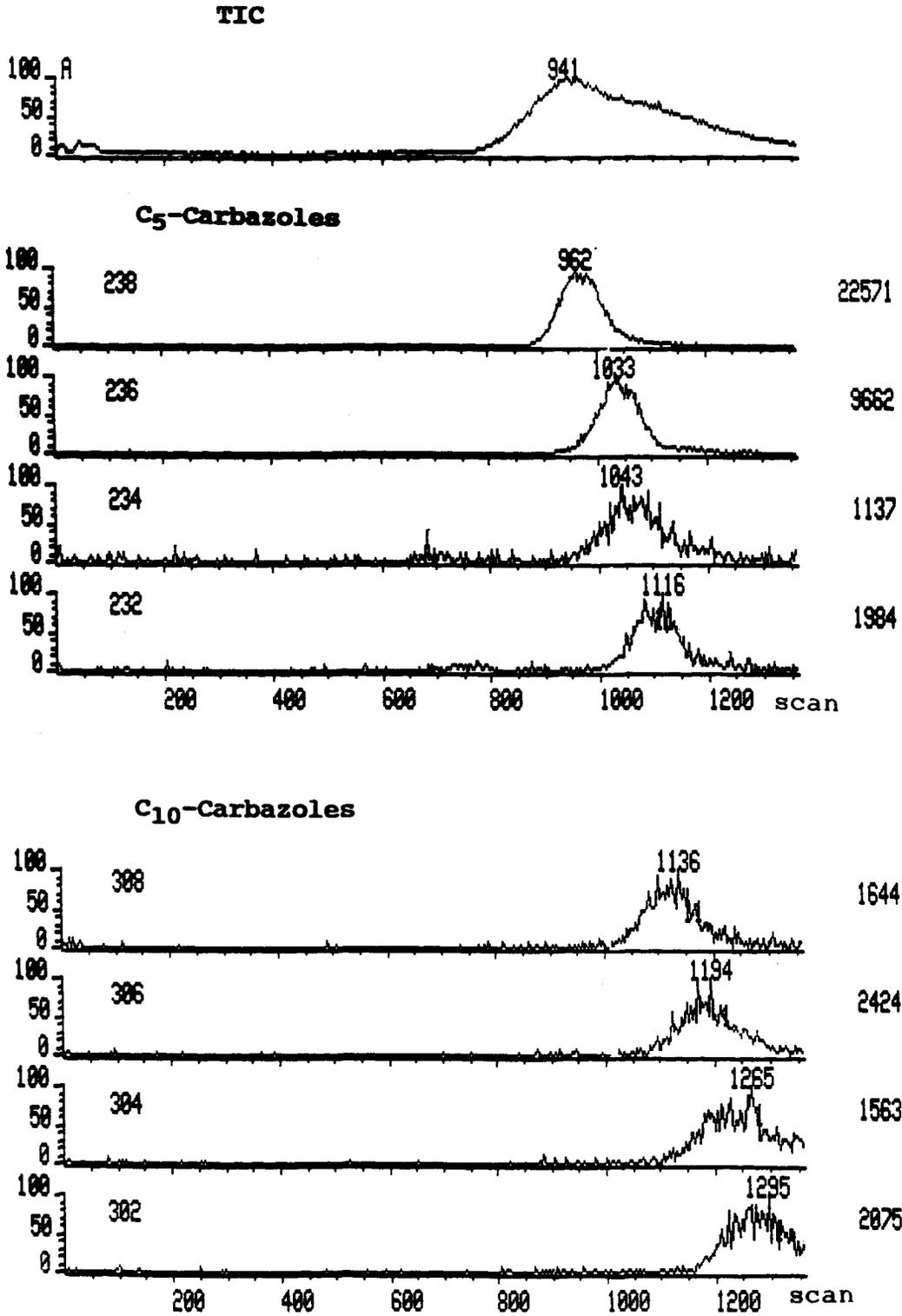


Fig.34 Mass chromatograms from the GC/MS analysis of the Tar Sand A3 fraction: C₅- and C₁₀-carbazoles with zero, 1, 2 and 3 degrees of unsaturation.

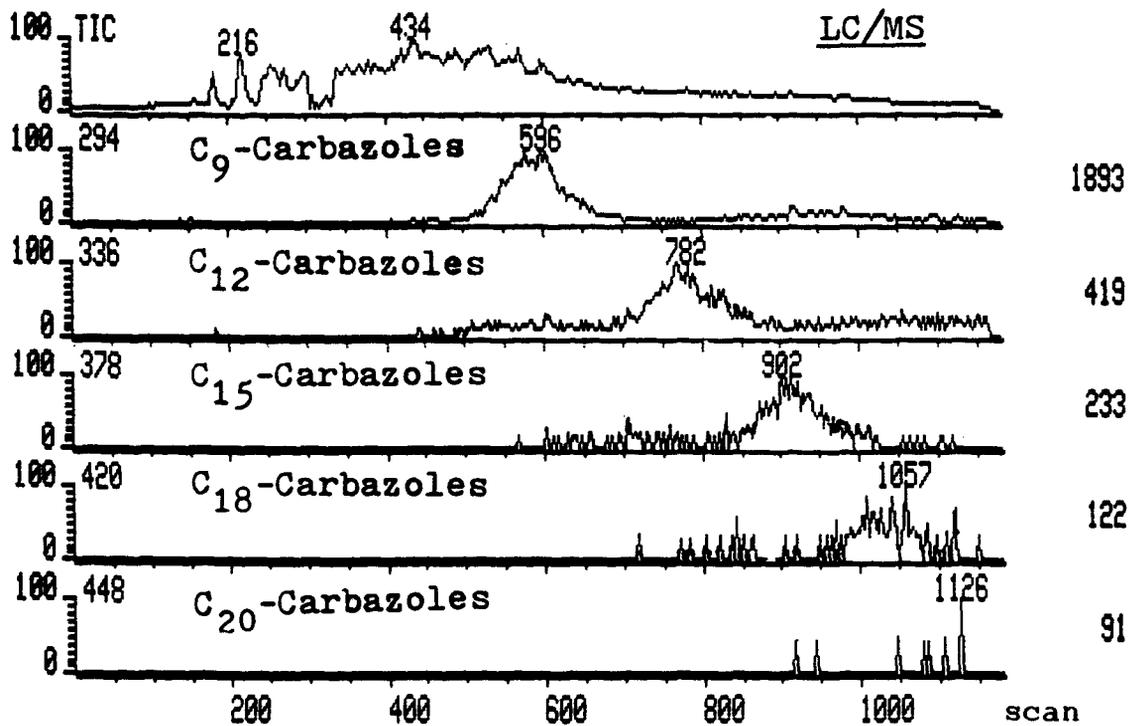
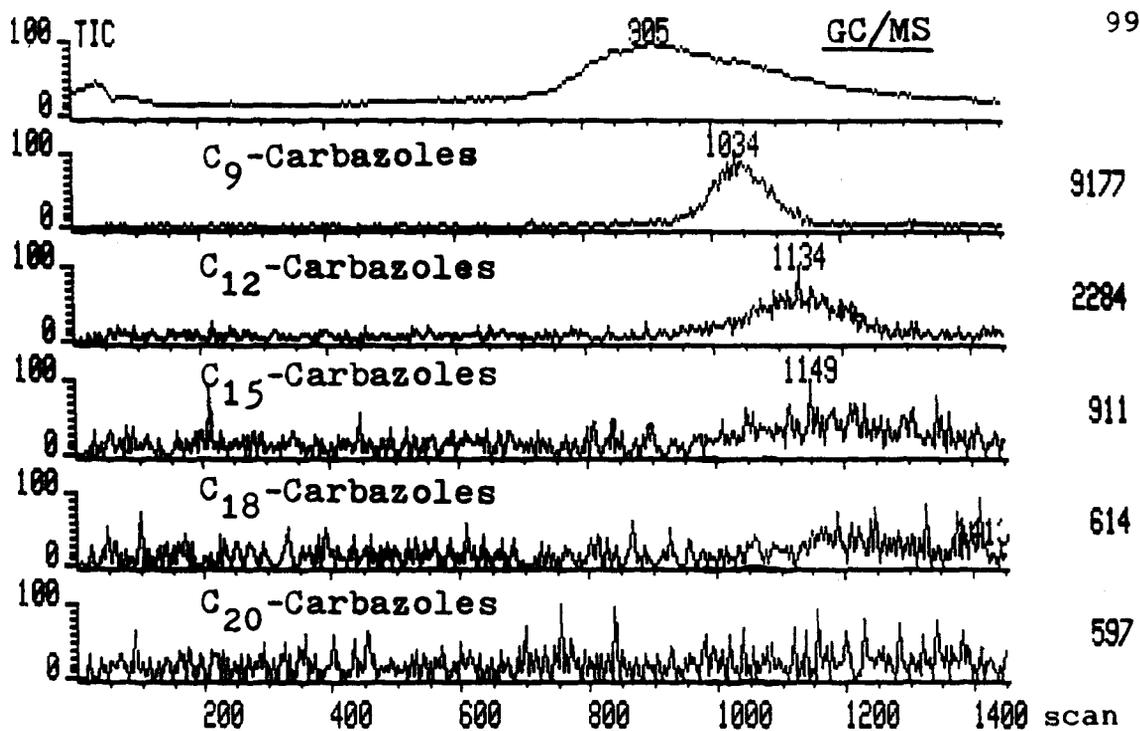


Fig.35 Mass chromatograms to show comparison of GC/MS (NH₃ CI) and LC/MS (NH₃ CI) analyses of the Tar Sand A3 fractions.

intensities decreased about 10-fold; no distinguishable peaks could be seen in the mass chromatograms for molecular ions of carbazoles with 16 or more carbons. In the LC/MS mode, however, the $m/z=420$ mass chromatogram still showed a peak easily distinguished from background; by $m/z=448$ this method also showed a negligible response. Clearly, the LC/MS method was more sensitive for the detection of higher molecular weight compounds than GC/MS. The relative areas of all the alkylated carbazoles with the same carbon number, irrespective of the degree of unsaturation, have been plotted as a function of carbon number (Fig. 36). Both the GC/MS and the LC/MS analyses results were added together and plotted from C_2 to C_{19} . This plot shows that GC/MS was more suitable for the lower molecular compounds and is less sensitive in the higher mass range (C_7 -carbazoles and above). The areas of carbazoles above C_{13} are so small as to be almost negligible. In contrast, LC/MS analyses was able to extend the detection range to C_{19} -carbazoles before the peak intensity was too small to measure.

The total ion current chromatogram of the GC/MS (NH_3 CI) analysis and a selection of mass spectra from the processed residue S1 fraction are shown in Fig. 37. The elution pattern of compounds found in this GC/MS experiment is very similar to that observed in the Tar Sand A3 fraction analysis; spectra from the beginning of the chromatogram were simpler compared to spectra from later scans. Six different

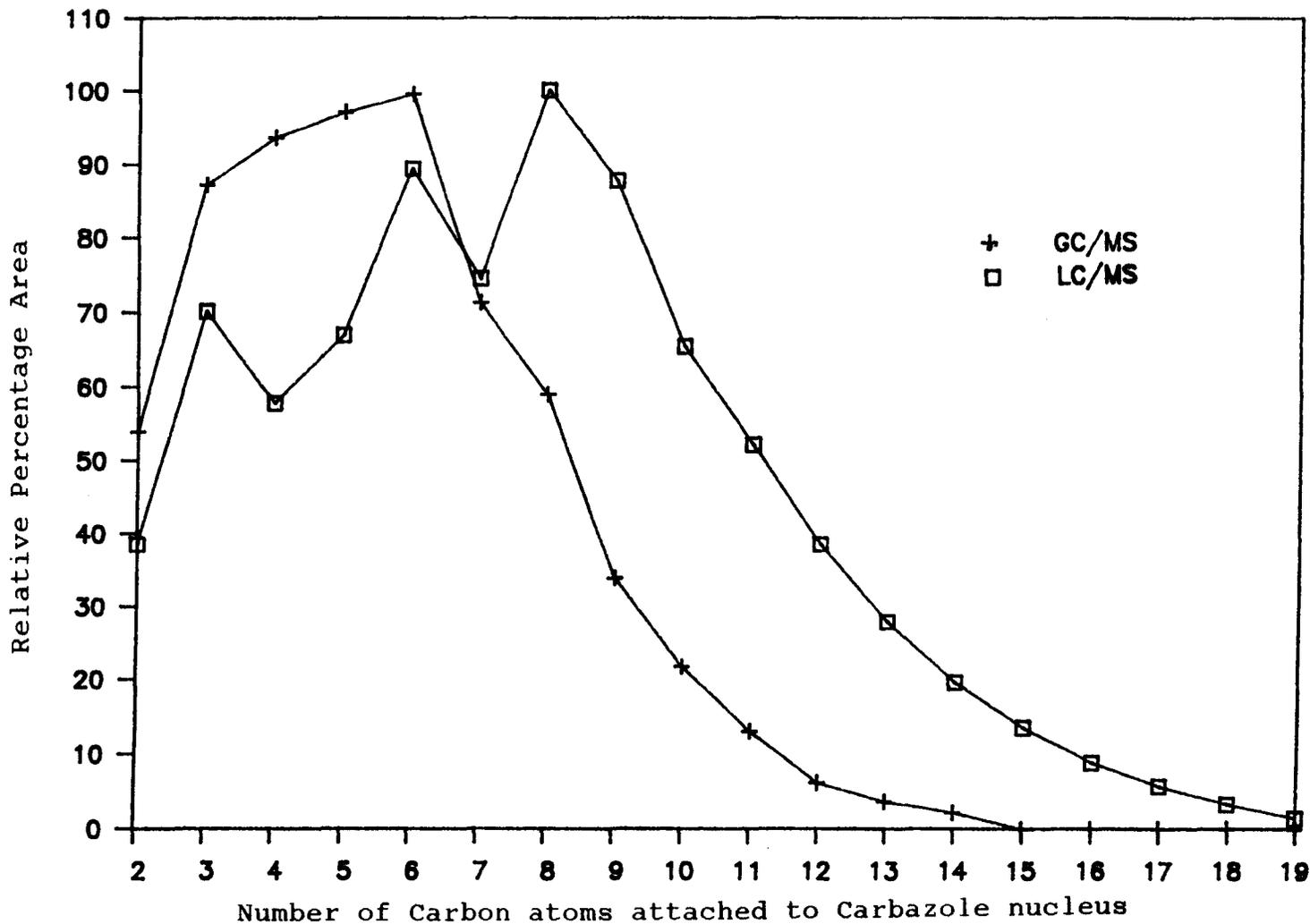


Fig.36 Distribution of alkylated carbazoles as determined by the areas of mass chromatograms for carbazoles containing the same number of carbons were added together and plotted as a function of carbon number.

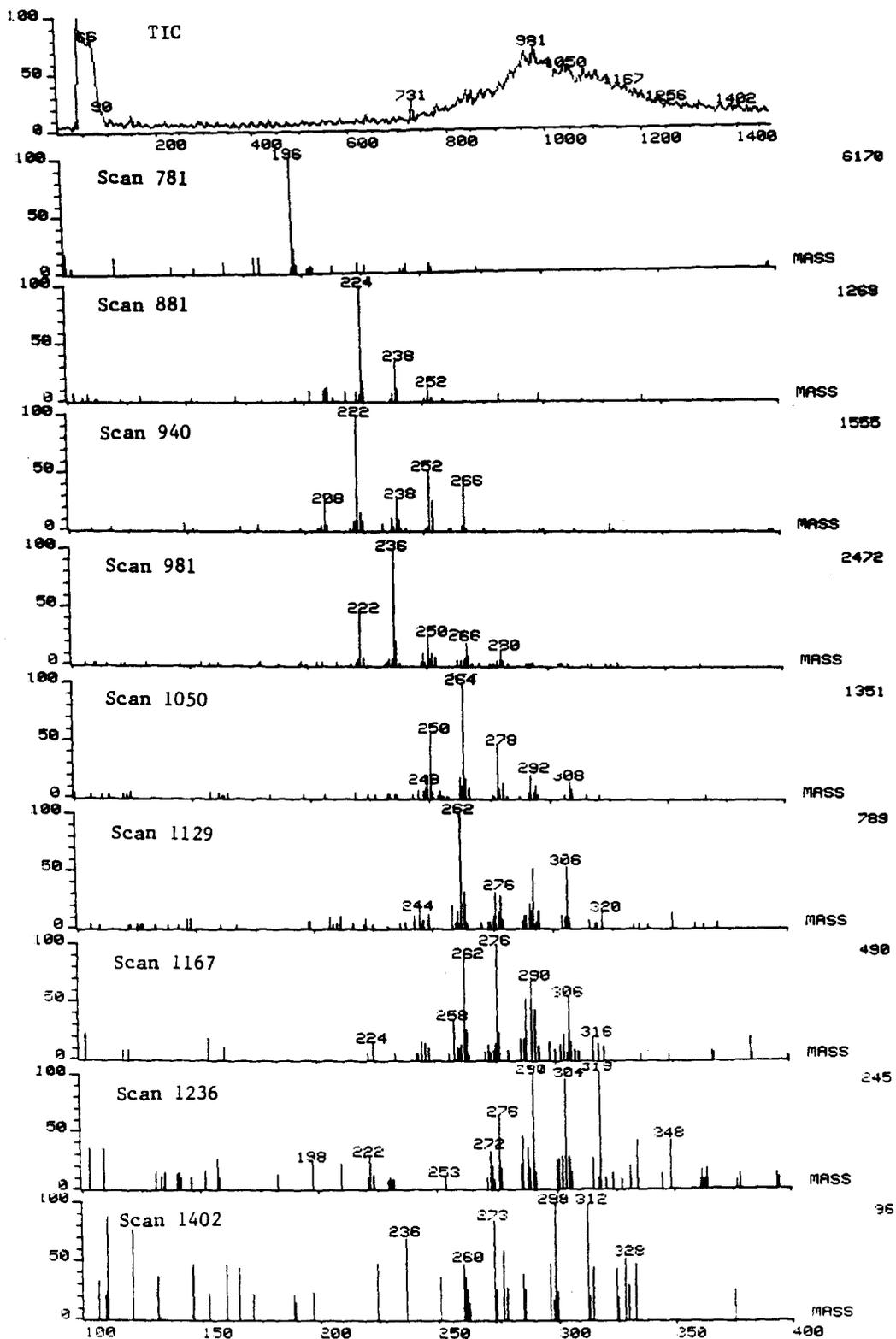


Fig.37 Total ion current chromatogram and selected mass spectra from the GC/MS (NH_3) analysis of the processed residue S1 fraction.

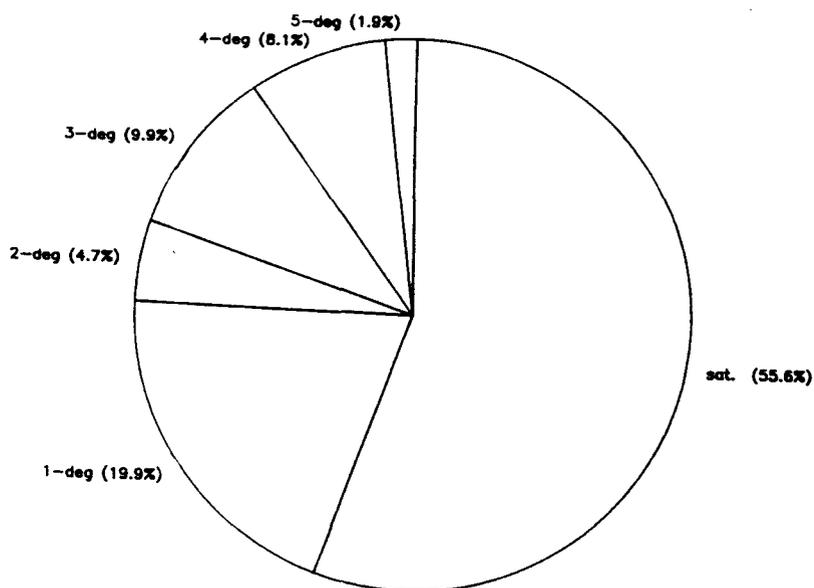
carbazole groups in different degrees of unsaturation were also found in this fraction. Peak areas from the mass chromatogram of each carbazole peak were measured and are listed in Appendix IV.

Pie charts showing the GC/MS area distributions of each carbazole group are plotted in Fig. 38ba and 38b. The major difference between the two oil samples is that in the Tar Sand, the major carbazole group was the saturated carbazoles (56%) while in the processed residue, the one-degree unsaturates were the dominant carbazole series (39%).

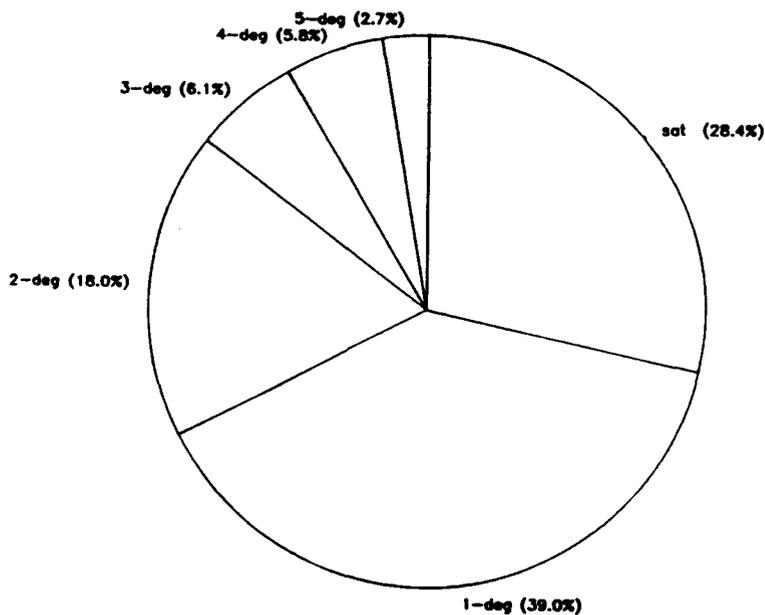
III.2.9 Summary

Results from the GC-FID analyses of the Tar Sand and processed residue fractions indicated that most of the nitrogenous components eluted in fraction S1. The complexity of these S1 fractions is obvious from the broad hump of eluting components in the two chromatograms.

The GC/MS analyses also showed the presence of alkylated carbazoles in different degrees of unsaturation in both S1 fractions. Saturated carbazoles were found to be the major carbazole series in Tar Sand sample while in the processed residue, the major series was the one degree unsaturated carbazoles. The LC/MS analysis gave very similar result to the GC/MS analyses. However, the LC/MS experiment was more sensitive to higher mass carbazoles than GC/MS.



(a) Tar Sand



(b) Processed residue

Fig.38 Relative distributions of carbazoles grouped according to their degree of unsaturation in (a) Tar Sand A3 fraction, (b) processed residue S1 fraction.

III.2.10 Comparison of Area Determined from the Probe
Ammonia CIMS Analysis and the LC/MS Analysis

The relative amounts of the alkylated carbazoles were determined by measuring the areas in a series mass chromatograms from GC/MS or LC/MS experiments. A substantial amount of time was needed to complete the chromatography, mass spectrometry and data analysis in order to prepare a figure such as Figure 29. Given the selectivity of ionization of nitrogenous compounds using NH_3 CI we proposed that such carbazole distributions might be obtained directly from the ion intensities of averaged ammonia CI mass spectra of A3 fractions. The averaged NH_3 CI mass spectrum of the Tar Sand A3 fraction is shown in Fig. 39 the relative intensities from the six carbazole series are listed in Appendix V and are plotted in Fig. 39b and 39c. The latter two figures are very similar to the LC/MS results obtained on the same sample. A pie chart presentation of the sums of each carbazole series shown in Fig. 39e is remarkably similar to the pie chart of the LC/MS data (Fig. 39d), suggesting that peak intensities from a simple probe NH_3 CI mass spectrum provide the same quantitative information as the much more complex GC/MS or LC/MS analyses. By obtaining this data from averaged probe NH_3 CI mass spectra (instead of from GC/MS or LC/MS mass chromatograms) a substantial reduction of time can be realized. It is estimated that this type of analysis of a

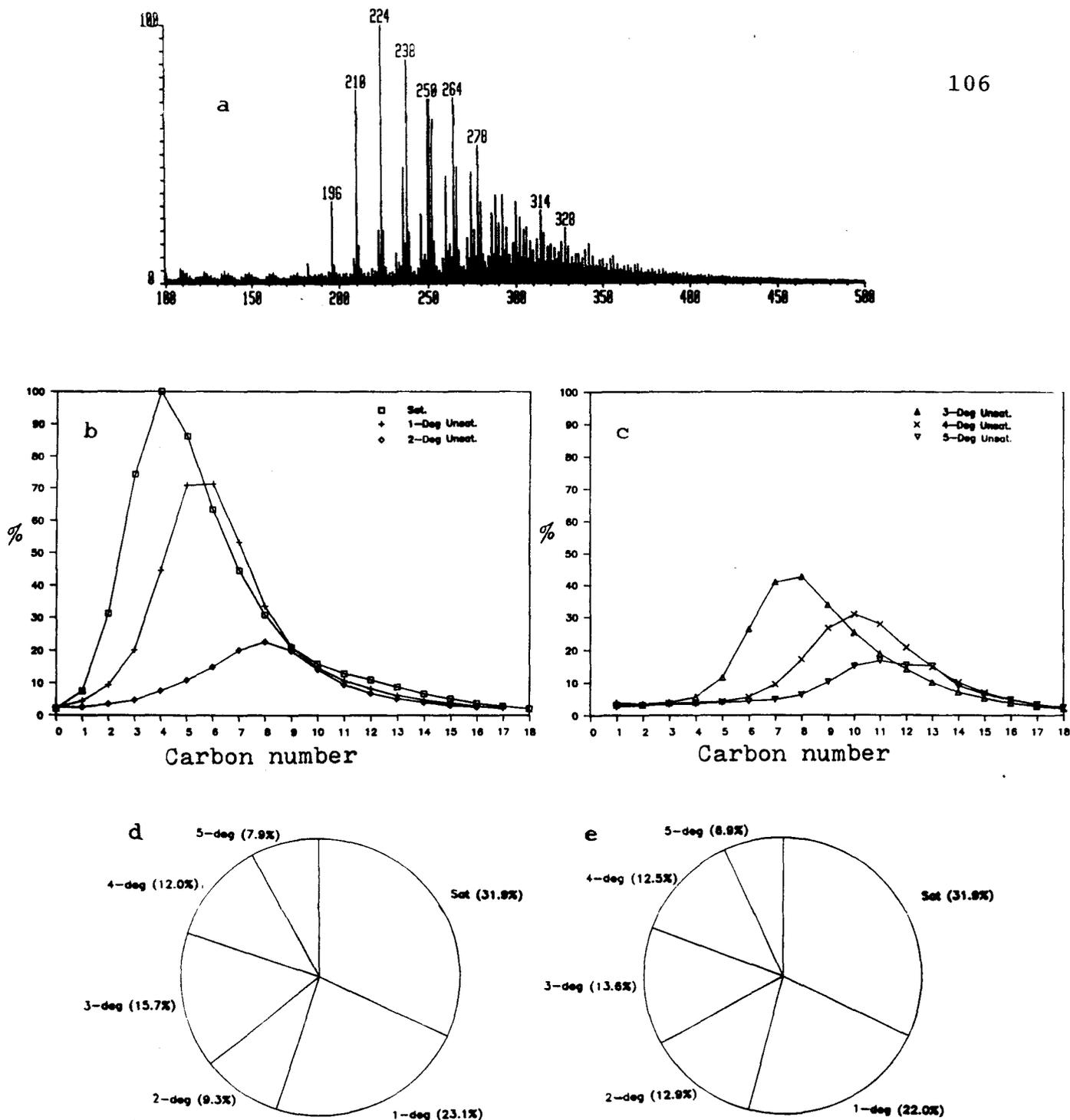


Fig.39 (a) Averaged probe NH₃ CI mass spectrum of Tar Sand A3 fraction, (b) distribution of the sat, 1- and 2-degree unsaturated carbazoles, (c) distribution of 3-, 4- and 5-degree unsaturated carbazoles. Relative distribution of different carbazole groups from (d) LC/MS analysis and (e) probe NH₃ CI analysis.

process stream (which would require an alumina chromatography and a probe MS analysis) could be done in 1-1.5 days.

III.2.11 Nuclear Magnetic Resonance (NMR)

While results from both the MS and LC/DAD experiments indicated that the oil samples contained alkylcarbazoles in different degrees of unsaturation, unfortunately neither the mass spectrometric nor the UV spectral data could give any indication as to the relative contribution of ring structures or alkene bonds to the degrees of unsaturation. By the application of Nuclear Magnetic Resonance (NMR) spectroscopy the protons attached to saturated rings and alkene bonds would show up in very different regions of the NMR spectrum; alkene protons would give peaks in the 5.5 ppm region while alkyl protons would resonate in the 1-2.5 ppm region.

Two Tar Sand A3 fractions from the two scaled-up alumina separations were combined (1.2 grams) and dissolved in 1.8 mL of benzene-d₆ then filtered into a 10 mm NMR tube. All NMR spectra were kindly obtained by Dr. D. Hughes.

In spite of the high resolution of the Bruker AM500 spectrometer, the 500 MHz ¹H spectrum showed only "broad" absorptions (Fig. 40). However, the resonances were grouped into three major regions: (1) the aliphatic region between 1 and 2.5 ppm was attributed to methyl, methylene and methine

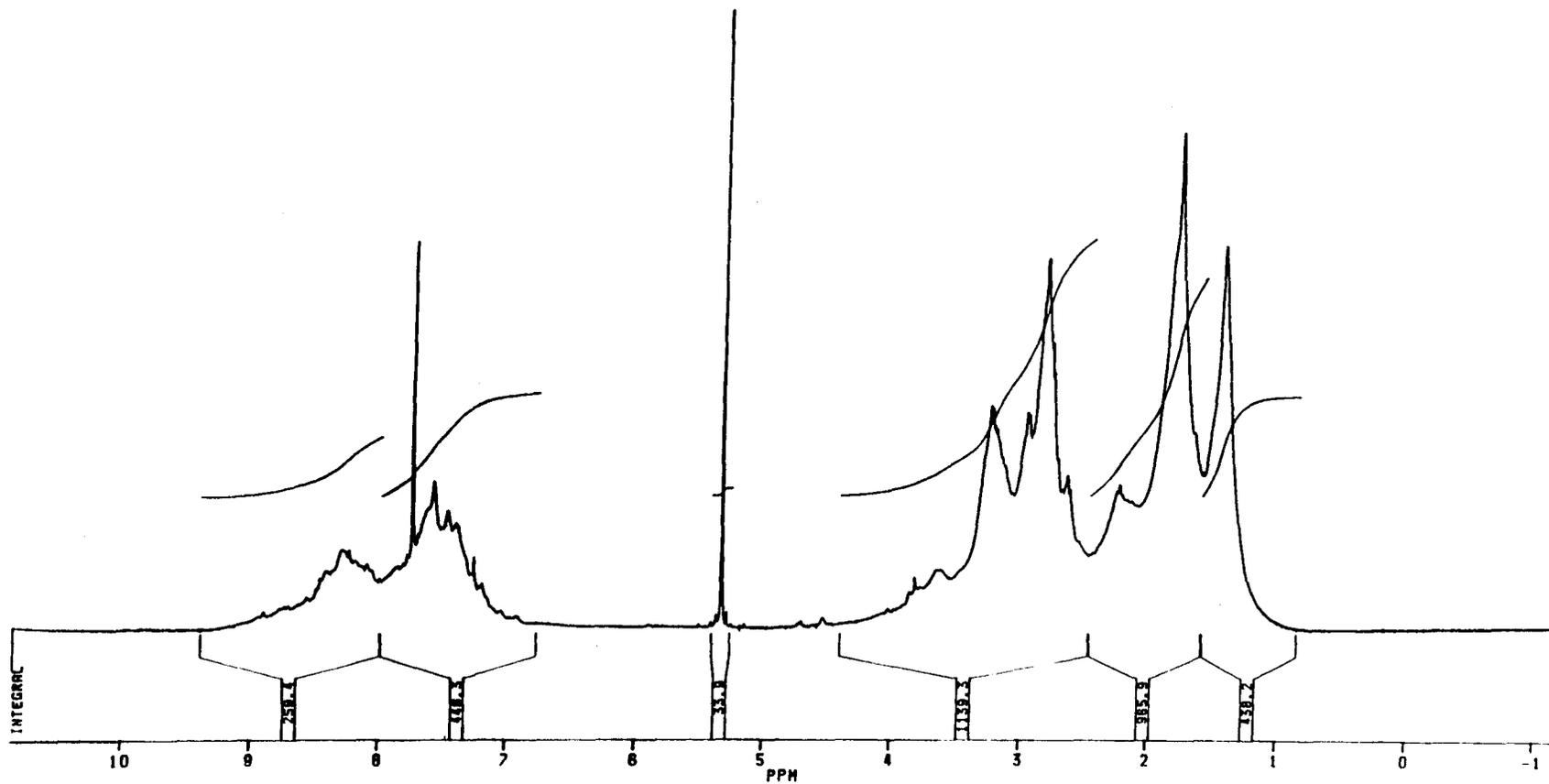


Fig.40 Proton NMR spectrum (500 MHz) of 1.2 g of Tar Sand A3 fraction. Residual CH_2Cl_2 peak at 5.45 ppm.

protons attached to saturated carbons, (2) the benzylic region between 2.5 and 4.4 ppm attributed to CH₃, CH₂ and CH benzylic protons and (3) the aromatic region (7 to 9 ppm) attributed to carbazole protons. Surprisingly, no alkene protons were observed in the 5 to 6.5 ppm range, suggesting that carbazole mixture contained few or no alkene bonds. The single peak at about 5.3 ppm was assigned to residual CH₂Cl₂, an assignment subsequently confirmed by a ¹³C-¹H 2-D shift correlation experiment. Clearly, the degrees of unsaturation in these carbazoles must be accounted for by saturated rings or additional aromatic rings and not by alkene bonds.

The relative areas of the three peak regions of the ¹H NMR spectrum were:

Proton Type:	aromatic	:	benzylic	:	alkyl
Spectral Region:	7-9 ppm	:	2.5-4.5 ppm	:	1-2.5 ppm
Relative Area:	1	:	1.6	:	2

The ratio of the integrated area of the benzylic and the alkyl protons was 1:1.25 (1.6:2), suggesting that a substantial percentage of the alkyl chains attached to the carbazole nucleus must be short alkyl chains. For example, an ethyl group attached to a carbazole would have a ratio of benzylic to alkyl protons of 2:3 (1:1.5); for an n-pentyl group this ratio would be 2:9 (1:4.5). Hence, the 1:1.25 benzylic:alkyl ratio found in the Tar Sand A3 spectrum

indicates that most of the alkyl chains are short chains on average. On the other hand, the 1:1.6 ratio between the aromatic and the benzylic protons suggests that many of the aromatic protons of carbazole have been replaced by alkyl chains. For example, methylcarbazole and butylcarbazole have, the relative area ratios of aromatic vs benzylic protons of 7:3 (1:0.42) and 7:2 (1:0.28), respectively, while trimethylcarbazole and tetra ethylcarbazoles, have ratios of 5:9 (1:1.8) and 4:8 (1:2), respectively; these latter ratios are close to the ratio found in the A3 spectrum.

The 125 MHz carbon-13 spectrum of the A3 fraction also showed only "broad" absorptions (Fig. 41). The carbon resonances can also be grouped into three regions: 10 to 50 ppm, 60 to 80 ppm and 110 to 150 ppm. In the aromatic carbon region (110-150 ppm), two peaks were observed at 111 and 113 ppm. These resonances are at a high field for aromatic carbons and correspond well with the chemical shifts of the carbons ortho to nitrogen in carbazoles (Appendix VI).

By application of the DEPT sequence (F1184, F1185) (distortionless enhancement by polarization transfer), individual subspectra corresponding to the CH, CH₂ and CH₃ carbons were obtained (Figure 42). A comparison of the three subspectra to the total carbon spectrum shows the resonances between 10 to 50 ppm are a superposition of CH₃ and CH₂ carbon resonances. The tiny resonances between 60 and 80 ppm in the CH₂ subspectrum were attributed to methylene carbons

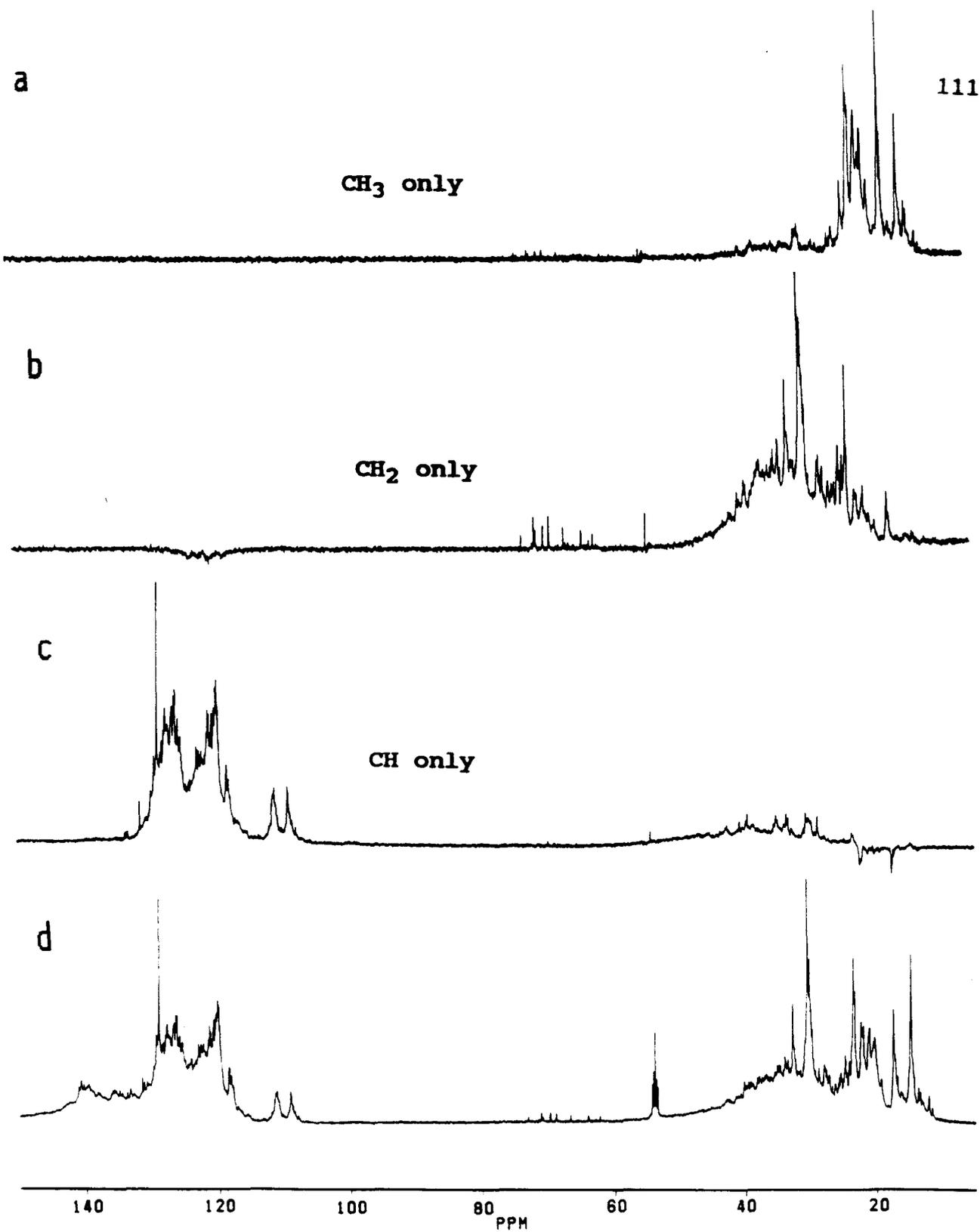


Fig.41 Carbon-13 spectrum (125 MHz) of 1.2 g Tar Sand A3 fraction (spectrum d). Carbon subspectra obtained using DEPT sequence: (a) CH₃ sub-spectrum, (b) CH₂ sub-spectrum, and (c) CH sub-spectrum.

attached to the carbazole nitrogen. Most of the aromatic carbons were observed in the CH subspectrum (110-130 ppm). Comparison of the complete ^{13}C spectrum with the CH subspectrum showed that the resonances in the 130-145 ppm region were due to quaternary aromatic carbons.

The ^{13}C - ^1H 2-D shift correlation spectrum is shown in Fig. 42; some plots of expanded regions can be found in Appendix VII. Not surprisingly two major regions of shift correlations were observed: the 10-50 ppm region of the ^{13}C spectrum correlated with the alkyl and benzylic protons (1-4.5 ppm) while the aromatic carbons (110-140 ppm) correlated with the aromatic protons (7-9 ppm). Within the higher field correlation region a trend was noted throughout; each hump in the ^1H spectrum corresponding to a narrow range of proton resonances correlated with a broad range of resonances in the carbon spectrum. However in the aromatic region, the opposite was observed; the narrow carbon resonances at 111 and 113 ppm correlated with a wide range of ^1H resonances (Appendix VII).

An inversion-recovery experiment was performed in order to obtain the carbon T_1 values listed in Table 9. The purpose of this experiment was to obtain some information about the motional characteristics of these compounds. For example, high molecular weight carbazoles should show shorter T_1 values than molecules of lower molecular weight. Such

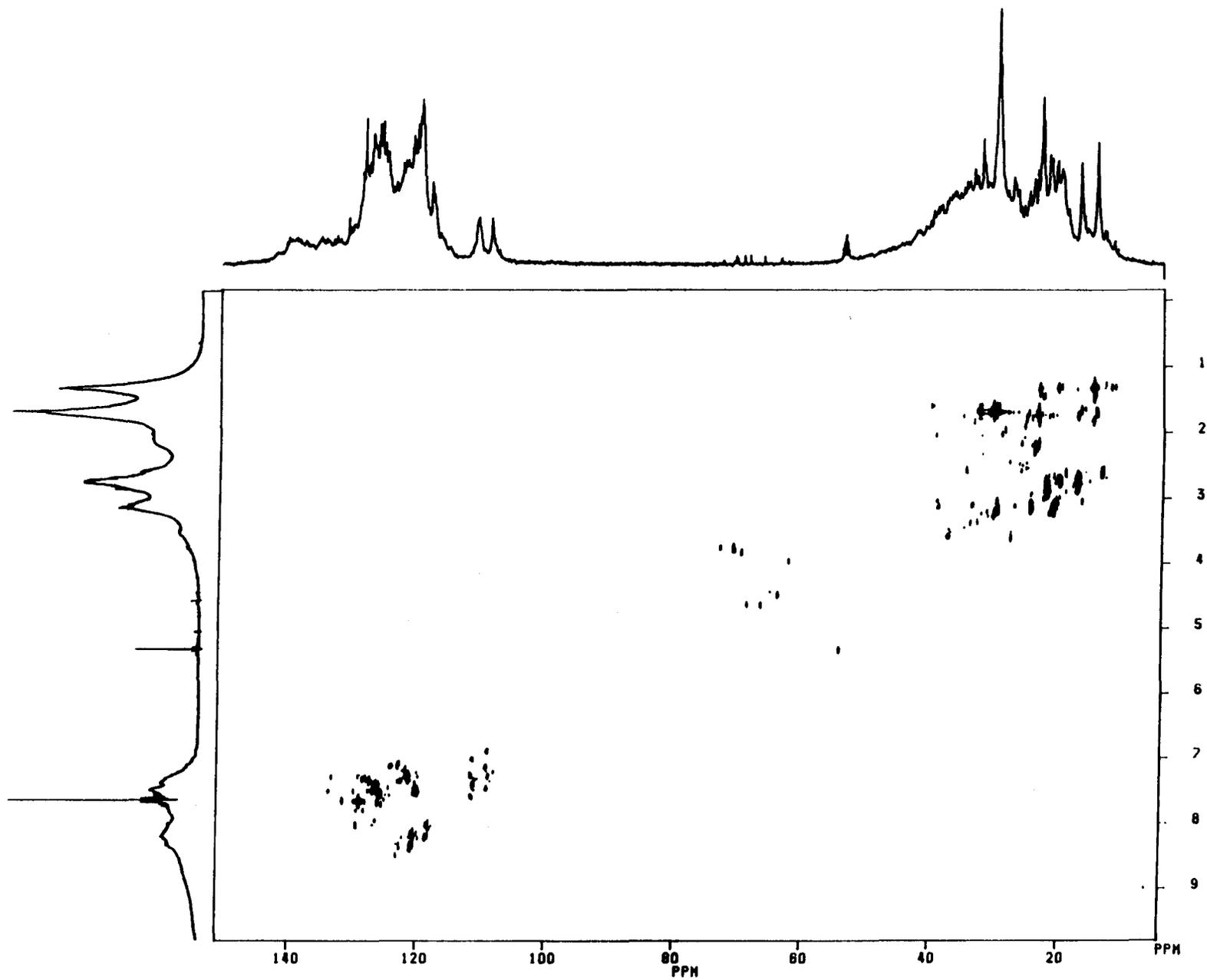


Fig.42 ^{13}C - ^1H 2-D shift correlation spectrum of Tar Sand A3 fraction.

high molecular weight components, should they exist, would not have been detected by the GC, GC/MS or LC/MS experiments.

Table 9: T_1 values at different carbon resonances

<u>Carbon Chemical Shifts (PPM)</u>	<u>T_1(sec)</u>	<u>Carbon Type</u>
127.6	0.43	CH
120.1	0.55	CH
111.2	0.37	CH
111.1	0.42	CH
109.1	0.45	CH
32.7	0.84	CH ₂
30.5	0.66	CH ₂
23.5	1.20	CH ₃ /CH ₂
22.3	1.01	CH ₃ /CH ₂
17.3	1.62	CH ₃
14.8	2.43	CH ₃

The CH carbons in the aromatic region (127.6-109.1 ppm) had a narrow range of relaxation times (0.37-0.66 sec), which are typical of molecules with molecular weight in the 200-400 range. There were no substantial evidence for a short T_1 component, i.e., no evidence for substantial higher molecular weight species. The methylene carbons (30.5 and 32.7 ppm) had longer T_1 's than the aromatic carbons indicating that there is substantial motion in the alkyl chains attached to the carbazole nucleus. The methyl carbons (14.8 and 17.3 ppm) showed ever longer T_1 's, typical of rapidly rotating CH₃ groups.

III.2.12 Summary

Results from the NMR analyses were extremely useful for interpretation of possible carbazole structures in the Tar Sand A3 fraction. The absence of the alkene protons in the ^1H NMR spectrum suggested that the degrees of unsaturation must be either saturated rings or benzo-annulated rings. Moreover, the alkyl chains in these carbazoles were, on average, short chains and that, on average, each carbazole nucleus was substituted by 3 to 4 alkyl chains.

NMR analysis was not applied to the examination of the carbazole structures in the processed residue. However, all the information from MS and LC analyses indicated that the nitrogenous components in the processed residue and the Tar Sand sample were very similar, it is possible to predict that the carbazoles in the processed residue oil were also very similar to the one found in the Tar Sand.

III.2.13 Compound Interpretation

The experimental results discussed thusfar have shown that carbazoles are the major nitrogen-containing compounds in the Tar Sand and processed residue oil samples. It is highly unlikely that these nitrogenous compounds were other nitrogen-containing compounds, such as alkylated amino-PAH or alkyl tertiary-PANH.

First, the elution pattern of nitrogenous compounds from the silicic acid column precludes substantial contamination by amino-PAH or tertiary PANH. The tertiary-PANH such as quinolines or the acridines only eluted in fractions S2 and S3, not in S1. In our modified method, the polarity of the S1 solvent (hexane:benzene=3:1) was even lower than the original solvent (1:1). Hence, the chances of eluting tertiary-PANH in fraction S1 was very low. Second, the UV spectra obtained throughout the LC chromatograms (Fig. 22 and 24) further support this view. The UV spectra of six different nitrogen-containing aromatics are shown in Appendix VII: carbazole, benzo(a)carbazole, dibenzo(c,f)carbazole, aminopyrene, quinoline and acridine. None of these spectra, except that of carbazole resembled the spectra observed across the S1 chromatograms (Fig. 22 and 24). Lastly, the two carbon resonances at 109 and 111 ppm in the ^{13}C spectrum were highly characteristic of a carbazole structure. Hence, we concluded that carbazole was the most abundant nitrogenous compounds in these oils.

IV. CONCLUSION

Separation of the nitrogenous components from the crude oil samples was successful. The two stage chromatographic method first separated the nitrogenous components (<2 wt % of original oil which contained more than 80% of the total nitrogen content) from the oil. The application of the silicic acid separation further fractionated the nitrogenous fraction according to their compound classes: i.e. the secondary-PANH in fraction S1 (62% total nitrogen), the amino-PAH and tertiary-APNH in fraction S2 (4%N) and the remaining tertiary-PANH in fraction S3 (9%N).

The modified medium pressure separation method enabled a cleaner and faster separation while the scaled-up alumina separation increased the separation scale by a factor of 100-fold.

In the three ionization modes (electron impact, methane CI and ammonia CI) used in the mass spectrometry, ammonia chemical ionization was found to be most suitable for the analysis of heavy oil nitrogenous compounds. The high proton affinity of ammonia resulted in selective protonation of nitrogenous compounds, affording very clean mass spectra of rather complex mixtures.

As compared to the capillary gas chromatography, reverse phase liquid chromatography provided a better separation of the complex nitrogenous fraction. The LC/MS

(NH₃ CI) analysis was also able to detect higher molecular weight compounds than the GC/MS (NH₃ CI) analysis.

Information from nuclear magnetic resonance spectroscopy (NMR) was extremely useful for the structural interpretation of nitrogenous compounds providing that there were sufficient samples available for the NMR analyses.

Separation results indicated that most nitrogenous compounds were eluted into the secondary-PANH S1 fraction. Alkylcarbazoles, ranging from saturated to 5-degrees of unsaturation, were found to be the most abundant nitrogenous components in both the Athabasca Tar Sand and the processed Peace River residue oil sample. Alkyl chains attached to the carbazole nucleus were short and the degrees of unsaturation were either saturated rings or benzo-annulated rings. The relative ratio of the saturated:1-degree:2-degree:3-degree:4-degree:5-degree unsaturated carbazoles was approximately 32%:23%:9%:16%:12%:8% in the Tar Sand sample and 28%:39%:18%:6%:6%:3% in the processed residue sample.

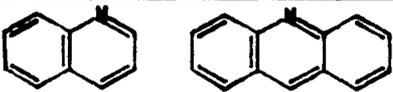
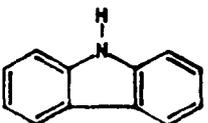
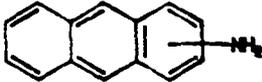
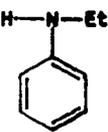
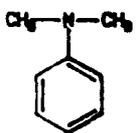
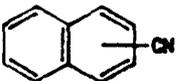
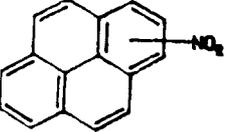
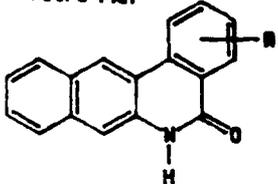
For future work, only the alumina separation would be needed since most nitrogenous compounds were carbazoles. The scaled-up alumina separation was highly recommended for its capability of separating hundreds of milligrams of nitrogenous compounds in each separation. The separated A3 fraction can then be analyzed by probe ammonia CI mass spectrometry and NMR. It is estimated that this type of analysis of a process stream could be done in 1 to 2 days.

Appendix ITABLE 1: Types of Oil Samples Analyzed for Organic Nitrogen Compounds

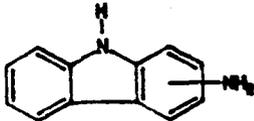
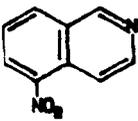
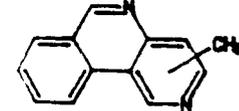
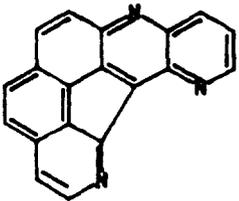
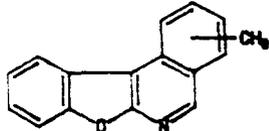
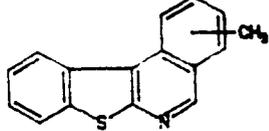
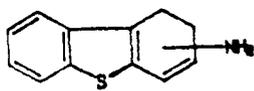
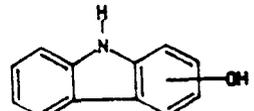
Sample Type	Examples	References
Coal Liquids	Solvent Refined Coal (SRCII)	F0008 F0009 F1031 F1129 F1139
	Coal Oil	F0007 F0026 F0028 F0236 F1105 F1119 F1136 F1148
	Anthracene oil	F0144
	Coal Tar	F0006 F0018 F1119 F1120 F1124 F1125
	Tar Base Concentrate	F1131
	Coal Liquefaction Product	F1116
Shale Oil		F0005 F0006 F0007 F0012 F0022 F0023 F0025 F0028 F0029 F0077 F1135 F1122 F0210 F1022 F1041 F1101 F1102 F1103 F1105 F1106 F1109 F1110 F1111 F1116 F1120 F1131 F1132 F1133 F1134 F1136 F1139 F1145 F1148 F1212
Petroleum Liquid	Gasoline	F1113
	Crude Oil	F0162 F0275 F0277 F0278 F1121 F1127
	Kerosene	F1107 F1113
	Petroleum	F0028 F1105 F1148
	Fossil Fuel	F0001
	Asphaltene	F1104
Syncrude		F0028 F0167 F0210 F0280
Tar Sands Oil		F1155 F1156 F1157 F1158

Appendix I (Cont.)

Table 2: Types of Nitrogen Compounds Found in Different Oil Samples

Compound Types	Examples	References
3°-PANH	 <p>Guanine Acridine</p>	F0005 F0012 F0018 F0026 F0029 F0077 F0144 F0236 F0278 F1041 F1100 F1102 F1105 F1111 F1116 F1117 F1119 F1122 F1124 F1125 F1131 F1135 F1142
2°-PANH	 <p>Carbazole</p>	F0005 F0012 F0018 F0077 F0162 F0236 F1100 F1111 F1116 F1122 F1124 F1127 F1135 F1136 F1139 F1145
Amino-PAH (APAH)	 <p>Amino-PAH</p>	F0012 F0025 F0026 F0023 F0236 F1105 F1116 F1122 F1123 F1131 F1135 F1142 F1148
2°-APAH	 <p>N-ethyl aniline</p>	F0236 F1122
3°-APAH	 <p>N,N-dimethyl aniline</p>	F0236 F1122
Nitrile	 <p>Cyano-naphthalene</p>	F0018 F1124
Nitro-PAH	 <p>Nitro-PAH</p>	F0214 F1160
Amide	 <p>Nitro-PAH</p>	F1168

Appendix I (Cont.)

Amino-PANH		F0023
Nitro-PANH		F1160
PANNH (PAH with two Nitrogen)		F0018 F0023 F1125 F1139 F1141
PANNNH (PAH with three Nitrogen)		F1139
PANOH (PAH with one Nitrogen & one Oxygen)		F0018 F0144 F1112 F1125
PANSH (PAH with one Nitrogen & one Sulphur)		F0018 F0144 F1112 F1120 F1125
APASH		F1120
Hydroxy-PANH		F1183
	<p>Hydroxy-carbazole</p>	

Appendix I (Cont.)TABLE 3: Separation Methods used to Isolate Nitrogenous Components from Oil Samples

Methods	References
Liquid-Liquid Extraction	F0007 F0026 F0029 F0077 F0144 F0162 F1100 F1102 F1105 F1111 F1116 F1117 F1122 F1123 F1125 F1132 F1134 F1135 F1136 F1142 F1145 F1148
Soxhlet Extraction	F0021 F0214 F1128 F1135
Alumina Column	F0006 F0009 F0012 F0025 F0077 F0107 F1041 F1102 F1119 F1120 F1127 F1139 F1041 F1146 F1147 F1148
Silica Column	F0009 F0012 F0021 F0025 F0039 F0077 F0107 F1041 F1105 F1119 F1139 F1144 F1146 F1147
Thin Layer (TLC)	F1100 F1101 F1102 F1133 F1141
HPLC	
Bonded-NPLC	F0018 F0026 F0029 F0212 F1111 F1126 F1133 F1134
Bonded-RPLC	F0021 F0262 F0278 F1139
Ion Exchange Column	F1102 F1119 F1141 F1146
Sephadex LH-20 Column	F0162 F1105 F1123 F1126 F1131 F1148
Solid Phase Extraction	F1126

Appendix I (Cont.)

Distillation		F1011 F1129 F1147
Derivative Formation	Methyl-8	F1142
	TFA	F0012 F1116 F1123 F1148
	PFP	F0025 F0107
Fluoropak Column		F0008 F0009
Gel Permeation		F0025 F1127
FeCl ₃ Clay Column		F1102
Charcoal Column		F1146
H ₂ SO ₄ /SO ₂		F1101

Appendix I (Cont.)

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

Columns:

Reverse Phase Packed	F0029 F0212 F1108
Reversed Phase Capillary	F1139

Detectors:

Ultraviolet	F0029 F0212 F1100 F1111 F1126 F1139 F1141 F1146
Fluorescence	F0029 F0278 F1117 F1119 F1121 F1127 F1139
Refractive Index	F1100
Potentiometric Titration	F1117 F1140
Amperometric	F1108

SUPERCRITICAL FLUID CHROMATOGRAPHY

Columns:

Packed microbore	-
Wall Coated Open Tubular (WCOT)	F1149 F1160

Detectors:

Flame Ionization	F1149
Nitrogen-selective TSD	F1149 F1160

Appendix I (Cont.)

MASS SPECTROMETRY

Electron Impact Ionization

F0006 F0012 F0018 F0023
F0025 F0077 F0107 F0210
F0236 F1102 F1103 F1105
F1120 F1126 F1131 F1142
F1145

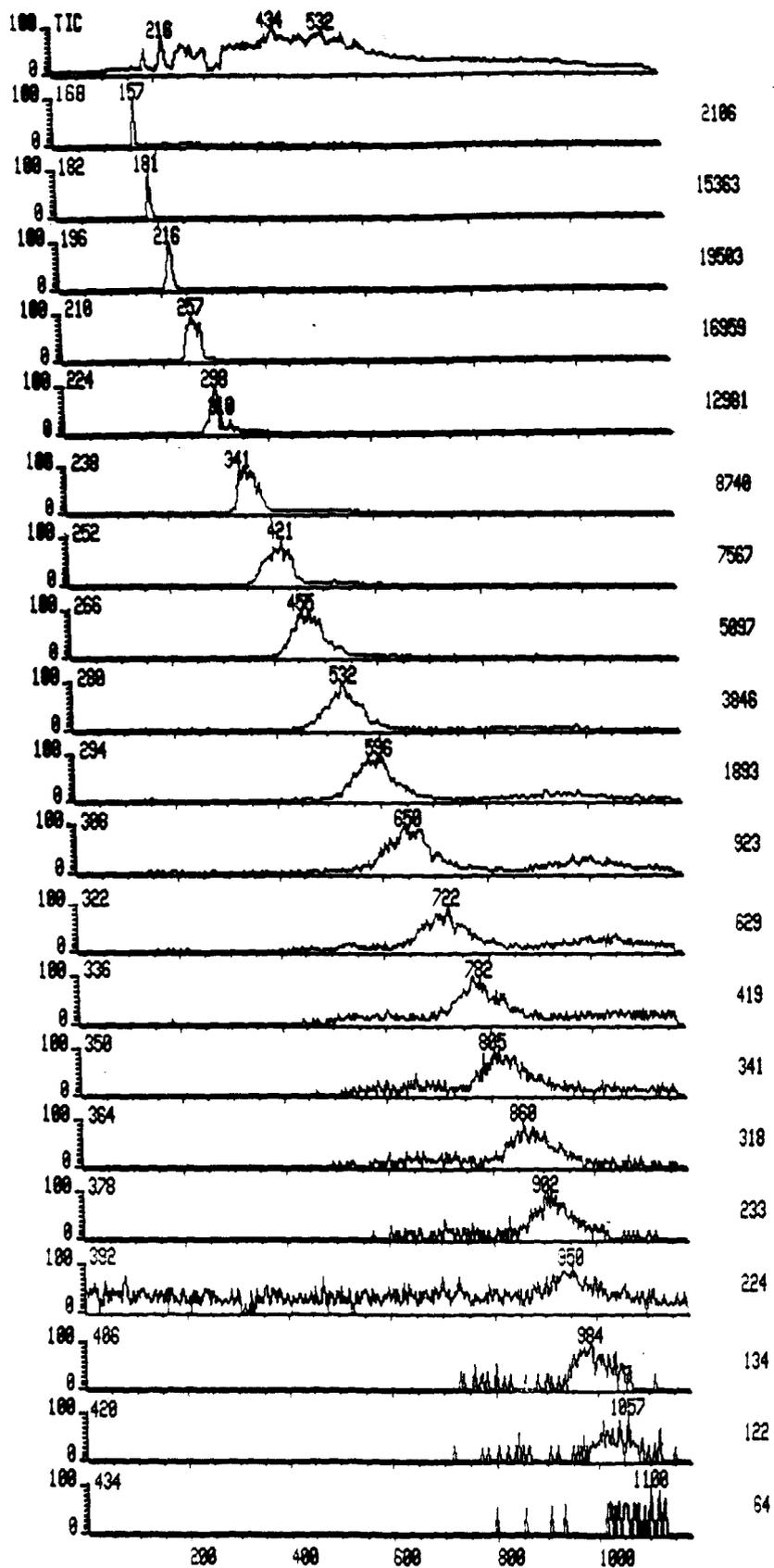
Chemical Ionization

F0236 F1105

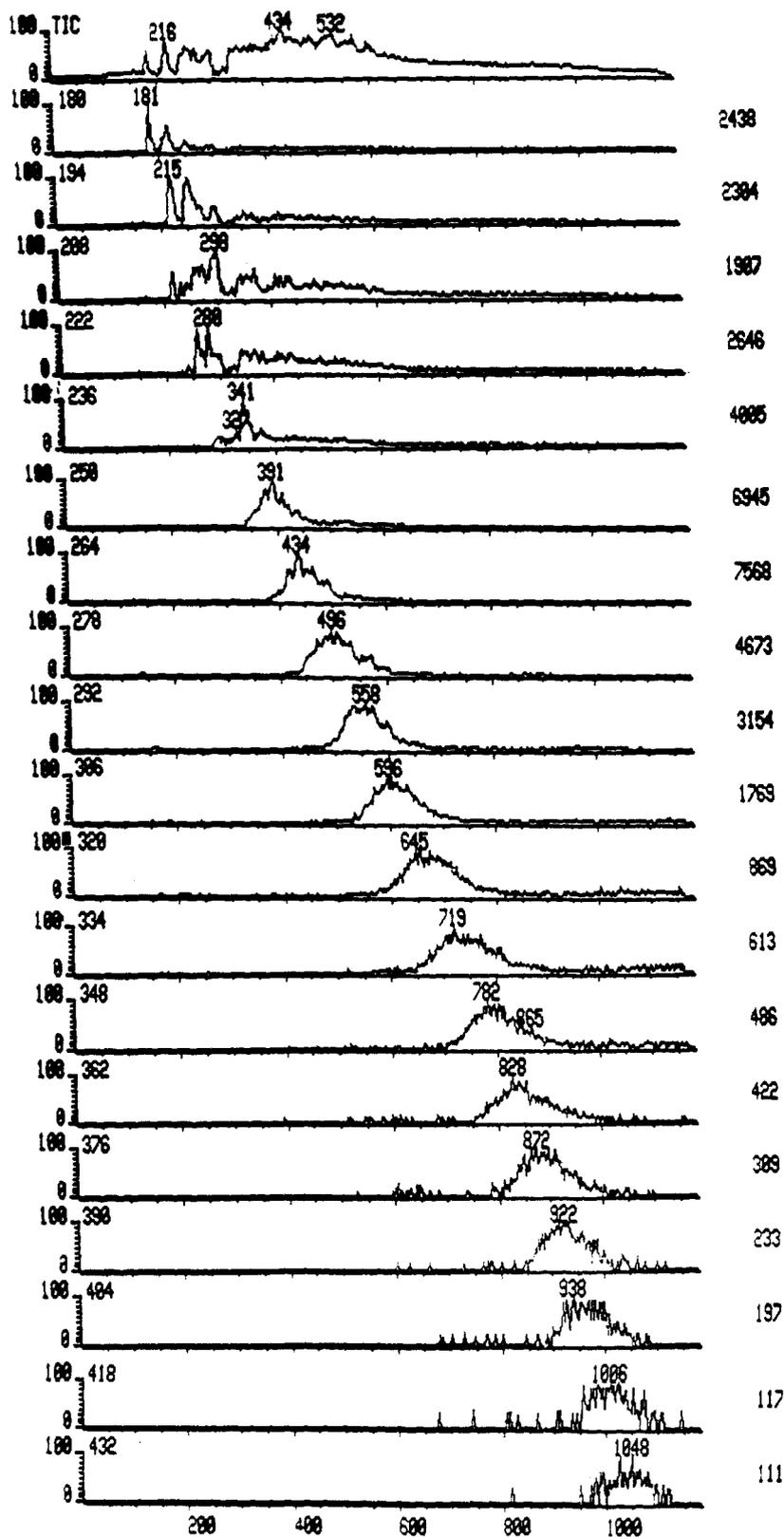
NUCLEAR MAGNETIC RESONANCE

F1101 F1102 F1117 F1127
F1131 F1134 F1136 F1140
F1141

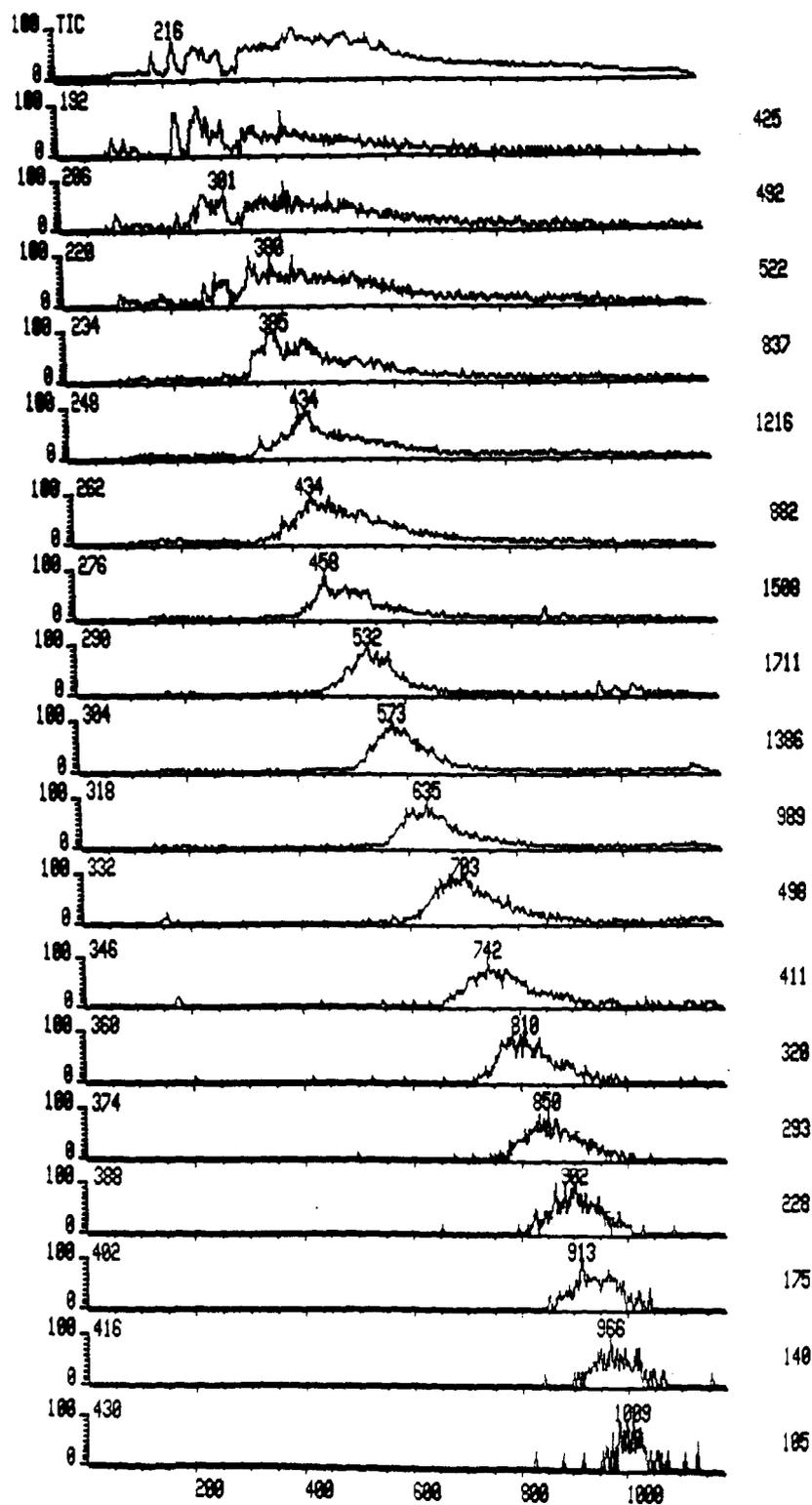
Saturated carbazole series



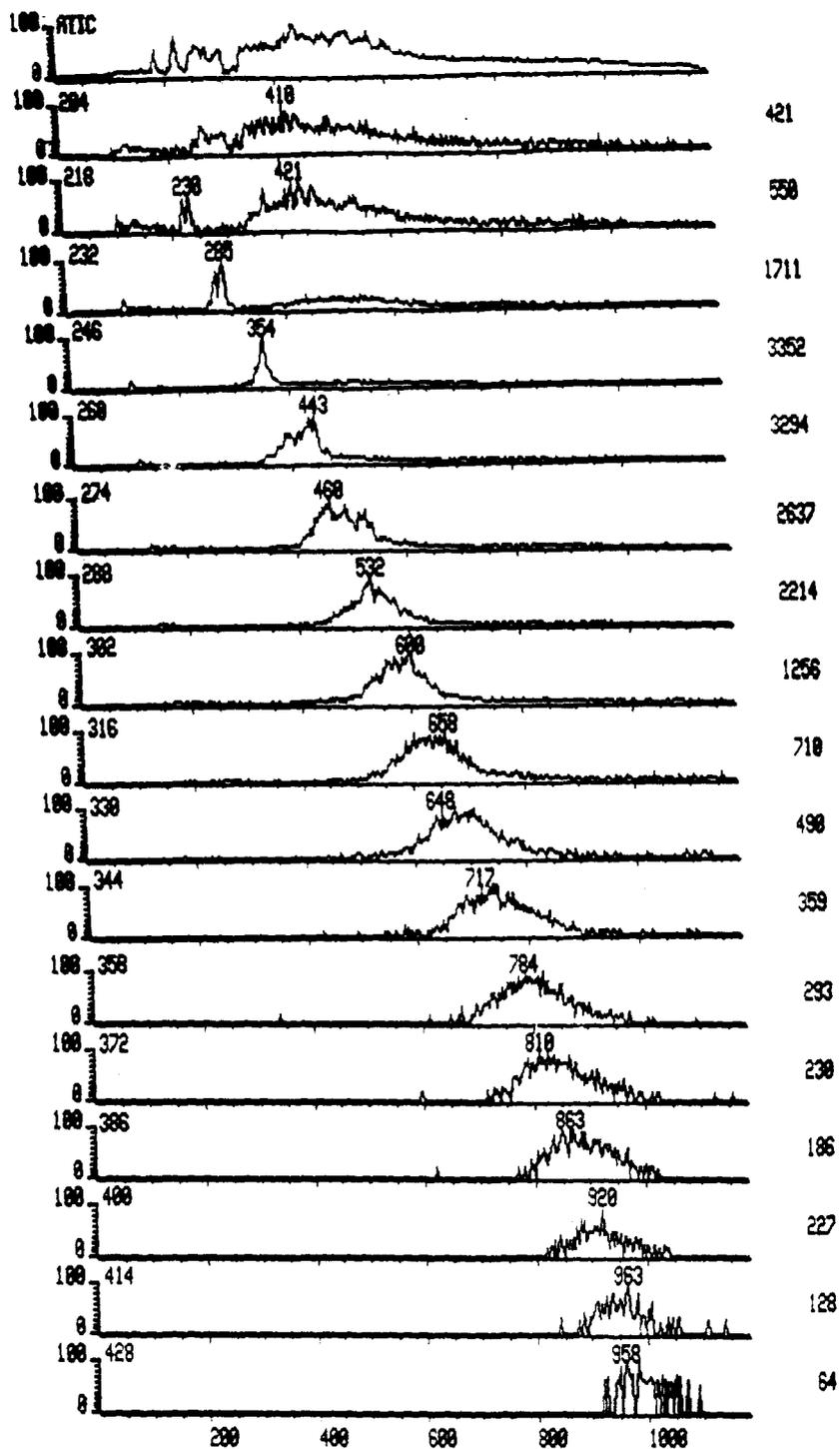
1^o-Unsaturated carbazole series



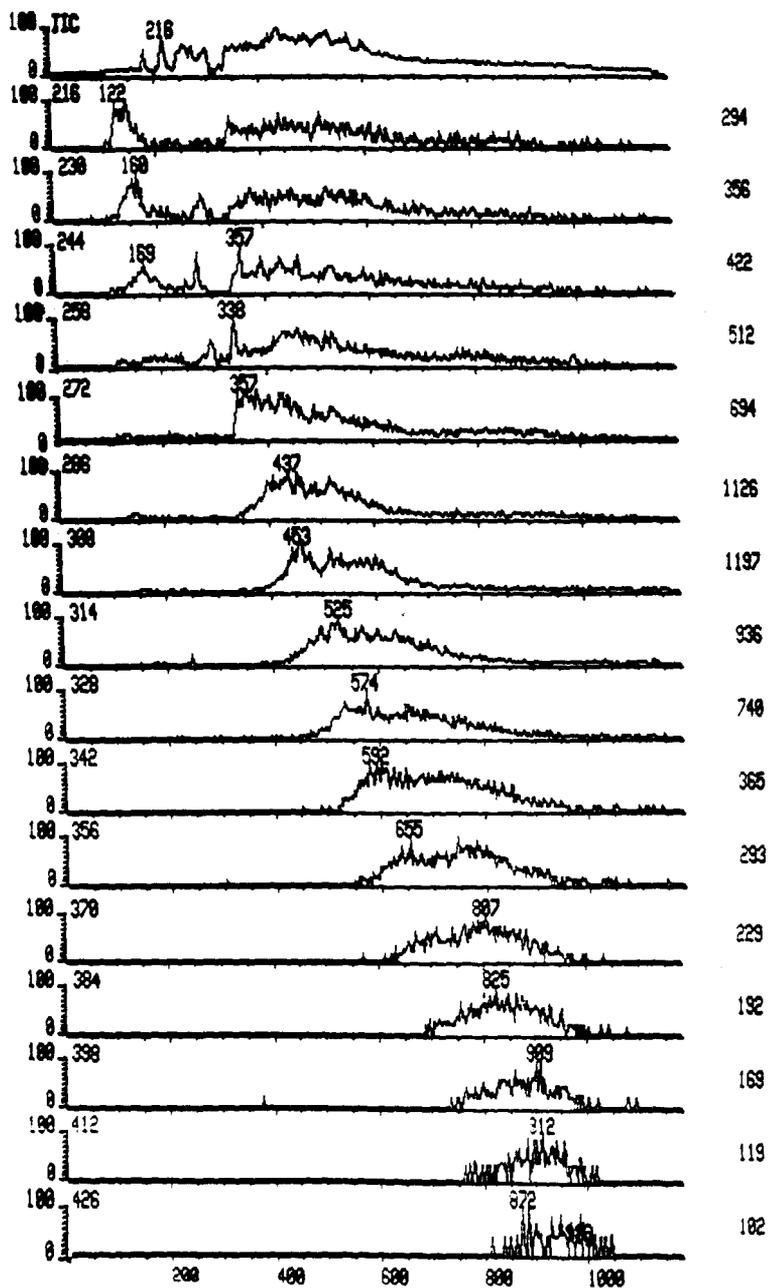
2^o-Unsaturated carbazole series



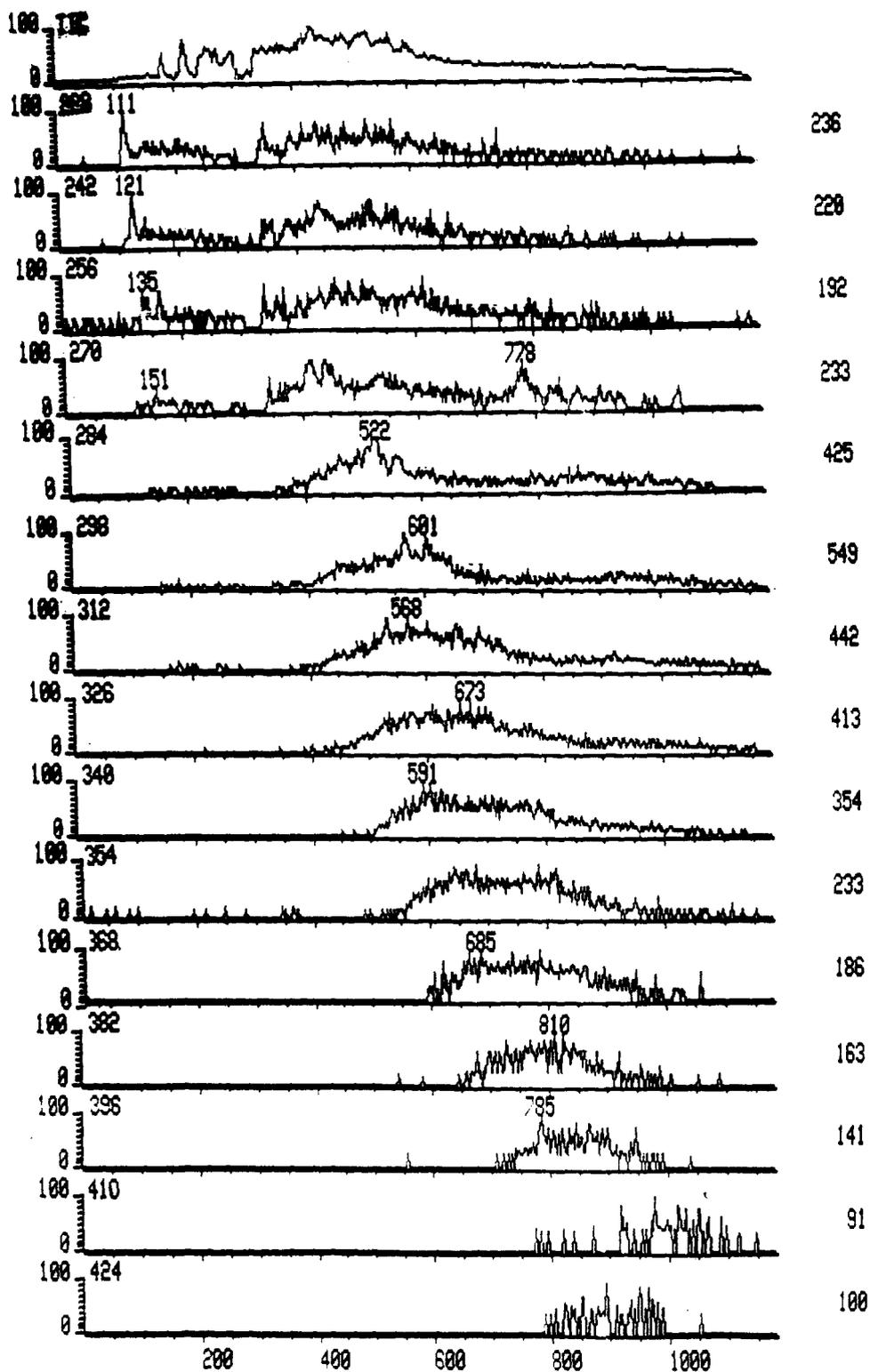
3^o-Unsaturated carbazole series



4^o-Unsaturated carbazole series



5^o-Unsaturated carbazole series



Area of Carbazoles derived from the LC/MS (NH3 CI)
Analysis of the Tar Sand A3 fraction

No. of carbons
attaching to
carbazoles

Carbazoles Series

	Sat		1-deg		2-deg		3-deg		4-deg		5-deg	
	m/z	Area	m/z	Area	m/z	Area	m/z	Area	m/z	Area	m/z	Area
0	168	6										
1	182	59	180	19								
2	196	173	194	94	192	30						
3	210	320	208	125	206	51	204	44				
4	224	163	222	135	220	59	218	63	216	25		
5	238	256	236	37	234	77	232	39	230	43	228	24
6	252	276	250	225	248	76	246	45	244	45	242	22
7	266	254	264	27	262	85	260	138	258	50	256	20
8	280	188	278	241	276	68	274	161	272	83	270	30
9	294	114	292	190	290	107	288	110	286	112	284	43
10	308	64	306	104	304	86	302	72	300	123	298	55
11	322	47	320	61	318	63	316	56	314	114	312	61
12	336	38	334	38	332	41	330	45	328	75	326	60
13	350	31	348	29	346	25	344	30	342	50	340	50
14	364	20	362	25	360	19	358	24	356	31	354	32
15	378	10	376	20	374	14	372	17	370	22	368	21
16	392	6	390	14	388	11	386	12	384	13	382	12
17	406	5	404	10	402	7	400	8	398	8	396	6
18	420	3	418	6	416	5	414	4	412	4	410	3
19	434	1	432	3	430	2	428	2	426	2	424	1
Sum of Area:	2033		1403		824		868		798		439	

Appendix IV

Area of Carbazoles derieved from the GC/MS (NH3 CI)
Analysis of the processed residue A3 fraction

No. of carbons
attaching to
carbazoles

Carbazoles Series

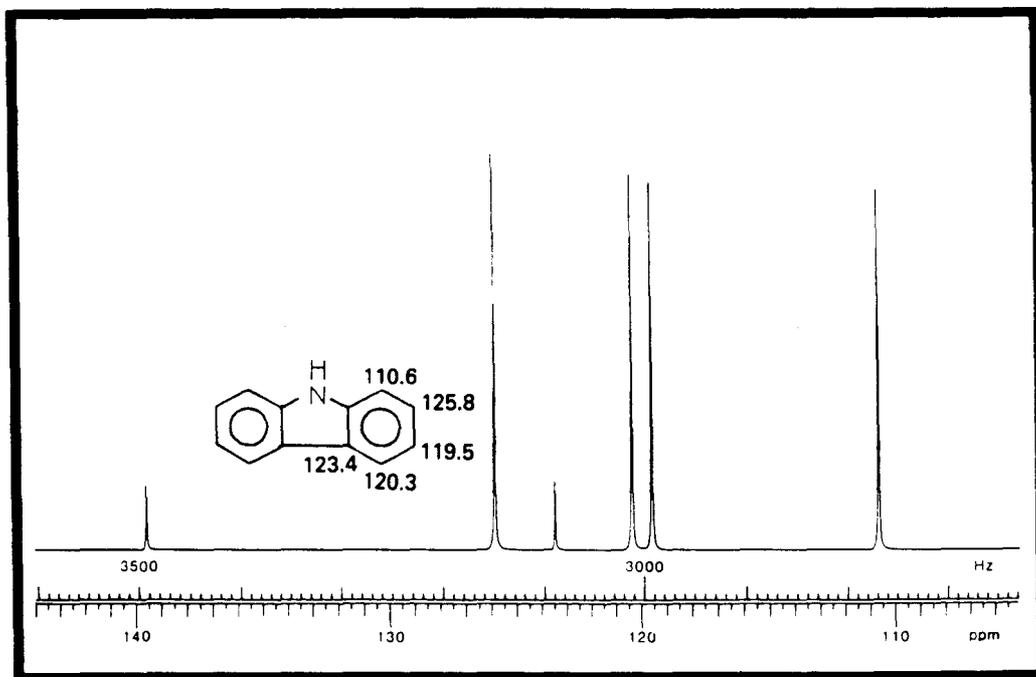
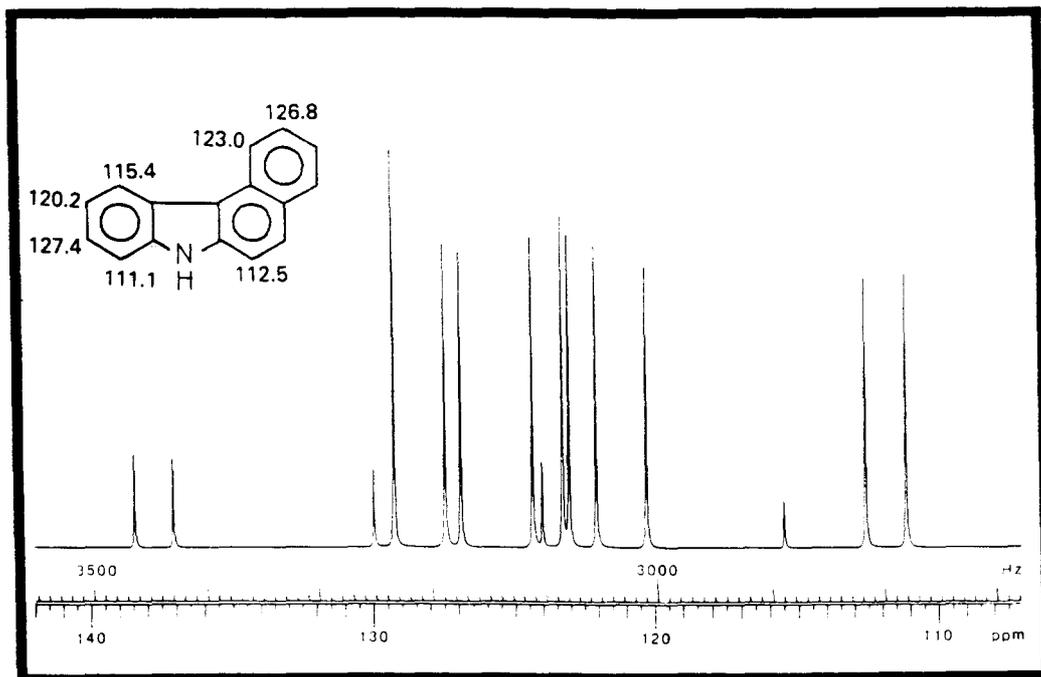
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	m/z	Area	m/z	Area	m/z	Area	m/z	Area	m/z	Area	m/z	Area
0	168	74										
1	182	1182	180	78								
2	196	5016	194	134	192	84						
3	210	7710	208	370	206	95	204	291				
4	224	7424	222	957	220	126	218	347	216	231		
5	238	6127	236	2235	234	184	232	504	230	248	228	126
6	252	3621	250	3040	248	447	246	974	244	1384	242	195
7	266	2067	264	2642	262	418	260	1346	258	320	256	126
8	280	988	278	1673	276	563	274	1176	272	1175	270	144
9	294	500	292	763	290	485	288	783	286	571	284	185
10	308	288	306	414	304	258	302	447	300	561	298	142
11	322	160	320	167	318	190	316	228	314	353	312	165
12	336	96	334	107	332	99	330	80	328	198	326	17
13	350	88	348	49	346	24	344	58	342	88	340	44
14	364	63	362	36	360	15	358	46	356	12	354	39
Sum of Area:		35404		12665		2988		6280		5141		1183

Appendix V

Area of Carbazoles derieved from the probe NH3 CI MS
Analysis of the Tar Sand A3 fraction

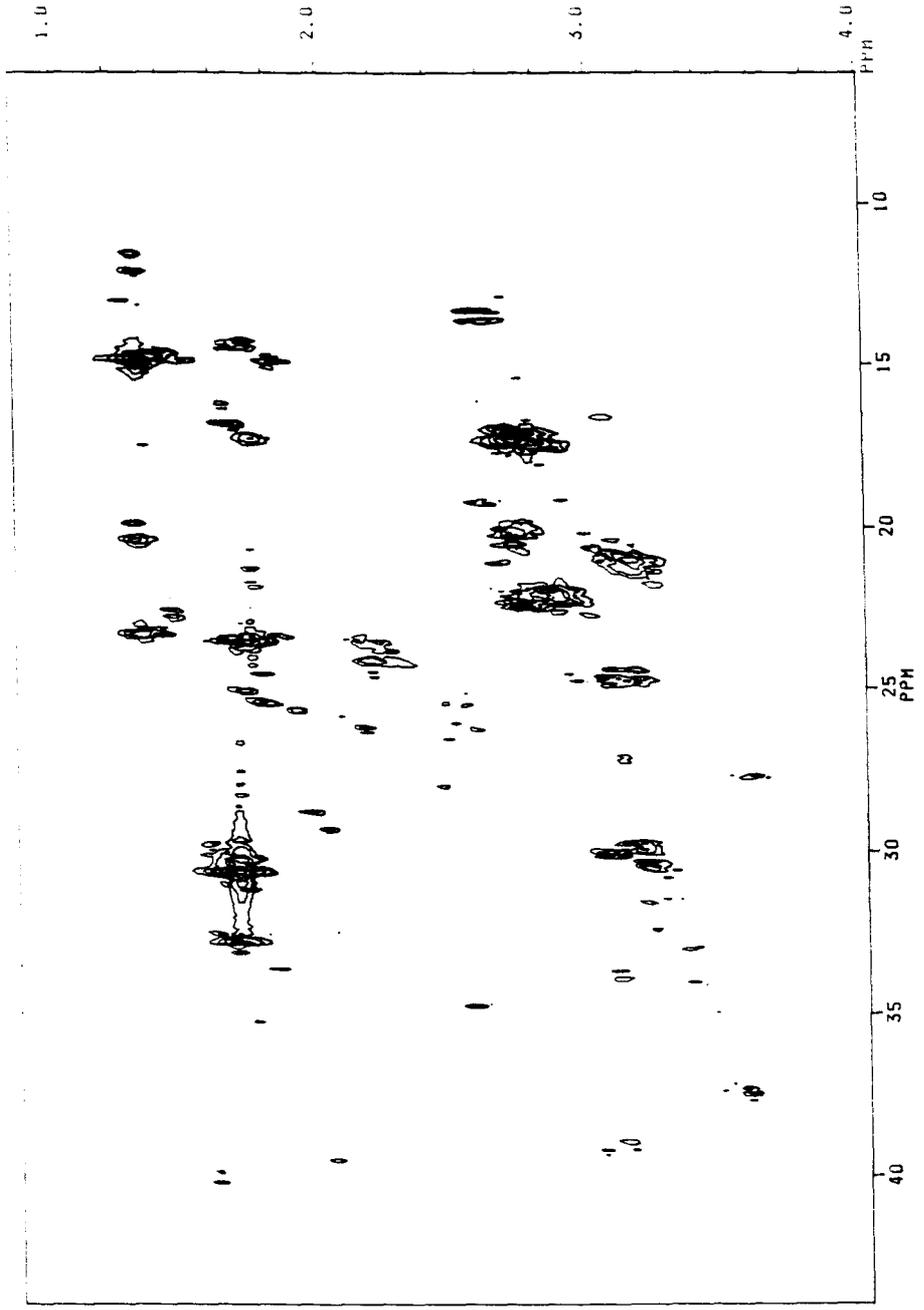
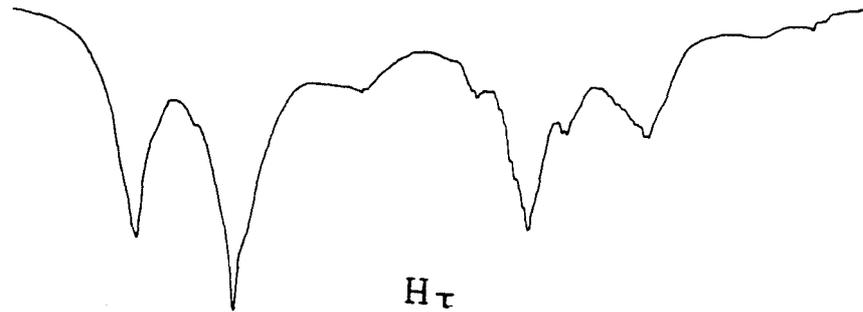
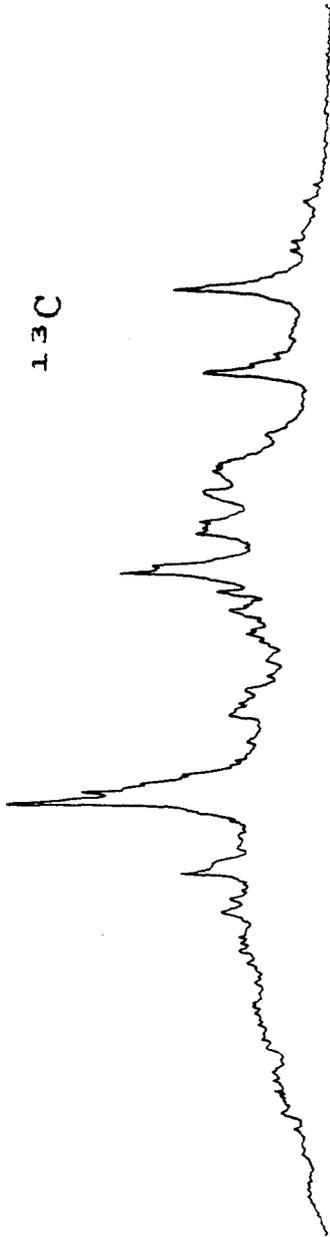
No. of carbons
attaching to
carbazoles

	Sat		1-deg		2-deg		3-deg		4-deg		5-deg	
	m/z	%	m/z	%	m/z	%	m/z	%	m/z	%	m/z	%
0	168	2										
1	182	8	180	2	178	2	176	4	174	3	172	3
2	196	31	194	4	192	3	190	3	188	3	186	3
3	210	74	208	9	206	3	204	4	202	4	200	3
4	224	100	222	20	220	5	218	6	216	4	214	4
5	238	86	236	45	234	8	232	12	230	4	228	4
6	252	63	250	71	248	11	246	26	244	6	242	4
7	266	45	264	71	262	15	260	41	258	10	256	5
8	280	31	278	53	276	20	274	43	272	17	270	6
9	294	21	292	34	290	23	288	34	286	27	284	10
10	308	16	306	21	304	20	302	25	300	31	298	15
11	322	13	320	15	318	14	316	19	314	28	312	17
12	336	11	334	11	332	10	330	14	328	21	326	15
13	350	9	348	8	346	7	344	10	342	15	340	15
14	364	7	362	6	360	5	358	7	356	10	354	9
15	378	5	376	5	374	4	372	5	370	7	368	7
16	392	4	390	4	388	3	386	4	384	5	382	5
17	406	3	404	3	402	3	400	3	398	3	396	3
18	420	2	418	2	416		414	2	412	2	410	3
		530		385		154		262		200		131



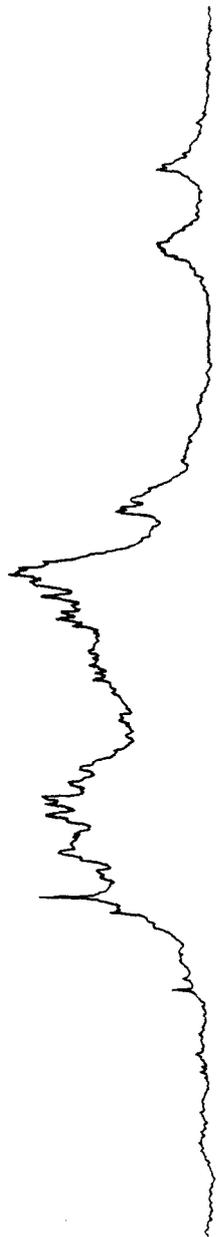
Appendix VII

^{13}C

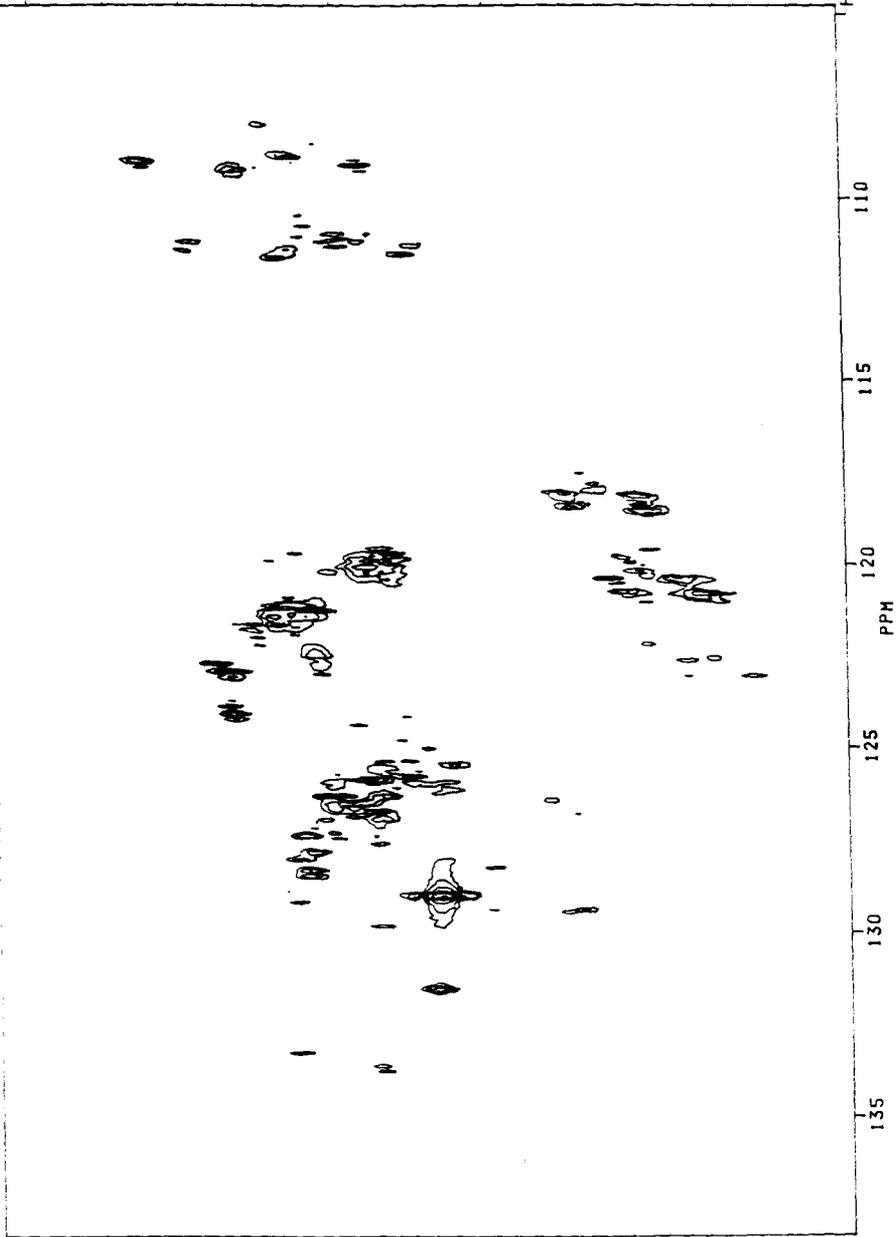


Appendix VII (Cont.)

^{13}C



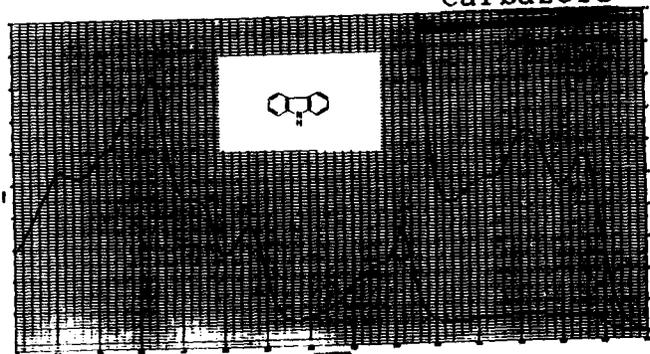
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6



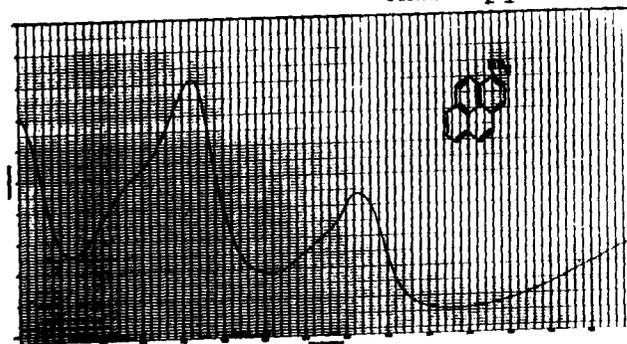
H_τ

Appendix VIII

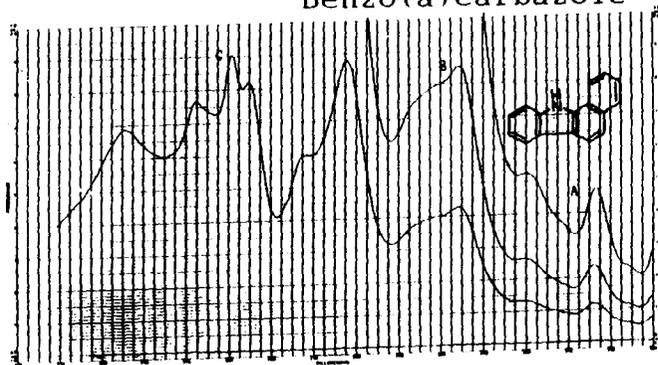
Carbazole



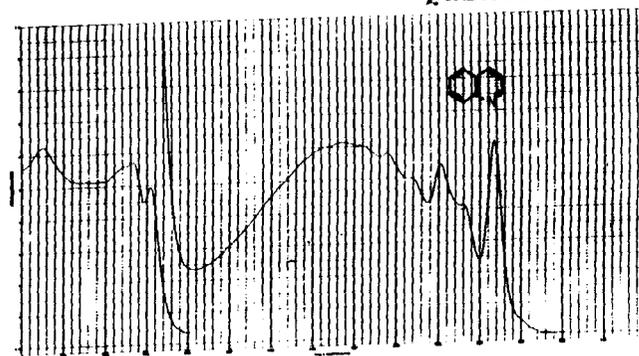
Aminopyrene



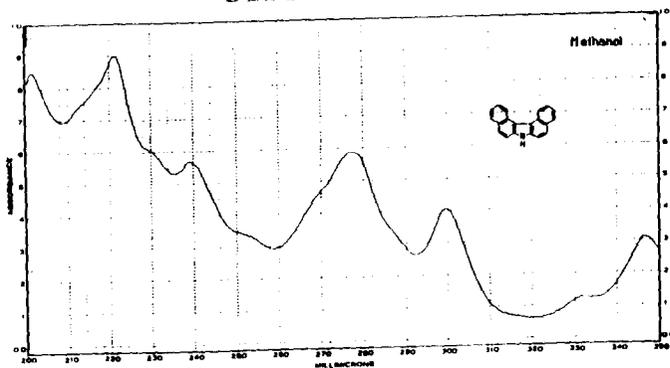
Benzo(a)carbazole



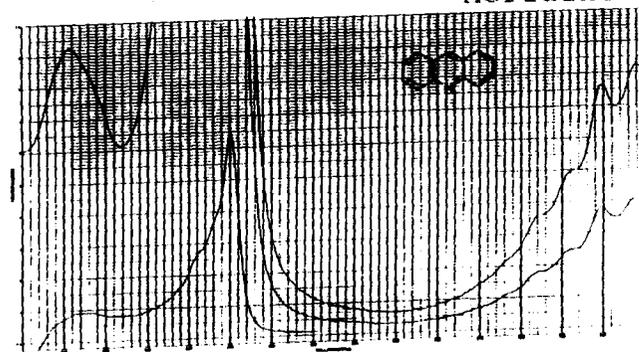
Quinoline



Dibenzo(c,f)carbazole



Acridine



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