

BAFFIN ISLAND OIL SPILL PROJECT -  
CHEMISTRY COMPONENT

VOLUME 2

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Foreward

Volume 2 of the BIOS - Chemistry Component **final report** includes all aspects of the organic chemistry analytical components of the program undertaken by **ERCO** (Energy Resources Co. Inc., Cambridge, Massachusetts, U.S.A.). The infrared (IR) analyses performed **on** seawater and sediments were generated by Seakem Oceanography Ltd. and thus appear in Volume 1 of this report.

## SECTION ONE

### INTRODUCTION

#### 1.1 Project Goals

The chemistry component of the Baffin Island oil spill project (BIOS) involved two basic tasks during the first year of the project: (1) to chemically characterize the marine environment of **the** Ragged Channel bays prior to the experimental oil spills (i.e., the **Nearshore** Study baseline), and (2) to perform chemical measurements of the oiled shoreline plots to determine the concentration and composition of residual **oil** in these experimental spills (i.e., the Shoreline Experiment). The undertaking of these tasks required specifically tailored sampling and analytical protocols designed to create the chemical foundation for a **multiyear** examination of the chemical fates and biological assimilation of the spilled **oils**.

The specific **goals** of the analytical chemistry (hydrocarbons) segment are stated in Table 1-1.

#### 1.2 Technical Plan

The analytical plan employed in the study involved the types of samples indicated in **Table** 1-2 and the types of analyses shown in **Table** 1-3. The rationale for each type of analysis is presented in detail in Section Two of this report. **It** should be stated that the overall plan was to blend analytical techniques of varying sophistication and resolution to best enable the program's goals to be achieved within

TABLE 1-1

HYDROCARBON CHEMISTRY (YEAR 1) GOALS

- 
1. To characterize the unweathered, weathered crude, and **crude/dispersant** mixtures
  2. Establish baseline levels and compositions of hydrocarbon compounds in seawater, **sediment**, and animal tissues
  3. To utilize a combination of non-specific screening and sophisticated chemical techniques to investigate the **pre-spill biogeochemical** environment
  4. To evaluate the analytical combination in terms of its use in post-spill investigations
  5. To investigate the detailed chemical weathering of spilled oil in the shoreline study
  6. To research the fate of **minor**, but Persistent classes of marker compounds - establish baseline levels and obtain initial results on spilled oil
-

TABLE 1-2  
 CHEMISTRY COMPONENT - TYPES OF SAMPLES ANALYZED

Sample Type	Nearshore - Baseline	Shoreline - Weathering
Seawater (pre-spill)	x	x
Sediment (offshore)	x	
Sediment (beach)	x	x
Oiled sediment (beach)		x
Tissues	x	
Crude oil	x	x

TABLE 1-3  
ANALYTICAL CHEMISTRY MATRIX

	UV/F	SILICIC ACID CHROMA- TOGRAPHY	CAPIL- LARY GC	CAPIL- LARY GC HO- PANES	CAPIL- LARY GC AZA- ARENES	CAPIL- LARY GC AROMATIC H.C.	PHYS- ICAL PROP- ERTIES	TRACE METALS
Crude oils	x	x	x	x	x	x	x	x
Seawater	x	x	x			x		
Sediment (offshore baseline)	x	x	x	x	x	x		
Sediment (beach baseline)	x	x	x	x	x	x		
Sediment (oiled beach)		x	x	x	x	x		
<b>Tissues</b>		<b>x</b>	<b>x</b>	<b>x</b>		<b>x</b>		

the budgetary constraints. We have employed such blends successfully in the past (Fiest and Boehm, 1981; Boehm and Fiest, 1981a, 1981b; Boehm et al., 1981a).

### 1.3 Background

#### 1.3.1 Pollutant Compounds in the Arctic

Although an abundance of data is not readily available, several studies have been undertaken in recent years to determine levels of organic pollutants, most notably petroleum hydrocarbons (PHC), in remote and/or undeveloped arctic marine environments. A general chemical picture emerges of an environment with very low levels of hydrocarbons, but one that is not free from "contaminants" distributed on a global basis by natural and anthropogenic processes.

Wong et al. (1976), Shaw et al. (1979), Shaw and Baker (1978), and Johansen et al. (1977) have investigated petroleum hydrocarbon pollutant distributions in the offshore Beaufort Sea, the nearshore Beaufort Sea, the Port Valdez nearshore environment and the West Greenland coast respectively. There is little indication in any of these studies of inputs of chronic petroleum related inputs of hydrocarbons, although Shaw et al. (1979) suspect that fossil-fuel-related arenes (aromatic hydrocarbons) from coal outcrops or natural seeps are sources for low levels of sedimentary arenes found at several locations.

Long-range transport of polycyclic aromatic hydrocarbons (PAH = arenes) from pyrolytic sources (i.e., combustion of fossil fuels) are probable sources for observed distributions of low levels of PAH found in the Arctic (Wong et al.,

1976; Shaw et al., 1979) and elsewhere on a global scale (Laflamme and Hites, 1978; Lunde and Bjorseth, 1977).

Some PAH compounds are also produced **diagenetically** (i.e., after deposition of precursors in the sediment) in surface sediments and may therefore not be related to any pollutant sources. Wakeham et al. (1980), Aizenshtat (1973), and Simoneit (1977 a, 1977b), among others, describe the diagenetic production of PAH compounds including "the more commonly encountered retene (1-methyl-7-isopropylphenanthrene) and **perylene**, and other compounds (e.g., alkylphenanthrenes) that have pollutant sources as well.

Little evidence exists for the input of saturated petroleum hydrocarbons in any arctic environment studied in sufficient quantities to mask **natural** saturated hydrocarbon profiles consisting of marine and terrigenous **biogenic** compounds. **Alkane** compositions suggest **biogenic** sources (Shaw et al., 1979) as well.

### 1.3.2 Weathering of Petroleum in the Marine Environment

"Weathering" of oil at sea pertains to that collective set of processes which alter the chemical composition of petroleum mixture through evaporation, dissolution, **photochemical** oxidation, microbial degradation, and auto-oxidation. The physical processes mediating the chemical changes are mixing, emulsification, and sorption (NAS, 1975). A schematic diagram of the processes of weathering of oil is shown in Figure 1-1.

Incorporation of petroleum in the sediment usually results in accelerated weathering of oil in oxygenated substrate **mainly** through microbial degradation (Teal et al., ,

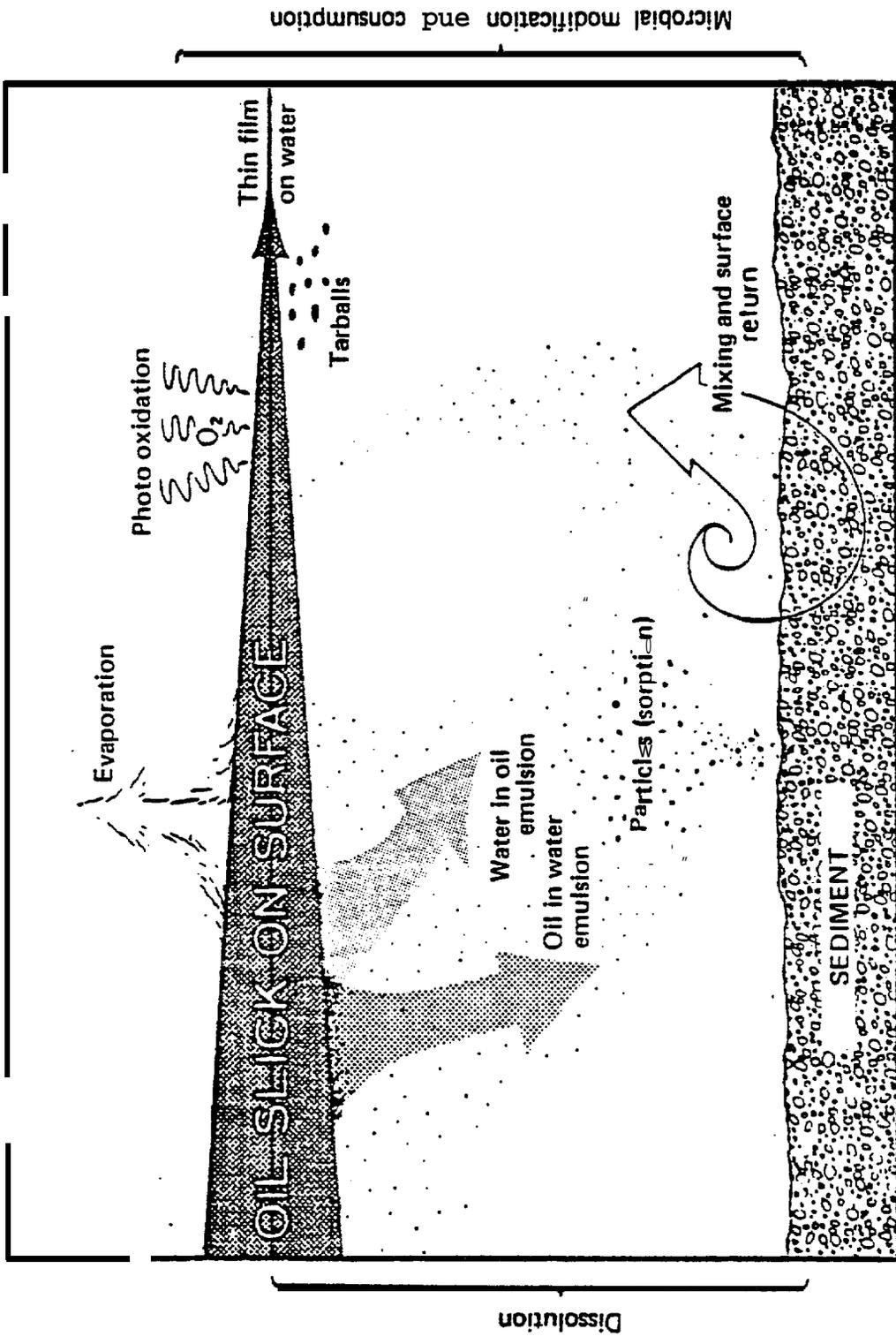


Figure 1.1. Schematic of the transport processes affecting spilled oil in the marine environment

1978; Cretney et al., 1978; Keizer et al., 1978; **Beslier** et al., 1981; **Atlas** et al., 1981; **Boehm** and **Fiest**, 1981b). **Boehm** et al. (1981b) have conducted a comprehensive study of how Amoco Cadiz oil changed markedly in its composition with time after deposition in intertidal sediments (Figure 1-2). Oil buried beneath the aerobic zone is subject to little or very slow anaerobic degradation (Ward and **Boehm**, unpublished data). Oil may be transported to the benthos by several processes illustrated in Figure 1-3. In the case of chemical dispersion of oil, the magnitude of incorporation of oil into the benthos after dispersion is unknown. Therefore, oil transported to the **benthos** in **small** to moderate quantities can be expected to lose much of its obvious fingerprint if the hydrocarbons are available to microorganisms. The **paraffinic** fraction can first be altered by oxidation and **isomerization**, followed next by the aromatic fraction. Oil which has been highly weathered requires study by sophisticated and extensive analytical procedures **prior to** successful characterization. pelagic tar balls are notorious exceptions to this rule, maintaining characteristic paraffinic patterns for considerable periods of time (Butler et al., 1973).

The use of molecular marker compounds for the long-term identification and detection of oil residues have been used previously. These compound **classes** are more resistant to environmental degradation than the commonly used **fingerprintable** material (*i.e.*, **alkanes**). Of particular interest have been **pentacyclic** triterpanes (**Dastillung** and **Albrecht**, 1976; **Boehm** et al., 1981b; **Atlas** et al., 1981) **alkylated phenanthrenes** and **dibenzothiophenes** (**Boehm** et al., 1981b, **Teal** et al., 1978) and **azaarene** compounds (**heterocyclic** nitrogen aromatic compounds) (**Jewell**, 1980). Use of these markers requires their characterization in **the** source material, the **pre-spill environment**, and the **post-spill** contaminated **samples**.

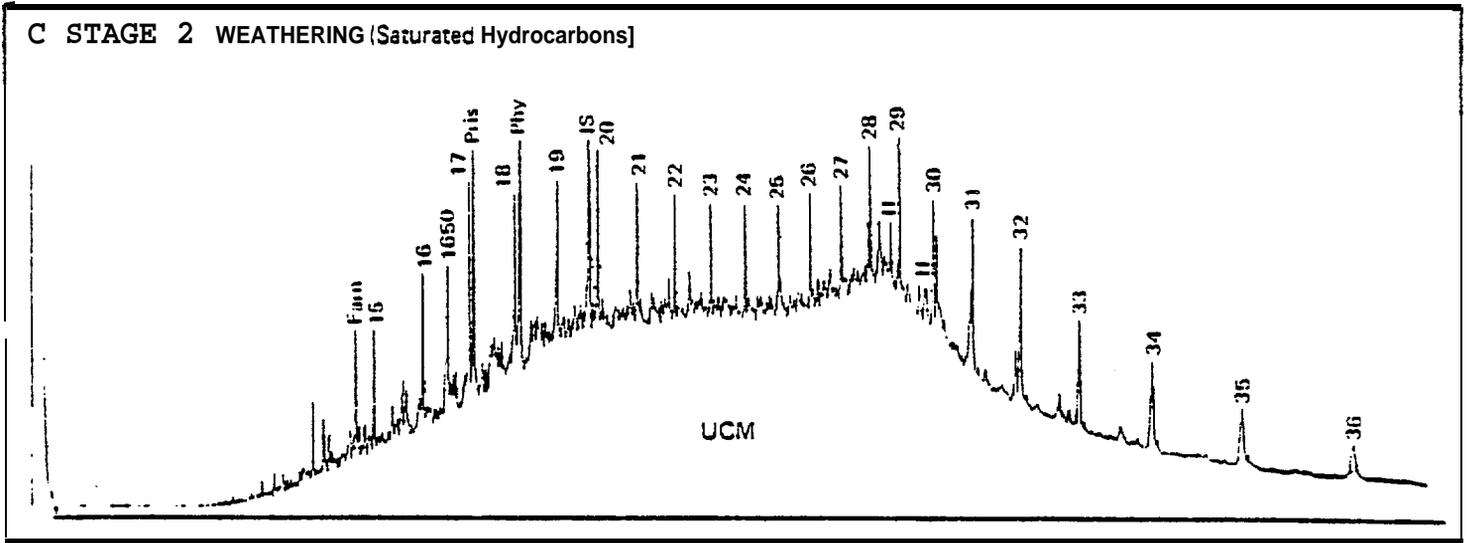
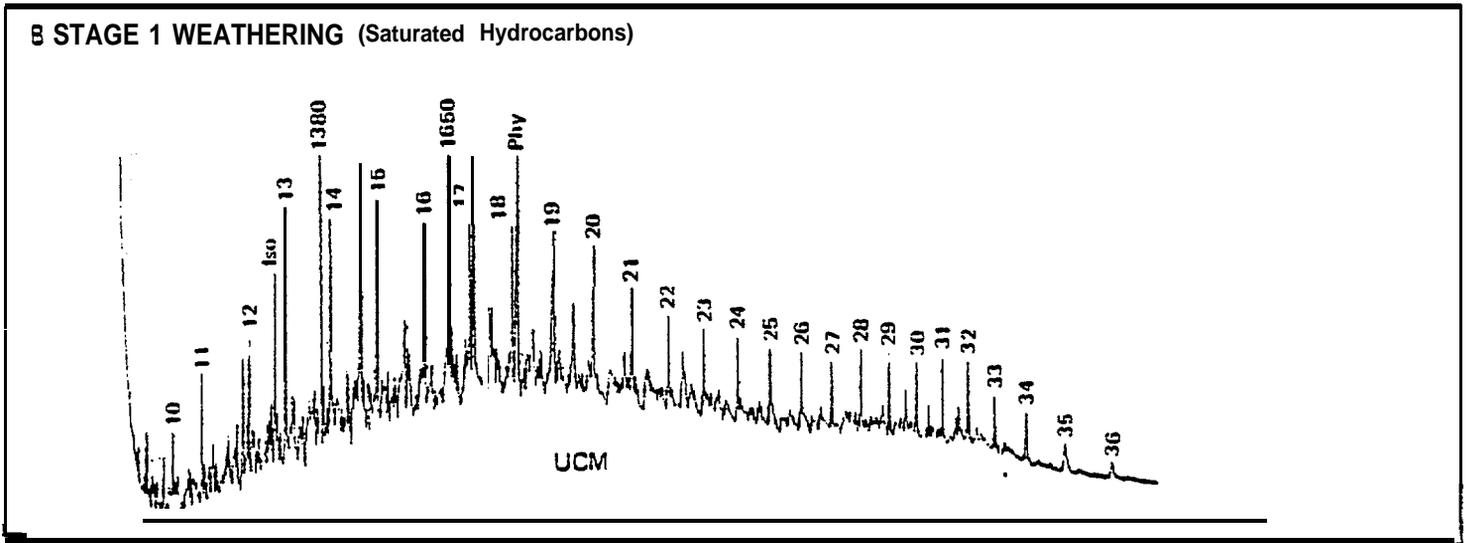
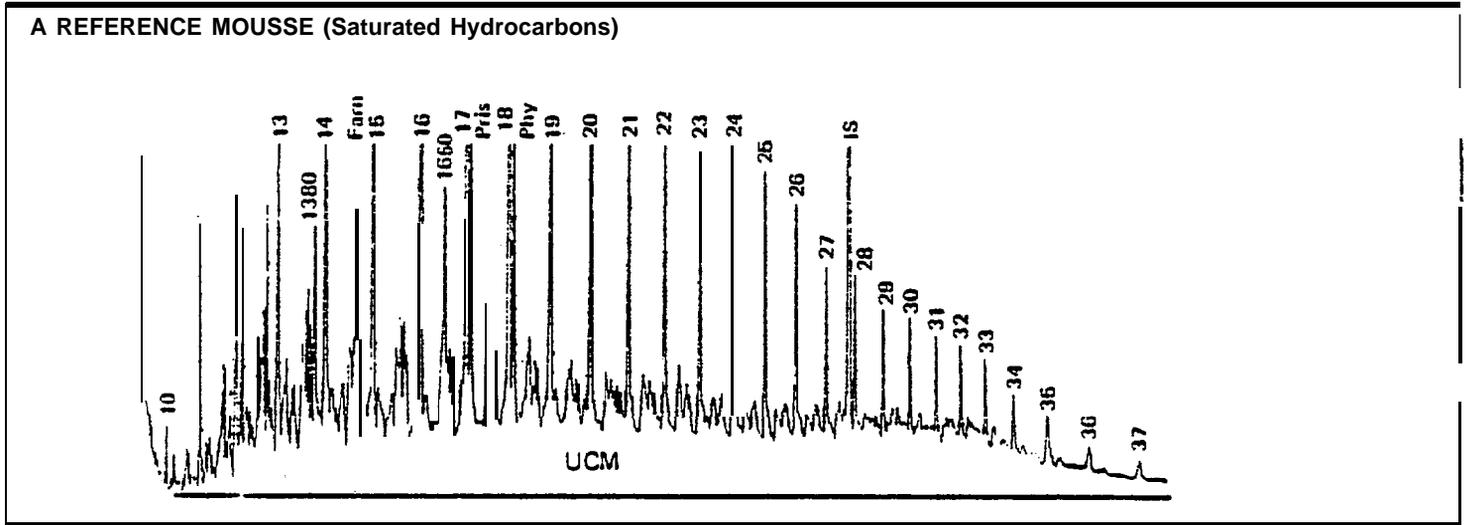
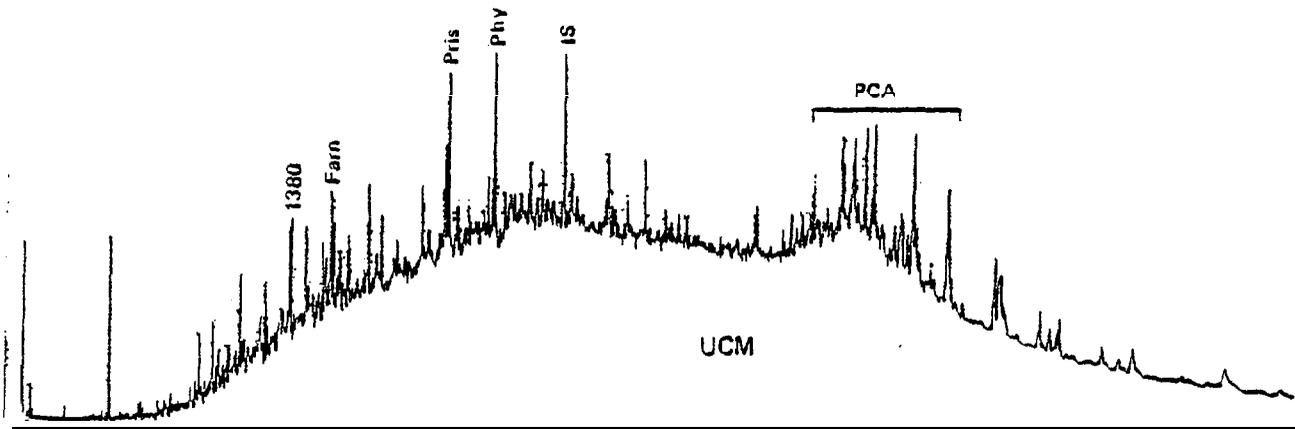


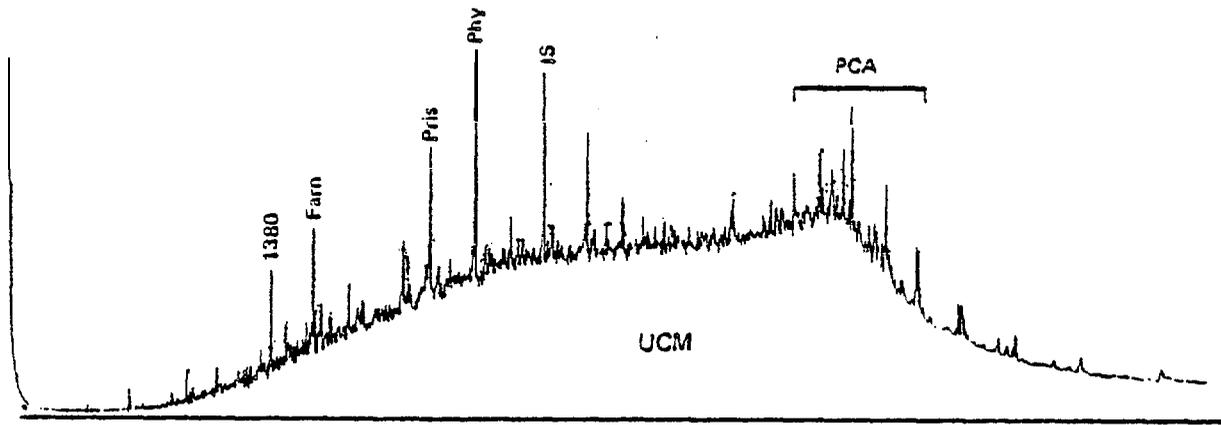
Figure 1.2. Weathering patterns of saturated hydrocarbons in *Amoco Cadiz* oil (from Boehm et al., 1981 b).

O STAGE 3 WEATHERING (Saturated Hydrocarbons)

PCA=Polycyclic Aliphatics



ESTAGE 4 WEATHERING (Saturated Hydrocarbons)



F BACKGROUND (saturated Hydrocarbons)

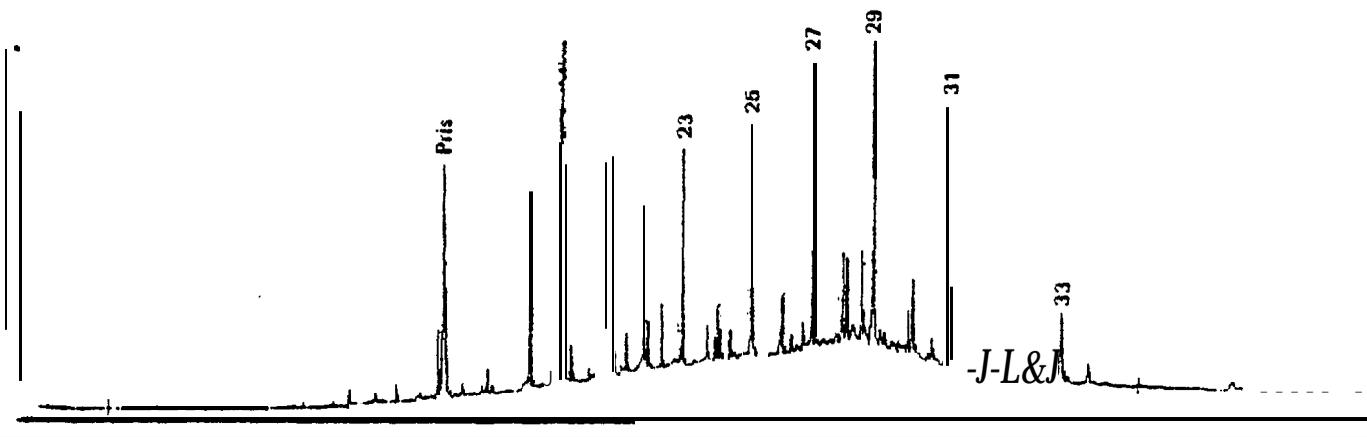


Figure 1.2. (Continued).

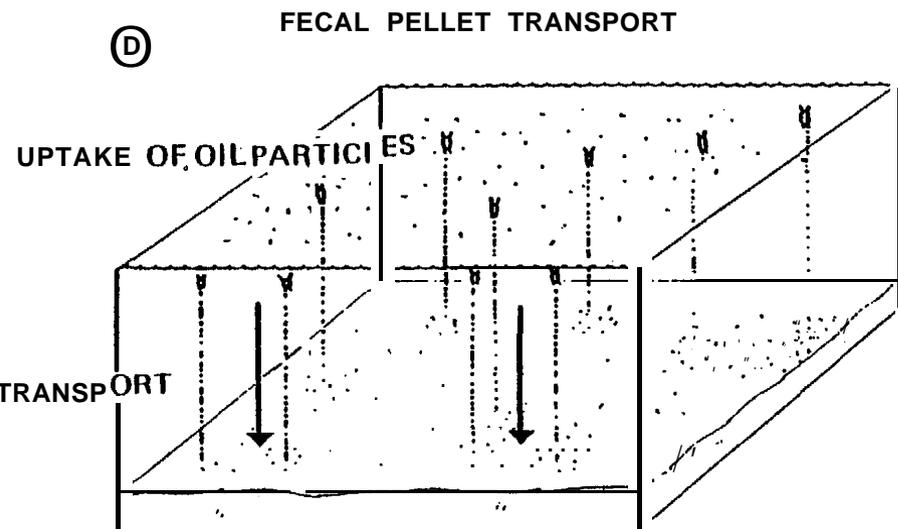
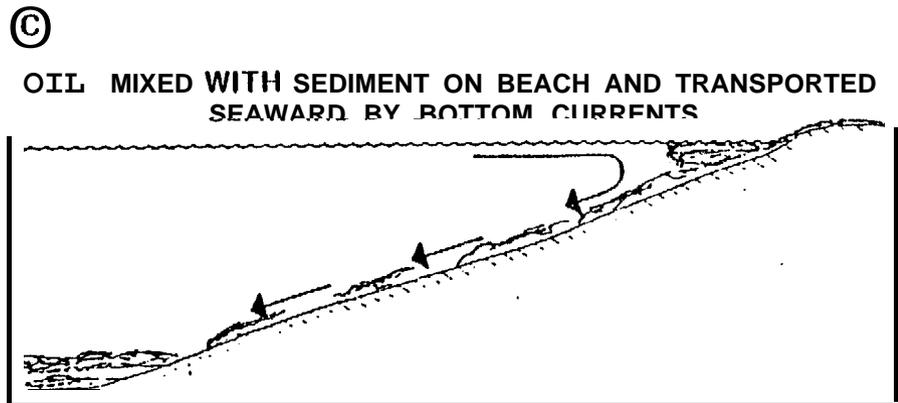
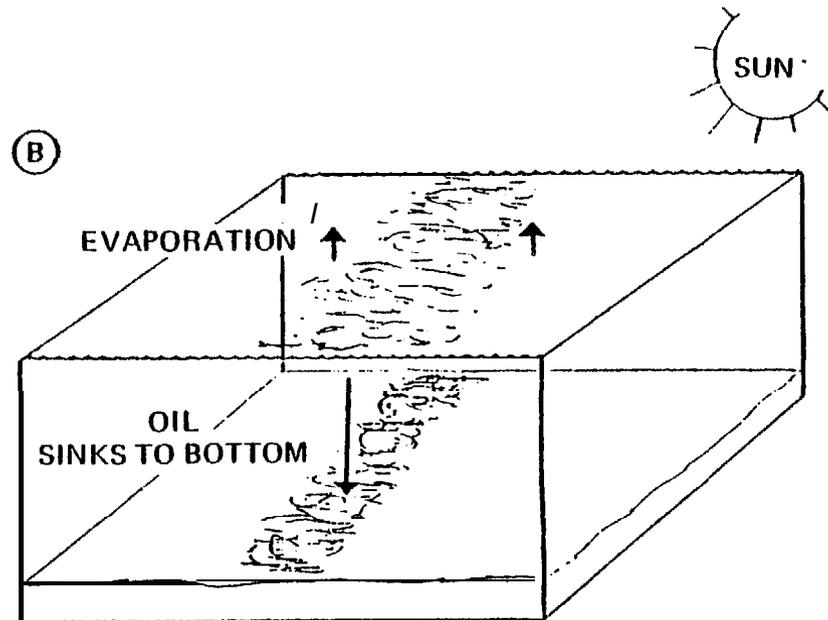
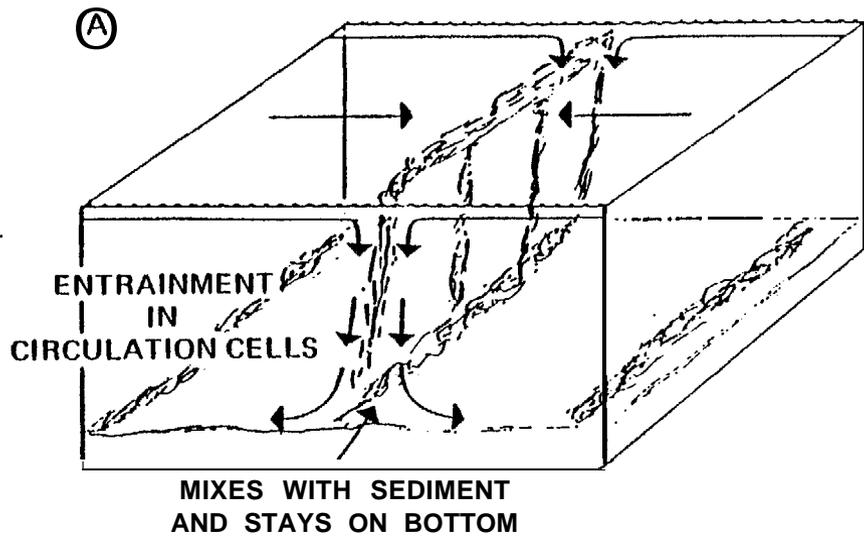


Figure 1.3. Hypothesized methods by which oil may be caused to sink and remain on the bottom.

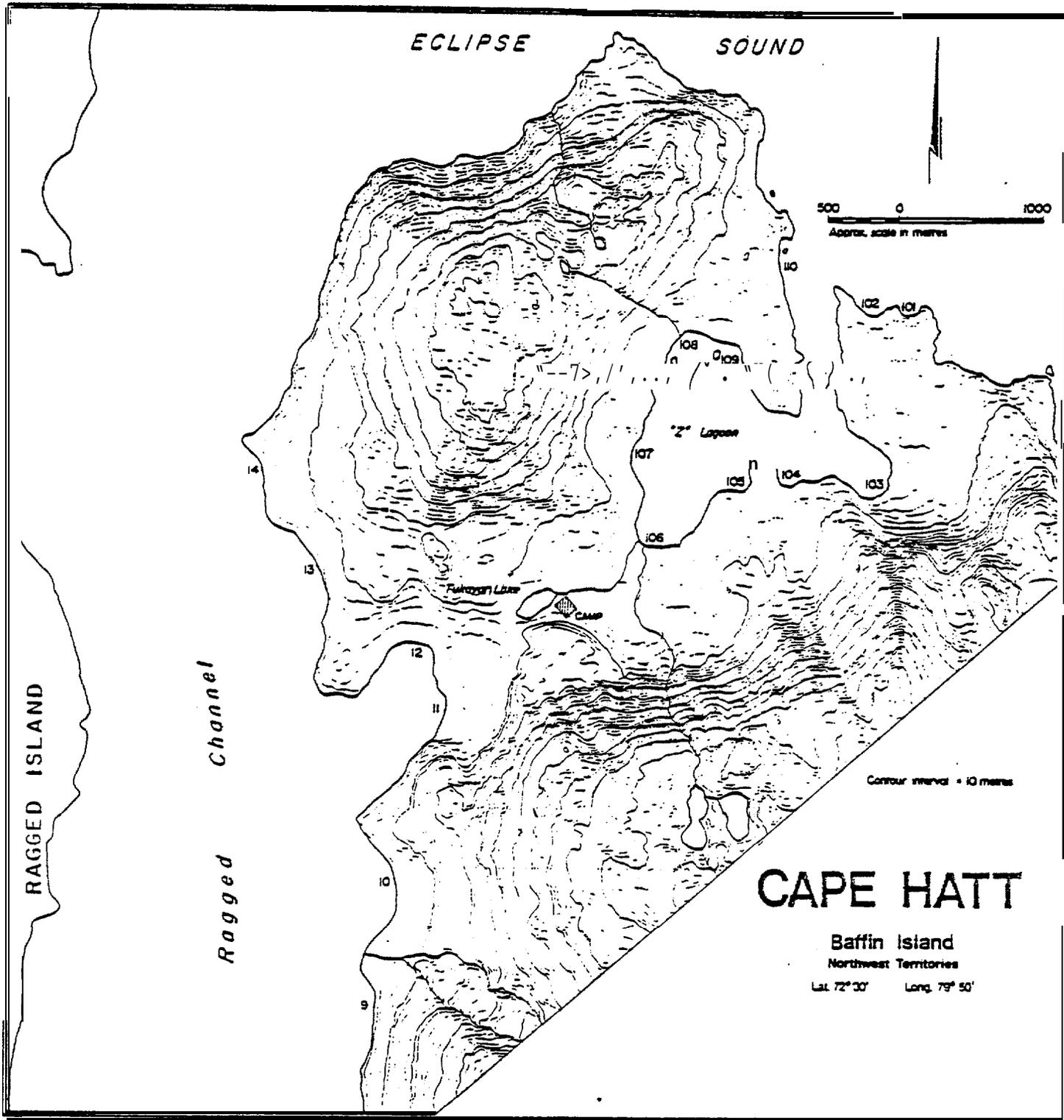


Figure 2.2. The Cape Hatt Site, Showing the Numbering of the Experimental Bays.



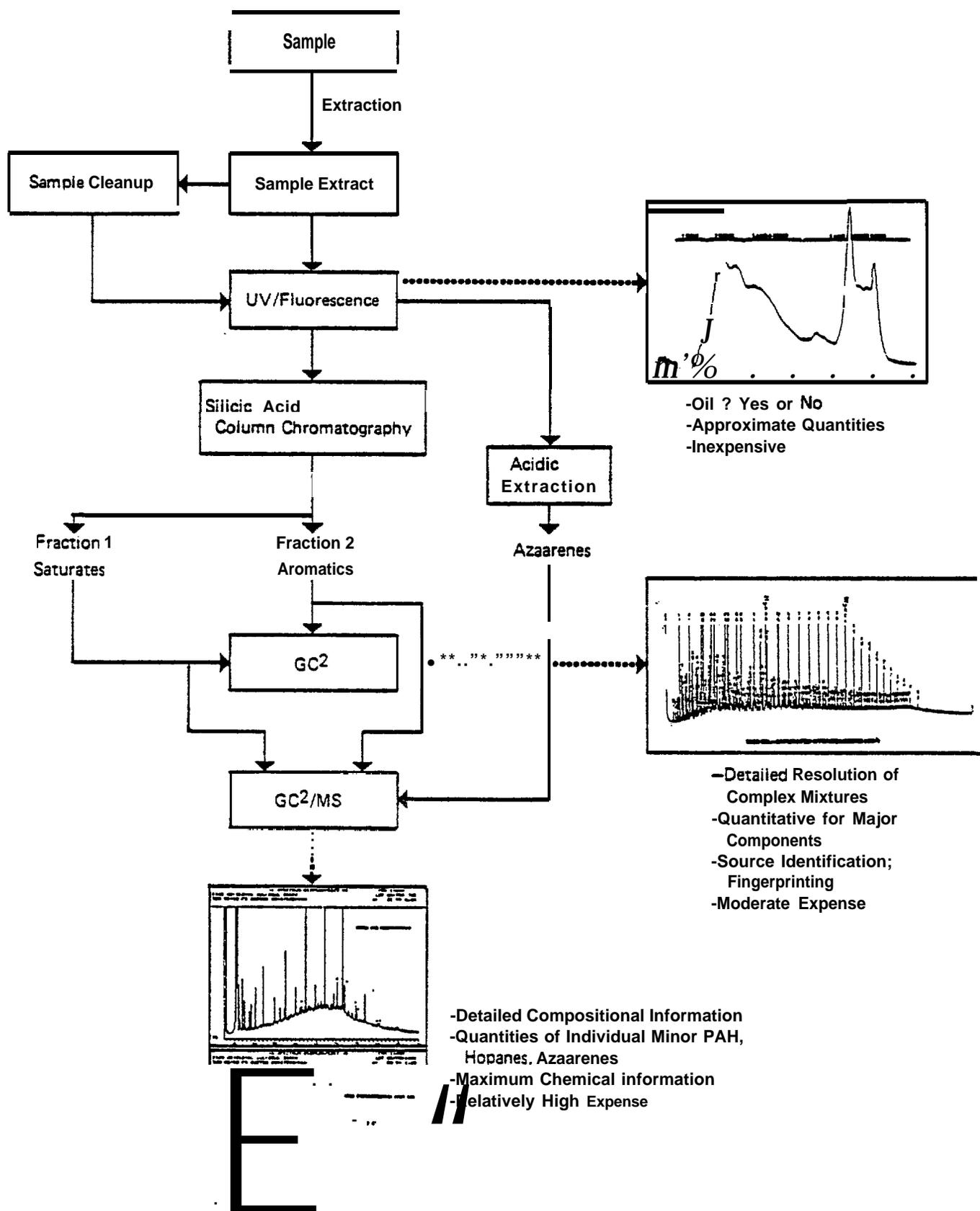


Figure 2.4. Schematic of Analytical Strategy.



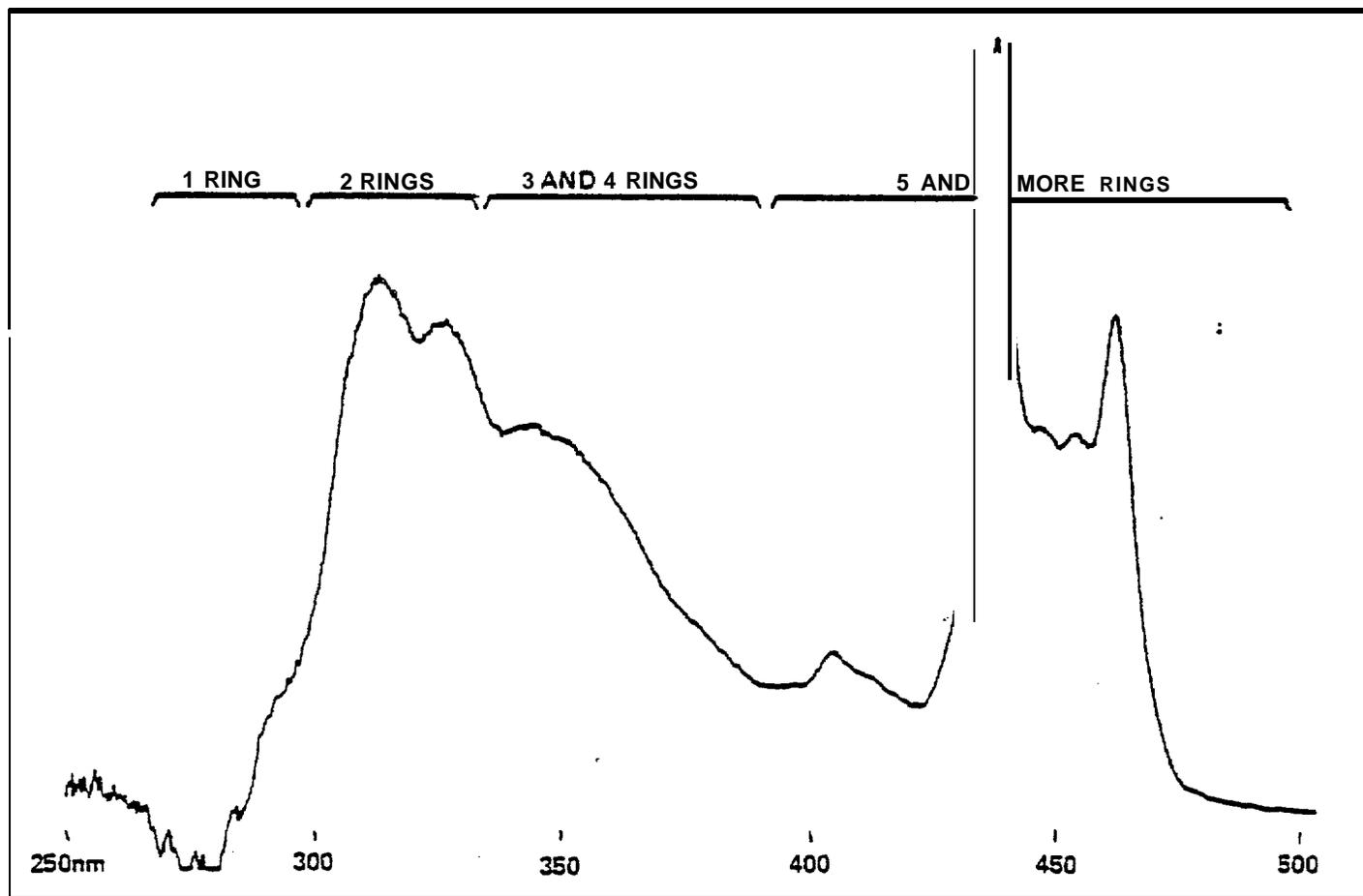


Figure 2.5. Synchronous Spectrofluorometry Spectrum of a Sediment Extract Showing the Resolution of Ring Classes and Perylene in the Right-Hand Side of the Spectrum.



TABLE 2-1

SUMMARY OF METHODS USED IN THIS ANALYTICAL PROGRAM

SAMPLE TYPE	ANALYSIS	METHOD SUMMARY	REFERENCES
Seawater	Synchro- nous UV/F	Freon extraction; analysis of unfractionated extract	Wakeham, 1977; Gordon et al., 1976; Vo-Dinh, 1978; Lloyd, 1971
Seawater	GC <sup>2</sup>	Temperature-programmed capillary analysis; SE52 fused silica columns; internal standard quantification; GC <sup>2</sup> and gravimetric analysis of f <sub>1</sub> and f <sub>2</sub> silicic acid column eluates; computation of individual component levels and key diagnostic parameters	Boehm, 1980; Cram & Young, 1980; Boehm & Fiest, 1981a
Seawater	GC <sup>2</sup> /MS	GC/MS/computer system (HP5985); quantification by mass fragmentography	Boehm et al., 1981a, 1981b
Sediments	Synchro- nous UV/F	Azeotropic room temperature extraction; analysis of whole extract	Wakeham, 1977; Boehm & Fiest, 1981a; Boehm et al., 1981b; Boehm et al., 1979;
Sediments	GC <sup>2</sup>	(see GC <sup>2</sup> for seawater)	Barrington et al., 1976; Boehm et al., 1981b; Boehm & Fiest, 1981b



TABLE 2-2

STEAM DISTILLATION RECOVERY/EFFICIENCY -  
MIXED SATURATED/AROMATIC STANDARD

COMPONENT	% RECOVERY
n-C <sub>10</sub>	35
n-C <sub>11</sub>	43
Naphthalene	91
n-C <sub>12</sub>	47
n-C <sub>13</sub>	56
n-C <sub>14</sub>	80
Hexamethyl benzene	103
n-C <sub>15</sub>	106
n-C <sub>16</sub>	117
n-C <sub>17</sub>	115
Pristane	105
phenanthrene	113
Anthracene	105
n-C <sub>18</sub>	112 "
Phytane	110
n-C <sub>19</sub>	98
n-C <sub>20</sub>	96
n-C <sub>21</sub>	76
n-C <sub>22</sub>	75
n-C <sub>23</sub>	85
n-C <sub>24</sub>	80
n-C <sub>25</sub>	89
Chrysene	38
n-C <sub>26</sub>	98
n-C <sub>28</sub>	102
Perylene	56
n-C <sub>29</sub>	101
n-C <sub>30</sub>	101
n-C <sub>31</sub>	108
n-C <sub>32</sub>	110
Benzoperylene	85



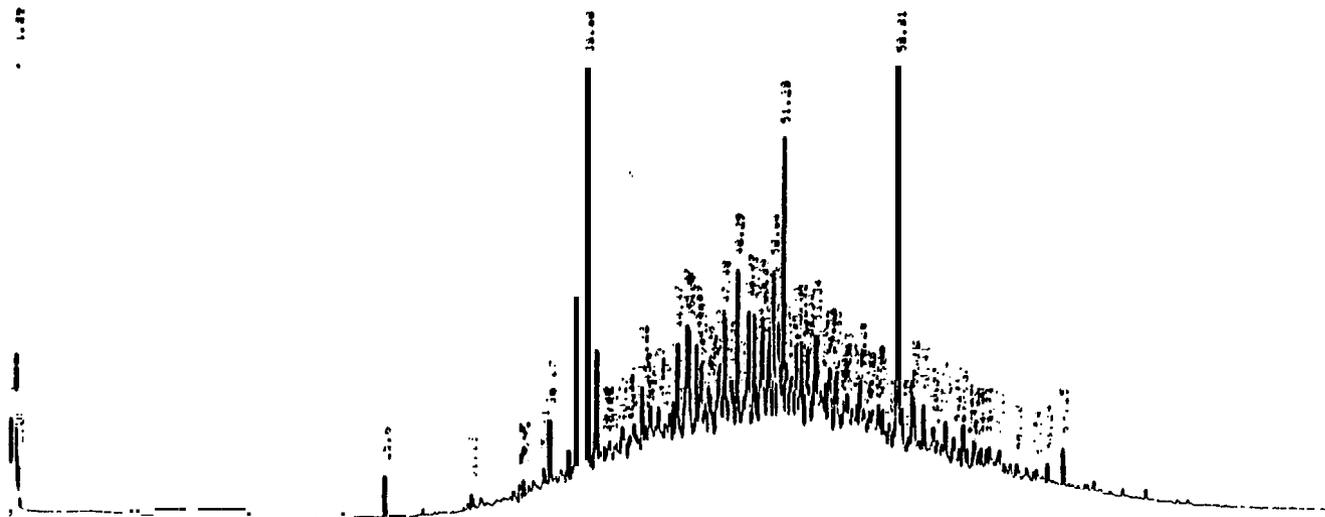
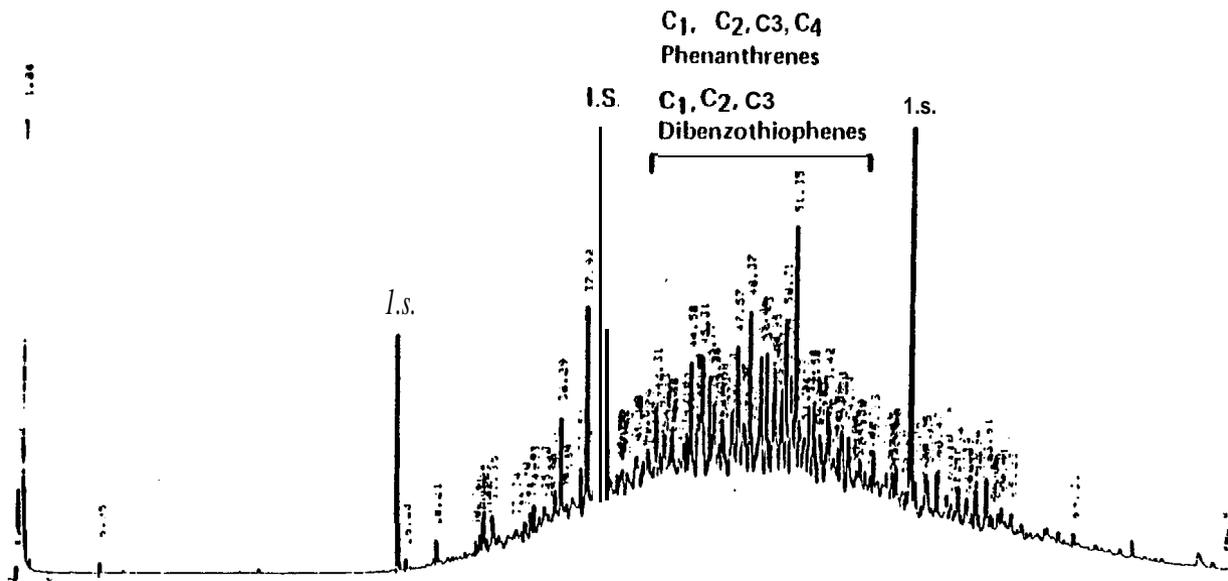


Figure 2.6. Steam Distillation Recovery of Polluted Tissue Aromatic Extract, A-Aromatics (Original); B-Aromatics (After Steam Distillation).

## SECTION THREE

### RESULTS

#### 3.1 Oil Characteristizations

##### 3.1.1 Gross Composition

The quantitative breakdown between saturated, aromatic polar (**NSO**), and residual (**asphaltene**) fractions of the fresh and aged **Lagomedio** crude oil and a **10:1 oil/corexit** mixture are presented in Table 3-1.

##### 3.1.2 Saturated Hydrocarbons

The saturated hydrocarbons of the **Lagomedio** crude oil include **n-alkanes** in the boiling range of n-C<sub>9</sub> to n-C<sub>34</sub> (Figure 3-1). Approximately 70% of the fresh, unweathered crude **elutes** prior to n-C<sub>15</sub> compared to 50% for the weathered (or aged) oil. The comparative **GC<sup>2</sup>** traces are shown in Figure 3-1 with the major normal alkane and branched **alkane** (**isoprenoid**) components **labelled**.

Several other important parameters are presented in Table 3-2. Note how the artificial aging of the crude has influenced the saturate composition through the boiling range n-C<sub>9</sub> to pristane. The changing saturated hydrocarbon weathering ratio (**SHWR**) is a measure of the evaporative weathering process. The **alkane** to isoprenoid ratio (**ALK/ISO**) quantifies the relative composition of the more **easily** biodegraded **n-alkanes** to the **less** readily degraded **isoprenoids**.



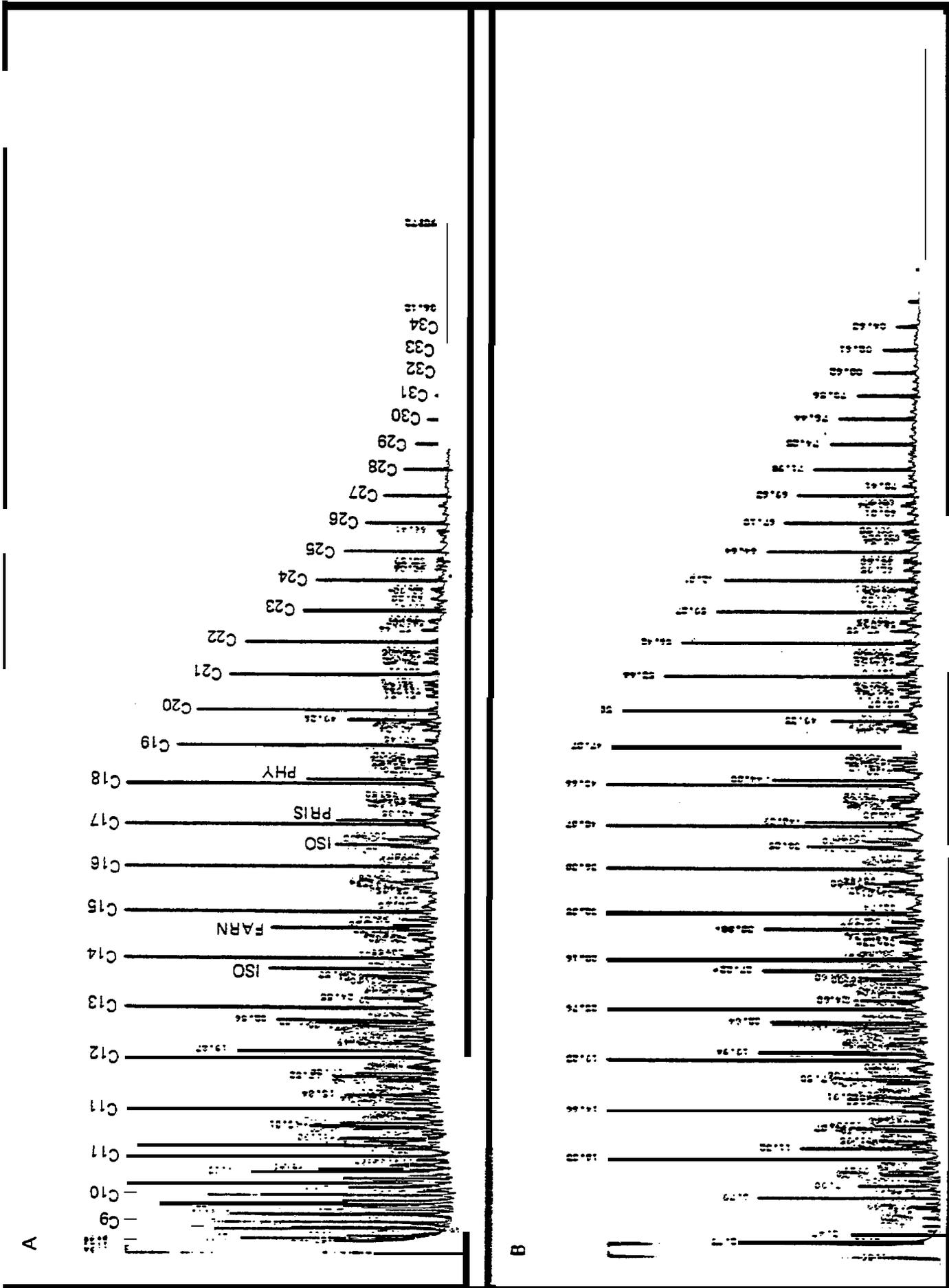


Figure 3.1. GC<sup>2</sup> Traces of Saturated Hydrocarbons of A—Unweathered Lagomedio Crude Oil, B—Aged Oil.



A graphical comparison of the saturated hydrocarbon composition is shown in Figure 3-2. Note from this presentation how significant compositional changes appear throughout the boiling range.

### 3.1.3 Pentacyclic Triterpanes

GC<sup>2</sup>/MS analysis of the hopane-type pentacyclic triterpanes reveals small quantities of four compounds (Figure 3-3): Compound C (norhopane; C<sub>29</sub>H<sub>50</sub>), Compound D (C<sub>30</sub>H<sub>52</sub>); Compounds E, E' (homohopanes C<sub>31</sub>H<sub>54</sub>) and a pattern of 12 secondary peaks of unknown structure.

### 3.1.4 Aromatic Hydrocarbons (UV/F)

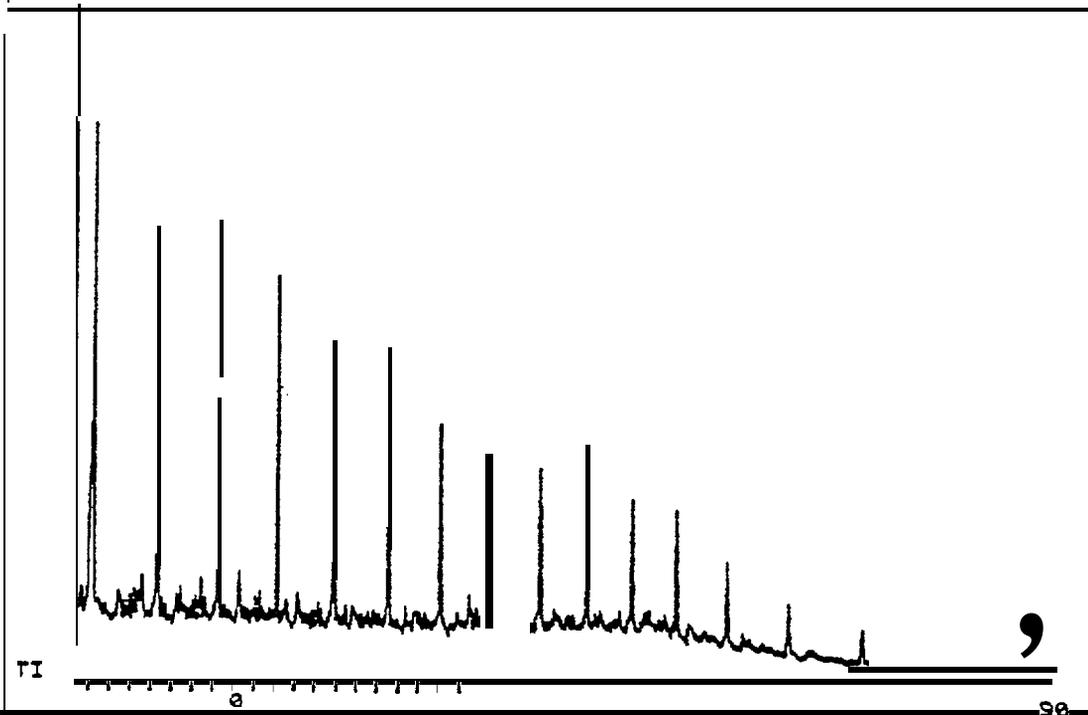
W/F analysis of several dilutions of the aged Lagomedio crude is presented in Figure 3-4. Major quantities of 2-, 3-, and 4-ring aromatics are apparent with lesser quantities of the 5-ring compounds.

### 3.1.5 Aromatic Hydrocarbons

GC<sup>2</sup>/MS analysis of the Lagomedio crude indicate that compounds from alkyl benzenes to the benzopyrenes are detected in the aged and fresh crudes. The GC<sup>2</sup>/MS data is presented in several different ways: (1) a semi-log plot of aromatic hydrocarbon concentrations (Figure 3-5) of the aged oil, (2) comparative GC<sup>2</sup> traces of the fresh and aged crude oil aromatic fraction (Figure 3-6), (3) a comparative plot of the aromatic compositions normalized to trimethyl dibenzothiophene (Figure 3-7), and (4) GC<sup>2</sup>/MS mass fragmentograms (Appendix A).



\*\* SPECTRUM DISPLAY/EDIT \*\*  
 FUN 14734  
 EIOS OIL LMF1 1UL/7SUL 2000U A/ D-3 1ST SC/PG: 761  
 30M SE-52 FS 70CT80 60-27503/MIN X= .25 Y= 2.00



\*\* SPECTRUM DISPLAY/EDIT \*\*  
 FRN 14734  
 EIOS OIL LMF1 1UL/7SUL 2000U A/D-3 1ST SC/PG: 1112  
 30M SE-52 FS 70CT80 60-27503 MIN X= .50 Y= 1.00

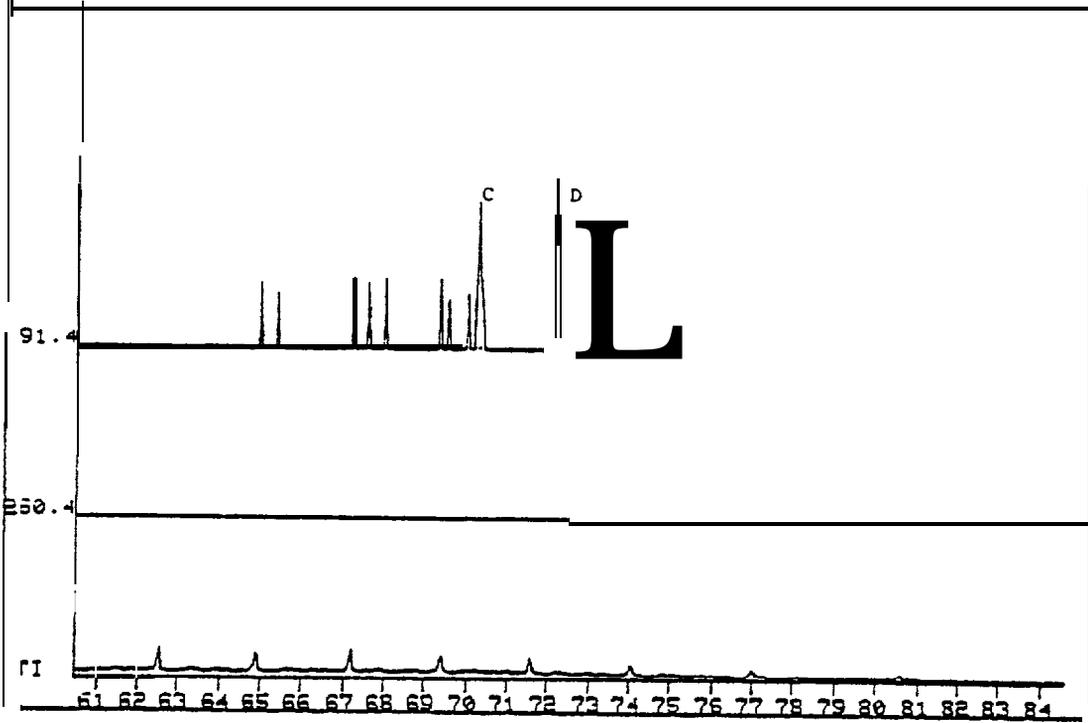


Figure 3.3. Bios Oil—Hopane Analysis (GC<sup>2</sup>/MS).



(ppm)

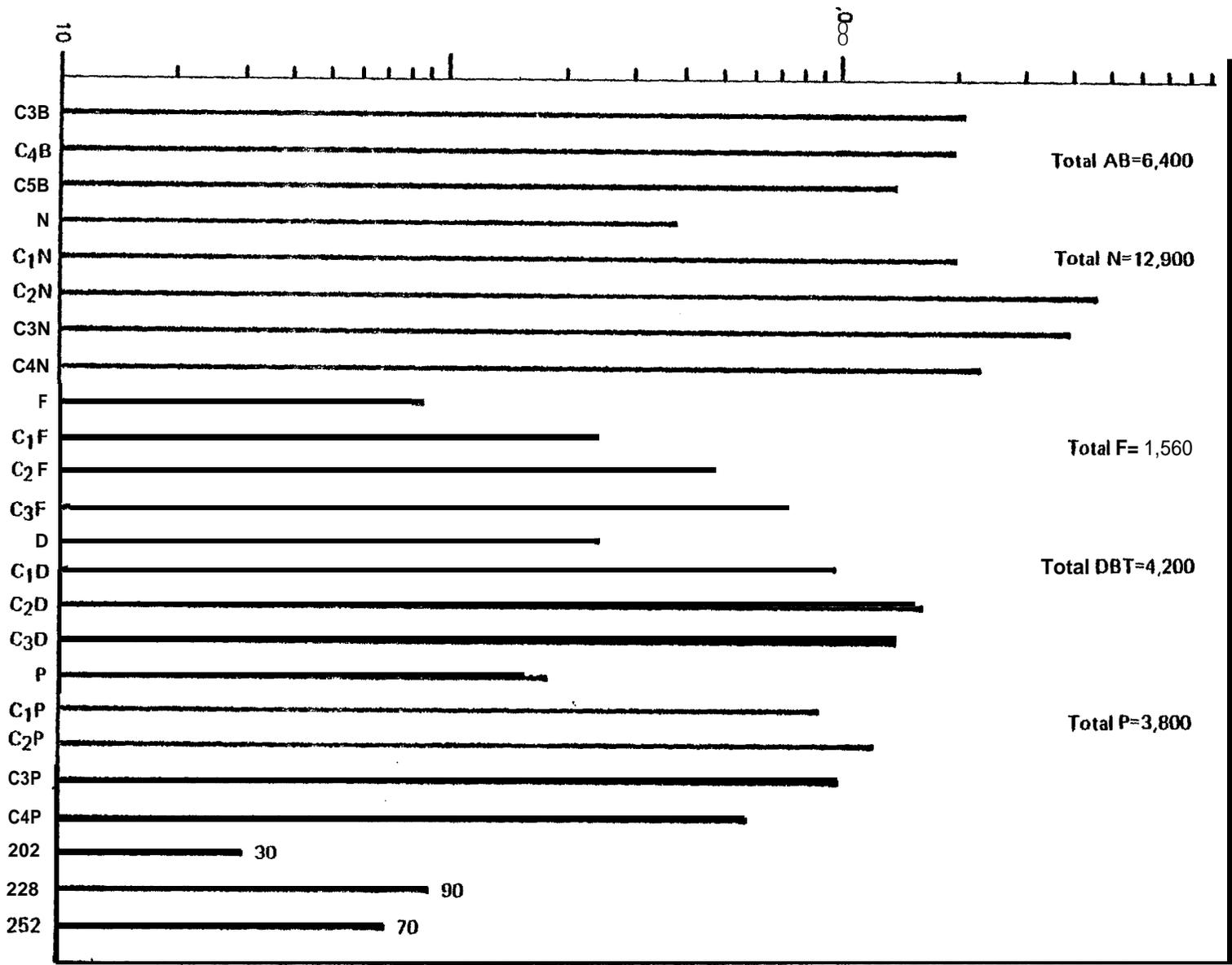


Figure 3.5. PAH Composition of Weathered Lagomedio Crude Oil (ppm).

(B=Benzene, N=Naphthalene, F=Fluorene, D=Dibenzothiophene, P=Phenanthrene, 202=Fluoranthene/Pyrene, 228=Chrysene, 252=Benzopyrenes)



3-11

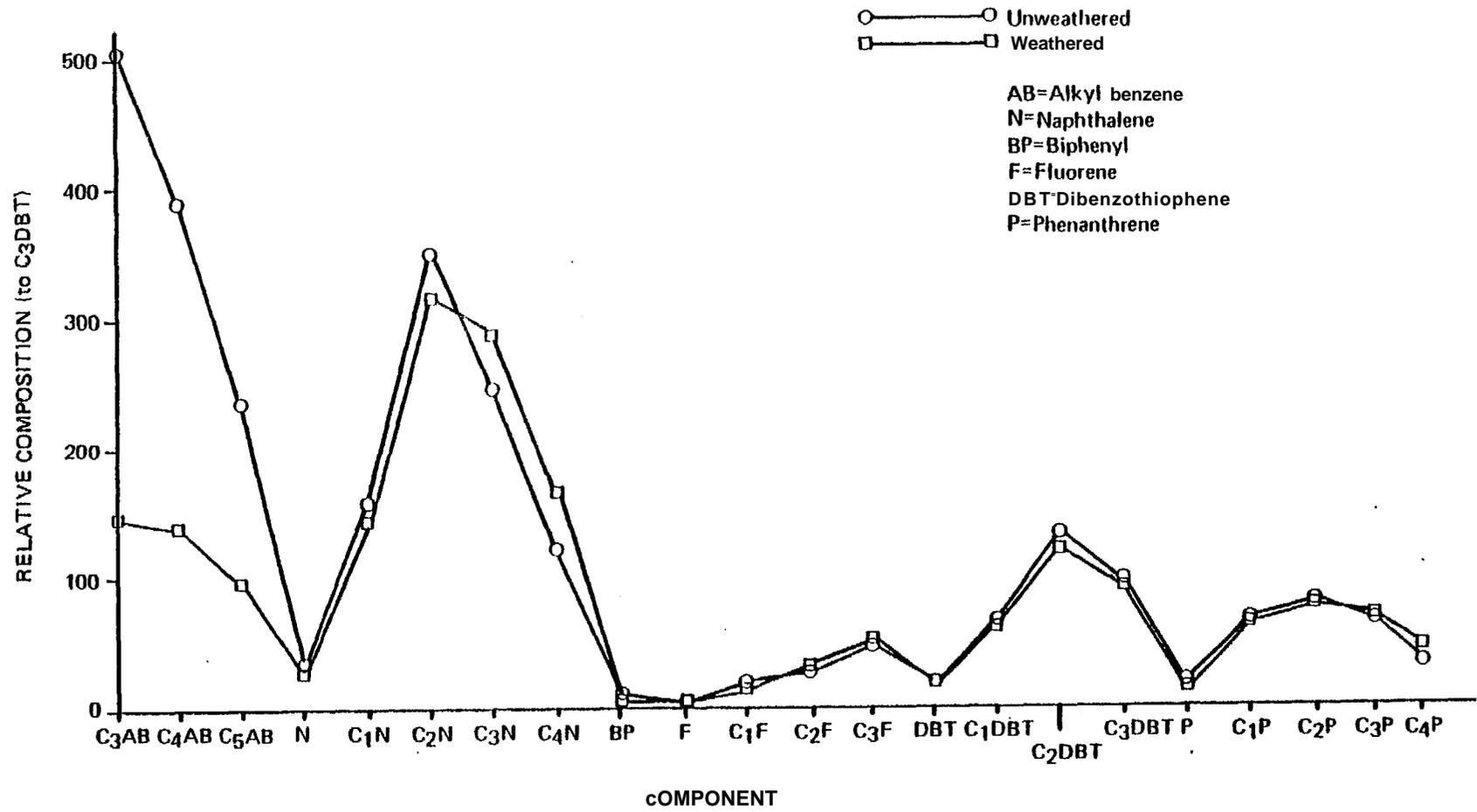


Figure 3.7. Aromatic Hydrocarbon Composition of Weathered vs. Unweathered Lagomedio Crude Oil.



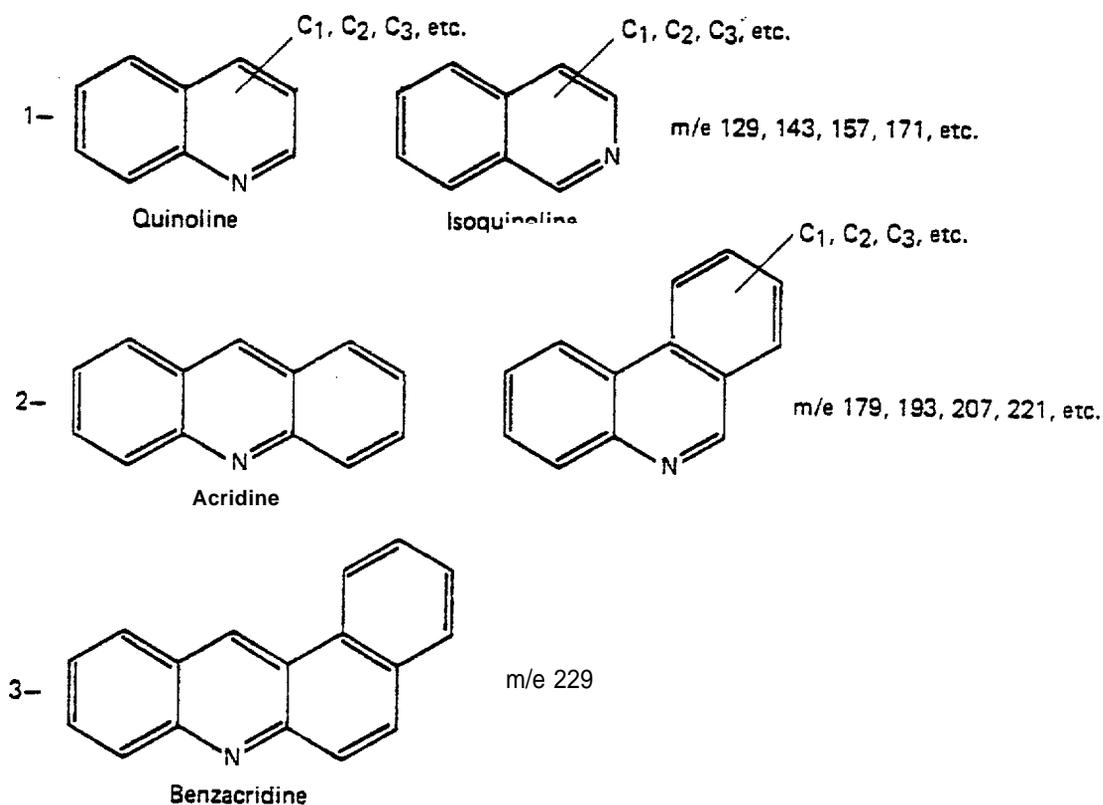
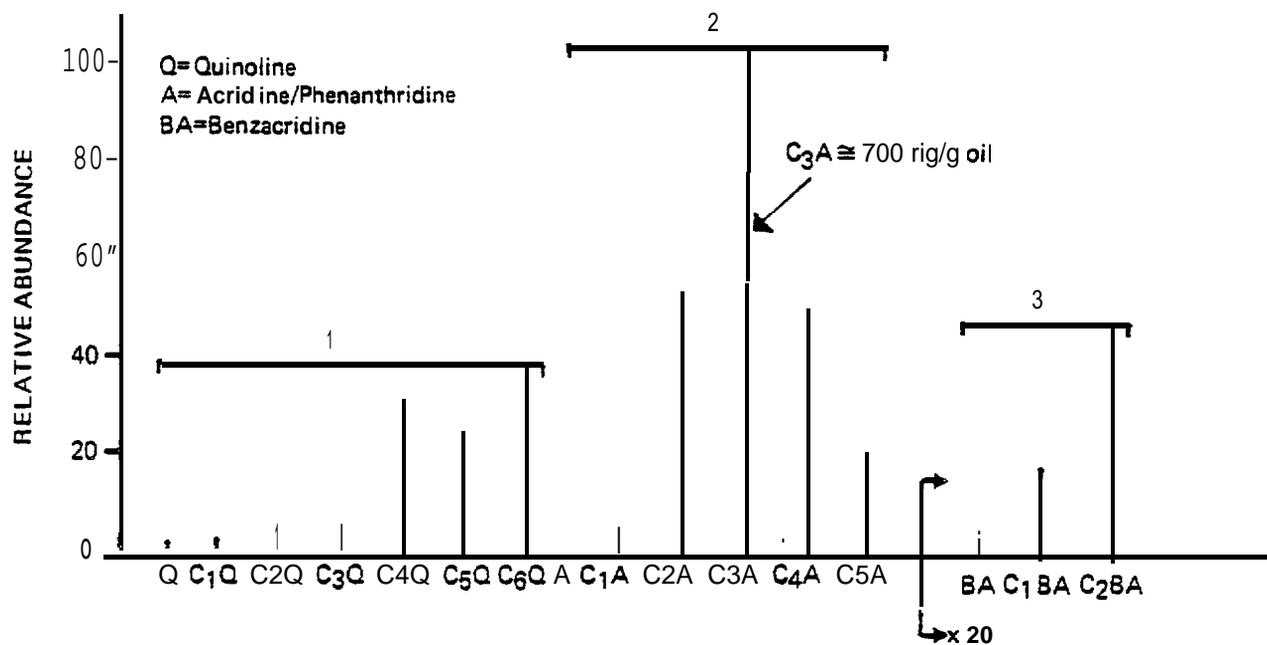


Figure 3.8. Azaarene composition of Lagomedio crude oil.



(10:1); aged **Lagomedio** crude:Corexit 9527 (1:1). The results are presented in Tables 3-3, 3-4, and 3-5.

As the note in Table 3-3 indicates, significant wax precipitation precluded the obtaining of absolute viscosity measurements. The viscosity values reported in the note (Table 3-3) were found to be both time dependent and influenced by the capillary size of the viscometer used. The samples are non-Newtonian at the temperatures in question and their viscosities cannot be determined by capillary **viscometry**. Apparent viscosity data, if required, may be determined by the use of the Brookfield **viscometer**.

The data reported for the 1:1 sample and at 5°C for the crude oil and 10:1 mix samples were obtained under conditions under which wax formation was minimal and under which the samples behaved in a Newtonian manner.

These results have **great** bearing on the behavior of the oil under the proposed spill conditions. Wax formation is to be expected and must be dealt with both in the diffuser system and in the sampling scheme.

#### 3.1.8 Trace Metal Composition

The trace metal composition of the aged **Lagomedio** crude oil is given in Table 3-6. The analyses are presented in comparison to another Venezuelan crude? a Kuwait crude, and a Louisiana crude. Of greatest interest are the high nickel and vanadium (12.4 ppm and 135 ppm, respectively) contents of the **Lagomedio** crude.



TABLE 3-4

INTERFACIAL TENSION OF CRUDE OIL AND OIL/DISPERSANT MIXTURES  
VERSUS STANDARD SEAWATER (35 o/oo) (dynes/cm)

	AT -5°C	AT 0°C	AT +5°C
Lagomedio crude	ND <sup>a</sup>	16.7	19.8
Lagomedio crude:Corexit 9527 (10:1)	1.7	1.3	3.4
Lagomedio crude:Corexit 9527 (1:1)	1.3	1.3	2 . 0

<sup>a</sup>Not determined.

TABLE 3-5

DENSITY OF CRUDE OIL AND OIL/DISPERSANT MIXTURES (g/cm<sup>3</sup>)

	AT -5°C	AT 0°C	AT +5°C
Lagomedio crude	0.8990	0.8958	0.8923
Lagomedio crude:Corexit 9527 (10:1)	0.9118	0.9082	<b>0.9045</b>
Lagomedio crude:Corexit 9527 (1:1)	<b>0.9621</b>	0.9586	<b>0.9551</b>



TABLE 3-6 (Cont.)

SAMPLE	Cr	Cu	Fe <sup>a</sup>	Mn	Pb	Ti <sup>a</sup>	Zn <sup>a</sup>
Aged Venezuelan Crude	<0.5	<0.05	1.9	<0.05	<0.5	0.05	1.5
Venezuelan Crude <sup>b</sup>	0.04 ±0.05	0	0.76 ±0.10	0.007 ±0.002	-- <sup>c</sup>	-.c	--c
Kuwait Standard Oil (API)							
ERCO Analysis	<0.5	0.10	1.1	<0.05	<0.5	0.29	<1.0
Certified Value	--d	--d	--d	--d	--d	--d	--d
Louisiana Standard Oil (API)							
ERCO Analysis	<0.5	0.06	3.9	<0.05	<0.5	0.13	<1.0
Certified Value	--d	--d	--d	--d	--d	--d	--d
Blank	<0.5	<0.05	2.4	<0.05	<0.5	0.04	3.2

<sup>a</sup>Values are blank corrected.

<sup>b</sup>Leone and Church (1976), p. 42.

<sup>c</sup>Not reported.

<sup>d</sup>Not certified.



TABLE 3-7

UV/FLUORESCENCE RESULTS OF JUNE WATER SAMPLES

	SAMPLE	COLLECTION DATE	SAMPLING DEPTH (m)	$\mu\text{g/l}$ <sup>a</sup>
Bay 9	H5 (extract)	6/14/80	1	<b>ND<sup>b</sup></b>
Bay 9	H5 (extract)	6/14/80	5	<b>ND</b>
Bay 9	H5 (extract)	6/14/80	10	ND
Bay 10	H3 (extract)	6/14/80	1	ND
Bay 10	H3 (extract)	6/14/80	5	ND
Bay 10	H3 (extract)	6/14/80	10	ND
Bay 11	<b>H1</b> (extract)	6/14/80	1	ND
Bay 11	<b>H1</b> (extract)	6/14/80	5	ND
Bay 11	<b>H1</b> (extract)	6/14/80	10	ND
Bay 9	H5 (whole water)	6/22/80	1	ND
Bay 9	H5 (whole water)	6/22/80	5	<b>ND</b>
Bay 9	H5 (whole water)	6/22/80	10	ND
Blank (solvent and field extraction)				9-50

<sup>a</sup>As equivalents of No. 2 fuel oil measured at 312 nm:  
corrected for blank.

<sup>b</sup>Not detected.

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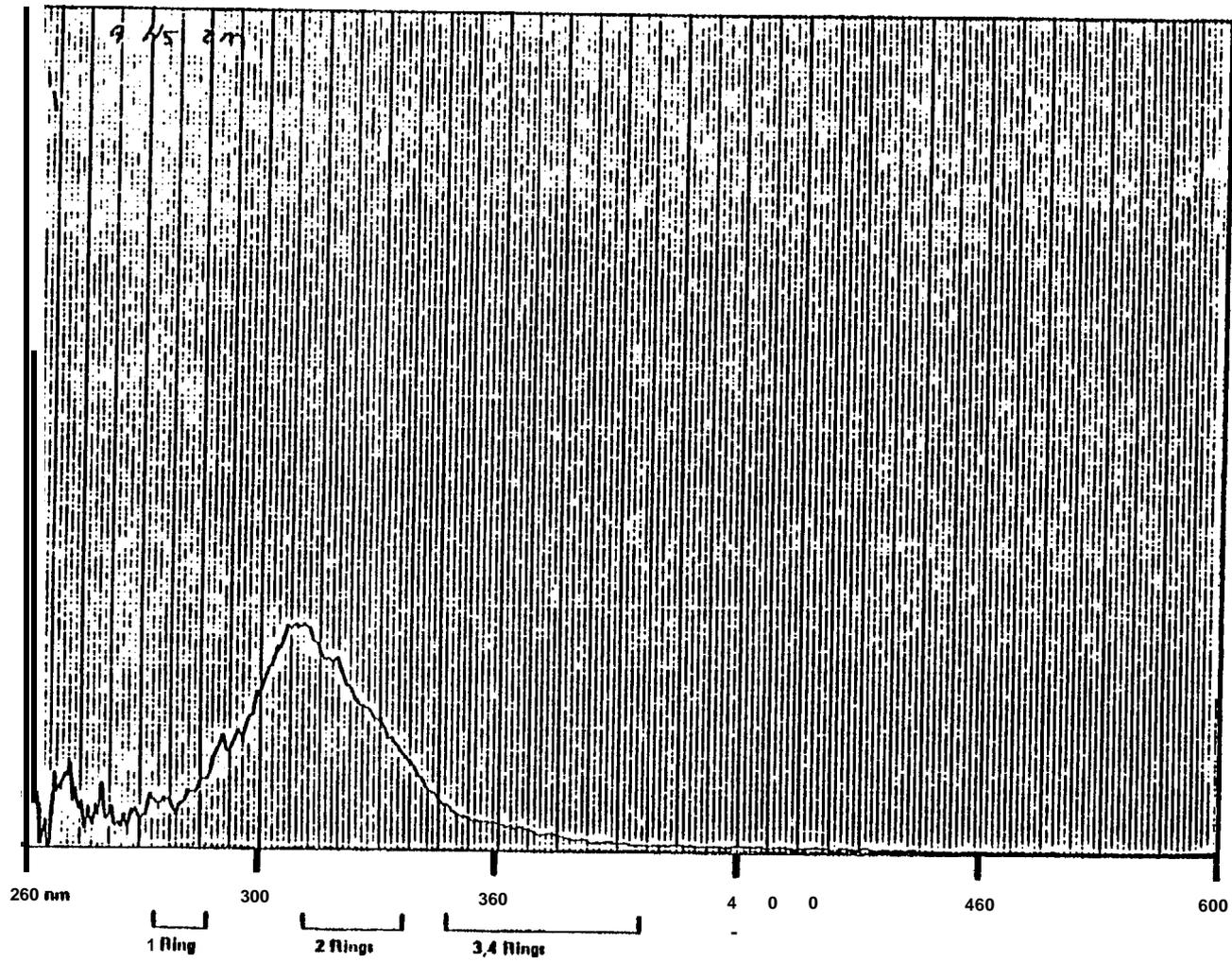


Figure 3.11. UV/Fluorescence (Synchronous Scan) of Bios Water-Baseline.



TABLE 3-8 (Cont. )

SAMPLE	COLLEC- TION DATE	SAMPLING DEPTH {m}	CONCEN- TRATION <sup>a, b</sup> ( $\mu\text{g}/\text{l}$ )
Blank #1	9/19/80		ND <sup>c</sup>
Blank #1 (leaked; probably contaminated)	9/20/80		ND
Blank #2 (120 ml Freon)	<b>9/17/80</b>		<b>ND</b>
Blank #1	<b>9/17/80</b>		ND
Blank #2 <b>W/F</b>	<b>9/19/80</b>		3
Blank #3	<b>9/19/80</b>		ND
Blank #3	<b>9/20/80</b>		ND
Blank (leaked; probably contaminated)	<b>9/18/80</b>		ND

<sup>a</sup>Concentrations expressed as micrograms of API No. 2 fuel oil equivalents/liter of seawater extracted.

<sup>b</sup>Detection limit is .3  $\mu\text{g}/\text{l}$ .

<sup>c</sup>Not detected.



TABLE 3-9

SEAWATER SAMPLES OBTAINED FOR GC<sup>2</sup> AND GC<sup>2</sup>/MS ANALYSES

LOCATION	DATE	DEPTH (m)	VOLUME (liter)	TYPE
<b>Bay 10</b>	9/19/80	1	20.5	<b>NBS<sup>a</sup></b>
<b>Bay 10</b>	9/19/80	5	<b>19.5</b>	<b>NBS</b>
<b>Bay 10</b>	9/19/80	5	19.5	<b>NBS</b>
<b>Bay10 (Filtered Seawater)</b>	9/7/80	1	210	<b>Risebrough LVWS<sup>b</sup></b>
Bay 10 (Particulate	<b>9/7/80</b>	1	21(I	<b>Risebrough LVWS</b>
Bay 11	9/1/80	1	16	<b>NBS</b>
Bay 11	9/17/80	5	20	<b>NBS</b>
Bay 11 (Filtered Seawater)	9/11/'80	8	130	<b>Risebrough LVWS</b>
Bay 11 (Particulate	9/11/80	<b>8</b>	130	<b>Risebrough LVWS</b>
Z Lagoon	9/20/80	1	16.2	<b>NBS</b>
Z Lagoon	9/20/80	5	15.5	<b>NBS</b>
Blank Polyplug #1				
Blank Filter #1				
<b>Blank Polyplug #2</b>				
Blank Filter #2				

Key:

NBS = 4-liter drop sampler

LVWS = large-volume water sampler



TABLE 3-10  
ANALYTICAL RESULTS - SEAWATER SAMPLES

SAMPLE	LIPID WEIGHT ( $\mu$ g/l)	HYDROCARBONS ( $\mu$ g/l)	GC-TYPE (FRAC-TIONATED)
<u>June</u>			
Bay 9 (1 m)	ND	ND <sup>a</sup>	3
Bay 9 (5 m)	ND	ND <sup>a</sup>	3
Bay 9 (10 m)	ND	ND <sup>a</sup>	3
<u>September</u>			
Bay 10 (1 m) - NBS	2.8	ND <sup>b</sup>	3/1
Bay 10 (5 m) - NBS	1.2	ND <sup>b</sup>	3
Bay 10 (5 m) - NBS	0.5	ND <sup>b</sup>	3
Bay 11 (1 m) - NBS	2.7	ND <sup>b</sup>	3/1
Bay 11 (5 m) - NBS	3.4	ND <sup>b</sup>	3
Z Lagoon (1 m) - NBS	3.2	ND <sup>b</sup>	3
Z Lagoon (5 m) - NBS	2.7	ND <sup>b</sup>	3
-----			
	f1 (ng/l) <sup>c</sup>	f2 (ng/l) <sup>c</sup>	
Bay 10 (1 m) LVWS - filtered seawater	1.4	2.0	4
Bay 10 (1 m) LVWS - particulate	0.6	0.7	1
Bay 11 (8 m) LVWS - filtered seawater	0.9	1.1	4/1
Bay 11 (8 m) LVWS - filtered seawater	0.7	0.6	1

<sup>a</sup>ND = <5  $\mu$ g/l.

<sup>b</sup>ND = <0.3  $\mu$ g/l.

<sup>c</sup>Gravimetric weight.

GC-type:

1. Petrogenic -tarry material
2. Terrigenous biogenics (sediments)
3. Marine biogenics (plankton)
4. Aromatic hydrocarbon residues



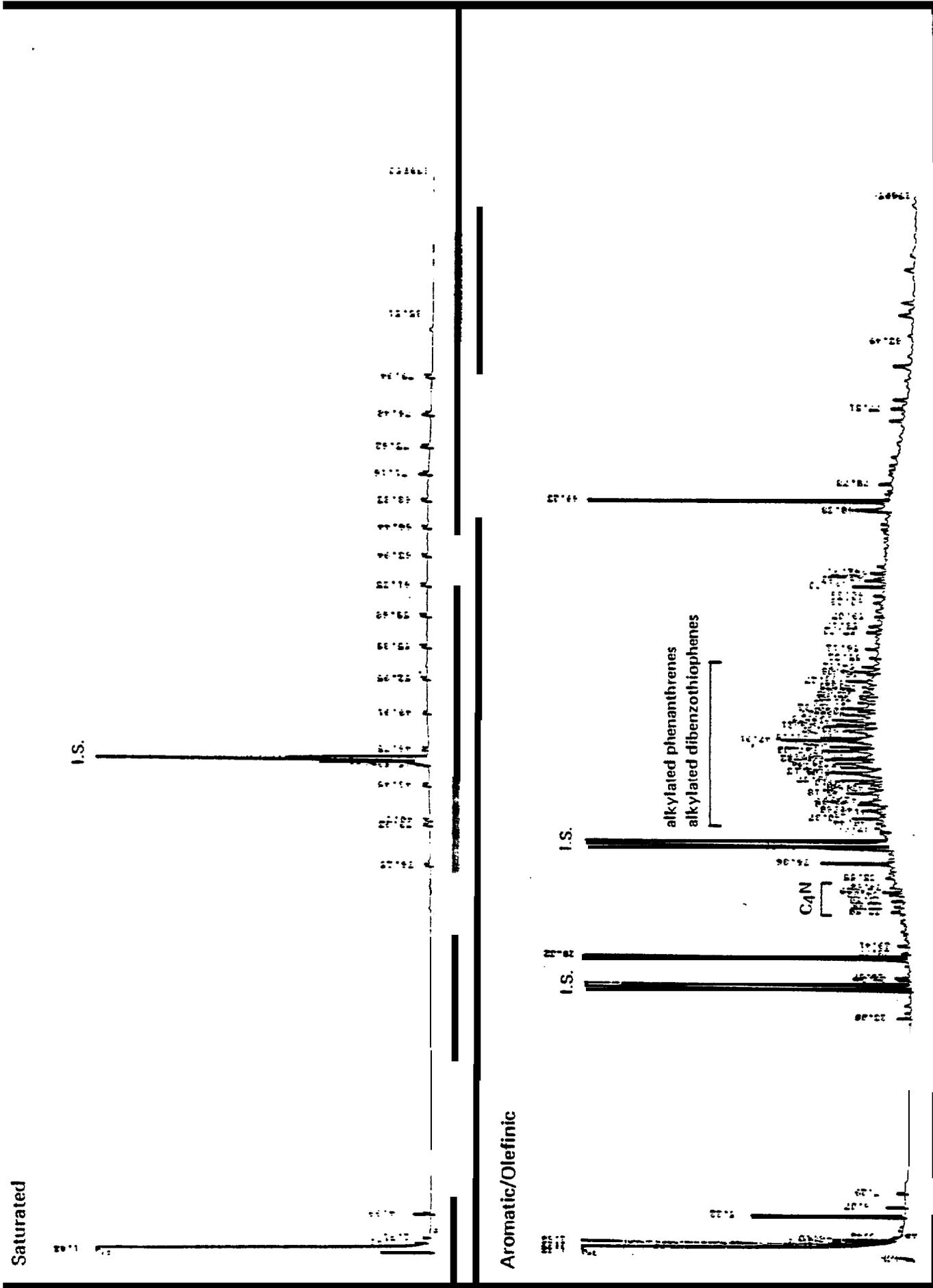


Figure 3.13. GC<sup>2</sup> Traces of Hydrocarbons in Bay 10 Filtered Seawater (LVWS).



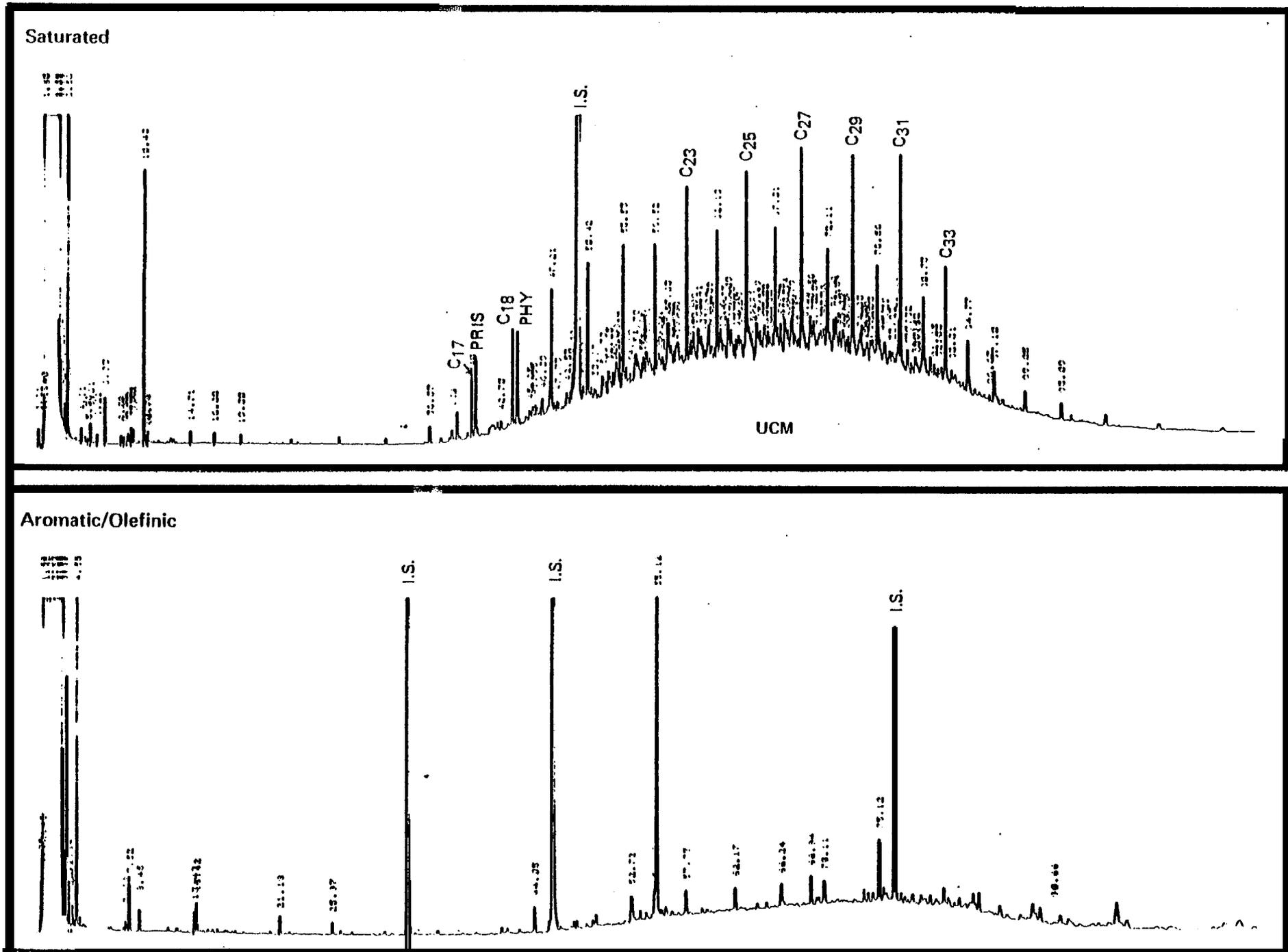


Figure 3.14. GC<sup>2</sup> Traces of Hydrocarbons in Particulate from Bay 10 (LVWS).



TABLE 3-12

UV/FLUORESCENCE-DETERMINED CONCENTRATIONS  
OF HYDROCARBONS IN SEDIMENT SAMPLES -  
JUNE 1980

SAMPLE NUMBER	CONCENTRATION <sup>a</sup> ( $\mu\text{g/g}$ )
13-A-2-17-CC4	1.0
13-A-3-24-CC5	0.5
1(I-2-13-cc10	0.8
10-3-22-CC11	ND
14-1-2-CC12	ND
14-2-15-CC16 (0-4 cm)	0.6
14-2-15-CC16 (10-15 cm) #1	2.2
14-2-15-CC16 (10-15 cm) #2	3.0
14-2-15-CC16 (28-33 cm)	1.3
14-3-26-CC17	7.5
105-1-10-CC20 #1	0.9
105-1-10-CC20 #2	0.7
Core caps	ND
Procedural blank	ND

<sup>a</sup>Weathered Lagomedio equivalents @356 nm.



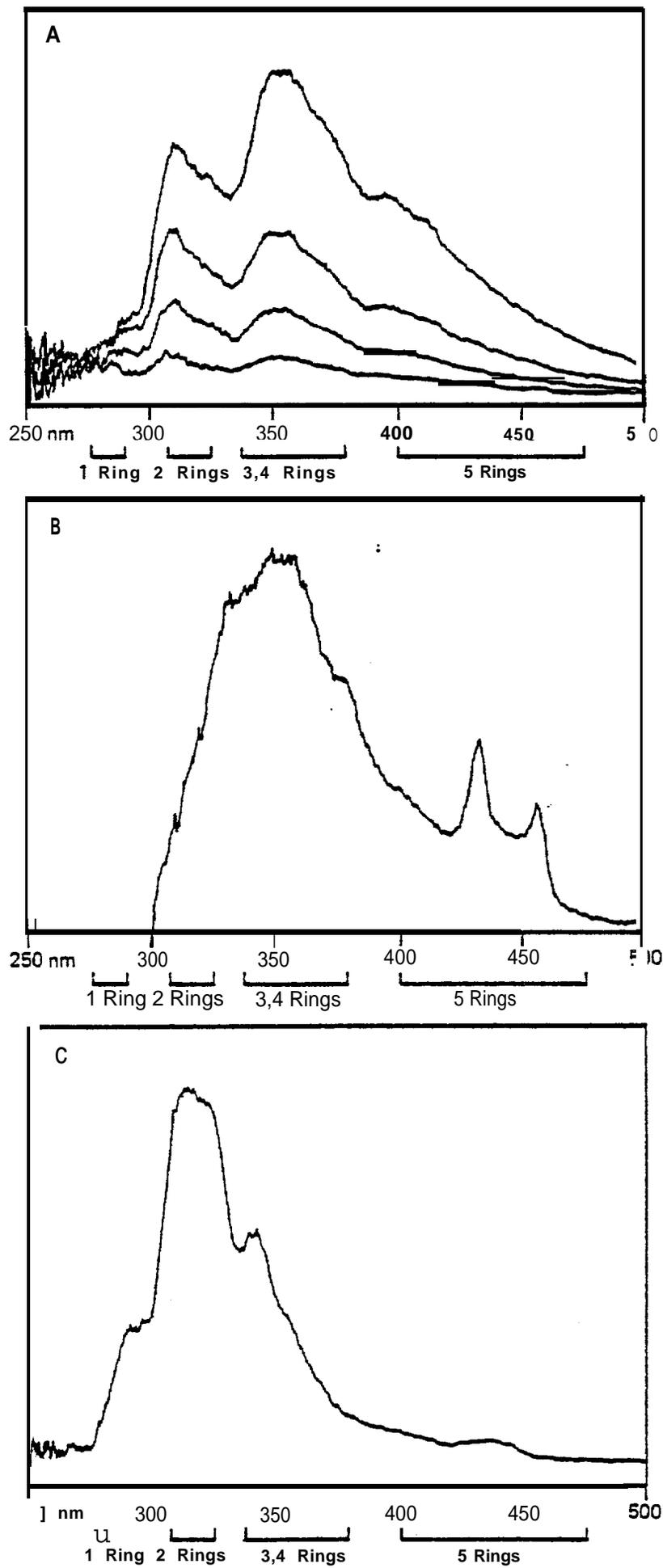


Figure 3.15. UV/Vis Spectra of A-Several Dilutions of Lagomedio Crude; B-A Beach Sediment; C-An Offshore Sediment.



The "**total extractable**" number indicates the total **lipoidal**, or solvent extractable organic material, only a small part of which is hydrocarbon {i.e., **f<sub>1</sub>** or **f<sub>2</sub>**}. The **f<sub>3</sub>** fraction corresponds to material **eluting** off the **silicic** acid column in the so-called polar (mainly oxygenated compounds) fraction. The **total extractable** and Fraction 3 values will be of more use in the post-spill assessment.

There appears to be little variation in the analytical plus small-scale spatial (i.e., two **subsamples** of the same sediment) variability (Table 3-14). Furthermore there is little variation in the concentration and composition of hydrocarbons within the top 30 cm of the sedimentary record . (Core Sample 14-2-15-CC16; Table 3-14).

The concentrations of hydrocarbons in the beach samples range from being much lower to equal to the offshore samples. The source of saturated hydrocarbons to both sets of samples is similar, but both qualitative and quantitative differences occur in the **aromatic/olefinic** fraction. This is apparent in comparing (1) total resolved and (2) total **gravimetric** Fraction 2 values and perhaps more importantly, by examining **GC<sup>2</sup>** traces.

The Fraction 2 **GC<sup>2</sup>**-determined compositions of all offshore samples are similar (Figure 3-16) and different than the beach **f<sub>2</sub>** assemblage (Figures 3-17 and 3-18). The primary difference is in the amount of **olefinic** clusters which have strictly a marine origin and are thus deposited offshore. The saturated (**f<sub>1</sub>**) fractions of both sets of samples are **similar**, illustrating major **terrigenous** inputs for both sets and a marine biogenic component for the offshore samples. The presence of an unresolved complex mixture in several offshore samples is in this case suggestive of the



TABLE 3-15

## BEACH SEDIMENT GEOCHEMISTRY DATA SUMMARY - AUGUST/SEPTEMBER 1980

SAMPLE NUMBER	FRACTION 1					FRACTION 2		TOTAL EXTRACTABLES ( $\mu\text{g/g}$ )	
	RESOLVED (GC <sup>2</sup> ) ( $\mu\text{g/g}$ )	TOTAL (GRAV) ( $\mu\text{g/g}$ )	PRISTANE ( $\mu\text{g/g}$ )	PHYTANE ( $\mu\text{g/g}$ )	PRIS/ PHY	CP I	RESOLVED (GC <sup>2</sup> ) ( $\mu\text{g/g}$ )		TOTAL (GRAV) ( $\mu\text{g/g}$ )
9-N-L	0.03	0.17	ND	ND		2.5	0.007	0.26	0.7
9-N-ii	0.1	0.12	ND	ND		4.1	0.06	0.12	6.2
9-C-L	0.03	0.1	ND	ND		9.3	ND	0.1	1.0
9-c-ii	0.02	1.7	1	ND		2.0	0.008	0.1	4.5
9-S-L	0.03	0.2	2	0.2	10	ND	0.013	0.4	2.0
9-s-ii	0.04	0.6	ND	ND		4.0	0.05	0.2	3.9
10-N-L	0.28	10.6	17	1	17	3.5	0.11	3.0	65.8
10-N-H	0.05	0.2	5	0.2	25	4.2	0.02	0.3	1.3
10-C-L	0.35	2.5	22	1.3	17	4.0	0.15	5.2	81.3
10-C-H	0.04	0.3	1	ND		2.1	0.05	0.2	3.5
10-S-L	0.00	3.1	5.0	0.3	17	5.5	0.1	1.2	13.9
10-s-ii	0.04	3.0	1	ND		2.3	0.02	1.1	14.8
11-N-L	0.12	5.9	17	0.1	170	4.6	0.17	2.4	38.6
n-N-ii	0.10	2.7	2	0.2	10	8.8	0.5	2.5	55.7
11-C-L	0.04	2.1	5.8	0.2	29	4.5	0.04	1.0	14.7
11-c-ii	0.28	4.0	3.4	0.1	34	4.6	0.39	2.1	54.1
11-S-L	0.30	2.2	6.5	0.5	13	9.5	0.10	1.7	26.0
n-s-ii	0.45	2.9	10	0.2	50	10.8	0.37	2.7	70.0
BSB-T1	0.5	0.6	75	0.05	1500	12.4	0.17	0.3	2.2
Bay 102 (pre-spill)	0.01	0.2	ND	ND		7.8	0.04	0.3	1.3
Bay 103 (pre-spill)	0.07	0.1	ND	ND		7.3	0.05	0.1	1.5



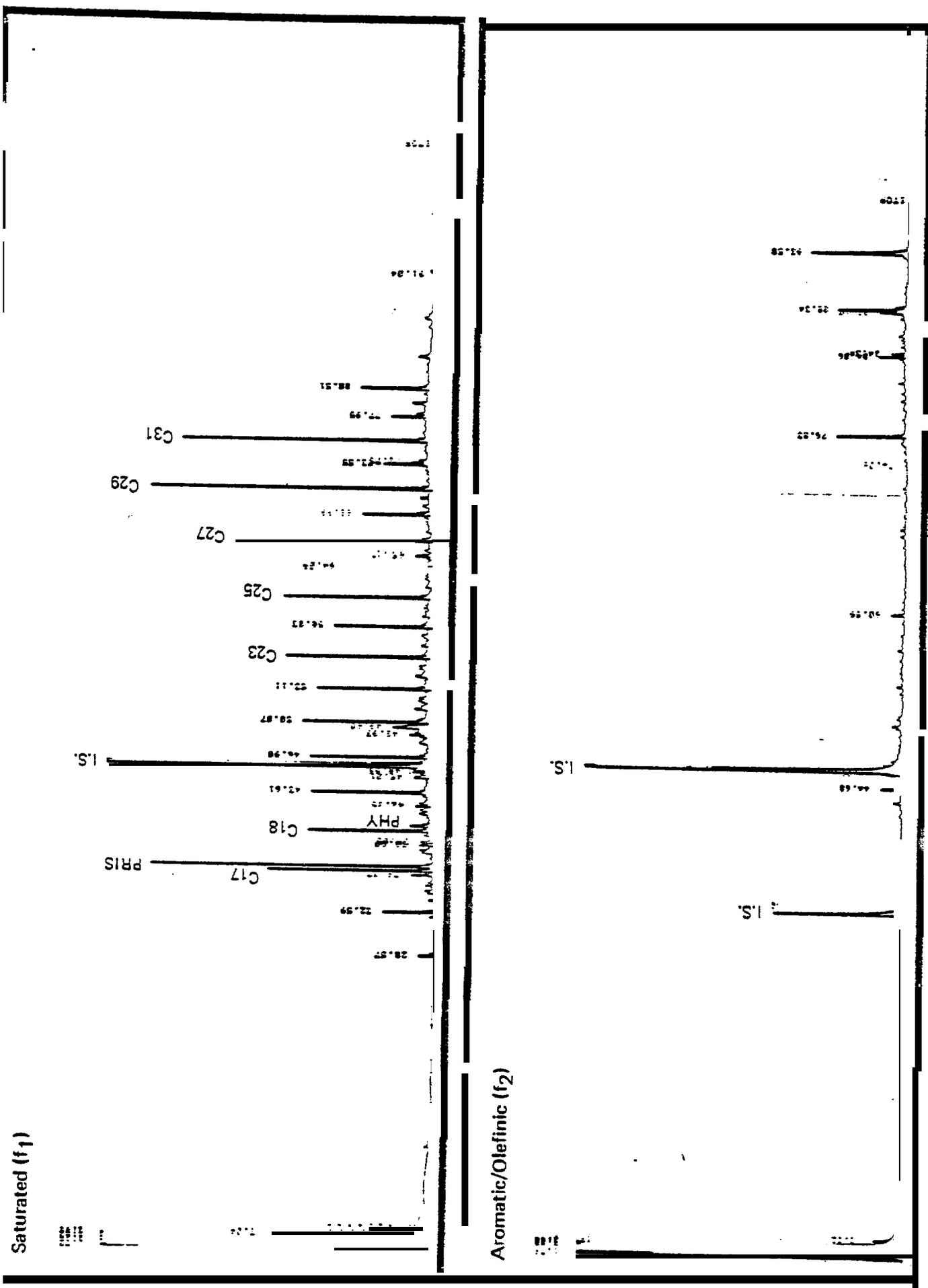


Figure 3.17. Representative GC<sup>2</sup> Traces of Hydrocarbons in Beach Samples (No. 1).

2

2

2

addition of anthropogenic material, the result of long-range transport of a global nature.

An illustrative set of generic GC2 traces of hydrocarbons of various marine sediment samples illustrating the variety of possible source material is presented in Figure 3-19 for comparison.

### 3.2.5 Sediment Samples - GC 2/MS

GC<sup>2</sup>/MS analyses were utilized to examine (1) the identities and levels of PAH compounds in f2 fractions of selected samples, (2) the nature of the background **penta-**cyclic triterpane (hopane) compounds, and (3) the nature of the azaarene composition.

#### 3.2.5(a) PAH Compounds

Very low, but detectable, **levels** of PAH compounds containing 3 to 5 rings were detected in both the beach samples and the offshore sediment samples. The PAH distributions have a markedly pyrolytic and/or diagenetic source, being comprised mainly of the phenanthrenes, the **fluoranthene**/pyrene doublet, and **perylene**. Other minor quantities of benzanthracene, **chrysene**, and **fluorene** compounds are present as well (Table 3-16).

The amount of **perylene**, a diagenetic **pentacyclic** PAH compound, appears strongly related to the quantity of total extractable organic material and to the level of hydrocarbons in the samples.



TABLE 3-16

BASELINE PAN CONCENTRATIONS IN OFFSHORE AND BEACH SEDIMENT BY GC<sup>2</sup>/MS

BAY: SAMPLE ID	OFFSHORE			BEACH				
	13 13-3-24-CC5	9 14-2-15-CC16	10 10-2-13-CC10	9 9-C-L	9 9-c-H	10 10-N-L	10 10-N-H	11 11-C-L
<u>COMPOUND</u>								
Phenanthrene ( m/e 170)	1.6	1.6	1.4	0.3	0.3	2.6	0.5	0.3
Methyl phenanthrene (m/e 190)	1.9	2.0	1.2	0.4	ND	5.6	0.9	0.5
Dimethyl phenanthrene (m/e 206)	ND	ND	ND	0.2	ND	3.1	0.5	ND
Trimethyl phenanthrene (m/e 220)	ND	ND	ND	0.1	ND	1.9	0.3	ND
<b>Σ Phenanthrenes</b>	3.5	3.6	2.6	1.0	0.3	13.2	2.2	<b>0.8</b>
Fluorene (m/e 166)	ND	ND	ND	0.03	ND	<b>0.4</b>	0.03	ND
Methyl fluorene (m/e 180)	ND	ND	ND	0.1	ND	1.6	0.2	ND
Dimethyl fluorene (m/e 194)	ND	ND	ND	ND	ND	<b>1.7</b>	0.2	ND
Trimethyl fluorene (m/e 200)	ND	ND	ND	ND	ND	1.0	ND	ND
Methyl dibenzothiophene (m/e 198)	ND	ND	ND	ND	ND	0.8	ND	ND
Benzanthracene (m/e 228)	ND	ND	ND	<b>0.1</b>	ND	1.0	<b>0.1</b>	0.07
Chrysene (m/e 228)	0.6	ND	ND	0.1	ND	<b>1.0</b>	<b>0.1</b>	0.07
Fluoranthene (m/e 202)	0.3	ND	ND	0.4	ND	0.3	<b>0.1</b>	0.05
Pyrene (m/e 202)	0.4	0.5	ND	0.3	ND	<b>1.6</b>	0.2	0.15
Benzofluoranthene	ND	ND	ND	0.1	ND	<b>1.6</b>	0.2	0.02
Benzoyrenes	ND	ND	ND	0.1	ND	1.8	0.2	<b>0.04</b>
Perylene	<b>0.9</b>	<b>2.9</b>	<b>10.4</b>	ND	ND	3.3	0.1	<b>0.2</b>
Total extractable organics (µg/g)	155	228	660	<b>1.0</b>	4.5	65.8	1.3	<b>14.7</b>
Total hydrocarbons (µg/g)	<b>17.4</b>	<b>33.2</b>	<b>176.0<sup>a</sup></b>	0.2	<b>1.8</b>	<b>13.6</b>	0.5	<b>3.1</b>

<sup>a</sup>May contain non-chromatographable pigment material  
 ND = none detected



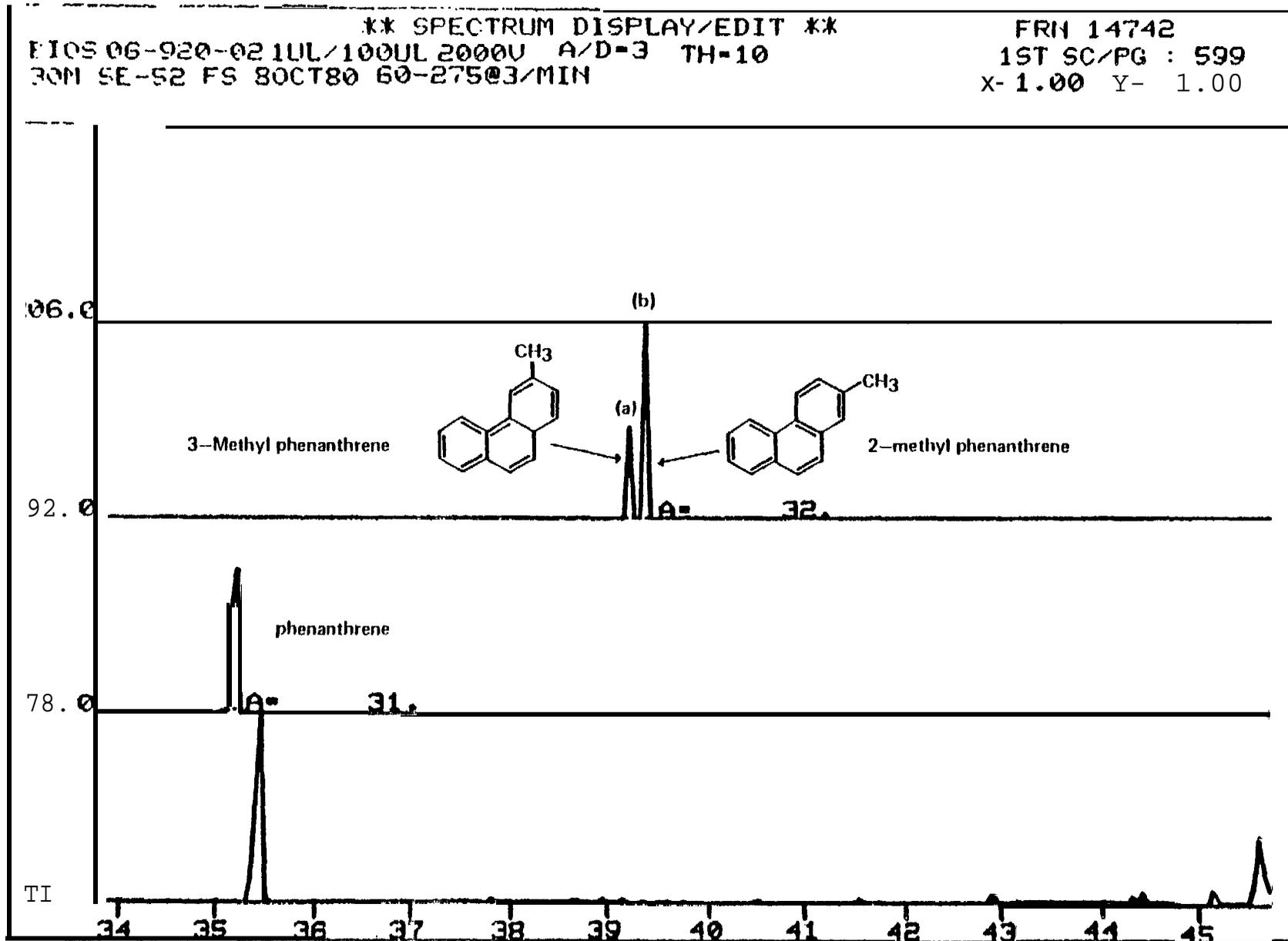


Figure 3.20. Phenanthrene mass chromatograms of offshore sediment sample.



\*\* SPECTRUM DISPLAY/EDIT \*\*

FRN 14735

FIOS OIL LM F21UL/75UL2000VA/D=3  
30M SE-52 FS 70CT80 60-27503/MIN

1ST SC/PG: 610  
X= 1.00 Y= 1.00

3-51

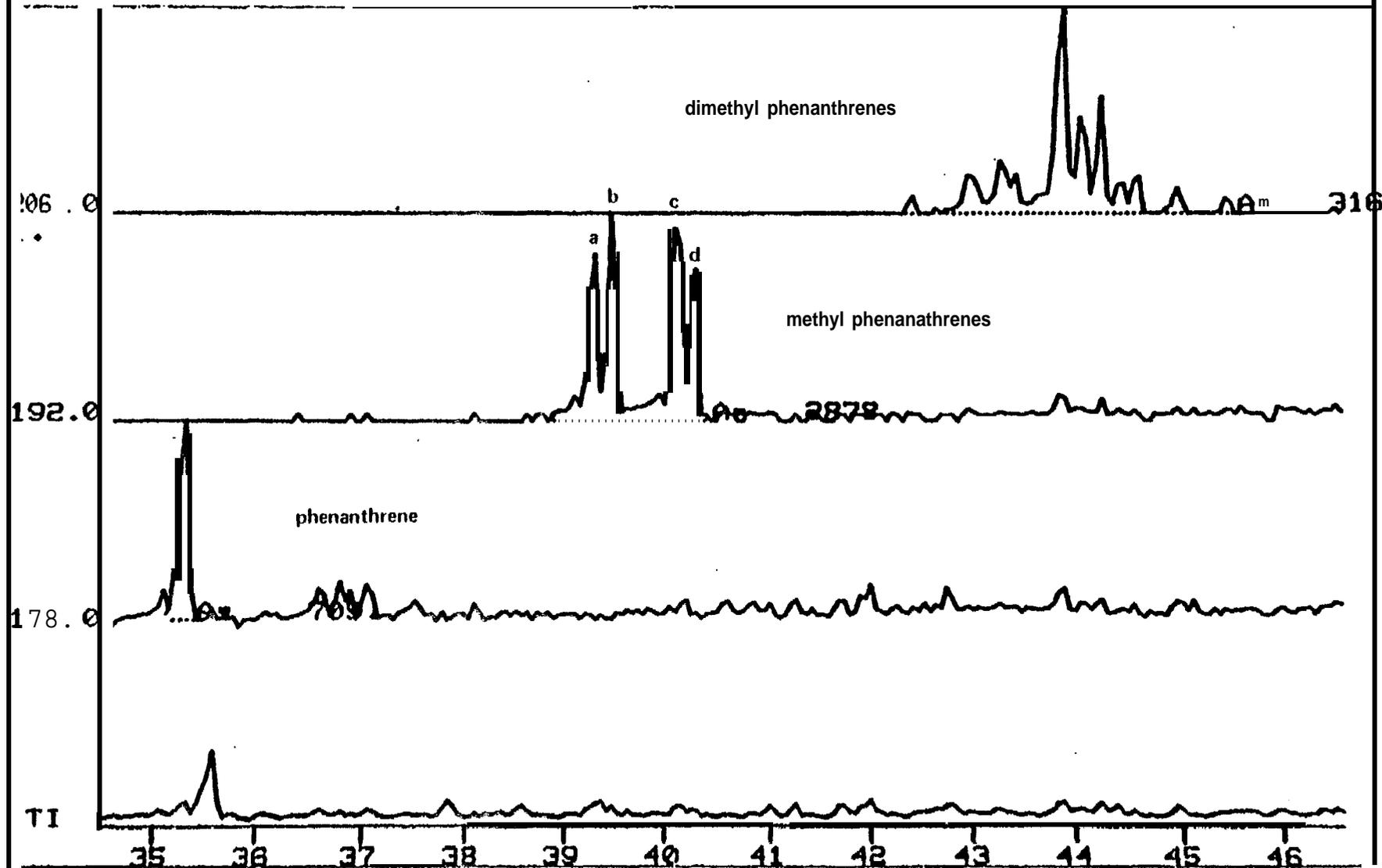


Figure 3.22. Phenanthrene Mass Chromatograms of Lagomedio Crude Oil.



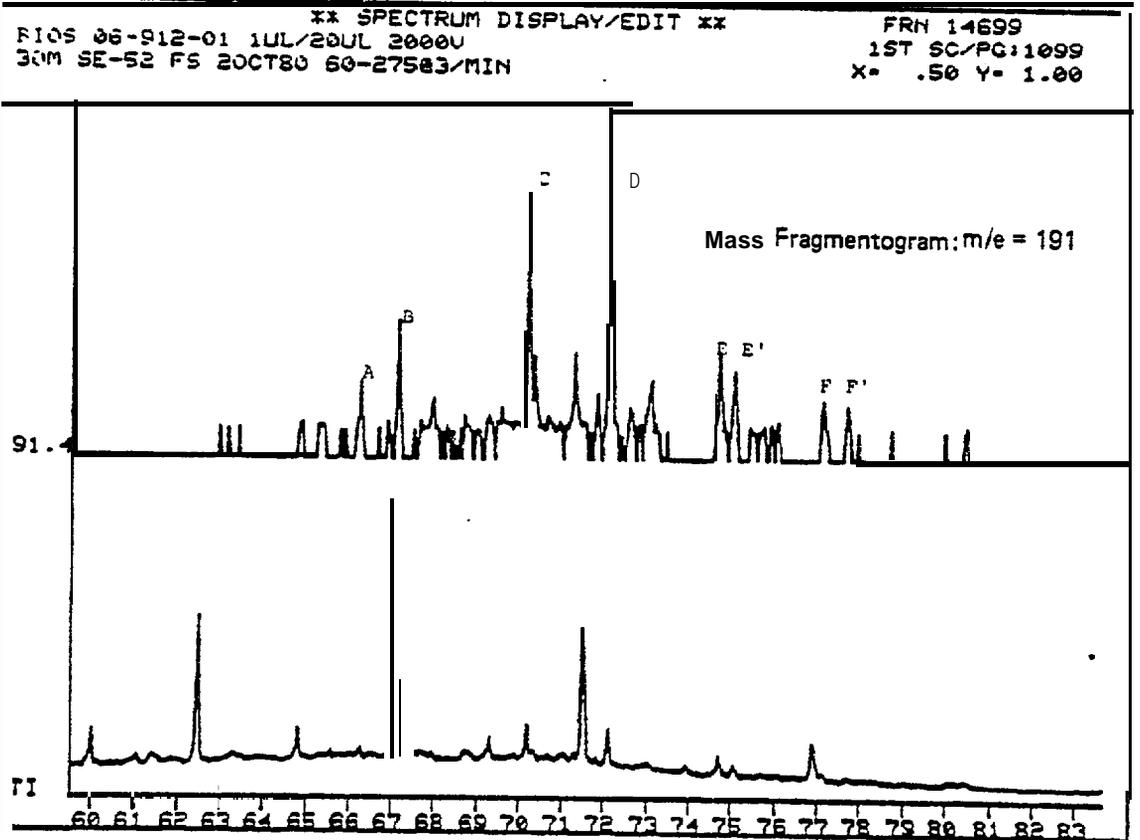
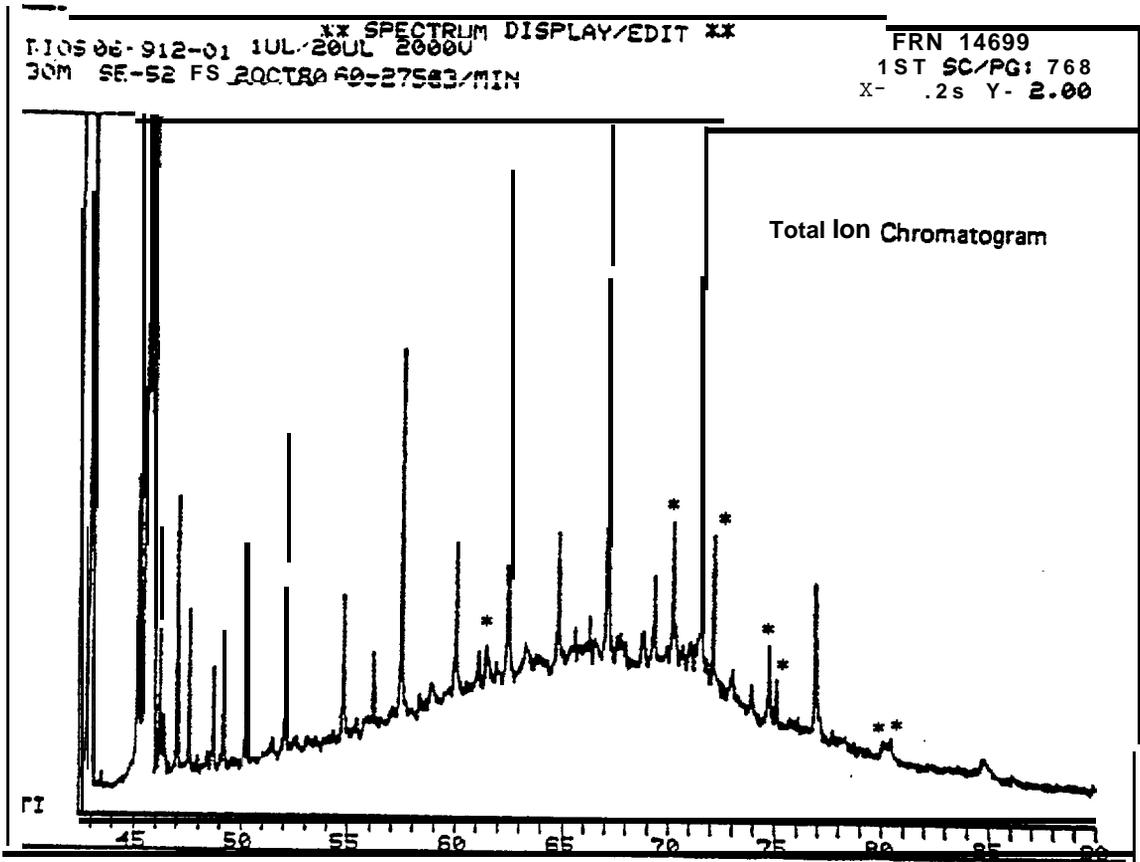


Figure 3.23. Bios Sediment-Hopane Analysis (GC<sup>2</sup>/MS).

100

100

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100

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100

### 3.2.5(c) Azaarenes

Two baseline samples (beach samples) were analyzed to determine if azaarenes were found as baseline components of the organic **geochemical** makeup of the sediment. Trace levels (<1 **ppb**) of several azaarenes were detected (e.g., Figure 3-24 and 3-25). Table 3-18 shows that one of the samples (1C1-C-L) appeared to contain compounds in the 3-ring **acridine/phenanthridine** series (m/e 207,221,235) while only questionable identifications of several **alkyl quinolines** were noted in sample 11-C-L. Thus the existence of these prominent series of **quinolines**, **acridine**, and **benzacridine** series in the Lagomedio **crude** (see Section 3.1) suggests that azaarenes may be sensitive long-term chemical markers.

### 3.2.6 Tissue Hydrocarbons (GC<sup>2</sup>)

Seventy-two tissue samples were analyzed for their hydrocarbon content and composition by GC<sup>2</sup>. Hydrocarbon concentrations were measured using two techniques:

1. The sum of components as determined by GC<sup>2</sup>.
2. The **microgravimetric** weights of the saturated (**f<sub>1</sub>**) and **aromatic/olefinic** (**f<sub>2</sub>**) fractions.

The results are presented in Tables 3-19 and 3-20. As **gravimetrically-determined** hydrocarbon values often include **non-chromatographable lipoidal** material, the weights are often gross overestimates of the **GC<sup>2</sup>-analyzable** material. Thus, the more relevant numbers with respect to "**before-and-after-spill**" comparisons are the **GC<sup>2</sup>-determined** values in Table 3-18.



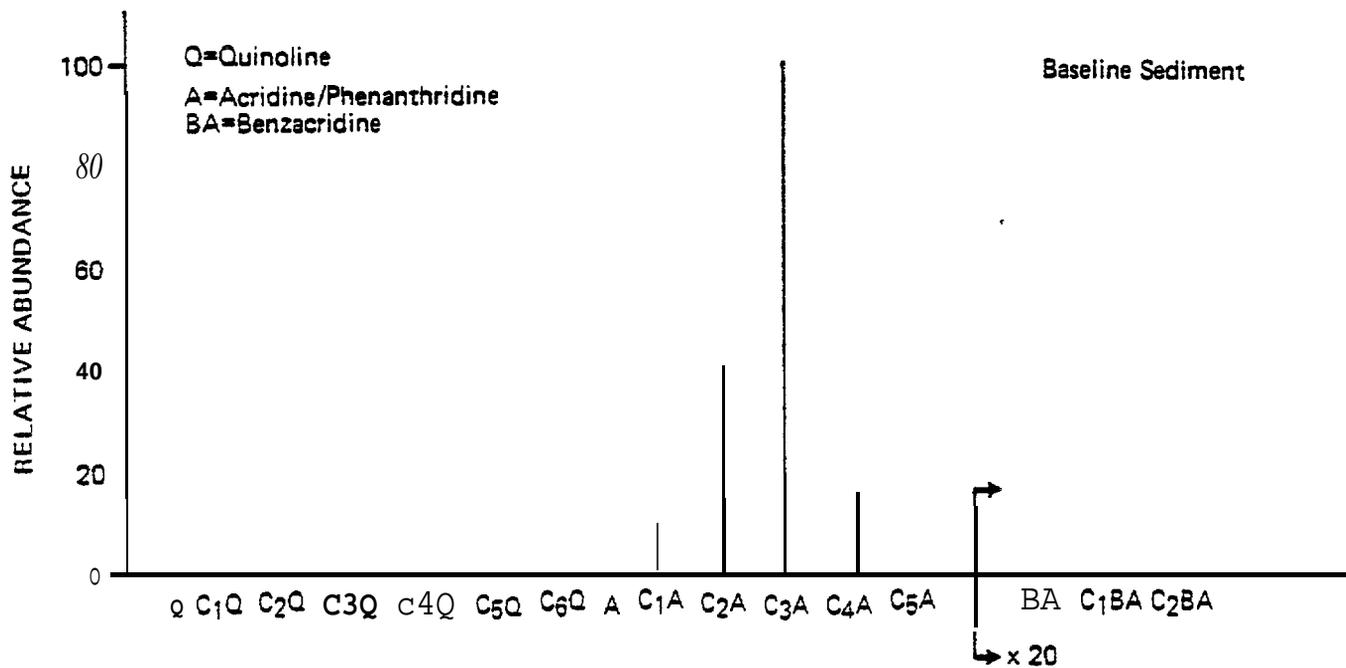
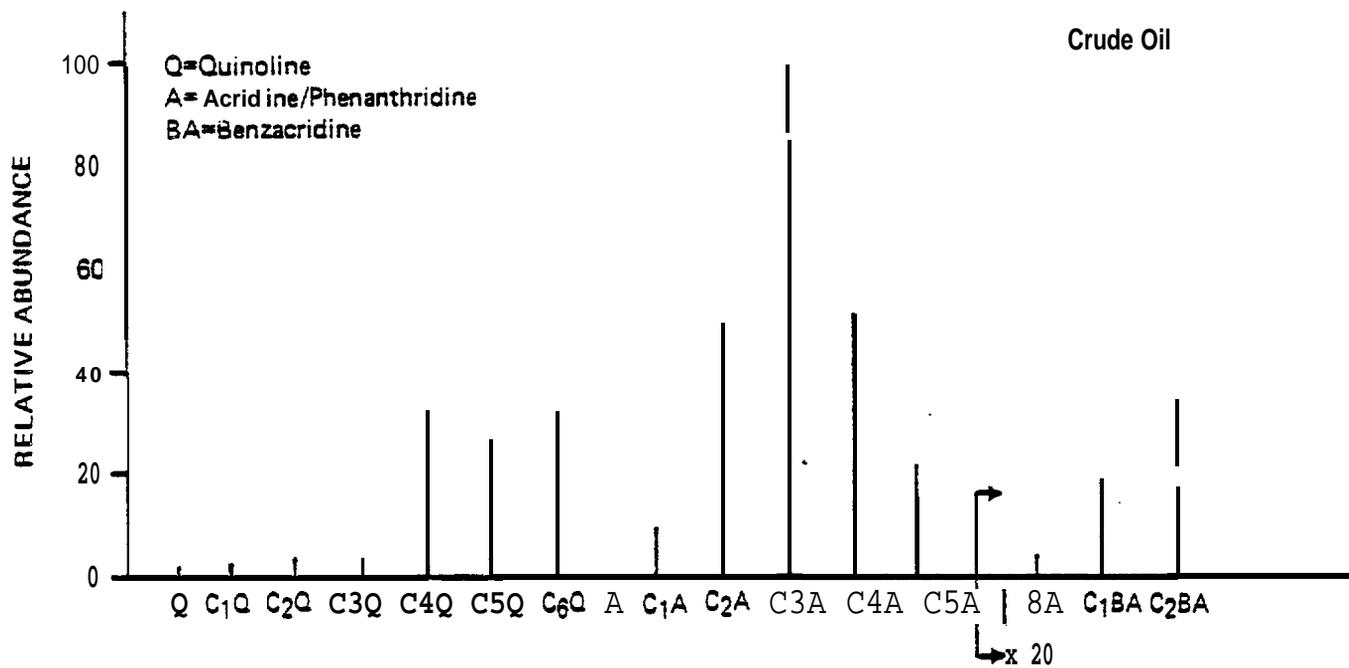


Figure 3.25. Comparison of Azarene Composition in Baseline Sediment Samples with Lagomedio Crude Oil



TABLE 3-19

SUMMARY OF BIOS TISSUE ANALYTICAL RESULTS

BAY	ERCO ID	SPECIES <sup>a</sup>	COLLEC- TION DATE	DEPTH (m)	HYDROCARBON CONCENTRATIONS (GC)		HYDROCARBON CONCENTRATIONS (GRAVIMETRIC)	
					f1 ( µg/g )	f2 ( µg/g )	f1 ( µg/g )	f2 ( µg/g )
9	728	<u>Fucus</u>	9/13/80	4	1.0	17.1	12.6	21.9
9	729	<u>Leptosterias polaris (L)</u>	9/10/80	9	0.1	3.3	0.3	5.5
9	730	<u>L. polaris (L)</u>	9/10/80	9	1.8	3.4	1.0	7.6
9	731	<u>L. polaris (L)</u>	9/10/80	9	1.9	3.6	0.1	3.1
9	732	<u>L. polaris (M)</u>	9/10/80	9	2.9	13.3	8.4	53.9
9	733	<u>L. polaris (M)</u>	9/10/80	9	1.0	2.8	0.3	6.0
9	734	<u>L. polaris (S)</u>	9/10/80	9	0.3	0.2	0.1	3.2
9	735	<u>Psolus sp.</u>	9/10/80	17	3.9	10.6	12.4	33.1
9	736	<u>Psolus sp.</u>	9/10/80	17	0.6	29.2	1.0	15.3
9	737	<u>Psolus sp.</u>	9/10/80	17	0.8	6.5	2.4	6.4
9	738	<u>Psolus frabricii</u>	9/10/80	17	4.9	43.2	0.1	13.3
9	739	<u>Strongylocentrus droebachiensis (M to L)</u>	9/10/80	9	17.0	35.5	13.7	91.8
9	740	" <u>S. droebachiensis (M)</u>	9/10/80	9	1.0	45.0	4.1	20.0

a(L) = large; (M) = medium; (S) = small.



TABLE 3-19 (Cont.)

BAY	ERCO ID	SPECIES	COLLEC- TION DATE	DEPTH (m)	HYDROCARBON CONCENTRATIONS (GC)		HYDROCARBON CONCENTRATIONS (GRAVIMETRIC)	
					f1 (µg/g)	f2 (µg/g)	f1 (.19/9)	f2 (µg/g)
10	757	<u>Mya truncata</u> (L)	9/13/80	7	0.3	1.1	0.9	6.4
10	758	<u>Mya truncata</u> (M)	9/13/80	7	1.7	32.3	6.9	23.9
10	759	<u>Mya truncata</u> (S)	9/13/80	7	1.7	25.1	1.5	21.9
11	777	<u>Agarum</u>	9/8/80	20	3.5	48.7	1.3	4.8
11	778	<u>Fucus</u>	9/13/80	3	5.3	6.7	2.3	7.6
11	779	<u>L. polaris</u>	9/8/80	15-20	5.2	37.4	7.9	61.1
11	780	<u>L. polaris</u>	9/8/80	15-20	1.4	24.1	2.4	37.4
11	781	<u>L. polaris</u>	9/8/80	15-20	1.5	29.3	3.3	32.9
11	782	<u>L. polaris</u>	9/8/80	15-20	8.9	20.6	7.9	27.8
11	783	<u>L. polaris</u>	9/8/80	15-20	3.4	24.5	3.3	34.4
11	784	<u>Psolus frabricii</u> (L)	9/8/80	15-20	2.6	33.9	22.4	90.4
11	785	<u>Psolus frabricii</u> (L)	9/8/80	15-20	2.5	33.3	5.2	74.5
11	786	<u>Psolus frabricii</u> (s)	9/8/80	15-20	4.1	44.8	14.0	158.0
11	787	<u>S. droebachiensis</u> (L)	9/8/80	15-20	30.3	156.0	51.0	321.1
11	788	<u>S. droebachiensis</u> (M)	9/8/80	15-20	16.3	79.8	45.7	123.5
11	789	<u>S. droebachiensis</u> (M)	9/8/80	15-20	17.1	82.4	30.8	167.0



TABLE 3-19 (Cont.)

BAY	ERCO ID	SPECIES	COLLEC- TION DATE	DEPTH (m)	HYDROCARBON CONCENTRATIONS (GC)		HYDROCARBON CONCENTRATIONS (GRAVIMETRIC)	
					f1 (µg/g)	f2 (µg/g)	f1 (µg/g)	f2 (µg/g)
Z	766	<u>S. droebachiensis</u> (L)	9/16/80	-	10.4	59.9	42.3	185.0
La-	767	<u>S. droebachiensis</u> (M)	9/16/80'	-	14.6	125.1	24.4	177.4
goon	768	<u>S. droebachiensis</u> (s)	9/16/80	-	39.0	45.4	" 157	392
	769	<u>Serripes</u>	9/16/80		16.2	112.0	16.9	129.5
	770	<u>Astarte borealis</u>	9/16/80		0.3	1.2	1.0	6.3
	771	<u>Mya truncata</u> (L)	9/16/80		7.3	4.8	1.4	1.7
	772	<u>Mya truncata</u> (M)	9/16/80		8.0	20.6	1.9	42.0
	773	<u>Mya truncata</u> (M)	9/16/80		2.8	6.1	4.7	25.1
	774	<u>Mya truncata</u> (S)	9/16/80		0.4	9.0	1.6	34*5
	775	Scallop	9/16/80		1.4	27.0	6.3	22.8
	, 776	<u>Myoxocephalus</u> <u>scorpius</u>	9/16/80		2.3	4.5	3.4	4.9

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As presented in Table 3-20, there is a wide range of hydrocarbon concentrations within each species, reflecting variations mainly in **biogenic** components. For example, concentrations of **f<sub>1</sub>** and **f<sub>2</sub>** hydrocarbons in Mya range over an order of magnitude within a given bay. However variations between bays are **small**. These large variations in the **biogenic** hydrocarbon makeup of a particular species **are** common in baseline investigations (e.g., Boehm et al., 1979). **Rather** than suggesting analytical "chaos," these observed variations **fall** into definable compositional groups if one views the information given in Table 3-20 for each species over the four-bay region **in** light of the GC<sup>2</sup>-determined compositions.

Perhaps the most important information on these baseline tissue hydrocarbons comes from the GC<sup>2</sup> traces. Representative GC<sup>2</sup> traces reveal that each species groups into one **or** two main compositional patterns. **For** example, Mya fall into one of the three related compositional patterns which are similar in their **f<sub>1</sub>** compositions or combinations thereof (Figures 3-26, 3-27, and 3-28). These compositions are mainly of a biogenic origin although there is some evidence of the presence of small amounts of aromatic hydrocarbon compounds (see Figure 3-25 and next section) .

The sea urchins, Strongylocentrotus droebachiensis, contain **large** amounts of natural lipid material and hence **biogenic** hydrocarbons. **No** evidence of petroleum contamination was observed in this species. The hydrocarbon compositions are strikingly similar in **all** samples of this species examined {e.g., Figure 3-29).

Similarly Psolus samples are free of petroleum inputs and are characterized by biogenic hydrocarbon compositions (Figure 3-30).



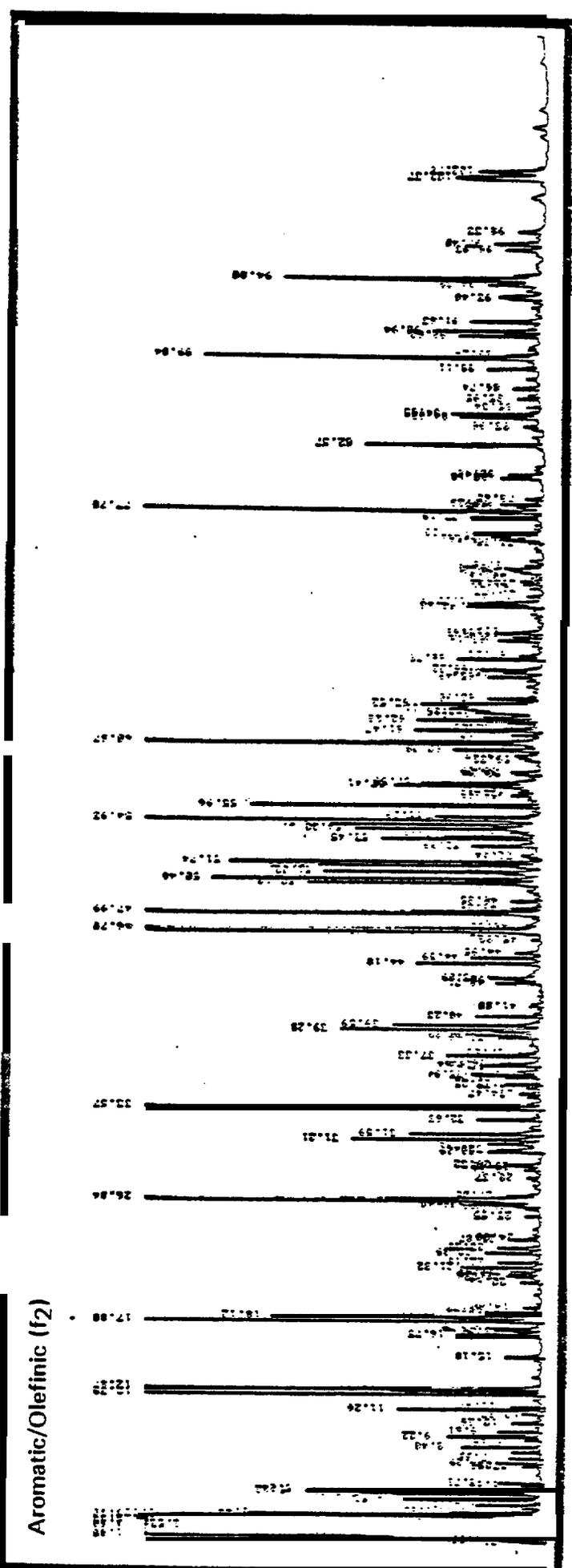
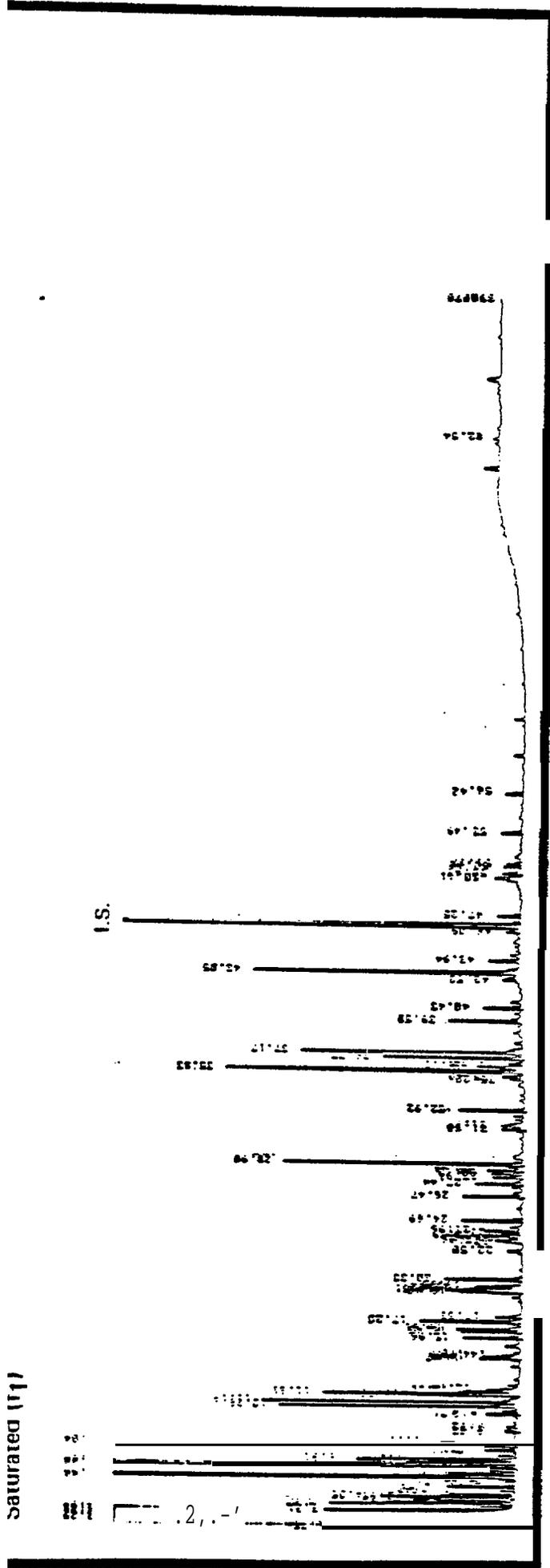


Figure 3.27. GC2 Traces of *Mya truncata*—Bay 11.



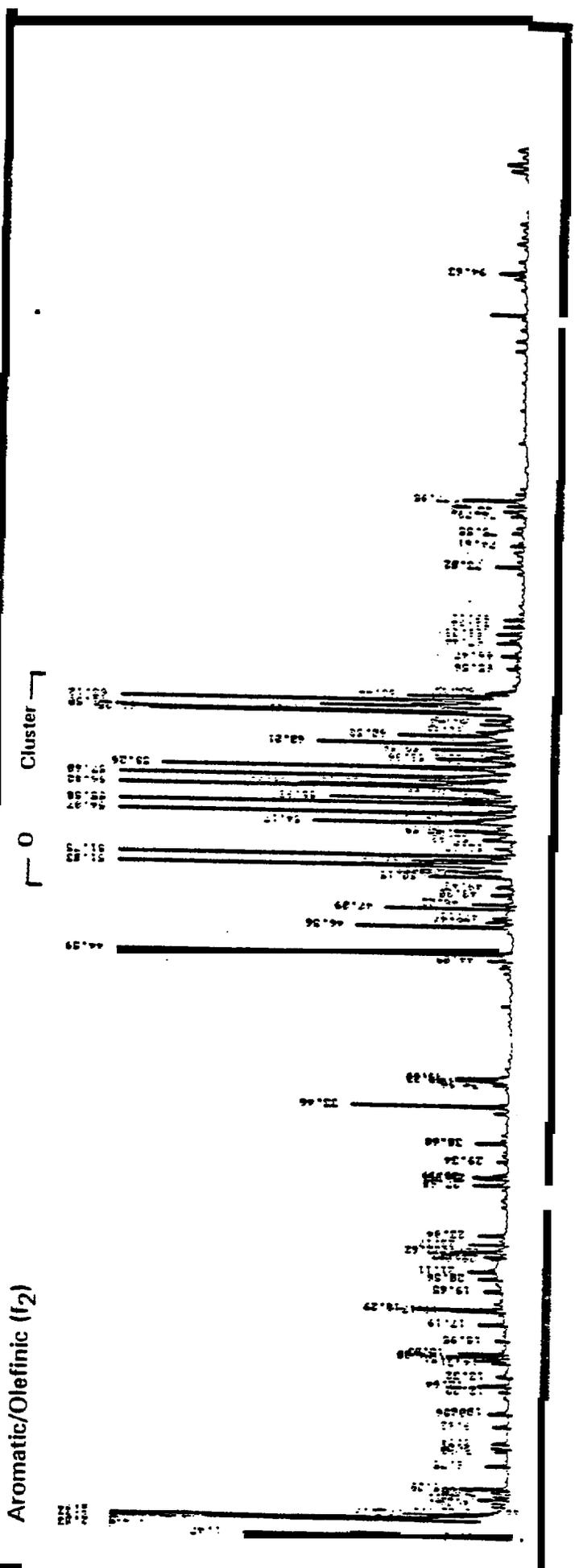
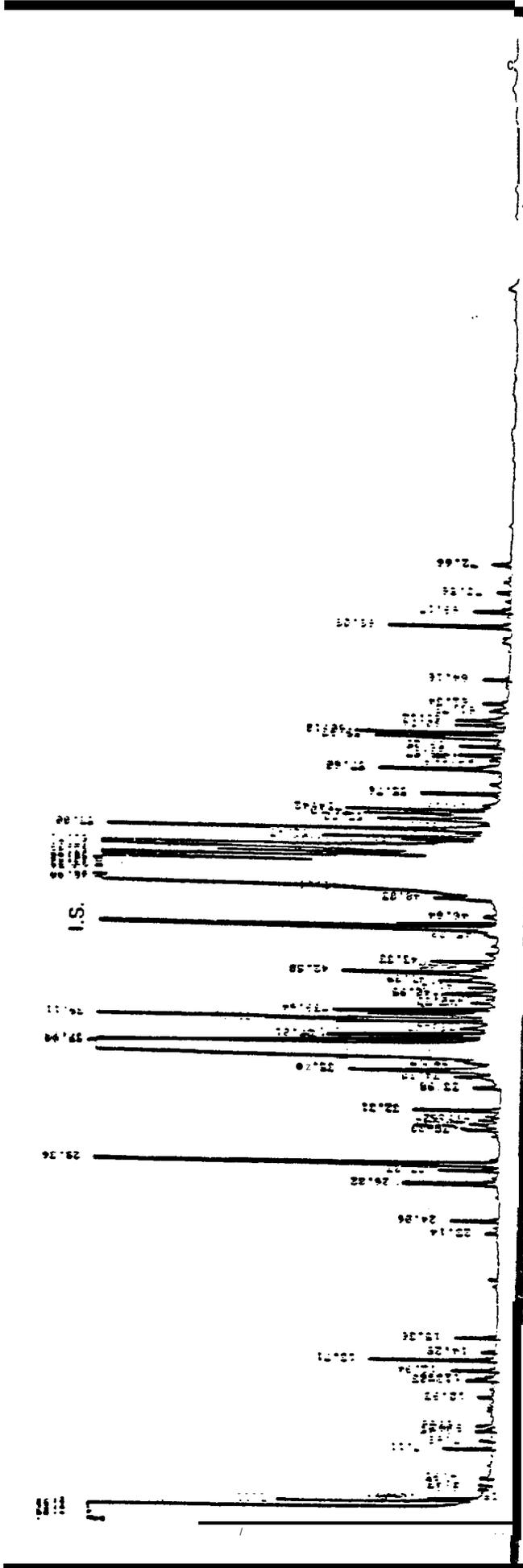


Figure 3.29. GC<sup>2</sup> Traces of *Strongylocentrotus droebachiensis*—Bay 9.



Samples of Leptosterias were comprised of a more complex set of saturated and aromatic/o **lefinic** (f2) hydrocarbons (Figure 3-31). While no evidence for petroleum hydrocarbon input is seen in the **f<sub>1</sub>** fraction, **GC<sup>2</sup>/MS** analyses of the f2 fraction (e.g., Figure 3-29) (see next section) reveal important levels of light aromatic hydrocarbons (**alkyl benzenes, naphthalenes**) suggestive of low level contaminant input. While most of the samples were comprised of **f<sub>1</sub>** and f2 hydrocarbons similar to those shown in Figures 3-31 and 3-32, several of the samples (4 out of a total of 17) appeared to contain obvious petroleum contaminants (2-100 ppm) **presumably** due to sampling-related contamination (Figure 3-33).

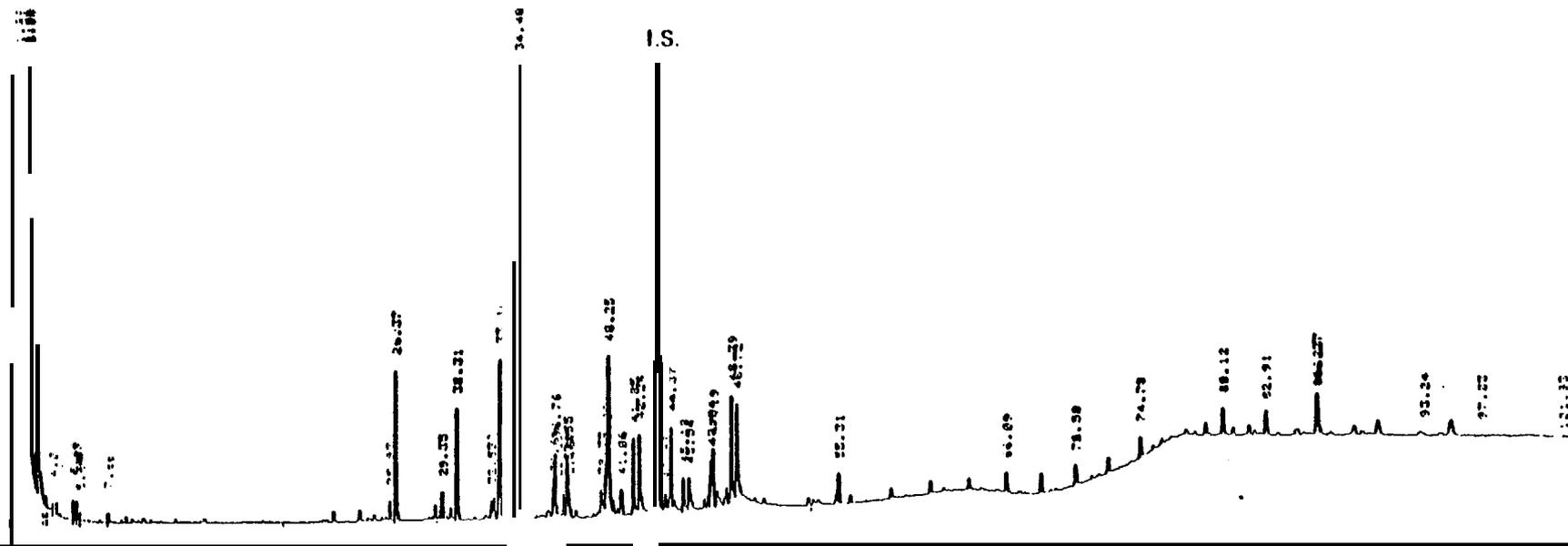
Note that the compositional pattern shown in **Figure 3-31** very much resembles the seaweed compositions. All of the remaining sample types contained a variety of biogenic hydrocarbons and no petroleum-related inputs. Several of the seaweeds (Laminaria, Fucus) (Figures 3-34 and 3-35) were comprised of sets of **biogenic** hydrocarbons very similar in composition to Leptosterias (Figure 3-31) and Strongylocentrotus (Figure 3-31) compositions thus implying a food chain relationship.

### 3.2.7 Tissue Hydrocarbons (GC/MS)

In order to ferret out any low levels of aromatic hydrocarbons in the biogenic-dominated f2 distributions, **G<sup>2</sup>C/MS** was used. The **GC<sup>2</sup>/MS/computer** system focused on levels of 1- to 5-ring aromatics in 14 samples chosen on the basis of their GC<sup>2</sup> traces and in an effort to get adequate areal and species coverage.



Saturated (f1).



Aromatic/Olefinic (f2)

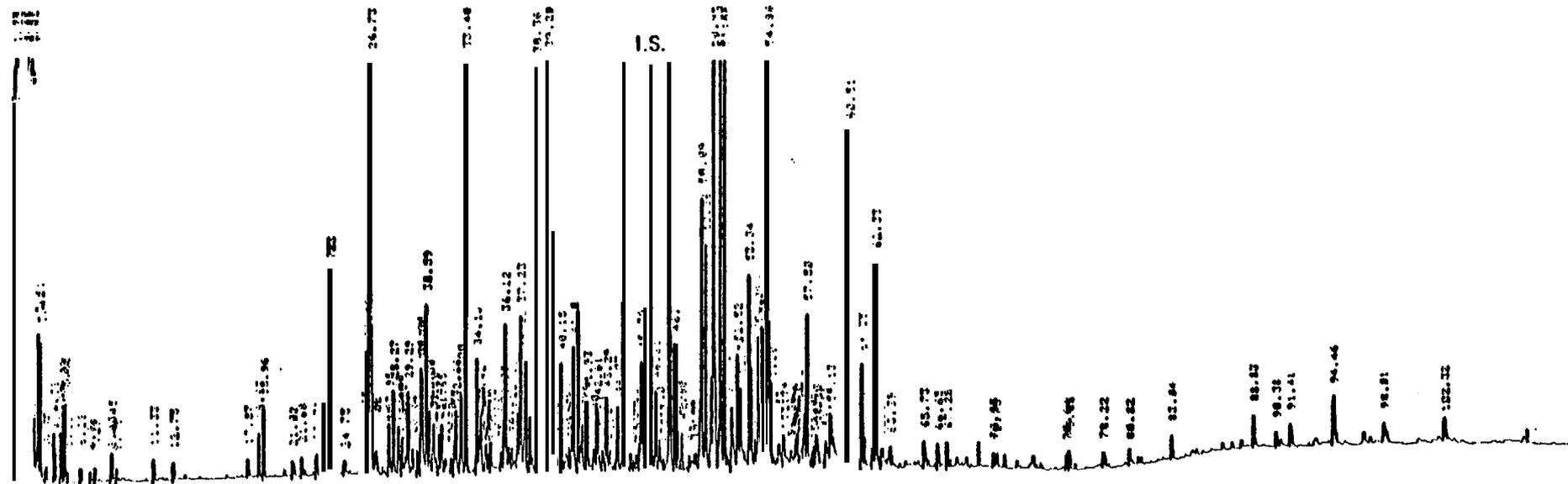


Figure 3.32. GC<sup>2</sup> Traces of *L. polaris*-Bay 9.

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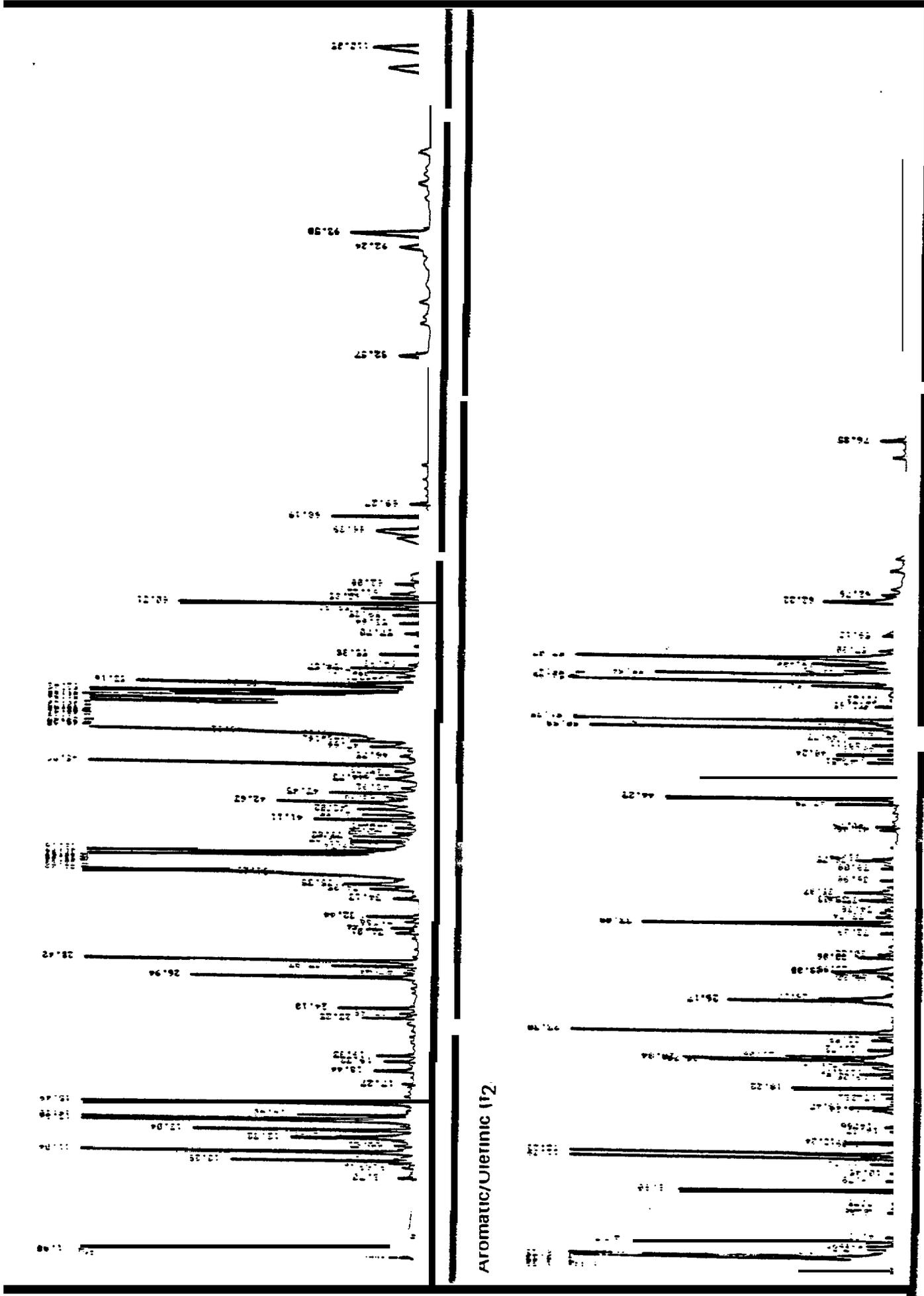


Figure 3.34. GC2 Traces of Laminaria-Z-Lagoon.



## SECTION TWO

### SAMPLING AND ANALYTICAL METHODS

#### 2.1 Sampling

Samples of seawater, offshore sediments, beach sediments (baseline), beach sediments (oiled test plots), and animal tissues were obtained from stations within the bays shown in Figures 2-1 and 2-2. Details of the sampling locations and sampling methods are given in Volume 1 of this report.

#### 2.2 Analytical Methods

The choice of analytical methods used in this program (**Table 1.3**) was inspired by a need to generate a **cost-effective** set of data usable to two groups: (1) those requiring information on the presence and approximate concentrations of petroleum hydrocarbons in samples and (2) those requiring detailed information on the composition of the hydrocarbon assemblage and the concentration of individual petroleum hydrocarbon components and marker compounds (e.g., Figure 2-3). Three analytical methods were employed sequentially: (1) **UV/fluorescence-synchronous scan (UV/F)**, (2) glass capillary gas chromatography (**GC<sup>2</sup>**), and (3) glass capillary gas chromatographic mass spectrometry (**GC<sup>2</sup>/MS**) (Figure 2-4).

In recent years, **UV/F** spectra of environmental samples obtained when emission and excitation wavelengths are simultaneously scanned have yielded important, useful, compositional information on extracts of environmental samples (John and

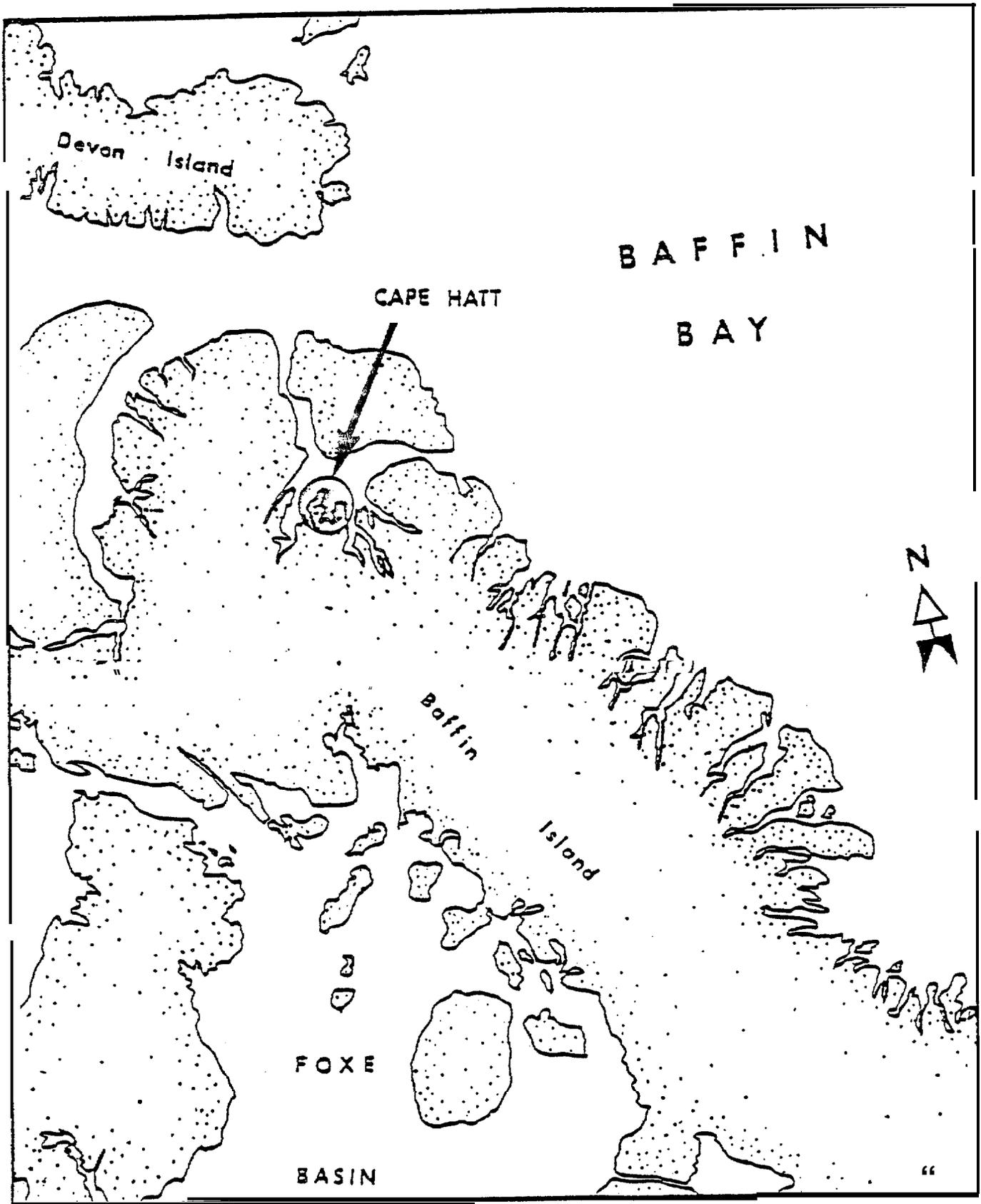


Figure 2.1. Location of Cape Hatt, Baffin Island.

The resultant data is summarized in Table 3-21. Low levels (2-12 ppb) of **naphthalenes**, and phenanthrene compounds were found in most of the samples. In the samples with extremely low levels (e.g., all of the Mya samples) the parent (**unsubstituted**) **naphthalene** and phenanthrene compounds were detected with none of their **alkylated homologues** present. In those samples showing moderate to **gross** petroleum contamination, entire families (**C<sub>0</sub> to C<sub>4</sub>**) of **naphthalene, fluorene, and C<sub>3</sub> to C<sub>5</sub> alkylated benzenes** were readily detected.

Note that these incidents of contamination affected several Leptosterias samples, as previously mentioned, and may have affected several seaweed samples. The presence of aromatic hydrocarbons in the seaweed was not readily apparent in the GC<sup>2</sup> traces due to the much higher levels of **biogenic** hydrocarbons present. The results of the Mya analyses indicate that, except for minor inputs of **phenanthrene** and **naphthalene** from long-range transport sources (e.g., fallout), this species is quite free of any contamination and is thus quite suitable for use as a sensitive monitor of inputs of low levels of petroleum to the suspended particulate load.

TABLE 3-21

BASELINE STUDY - AROMATIC HYDROCARBON LEVELS IN TISSUES (BY GC/MS)(nanograms/gram dry weight)

	LAB ID													
	749	772	758	797	743	731	732a	762	753	729	733a	750a	777	751
<b>SPECIES:<sup>b</sup></b>	<b>1</b>	<b>1</b>	1	<b>1</b>	2	3	3	3	3	3	3	<b>4</b>	<b>5</b>	6
<b>BAY:</b>	9	2	10	<b>11</b>	<b>9</b>	9	9	<b>2</b>	<b>10</b>	9	9	10	<b>11</b>	<b>10</b>
<b>Naphthalenes</b> (m/e 128, 142, 156, 170)	7	5	ND	ND	2	28	1270	140	<b>140</b>	8	5100	6700	<b>150</b>	20
<b>Alkyl Benzenes</b> (m/e 120, 134, 148)	ND	ND	ND	NO	ND	<b>11</b>	1300	220	<b>190</b>	3	3500	1700	<b>10</b>	<b>10</b>
<b>Phenanthrenes</b> (m/e 178, 192, 206, 220, 234)	<b>3</b>	<b>6</b>	<b>8</b>	1	<b>10</b>	ND	ND	10	5	ND	40	490	<b>11</b>	<b>8</b>
<b>Fluorenes</b> (m/e 166, 180, 194, 208)	ND	ND	ND	ND	ND	ND	<b>100</b>	ND	ND	ND	130	70	<b>2</b>	<b>1</b>
<b>Biphenyl</b> (m/e 154)	ND	ND	ND	ND	ND	ND	100	8	<b>11</b>	ND	360	200	<b>8</b>	2
<b>Fluoranthene/Pyrene</b> (m/e 202)	ND	ND	ND	ND	4	ND	ND	ND	<b>19</b>	ND	ND	ND	<b>5</b>	ND
<b>Benzopyrenes</b> (m/e 252)	ND	ND	ND	ND	ND	ND	ND	ND	<b>14</b>	ND	ND	ND	ND	ND

<sup>a</sup>GC<sup>2</sup> trace indicates gross contamination.

<sup>b</sup>Species 1 = Mya truncata

2 = Serripes groenlandica

3 = Leptosteroias polaris

4 = Fucus

5 = Laminaria

ND = not detected.

3-78

### 3.3 Shoreline Experiments

Samples from four pairs of oiled test plots were analyzed to determine the detailed hydrocarbon chemical composition in order to discern subtle time-dependent changes owing to weathering processes. The samples, taken at times from 1 to 16 days after the oil applications, consisted of a single composite surface sample (see details in Volume 1).

#### 3.3.1 Hydrocarbon Concentrations

A summary of the analytical data on the gross compositional features (i.e. resolved by GC<sup>2</sup>) and total (by **micro-gravimetry**) hydrocarbons are presented in Table 3-22 for the 16 test plots. These results indicate large differences in residual concentrations of oil in the test plots from the intertidal zone, dependent mainly on whether the spilled oil was emulsified (site L-2; H-2) or **unemulsified** (site L-1; H-1). The **unemulsified** (or aged) oil concentrations remained high throughout the experiments (after day 1 at H-1), but increased at the sites with the emulsified oil, probably due to oil removal followed by **redeposition**. The oil concentrations at the **backshore** plots were higher than the intertidal plots throughout the experiments, although some temporal variations were noted at all plots.

#### 3.3.2 Saturated Hydrocarbon Composition (GC<sup>2</sup>)

The detailed saturated hydrocarbon compositional information is presented for each test plot in a tabular form and in a graphic form. The tabular information (Tables 3-23 to 3-30) presents concentrations of individual **n-alkanes**

TABLE 3-22

SHORELINE STUDY - PETROLEUM HYDROCARBON CONCENTRATIONS

SITE	DAY	SAMPLE ID NO.	SATURATED HYDROCARBONS		AROMATIC HYDROCARBONS	
			TOTAL RESOLVED (GC) ( µg/g )	TOTAL <b>GRAVI-</b> METRIC ( µg/g )	TOTAL RESOLVED (GC) ( µg/g )	TOTAL <b>GRAVI-</b> METRIC ( µg/g )
L-1	1	GC-11	307	2,650	166	1,970
	2	GC-12	421	2,650	134	1,971
	4	GC-13	301	4,300	201	2,542
	8	GC-14	824	<b>4,210</b>	350	3,890
L-2	2	GC-17	6.0	78	1.8	65
	4	GC-18	57.1	469	30.7	385
	8	GC-19	60.8	278	20.0	188
H-1	1	GC-1	0.7	15.1	ND	0.2
	2	GC-2	84.4	<b>1,100</b>	46.0	905
	4	GC-3	244	1,880	99.3	1,850
	8	GC-4	236	2,790	57.9	1,360
	16	GC-5	98.9	<b>1,290</b>	29.8	963
H-2	1	GC-6	0.14	1.0	0.005	1.8
	2	GC-7	0.4	0.8	0.002	1.6
	4	GC-8	14.8	95.0	9.0	58.1
	8	GC-9	17.5	206	4.0	158
	16	GC-10	250	4,420	77.8	2,840
LT-1	1	GC-21	696	19,900	863	14,700
	2	GC-22	1,350	17,300	632	10,500
	4	GC-23	150	5,170	220	5,240
	8	GC-24	1,550	10,200	758	10,500
LT-2	1	GC-26	2,710	11,300	399	8,970
	2	GC-27	4,380	11,900	835	7,480
	4	GC-28	<b>961</b>	4,400	106	3,720
	8	GC-29	3,520	20,900	487	16,700

TABLE 3-22 (Cont.)

SITE	DAY	SAMPLE ID NO.	SATURATED HYDROCARBONS		AROMATIC HYDROCARBONS	
			TOTAL RESOLVED (GC) ( µg/g )	TOTAL <b>GRAVI-</b> METRIC ( µg/g )	TOTAL RESOLVED (GC) ( µg/g )	mTAL <b>GRAVI-</b> METRIC ( µg/g )
HT-1	1	GC-40	623	3,990	185	2,560
	2	GC-42	490	4,480	155	3,020
	4	GC-44	403	5,030	140	4,030
	8	GC-46	2,270	12,000	872	8,660 "
HT-2	1	GC-41	3,970	18,300	520	16,500
	2	GC-43	1,100	5,790	<b>361</b>	4,680
	4	GC-45	1,350	13,700	373	6,900
	8	GC-47	1,337	9,120	646	6,920
	16	GC-49	1,260	7,880	304	4,840

TABLE 3-23

SHORELINE STUDY - SATURATED HYDROCARBONS (SITE L-1)

	DAY				
	1	2	4	8	16
Sample ID No.	<b>GC-11</b>	<b>GC-12</b>	<b>GC-13</b>	<b>GC-14</b>	None
Lab ID No.	06-1060	06-1061	06-1104	06-1062	
Constituent ( $\mu\text{g/g}$ )					
n-C <sub>10</sub>	9.2	4.5	3.6	20.1	
n-C <sub>11</sub>	13.8	13.9	<b>11.6</b>	<b>36.1</b>	
n-C <sub>12</sub>	15.9	<b>20.1</b>	17.1	<b>43.9</b>	
n-C <sub>13</sub>	<b>15.6</b>	22.3	20.0	45.0	
n-C <sub>14</sub>	15.3	23.1	18.2	43.5	
Farnesane	6.1	9.3	8.5	15.3	
n-C <sub>15</sub>	14.6	22.7	20.5	42.4	
n-C <sub>16</sub>	12.9	20.0	18.6	37.9	
n-C <sub>17</sub>	11.2	<b>18.1</b>	16.7	34.8	
Pristane	4.9	7.3	5.7	15.2	
n-C <sub>18</sub>	10.1	14*9	13.6	2.8	
Phytane	<b>5.5</b>	9.4	8.2	17.7	
n-C <sub>19</sub>	9.8	15.8	<b>10.0</b>	31.5	
n-C <sub>20</sub>	7.6	12.5	10.6	25.3	
n-C <sub>21</sub>	6.3	10.7	8.3	21.2	
n-C <sub>22</sub>	5.6	9.7	7*5	21.9	
n-C <sub>23</sub>	4.4	8.2	6.1	15.0	
n-C <sub>24</sub>	4.8	7.4	5.3	13.5	
n-C <sub>25</sub>	3.6	6.0	4.2	11.2	
n-C <sub>26</sub>	2.9	5.1	3.5	10.9	
n-C <sub>27</sub>	2.7	4.3	2.8	8.0	
n-C <sub>28</sub>	2.2	3.7	2.2	5.3	
n-C <sub>29</sub>	2.2	3.0	1.8	6.0	
n-C <sub>30</sub>	1.5	2.7	1.4	3.5	
n-C <sub>31</sub>	1.6	2.1	1*3	4.2	
n-C <sub>32</sub>	1.0	1.5	<b>1.0</b>	<b>ND<sup>a</sup></b>	

<sup>a</sup>ND not detected.

TABLE 3-23 (Cont.)

	DAY				
	1	2	4	8	16
Total Alkanes (GC) ( $\mu\text{g/g}$ )	175	288	206	" 483	None
Total Resolved (GC) ( $\mu\text{g/g}$ )	307	421	301	829	
Total Saturates (grav. wt.) ( $\mu\text{g/g}$ )	2,650	2,650	4,300	4,210	
ALK/ISO	2.36	2.48	2.64	2.55	
SHWR	2.54	<b>1.89</b>	2.33	2.52	

TABLE 3-24

SHORELINE STUDY - SATURATED HYDROCARBONS (SITE L-2)

	DAY				
	1	2	4	8	16
Sample ID No.	None	<b>GC-17</b>	<b>GC-18</b>	<b>GC-19</b>	None
Lab ID No.		06-1064	06-1065	06-1066	
Constituent ( µg/g )					
n-C <sub>10</sub>		<b>ND<sup>a</sup></b>	0.26	0.30	
n-C <sub>11</sub>		0.03	<b>1.5</b>	1.2	
n-C <sub>12</sub>		<b>0.16</b>	2.9	2.3	
n-C <sub>13</sub>		0*31	3.6	3.0	
n-C <sub>14</sub>		<b>0.40</b>	3.7	3.5	
Farnesane		<b>0.15</b>	1.2	1.4	
n-C <sub>15</sub>		0.44	3.5	3.7	
n-C <sub>16</sub>		0.40	3.2	3.3	
n-C <sub>17</sub>		0,38	2.9	3.1	
Pristane		0.14	1.1	1.2	
n-C <sub>18</sub>		0.35	2.7	2.8	
Phytane		0.20	1.6	1.6	
n-C <sub>19</sub>		<b>0.35</b>	2.6	<b>1.9</b>	
n-C <sub>20</sub>		0.29	2.2	2.3	
n-C <sub>21</sub>		0.25	1.9	1.9	
n-C <sub>22</sub>		0.22	1.7	<b>1.7</b>	
n-C <sub>23</sub>		<sup>u</sup> 0.18	<b>1.4</b>	1.4	
n-C <sub>24</sub>		<b>0.15</b>	12.0	1.2	
n-C <sub>25</sub>		0.12	<b>1.0</b>	<b>1.1</b>	
n-C <sub>26</sub>		0.10	0.82	0.86	
n-C <sub>27</sub>		0.07	0.72	0.69	
n-C <sub>28</sub>		0.05	0.60	0.60	
n-C <sub>29</sub>		0.05	0.61	0.50	
n-C <sub>30</sub>		0.04	0.58	0.45	
n-C <sub>31</sub>	.	0.03	0.47	0.36	
n-C <sub>32</sub>		0.02	0.37	0.23	

TABLE 3-24 (Cont.)

	DAY				
	1	2	4	8	16
Total Alkanes (GC) ( $\mu\text{g/g}$ )	None	5.1	39.7	38.6	None
Total Resolved (GC) ( $\mu\text{g/g}$ )		5.98	57.1	60.8	
Total Saturates (grav. wt.) ( $\mu\text{g/g}$ )		78.3	469	278	
ALK/ISO		2.70	2.62	2.80	
SHWR		2.09	2.25	2.00	

TABLE 3-25

SHORELINE STUDY - SATURATED HYDROCARBONS (SITE H-1)

	DAY				
	1	2	4	8	16
Sample ID No.	<b>GC-1</b>	GC-2	GC-3	GC-4	GC-5
Lab ID No.	06-1097	06-1073	06-1074	06-1075	06-1076
Constituent ( µg/g )					
n-C <sub>10</sub>	<b>ND<sup>a</sup></b>	ND	5.	<b>ND</b>	ND
n-C <sub>11</sub>	ND	<b>0.8</b>	<b>10.4</b>	0.29	ND
n-C <sub>12</sub>	<b>ND</b>	2.8	13.2	3.0	0.44
n-C <sub>13</sub>	ND	4.5	<b>13.1</b>	9.7	2.6
n-C <sub>14</sub>	<b>0.01</b>	5.5	12.7	15.0	<b>5.4</b>
Farnesane	0.002	<b>2.2</b>	4.4	6.4	<b>2.5</b>
n-C <sub>15</sub>	0.03	5.6	12.3	16.9	6.7
n-C <sub>16</sub>	0.05	5*1	11.1	15.0	6.6
n-C <sub>17</sub>	0.05	4.5	<b>10.2</b>	<b>13.9</b>	6.0
Pristane	0.02	2.0	4.2	5.4	2.6
n-C <sub>18</sub>	0.05	4.0	9.3	12.5	5 . 1
Phytane	0.03	2.2	5.5	6.8	2.9
n-C <sub>19</sub>	<b>0.04</b>	2.4	9.2	7.7	3.8
n-C <sub>20</sub>	0.04	3.1	7.8	9.5	<b>4.5</b>
n-C <sub>21</sub>	0.04	<b>2.5</b>	6.6	8.0	3.8
n-C <sub>22</sub>	0.03	2.2	5.7	7.0	3.3
n-C <sub>23</sub>	0.03	1.9	4.9	5.9	2.8
n-C <sub>24</sub>	0.03	1.7	4.3	5.3	<b>2.5</b>
n-C <sub>25</sub>	0.03	1.4	3.7	4.3	2.3
n-C <sub>26</sub>	0.02	1.2	3.4	3.8	1.8
n-C <sub>27</sub>	0.03	1.0	2.8	3.3	1.5
n-C <sub>28</sub>	0.02	0.89	2.3	2.9	1.3
n-C <sub>29</sub>	0.02	0.79	<b>2.1</b>	2.6	1*0
n-C <sub>30</sub>	0.02	0.70	1.7	2.4	0.88
n-C <sub>31</sub>	0.02	0.64	<b>1.6</b>	2.0	0.73
n-C <sub>32</sub>	0.01	0.44	1.3	1.6	0.43

<sup>a</sup>ND · not detected.

TABLE 3-25 (Cont.)

	DAY				
	1	2	4	8	16
Total Alkanes (GC) ( $\mu\text{g/g}$ )	0.55	54.4	155	145	63.6
Total Resolved (GC) ( $\mu\text{g/g}$ )	0.74	84.4	244	236	98.9
Total Saturates (grav. wt.) ( $\mu\text{g/g}$ )	15.1	1,100	1,880	2,790	1,290
ALK/ISO	2.67	2.54	2.53	2.78	2.58
SHWR	1.27	2.03	2.26	1.81	1.63

TABLE 3-26

SHORELINE STUDY - SATURATED HYDROCARBONS (SITE H-2)

	DAY				
	1	2	4	8	16
Sample ID No.	GC-6	GC-7	<b>GC-8</b>	GC-9	<b>GC-10</b>
Lab ID No.	06-1077	06-1078	06-1079	06-1080	06-1081
Constituent ( $\mu\text{g/g}$ )					
n-C <sub>10</sub>	ND <sup>a</sup>	ND	ND	ND	2.5
n-C <sub>11</sub>	ND	ND	ND	ND	18.0
n-C <sub>12</sub>	ND	ND	0.04	0.14	38.3
n-C <sub>13</sub>	ND	ND	0.25	0.47	52.8
n-C <sub>14</sub>	ND	ND	0*57	0.82	22.0
Farnesane	ND	ND	0.27	0.40	23.5
n-C <sub>15</sub>	0.5 <sup>b</sup>	ND	0.88	0.95	57.6
n-C <sub>16</sub>	2.0 <sup>b</sup>	0.2 <sup>b</sup>	0.96	1.1	52.3
n-C <sub>17</sub>	3.4 <sup>b</sup>	1.5 <sup>b</sup>	0.99	1.0	46.5
Pristane	4.5 <sup>b</sup>	2.2 <sup>b</sup>	0.43	0.45	20.8
n-C <sub>18</sub>	4.8 <sup>b</sup>	3.0 <sup>b</sup>	0.97	0.88	40.2
Phytane	2.4 <sup>b</sup>	1.4 <sup>b</sup>	0.58	0.53	24.2
n-C <sub>19</sub>	1.6 <sup>b</sup>	0.2 <sup>b</sup>	0.90	0.67	44.5
n-C <sub>20</sub>	5.4 <sup>b</sup>	3.0 <sup>b</sup>	0.76	0.76	35.3
n-C <sub>21</sub>	4.7 <sup>b</sup>	2.8 <sup>b</sup>	0.62	0.78	30.6
n-C <sub>22</sub>	5.3 <sup>b</sup>	2.4 <sup>b</sup>	<b>0.51</b>	0.58	26.4
n-C <sub>23</sub>	6.2 <sup>b</sup>	2.0 <sup>b</sup>	0.44	0.51	22.7
n-C <sub>24</sub>	8.9 <sup>b</sup>	1.6 <sup>b</sup>	0.38	0.46	19.4
n-C <sub>25</sub>	11.5 <sup>b</sup>	1.6 <sup>b</sup>	0.31	0.39	18.1
n-C <sub>26</sub>	14.0 <sup>b</sup>	1.2 <sup>b</sup>	0.27	0.35	14.8
n-C <sub>27</sub>	10.2 <sup>b</sup>	1.2 <sup>b</sup>	0.25	0.30	13.0
n-C <sub>28</sub>	8.0 <sup>b</sup>	1.0 <sup>b</sup>	0.22	0.25	11.0
n-C <sub>29</sub>	6.1 <sup>b</sup>	1.0 <sup>b</sup>	0.21	0.24	9.5
n-C <sub>30</sub>	4.6 <sup>b</sup>	0.6 <sup>b</sup>	0.20	0.25	11.2
n-C <sub>31</sub>	3.4 <sup>b</sup>	0.6 <sup>b</sup>	0.16	0.18	7.7
n-C <sub>32</sub>	2.2 <sup>b</sup>	0.4 <sup>b</sup>	<b>0.12</b>	0.17	6.6

<sup>a</sup>ND - not detected.

<sup>b</sup>ng/g.

TABLE 3-26 (Cont.)

	DAY				
	1	2	4	8	16
Total Alkanes (GC) ( $\mu\text{g/g}$ )	64 <sup>b</sup>	26 <sup>b</sup>	11.0	8.7	591
Total Resolved (GC) ( $\mu\text{g/g}$ )	141 <sup>b</sup>	444 <sup>b</sup>	14.8	17.5	1,000
Total Saturates (grav. wt. ) ( $\mu\text{g/g}$ )	970 <sup>b</sup>	810 <sup>b</sup>	95.0	206	4,220
ALK/ISO	3.73	3.06	2.54	2.36	2.06
SHWR	1.04	1.02	1.40	1.18	1.82

<sup>a</sup>ND - not detected.

<sup>b</sup>ng/g.

TABLE 3-27

SHORELINE STUDY - SATURATED HYDROCARBONS (SITE LT-1)

	DAY				
	1	2	4	8	16
Sample ID No.	<b>GC-21</b>	<b>GC-22</b>	<b>GC-23</b>	<b>GC-24</b>	None
Lab ID No.	06-1067	06-1082	06-1068	06-1084	
Constituent ( µg/g )					
n-C <sub>10</sub>	17.1	23.3	<b>4.3</b>	8.9	
n-C <sub>11</sub>	<b>28.3</b>	60.8	<b>6.7</b>	36.7	
n-C <sub>12</sub>	<b>33.5</b>	82.3	<b>7.6</b>	58.2	
n-C <sub>13</sub>	33.8	<b>86.1</b>	7.5	64.6	
n-C <sub>14</sub>	34.4	84.2	<b>7.4</b>	68.6	
Farnesane	<b>13.6</b>	28.7	3.0	27.5	
n-C <sub>15</sub>	33.0	<b>81.4</b>	7.2	68.1	
n-C <sub>16</sub>	29.8	68.2	6.2	59.9	
n-C <sub>17</sub>	26.8	<b>76.1</b>	5.6	53.7	
Pristane	<b>11.9</b>	24.8	2.5	23.5	
n-C <sub>18</sub>	<b>22.7</b>	58.8	<b>4.5</b>	43.9	
Phytane	13.0	34.4	2.8	27.8	
n-C <sub>19</sub>	22.9	41.3	4*7	33.6	
n-C <sub>20</sub>	<b>19.5</b>	48.9	<b>4.1</b>	37.9	
n-C <sub>21</sub>	16.3	<b>41.7</b>	3*4	31.1	
n-C <sub>22</sub>	14.8	36.9	3.7	27.4	
n-C <sub>23</sub>	12.5	30.6	2.6	23.1	
n-C <sub>24</sub>	<b>11.0</b>	26.9	2.3	20.3	
n-C <sub>25</sub>	9.4	21.5	<b>1.9</b>	19.9	
n-C <sub>26</sub>	8.1	17.8	1.6	16.7	
n-C <sub>27</sub>	7.5	14.0	<b>1.4</b>	15.6	
n-C <sub>28</sub>	6.7	11.6	1.2	13.2	
n-C <sub>29</sub>	6.6	10.9	1.0	10.9	
n-C <sub>30</sub>	6.5	7.9	0.91	10.5	
n-C <sub>31</sub>	5.7	<b>5.2</b>	0.74	8.9	
n-C <sub>32</sub>	4.2	4.2	0.48	6.3	

TABLE 3-27 (Cont.)

	DAY				
	1	2	4	8	16
<b>Total Alkanes (GC) (µg/g)</b>	411	930	87.2	<b>738</b>	None
Total Resolved (GC) (µg/g)	696	1,350	150	1,550	
Total Saturates (grav. wt.) (µg/g)	19,000	17,300	5,170	10,200	
ALK/ISO	2.43	2.57	2.45	2.96	
SHWR	2.35	2.30	2.42	2.25	

TABLE 3-28

SHORELINE STUDY - SATURATED HYDROCARBONS (SITE LT-2)

	DAY				
	1	2	4	8	16
Sample ID No.	<b>GC-26</b>	GC-27	<b>GC-28</b>	GC-29	None
Lab ID No.	06-1085	06-1086	06-1087	06-1088	
Constituent ( µg/g )					
n-C 10	9.9	<b>13.7</b>	<b>3.6</b>	47.7	
n-C <sub>11</sub> 1	55.6	<b>56.9</b>	<b>17.9</b>	<b>127</b>	
n-C <sub>12</sub> 2	<b>114</b>	104	<b>36.4</b>	<b>169</b>	
n-C <sub>13</sub> 3	<b>141</b>	<b>119</b>	47.8	199	
n-C <sub>14</sub> 4	<b>140</b>	127	41.5	204	
Farnesane	60.9	46.4	17.89	65.9	
n-C <sub>15</sub> 5	140	119	43.0	200	
n-C <sub>16</sub> 6	139	113	56.5	188	
n-C <sub>17</sub> 7	124	126	52.9	172	
Pristane	57.3	48.1	21.8	76.9	
n-C <sub>18</sub> 8	115	97.2	47.3	165	
Phytane	61.8	153.7	28.0	91.6	
n-C <sub>19</sub> 9	<b>119</b>	67.7	48.8	164	
n-C 20	95.1	74.5	39.8	135	
n-C <sub>21</sub> 10	<b>86.0</b>	61.7	34.4	121	
n-C <sub>22</sub> 11	77.0	49.6	29.3	105	
n-C 23	76.2	39.8	25.7	90.6	
n-C <sub>24</sub> 12	60.4	33.3	22.9	81.8	
n-C <sub>25</sub> 13	52.6	<b>33.4</b>	18.4	68.8	
n-C <sub>26</sub> 14	48.3	23.7	16.5	70.3	
n-C <sub>27</sub> 15	45.1	22.0	<b>13.5</b>	59.9	
n-C 28	42.6	18.5	10.1	52.6	
n-C <sub>29</sub> 16	35.0	<b>15.0</b>	8.99	48.9	
n-C30	33.7	14.7	8.97	38.2	
n-C31	35.2	10.6	4.97	23.9	
n-C32	25.9	9.21	4.89	19.9	

TABLE 3-28 (Cont.)

	DAY				
	1	2	4	8	16
Total <b>Alkanes</b> (GC) ( $\mu\text{g/g}$ )	1,800	1,330	655	1,450	None
Total Resolved (GC) ( $\mu\text{g/g}$ )	2,710	4,380	961	3,920	
Total Saturates (grav. wt.) ( $\mu\text{g/g}$ )	11,300	<b>11,900</b>	4,400	20,900	
<b>ALK/ISO</b>	2.58	2.45	2.08	2.29	
SHWR	1.93	2.12	<b>1.79</b>	2.03	"

TABLE 3-29

## SHORELINE STUDY - SATURATED HYDROCARBONS (SITE HT-1)

	DAY			
	1	2	4	8
Sample ID No.	<b>GC-40</b>	GC-42	<b>GC-44</b>	Gc-46
Lab ID No.	06-1089	06-1091	06-1093	06-1044
Constituent ( µg/g )				
n-C <sub>10</sub>	<b>4.1</b>	5.0	2.4	26.9
n-C <sub>11</sub>	<b>18.6</b>	16.7	9.5	78.6
n-C <sub>12</sub>	<b>30.1</b>	26.5	<b>17.2</b>	122
n-C <sub>13</sub>	33.0	29.3	20.8	125
n-C <sub>14</sub>	33.8	29.3	<b>21.4</b>	<b>130</b>
Farnesane	13.4	<b>10.0</b>	7.6	53.1
n-C <sub>15</sub>	32.8	28.2	21.6	137
n-C <sub>16</sub>	28.9	24.0	19.4	<b>121</b>
n-C <sub>17</sub>	25.3	21.5	18.3	<b>112</b>
Pristane	7.1	<b>9.3</b>	<b>8.1</b>	39*9
n-C <sub>18</sub>	21.3	19.6	16.2	100
Phytane	13.0	10.7	9.5	56.8
n-C <sub>19</sub>	15.1	19*7	15.7	93.8
n-C <sub>20</sub>	18.6	15.0 "	<b>13.4</b>	75.8
n-C <sub>21</sub>	16.0	13.6	11.9	62.6
n-C <sub>22</sub>	16.5	<b>11.9</b>	10.4	54.2
n-C <sub>23</sub>	12.1	<b>9.9</b>	9.0	44.2
n-C <sub>24</sub>	11.0	<b>8.6</b>	8.0	37.4
n-C <sub>25</sub>	<b>11.5</b>	7.9	6.3	31.8
n-C <sub>26</sub>	7.8	6.0	5.3	26.0
n-C <sub>27</sub>	7.3	4.9	4.1	24.2
n-C <sub>28</sub>	5.5	3.8	3.6	18.3
n-C <sub>29</sub>	4.1	3.1	<b>3.2</b>	<b>16.0</b>
n-C <sub>30</sub>	3.8	2.1	<b>1.9</b>	11.1
n-C <sub>31</sub>	2.9	<b>2.1</b>	1.9	7.4
n-C <sub>32</sub>	1.8	1.3	1.1	6.8

TABLE 3-29 (Cont.)

	DAY			
	1	2	4	8
Total Alkanes (GC) ( $\mu\text{g/g}$ )	362	310	242	1,460
Total Resolved (GC) ( $\mu\text{g/g}$ )	623	490	403	2,270
Total Saturates (grav. wt.) ( $\mu\text{g/g}$ )	3,990	4,500	5,030	12,000
ALK/ ISO	2.63	2.60	2.52	2.84
SHWR	2.23	2.24	2.18	2.21

TABLE 3-30

SHORELINE STUDY - SATURATED HYDROCARBONS ( SITE HT-2 )

	DAY				
	1	2	4	8	16
Sample ID No.	<b>GC-41</b>	<b>GC-43</b>	<b>GC-45</b>	GC-47	GC-49
Lab ID No.	06-1090	06-1092	06-1105	06-1095	06-1096
Constituent ( µg/g )					
n-C <sub>10</sub>	46.2	2.65	<b>4.0</b>	8.10	6.96
n-C <sub>11</sub>	<b>139</b>	<b>18.9</b>	67.2	32.0	29.3
n-C <sub>12</sub>	<b>215</b>	45.0	77.2	62.9	49.8
n-C <sub>13</sub>	<b>219</b>	63.0	<b>73.2</b>	69.9	69.5
n-C <sub>14</sub>	215	69.8	68.8	81.0	73.9
Farnesane	90.0	20.5	28.4	35.9	31.0
n-C <sub>15</sub>	205	70.0	63.6	89.8	75.2
n-C <sub>16</sub>	198	62.3	63.2	78.4	68.2
n-C <sub>17</sub>	180	56.6	57.2	70.4	63.2
Pristane	78.5	25.4	24.8	32.5	28.4
n-C <sub>18</sub>	165	50.9	51.2	63.3	52.8
Phytane	91.1	30.0	26.4	36.3	<b>31.2</b>
n-C <sub>19</sub>	166	51.4	52.4	54.0	36.6
n-C <sub>20</sub>	<b>131</b>	41.5	42.4	49.2	43.8
n-C <sub>21</sub>	114	36.0	36.8	43.8	37.2
n-C <sub>22</sub>	100	30.7	<b>31.2</b>	36.6	32.5
n-C <sub>23</sub>	87.1	26.0	26.0	31.2	26.5
n-C <sub>24</sub>	78.4	24.4	24.0	25.1	22.8
n-C <sub>25</sub>	80.7	20.7	22.4	22.3	18.2
n-C <sub>26</sub>	56.5	18.2	18.4	15.3	15.7
n-C <sub>27</sub>	52.3	15.2	18.4	11.9	10.5
n-C <sub>28</sub>	41.1	13.9	14.8	11.4	7.53
n-C <sub>29</sub>	36.6	13.6	15.6	8.75	<b>6.88</b>
n-C <sub>30</sub>	30.0	13.0	14.4	<b>6.0</b>	5.65
n-C <sub>31</sub>	21.0	6.56	12.4	4.0	4.12
n-C <sub>32</sub>	21.7	7.18	<b>9.2</b>	1.6	2.80

TABLE 3-30 (Cont.)

	DAY				
	1	2	4	8	16
Total Alkanes (GC) (µg/g)	2,600	763	864	877	760
Total Resolved (GC) (µg/g)	3,970	<b>1,110</b>	1,350	1,337	1,260
Total Saturates (grav. wt. ) (µg/g)	18,300	5,790	13,700	9,120	7,880
ALK/ I SO	2.57	2.80	2.98	2.64	2.38
<b>SHWR</b>	2.12	1.96	2.31	2.07	<b>2.12</b>

(C<sub>10</sub>-C<sub>32</sub>) and three key isoprenoids (branched **alkanes**) farnesane, pristane, and **phytane**. The **alkanes** are summed and presented in relation to the entire suite of resolved (GC<sup>2</sup>) saturates. The total saturates (= resolved plus unresolved complex mixture plus **non-chromatographables**) was determined by microgravimetry. Two key ratios, the **ALK/ISO** (**alkanes** from n-C<sub>14</sub> through n-C<sub>18</sub> ÷ five key isoprenoids in this boiling range including **farnesane**, pristane **phytane** and two others), and the SHWR - saturated hydrocarbon weathering ratio:

$$\text{SHWR} = \frac{\text{Sum of alkanes from n-C}_{10} \text{ to n-C}_{25}}{\text{Sum of alkanes from n-C}_{17} \text{ to n-C}_{25}}$$

are calculated. The **ALK/ISO** is sensitive to biodegradation as **alkanes** are preferentially biodegraded (Boehm et al., 1981a; Boehm et al., 1981b; Atlas et al., 1981). The SHWR approaches unity as the lighter components are lost due mainly to evaporation and some dissolution (Boehm and Fiest, 1981a).

The **ALK/ISO** and SHWR values in the "fresh" and "aged" Lagomedio crude oils are:

	<u>ALK/ISO</u>	<u>SHWR</u>
Fresh	2.36	2.87
Aged	2.50	2.28

The graphic results (Figures 3-36 to 3-43) are derived from the tables and present compositional information relative to n-C<sub>24</sub>, which is **assumed** to be unaffected by weathering processes. The compositional information can be compared to the fresh oil in the figures. Perhaps it **would** be more appropriate to compare the results to the "aged" oil but, as discussed previously (Section One), the "aged" oil's composition is more weathered than most of the residues in the test

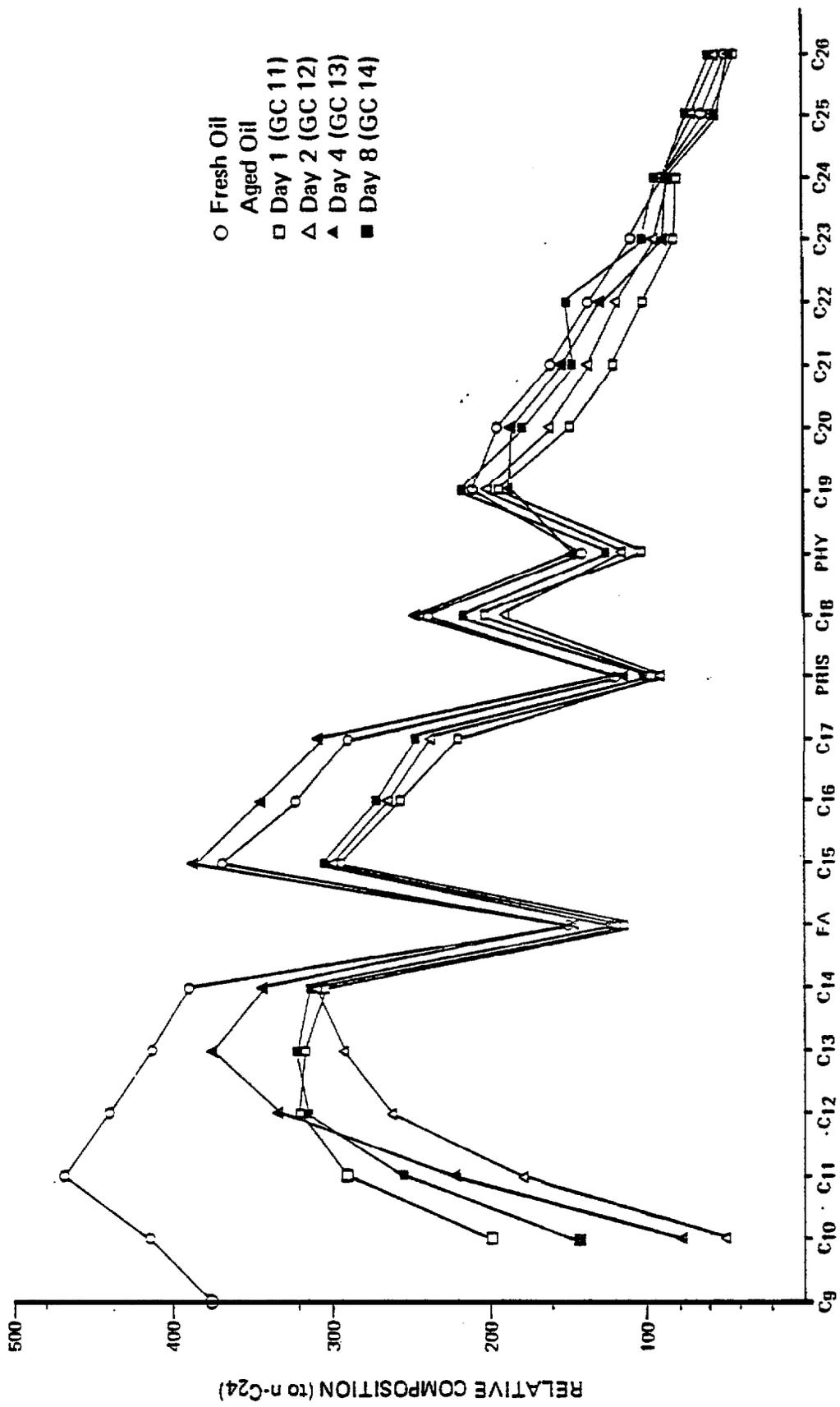


Figure 3.36. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site L-1.

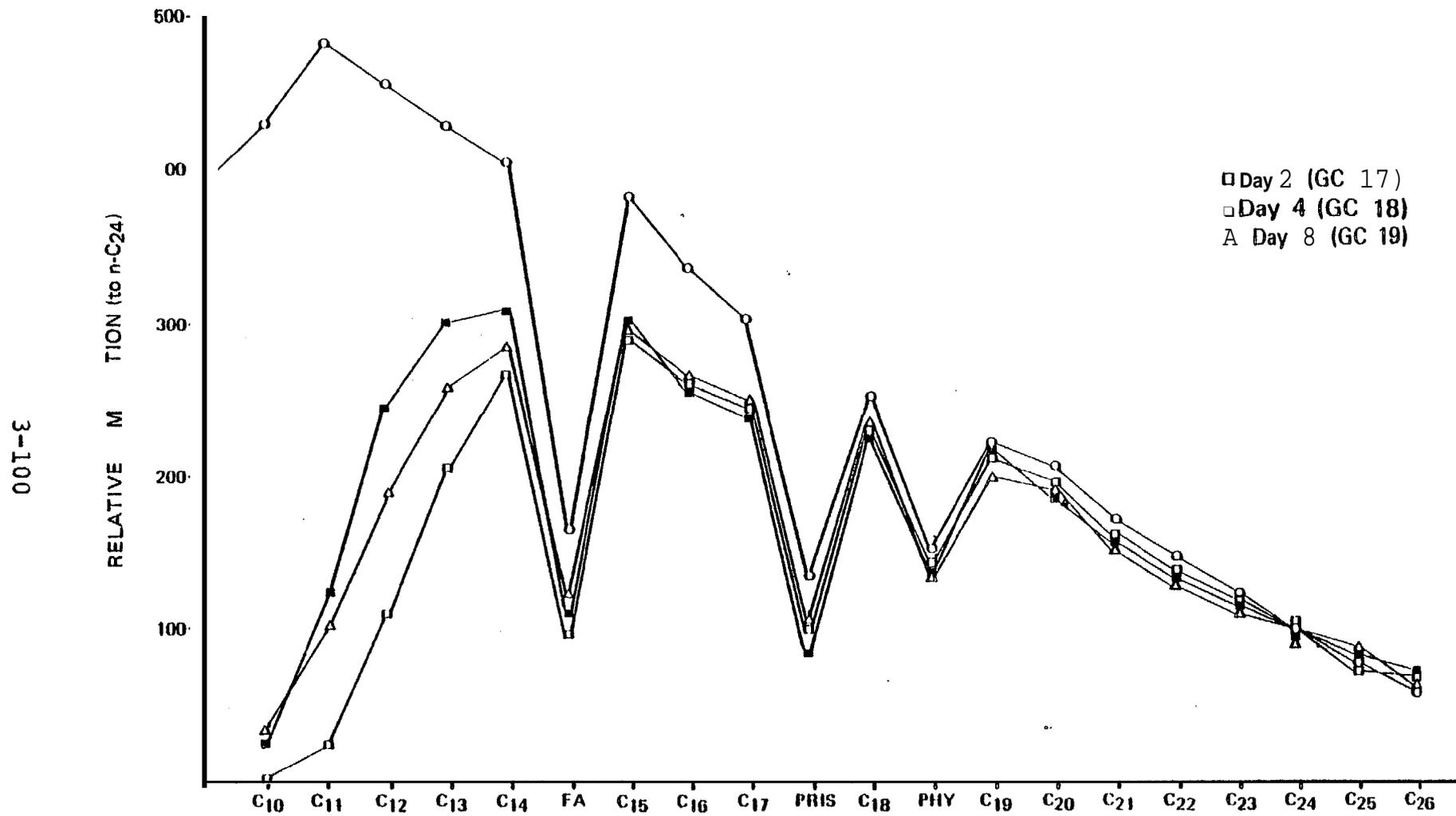


Figure 3.37. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site L-2.

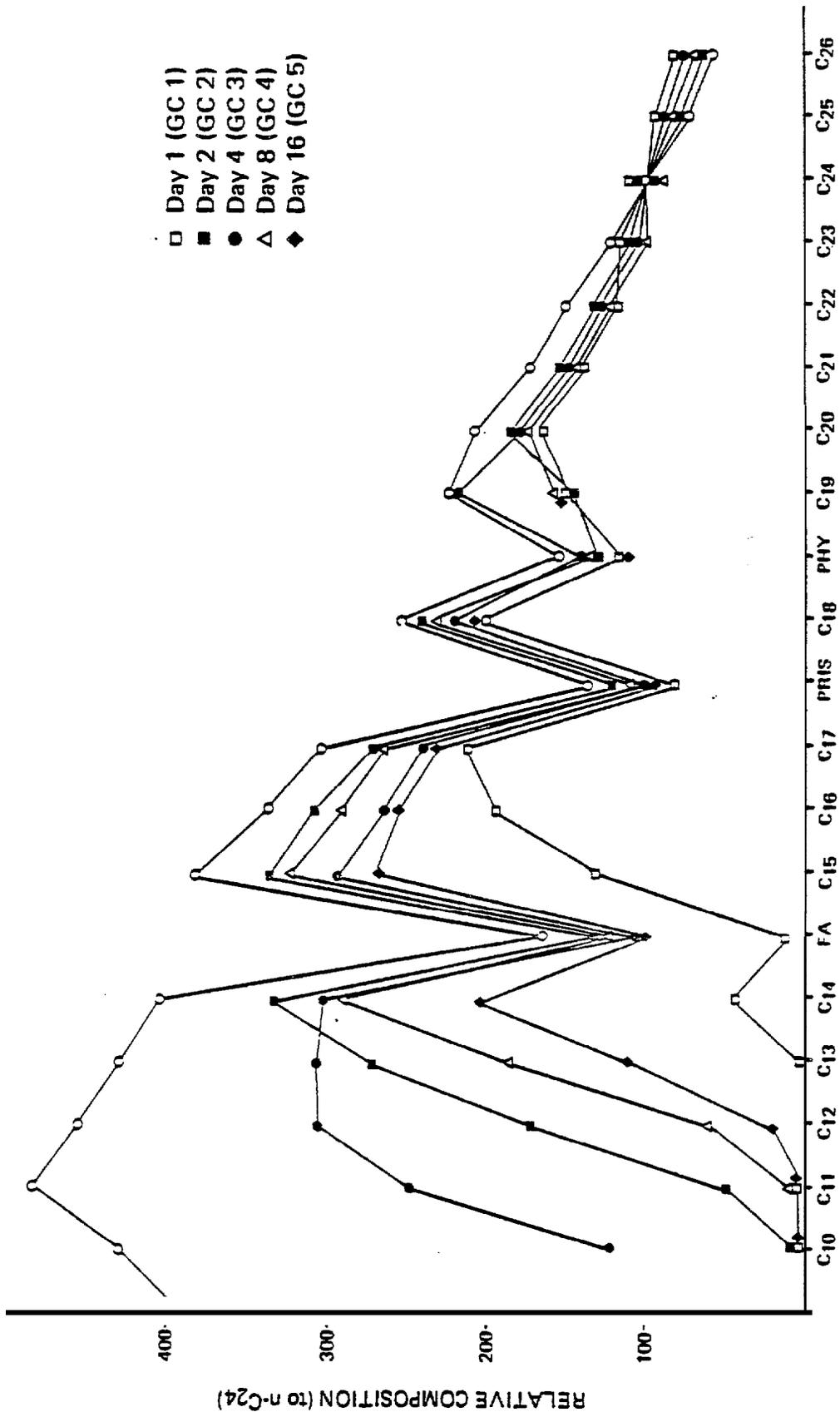


Figure 3.38. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site H-1.

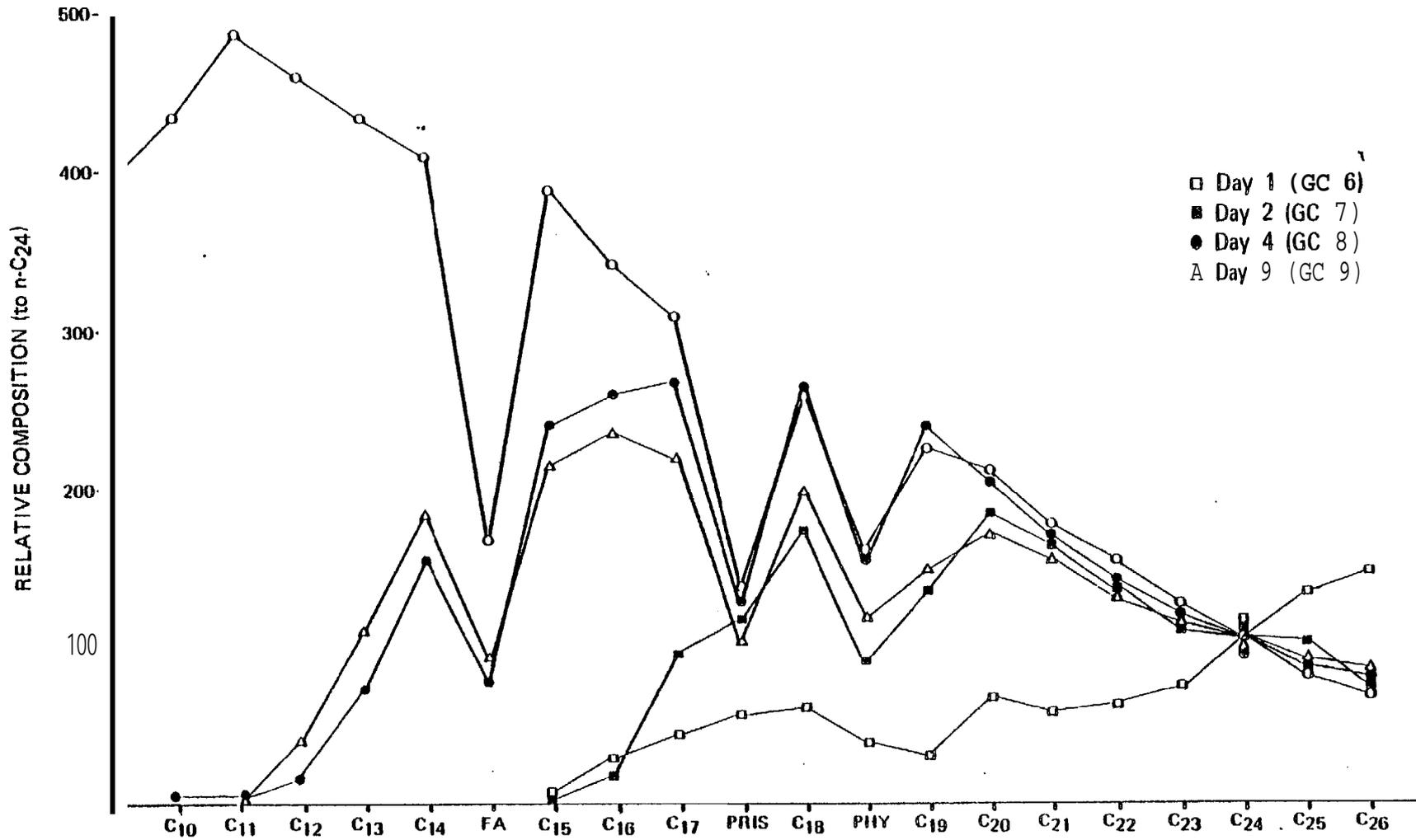


Figure 3.39. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site H-2.

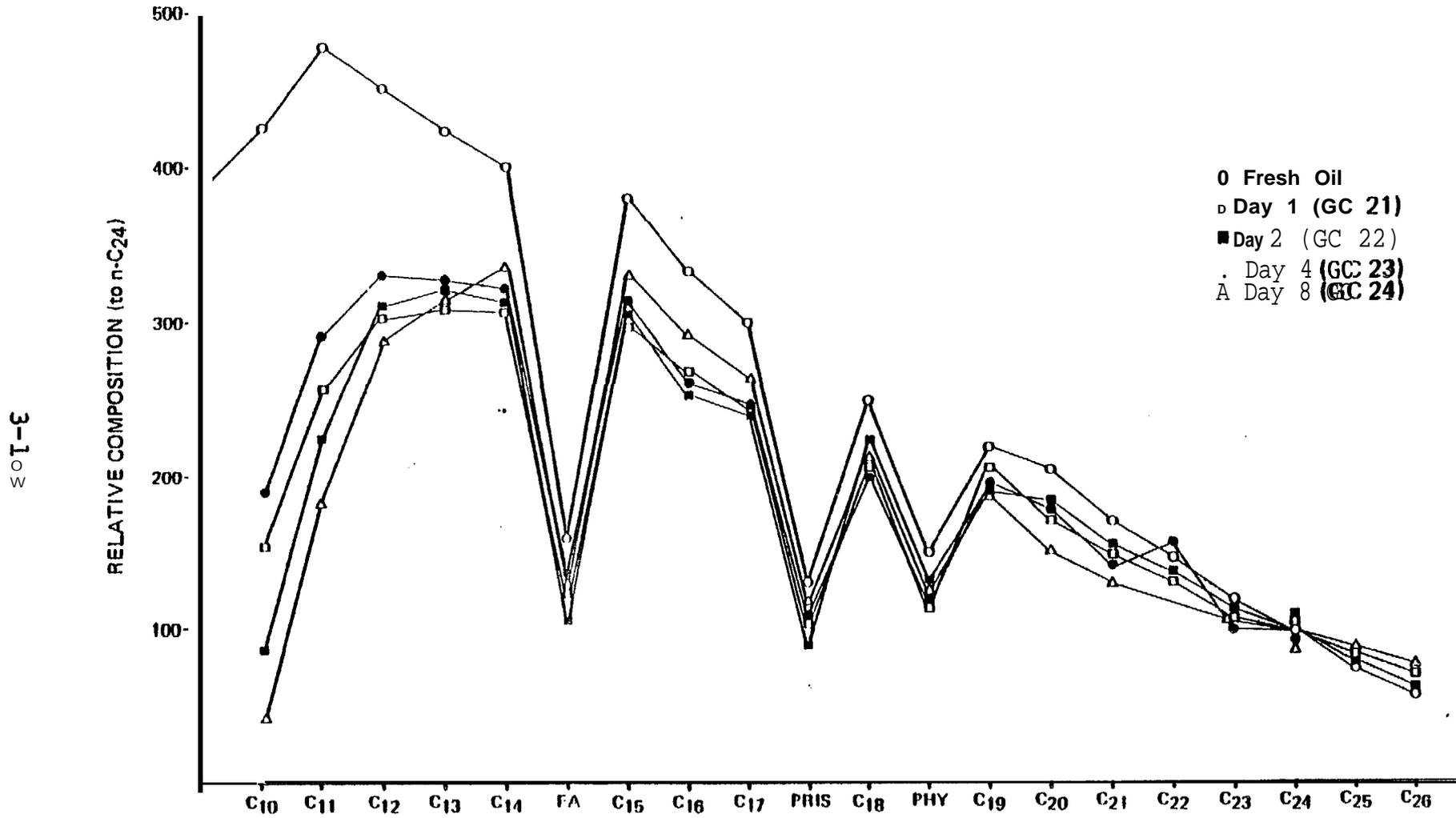


Figure 3.40. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site LT-1.

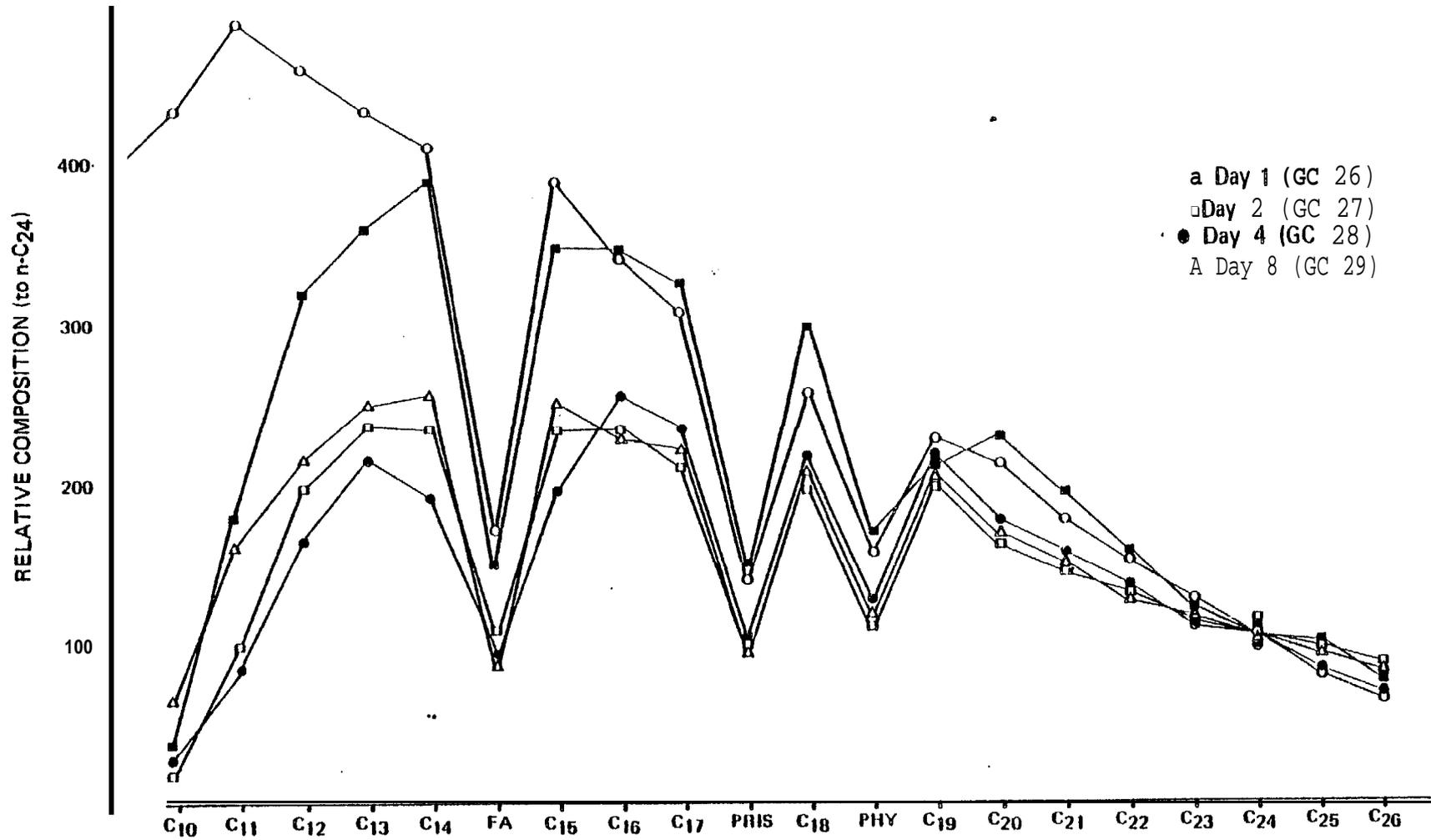


Figure 3.41. Comparative Saturated Hydrocarbon Composition " of Lagomedio Crude-Shoreline Experiment, SiteLT-2.

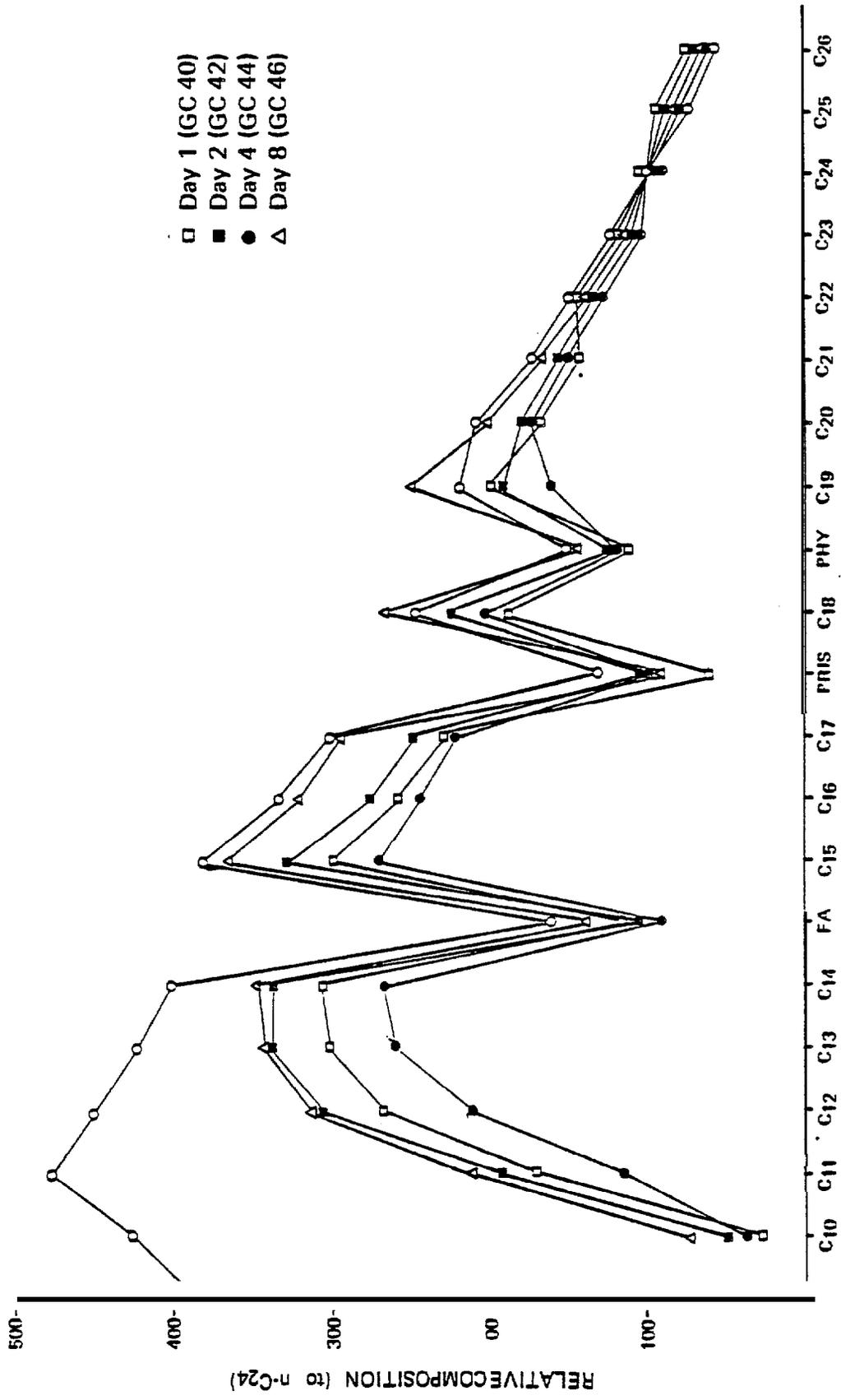


Figure 3.42. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site HT-1.

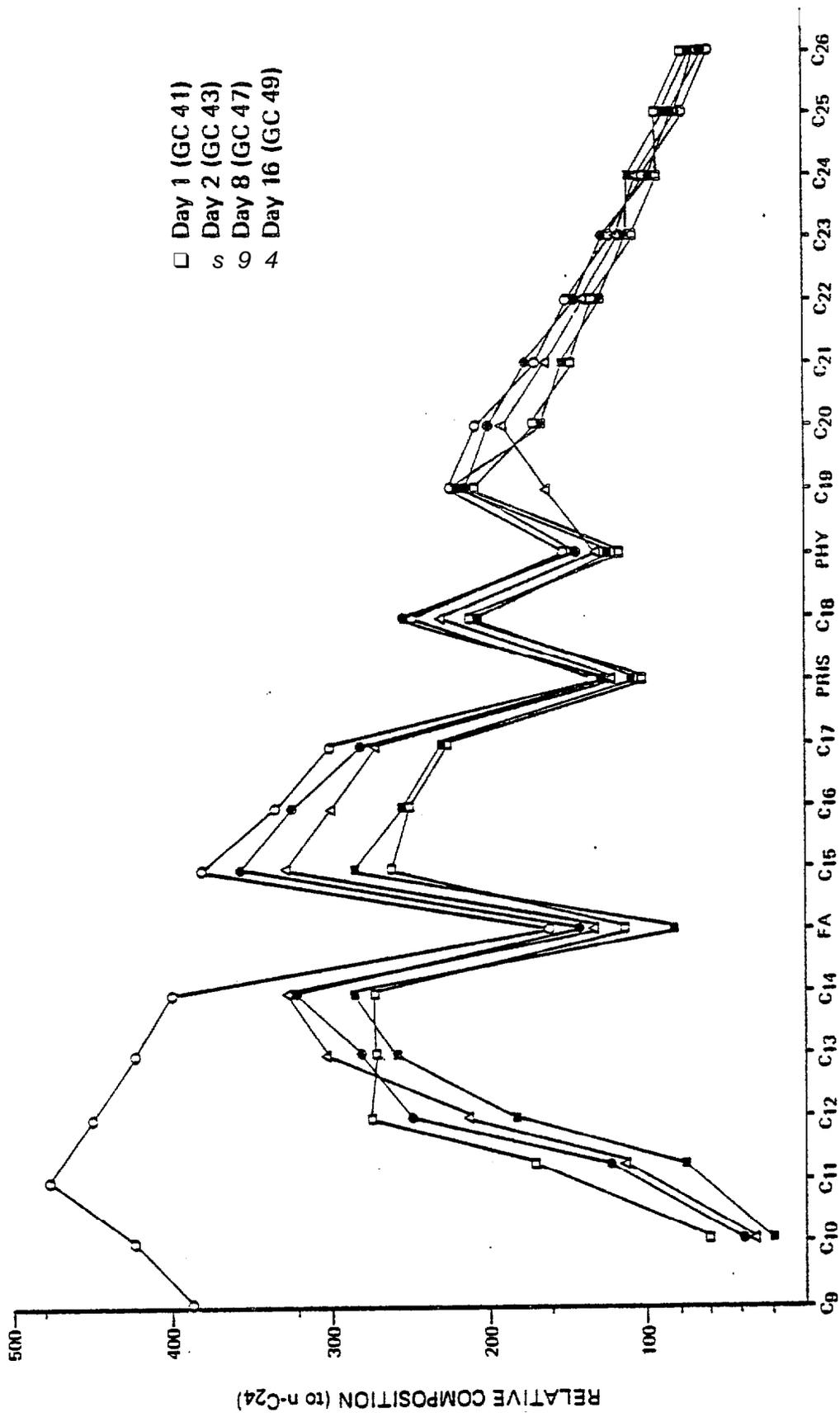


Figure 3.43. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site HT-2.

plots . Note, however, that we did not **analyze oil from the field prior to application.** Our "aged" oil was supplied by **the project office** as sampled from the railroad car (aging chamber) and thus must differ significantly from that used in the field. We suspect that the test **oil** actually used in the field was intermediate in composition between the **fresh** and "aged" oil supplied by the project office.

The compositional **plots** indicate much non-predicted behavior with the "older" residues (4 to **16** days) often "fresher" or less weathered than the early samples. However, it is probable that compositional heterogeneity occurs in the test plots and it is certain that most of the 16 days of weathering occurred within several (1-2) days in **all** plots other than perhaps Site H-1. Note how the samples containing much lower concentrations (e.g., site **H-1** day 1; H-2 days 1 and 2) are more highly weathered. This is probably due to gross removal of oil by waves leaving the remaining **low** level oil residues more highly leached. Subsequently, fresher oil is redeposited.

The results from one site, H-1, illustrate that evaporative weathering does proceed during the entire 16 days although the compositional situation during days 1 through 4 appears highly variable. Thereafter (days 8 and 16), weathering proceeds steadily (**SHWR** = 2.26, day 4; 1.81, *day 8*; **1.63**, day 16).

### 3.3.3 Aromatic Hydrocarbons (GC/MS)

The samples from two test plots, L-1 and **LT-1**, formed a subset of shoreline **plots** which were analyzed by **GC<sup>2</sup>/MS** to determine the detailed aromatic hydrocarbon compositions and,

hence, weathering patterns. The analytical results are summarized in Table 3-31. Four families of aromatic hydrocarbon compounds and one **organo-sulfur** family were focused on: **naphthalenes** and **alkyl naphthalenes**; **alkyl benzenes**; **fluorenes**; **phenanthrenes** and **alkyl phenanthrenes**; **dibenzothiophanes** and **alkyldibenzothiophenes**. The total **polynuclear aromatics (PAH)** represent the sum of the compounds of interest. The AWR or aromatic weathering ratio is similar in concept to the SHWR (Section 3.3.2)

$$AWR = \frac{\sum (\sum AB + \sum N + \sum F + \sum P + \sum DBT)}{\sum (\sum P + \sum DBT)}$$

and approaches unity as the more volatile, **soluble** compounds (N, AB, F) are weathered. The **AWR values** in fresh and aged Lagomedio oil are 4.29 and 3.47, respectively.

The values in Table 3-31 parallel the trends previously noted. For the **L-1** test plots weathering of the aromatic fraction is complete by the first day after application. This is supportive of **the** saturated hydrocarbon data (see Section 3.3.2). The **LT-1 plot** results also parallel the saturated hydrocarbon trends. Figures 3-44 and 3-45 graphically illustrate the comparison of the "aged" oil to the "fresh" oil and to the test samples as well. In these plots the aromatics are normalized to **trimethyl (C3) dibenzothiophene**. Most of the compositional change is seen in the lighter compounds (i.e., **alkyl benzenes** and, to a lesser extent, **naphthalenes**).

#### 3.3.4 Azaarenes (GC<sup>2</sup>/MS)

Detailed analyses of three families of prominent nitrogen **heterocyclics (azaarenes)** in the Lagomedio Crude

TABLE 3-31

SHORELINE STUDY - GC/MS DATA SUMMARY  
OF' AROMATIC HYDROCARBON RESULTS

	Site L-1			Site LT-1			
	Day 1 GC-11 ( µg/g )	Day 2 GC-12 ( µg/g )	Day 8 GC-14 ( µg/g )	Day 1 GC-21 ( µg/g )	Day 2 GC-22 ( µg/g )	Day 4 GC-23 ( µg/g )	Day 8 GC-24 ( µg/g )
N	1.2	1.2	2.9	<b>13.0</b>	6.8	2.4	6.9
C <sub>1</sub> N	7.1	7.6	15.7	66.0	44.2	12.0	43.4
C <sub>2</sub> N	17.7	17.7	38.0	139.0	102.2	28.1	106.0
C <sub>3</sub> N	14.7	16.3	30.0	114.0	87.2	22.6	90.5
C <sub>4</sub> N	7.7	7.9	15.9	694.0	54.0	13.3	48.3
ΣN	48.4	<b>50.7</b>	102.5	426.0	294.4	78.4	295.1
C <sub>3</sub> AB	3.7	3.2	4.1	99.6	21.8	7.3	19.0
C <sub>4</sub> AB	6.4	5.7	4.2	86.6	35.6	11.4	33.3
c 5AB	5.3	5.1	3.4	61.0	31.8	9.9	32.2
ΣAB	15.4	14.0	11.7	246.2	89.2	28.6	84.5
BP	0.6	0.6	1.2	4.6	3.2		3.2
F'	0.4	0.4	0.6	3.2	2.4	<b>0.6</b>	2.2
C <sub>1</sub> F	1.2	1.3	2.4	8.2	6.2	<b>1.7</b>	6.6
C <sub>2</sub> F	1.8	1.9	3.3	16.6	11.2	3.1	12.3
C <sub>3</sub> F	2.4	2.5	4.4	21.0	15.4	3.8	13.4
ΣF	5.8	6.1	10.7	49.0	35.2	9.2	34.5
P	0.8	0.9	1.8	7.6	4.8	1.4	<b>5.0</b>
C <sub>1</sub> P	4.1	3.8	7.2	32.0	18.9	5.1	22.5
C <sub>2</sub> P	5.0	5.2	8.6	40.0	25.4	6.6	28.2
C <sub>3</sub> P	3.5	3.1	6.0	37.8	22.0	5.8	21.7
C <sub>4</sub> P	2.8	2.4	2.1	22.6	<b>13.2</b>	3.4	<b>18.1</b>
ΣP	16.2	15.4	25.7	140.0	84.3	22.3	95.5

TABLE 3-31 (Cont.)

	Site L-1			Site LT-1			
	Day 1 GC-11 ( µg/g)	Day 2 GC-12 ( µg/g)	Day 8 GC-14 ( µg/g)	Day 1 GC-21 ( µg/g)	Day 2 GC-22 ( µg/g)	Day 4 GC-23 ( µg/g)	Day 8 GC-24 ( µg/g)
DBT	1.0	1.1	2.0	8.4	5.6	1.4	5.2
C <sub>1</sub> DBT	3.8	3.7	6.9	30.8	20.4	5.2	20.2
C <sub>2</sub> DBT	6.9	7.2"	13.7	62.2	41.4	9.9	38.9
C <sub>3</sub> DBT	5.6	5.6	10.0	50.8	35.2	7.6	37.5
ΣDBT	17.3	17.6	32.6	152.2	102.6	24.1	101.8
Total PAH ( µg/g )	103.7	104.4	184.4	1,018	608.9	162.6	614.6
Total Aromatics (Grav.) [ µg/g )	1,970	1,971	3,890	19,900	17,300	5,170	10,200
AWR	3.08	3.15	3.14	3.46	3.24	3.50	3.10

N = naphthalenes

AB = alkyl benzenes

BP = biphenyl

F = Fluorenes

P = phenanthrenes

DBT = dibenzothiophenes

C<sub>1</sub>,C<sub>2</sub>,C<sub>3</sub>,C<sub>4</sub>,C<sub>5</sub> = mono-, di-, tri-, tetra- and  
penta-methyl homologues.

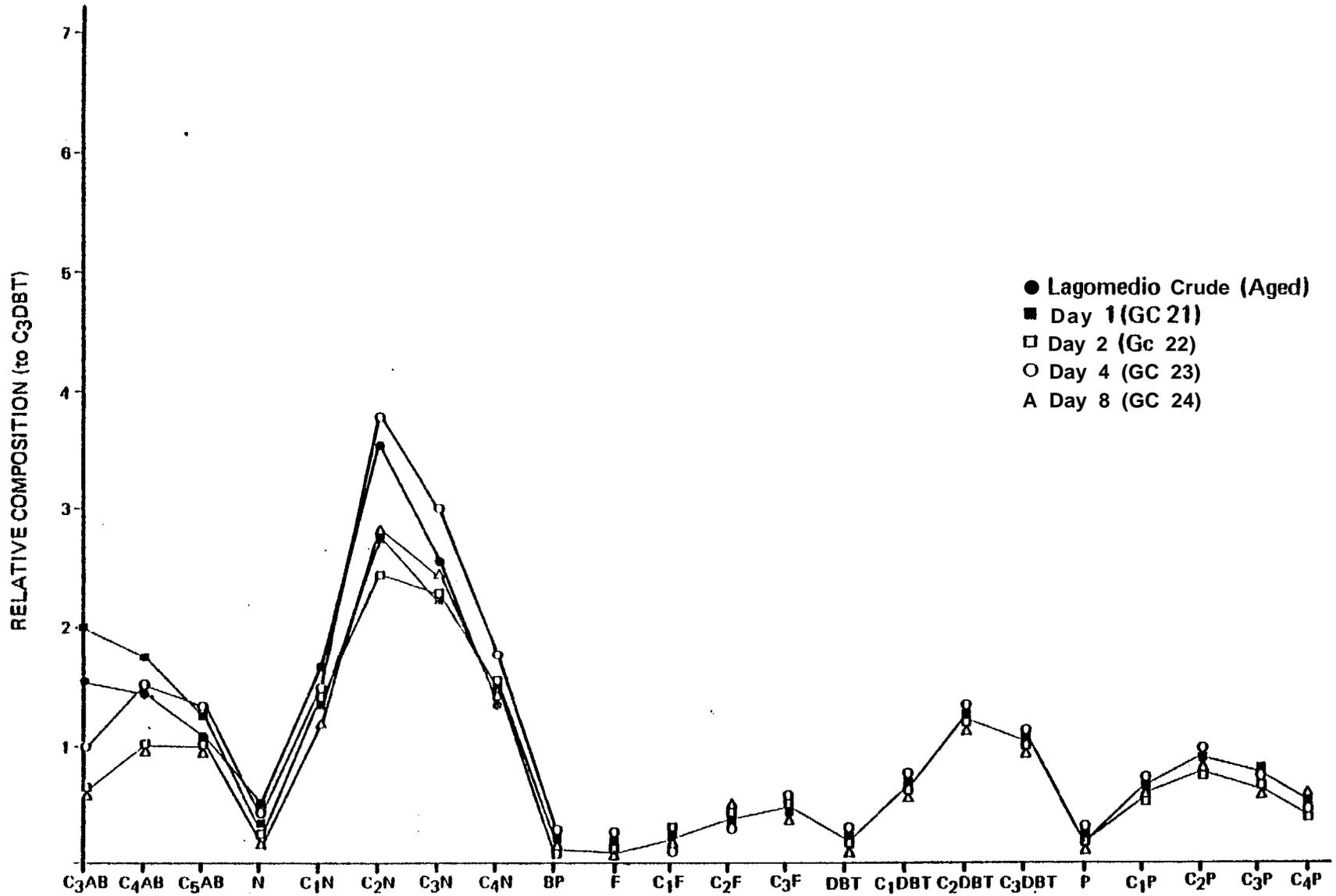


Figure 3.44. Comparative Aromatic Hydrocarbon Compositions, Site L-1 : Aged Oil.

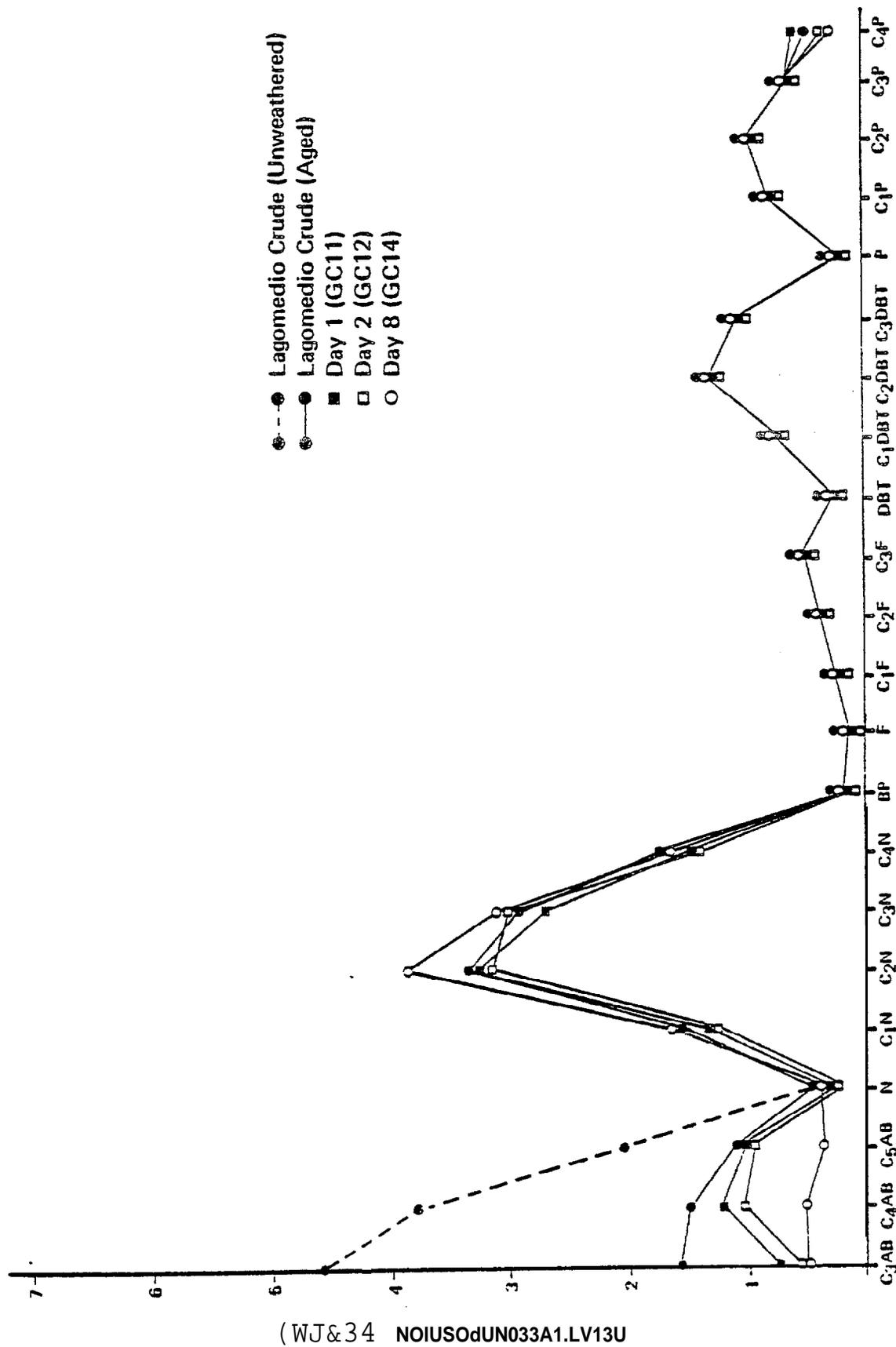


Figure 3.45. Comparative Aromatic Hydrocarbon Compositions, Site LT-1: Aged Oil.

were performed on a set of samples (Table 3-32) from the **oiled** test plots. The compositions of the **quinoline, acridine/phenanthridene** families remained invariant throughout the 8 days of sampling. A substantial, unique data base on the range (however narrow) of azaarene compositions has been amassed which will be extremely important for the use of these compounds as markers for this oil.

Figure 3-46 compares the azaarene composition in the test oils with that in the samples confirming the narrow range of variation of these compounds. Differences between fresh and aged Lagomedio are also **small**. Significant variations do occur in the benzacridine samples. The **low** relative amounts of these compounds (note scale expansion) probably account **for** the noticeable variability.

### 3.3.5 Pentacyclic Triterpanes (GC<sup>2</sup>) "

**Pentacyclic** triterpane hydrocarbons (**PT**) were the subject of a **GC<sup>2</sup>/MS** analytical program involving nine heavily oiled shoreline samples. The objective was to examine post-spill PT compositional changes to document weathering-induced **changes, if any**. As shown in **Table 3-33**, the PT compounds identified in the **oil** itself are **present** in the oiled samples throughout the time period studied in nearly the same ratios to each other. However, the compounds are present in very low levels and are often barely detectable above instrumental noise. The PT fingerprint is certainly less *clear* than that revealed by other oils in spill situations (e.g., Amoco Cadiz; **Atlas et al.**, 1981) (Figure 3-47) and hence, although the weak **Lagomedio** PT fingerprint persists, it is doubtful whether it will be useful as a long-term marker, especially in view of the background PT fingerprint (see Section 3.2.5) .

TABLE 3-32

AZAARENES IN OIL RESIDUES FROM  
SHORELINE TEST PLOTS - RELATIVE CONCENTRATIONS<sup>a</sup>

M/e	SITE L-1		
	DAY 1 GC-11	DAY 2 GC-12	DAY 8 GC-14
129 Q	0.8	0.7	--
143 C <sub>1</sub> Q	<b>2.2</b>	<b>1.6</b>	1
157 C <sub>2</sub> Q	<b>1.9</b>	<b>2.9</b>	<b>1.4</b>
171 C <sub>3</sub> Q	<b>7.8</b>	<b>10</b>	<b>15</b>
185 C <sub>4</sub> Q	25	<b>31</b>	41
199 C <sub>5</sub> Q	21	25	32
213 C <sub>6</sub> Q	29	30	30
<b>179A</b>	0.3	0.2	0.5
193 C <sub>1</sub> A	8	11	11
207 C <sub>2</sub> A	55	51	71
221 C <sub>3</sub> A	100	<b>100</b>	100
235 C <sub>4</sub> A	54	63	39
249 C <sub>5</sub> A	<b>18</b>	22	10
229 BA	0.2	0.3	0.1
243 C <sub>1</sub> BA	3	3	1
257 C <sub>2</sub> Ba	4	4	2

<sup>a</sup> = Concentrations normalized to C<sub>3</sub>A

A = Acridines/phenanthridines

Q = **Quinolines**

BA = Benzacridines

C<sub>n</sub> = **Alkyl** homologies with n-Carbon atoms

TABLE 3-32 (Cont.)

	SITE LT-1			
	DAY 1 GC-21	DAY 2 GC-22	DAY 4 GC-23	DAY 8 GC-24
M/e				
129 Q	4	3	.3	0.9
143 C <sub>1</sub> Q	6	5	3	1.7
<b>157 C<sub>2</sub>Q</b>	5	4	<b>1</b>	2.5
171 C <sub>3</sub> Q	15	<b>11</b>	8	<b>11</b>
185 C <sub>4</sub> Q	43	33	26	32
199 C <sub>5</sub> Q	31	<b>27</b>	23	28
213 C <sub>6</sub> Q	<b>30</b>	29	25	28
179A	0.4	0.2	0.3	0.3
193 C <sub>1</sub> A	14	10	8	11
207 C <sub>2</sub> A	69	58	49	52
221 C <sub>3</sub> A	100	100	100	100
235 C <sub>4</sub> A	41	53	51	59
249 C <sub>5</sub> A	12	19	20	21
229 BA	0.2	0.2	0.3	0.2
243 C <sub>1</sub> BA	1	2.4	3	2.5
257 C <sub>2</sub> Ba	1	3.0	5	3.4

<sup>a</sup> = Concentrations normalized to C<sub>3</sub>A

A = Acridines/phenanthridines

Q = Quinolines

BA = Benzacridines

C<sub>n</sub> = Alkyl homologies with n-Carbon atoms

TABLE 3-32 (Cont.)

	Site H-1				
	Day 1 GC-1	Day 2 GC-2	Day 4 GC-3	Day 8 GC-4	Day 16 GC-5
<b>M/e</b>					
129 Q	0.5	0.3	0.3	0.6	1.0
143 C <sub>1</sub> Q	1.1	0.7	<b>1.4</b>	2.3	2.6
<b>157</b> C <sub>2</sub> Q	<b>1.8</b>	2	1	1.5	1*5
171 C <sub>3</sub> Q	8	7	8	<b>10</b>	9.5
185 C <sub>4</sub> Q	25	22	27	<b>32</b>	30
199 C <sub>5</sub> Q	<b>19</b>	<b>16</b>	24	22	23
<b>213</b> C <sub>6</sub> Q	<b>28</b>	22	27	28	<b>27</b>
179A	0.3	0.2	<b>0.2</b>	0.3	0.3
193 C <sub>1</sub> A	10	9	9	<b>10</b>	9
207 C 2A	<b>49</b>	47	57	55	47
221 C <sub>3</sub> A	100 "	100	<b>100</b>	100	<b>100</b>
235 C <sub>4</sub> A	51	47	56	55	51
249 C <sub>5</sub> A	18	<b>15</b>	20	20	<b>0.9</b>
229 BA	0.2	0.2	<b>0.3</b>	0.3	<b>0.1</b>
243 C <sub>1</sub> BA	2.1	2	1.5	3.2	3.0
257 C <sub>2</sub> Ba	4.3	5	3	5.1	4.6

<sup>a</sup> = Concentrations normalized to C<sub>3</sub>A

A = Acridines/phenanthridines

Q = Quinolines

BA = Benzacridines

C<sub>n</sub> = Alkyl homologies with n-Carbon atoms

TABLE 3-32 (Cont.)

	Site HT-1		
	Day 1 GC-40	Day 2 GC-42	Day 4 GC-44
M/e			
129 Q	0.5	0.3	0.2
143 C <sub>1</sub> Q	1.7	0.7	0.7
157 C <sub>2</sub> Q	<b>1.7</b>	1,6"	1.1
171 C <sub>3</sub> Q	9	9	6.5
185 C <sub>4</sub> Q	27	25	20
199 C <sub>5</sub> Q	24	22	20
213 C <sub>6</sub> Q	29	29	29
179A	0.3	0.2	0.1
193 C <sub>1</sub> A	<b>9</b>	10	9
207 C <sub>2</sub> A	52	53	50
<b>221</b> C <sub>3</sub> A	100	<b>100</b>	100
235 C <sub>4</sub> A	58	58	58
249 C <sub>5</sub> A	24	24	24
229 BA	0.2	0.3	0.2
243 C <sub>1</sub> BA	3.4	3.1	2.9
257 C <sub>2</sub> Ba	5.6	5.4	4.6

<sup>a</sup> = Concentrations normalized to C<sub>3</sub>A

A = Acridines/phenanthridines

Q = **Quinolines**

BA = Benzacridines

Cn = **Alkyl** homologies with n-Carbon atoms

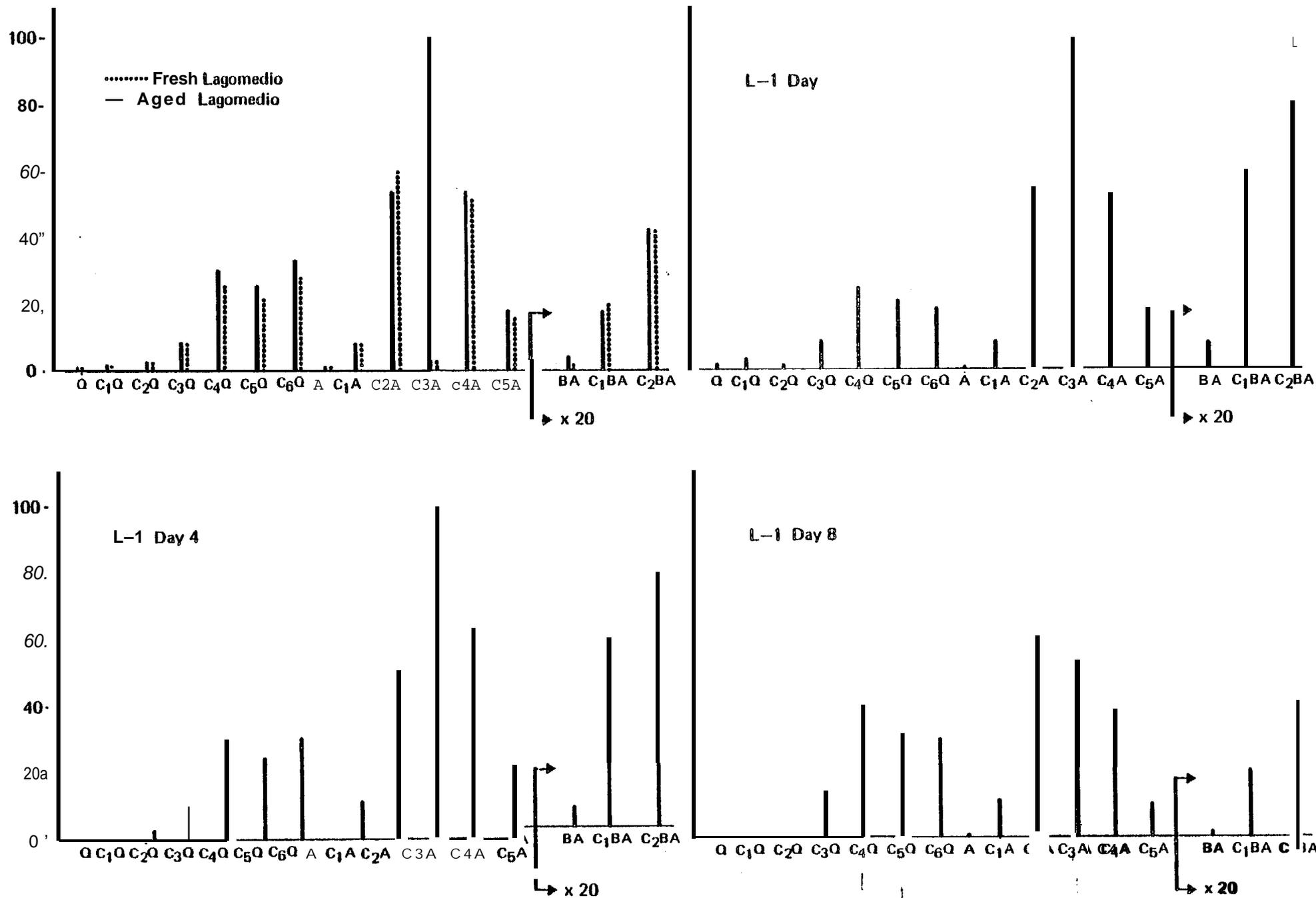


Figure 3.46. Comparative compositional plots of Azaarenes in aged Lagomedio oil and oil residues from Site L-1.

TABLE 3-33

QUALITATIVE GC/MS ANALYSES OF OILED SHORELINE SAMPLES  
FOR PENTACYCLIC TRITERPANE COMPOUNDS

SITE:		L-1	L-1	L-1	LT-1	LT-1	LT-1	LT-1	HT-1	HT-1
DAY :		1	2	8	1	2	4	8	1	4
SAMPLE :	AGED OIL	GC-11	GC-12	GC-14	GC-21	GC-22	GC-23	GC-24	GC-40	GC-44
COMPOUNDa										
A	+	+	+	+	+	+	+	+	+	+
B	+	+	+	+	+	+	+	+	+	+
C	+	+	+	+	+	+	+	+	+	+
D	+	+	+	+	+	+	+	+	+	+
E	+	+	+	+	+	+	+	+	+	+
E'	+	+	+	+	+	+	+	+	+	+
F										
F'										

<sup>a</sup>See Section 3.2.5(b) for explanation of compound identification.

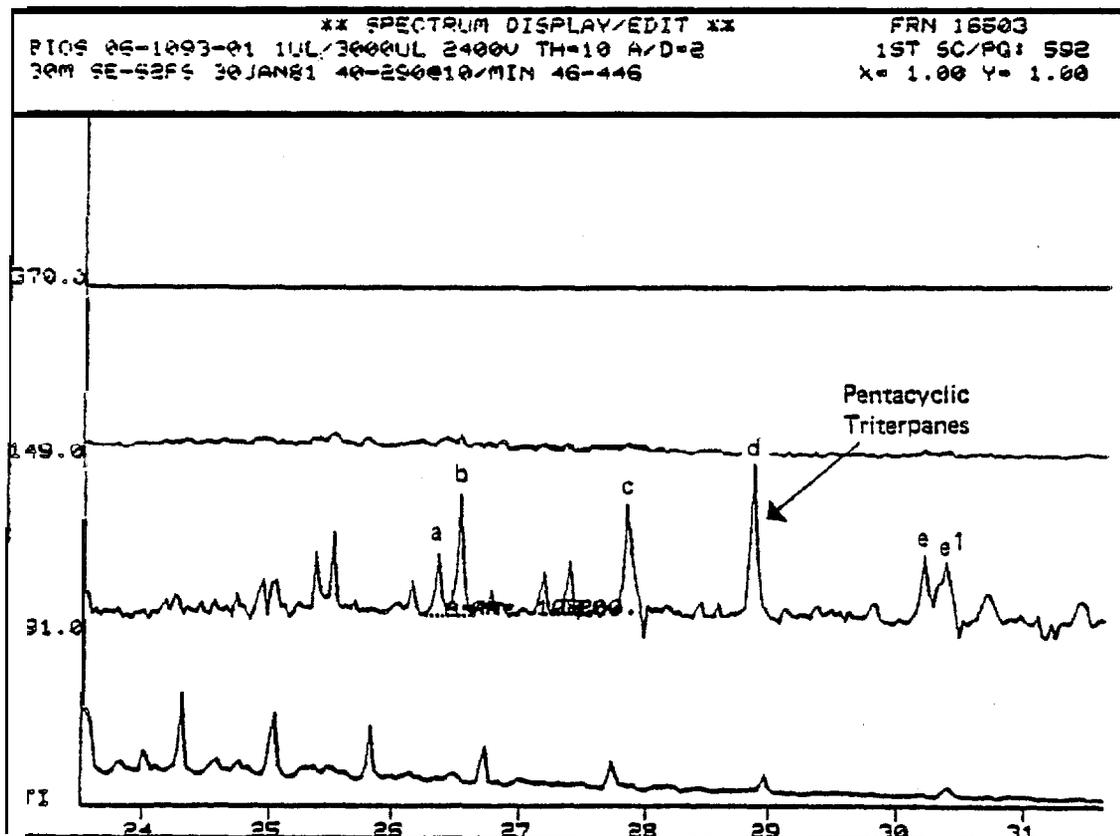
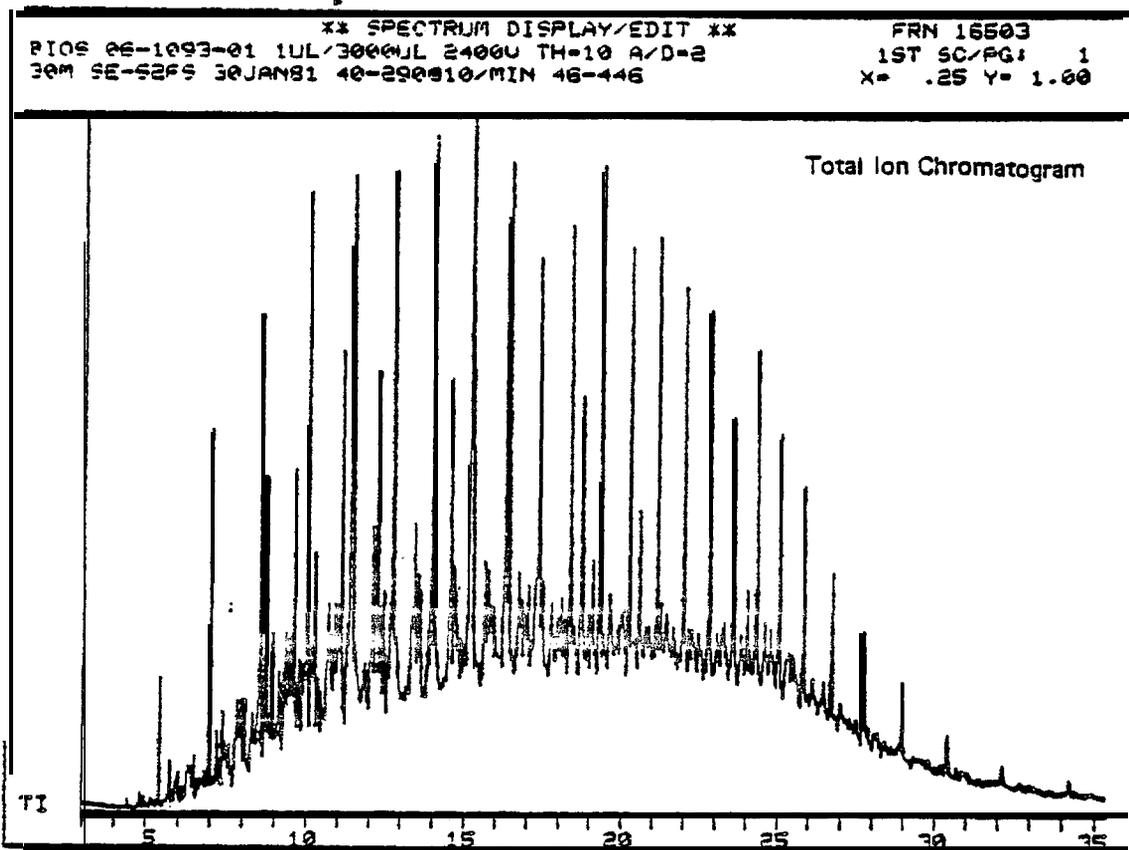


Figure 3.47. GC/MS of Pentacyclic Triterpanes in Oil Sample from shoreline sample.

## SECTION FOUR

### DISCUSSION

The marine environment of the Cape **Hatt**, N.W.T., area is comparable to other Arctic environments studied recently (e.g., Wong et al., 1976; Johansen et al., 1977; Shaw et al., 1978) with respect to its pristine nature. This similarity is reflected in the low petroleum hydrocarbon concentrations observed in the seawater, sediment, and tissue samples examined. As analytical methods have improved in recent years, the ability to measure minute levels of pollutant compounds has increased. Consequently, we find low levels (<1 ppb) of **polynuclear** aromatic hydrocarbons (**PAH**) and **polycyclic** aromatic nitrogen compounds (**PAN** = **azaarenes**), in both offshore and beach sediment. These levels of **PAH** and **PAN** compounds can be ascribed to the global atmospheric transport of a high-temperature combustion (mainly **anthropogenic**) origin (Lee et al., 1977). The other source for some of these aromatic compounds (e.g., **perylene**) is through **early** diagenesis of organic matter deposited in the sediments and preserved in a reducing environment.

Along with **PAH** and **PAN** compounds, an array of **polycyclic** saturated hydrocarbons (**PSH** = diterpane and triterpane) of an anthropogenic source are also detected in the sediment.

Tissue samples would be expected to be influenced by the deposition of these minute **levels** of **PAH**, **PAN**, and **PSH** compounds. However, for the most part, the tissue hydrocarbon components are of a **biogenic** origin. A complex array of **biogenic** compounds characterizes the hydrocarbon distribution of the species examined. **Intraspecies** compositional

uniformity was revealed through compositional similarities in GC<sup>2</sup> traces. Low **levels** of **naphthalene** and phenanthrene compounds (1-5 ppb) were identified in a set of Mya truncata samples. Thus the uniform **levels** and the composition of the very low, but detectable levels of petroleum-related aromatics, as opposed to the widely varying absolute levels of biogenic hydrocarbons, create a solid baseline for future oil-spill impact studies.

Seawater samples **revealed** little indication of petroleum inputs **until** the large volume water samples (LVWS) (150 to 200 liters) were analyzed. **Subpart-per-trillion** levels of petrogenic saturates were observed in the particulate hydrocarbons **while smaller levels** of petroleum-related **alkylated naphthalene**, phenanthrene and dibenzothiophene were observed by GC<sup>2</sup>/MS in the filterable or dissolved fraction. These findings point to four important facets of the study: (1) the LVWS are essential for the scrutiny of background and low-level post-spill water column investigations, (2) the Cape Hatt waters do contain minute levels of weathered petroleum-related material, (3) it is necessary to fractionate the water column into "dissolved" and **particulate** fractions to reveal the true physical-chemical nature of the hydrocarbon distribution (strongly related to their **bioavailability**), and (4) the "dissolved" and particulate fractions are decoupled with respect to chemical nature and probable transport mechanisms, thus confirming previous such baseline hydrocarbon measurements (**Boehm**, 1980).

The results of the study confirm the appropriateness of blending types of analyses to balance informational needs and cost aspects of the study. The low background levels of fluorescing material (i.e., aromatic hydrocarbons) make the UV/F technique extremely useful for screening both post-spill

seawater and sediment samples for the existence of petroleum contamination prior to sample selection for more detailed methods. During the spills **UV/F** can be used effectively, with appropriate standardization, in a continuous mode to monitor levels in the water column.

In order to examine (1) weathering of oil in shoreline and nearshore **spillages**, (2) the existence and the chemical nature of petroleum components in the dissolved and particulate forms in the water column, (3) the exposure levels and chemical fractionation of oil in biological samples, and (4) the detailed chemical fate of oil in sediments, **GC<sup>2</sup>** analysis must parallel or **follow UV/F** analysis.

Specified chemical marker compounds (**PAH, PAN, PSH**) must be analyzed by **GC<sup>2</sup>/MS** to accurately identify and quantify components. Analysis **for** those marker compounds in baseline and post-spill shoreline sediment samples indicates that the **most** promising markers are the PAH (**organo-sulfur** and three-ringed **alkylated** aromatics) and PAN compounds. The **pentacyclic** triterpanes seem to be both too abundant in offshore sediments and too "unimportant" as components of the oil to be used effectively as post-spill **biogeochemical** marker compounds. In addition, the PAH and PAN are the most biologically active components with the potential to cause long-term biological effects.

The character of the oil **was** revealed in great detail in this study and consists of a surprisingly strong suite of azaarenes and an equally surprisingly weak suite of pentacyclic triterpanes. Analysis of the composition of the artificially **aged oil** compared to the freshest residues (1 day) obtained in the shoreline experiments indicates that

much heterogeneity exists in what is being termed as the test oil. **This** fact added to the very important **determination** of non-Newtonian behavior through precipitation of wax from the oil and the **10:1 oil/dispersant** mix at **0°C**, suggests that close scrutiny of both field oil storage and the application of **the** oil should occur in order to avoid and/or monitor wax precipitation. Also, samples of oil for chemical analysis from the field should never be replaced by other surrogate sources.

Finally, **the** first year of **oil** weathering studies from the Z Lagoon and Eclipse Bay shorelines indicates that a **small** degree of weathering due to evaporation and dissolution occurs shortly (1 day) after the application but only minimal (but measurable) weathering proceeds further during the **first** 16 days. No indication for biodegradation was noted, probably due to the very high oil levels versus available nutrients,

Thus the BIOS project is in an excellent position to proceed, having obtained a comprehensive knowledge of (1) the baseline organic chemical aspects of the Cape **Hatt** marine environment, (2) the chemical and physical nature of the test oil, (3) the applicability of long-term marker compound analysis, (4) the expected **early** shoreline **weathering-**induced chemical changes in the **oil's** composition, and (5) the appropriate blend of analytical techniques to be used in the real-time spill monitoring and post-spill assessment.

## SECTION FIVE

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APPENDIX A

GC<sup>2</sup>/MS ANALYSIS OF AROMATIC  
FRACTION OF LAGOMEDIO CRUDE OIL

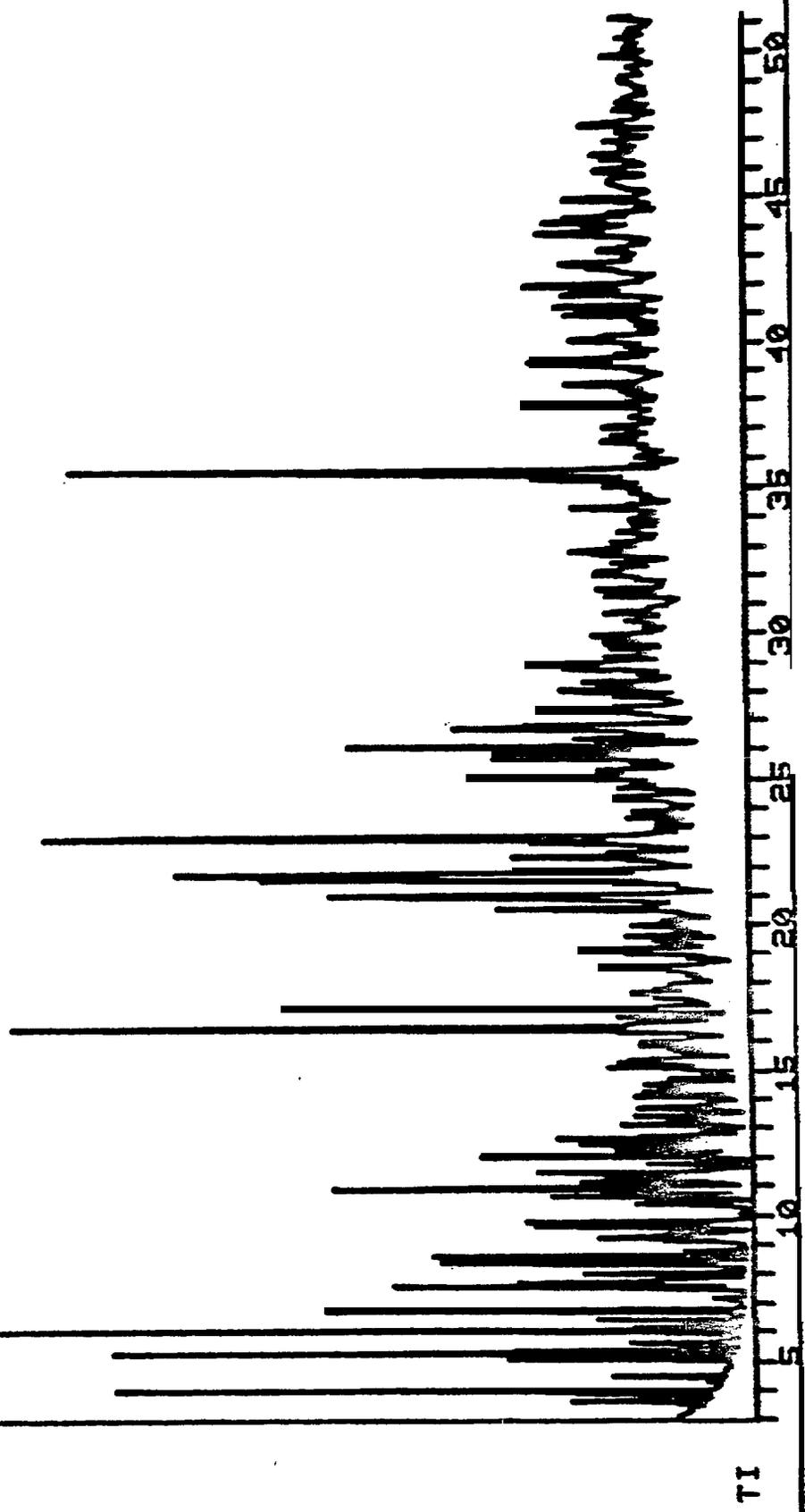
Key to mass spectral searches:

<u>m/e</u>	<u>Compound</u>
120	<b>C<sub>3</sub> alkyl benzenes</b>
134	<b>C<sub>4</sub> alkyl benzenes</b>
148	<b>C<sub>5</sub> alkyl benzenes</b>
128	Naphthalene (N)
142	<b>C<sub>1</sub> N</b>
156	C <sub>2</sub> N
170	C <sub>3</sub> N
184	<b>C<sub>4</sub> N</b>
188	Deuterated anthracene ( internal standard)
184	Dibenzothiophene ( <b>DBT</b> )
198	<b>C<sub>1</sub> DBT</b>
212	C <sub>2</sub> DBT
226	C <sub>3</sub> DBT
154	<b>Biphenyl</b>
166	<b>Fluorene (F)</b>
180	<b>C<sub>1</sub> F</b>
194	C <sub>2</sub> F
208	C <sub>3</sub> F
202	Fluoranthene/pyrene
178	Phenanthrene (P)
192	<b>C<sub>1</sub> P</b>
206	<b>C<sub>2</sub> P</b>
220	C <sub>3</sub> P
234	C <sub>4</sub> P
228	<b>Benzanthracene/chrysene</b>
252	<b>Benzopyrenes</b>

APPENDIX A: GC/MS OF LAGOMEDIO CRUDE AROMATICS

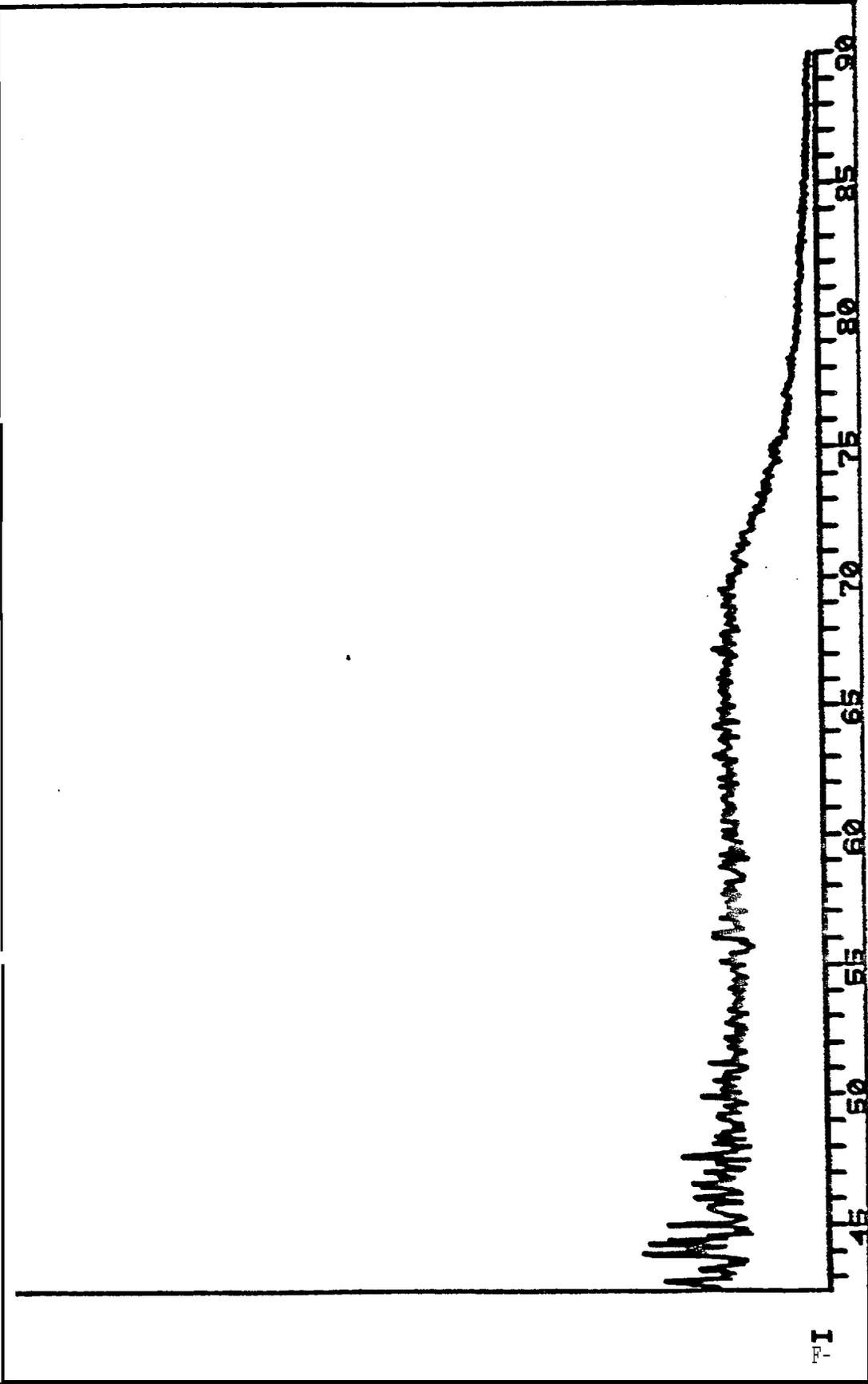
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X= .25 Y= 2.00

TOTAL ION



FRN 14735  
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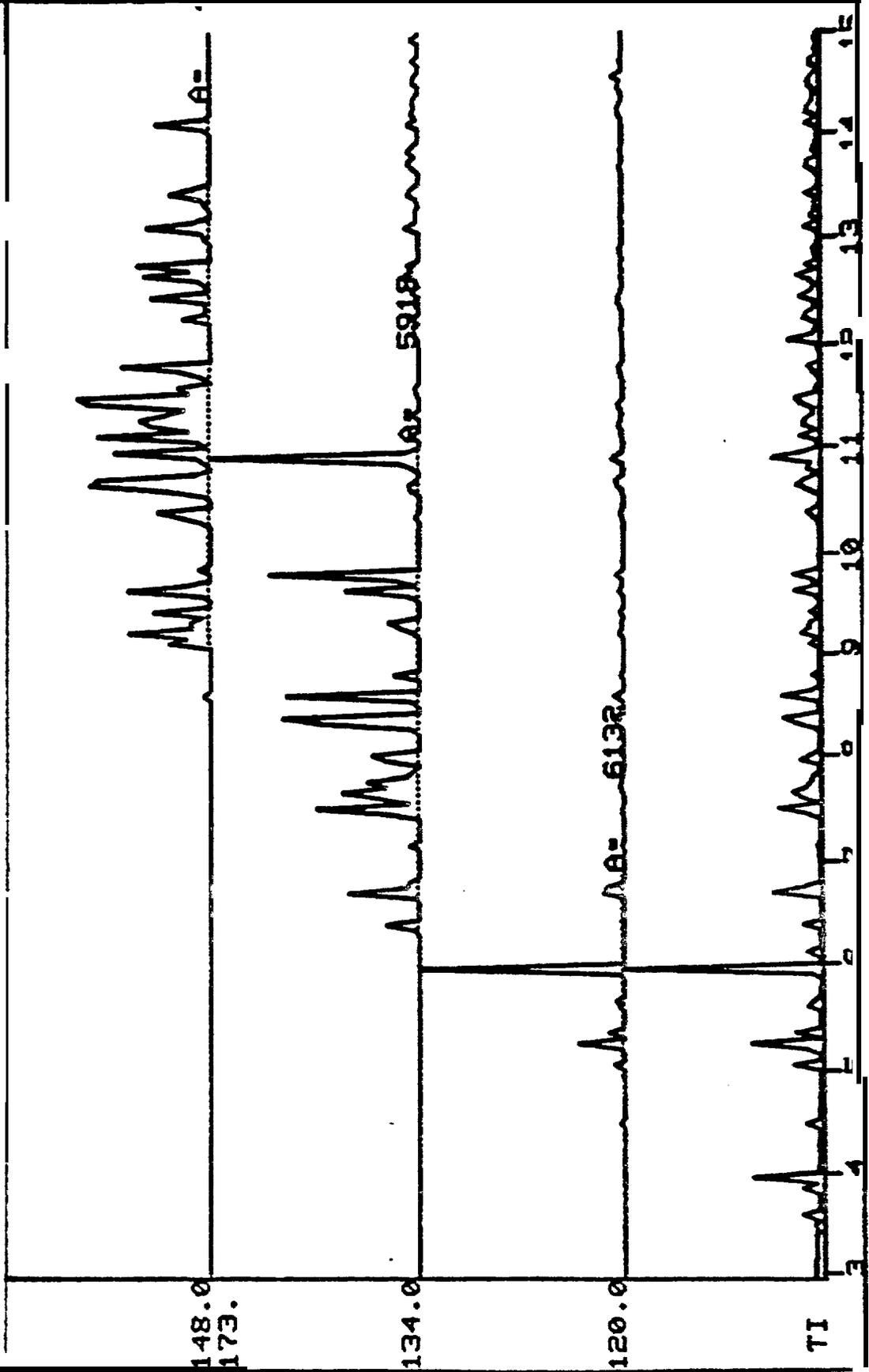


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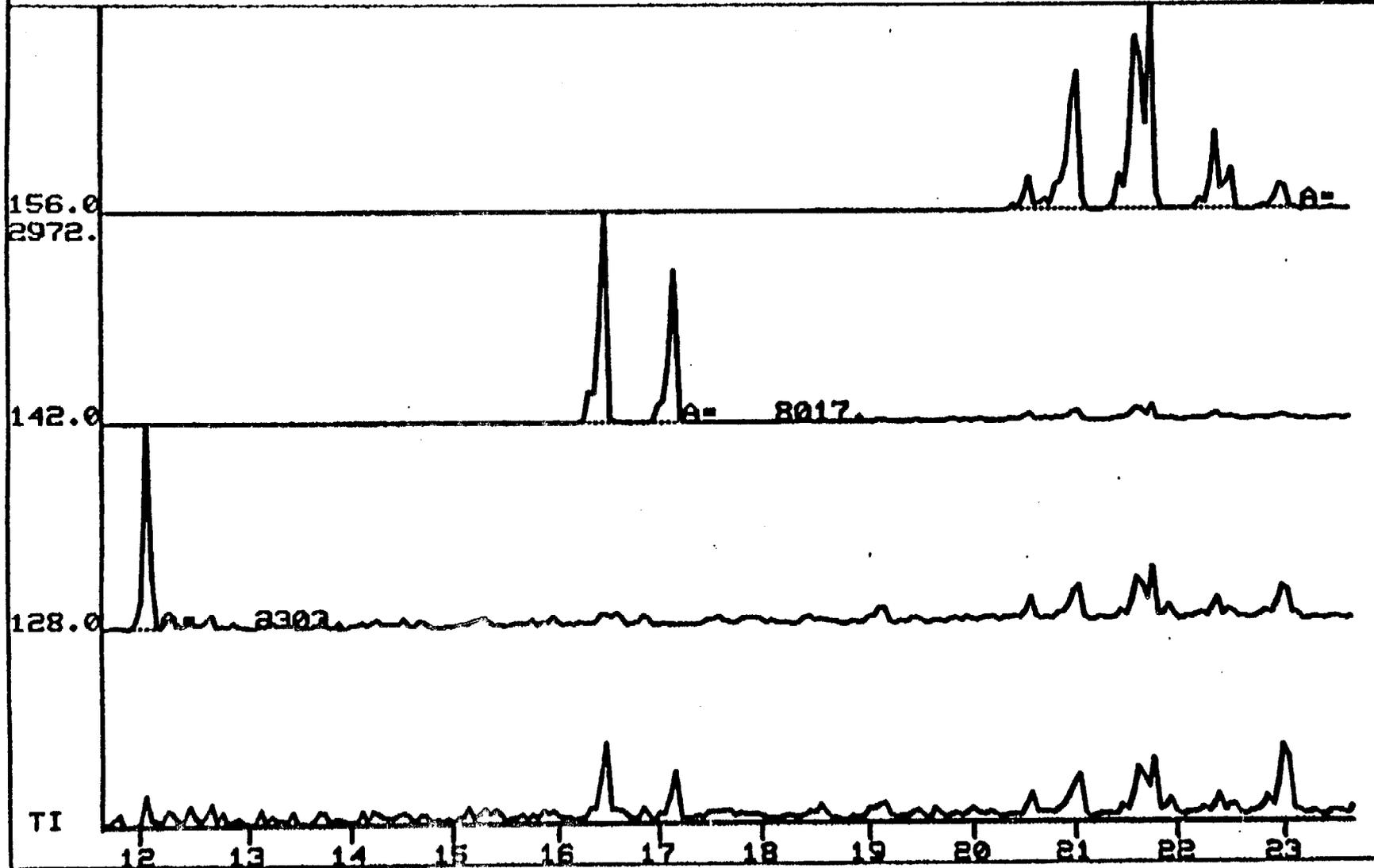


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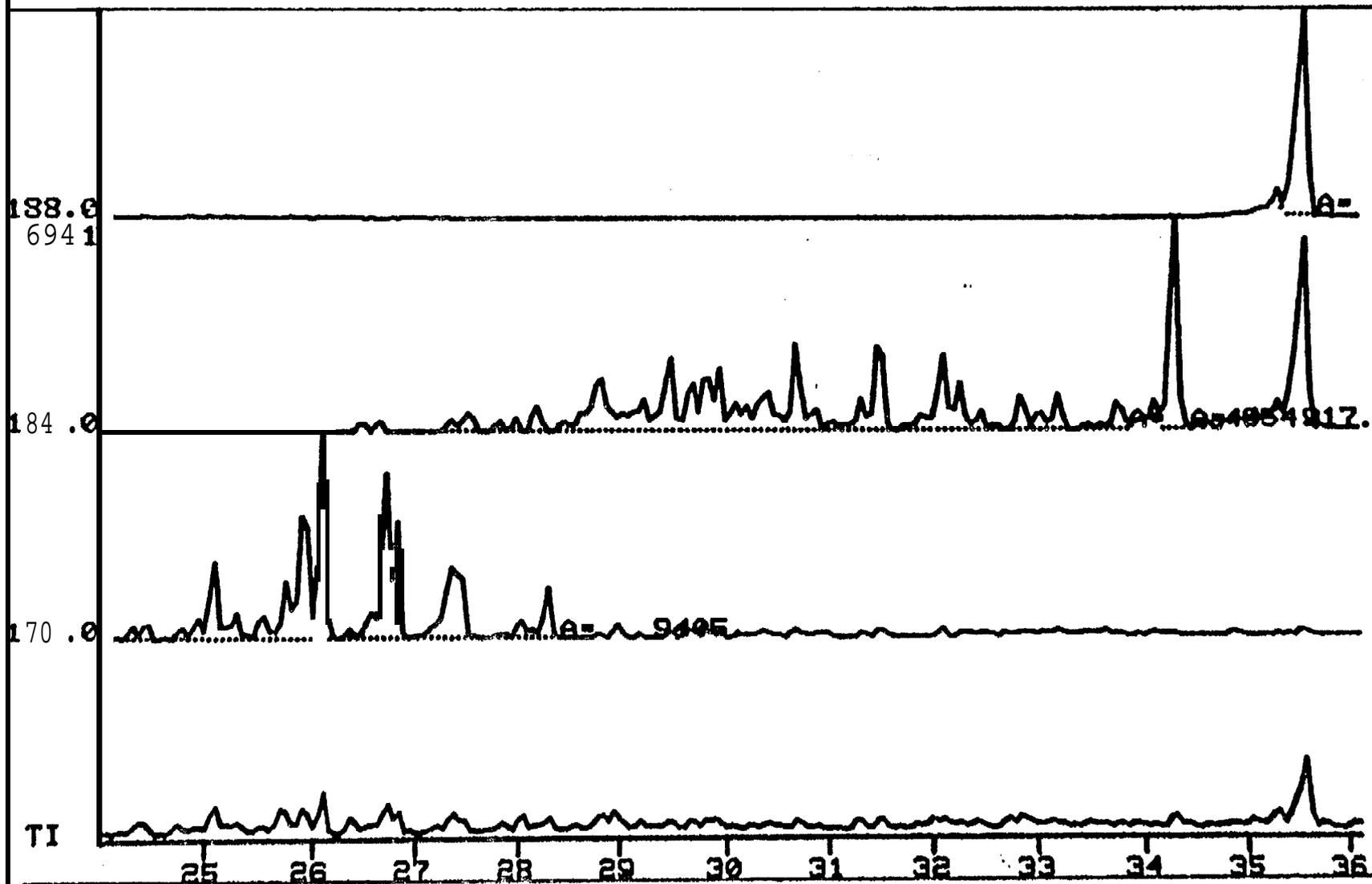


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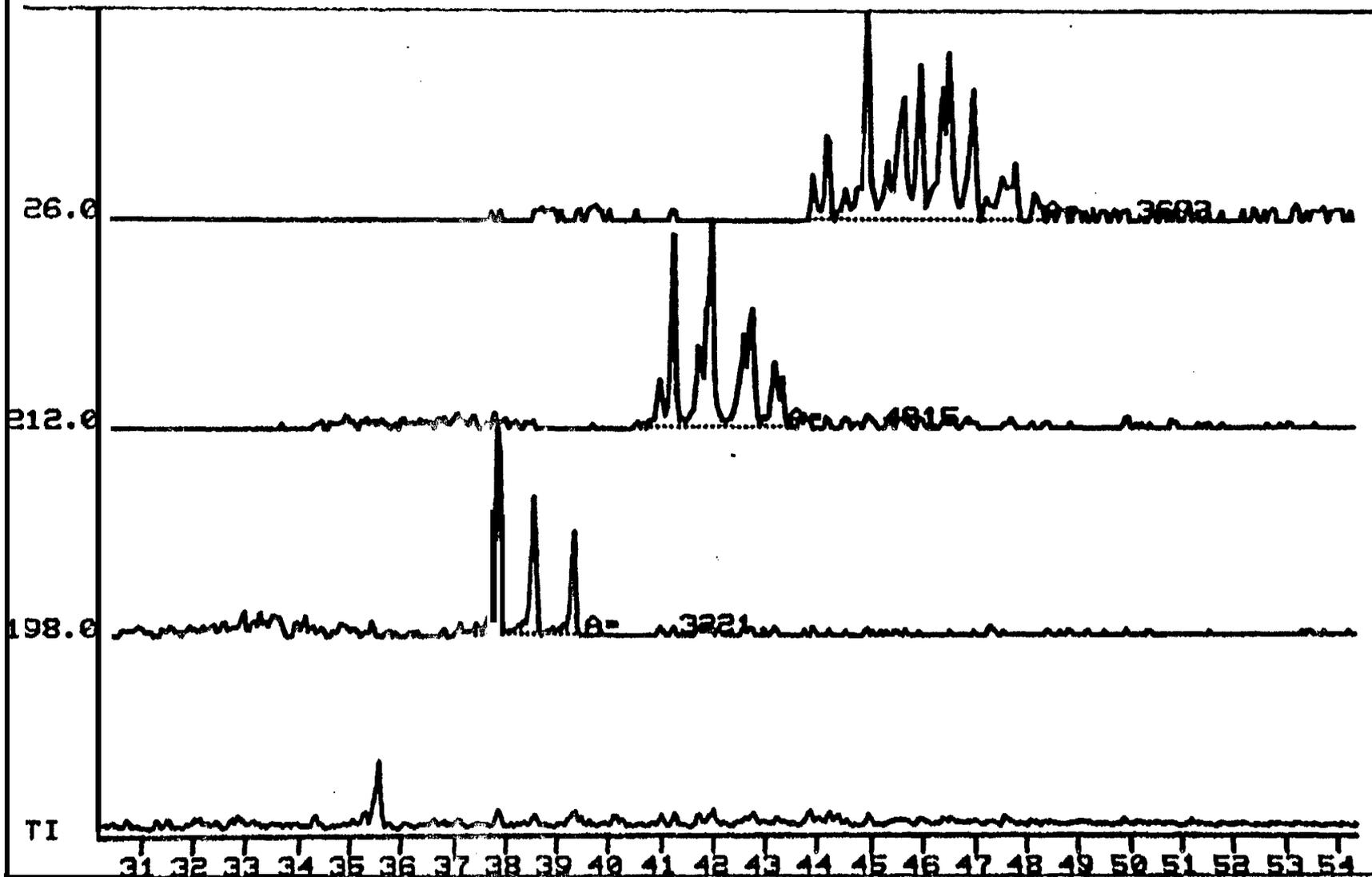


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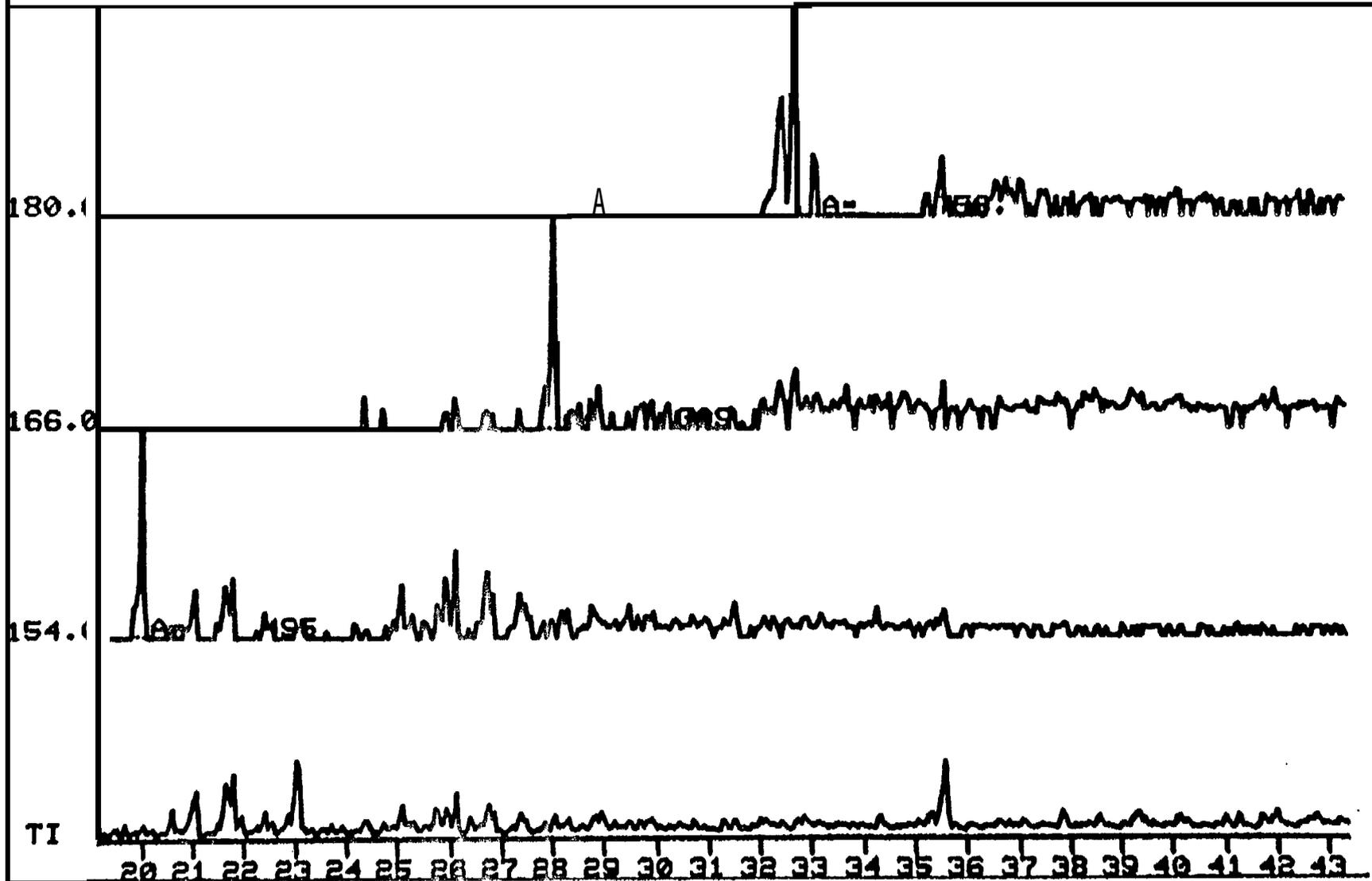
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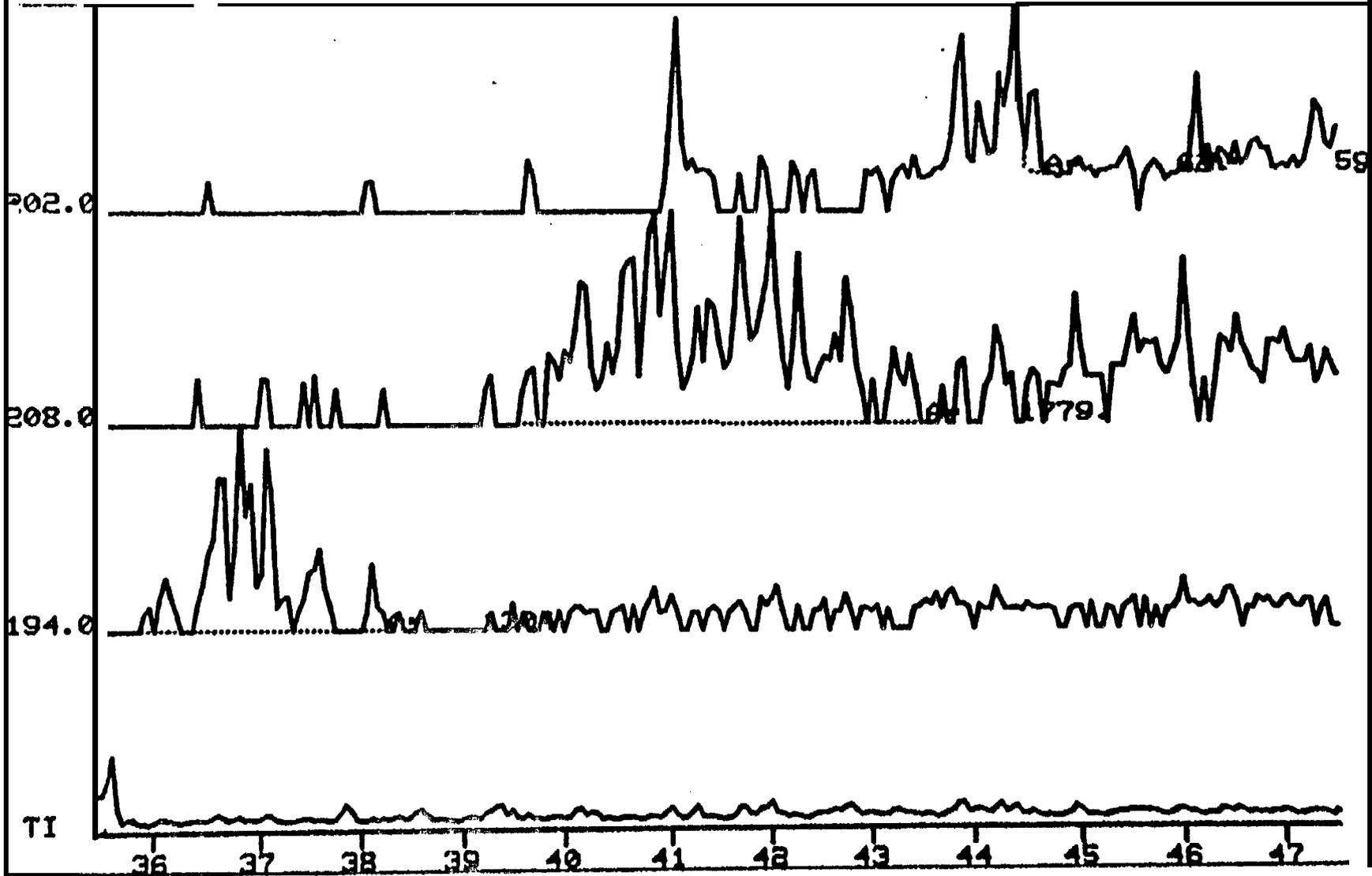
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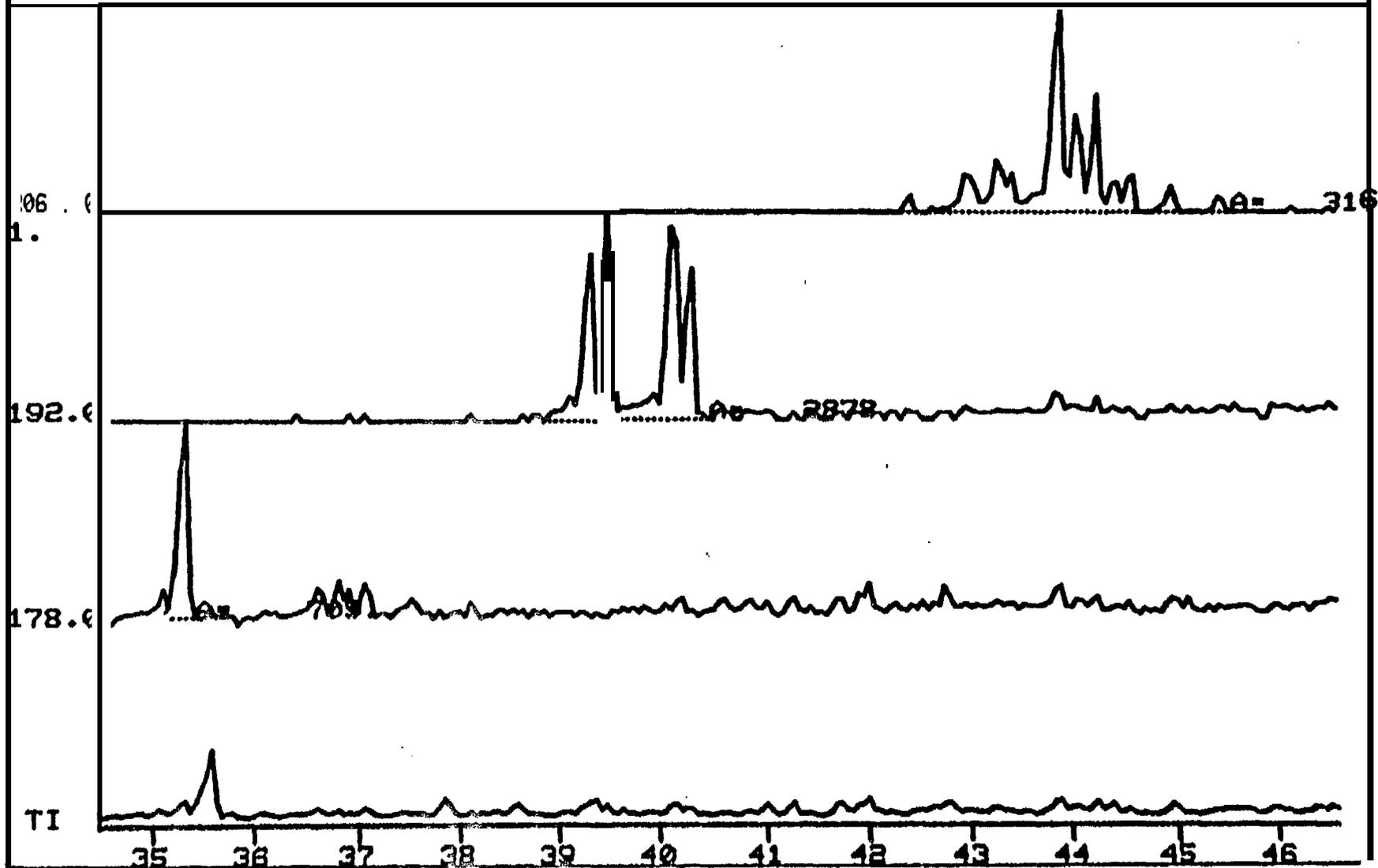
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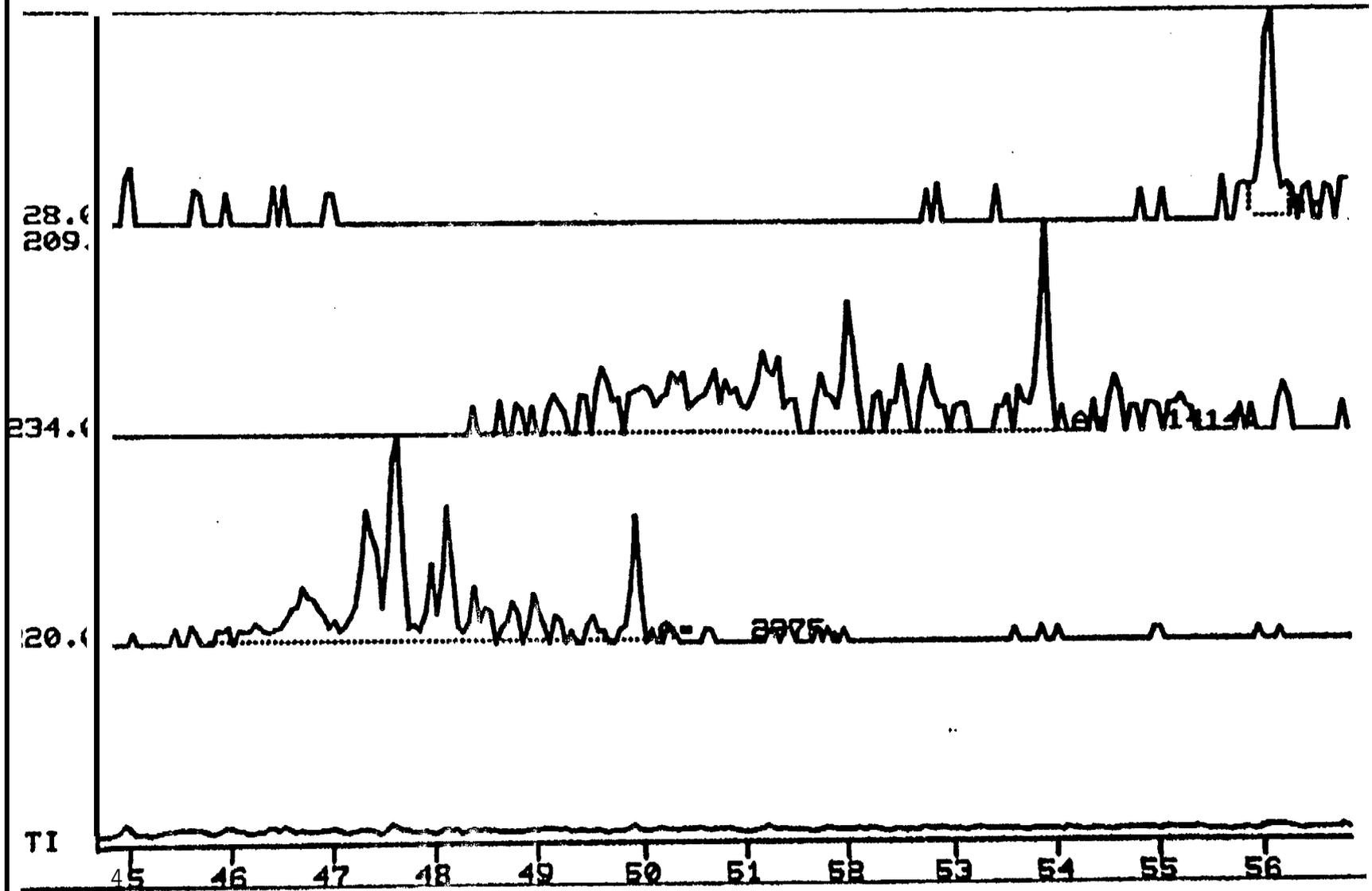
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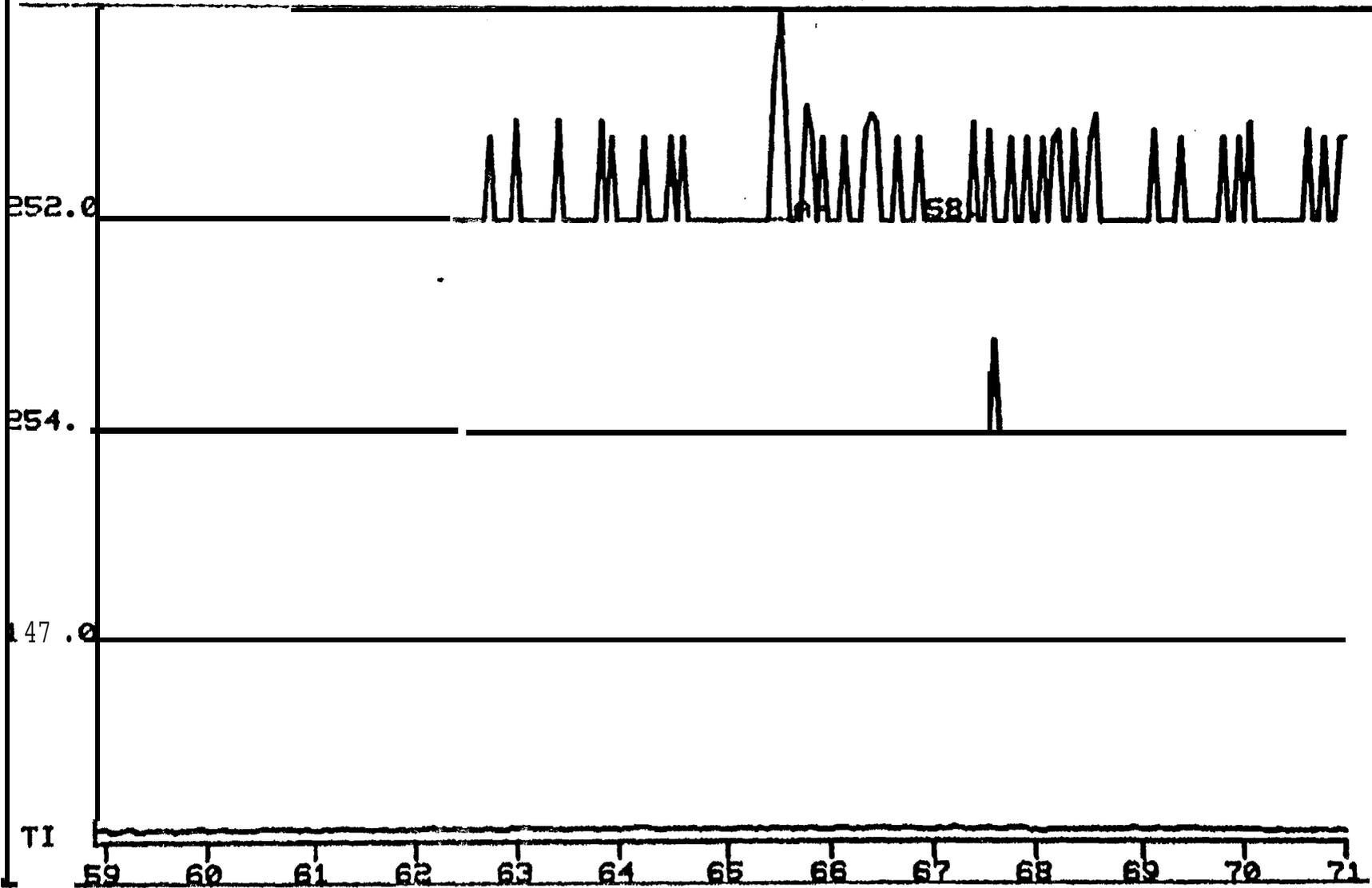
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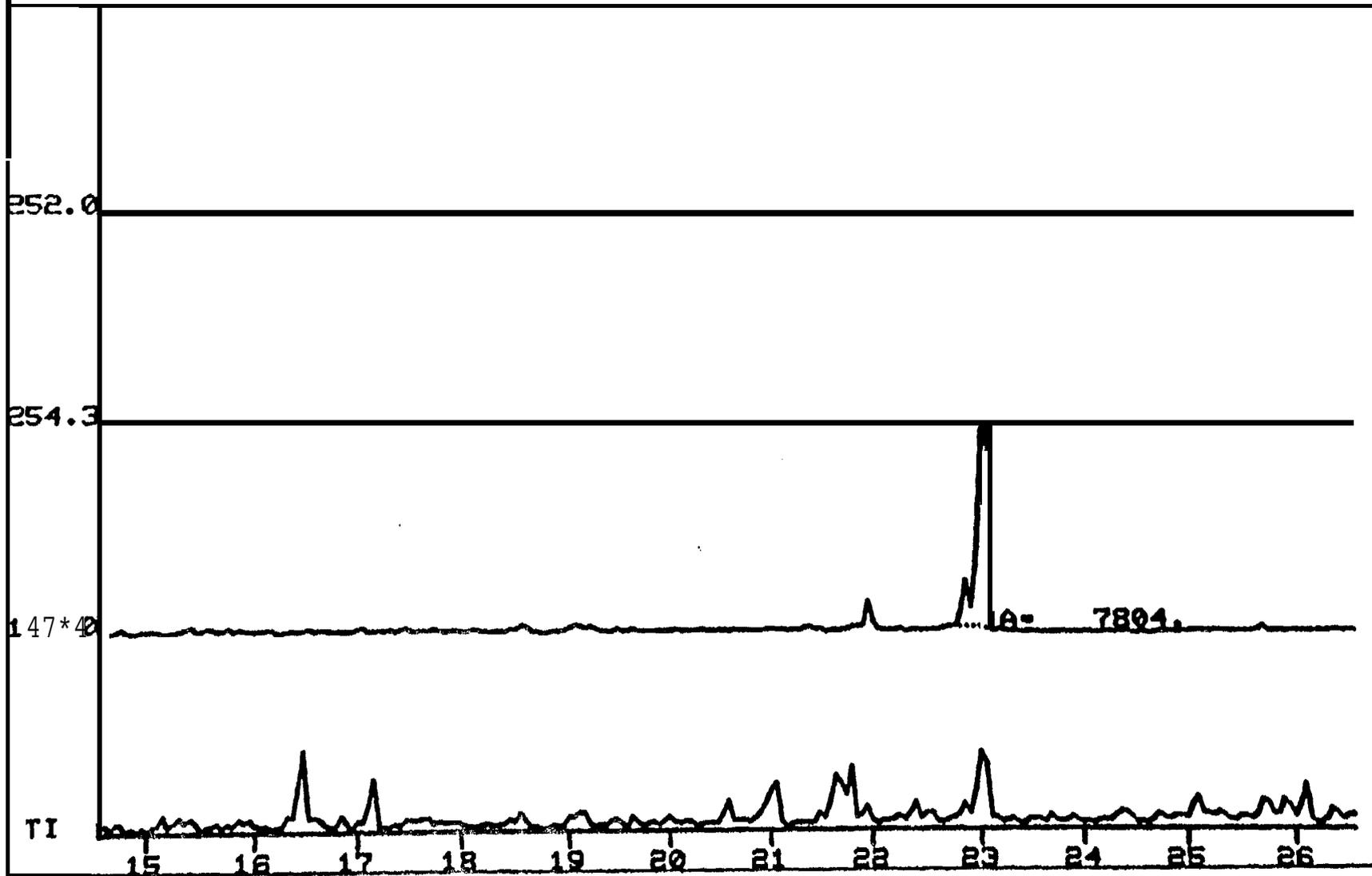


b

\*\* SPECTRUM DISPLAY/EDIT \*\*

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FILE NUMBER 14735

ENTRY	TIME	MASS	AREA	%
1	35.6	188.0	7078.	100.00
2	30.7	184.0	4780.	6?. 54
3	34*3	184.0	879.	12.42
4	26.2	170.0	9415.	133.02
5	12.0	128.0	2303.	32.54
6	16. S	142.0	8017.	113.27
7	21.8	156.0	12972.	183.27
8	20.0	154.0	517.	7.30
9	28.1	166.0	309.	4*37
10	32.7	180.0	730.	10.32
11	36.8	194.0	1304.	18.42
12	41*1	208.0	1779.	25.13
13	44.6	202.0	62.	.88
14	46.2	202.0	59.	.83
15	3s.3	178.0	709.	10. 02
16	39.5	192.0	2878.	40 .66
17	43.9	206 .0	3161.	44,66
18	23.1	147.0	8075.	114.10

CAL %ON ENTRY?

FILE NUMBER 14735

ENTRY	TIME	MASS	AREA	%
1	66.4	252.0	35 .	.49
2	65.8	2s2 .0	34 .	.48
3	65*S	252.0	58.	.82
4	23.1	147.0	7985 .	112.82
5	4?.6	220.0	237s .	33.56
6	53.9	234 .0	1414.	19.97
?	S6.1	228 .0	209.	2.9s
8	37*9	198.0	3221.	45.50
9	42.0	212.0	4815.	68 .03
10	45.0	226 .0	3693.	52* 17
11	6.0	120.0	6132.	86 .64
12	10.9	134.0	5918.	83.62
13	11.5	148.0	4173.	58 .95
14	35.6	188.0	7078.	100.00

CAL % ON ENTRY?

FILE NUMBER 14735

ENTRY	TIME	MASS	AREA	%
1	3S.6	188.0	7078.	87.65
2	30.7	184.0	4780.	59.20
3	34*3	184.0	879.	10.88
4	26.2	170.0	9415.	116.59
5	12.0	128.0	2303.	28.52
6	16.5	142.0	8017.	99.28
7	21.8	156.0	12972.	160.63
8	20.0	154.0	517.	6.40
9	28.1	166.0	309.	3.83
10	32.7	180.0	730.	9.04
11	36.8	194.0	1304.	16.15
12	41*1	208.0	1779.	22.03
13	44*6	202.0	62.	*77
14	46.2	202.0	59.	.73
15	35*3	178.0	709.	8.78
16	39*5	192.0	2878.	35.64
17	43.9	206.0	3161.	39*14
18	23.1	147.0	8075.	100.00

CAL % ON ENTRY?

FILE NUMBER 1473S

ENTRY	TIME	MASS	AREA	%
1	66.4	252.0	35.	.44
2	65.8	252.0	34.	.43
3	65.5	252.0	58.	.72
4	23.1	147.0	7985.	100.00
s	47.6	220.0	2375.	29.7s
6	53*9	234.0	1414.	17.70
7	S6.1	228 .@	209.	2.61
8	37.9	198.0	3221.	40.33
9	42.0	212.0	4815.	60.31
10	45.0	226,0	3693.	46.25
11	6.0	120.0	6132.	76.79
12	10*9	134.0	5918.	74.12
13	11.5	148.0	4173.	52.26
14	35.6	188.0	7078.	80,64

CAL % ON ENTRY?

APPENDIX B

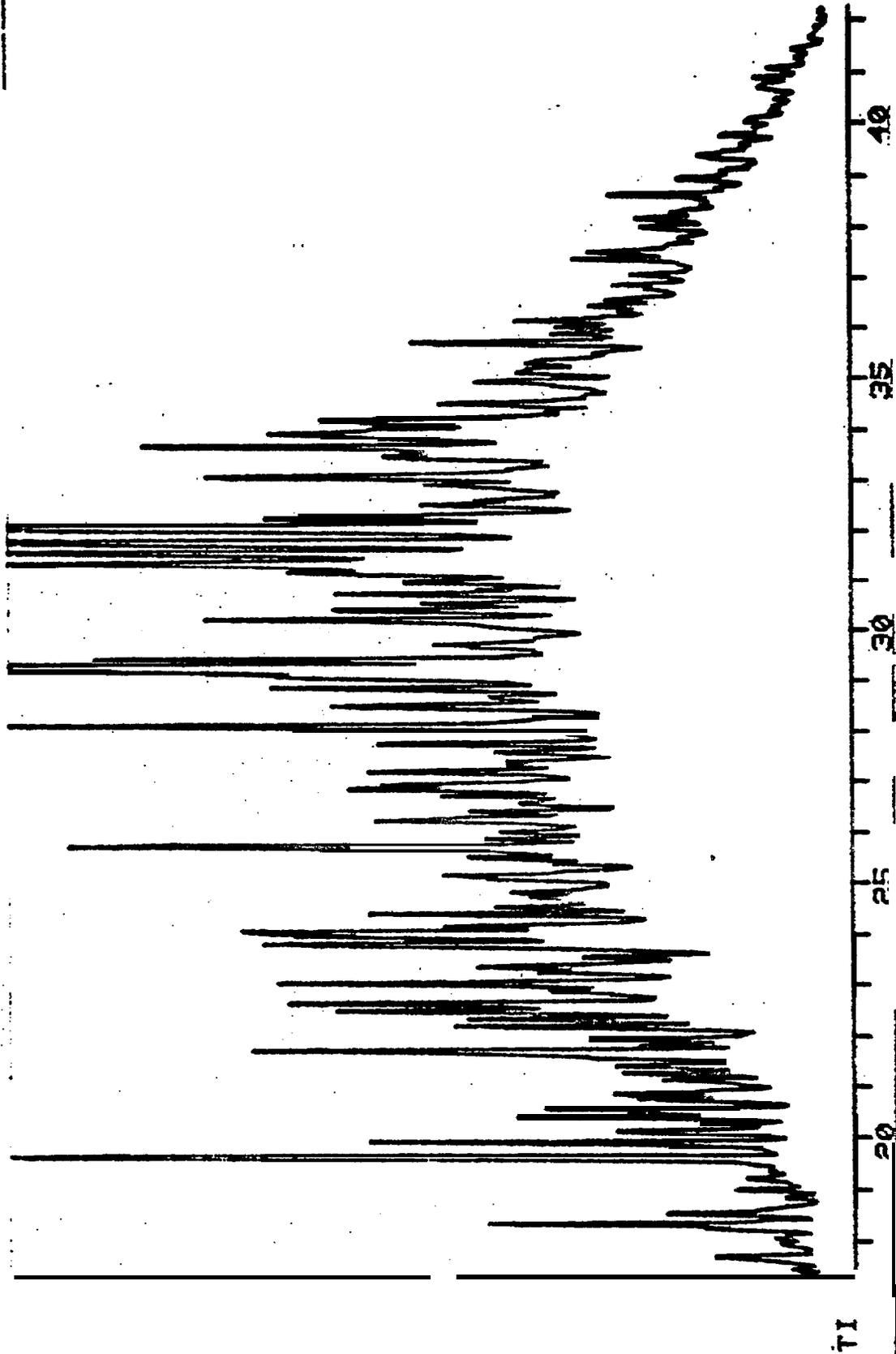
GC<sup>2</sup>/MS ANALYSIS OF AZAARENE  
FRACTION OF LAGOMEDIO CRUDE OIL

Key to mass spectral searches:

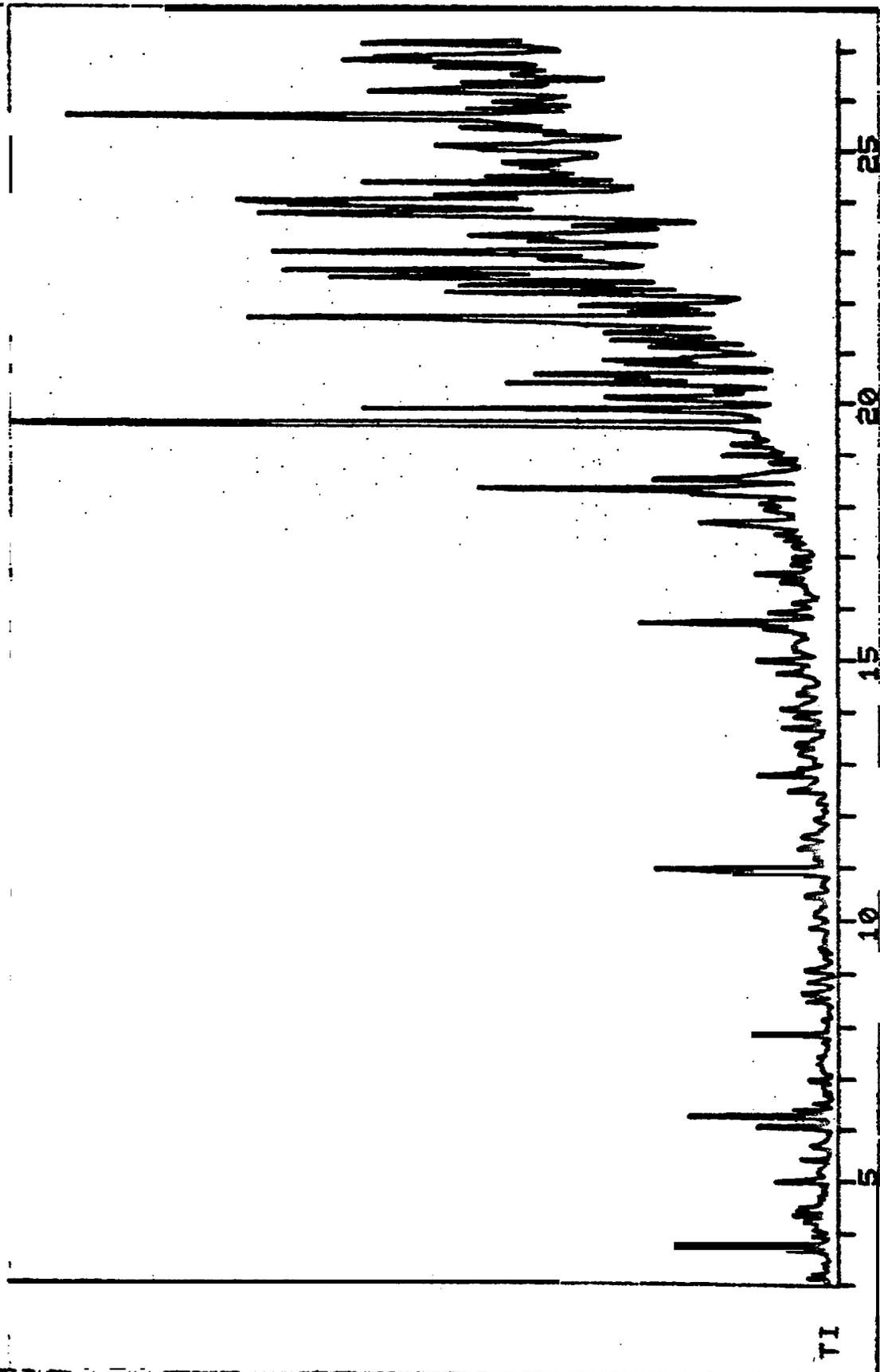
<u>m/e</u>	<u>Compound</u>
129	Quinoline, isoquinoline (Q)
143	C <sub>1</sub> Q
157	C <sub>2</sub> Q
171	C <sub>3</sub> Q
185	C <sub>4</sub> Q
199	C <sub>5</sub> Q
213	C <sub>6</sub> Q
179	Acridine/phenanthridine (AP)
193	C <sub>1</sub> AP
207	C <sub>2</sub> AP
221	C <sub>3</sub> AP
235	C <sub>4</sub> AP
249	C <sub>5</sub> AP
167	Carbazole (C)
181	C <sub>1</sub> C
195	C <sub>2</sub> C
209	C <sub>3</sub> C
223	C <sub>4</sub> C
229	Benzacridine (BA)
243	C <sub>1</sub> BA
257	C <sub>2</sub> BA

BIOS 06-1100-04 1UL/20UL 2200U TH=10 A/D=2  
30M SE=52FS 6JAN81 60-29005/MIN 46-346AM  
XX SPECTRUM DISPLAY/EDIT \*\*

FRN 16308  
1ST SC/PG: 560  
X= .25 Y= 2.00



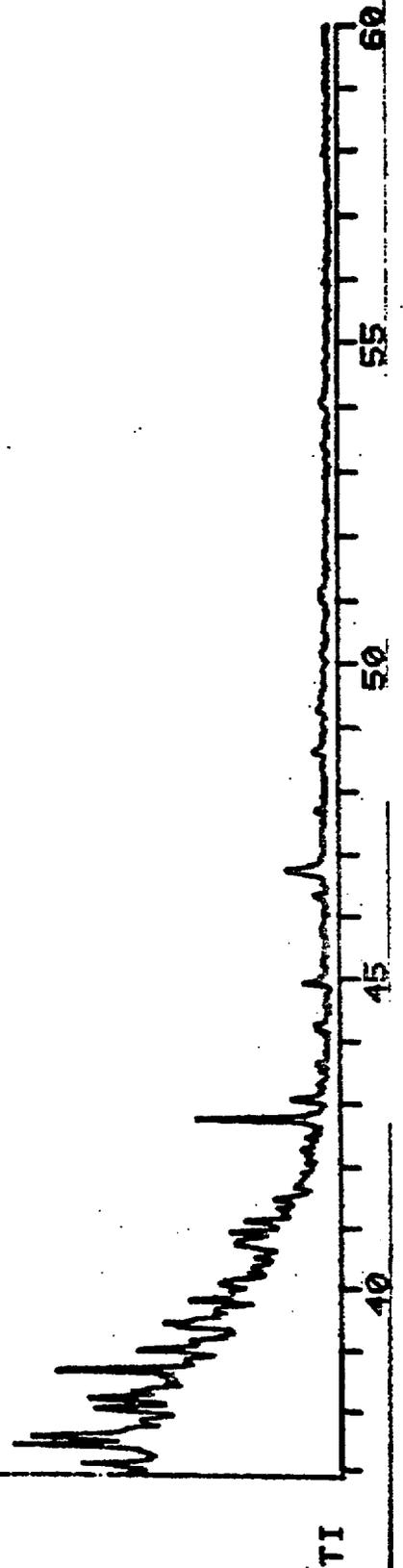
BIOS 03-1100-04 1UL/20UL 2200V TH-10 A/D-2  
30M SE-52FS 6JAN81 60-230@5/MIN 46-346AM  
\*\* SPECTRUM DISPLAY/EDIT \*\*  
FRN 16308  
1ST SC/PG: 1  
X- .25 Y- 2.00



TI

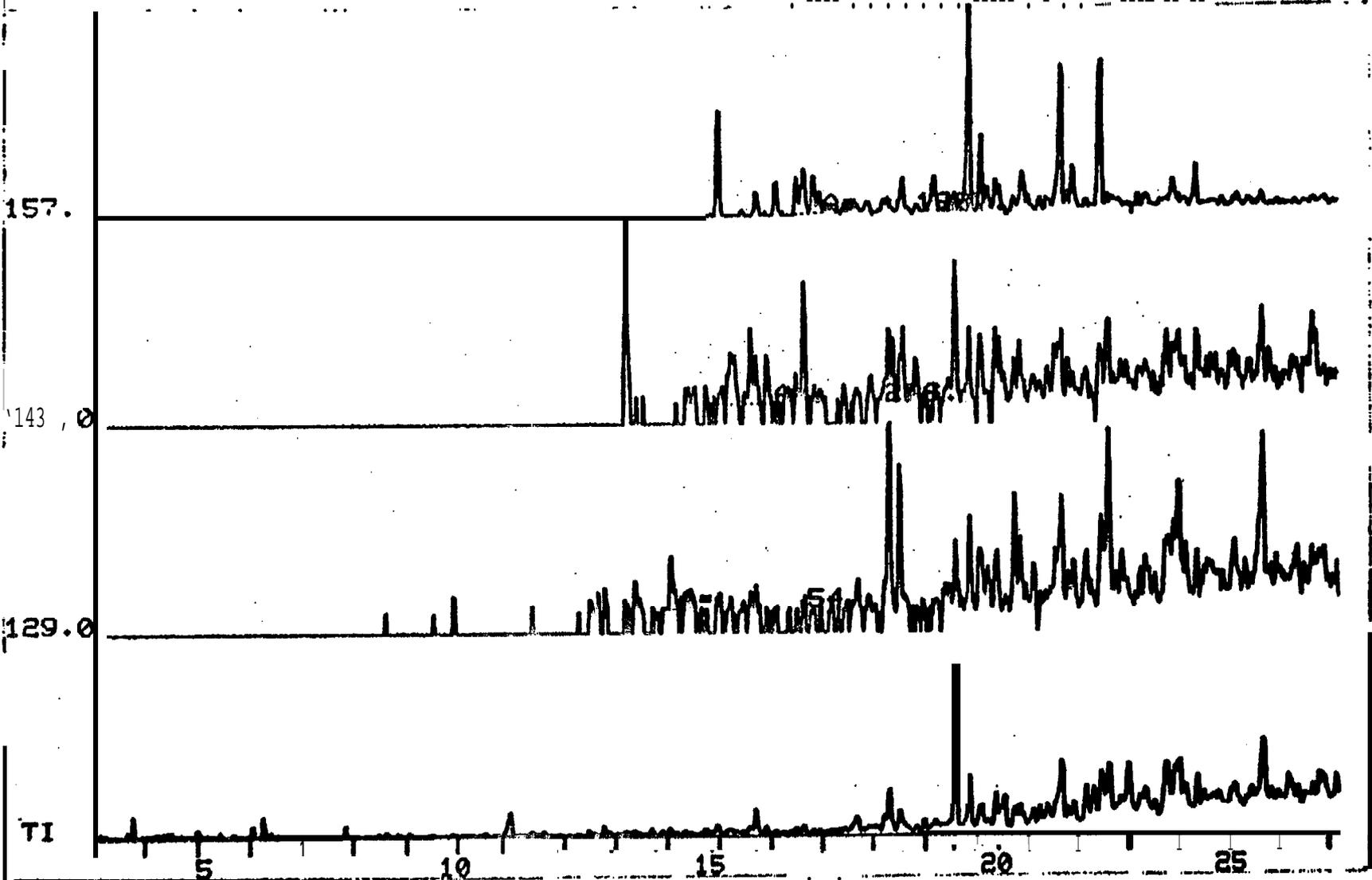
FKN 16308  
1ST SC/PG:1291  
X- .25 Y- 2.00

\*X SPECTRUM DISPLAY/EDIT \*X  
BIOS 06-1100-04 1UL/20UL 2200U TH-10 A/D-2  
30M SE-52FA 6JAN81 00 29005/MIN. 46-346AM



YK SPEC 1%. IN DIS PLAY EDI. XX  
BIOS W- I 100-041UL/20UL 2200U TH= 10 A/D=2  
30M SE -52FS 6JAN81 60-29005/MIN 46-346AM

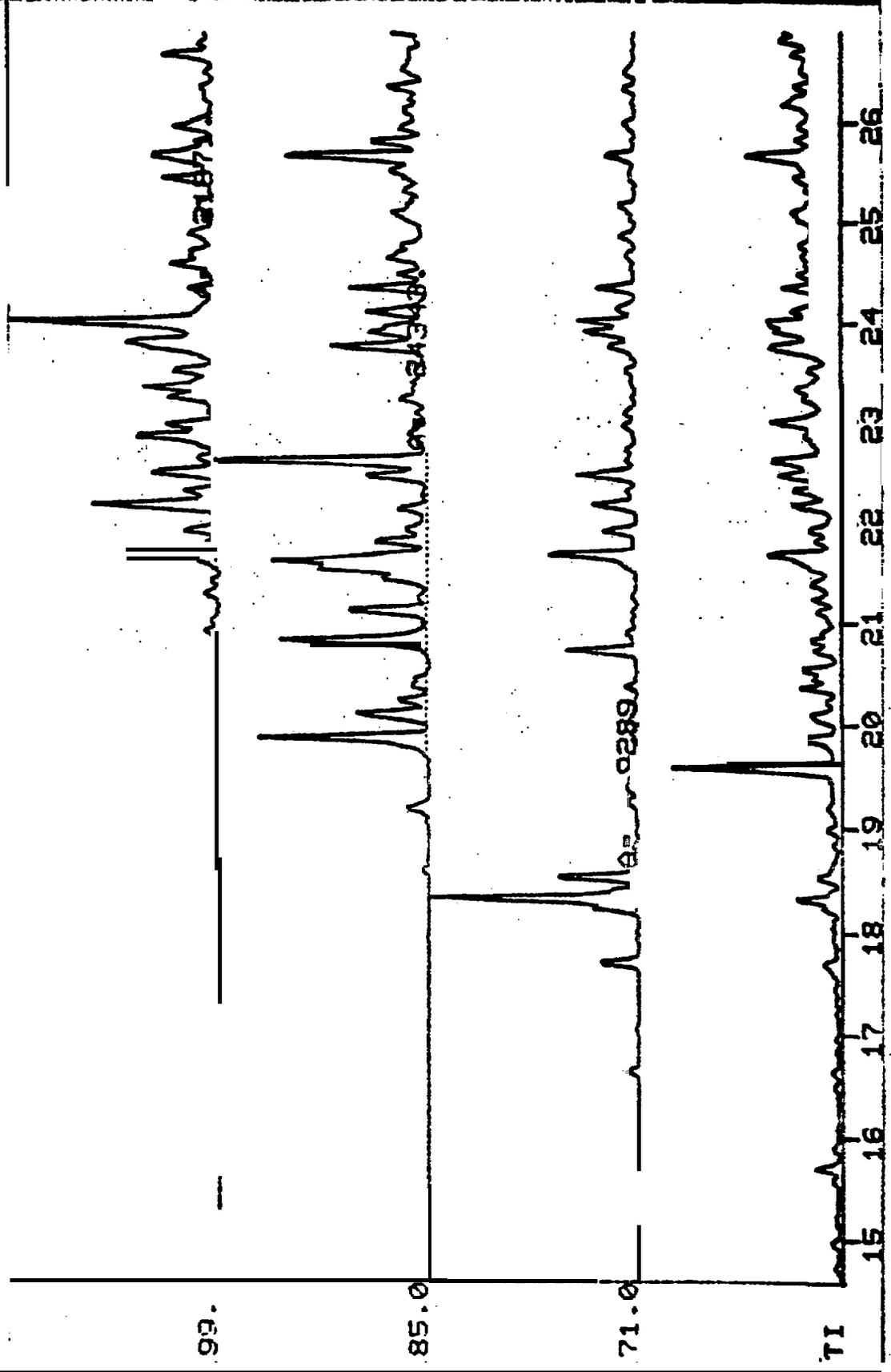
FRN 16308  
157 SC/PG: 1  
X= .25 Y= 1.00



\*\* SPECTRUM DISPLAY EDIT \*\*

FRM 16308  
1ST SC/PG: 455  
X- .50 Y- 1.00

BIDS 06-1100-04 1UL-20UL 2200U TH-10 A/D-2  
30M SE-52FS 6JAN81 50-23005/MIN 46-346AM



\*X SPECTRUM DISPLAY/EDIT \*X

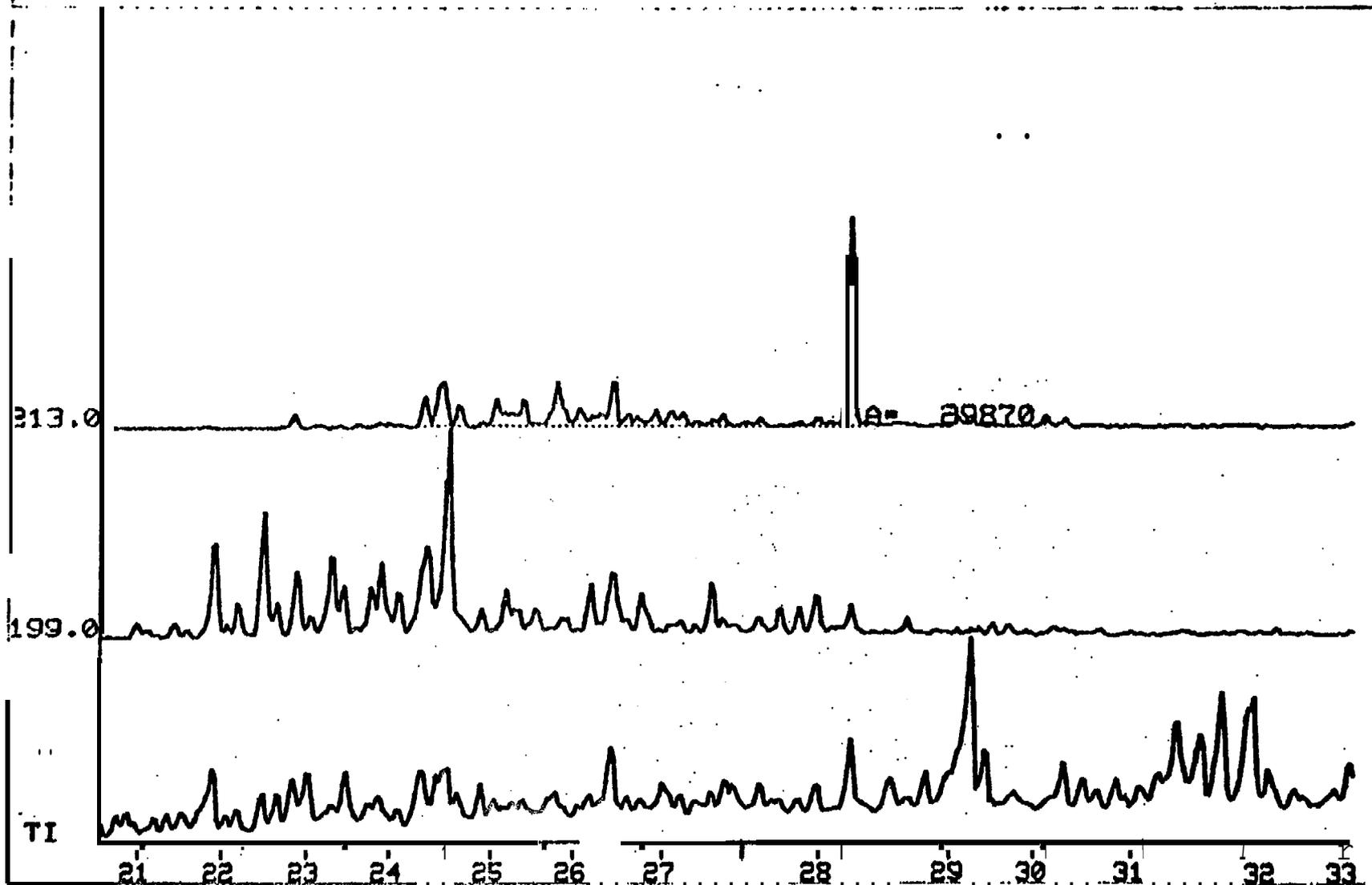
FRN 16308

BIOS 06-1100-04 1UL/20UL 2200U TH=10 A/D=2

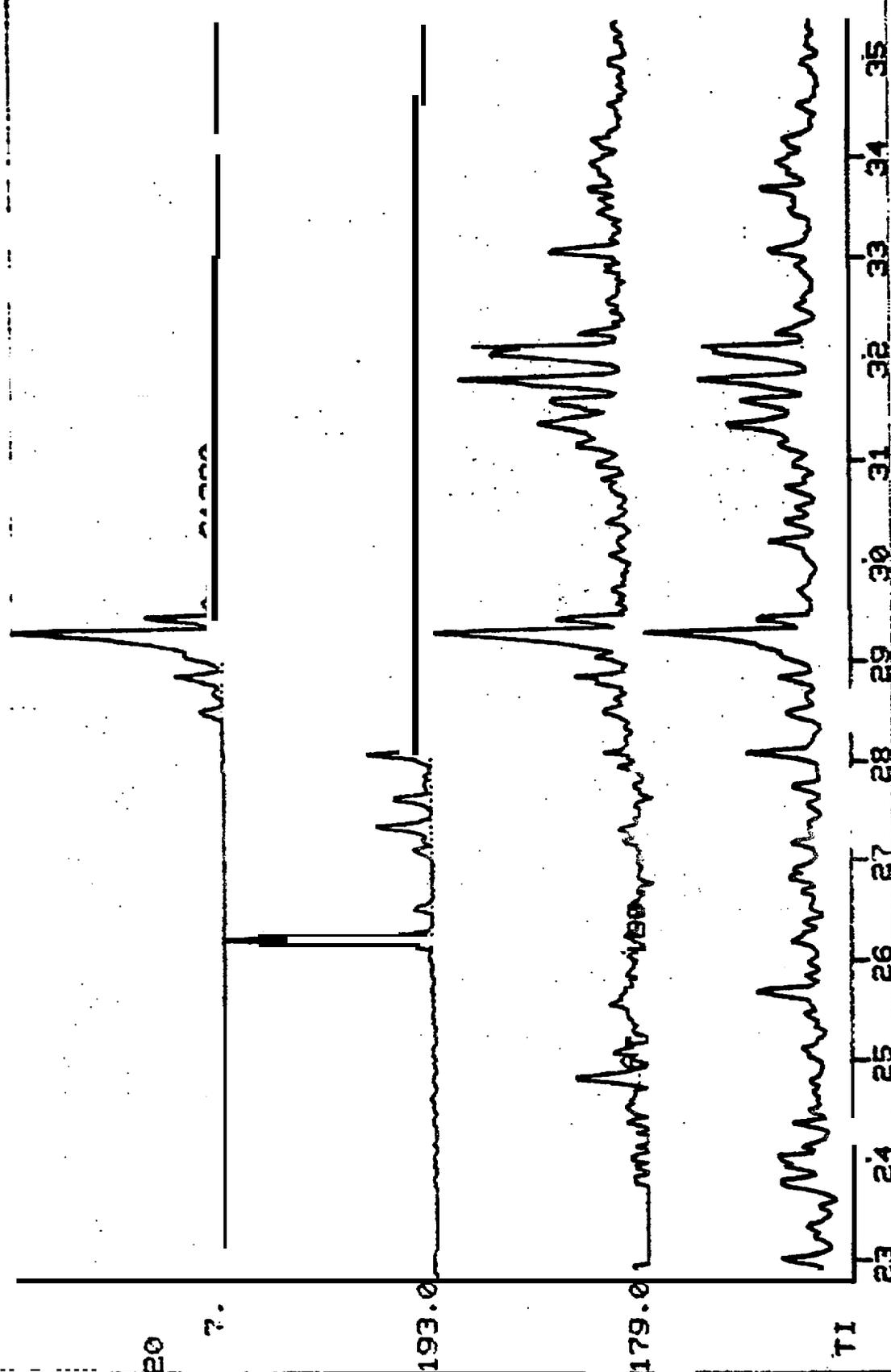
1ST SC/PG: 685

30M SE-52FS 6JAN81 50-29005/MIN 46-346AM

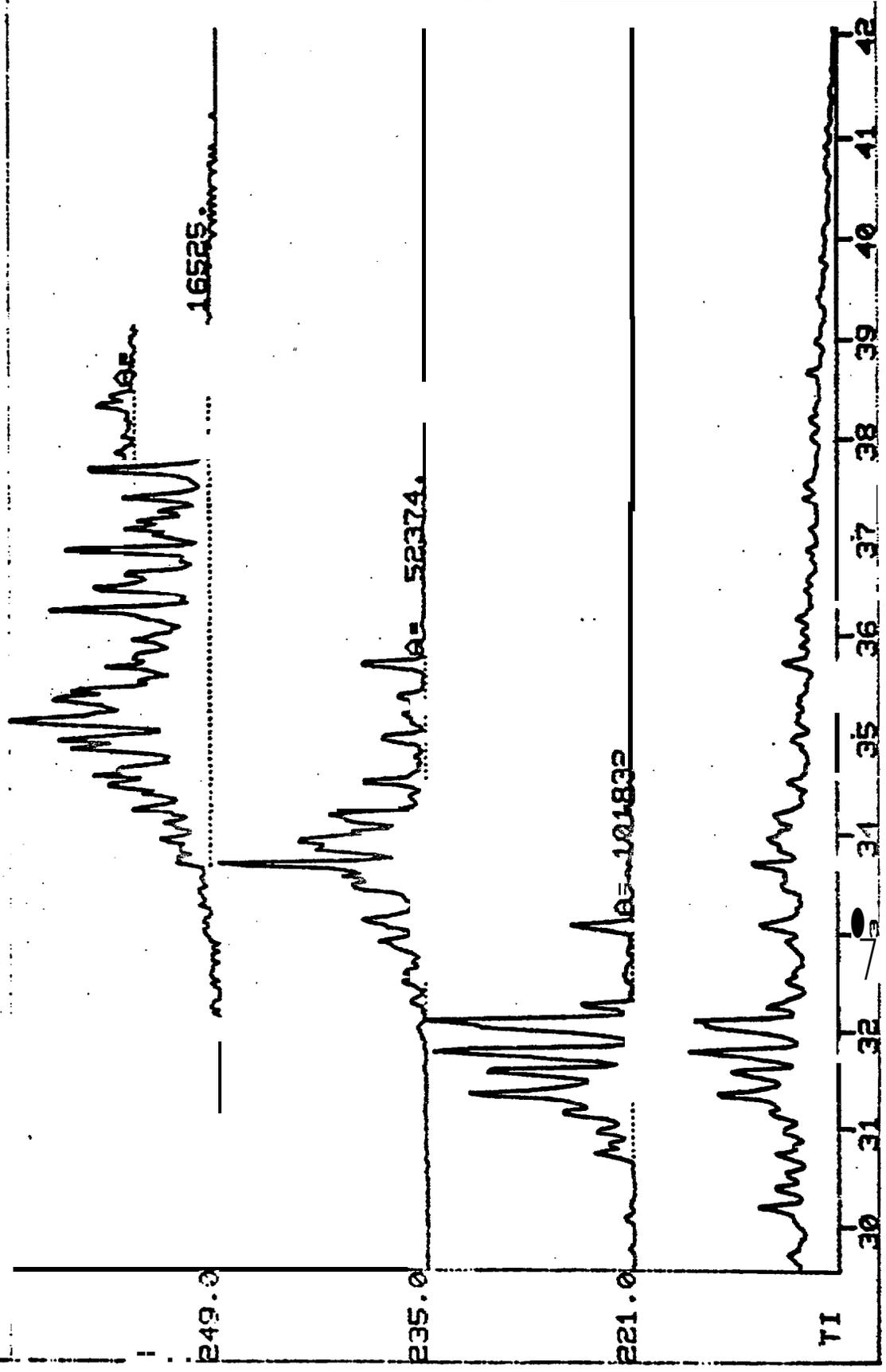
X= .50 Y= 1.00



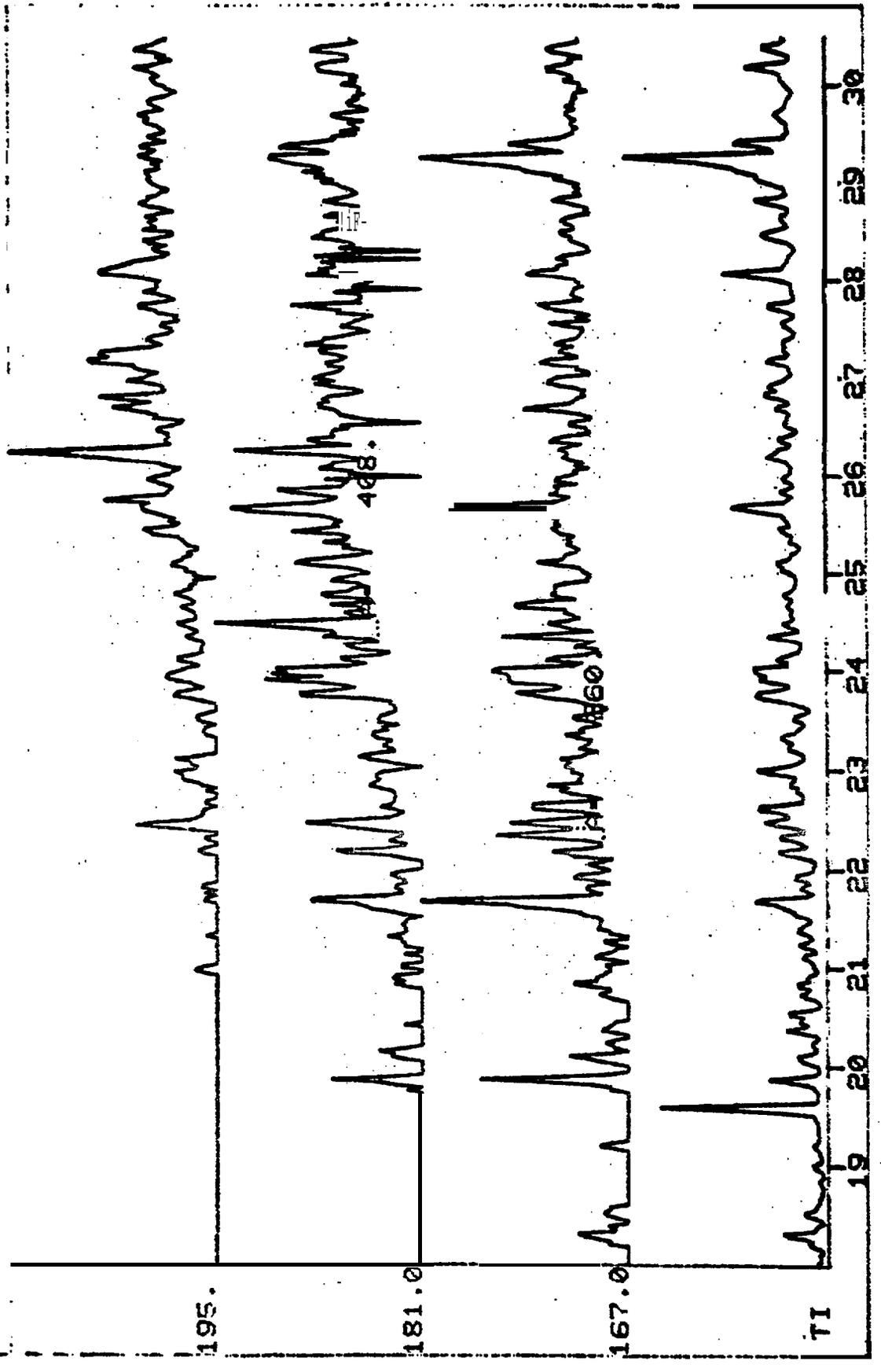
BIOS 06-1100-04 1UL/20UL 2000V TH-10 A/D-2  
30M SE-52FS 6JHN31 60-29005/MIN 46-346AM  
\*\* X SPECTRUM DISPLAYED \*\*  
FRM 16308  
1ST SC-PG: 769  
X- .50 Y- 1.00



XX SPECTRUM DISPLAY/EDIT XX  
FRN 16308  
R105 06-1100-04 JUL/20UL 2200U TH=10 A/D=2  
30M SE-52FS 6JAN81 60-29005.MIN 46-346AM  
X= .50 Y= 1.00

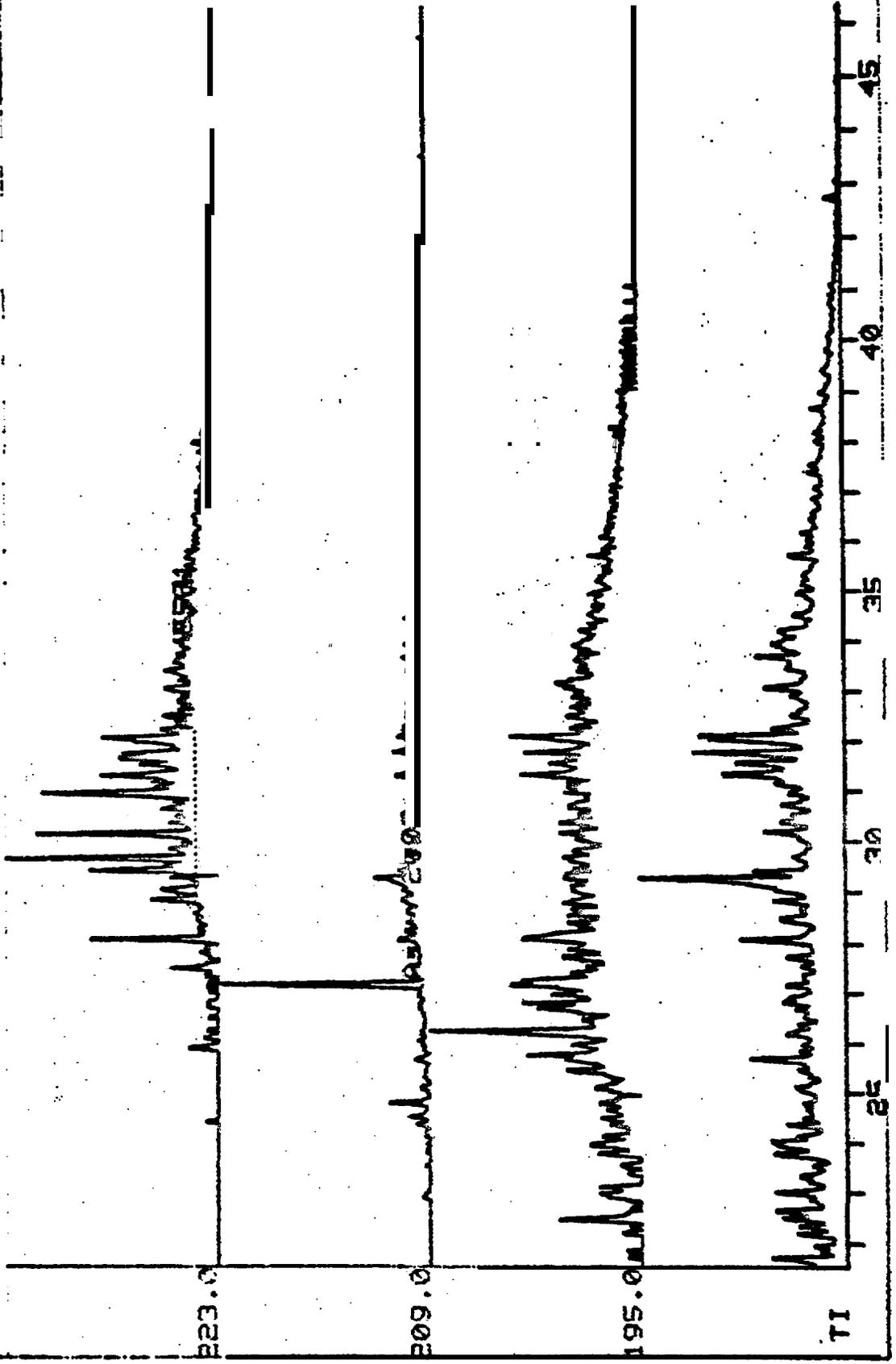


XX SPECTRUM DISPLAY EDIT XX  
FIRN 16308  
EJUS 06-1100-04 1UL-20UL 2200V TH-10 A/D-2 15F 5C/PG: 588  
30M SE-52FS 6JAN81 60-25005/MIN 46-346AM X. .50 Y. 1.00

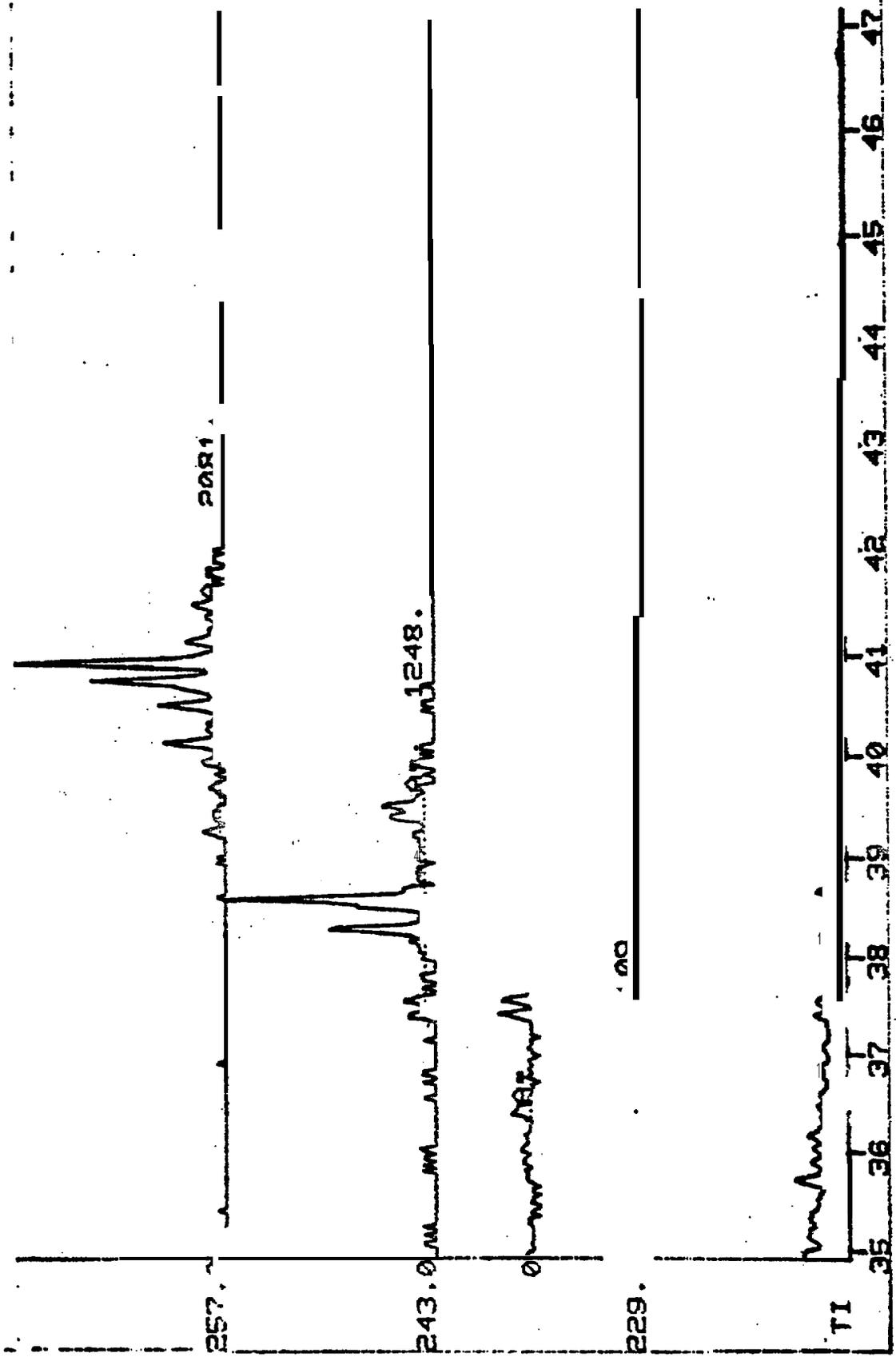


FRN 16308  
:ST 30/PG: 721  
X. .25 Y. 1.00

44 SPECTRUM DISPLAY EDIT \*\*  
R105 06-11:00-04 1UL/20UL 2300U TH-10 A/D-2  
30M SE 52FS 6JAN81 60-2900S/MIN 46-346AM



\*\* SPECTRUM DISPLAY EDIT \*\*  
 FPN 16308  
 06-1100-04 1UL/20UL 2200V TH=10 A/D=2  
 1ST SC/PG:1218  
 30M SE-52FS 6JAN81 60-25005/MIN 46-346AM  
 X= .50 Y= 1.00



FILE NUMBER 16308

ENTRY	TIME	MASS	AREA	%
1	14.0	129.0	54.	.0s
2	15.6	143.0	296.	.29
3	16.7	157.0	1287.	1.26
4	18.3	171.0	9289.	9.12
5	22.6	185.0	24343.	23.90
6	24.0	199.0	21871.	21.48
7	28.1	213.0	29870.	29.33
8	24.8	179-0	169.	.17?
9	26.2	193.0	8092.	7.95
10	29.3	207.0	61390.	60+ 29
11	32.1	221.0	101832.	100.00
12	33.7	238.0	52374.	51.43
13	35.2	249.0	16525.	16.23

CAL % ON ENTRY?

FILE NUMBER 16308

ENTRY	TIME	MASS	AREA	%
1	27.2	209.0	2006.	1.94
2	29.7	223.0	5521.	5.34 <sup>(2)</sup>
3	26.2	195.0	1092.	1.06?
4	22.3	167.0	260.	.25?
5	24.5	181.0	408.	.39?
6	36.4	229.0	109.	.11
7	38.6	243.0	1248.	1.21
8	40.9	257.0	2081.	2.01
9	32.1	221.0	103353.	100.00
10	32.1	221.0	100268.	97.01

CAL % ON ENTRY?

FILE NUMBER 16308

ENTRY	TIME	MASS	AREA	%
1	27.2	209.0	2006.	1.94
2	29.7	223.0	5521.	5.34 <sup>(2)</sup>
3	26.2	195.0	1092.	1.06?
4	22.3	167.0	260.	.25?
5	24.5	181.0	408.	.39?
6	36.4	229.0	109.	.11
7	38.6	243.0	1248.	1.21
8	40.9	257.0	2081.	2.01
9	32.1	221.0	103353.	100.00
10	32.1	221.0	100268.	97.01

CAL % ON ENTRY?