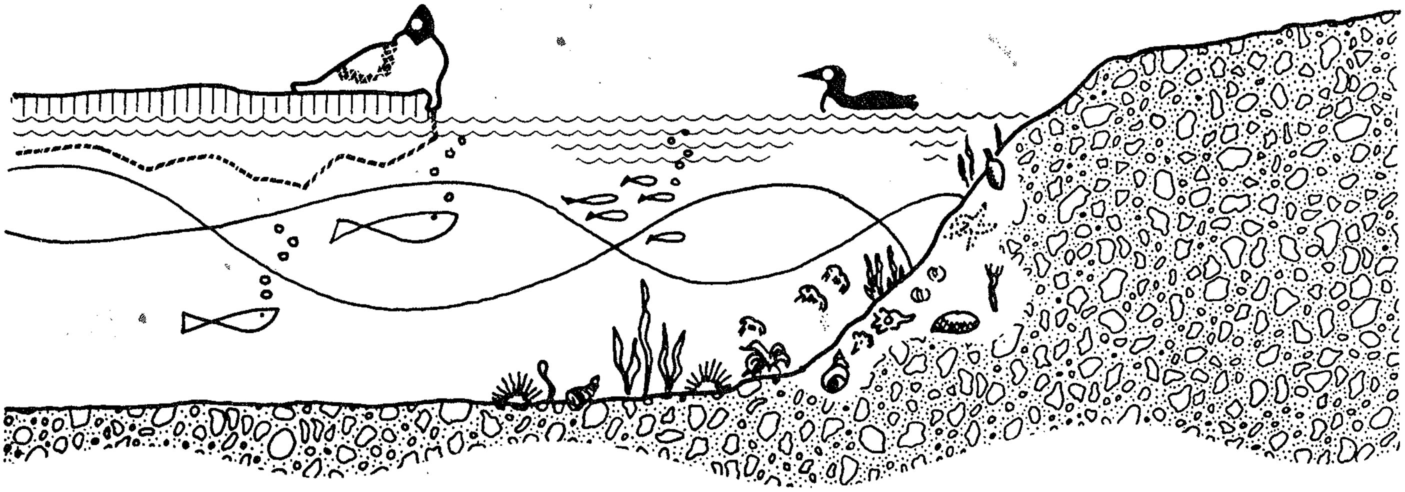
CHEMISTRY

2. Hydrocarbon Chemistry



Baffin Island Oil Spill Project

WORKING REPORT SERIES

1980 STUDY RESULTS

BIOS Working Report Series

This report is the result of a contract let under the Baffin Island Oil Spill Project. This unedited version is undergoing a limited distribution to transfer the results to people working in related research. The report has not undergone rigorous technical review by the BIOS management or technical committee and does not necessarily reflect the views or policies of these groups.

For further information on the BIOS project contact:

BIOS Project Office
Room 804
9942-108th Street
Edmonton, Alberta
T5K 2J5

Phone: (403) 420-2592

Correct citation for this publication:

Boehm, P.D., 1981, Chemistry:2. Hydrocarbon Chemistry - 1980 Study Results. (BIOS) Baffin Island Oil Spill Working Report 80-2: 184 p.

BAFFIN ISLAND OIL SPILL PROJECT - CHEMISTRY COMPONENT

VOLUME 2

Final Report
Contract No. 05580-00074

Prepared for:

Environmental Protection Service
Department of the Environment
Edmonton, Alberta T5K 2J5
Canada

Prepared by:

Paul D. Boehm, Ph.D.
Environmental Sciences Division
ERCO (Energy Resources Co. Inc.)
185 Alewife Brook Parkway
Cambrige, Massachusetts 02138
U.S.A.

(under subcontract to
Seakem Oceanography Ltd.)

March 1981

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont.)

LIST OF FIGURES

LIST OF FIGURES (Cont.)

LIST OF FIGURES (Cont.)

LIST OF TABLES

LIST OF TABLES (Cont.)

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 CEHMISTRY (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 CHROMATOGRAPHY	CAPILLARY GC	CAPILLARY GC HOPANES	CAPILLARY GC AZAARENES	CAPILLARY GC AROMATIC H.C.	PHYSICAL PROPERTIES	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		
Tissues		x	x	x		x		

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 hydrcarbons in any arctic environment studied in sufficient quantities to mask natural saturated hydrocarbon profiles consisting of marine and tenigenous 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.,

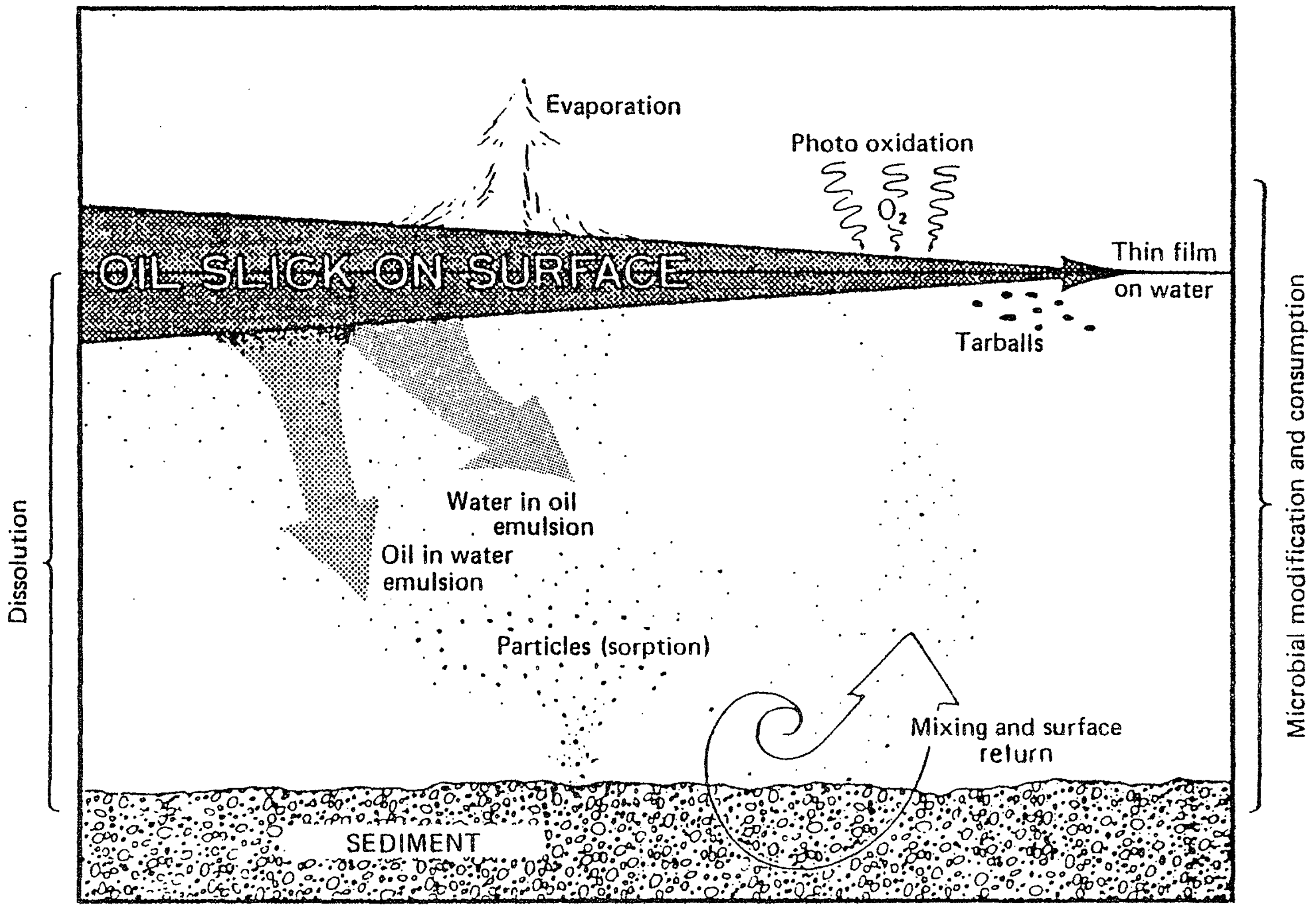


Figure 1.1. Schematic of the transport processes affecting spilled oil in the marine environment.

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.

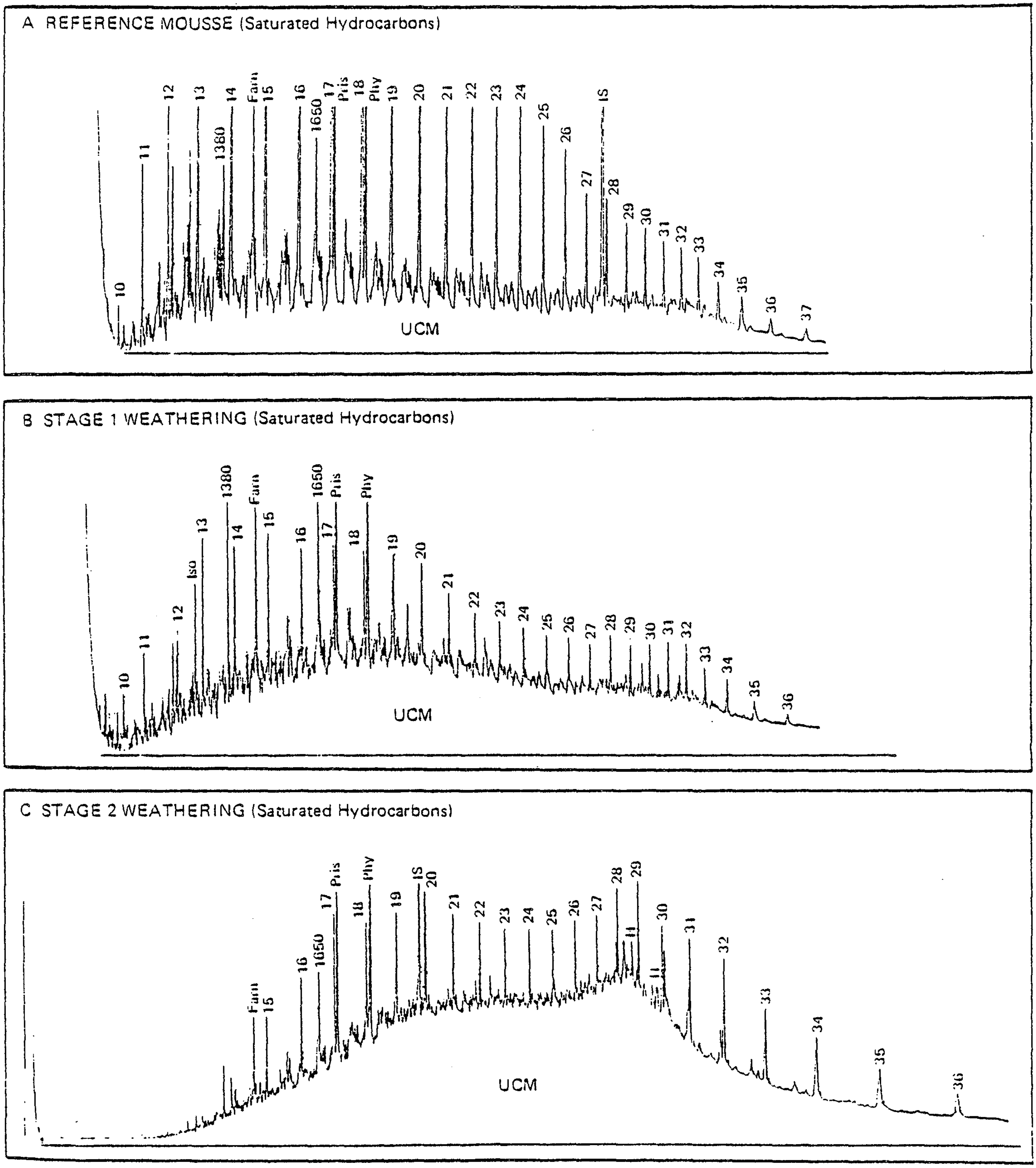
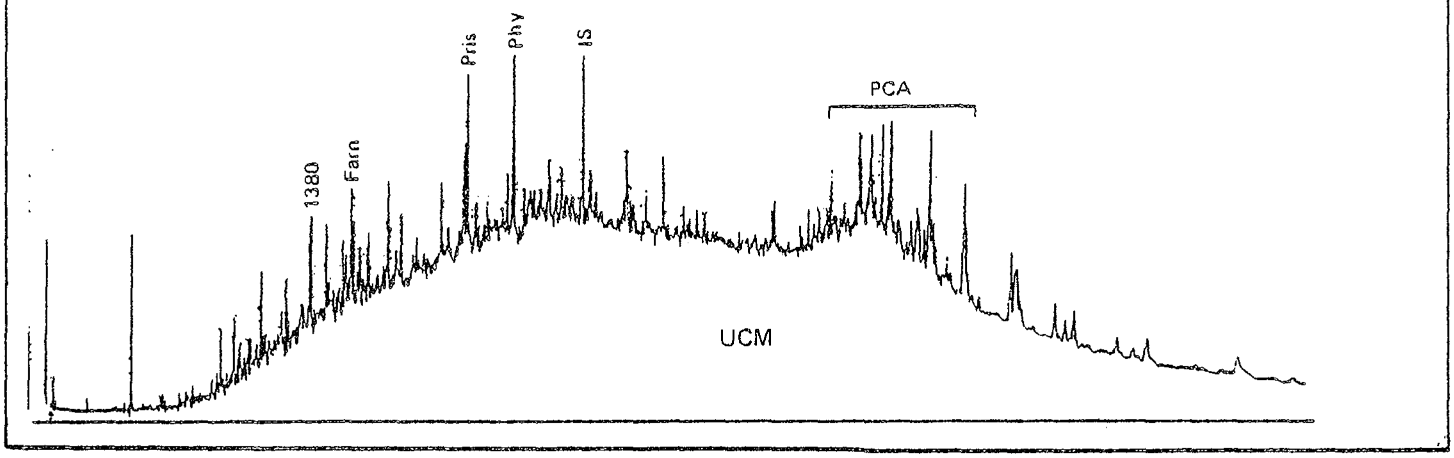


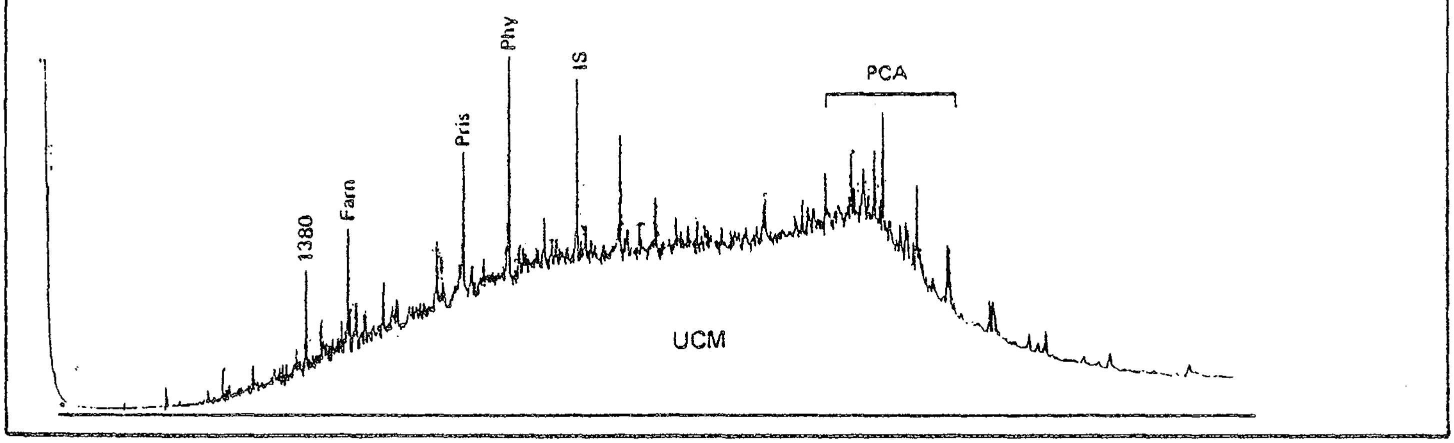
Figure 1.2. Weathering patterns of saturated hydrocarbons in *Amoco Cadiz* oil (from Boehm et al., 1981b).

D STAGE 3 WEATHERING (Saturated Hydrocarbons)

PCA=Polycyclic Aliphatics



E STAGE 4 WEATHERING (Saturated Hydrocarbons)



F BACKGROUND (Saturated Hydrocarbons) -bons)

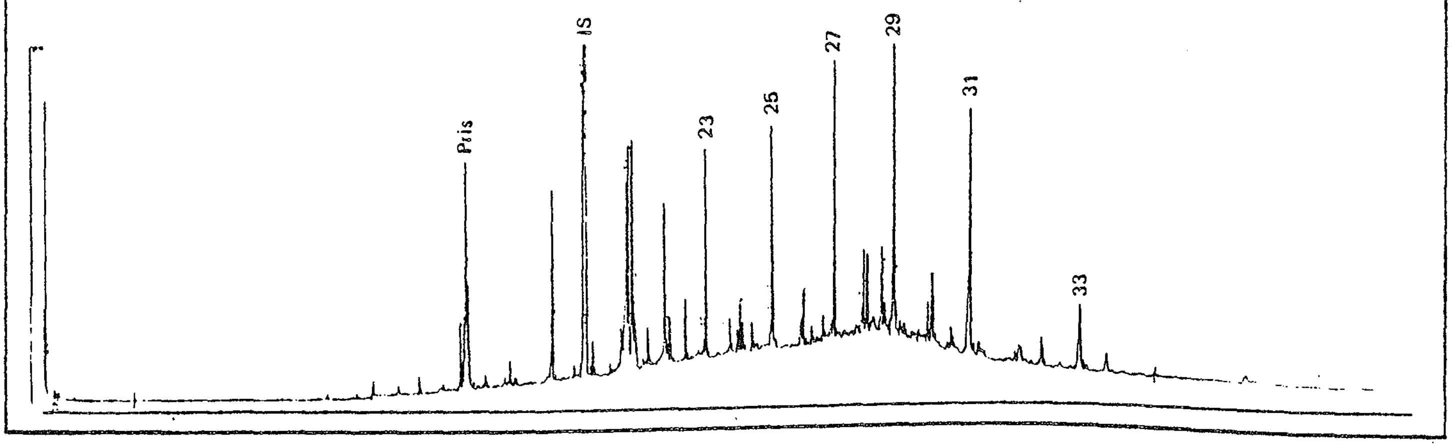


Figure 1.2. (Continued).

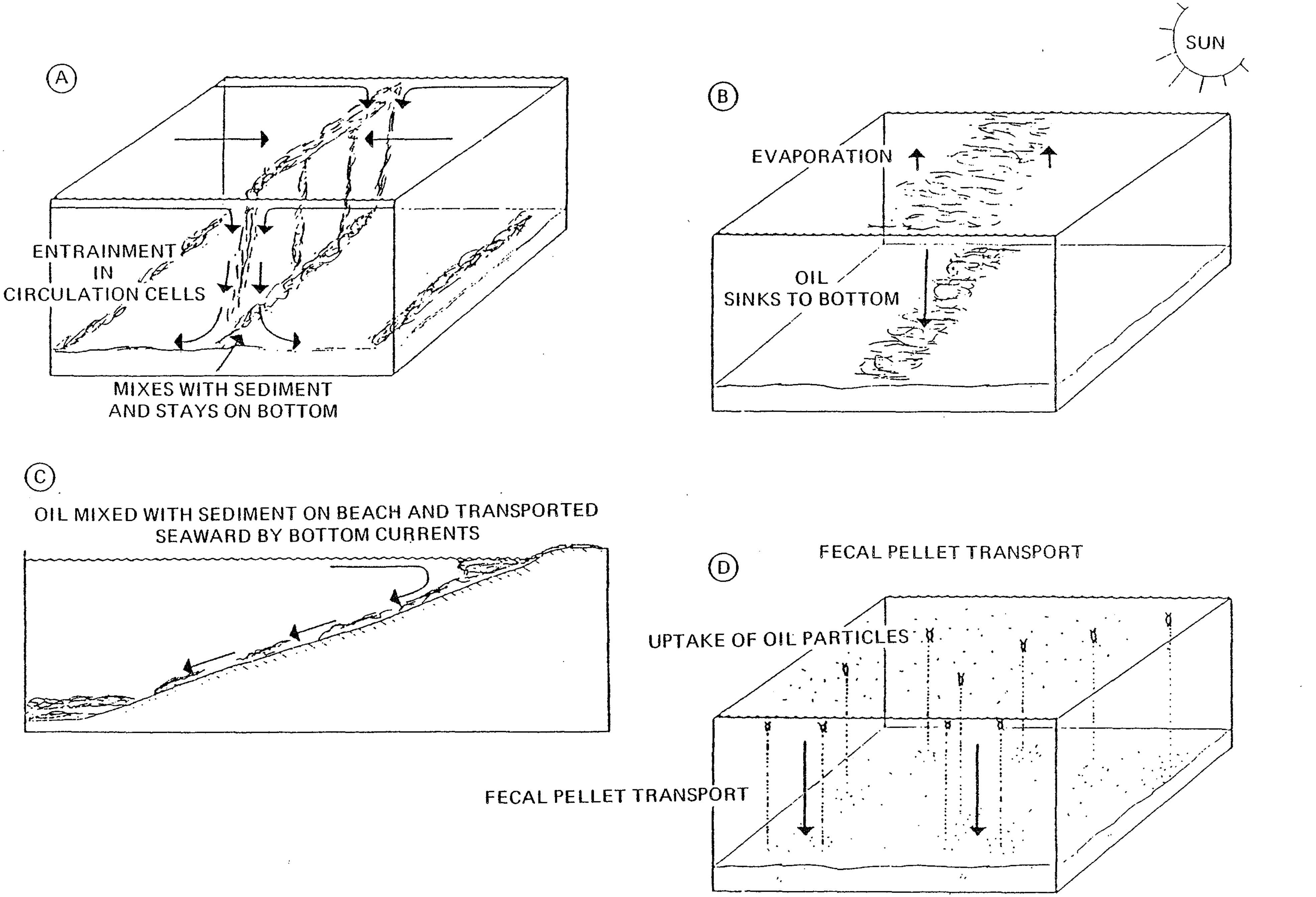


Figure 1.3. Hypothesized methods by which oil may be caused to sink and remain on the bottom.

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 approxinate 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^2), and (3) glass capillary gas chromatographic mass spectrometry (GC^2/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

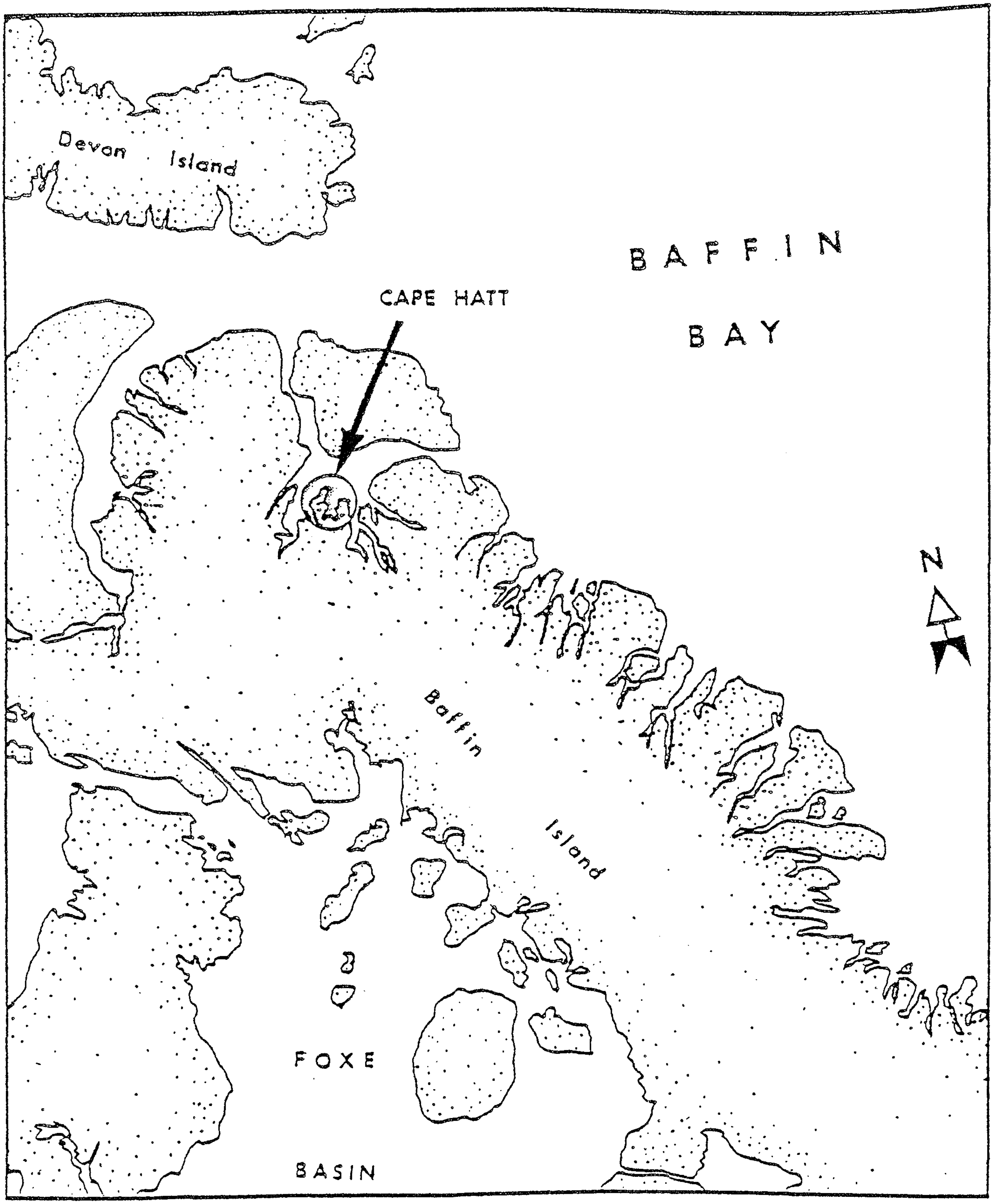


Figure 2.1. Location of Cape Hatt, Baffin Island.

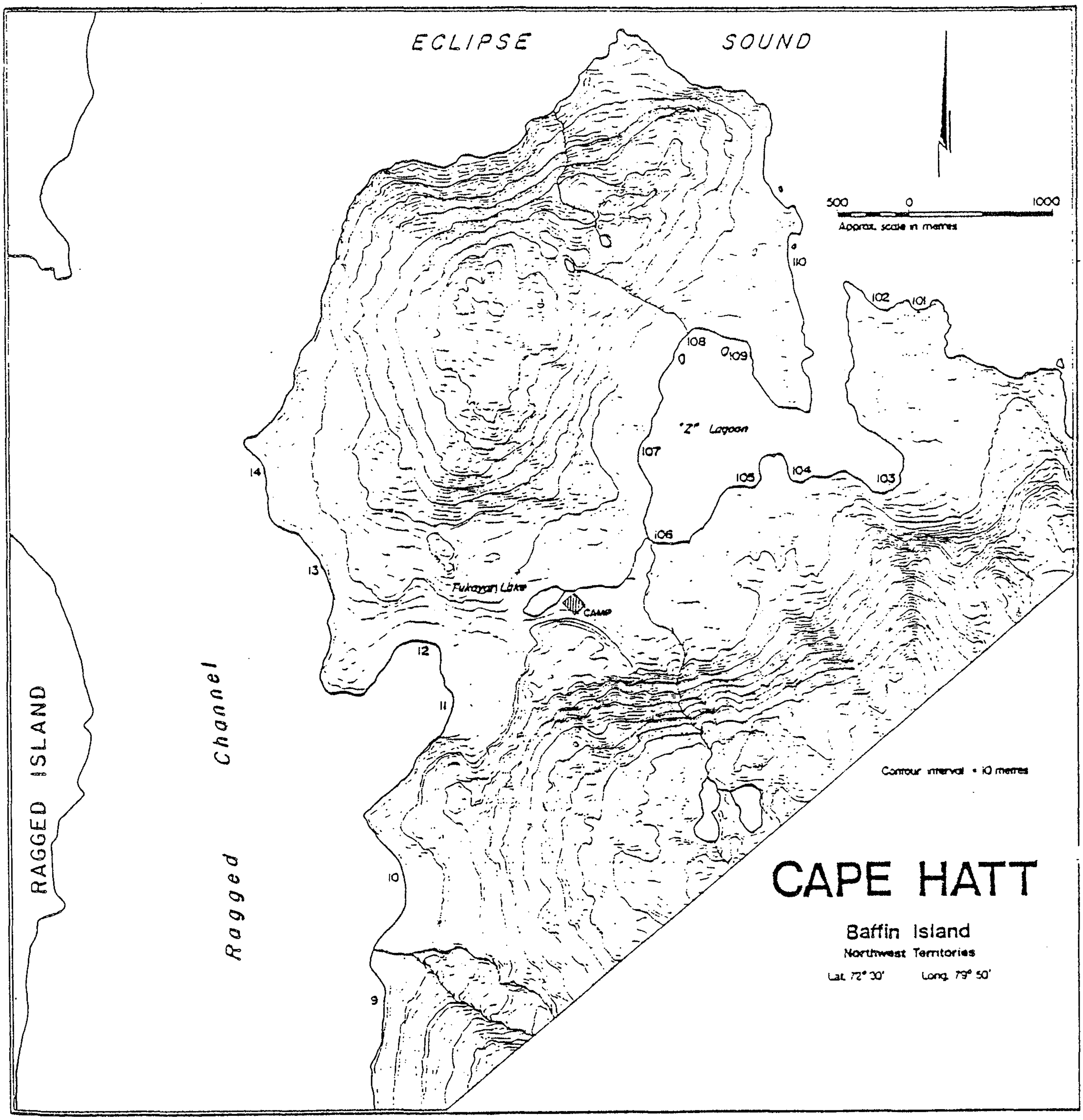
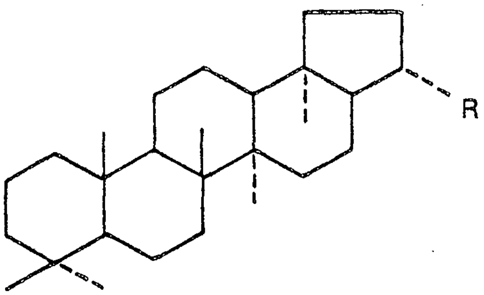


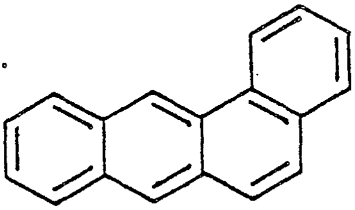
Figure 2.2. The Cape Hatt Site, Showing the Numbering of the Experimental Bays.

Pentacyclic Triterpanes—Marker Compounds



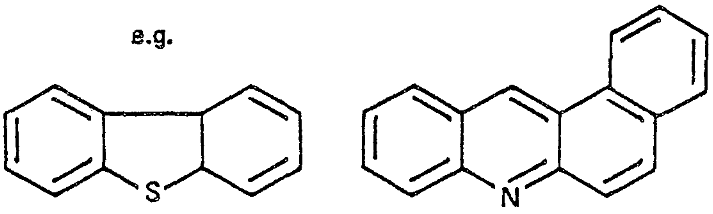
Aromatic Hydrocarbons—Toxicants, Carcinogens

e.g.



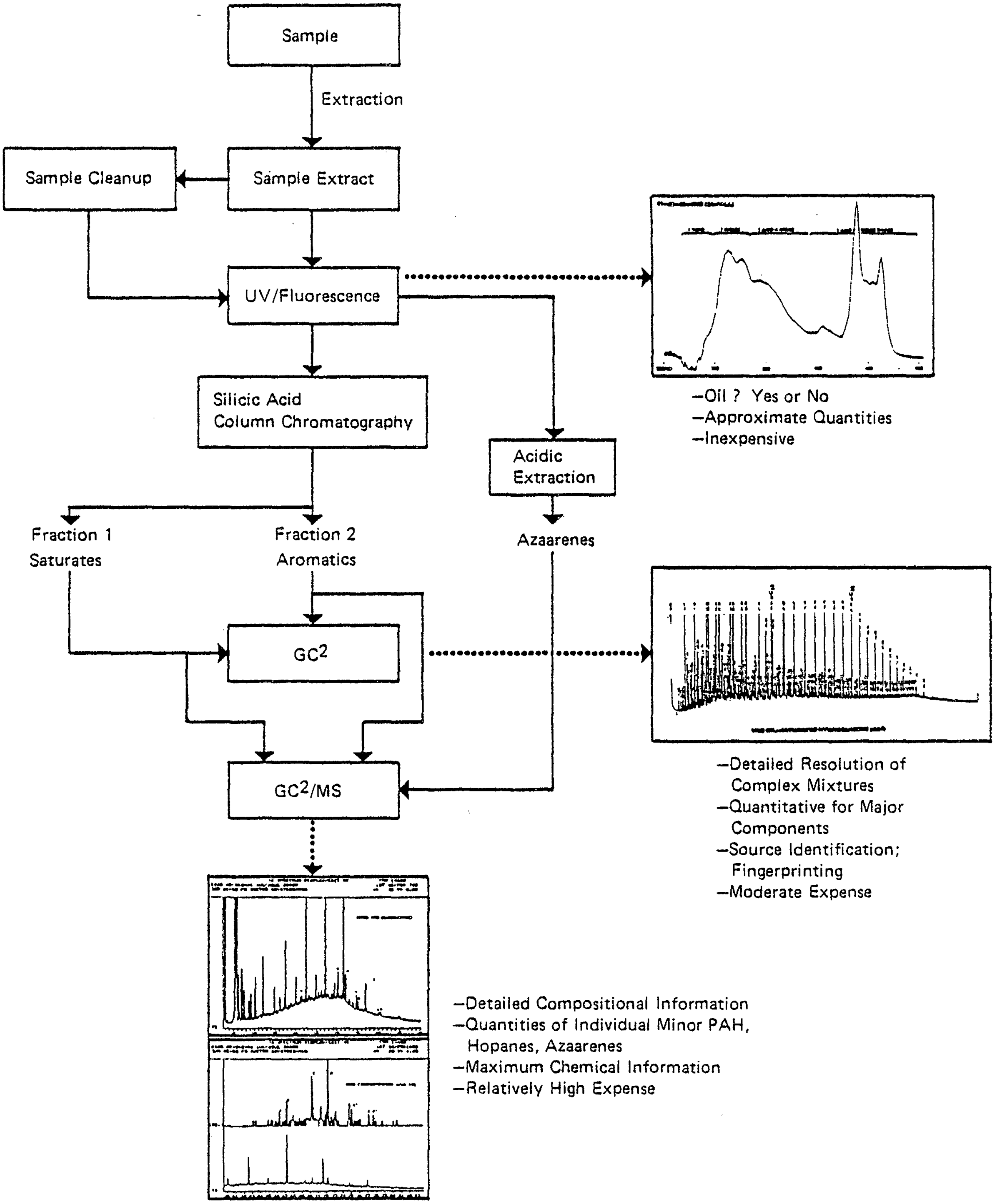
Aromatic Heterocyclics—Marker Compounds, Carcinogens

e.g.



(aromatic sulfur compounds) (azaarenes)

Figure 2.3. Typical molecular structures of petroleum marker compounds analyzed by GC^2/MS.



–Oil ? Yes or No
–Approximate Quantities
–Inexpensive

–Detailed Resolution of Complex Mixtures
–Quantitative for Major Components
–Source Identification; Fingerprinting
–Moderate Expense

–Detailed Compositional Information
–Quantities of Individual Minor PAH, Hopanes, Azaarenes
–Maximum Chemical Information
–Relatively High Expense

Figure 2.4. Schematic of Analytical Strategy.

Soutar, 1976; Wakeham, 1977; Gordon et al., 1976; Lloyd, 1971; VoDinh, 1978; Fiest and Boehm, 1981; Boehm and Fiest, 1981b). By appropriate selection of the solvent system and the offset of the excitation and emission monochronometers, aromatic (fluorescing) compounds in a mixture are resolved into distinct aromatic ring classes. By choosing an offset of 25 nm, 1-, 2-, 3-, 4-, and 5-ring aromatic compounds are resolved into discrete fluorescent bands (Lloyd, 1971). The wavelength bands are for benzenes, 280-290 nm; naphthalenes, 310-330; 3- and 4-ring compounds, 340-380 nm; and 5-ring compounds, >450 (Figure 2-5). The technique is quite useful for examining the relative weathering of oil in environmental samples and for comparing pre-spill and post-spill samples to determine if oil is present. Accurate quantitative information on hydrocarbon content is more difficult to obtain due to the specificity of the method for fluorescing (aromatic) compounds and the exclusion of, for example, saturates. If differential weathering affects the saturated and aromatic fractions then the use of a "spilled oil standard" is inappropriate unless corrected. Baseline measurements are more difficult to quantify unless the method is cross-calibrated with quantitatively more rigorous methods (e.g., microgravimetry and GC^2). The results obtained yield no information on individual component concentrations and on marker compounds. The method is widely used as a relatively inexpensive screening tool where extensive sample preparation is not involved.

If one desires information on the source of hydrocarbons, the concentrations of compound groups (i.e., saturated and aromatic hydrocarbons) and on concentrations and ratios of saturated hydrocarbons then GC^2 is employed. The method results in more detailed information by virtue of separating complex mixtures into individual components (e.g., Section One,

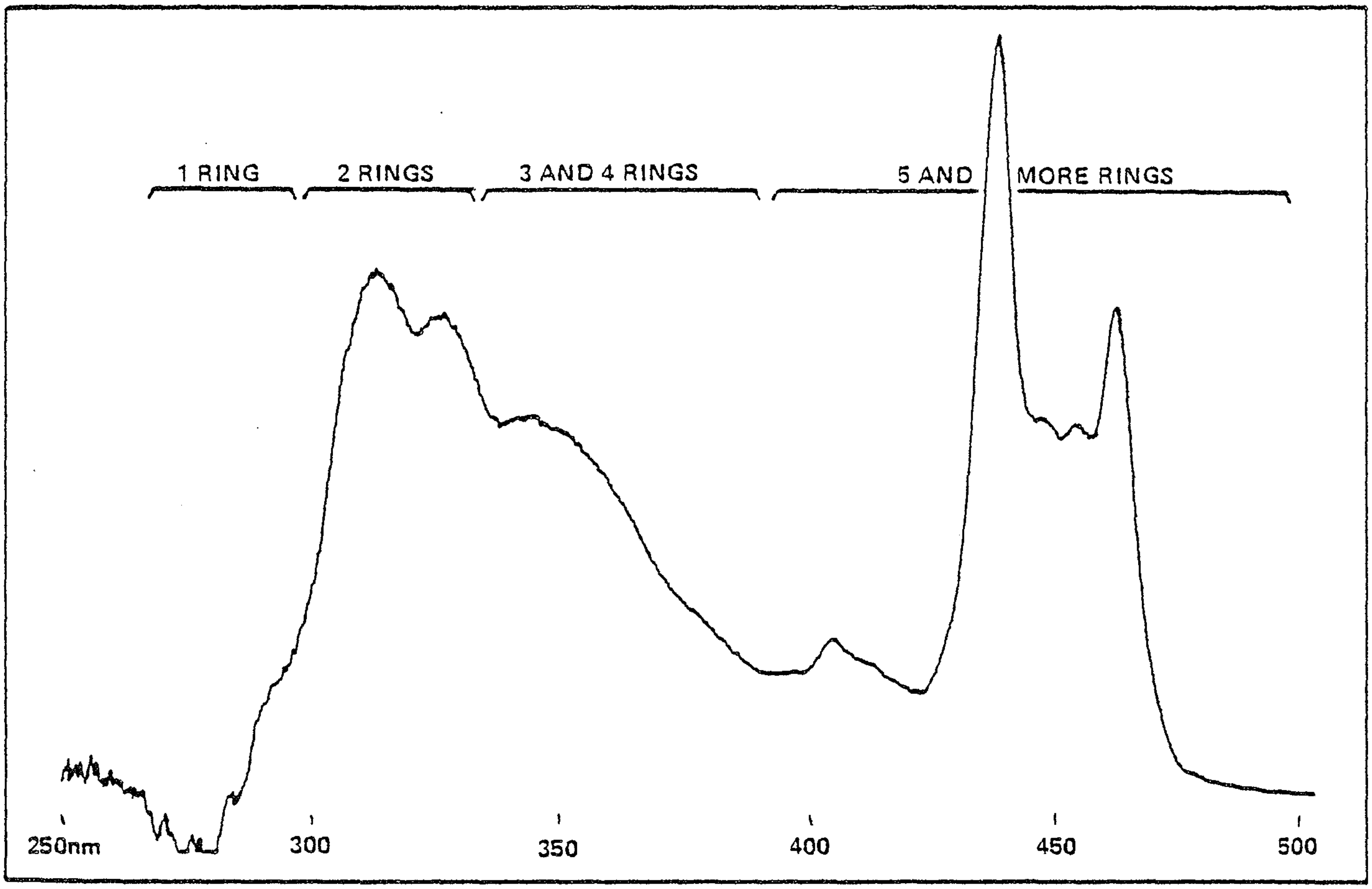


Figure 2.5. Synchronous Spectrofluorometry Spectrum of a Sediment Extract Showing the Resolution of Ring Classes and Perylene in the Right—Hand Side of the Spectrum.

Figure 1-2) thus yielding information on baseline compositions, petroleum weathering patterns, source identifications, and on differential uptake by marine organisms. The method is moderately expensive, requiring sample cleanup, fractionation and a mechanism for handling a large quantity of data. Most major components can be identified and quantified by this method.

GC^2/MS/computer is employed on sample fractions where the definitive identification and quantification of minor compounds (PAH, hopanes, azaarenes) is required. The method is of critical importance in baseline studies to identify and determine concentrations of specific trace level organics. In post-spill studies, the method yields concentrations of individual pollutant toxicants and carcinogens to relate to biological studies. Low-level molecular marker compounds are identified and quantified by GC^2/MS as well. The method is more expensive than GC^2 but yields the maximum amount of analytical information.

A summary of the specific analytical methods used in this project is presented in Table 2-1 for the sake of brevity.

Only the tissue analytical method deserves further mention. The steam distillation technique was adapted from that of Veith and Kiwus (1977). To examine the method in more detail we undertook a short study to determine the absolute recoveries of the range of compounds of interest. This included:

1. Analysis of BIOS tissue samples by the steam distillation and aqueous digestion (Warner, 1976; Boehm et al., 1981a) procedure.

TABLE 2-1

SUMMARY OF METHODS USED IN THIS ANALYTICAL PROGRAM

SAMPLE TYPE	ANALYSIS	METHOD SUMMARY	REFERENCES
Seawater	Synchronous UV/F	Freon extraction; analysis of unfractionated extract	Wakeham, 1977; Gordon et al., 1976; Vo-Dinh, 1978; Lloyd, 1971
Seawater	GC^2	Temperature-programmed capillary analysis; SE52 fused silica columns; internal standard quantification; GC^2 and gravimetric analysis of f_1 and f_2 silicic acid column eluates; computation of individual component levels and key diagnostic parameters	Boehm, 1980; Cram & Young, 1980; Boehm & Fiest, 1981a
Seawater	GC^2/MS	GC/MS/computer system (HP5985); quantification by mass fragmentography	Boehm et al., 1981a, 1981b
Sediments	Synchronous 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^2	(see GC^2 for seawater)	Farrington et al., 1976; Boehm et al., 1981b; Boehm & Fiest, 1981b

TABLE 2-1 (Cont.)

SAMPLE TYPE	ANALYSIS	METHOD SUMMARY	REFERENCES
Sediments	GC^2/MS	Computer search for 1- to 5-ring aromatics; pentacyclic triterpanes; azaarenes	Teal et al., 1978; Farrington, 1980; Pym et al., 1975 Ensminger et al., 1974; Overton et al., 1981; Boehm et al., 1981b
Tissues	GC^2, GC^2/MS	Steam distillation; isolation of extracted distillate; silicic acid fractionation; GC^2, GC^2/MS	Ackman & Noble, 1973; Veith & Kiwus, 1977; this report; Boehm et al., 1981a; Clark, 1974; Warner et al., 1980
Oils	Physical measurements	Absolute viscosity; interfacial tension; density	ASTM, D455; ASTM, D971
Oils	Chemical characterization (GC^2, GC^2/MS)	Saturates, aromatics, azaarenes, triterpanes	Overton et al., 1981 Boehm & Fiest, 1981a; Pym et al., 1975
Oils	Trace metals	High-temperature ashing; ICAP analysis	Leone & Church, 1976

TABLE 2-2

STEAM DISTILLATION RECOVERY/EFFICIENCY - MIXED SATURATED/AROMATIC STANDARD

COMPONENT	% RECOVERY
n-C_{10}	35
n-C_{11}	43
Naphthalene	91
n-C_{12}	47
n-C_{13}	56
n-C_{14}	80
Hexamethyl benzene	103
n-C_{15}	106
n-C_{16}	117
n-C_{17}	115
Pristane	105
Phenanthrene	113
Anthracene	105
n-C_{18}	112
Phytane	110
n-C_{19}	98
n-C_{20}	96
n-C_{21}	76
n-C_{22}	75
n-C_{23}	85
n-C_{24}	80
n-C_{25}	89
Chrysene	38
n-C_{26}	98
n-C_{28}	102
Perylene	56
n-C_{29}	100
n-C_{30}	101
n-C_{31}	108
n-C_{32}	110
Benzoperylene	85

2. Determining absolute recoveries of a complex mixture of standards.

3. The steam distillation of an actual polluted tissue extract to determine recoveries of a "real world" pollutant assemblage.

Approach 1 was not undertaken after it became apparent that a large intrinsic variation hydrocarbon composition existed in the animals (see Section 3.2.6). A tabulation of the absolute recoveries of the complex standard mixture is given in Table 2-2.

Although the recoveries of several of the compounds are low, they are no lower than those achieved by other techniques. That is, the light saturates and aromatics ($<n-C_{14}$) are subject to procedural losses in most methods geared for "high-molecular-weight" hydrocarbon analysis. Figure 2-6 illustrates that a complex aromatic hydrocarbon extract from an Amoco Cadiz polluted oyster consisting of alkylated naphthalenes, phenanthrenes, and dibenzothiophenes was quantitatively recovered after its steam distillation.

Thus, the steam distillation method used is quite satisfactory for use in this project.

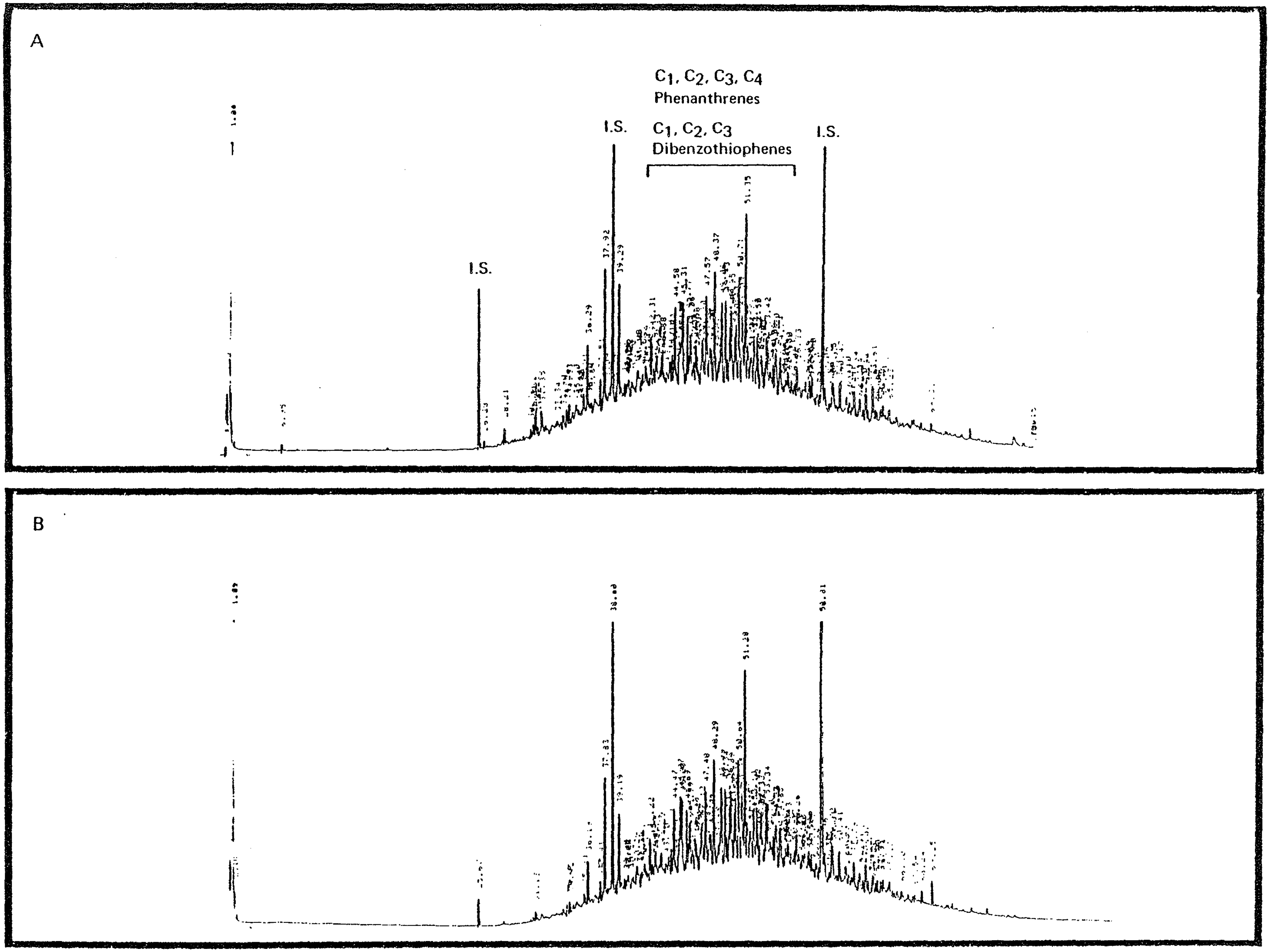


Figure 2.6. Steam Distillation Recovery of Polluted Tissue Aromatic Extract, A—Aromatics (Original); B—Aromatics (After Steam Distillation).

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_9 to n-C_{34} (Figure 3-1). Approximately 70% of the fresh, unweathered crude elutes prior to n-C_{15} compared to 50% for the weathered (or aged) oil. The comparative GC^2 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_9 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.

TABLE 3-1

GROSS CHEMICAL CHARACTERIZATIONS OF LAGOMEDIO CRUDE OIL AND OIL/COREXIT 9527 MIXTURE

SAMPLE	% SATURATES[a]	% AROMATICS[a]	% POLARS[a]	% RESIDUAL[a]	% ASPHALTENES[b]
Fresh (unweathered) oil	59.1	35.2	6.3	0	1.2
Aged oil	58.8	30.0	14.8	0	2.5
Aged: dispersant (10:1)	44.2	27.5	24.7	3.6	ND

[a] Determined from silicic acid column chromatographic fractionation; f_1 = hexane eluate; f_2 = hexane:methylene chloride (60:40) eluate; f_3 = methanol eluate; residual = material not eluting off column.

[b] Asphaltenes = pentane-insoluble material. <u>Note</u>: asphaltenes may elute in both f_2 and f_3 fractions.

ND = not determined

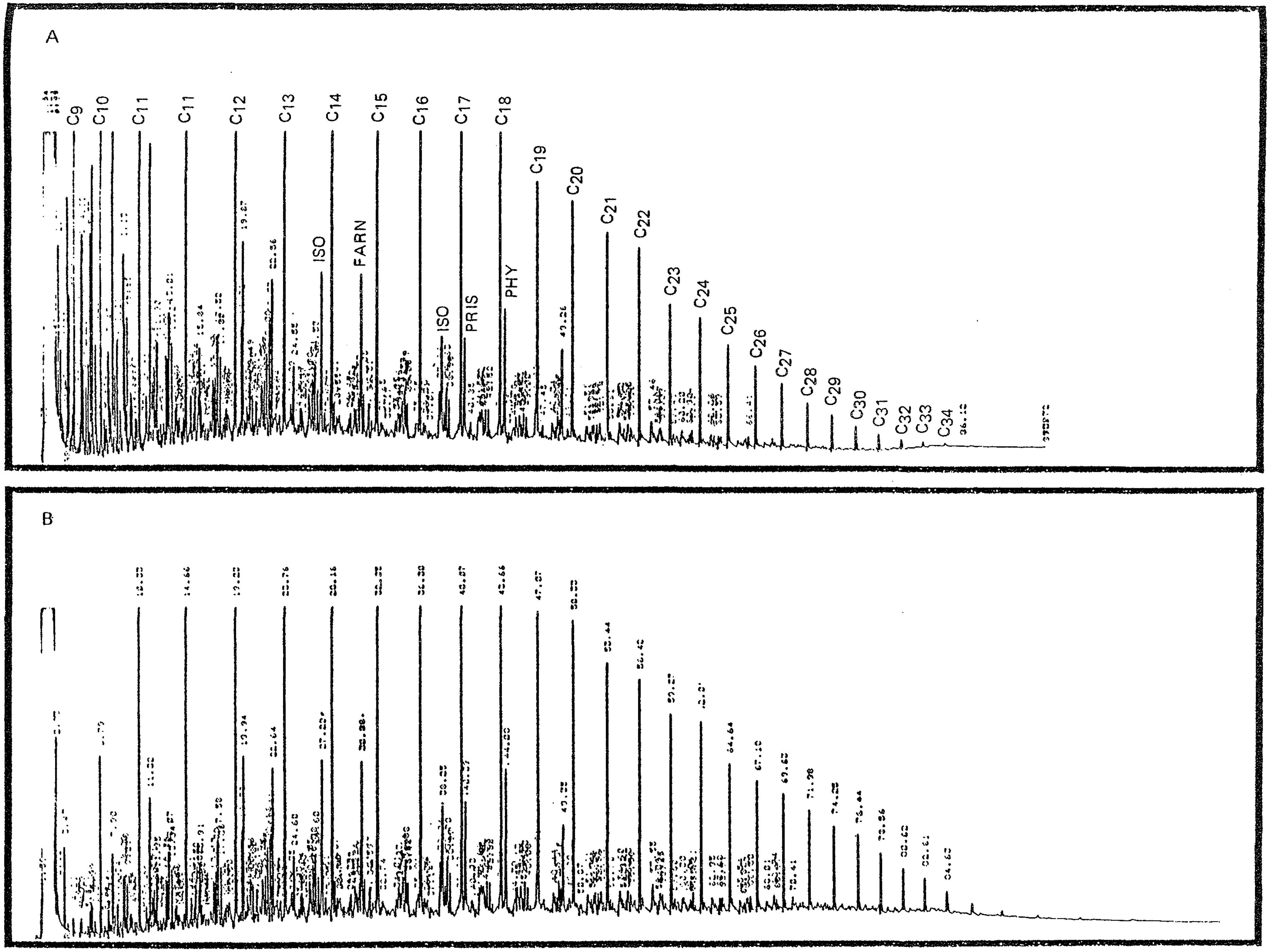


Figure 3.1. GC^2 Traces of Saturated Hydrocarbons of A—Unweathered Lagomedio Crude Oil, B—Aged Oil.

TABLE 3-2

SATURATED AND AROMATIC HYDROCARBON PARAMETERS OF LAGOMEDIO CRUDE OIL[a]

	FRESH OIL	AGED OIL
Saturates		
SHWR	2.87	2.28
ALK/ISO	2.36	2.50
PRIS/PHY	0.85	0.74
PRIS/n-C_{17}	0.51	0.38
PHY/n-C_{18}	0.61	0.62
Aromatics		
AWR	4.29	3.47

[a] Key:

$$\text{SHWR} = \frac{(\Sigma\ \text{n-alkanes};\ C_{10}-C_{25})}{(\Sigma\ \text{n-alkanes};\ C_{17}-C_{25})}$$

$$\text{AWR} = \frac{(\text{Alkyl Benzenes} + \text{Naphthalenes} + \text{Fluorenes} + \text{Phenanthrenes} + \text{Dibenzothiophenes})}{\text{Phenanthrenes} + \text{Dibenzothiophenes}}$$

$$\text{ALK/ISO} = \frac{(\Sigma\ \text{alkanes};\ C_{14}-C_{18})}{(\Sigma\ 5\ \text{isoprenoids; in n-}C_{13}\ \text{boiling range})}$$

PRIS = pristane

PHY = phytane

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^2/MS analysis of the hopane-type pentacyclic triterpanes reveals small quantities of four compounds (Figure 3-3): Compound C (norhopane; $C_{29}H_{50}$), Compound D ($C_{30}H_{52}$); Compounds E, E' (homohopanes $C_{31}H_{54}$) and a pattern of 12 secondary peaks of unknown structure.

3.1.4 Aromatic Hydrocarbons (UV/F)

UV/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^2/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^2/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^2 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^2/MS mass fragmentograms (Appendix A).

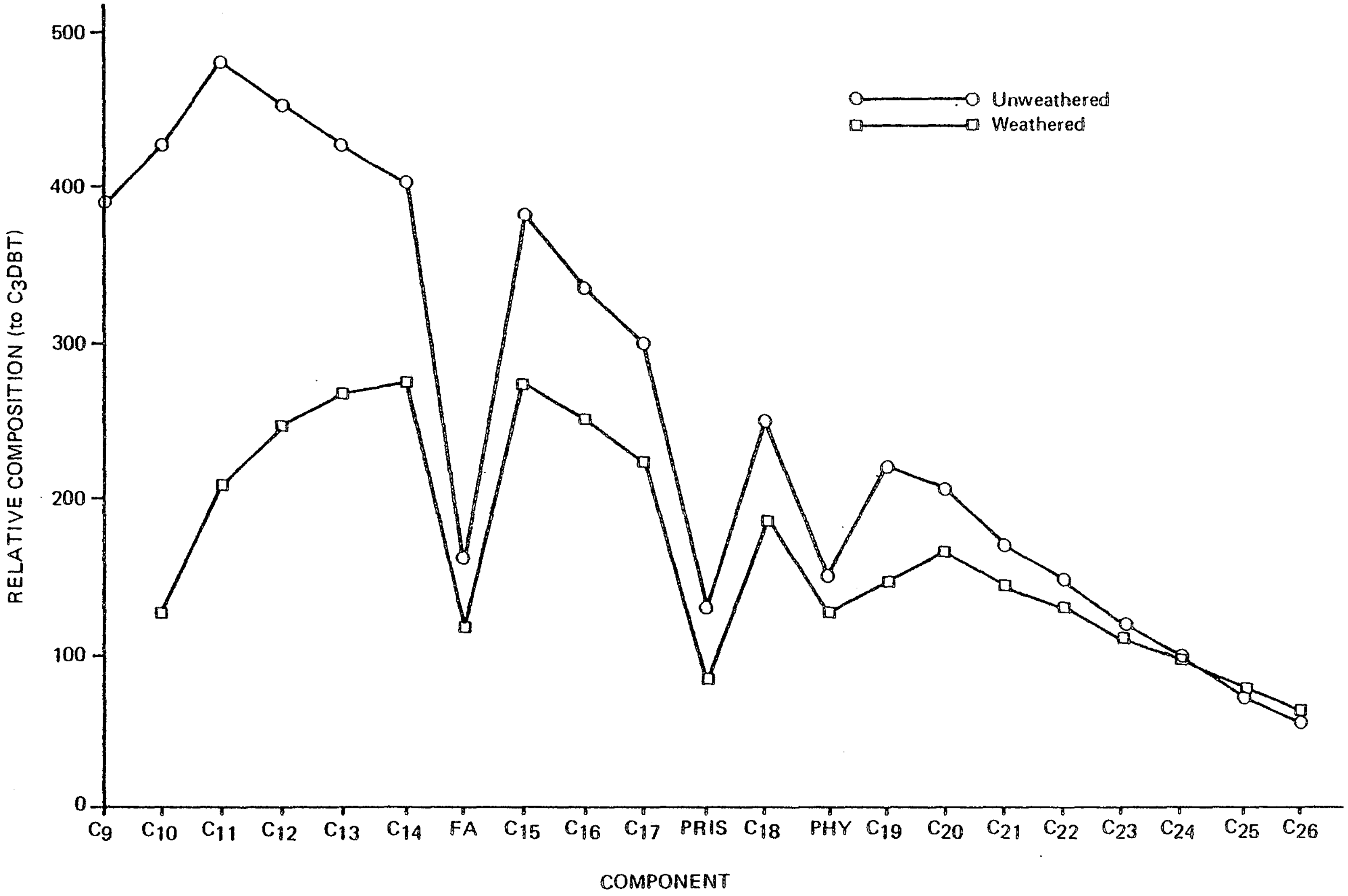


Figure 3.2. Saturated Hydrocarbon Composition of Weathered vs. Unweathered Lagomedio Crude Oil.

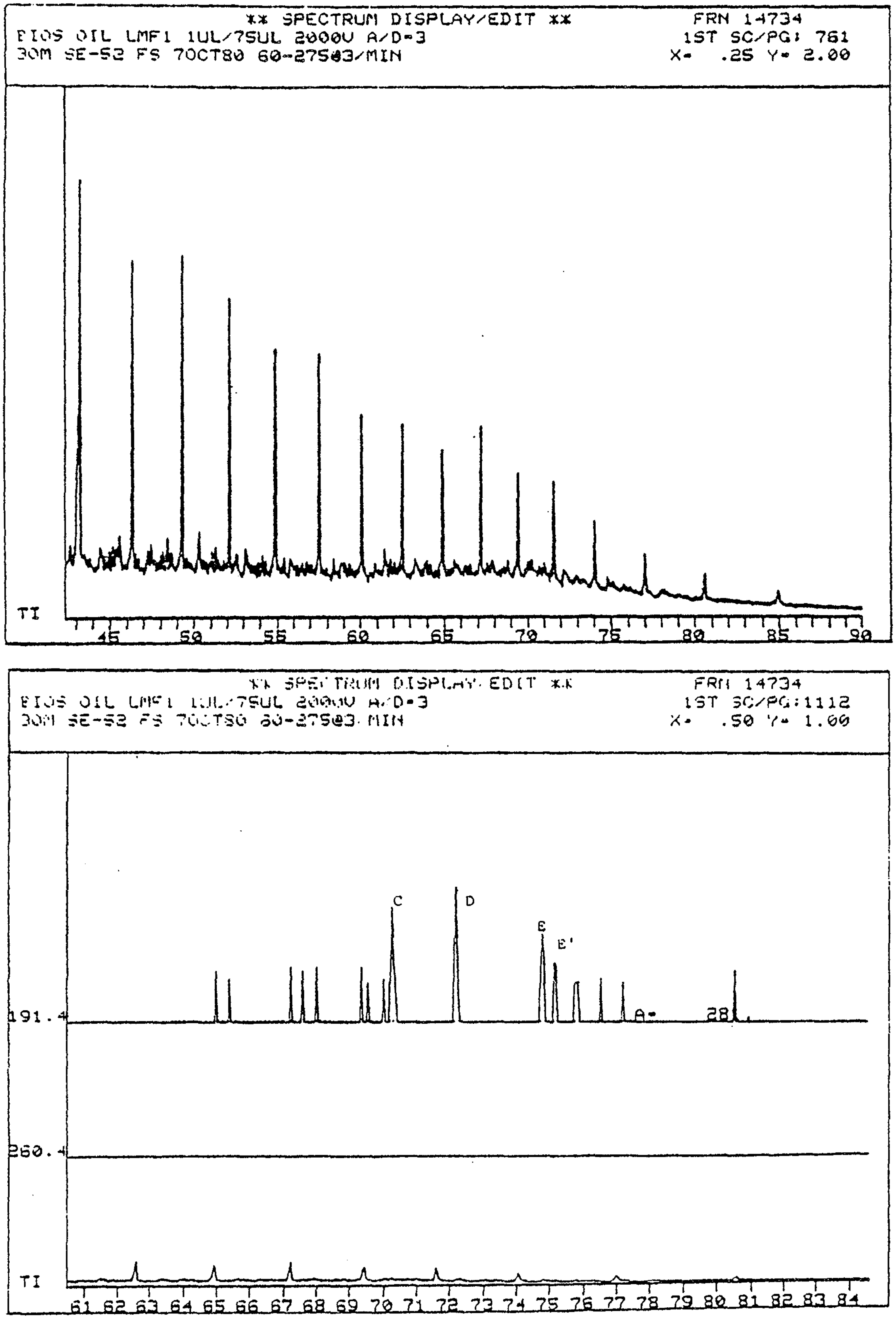


Figure 3.3. Bios Oil—Hopane Analysis (GC^2/MS).

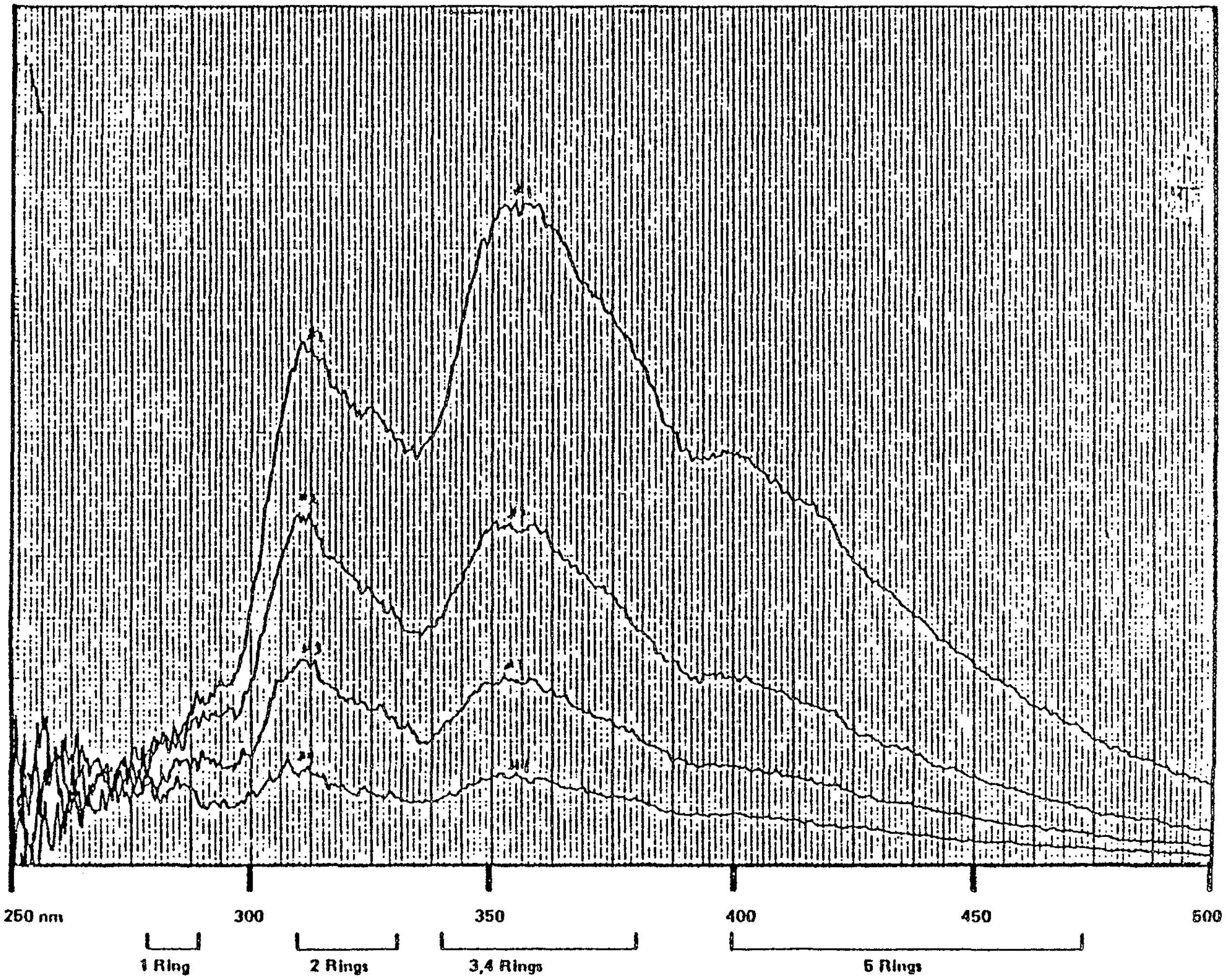


Figure 3.4. UV/Fluorescence (Synchronous Scan) of Lagomedio Crude.

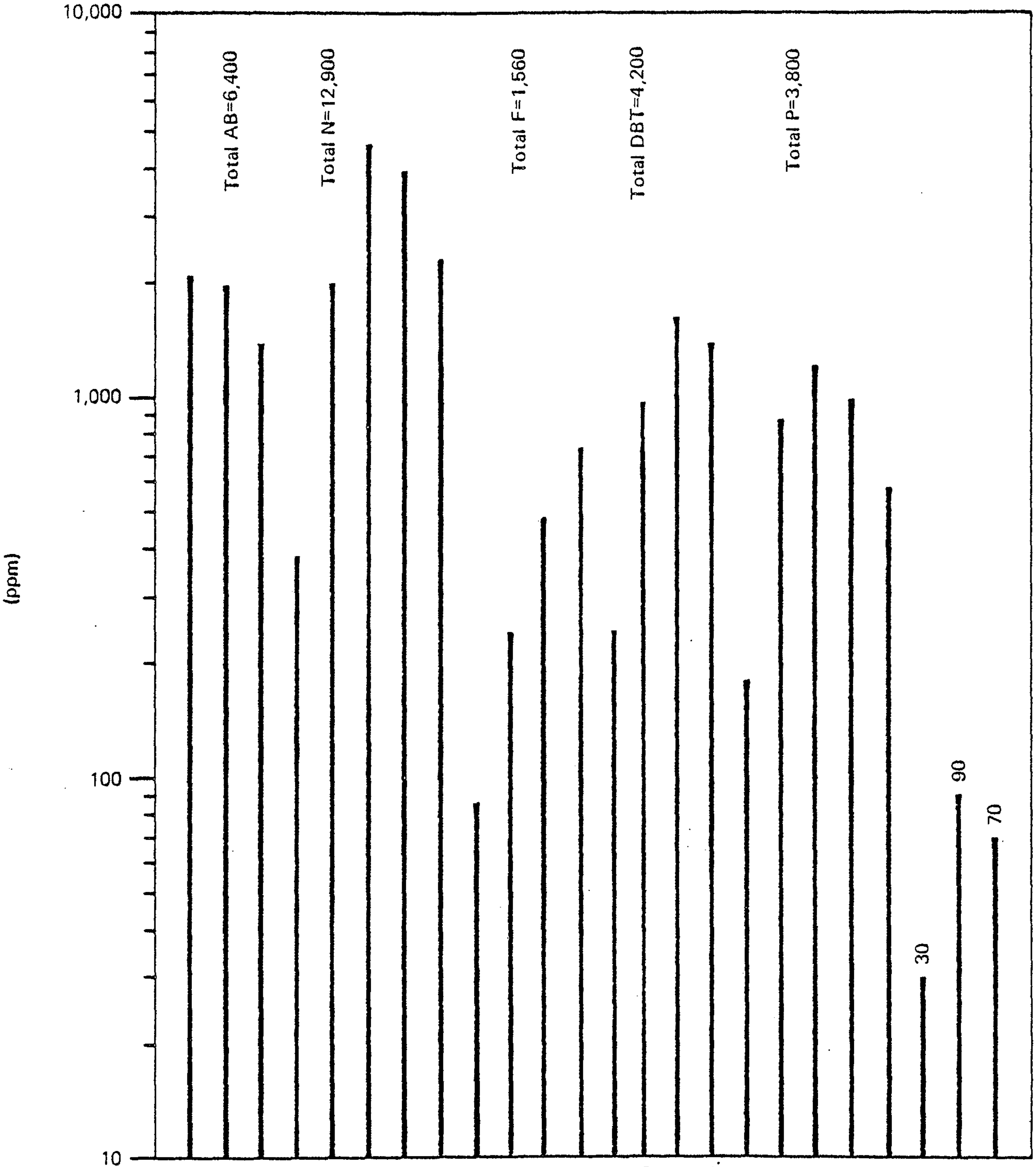


Figure 3.5. PAH Composition of Weathered Lagomedio Crude Oil (ppm).
(B=Benzene, N=Naphthalene, F=Fluorene, D=Dibenzothiophene, P=Phenanthrene, 202=Fluoranthene/Pyrene, 228=Chrysene, 252=Benzopyrenes)

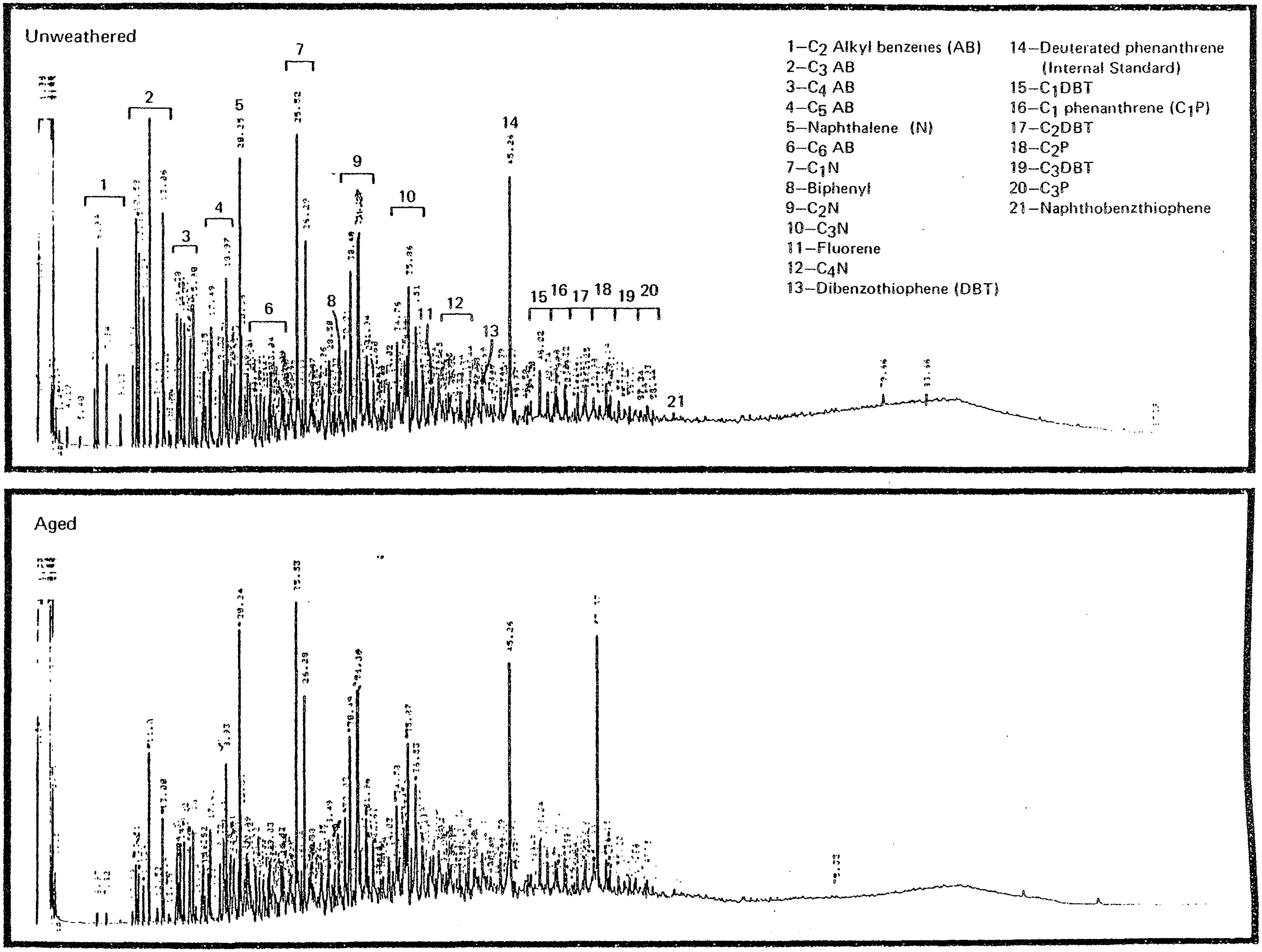


Figure 3.6. GC^2 Traces of Aromatic Hydrocarbons in Lagomedio Crude Oil

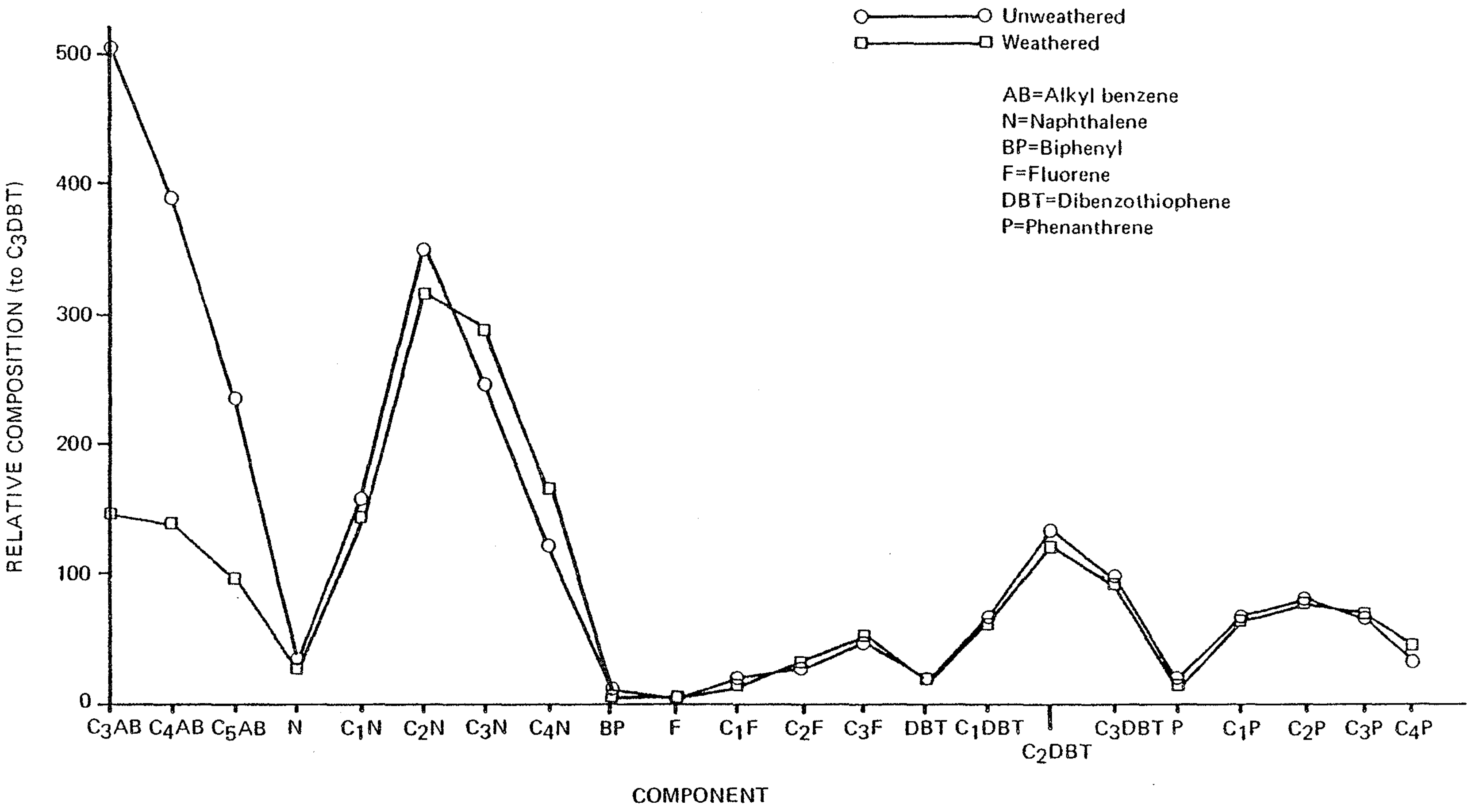


Figure 3.7. Aromatic Hydrocarbon Composition of Weathered vs. Unweathered Lagomedio Crude Oil.

In addition, a key compositional parameter, one sensitive to artificial and post-spill weathering, the aromatic weathering ratio (AWR), is presented in Table 3-2. The crude can be classified as a light crude being heavily dominated by naphthalene and alkyl benzene compounds. The dibenzothiophenes (heterocyclic aromatic sulfur compounds) are the third most abundant group followed by the 3-ring phenanthrenes and fluorenes. Lesser quantities of the 4- and 5-ring polycyclic aromatics are present.

3.1.6 Azaarenes

Acidic extractions of crude oils followed by GC^2/MS analyses of the acidic fraction yielded clean azaarene analysis. Note that the azaarenes are far less abundant than their aromatic hydrocarbon cousins (e.g., trimethyl phenanthrenes $\simeq$ 1,000 μg/g oil; trimethyl acridines/phenanthridines $\simeq$ 700 ng/g oil). The azarene composition of the aged crude is identical to that from the fresh oil. The complete GC^2/MS analysis of the azaarenes is presented in Appendix B. The relative abundance of the major azaarenes is shown in Figure 3-8. The major components of the azaarene assemblage are the C_3 (trimethyl) acridines (m/e 221) whose mass fragmentogram (Figure 3-9) reveals at least six isomers of the 3-ring azaarenes.

3.1.7 Physical Measurements

Measurements of absolute kinematic viscosity (ASTM method D445), interfacial (oil/seawater) tension (ASTM method D971), and density were performed at -5°C, 0°C, and +5°C for three oils: aged Lagomedio crude; aged Lagomedio crude:Corexit 9527

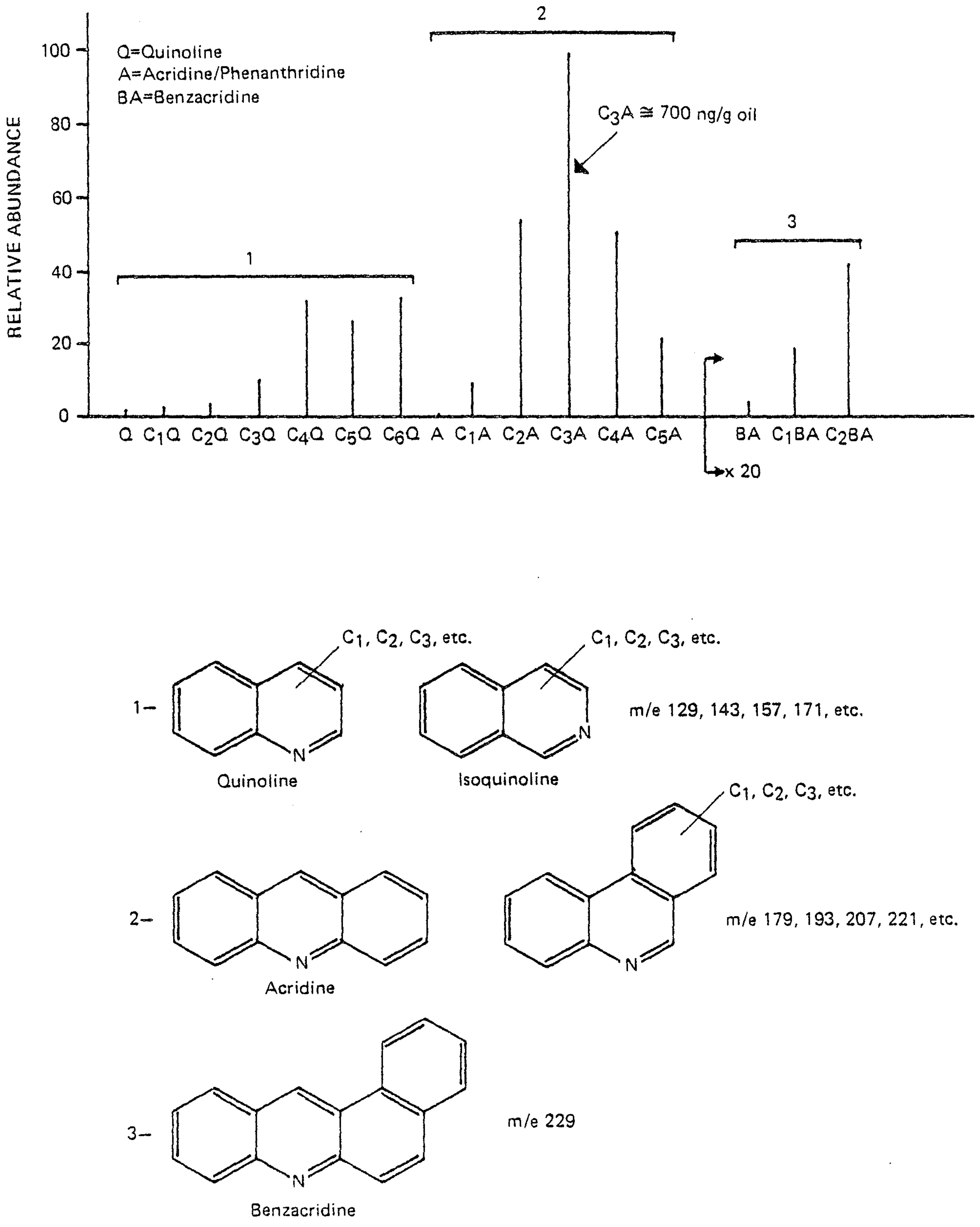


Figure 3.8. Azaarene composition of Lagomedio crude oil.

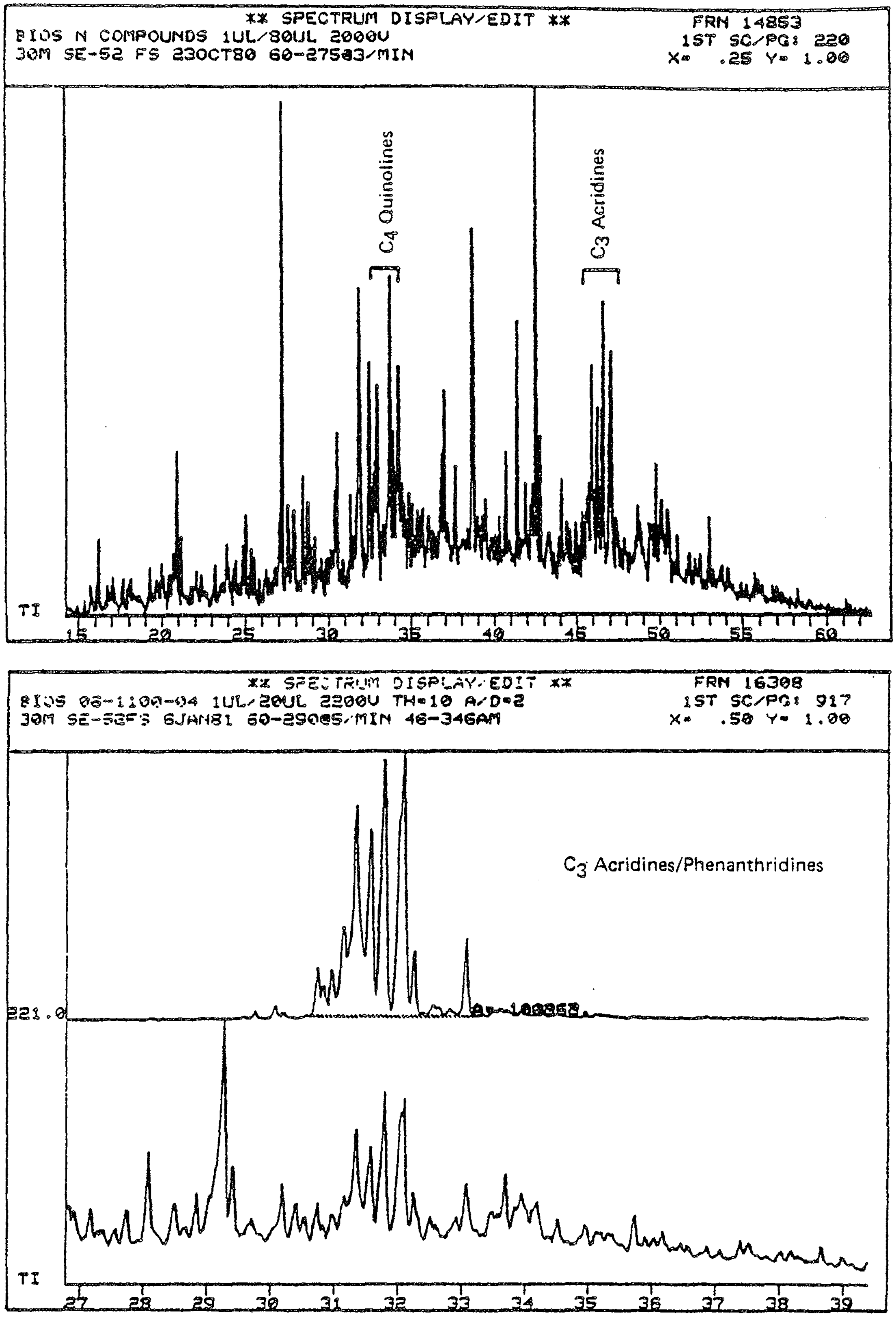


Figure 3.9. Lagomedio Crude Oil: Total Ion Chromatogram (A) and Mass Chromatogram of Trimethyl Acridines/Phenanthridines (m/e = 221) (B).

(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 3-3

ABSOLUTE VISCOSITY OF CRUDE OIL AND OIL/DISPERSANT MIXTURES (centistokes)

	AT -5°C	AT 0°C	AT +5°C
Lagomedio crude	Note[a]	Note[a]	154.1
Lagomedio crude:Corexit 9527 (10:1)	Note[a]	Note[a]	120.0
Lagomedio crude:Corexit 9527 (1:1)	218.0	144.6	100.3

[a] The samples appeared to precipitate waxy components at 0° C and -5° C. These prevented determination of the viscosity of the sample by clogging the orifice of the viscometer. The viscosities determined in the second section of the reverse flow viscometers used for the determinations were invariably higher than those determined in the first section.

Viscosity (centistokes)

At 0° C		At -5° C	
1st Section	2nd Section	1st Section	2nd Section
1,420	2,640	1,629	3,351
880	1,288	9,801	20,960

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[a]	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

[a] Not determined.

TABLE 3-5

DENSITY OF CRUDE OIL AND OIL/DISPERSANT MIXTURES (g/cm^3)

	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	0.9045
Lagomedio crude:Corexit 9527 (1:1)	0.9621	0.9586	0.9551

TABLE 3-6

SUMMARY OF TRACE METAL ANALYSIS OF OILS
(ppm)

SAMPLE	Ni	V	Al[a]	Ba	Be	Cd	Co
Aged Venezuelan Crude	12.4	135	2.5	0.06	<0.01	<0.02	0.05
Venezuelan Crude[b]	8.1 ±0.5	125 ±13	--[c]	--[c]	--[c]	--[c]	0.094 ±0.022
Kuwait Standard Oil (API)							
ERCO Analysis	7.5	24	0.96	0.05	<0.01	<0.02	0.05
Certified Value	7.7	16.8	--[d]	--[d]	--[d]	--[d]	--[d]
Louisiana Standard Oil (API)							
ERCO Analysis	1.3	0.73	0.58	0.11	<0.01	<0.02	0.10
Certified Value	1.4	0.67	--[d]	--[d]	--[d]	--[d]	--[d]
Blank	<0.2	<0.1	1.1	<0.02	<0.01	<0.02	<0.02

[a] Values are blank corrected.

[b] Leone and Church (1976), p. 42.

[c] Not reported.

[d] Not certified.

TABLE 3-6 (Cont.)

SAMPLE	Cr	Cu	Fe[a]	Mn	Pb	Ti[a]	Zn[a]
Aged Venezuelan Crude	<0.5	<0.05	1.9	<0.05	<0.5	0.05	1.5
Venezuelan Crude[b]	0.04 ±0.05	0	0.76 ±0.10	0.007 ±0.002	--[c]	--[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

[a] Values are blank corrected.

[b] Leone and Church (1976), p. 42.

[c] Not reported.

[d] Not certified.

3.2 Hydrocarbons Baseline Studies

3.2.1 Seawater Samples - UV/F Analyses

Forty-nine (49) 4-liter water samples, obtained by using an NBS-type drop sampler (see Volume 1) were extracted three times with 75 ml Freon 113. One-half of the resultant unfractionated extract representing 2 liters of seawater was analyzed by synchronous scanning spectrofluorometry (UV/F).

3.2.1(a) June Samples

The UV/F spectra of the June water samples showed very low levels of fluorescent material, not detectable above a significant freon blank (Table 3-7). The values presented in Table 3-7 were obtained by quantifying with respect to a No. 2 fuel oil standard (Figure 3-10A) and by subtracting the blank value. Thus, we relied mainly on quantitation of the 312-nm peak in the spectrum. The spectral characters of most of the water samples were quite similar (e.g., Figure 3-11), exhibiting a single main peak at 312 nm, presumably associated with the blank.

3.2.1(b) August/September Samples

A similar, but larger, suite of samples and field blanks were collected during the August/September sampling. The results in Table 3-8 indicate for the most part nondetectable (<3 µg/l) levels of petroleum-type hydrocarbons. Four samples, however, did contain detectable petrogenic material (Figure 3-10B). The concentrations in these samples ranged from 3 to 86 µg/l. All of these samples were pre-spill

TABLE 3-7

UV/FLUORESCENCE RESULTS OF JUNE WATER SAMPLES

SAMPLE		COLLECTION DATE	SAMPLING DEPTH (m)	μg/l[a]
Bay 9	H5 (extract)	6/14/80	1	ND[b]
Bay 9	H5 (extract)	6/14/80	5	ND
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	H1 (extract)	6/14/80	1	ND
Bay 11	H1 (extract)	6/14/80	5	ND
Bay 11	H1 (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	ND
Bay 9	H5 (whole water)	6/22/80	10	ND
Blank (solvent and field extraction)				9-50

[a] As equivalents of No. 2 fuel oil measured at 312 nm; corrected for blank.

[b] Not detected.

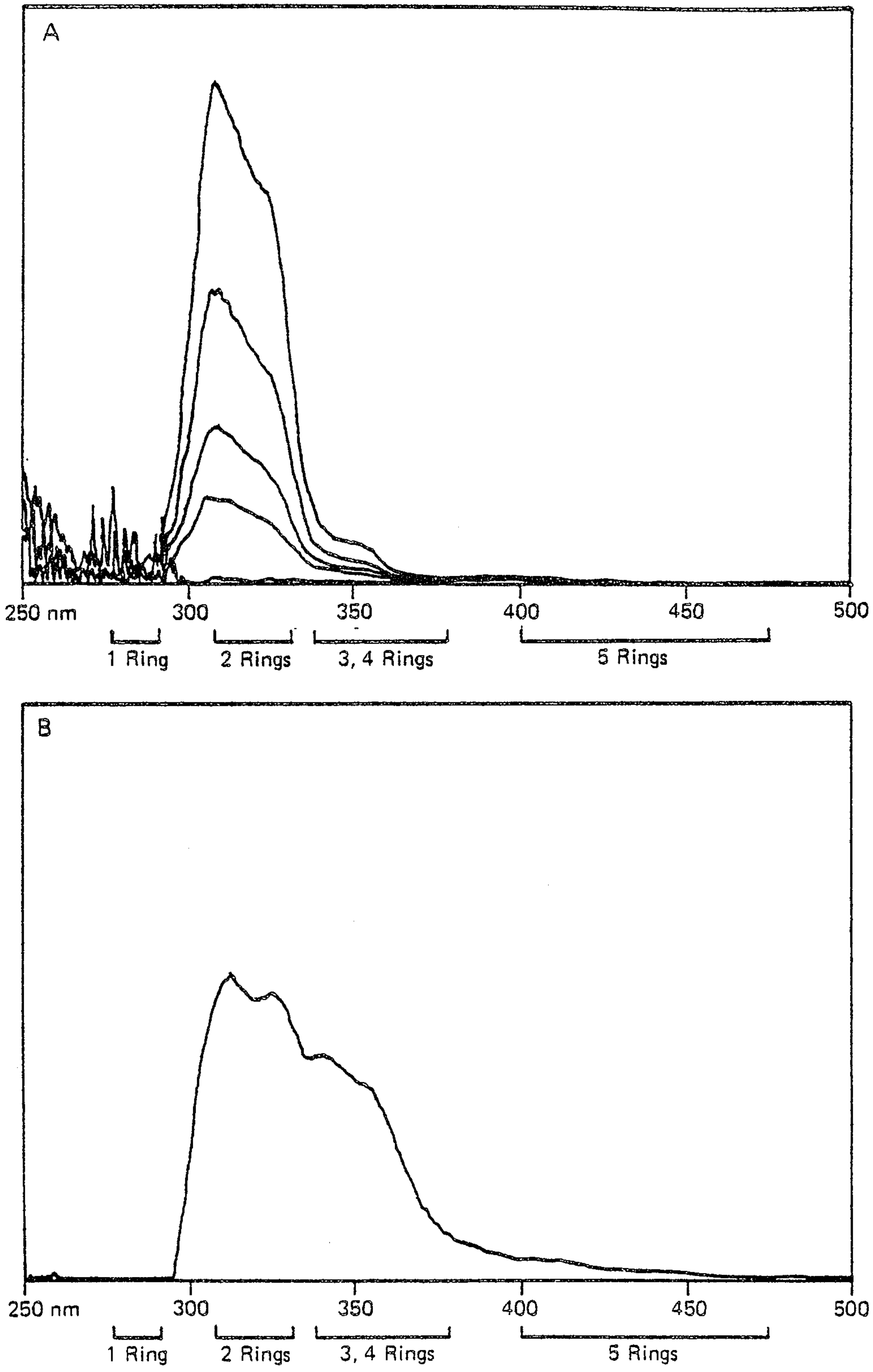


Figure 3.10. UV/F Spectra of A—Number 2 Fuel Oil and B—Water Sample with Detectable Petroleum Hydrocarbons.

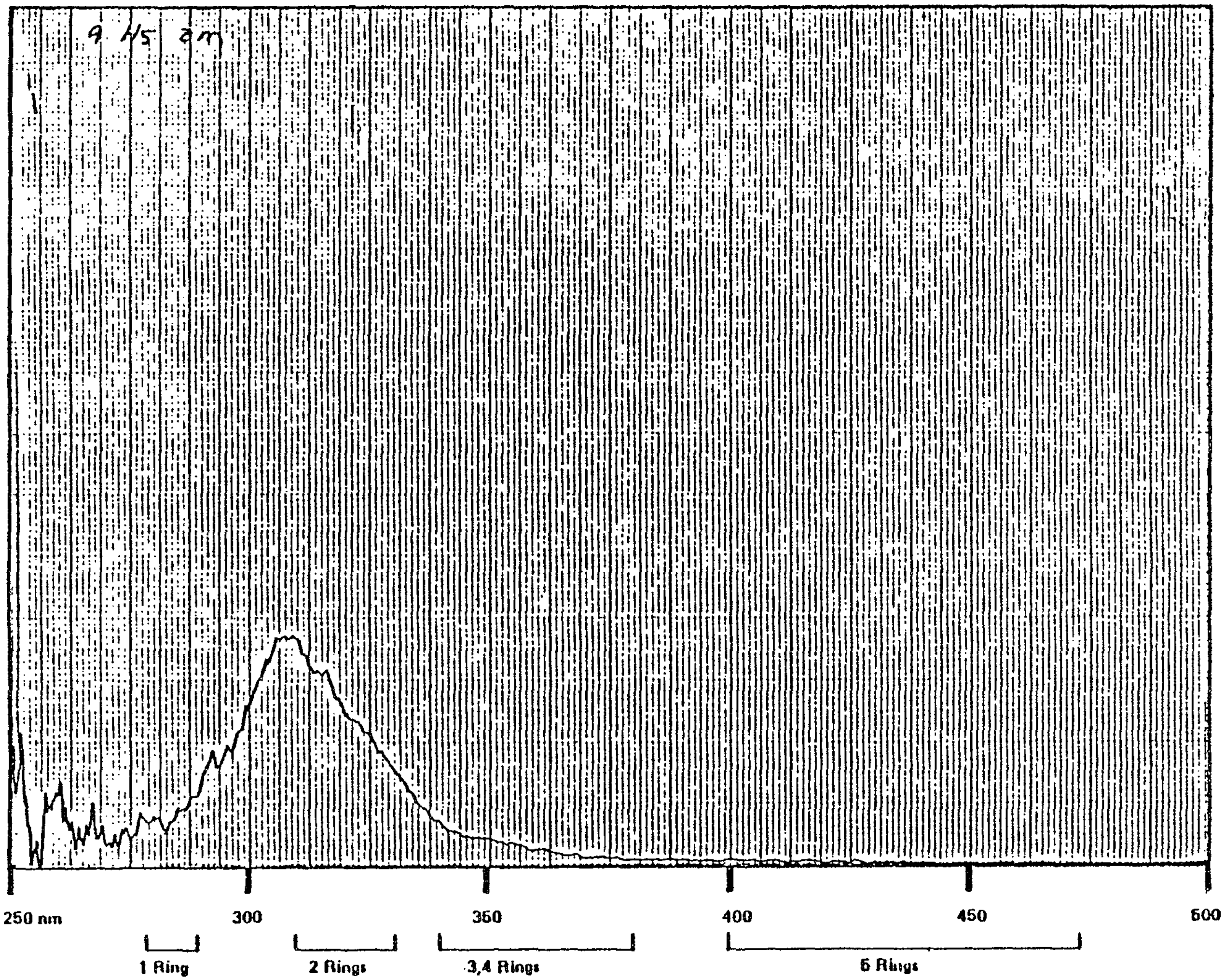


Figure 3.11. UV/Fluorescence (Synchronous Scan) of Bios Water—Baseline.

TABLE 3-8

UV/FLUORESCENCE RESULTS OF AUGUST/SEPTEMBER SAMPLES

SAMPLE	COLLEC-TION DATE	SAMPLING DEPTH (m)	CONCEN-TRATION[a,b] (µg/l)
Bay 9	8/26/80	1	ND[c]
Bay 9	8/26/80	5	ND
Bay 9	8/26/80	10	ND
Bay 9	9/20/80	1	ND
Bay 9	9/20/80	5	ND
Bay 10	8/26/80	1	ND
Bay 10	8/26/80	10	ND
Bay 10	8/26/80	10	86
Bay 10	9/19/80	1	ND
Bay 10	9/19/80	5	ND
Bay 10	9/19/80	10	ND
Bay 11	8/26/80	1	ND
Bay 11	8/26/80	5	ND
Bay 11	9/19/80	1	ND
Bay 11	9/19/80	5	ND
Bay 11	9/18/80	10	ND
Bay 102 Prespill	8/18/80	1	3
Bay 102 Prespill	8/18/80	4	ND
Z Lagoon Bay 103 Prespill NBS	8/17/80	1	ND
Z Lagoon Bay 103 Prespill NBS	8/17/80	10	13
Bay 103 Prespill	8/18/80	1	ND
Bay 103 NBS Prespill	8/18/80	7	67
Z Lagoon Prespill	8/20/80	1	ND
Z Lagoon Prespill	8/20/80	10	ND
Bay 103 Afterspill	8/21/80	1	ND
Bay 103 Afterspill	8/21/80	10	ND
Bay 103	9/20/80	1	ND
Bay 103	9/20/80		ND

TABLE 3-8 (Cont.)

SAMPLE	COLLECTION DATE	SAMPLING DEPTH (m)	CONCENTRATION[a,b] (μg/l)
Blank #1	9/19/80	-	ND[c]
Blank #1 (leaked; probably contaminated)	9/20/80	-	ND
Blank #2 (120 ml Freon)	9/17/80	-	ND
Blank #1	9/17/80	-	ND
Blank #2 UV/F	9/19/80	-	3
Blank #3	9/19/80	-	ND
Blank #3	9/20/80	-	ND
Blank (leaked; probably contaminated)	9/18/80	-	ND

[a] Concentrations expressed as micrograms of API No. 2 fuel oil equivalents/liter of seawater extracted.

[b] Detection limit is 3 μg/l.

[c] Not detected.

samples, three taken in Z Lagoon prior to the shoreline experiment, and one taken in Bay 10. We believe these determinations to be the result of sporadic sample contamination or of inclusion of significant amounts of sediment in the sample prior to extraction.

3.2.2 Seawater Samples (GC^2 GC^2/MS)

Three 4-liter seawater samples from Bay 9 (1, 5, and 10 m) were obtained and analyzed by UV/F (see previous section) and by GC^2 (Table 3-9). Whole, unfractionated extracts were analyzed by GC^2 as were fractionated (f_1 and f_2) extracts. No detectable hydrocarbons were observed in any of these 4-liter samples although the unfractionated (total lipid) extracts did reveal several non-hydrocarbon components (Figure 3-12).

The results from the September sampling were more definitive due to the larger volume of water sampled. The NBS-sampler-obtained set contained samples laden with total lipid material (primarily non-hydrocarbon) (Table 3-10). A typical GC^2 trace of the unfractionated extract (e.g., Figure 3-12) revealed a complex set of major (methyl esters, wax esters) and minor (unidentified) compounds, all having their origin in planktonic residues captured in the water samplers. Fractionation of these extracts into f_1 and f_2 hydrocarbon fractions removed most of this polar material and revealed very low levels (<1 ppb) of hydrocarbon material, most often of a biogenic origin (i.e., olefinic material in the f_2 fraction). In two samples (Table 3-10), a small amount of petrogenic material was detected in the f_1 fraction. This material resembled tar residues (tar specks), being

TABLE 3-9

SEAWATER SAMPLES OBTAINED FOR GC^2 AND GC^2/MS ANALYSES

LOCATION	DATE	DEPTH (m)	VOLUME (liter)	TYPE
Bay 10	9/19/80	1	20.5	NBS[a]
Bay 10	9/19/80	5	19.5	NBS
Bay 10	9/19/80	5	19.5	NBS
Bay 10 (Filtered Seawater)	9/7/80	1	210	Risebrough LVWS[b]
Bay 10 (Particulates	9/7/80	1	210	Risebrough LVWS
Bay 11	9/1/80	1	16	NBS
Bay 11	9/17/80	5	20	NBS
Bay 11 (Filtered Seawater)	9/11/80	8	130	Risebrough LVWS
Bay 11 (Particulates	9/11/80	8	130	Risebrough LVWS
Z Lagoon	9/20/80	1	16.2	NBS
Z Lagoon	9/20/80	5	15.5	NBS
Blank Polyplug #1				
Blank Filter #1				
Blank Polyplug #2				
Blank Filter #2				

Key:
NBS = 4-liter drop sampler
LVWS = large-volume water sampler

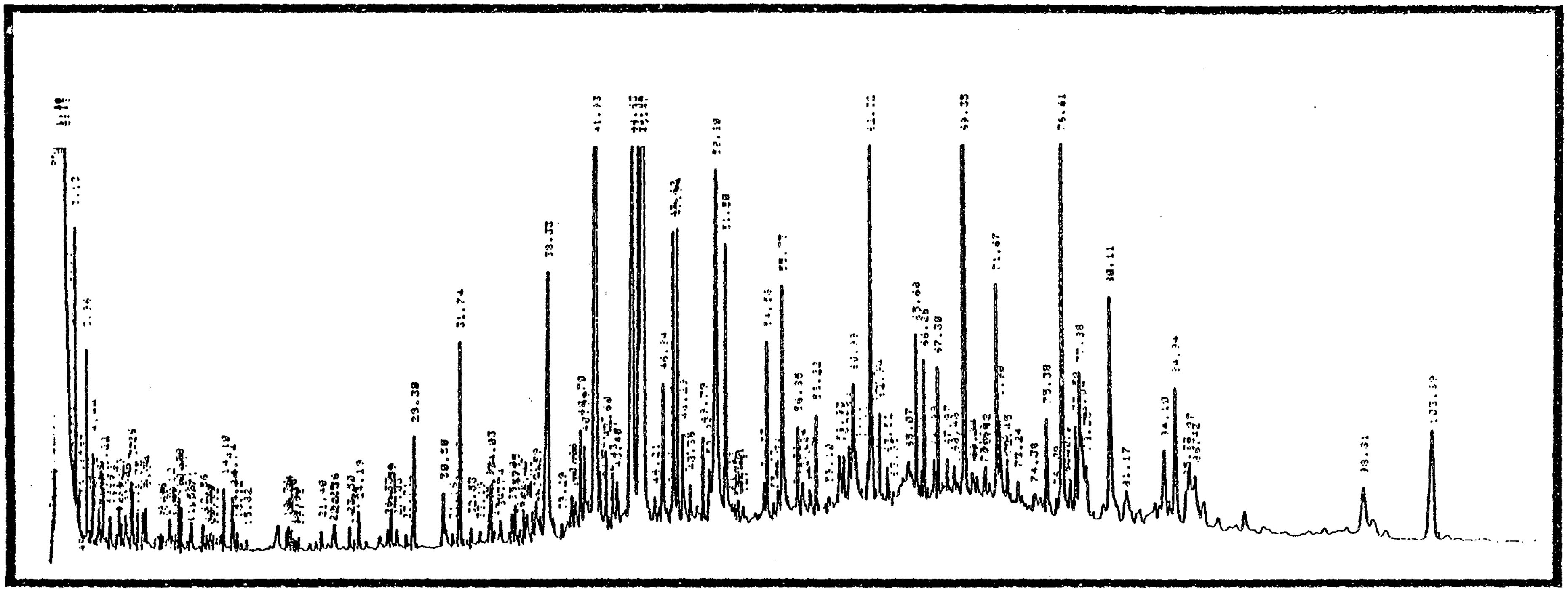


Figure 3.12. GC^2 of Unfractionated Seawater Extract Showing Polar Lipid Material.

TABLE 3-10

ANALYTICAL RESULTS - SEAWATER SAMPLES

SAMPLE	LIPID WEIGHT (UNFRACTIONATED) (µg/l)	HYDROCARBONS (FRACTIONATED) (µg/l)	GC-TYPE (FRACTIONATED
June			
Bay 9 (1 m)	ND	ND[a]	3
Bay 9 (5 m)	ND	ND[a]	3
Bay 9 (10 m)	ND	ND[a]	3
September			
Bay 10 (1 m) - NBS	2.8	ND[b]	3/1
Bay 10 (5 m) - NBS	1.2	ND[b]	3
Bay 10 (5 m) - NBS	0.5	ND[b]	3
Bay 11 (1 m) - NBS	2.7	ND[b]	3/1
Bay 11 (5 m) - NBS	3.4	ND[b]	3
Z Lagoon (1 m) - NBS	3.2	ND[b]	3
Z Lagoon (5 m) - NBS	2.7	ND[b]	3
	f1 (ng/l)[c]	f2 (ng/l)[c]	
Bay 10 (1 m) LVWS - filtered seawater	1.4	2.0	4
Bay 10 (1 m) LVWS - particulates	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

[a] ND = <5 µg/l.

[b] ND = <0.3 µg/l.

[c] Gravimetric weight.

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

highly paraffinic in nature. However, the absolute levels of this tarry material were less than half of the "hydrocarbon" values presented in Table 3-10.

The large-volume water samplers yielded information on particulate and filterable ("dissolved") hydrocarbons from Bays 10 and 11. Once again, the unfractionated extract contained substantial quantities (10-30 µg/l) of lipid material mainly of a planktonic origin. GC^2 and GC^2/MS analyses were performed on these samples and yielded the quantitative data shown in Table 3-10. The very low levels of petroleum-like hydrocarbons presented are real. The sampling technique allows very low levels of hydrocarbons to be detected (0.7-2.0 ng/l = parts per trillion).

The particulate/dissolved couples proved extremely interesting. The Bay 10 filtered seawater contained extremely low levels of hydrocarbons in the saturated fraction (f_1) with no GC^2 detectable components. However, the aromatic (f_2) fraction contained detectable alkylated naphthalene phenanthrene and dibenzothiophene by GC^2 (Figure 3-13) and quantifiable GC^2/MS (Table 3-11). Similarly, the Bay 11 water had very low, but detectable, levels of the same compounds.

The particulates were quite unlike the dissolved fraction, the composition of the former being dominated by saturated hydrocarbons of combined tar-like and terrigenous biogenic sources (Figure 3-14), and having no detectable aromatics. Thus, the dissolved and particulate fractions are decoupled with respect to source and probably transport paths as well.

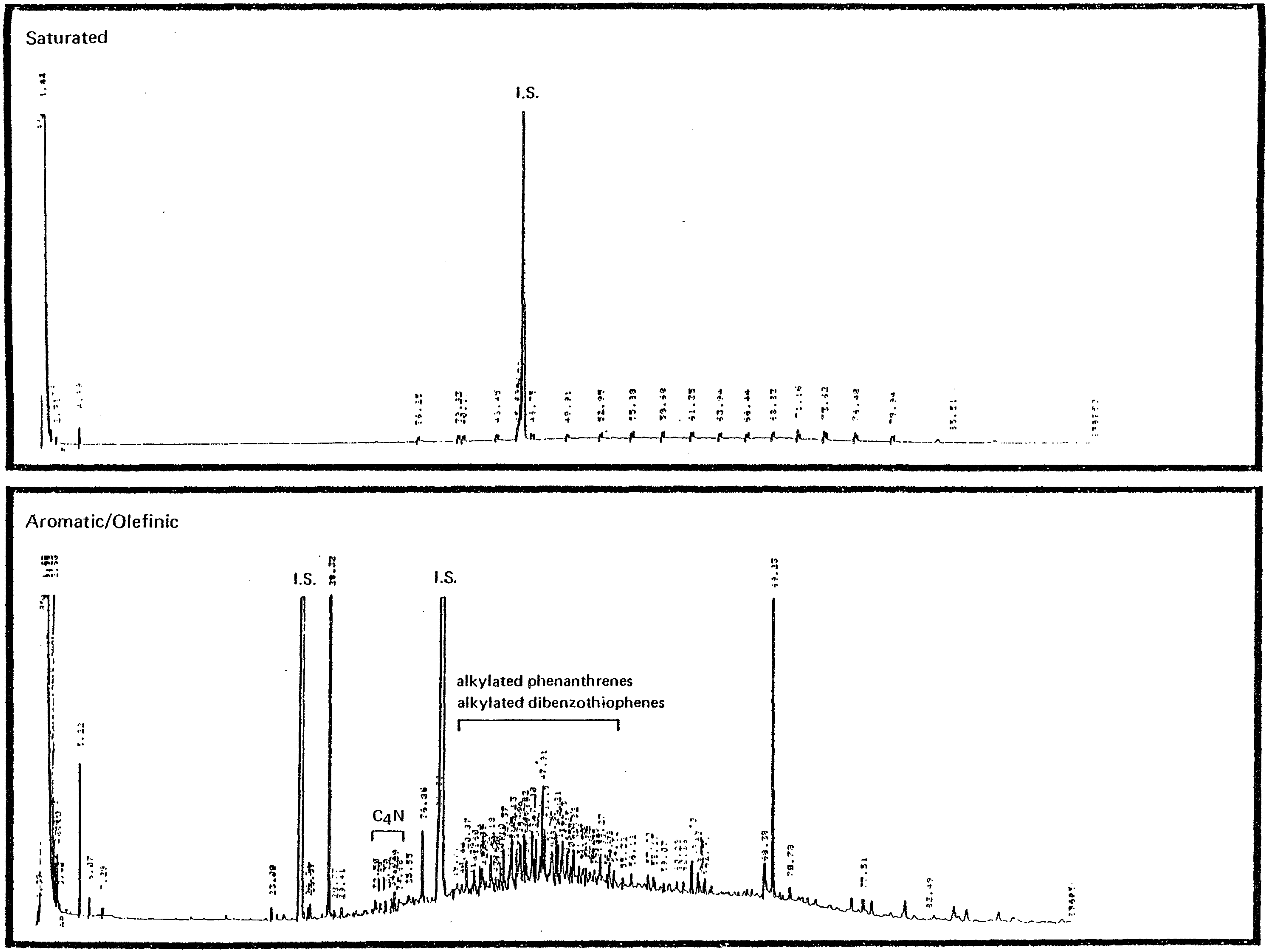


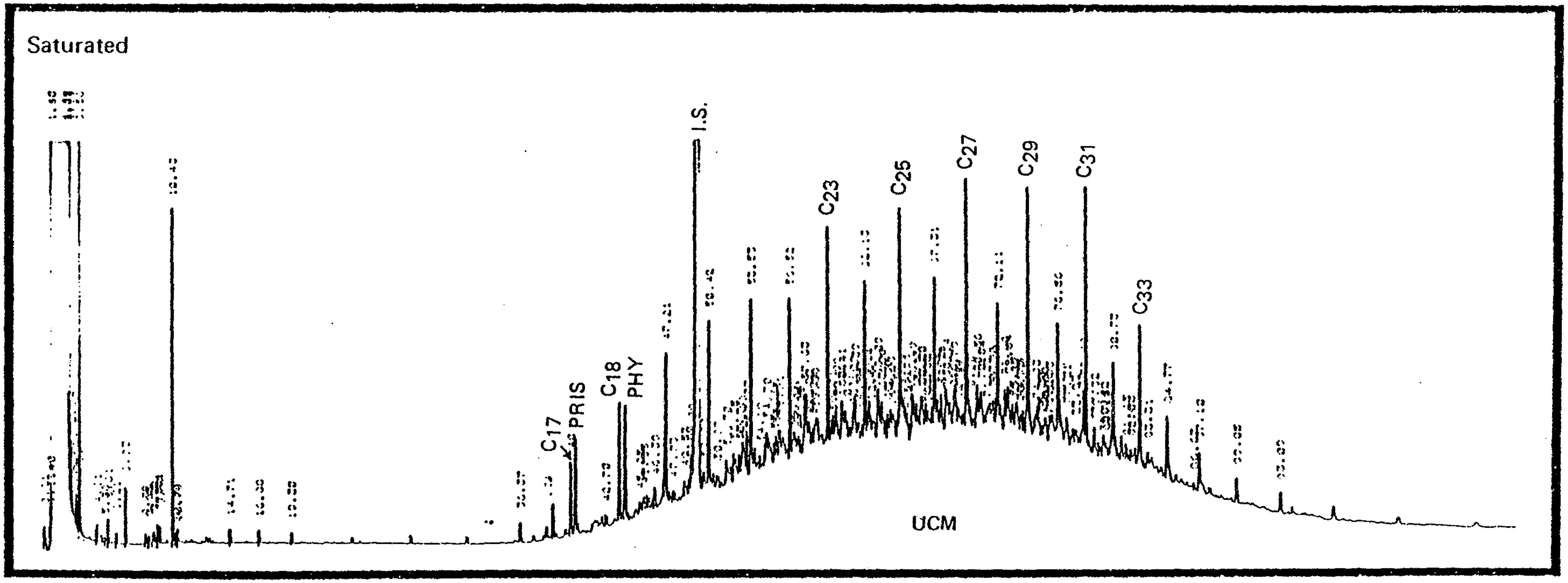
Figure 3.13. GC^2 Traces of Hydrocarbons in Bay 10 Filtered Seawater (LVWS).

TABLE 3-11

AROMATIC HYDROCARBON LEVELS IN LARGE-VOLUME WATER SAMPLES BY GC^2/MS

SAMPLE COMPOUND	BAY 10 FILTERABLE (ng/l)	BAY 10 PARTICULATE (ng/l)	BAY 11 FILTERABLE (ng/l)	BAY 11 PARTICULATE (ng/l)
Tetramethyl naphthalene	0.2	ND	ND	ND
Methyl phenanthrene	0.3	ND	0.05	ND
Dimethyl phenanthrene	0.5	ND	0.1	ND
Trimethyl phenanthrene	0.15	ND	ND	ND
Methyl dibenzothiophene	0.25	ND	0.05	ND
Dimethyl dibenzothiophene	0.4	ND	0.1	ND
Trimethyl dibenzothiophene	0.4	ND	0.1	ND

ND = <0.05 ng/l.



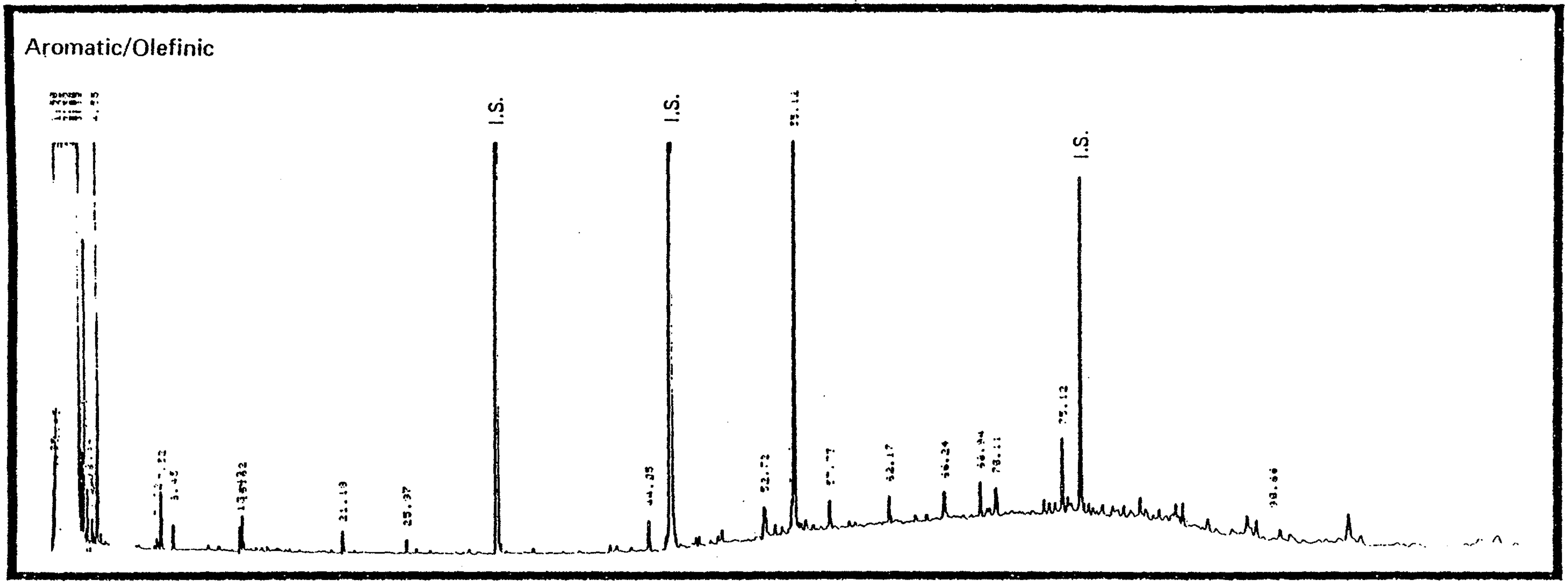


Figure 3.14. GC^2 Traces of Hydrocarbons in Particulates from Bay 10 (LVWS).

3.2.3 Sediment Samples - UV/F Analyses

The results of the UV/F analyses of sediments are presented in Tables 3-12 and 3-13 for the June offshore and August/September beach samples, respectively. Several replicate analyses (two subsamples) were performed in the June sample batch (#14-2-15-CC-16) and the results indicate that the quantification of hydrocarbons by this method is at least internally consistent.

UV/F measurements of one possible sample contaminant, the core caps, indicated this potential error was not a problem in this study.

Qualitatively, the UV/F spectra (Figure 3-15) reveal the presence of low levels of 3-, 4-, and 5-ring aromatic compounds and the readily identified perylene doublet. The spectra are quite unlike that of the Lagomedio crude (Figure 3-15A), thus pointing to a weakness in the quantification method used (i.e., Lagomedio as a standard) as well as a strength in the method for later distinguishing background from spill-related inputs. The perylene doublet was detected in many offshore sediments as well as several beach sediment samples.

3.2.4 Sediment Samples - GC^2 Analyses

To reveal the details of the hydrocarbons in the baseline sediments, GC^2 analyses were performed. The quantitative results are presented in Tables 3-14 and 3-15. The values presented give both the total saturated (Fraction 1) and aromatic/olefinic (Fraction 2) concentrations, determined gravimetrically and the amount of

TABLE 3-12

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

SAMPLE NUMBER	CONCENTRATION[a] (μg/g)
13-A-2-17-CC4	1.0
13-A-3-24-CC5	0.5
10-2-13-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

[a] Weathered Lagomedio equivalents @356 nm.

TABLE 3-13

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

SAMPLE NUMBER	CONCENTRATION[a] (μg/g dry weight)
9-C-H	0.3
9-C-L	0.6
9-N-H	0.2
9-N-L	0.2
9-S-H	0.2
9-S-L	0.1
10-C-H	0.2
10-C-L	0.6
10-N-H	0.3
10-N-L	0.6
10-S-H	0.1
10-S-L	0.2
11-C-H	0.1
11-C-L	0.1
11-N-H	ND
11-N-L	0.1
11-S-H	0.4
11-S-L	0.3
Bay 102 - Beach Sediment Prespill	ND
Bay 103 - Beach Sediment Prespill	0.3
Backshore Beach T-1	0.2
ERCO Blank	0.0

[a] Concentrations expressed as micrograms of Lagomedio crude oil equivalents/gram of dry sediment.

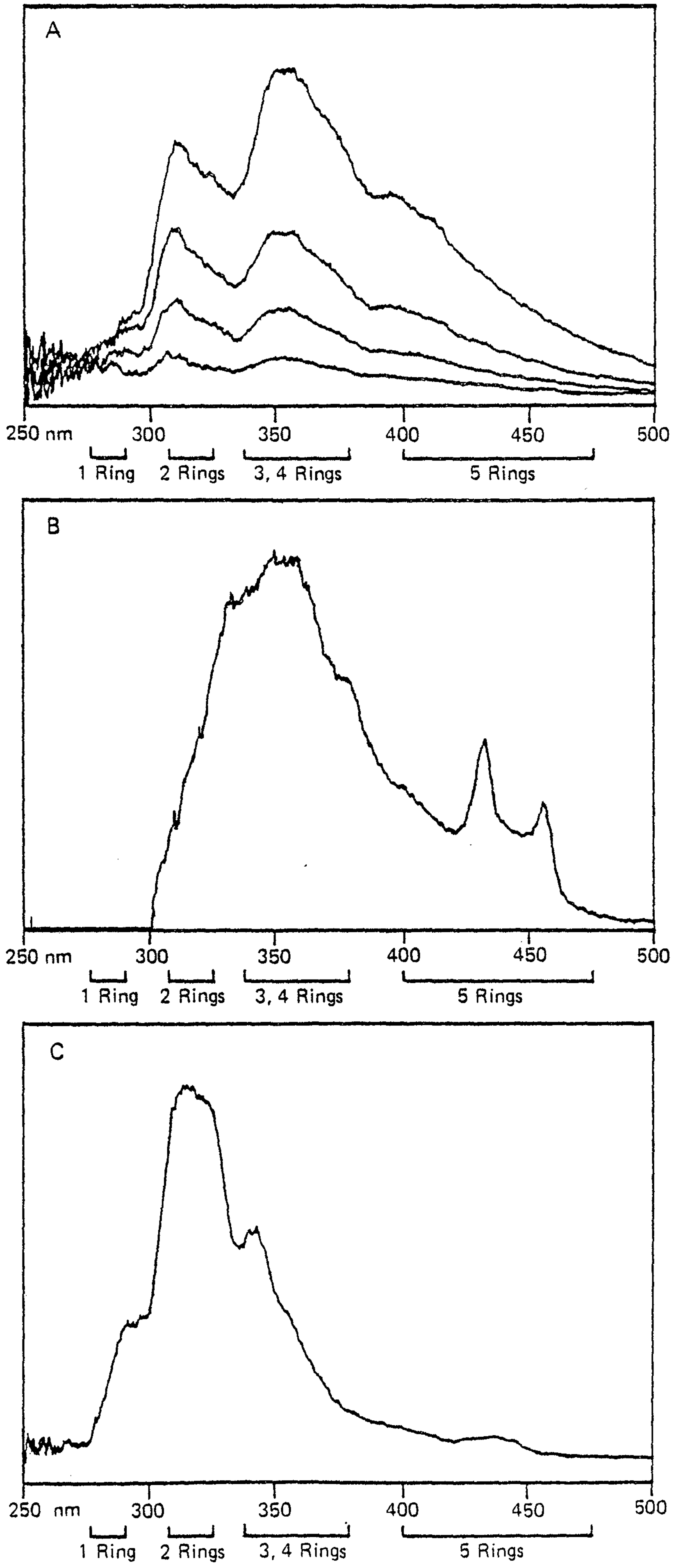


Figure 3.15. UV/F Spectra of A—Several Dilutions of Lagomedio Crude; B—A Beach Sediment; C—An Offshore Sediment.

chromatographically resolvable material (i.e., GC^2 peaks), the latter always being a part of the former. Fraction 1 contains two diagnostic parameters, the relative amounts of the isoprenoids pristane and phytane (PRIS/PHY) and the carbon preference index (CPI). Pristane is a commonly produced biogenic hydrocarbon originating in zooplankton and is also present in all fossil fuels. Phytane on the other hand is found only in fossil fuels. A PRIS/PHY near unity indicates a petroleum-related hydrocarbon source while clean sediments contain much more pristane. The PRIS/PHY ratios range from 3 to 20 in all offshore samples and 13 to 1,500 in the beach samples.

The second diagnostic ratio, CPI, examines the relative amount of n-alkanes containing an odd number of carbon atoms to those containing an even number, in the C_{26} to C_{30} range. Terrigenous plant waxes are abundant in odd carbon n-alkanes (i.e., CPI >>1) while crude oils have ratios near unity due to abiotic synthesis. CPI values in all samples are high, i.e., 3 to 12, indicating a preponderance of terrigenous plant detritus in these samples.

The data on the aromatic/olefinic fraction is fairly nonspecific as many of the compounds readily apparent by GC^2 are unidentified biogenic olefins. The total gravimetric f_2 values are higher than the GC traces would indicate, suggesting that much of the f_2 material does not elute from the GC column. This material is comprised of greenish-pigmented material which in spite of the fact that it elutes in the f_2 of the silicic acid column is either non-hydrocarbon in nature or thermally labile, but in any event of little consequence in this study.

The "total extractables" number indicates the total lipoidal, or solvent extractable organic material, only a small part of which is hydrocarbon (i.e., f_1 or f_2). The f_3 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^2 traces.

The Fraction 2 GC^2-determined compositions of all offshore samples are similar (Figure 3-16) and different than the beach f_2 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_1) 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 3-14

JUNE 1980 BIOCHEMISTRY DATA SUMMARY

		FRACTION 1						FRACTION 2			
	LAB CODE	RESOLVED (GC) (μg/g)	TOTAL (GRAV) (μg/g)	PRISTANE (ng/g)	PHYTANE (ng/g)	PRIS/ PHY	CPI	RESOLVED (G/C) (μg/g)	TOTAL (GRAV) (μg/g)	FRACTION 3 (μg/g)	TOTAL EXTRACT-ABLES (μg/g)
13A-2-17-CC4	06-910	0.4	1.6	5	1	5	5.1	0.5	32.3	143	329
13A-3-24-CC5	06-912	0.7	6.0	6	1	6	6.1	0.7	11.4	42.5	155
10-2-13-CC10	06-914	0.4	2.0	2	0.3	7	10.8	0.8	175	121	660
10-3-22-CC11	06-916	0.1	7.6	2	0.6	3	6.2	0.1	9.3	13.4	92
14-1-2-CC12	06-918	0.4	0.8	2	<0.1	20	7.2	0.7	29.4	69.6	301
14-2-15-CC16 (0-4 cm)	06-920	0.4	2.0	8	1	8	10.0	0.4	31.2	43.2	228
14-2-15-CC16 #1 (10-15 cm)	06-922	0.7	3.6	7	1	7	6.1	1.1	23.5	73.3	289
14-2-15-CC16 #2 (10-15 cm)	06-924	0.6	2.0	7	0.5	14	9.2	0.8	40.6	116	341
14-2-15-CC16 (28-33 cm)	06-926	0.7	1.6	15	1	15	5.8	0.7	18.8	94	333
14-3-26-CC17	06-928	0.2	1.6	12	1	12	3.3	0.1	11.3	33	89
105-1-10-CC20 #1	06-930	0.6	2.6	10	1	10	5.3	1.1	63.7	107	337
105-1-10-CC0 #2	06-932	0.6	1.9	9	1	9	5.5	1.4	47.4	115	323

$$\text{CPI} = \text{carbon preference index} = \frac{2([n\text{-}C_{27}] + [n\text{-}C_{29}])}{[n\text{-}C_{26}] + 2[n\text{-}C_{28}] + [n\text{-}C_{30}]}$$

TABLE 3-15

BEACH SEDIMENT GEOCHEMISTRY DATA SUMMARY - AUGUST/SEPTEMBER 1980

	FRACTION 1						FRACTION 2		
SAMPLE NUMBER	RESOLVED (GC^2) (µg/g)	TOTAL (GRAV) (µg/g)	PRISTANE (ng/g)	PHYTANE (ng/g)	PRIS/ PHY	CPI	RESOLVED (GC^2) (µg/g)	TOTAL (GRAV) (µg/g)	TOTAL EXTRACT-ABLES (µg/g)
9-N-L	0.03	0.17	ND	ND	-	2.5	0.007	0.26	0.7
9-N-H	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-H	0.02	1.7	1	ND	-	2.8	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-H	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	-	2.7	0.05	0.2	3.5
10-S-L	0.08	3.1	5.0	0.3	17	5.5	0.1	1.2	13.9
10-S-H	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
11-N-H	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-H	0.28	4.8	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
11-S-H	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

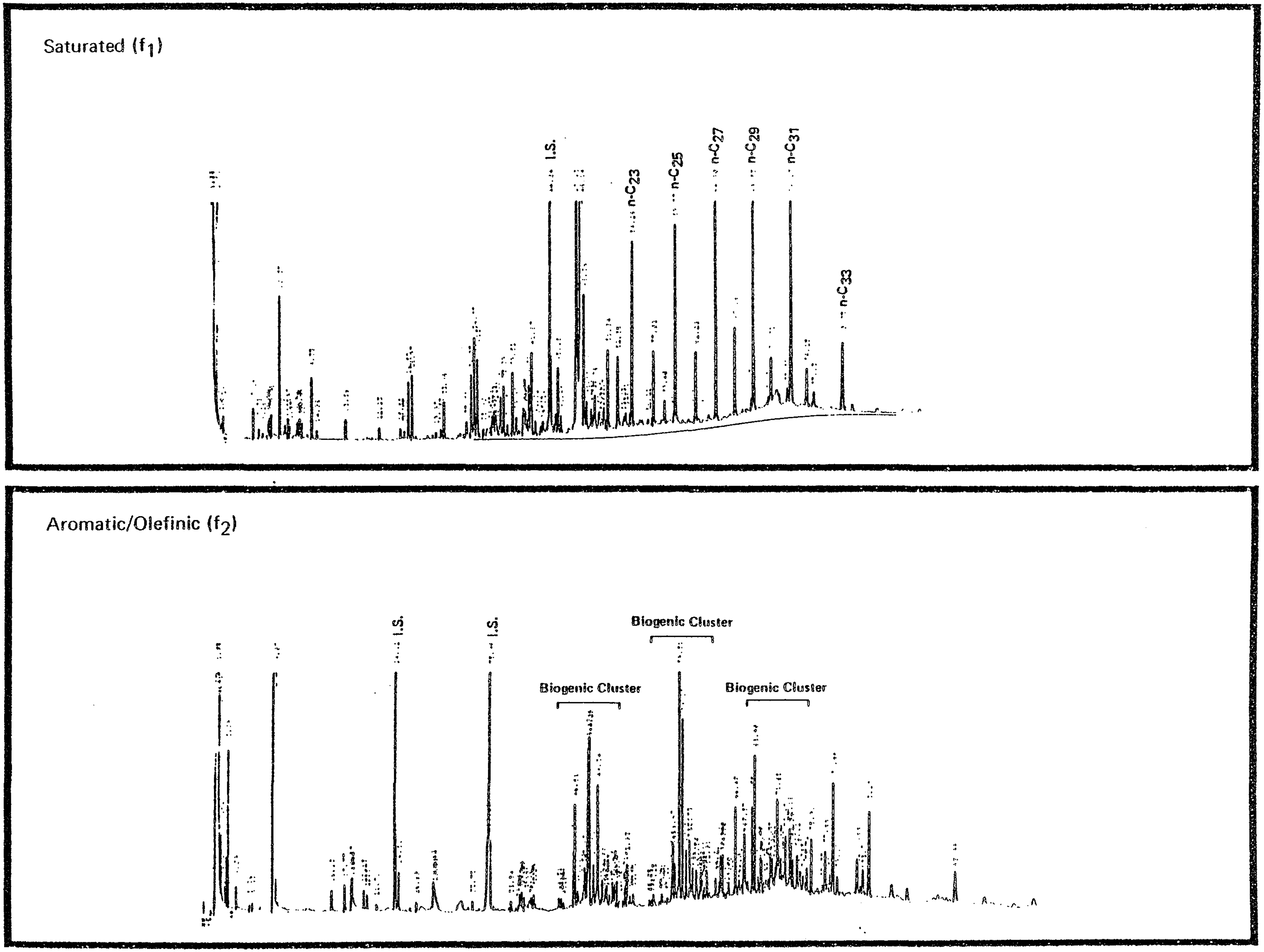


Figure 3.16. Representative GC^2 Traces of Hydrocarbons in Offshore Samples.

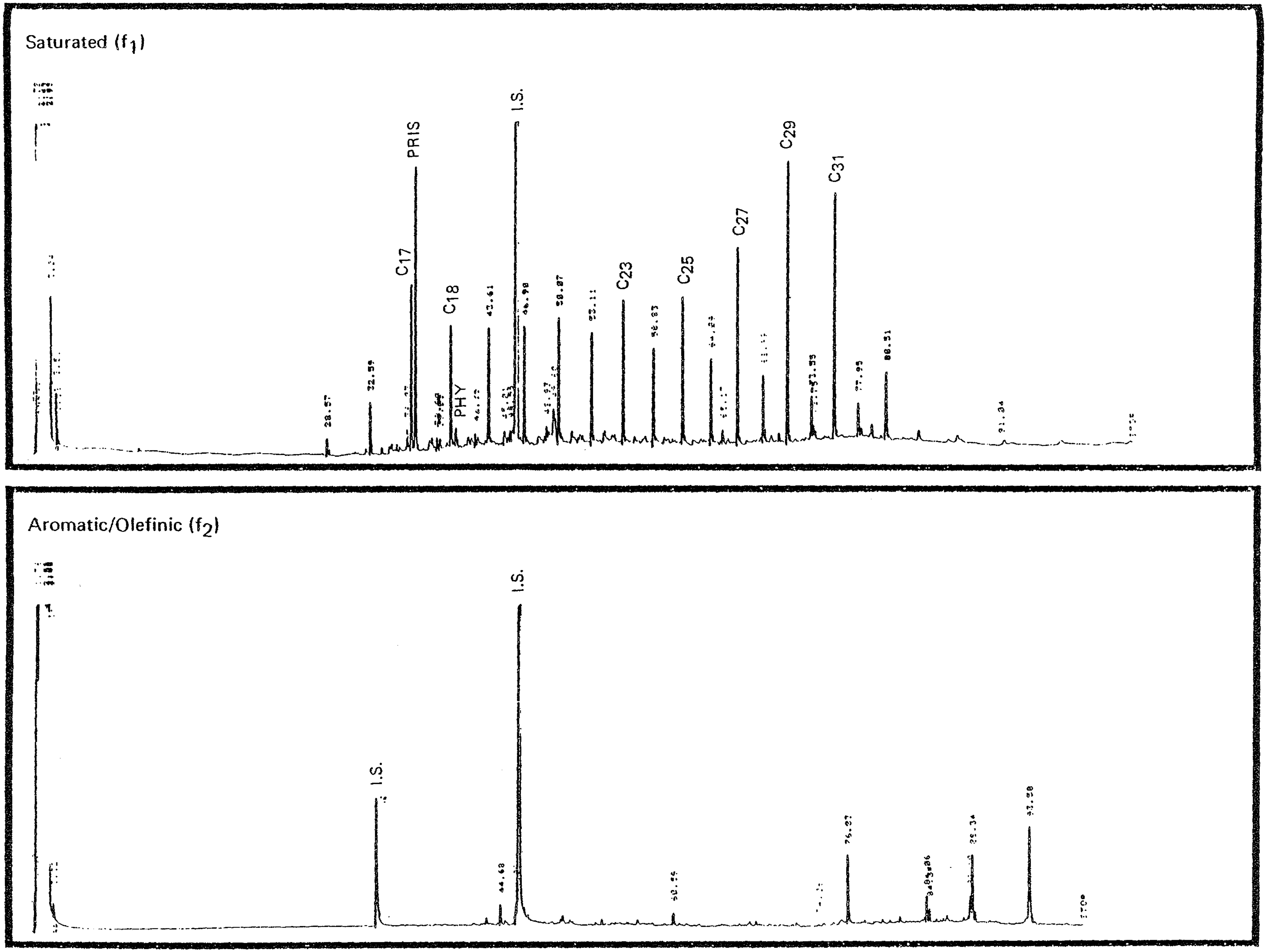


Figure 3.17. Representative GC^2 Traces of Hydrocarbons in Beach Samples (No. 1).

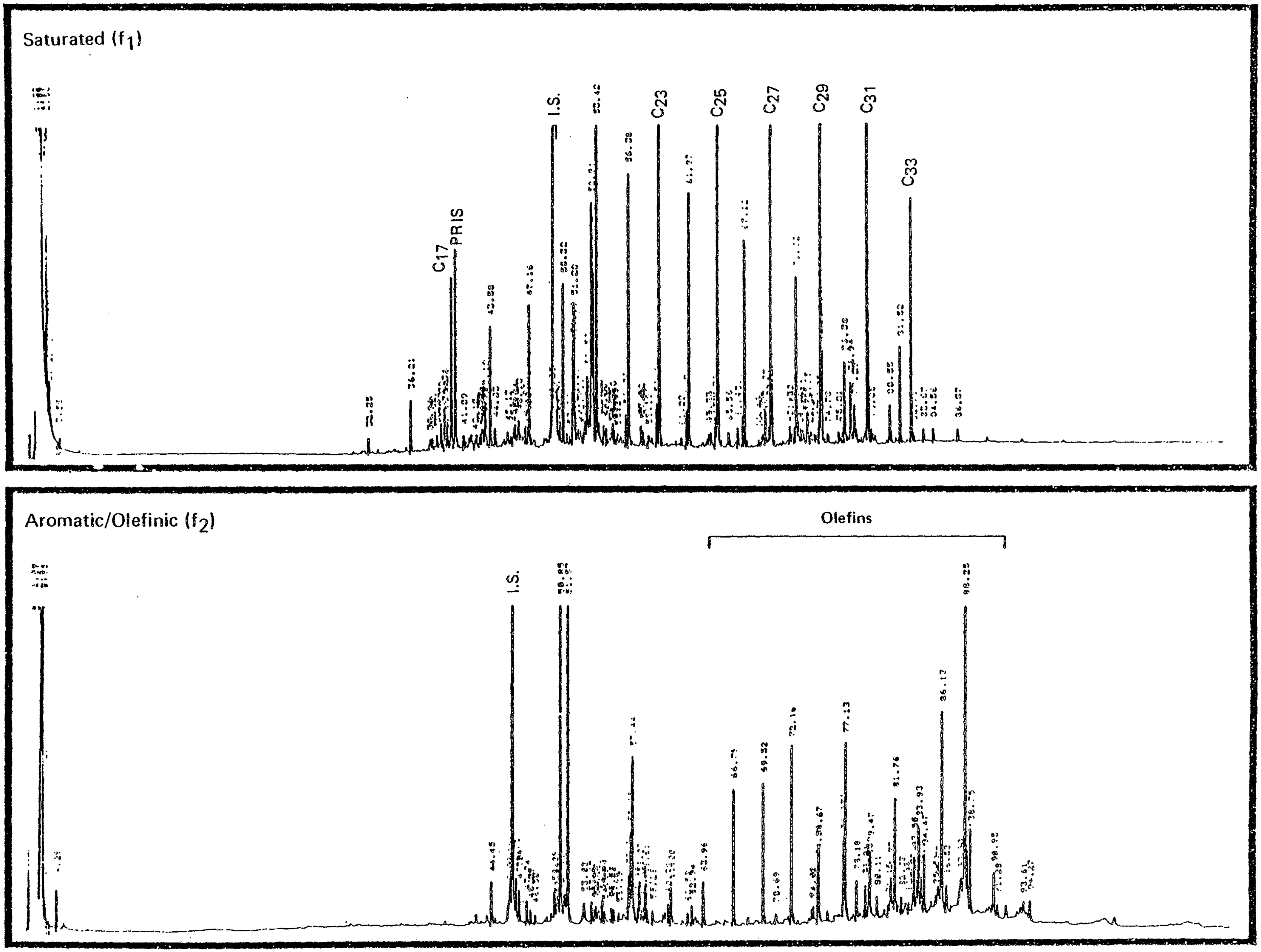


Figure 3.18. Representaive GC^2 Traces of Hydrocarbons in Beach Samples (No. 2).

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

An illustrative set of generic GC^2 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^2/MS analyses were utilized to examine (1) the identities and levels of PAH compounds in f_2 fractions of selected samples, (2) the nature of the background pentacyclic 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.

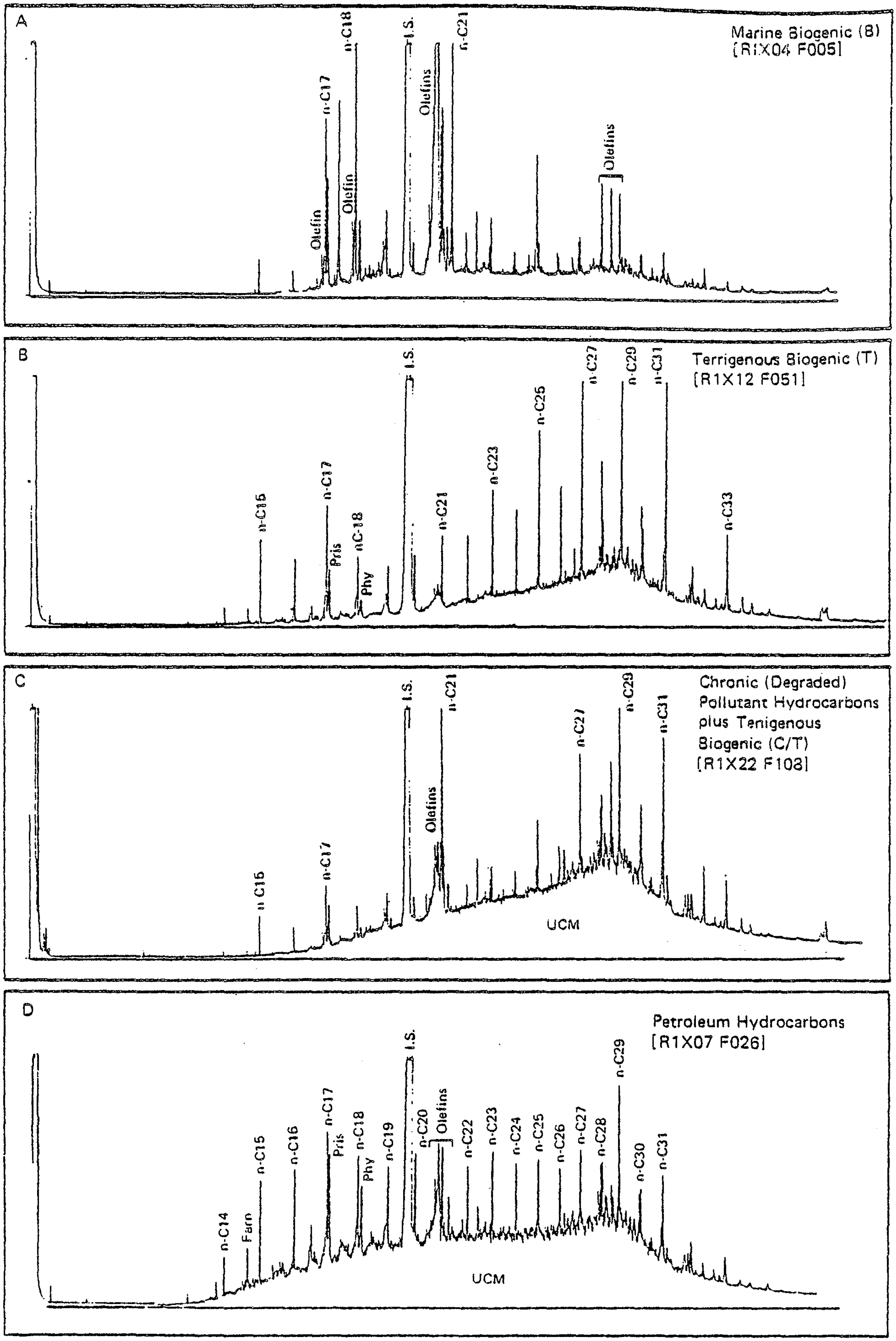


Figure 3.19. Glass capillary gas chromatograms of saturated hydrocarbons in non-oiled & oiled surface sediments.

TABLE 3-16

BASELINE PAH CONCENTRATIONS IN OFFSHORE AND BEACH SEDIMENT BY GC^2/MS

	OFFSHORE			BEACH				
BAY:	13	9	10	9	9	10	10	11
SAMPLE ID	13-3-24-CC5	14-2-15-CC16	10-2-13-CC10	9-C-L	9-C-H	10-N-L	10-N-H	11-C-L
COMPOUND								
Phenanthrene (m/e 178)	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
Σ Phenanthrenes	3.5	3.6	2.6	1.0	0.3	13.2	2.2	0.8
Fluorene (m/e 166)	ND	ND	ND	0.03	ND	0.4	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	1.7	0.2	ND
Trimethyl fluorene (m/e 208)	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	0.1	ND	1.0	0.1	0.07
Chrysene (m/e 228)	0.6	ND	ND	0.1	ND	1.0	0.1	0.07
Fluoranthene (m/e 202)	0.3	ND	ND	0.4	ND	0.3	0.1	0.05
Pyrene (m/e 202	0.4	0.5	ND	0.3	ND	1.6	0.2	0.15
Benzofluoranthene	ND	ND	ND	0.1	ND	1.6	0.2	0.02
Benzoyrenes	ND	ND	ND	0.1	ND	1.8	0.2	0.04
Perylene	0.9	2.8	10.4	ND	ND	3.3	0.1	0.2
Total extractable organics (μg/g)	155	228	660	1.0	4.5	65.8	1.3	14.7
Total hydrocarbons (μg/g)	17.4	33.2	176.0[a]	0.2	1.8	13.6	0.5	3.1

[a] May contain non-chromatographable pigment material
ND = none detected

One of the beach samples (10-N-L) differed considerably from the others in terms of its PAH content and composition. A petroleum-derived source for the PAH compounds is suggested by the larger quantity (13 ppb) of the phenanthrenes, by the relative abundance of the alkylated phenanthrenes and by the presence of a small quantity of alkylated dibenzothiophenes. However, whatever small quantities of petroleum material may contribute to the PAH, no evidence for petroleum contamination is seen in the saturated hydrocarbon fraction (see Section 3.2.5). Thus, the main contribution to both the total hydrocarbon (13.6 ppm) and total extractable (65.8 ppm) levels are biogenic inputs.

Two curious but unexplained differences exist between the beach samples and the offshore samples. The difference concerns the isomeric composition of the methyl phenanthrenes and the abundance of the higher alkylated phenanthrenes in the samples. The offshore samples examined showed the existence of only 3-methyl phenanthrene and 2-methyl phenanthrene (Figure 3-20) while the beach samples contained these two compounds plus the 9-methyl and 1-methyl isomers (Figure 3-21). Furthermore, the offshore samples do not contain detectable (>0.1 ng/g) levels of the dimethyl and higher alkylated phenanthrene homologs. (Compare Figures 3-20 and 3-21). The phenanthrene mass chromatograms of Lagomedio crude oil are presented in Figure 3-22 for comparison.

3.2.5(b) Pentacyclic Triterpanes (Hopanes)

A set of two offshore and six beach sediment samples was analyzed by GC^2/MS to determine the nature of the pentacyclic triterpane (PT) compounds and their approximate quantities, for use as baseline measurements of this set of

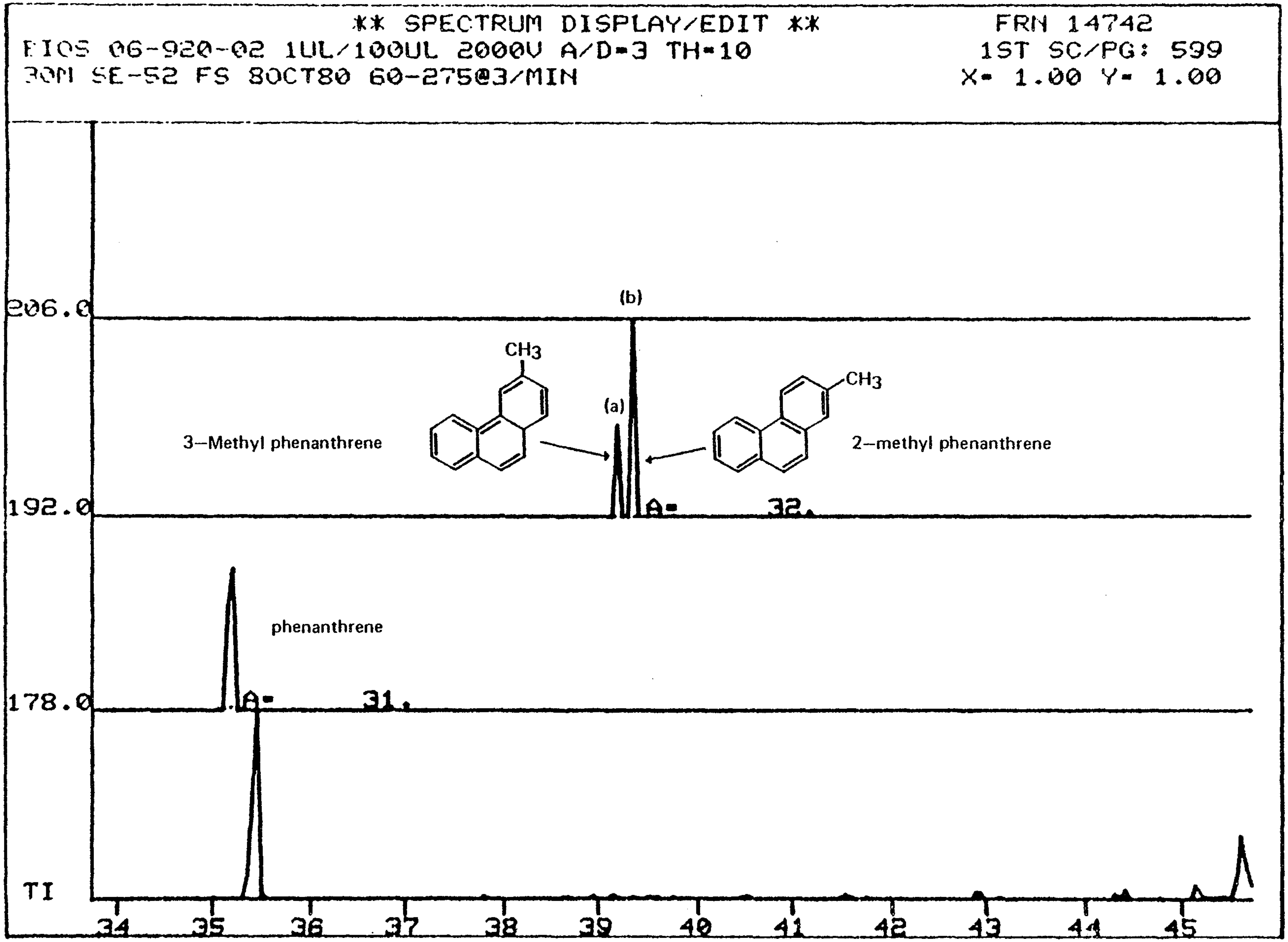


Figure 3.20. Phenanthrene mass chromatograms of offshore sediment sample.

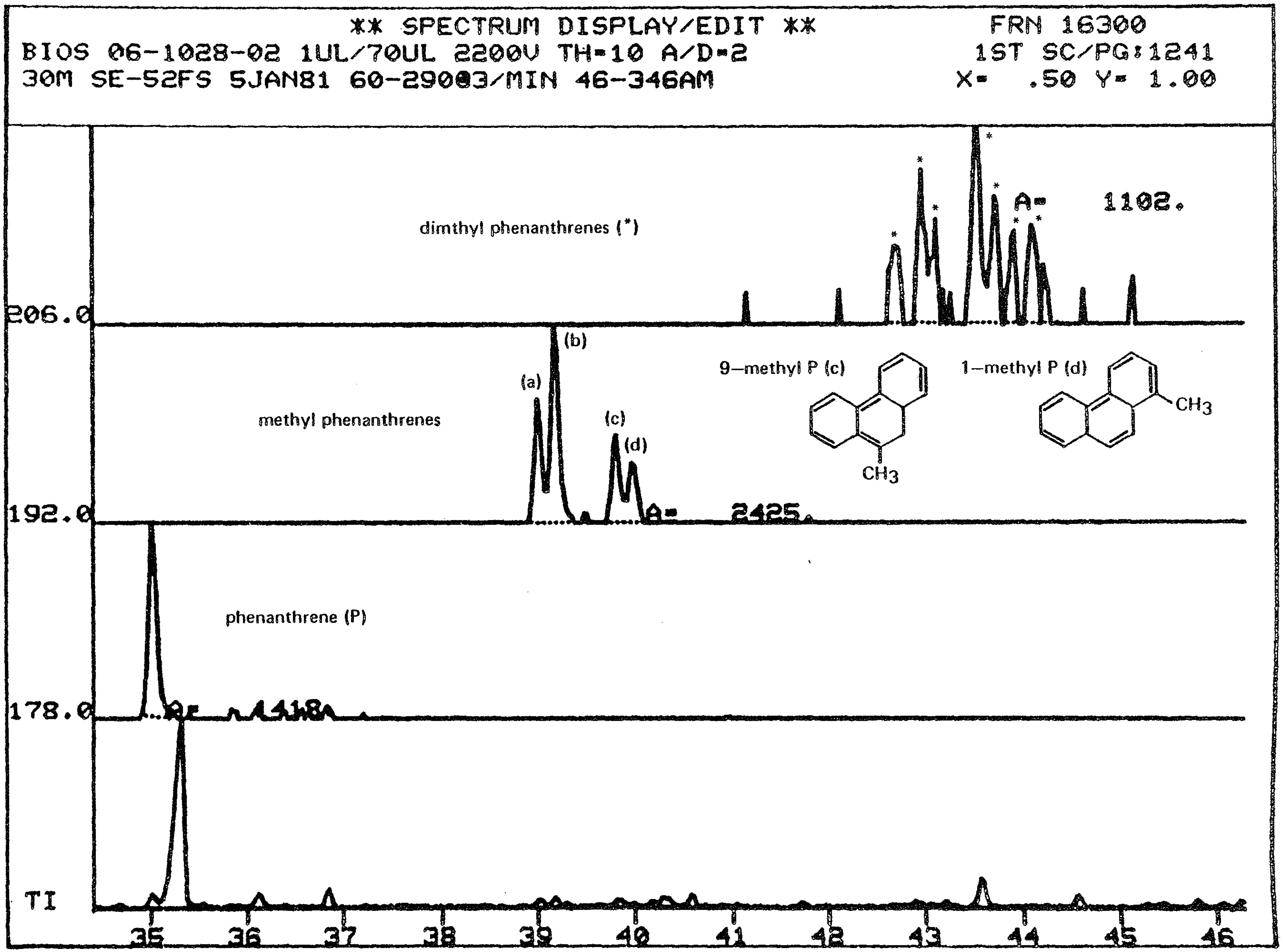


Figure 3.21. Phenanthrene mass chromatograms of beach baseline sample No. 10–N–L.

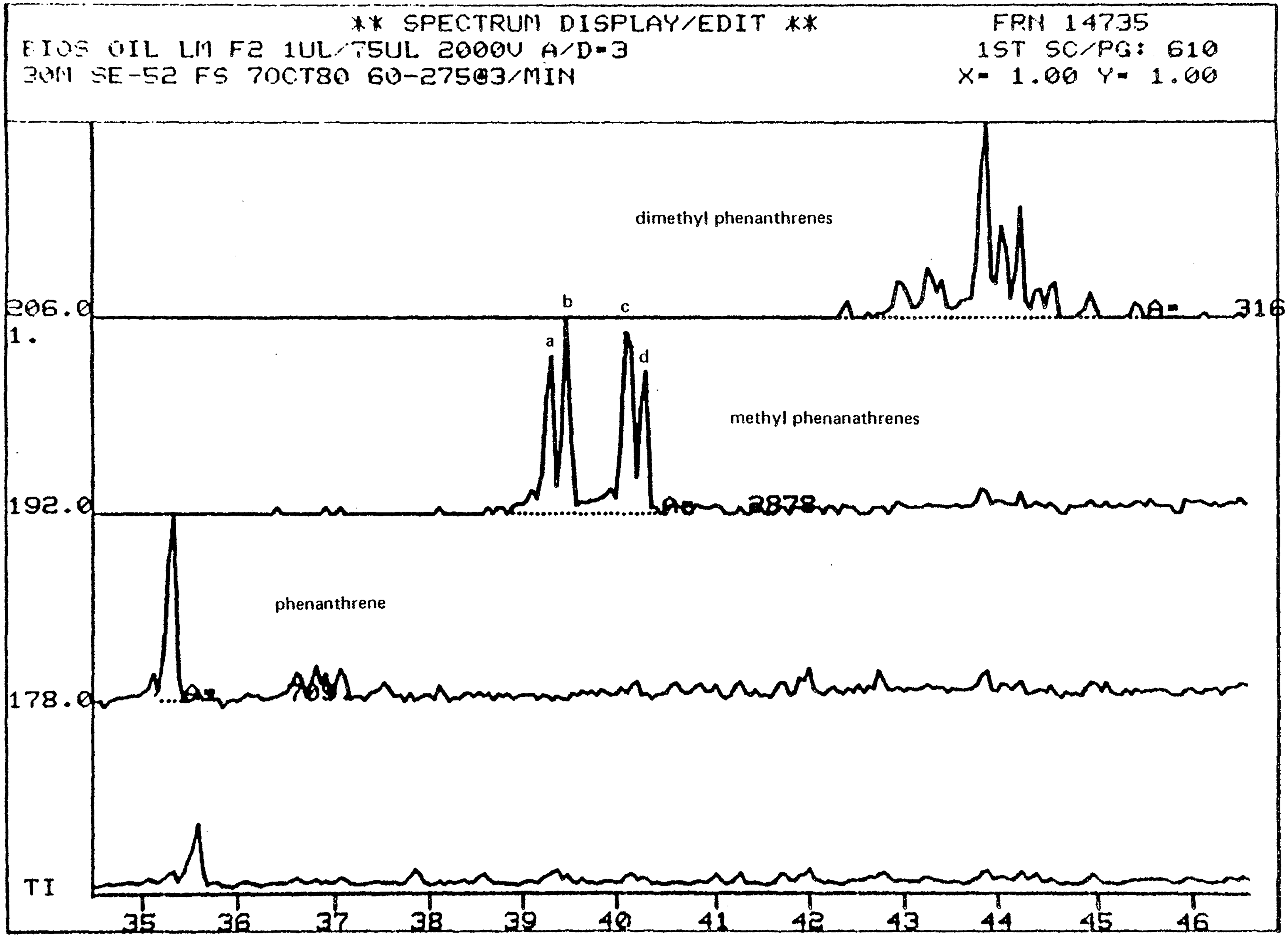


Figure 3.22. Phenanthrene Mass Chromatograms of Lagomedio Crude Oil.

petroleum marker compounds. Eight compounds have been focused on through selected ion searches for the characteristic fragment ion, m/e 191, and through confirmation of identity by molecular ion confirmations.

The distribution of compounds is shown in Figure 3-23.

The saturated fraction of the offshore sample 13-3-24-CC5 contains several prominent PT compounds as determined by m/e = 191 mass spectral searches. A series of eight of these compounds are observed: Compound A = C_{27} hopane ($C_{27}H_{44}$); Compound B = C_{27} trisnorhopane ($C_{27}H_{46}$); Compound C = C_{29} norhopane ($C_{29}H_{50}$); Compound D = C_{30} hopane ($C_{30}H_{52}$); Compounds E, E' = C_{31} homohopanes ($C_{31}H_{54}$); and Compounds F, F' = C_{32} bishomohopanes $C_{32}H_{56}$). All compounds appear to be of the 17α type and the nearly 1:1 ratio of the two C_{31} and C_{32} diastereomers indicates that the hopanes are representative of those associated with "mature" sediments and/or oils (anthropogenic inputs). This fact, coupled with the overall appearance of the GC trace with a prominent UCM (Figure 20), indicates that an anthropogenic input of hydrocarbons characterizes part of the hydrocarbon distribution of this sample.

The results are summarized in Table 3-17. The offshore samples do contain low levels of PT compounds with generally stronger m/e = 191 fragments than the Lagomedio oil itself (see Section 3.1; oil characterizations). The beach samples do not contain any detectable PT compounds. Thus the potential use of PT compounds for molecular markers of oil pollution in this environment may only be useful on the shore where PT compounds are absent.

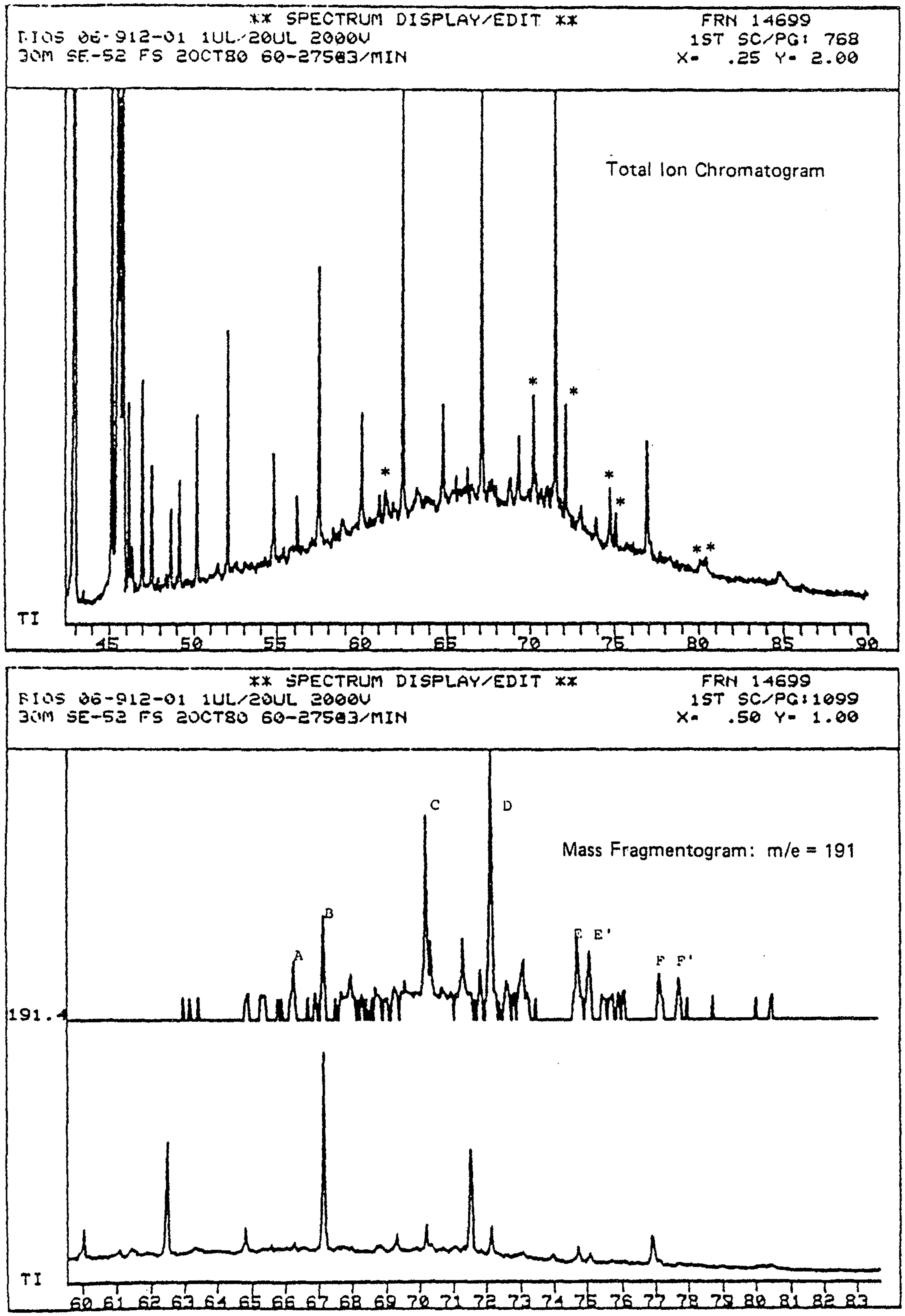


TABLE 3-17

RESULTS OF MASS SPECTRAL SEARCHES FOR PENTACYCLIC TRITERPANES IN BASELINE SEDIMENTS

	BEACH		BEACH					
COMPOUND[a]	13-3-24-CC5	10-2-13-CC10	10-C-L	10-N-L	10-N-H	9-C-L	9-C-H	11-C-L
A ($C_{27}H_{44}$)	+ (3)	+ (3)	–	–	–	–	–	–
B ($C_{27}H_{46}$)	+ (5)	+ (4)	–	–	–	–	–	–
C ($C_{29}H_{50}$)	+ (9)	+ (10)	–	–	–	–	–	–
D ($C_{30}H_{52}$)	+ (11)	+ (15)	–	–	–	–	–	–
E ($C_{31}H_{54}$)	+ (4)	+ (6)	+	–	–	–	–	–
E' ($C_{31}H_{54}$)	+ (3)	+ (5)	–	–	–	–	–	–
F ($C_{32}H_{56}$)	+ (3)	–	+	–	–	–	–	–
F' ($C_{32}H_{56}$)	+ (2)	–	+	–	–	–	–	–

[a] Refer to text for compound name.

Key:

( ) Numbers in parentheses refer to approximate concentrations of identified compounds (ng/g = ppb).

+ = positive detection and identification.

– = negative detection.

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 (10-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^2)

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

1. The sum of components as determined by GC^2.

2. The microgravametric weights of the saturated (f_1) and aromatic/olefinic (f_2) 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^2-analyzable material. Thus, the more relevant numbers with repect to "before-and-after-spill" comparisons are the GC^2-determined values in Table 3-18.

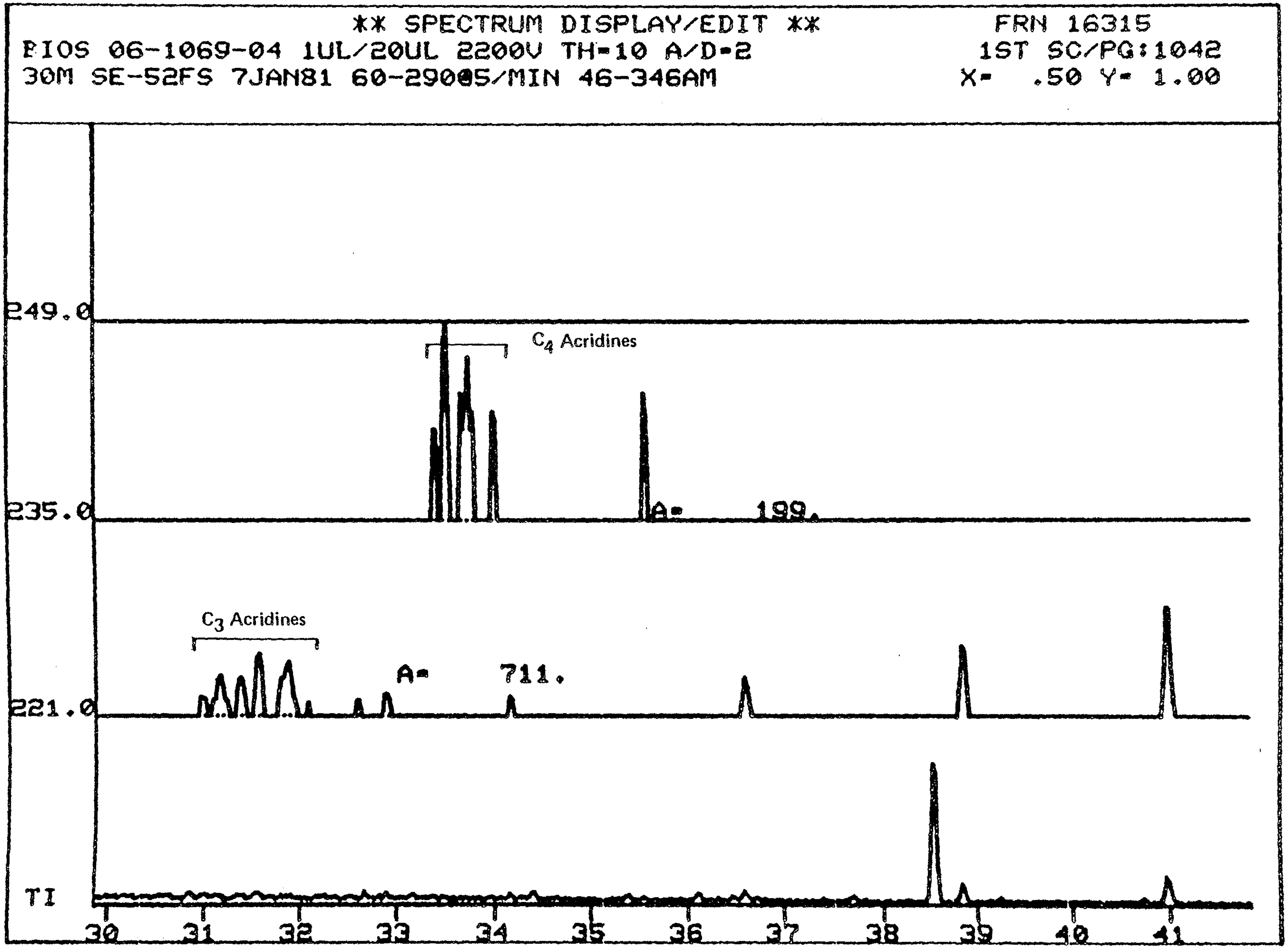
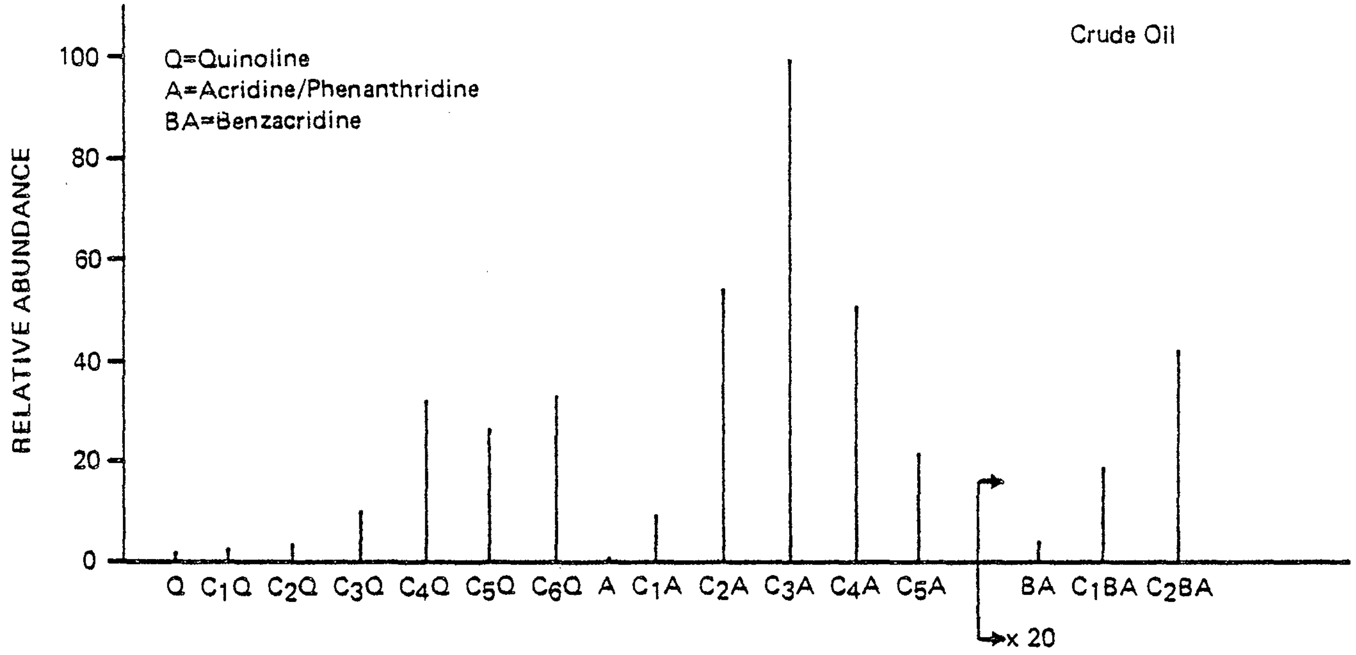


Figure 3.24. Azaarene Mass Spectral Searches—Beach Sediment.



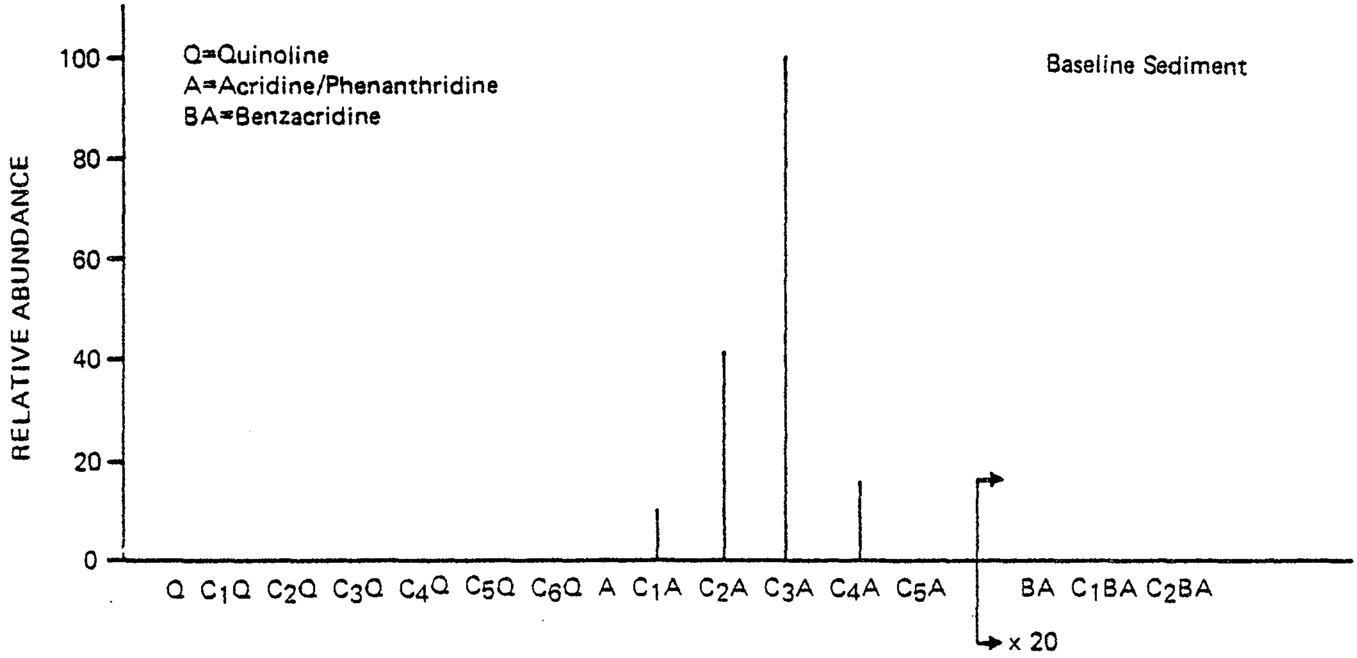


Figure 3.25. Comparison of Azaarene Composition in Baseline Sediment Samples with Lagomedio Crude Oil.

TABLE 3-18

MASS SPECTRAL RESULTS FOR AZAARENE CONTENT OF BASELINE BEACH SAMPLES

	10-C-L	11-C-L
Quinoline (Q)	-	-
C_1Q	-	-
C_2Q	-	-
C_3Q	-	-
C_4Q	-	-
C_5Q	-	-
C_6Q	-	-
Acridine/ Phenanthridine (AP)	+	-
C_1AP	+	-
C_2AP	+	+
C_3AP	+	+
C_4AP	+	-
C_5AP	-	-
Benzacridine (B)	-	-
C_1B	-	-
C_2B	-	-

TABLE 3-19

SUMMARY OF BIOS TISSUE ANALYTICAL RESULTS

					HYDROCARBON CONCENTRATIONS (GC)		HYDROCARBON CONCENTRATIONS (GRAVIMETRIC)	
BAY	ERCO ID	SPECIES[a]	COLLECTION DATE	DEPTH (m)	f^1 (μg/g)	f^2 (μg/g)	f^1 (μg/g)	f^2 (μg/g)
9	728	*Fucus*	9/13/80	4	1.0	17.1	12.6	21.9
9	729	*Leptosterias polaris* (L)	9/10/80	9	0.1	3.3	0.3	5.5
9	730	*L. polaris* (L)	9/10/80	9	1.8	3.4	1.0	7.6
9	731	*L. polaris* (L)	9/10/80	9	1.9	3.6	0.1	3.1
9	732	*L. polaris* (M)	9/10/80	9	2.9	13.3	8.4	53.9
9	733	*L. polaris* (M)	9/10/80	9	1.0	2.8	0.3	6.0
9	734	*L. polaris* (S)	9/10/80	9	0.3	0.2	0.1	3.2
9	735	*Psolus sp.*	9/10/80	17	3.9	10.6	12.4	33.1
9	736	*Psolus sp.*	9/10/80	17	0.6	29.2	1.0	15.3
9	737	*Psolus sp.*	9/10/80	17	0.8	6.5	2.4	6.4
9	738	*Psolus frabricii*	9/10/80	17	4.9	43.2	0.1	13.3
9	739	*Strongylocentratus droebachiensis* (M to L)	9/10/80	9	17.0	35.5	13.7	91.8
9	740	*S. droebachiensis* (M)	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	COLLECTION DATE	DEPTH (m)	HYDROCARBON CONCENTRATIONS (GC)		HYDROCARBON CONCENTRATIONS (GRAVIMETRIC)	
					f^1 (µg/g)	f^2 (µg/g)	f^1 (µg/g)	f^2 (µg/g)
9	741	*S. droebachiensis* (S)	9/10/80	9	38.5	42.0	13.0	62.0
9	742	*S. droebachiensis* (S)	9/10/80	9	51.0	10.0	20.0	9.0
9	743	*Serripes groenlandica* (L)	9/10/80	9	0.3	30.7	3.7	22.3
9	744	*S. groenlandica* (S)	9/10/80	9	8.7	9.6	3.7	15.5
9	745	*Mya truncata* (L)	9/10/80	9	0.8	5.9	11.4	35.8
9	746	*Mya truncata* (L)	9/10/80	9-12	1.3	7.0	6.5	54.2
9	747	*Mya truncata* (L)	9/10/80	9-10	2.6	13.7	48.4	95.5
9	748	*Mya truncata* (L)	9/10/80	9-10	0.6	2.5	2.3	11.6
9	749	*Mya truncata* (M)	9/10/80	9-10	1.7	22.0	1.2	21.3
10	750	*Fucus*	9/13/80	4	6.9	10.2	5.6	17.6
10	751	*Laminaria*	9/13/80	5	2.8	11.6	1.1	6.7
10	752	*L. polaris* (L)	9/13/80	5	2.3	1.7	0.1	1.5
10	753	*L. polaris* (M)	9/13/80	5	3.6	36.3	2.4	24.3
10	754	*L. polaris* (S)	9/13/80	5	0.3	10.5	1.0	30.1
10	755	*S. droebachiensis* (L)	9/13/80	7	6.7	15.4	13.8	34.5
10	756	*S. droebachiensis* (M)	9/13/80	7	25.1	40.2	22.1	44.1

TABLE 3-19 (Cont.)

					HYDROCARBON CONCENTRATIONS (GC)		HYDROCARBON CONCENTRATIONS (GRAVIMETRIC)	
BAY	ERCO ID	SPECIES	COLLECTION DATE	DEPTH (m)	f^1 (µg/g)	f^2 (µg/g)	f^1 (µg/g)	f^2 (µg/g)
10	757	*Mya truncata* (L)	9/13/80	7	0.3	1.1	0.9	6.4
10	758	*Mya truncata* (M)	9/13/80	7	1.7	32.3	6.9	23.9
10	759	*Mya truncata* (S)	9/13/80	7	1.7	25.1	1.5	21.9
11	777	*Agarum*	9/8/80	20	3.5	48.7	1.3	4.8
11	778	*Fucus*	9/13/80	3	5.3	6.7	2.3	7.6
11	779	*L. polaris*	9/8/80	15-20	5.2	37.4	7.9	61.1
11	780	*L. polaris*	9/8/80	15-20	1.4	24.1	2.4	37.4
11	781	*L. polaris*	9/8/80	15-20	1.5	29.3	3.3	32.9
11	782	*L. polaris*	9/8/80	15-20	8.9	20.6	7.9	27.8
11	783	*L. polaris*	9/8/80	15-20	3.4	24.5	3.3	34.4
11	784	*Psolus frabricii* (L)	9/8/80	15-20	2.6	33.9	22.4	90.4
11	785	*Psolus frabricii* (L)	9/8/80	15-20	2.5	33.3	5.2	74.5
11	786	*Psolus frabricii* (S)	9/8/80	15-20	4.1	44.8	14.0	158.0
11	787	*S. droebachiensis* (L)	9/8/80	15-20	30.3	156.0	51.0	321.1
11	788	*S. droebachiensis* (M)	9/8/80	15-20	16.3	79.8	45.7	123.5
11	789	*S. droebachiensis* (M)	9/8/80	15-20	17.1	82.4	30.8	167.0

TABLE 3-19 (Cont.)

BAY	ERCO ID	SPECIES	COLLECTION DATE	DEPTH (m)	HYDROCARBON CONCENTRATIONS (GC) f^1 (μg/g)	HYDROCARBON CONCENTRATIONS (GC) f^2 (μg/g)	HYDROCARBON CONCENTRATIONS (GRAVIMETRIC) f^1 (μg/g)	HYDROCARBON CONCENTRATIONS (GRAVIMETRIC) f^2 (μg/g)
11	790	*S. droebachiensis* (S)	9/8/80	15-20	2.5	24.7	9.9	39.5
11	791	*S. droebachiensis* (S)	9/8/80	15-20	5.0	25.5	17.4	79.7
11	792	*S. droebachiensis* (S)	9/8/80	15-20	41.5	11.6	38.8	177.6
11	793	*Serripes groenlandica*	9/12/80	5	1.5	7.5	1.6	10.7
11	794	*Mya truncata* (L)	9/8/80	15-20	1.9	30.1	1.5	27.5
11	795	*Mya truncata* --	9/8/80	15-20	0.8	31.1	0.8	18.6
11	796	*Mya truncata* (M)	9/8/80	15-20	2.5	7.6	0.5	11.9
11	797	*Mya truncata* (S)	9/8/80	15-20	0.7	13.3	5.5	16.6
11	798	*Mya truncata* (S)	9/8/80	15-20	7.3	20.9	2.4	20.2
11	799	*Myoxocephalus scorpius*	9/8/80	15-20	40.0	51.0	110.0	110.0
Z Lagoon	760	*Laminaria*	9/14/80	3	23.0	18.4	2.8	18.9
	761	*L. polaris*	9/16/80	-	0.4	4.1	1.1	10.3
	762	*L. polaris*	9/16/80	-	2.0	43.4	2.9	60.6
	763	*L. polaris*	9/16/80	-	0.1	1.0	0.9	6.5
	764	*Psolus frabricii*	9/16/80	-	3.0	43.6	7.5	88.2
	765	*S. droebachiensis* (L)	9/16/80	-	46.9	22.1	46.5	34.3

TABLE 3-19 (Cont.)

BAY	ERCO ID	SPECIES	COLLECTION DATE	DEPTH (m)	HYDROCARBON CONCENTRATIONS (GC) f^1 (μg/g)	f^2 (μg/g)	HYDROCARBON CONCENTRATIONS (GRAVIMETRIC) f^1 (μg/g)	f^2 (μg/g)
Z Lagoon	766	*S. droebachiensis* (L)	9/16/80	-	10.4	59.9	42.3	185.0
	767	*S. droebachiensis* (M)	9/16/80	-	14.6	125.1	24.4	177.4
	768	*S. droebachiensis* (S)	9/16/80	-	39.0	45.4	157	392
	769	*Serripes*	9/16/80	-	16.2	112.0	16.9	129.5
	770	*Astarte borealis*	9/16/80	-	0.3	1.2	1.0	6.3
	771	*Mya truncata* (L)	9/16/80	-	7.3	4.8	1.4	1.7
	772	*Mya truncata* (M)	9/16/80	-	8.0	20.6	1.9	42.0
	773	*Mya truncata* (M)	9/16/80	-	2.8	6.1	4.7	25.1
	774	*Mya truncata* (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	*Myoxocephalus scorpius*	9/16/80	-	2.3	4.5	3.4	4.9

TABLE 3-20

COMPARATIVE ANALYSIS OF CONCENTRATIONS OF HYDROCARBONS IN MARINE TISSUE

	BAY 9				BAY 10				BAY 11				Z LAGOON			
SPECIES	RANGE	MEAN	STD. DEVIATION	n	RANGE	MEAN	STD. DEVIATION	n	RANGE	MEAN	STD. DEVIATION	n	RANGE	MEAN	STD. DEVIATION	n
Mya truncata																
f_1: saturated	0.6-2.6	1.4	0.8	5	0.3-1.7	1.2	0.8	3	0.7-7.3	2.6	2.7	5	0.4-8.0	4.6	3.6	4
f_2: aromatic/ olefinic	2.5-22.0	10.2	7.7	5	1.1-32.3	19.5	16.3	3	7.6-31	20.6	10.3	5	4.8-21	10.1	7.2	4
Strongylocentratus droebachiensis																
f_1: saturated	1.0-51	26.8	22.2	4	6.7-25	15.9	13.0	2	2.5-41	18.8	14.9	6	15-47	27	18	4
f_2: aromatic/ olefinic	10-45	33.1	15.9	4	15-40	27.8	17.5	2	11-156	63.5	49.5	6	22-125	63	44	4
Leptosterias polaris																
f_1: saturated	0.1-2.9	1.3	1.1	6	0.3-3.6	2.0	2.3	3	1.4-8.9	4.1	3.1	5	0.1-2.0	0.8	1.0	3
f_2: aromatic/ olefinic	0.2-13	4.4	4.5	6	1.7-36	16	18	3	20-37	27	6.5	5	1-43.4	16	24	3
Psolus																
f_1: saturated	0.6-4.9	2.6	2.2	4	--	--	--	--	2.5-4.1	3.1	0.9	3	--	3.0	--	1
f_2: aromatic/ olefinic	6.5-43	22	17	4	--	--	--	--	33-45	37	6.5	3	--	46	--	1
Serripes groenlandica																
f_1: saturated	0.3-8.7	4.5	5.9	2	--	--	--	--	--	1.5	--	1	--	16	--	1
f_2: aromatic/ olefinic	9.6-31	20	15	2	--	--	--	--	--	7.5	--	1	--	112	--	1
Fucus																
f_1: saturated	--	1	--	1	--	6.9	--	1	--	5.3	--	1	--	--	--	--
f_2: aromatic/ olefinic	--	17	--	1	--	10	--	1	--	6.7	--	1	--	--	--	--
Laminaria																
f_1: saturated	--	--	--	--	--	2.8	--	1		--	--	--	--	23	--	1
f_2: aromatic/ olefinic	--	--	--	--	--	12	--	1		--	--	--	--	18	--	1
Agarum																
f_1: saturated	--	--	--	--	--	--	--	--	--	3.5	--	1	--	--	--	--
f_2: aromatic/ olefinic	--	--	--	--	--	--	--	--	--	49	--	1	--	--	--	--
Sculpin																
f_1: saturated	--	--	--	--	--	--	--	--	--	40	--	1	--	2.3	--	1
f_2: aromatic/ olefinic	--	--	--	--	--	--	--	--	--	51	--	1	--	4.5	--	1

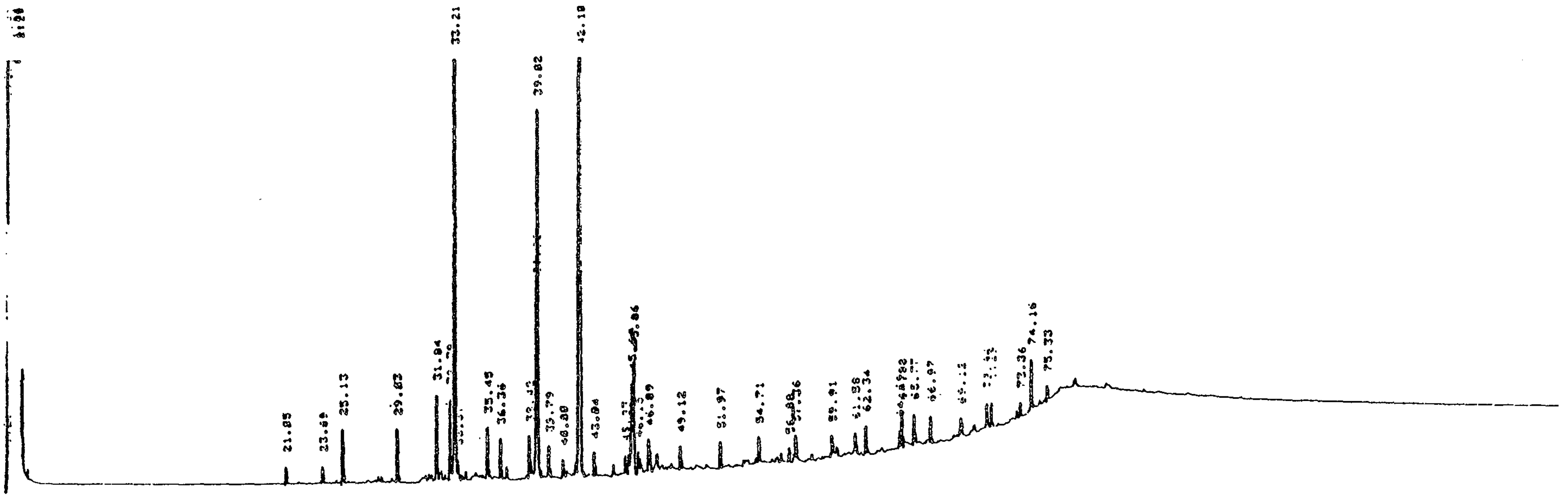
As presented in Table 3-20, there is a wide range of hydrocarbon concentrations within each species, reflecting variations mainly in biogenic components. For example, concentrations of f_1 and f_2 hydrocarbons in Mya range over an order of magnitude within a given bay. However variations between bays 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^2-determined compositions.

Perhaps the most important information on these baseline tissue hydrocarbons comes from the GC^2 traces. Representative GC^2 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_1 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).

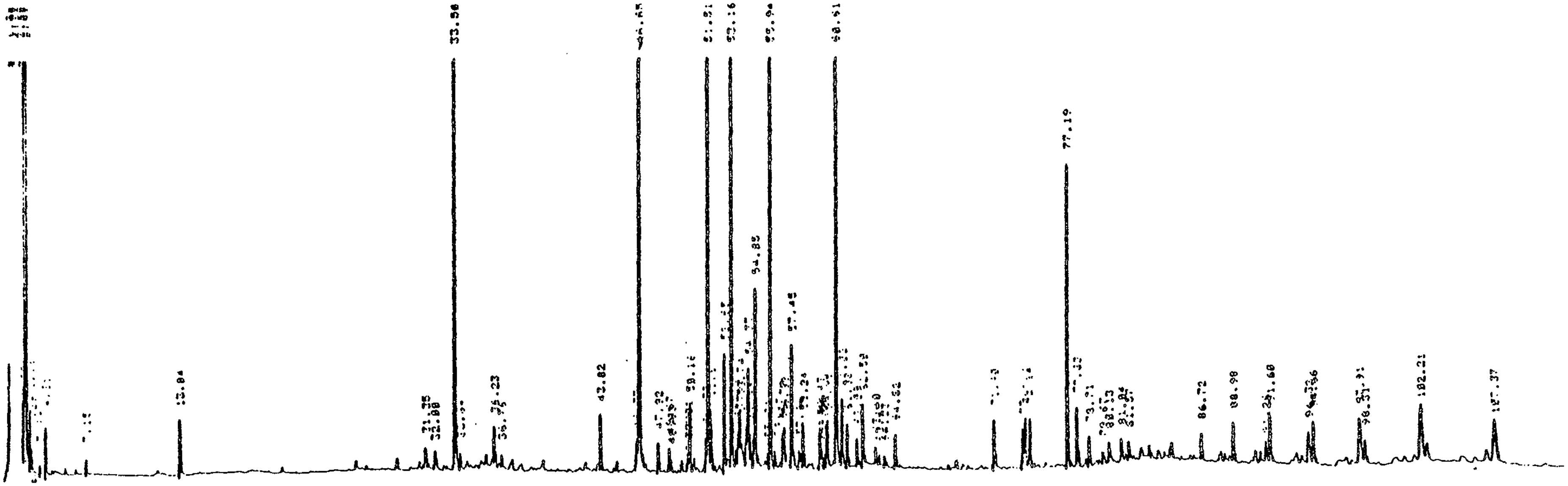
The sea urchins, Strongylocentrotus droebachiensis, contain large amounts of natural lipid material and hence biogenic hydrocarbons. No evidence of petroleum contamination was observed in this species. The hydrocarbon compositions are strikingly similar in all samples of this species examined (e.g.,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

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

Saturated (f_1)



Aromatic/Olefinic (f_2)



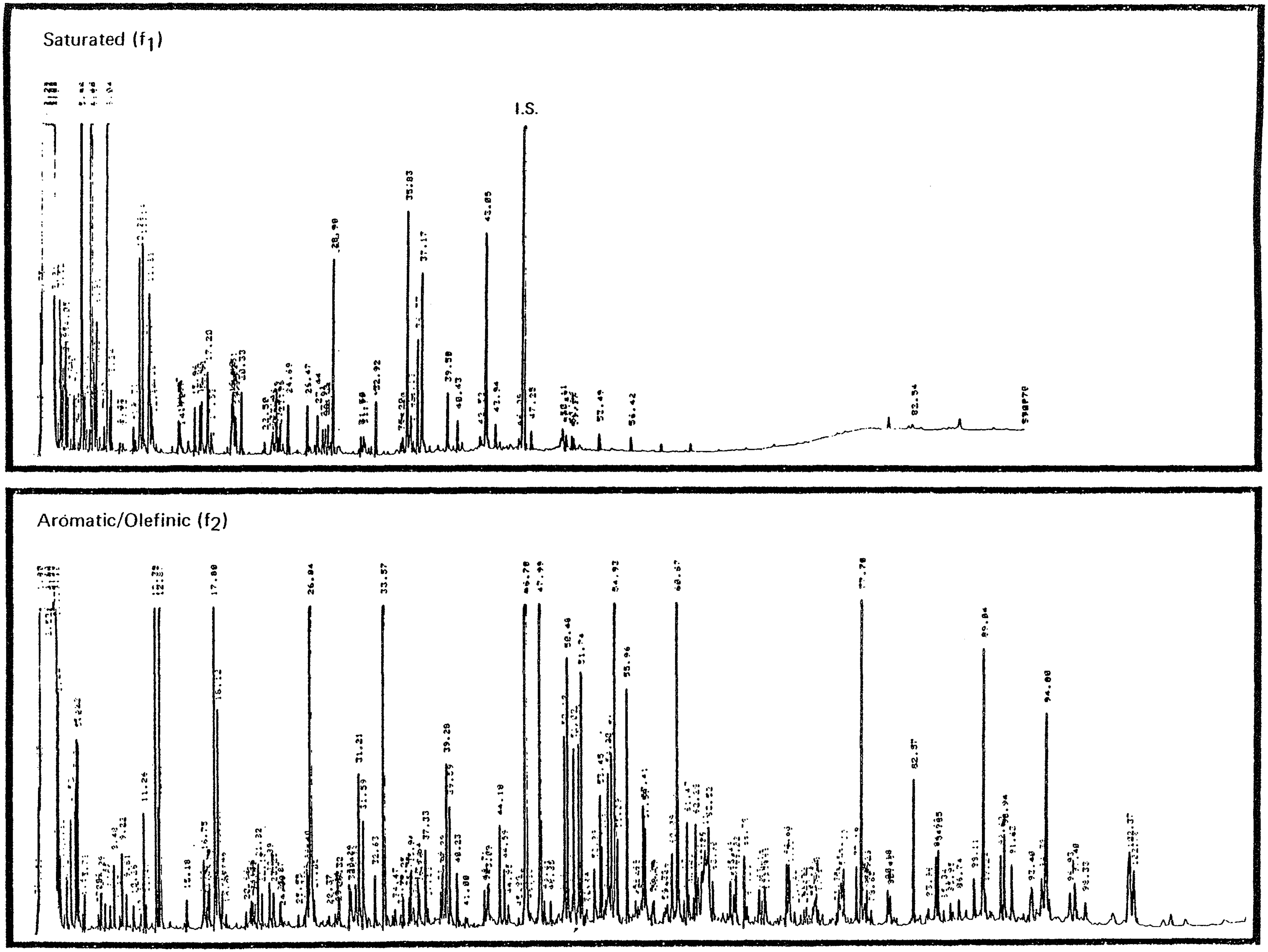
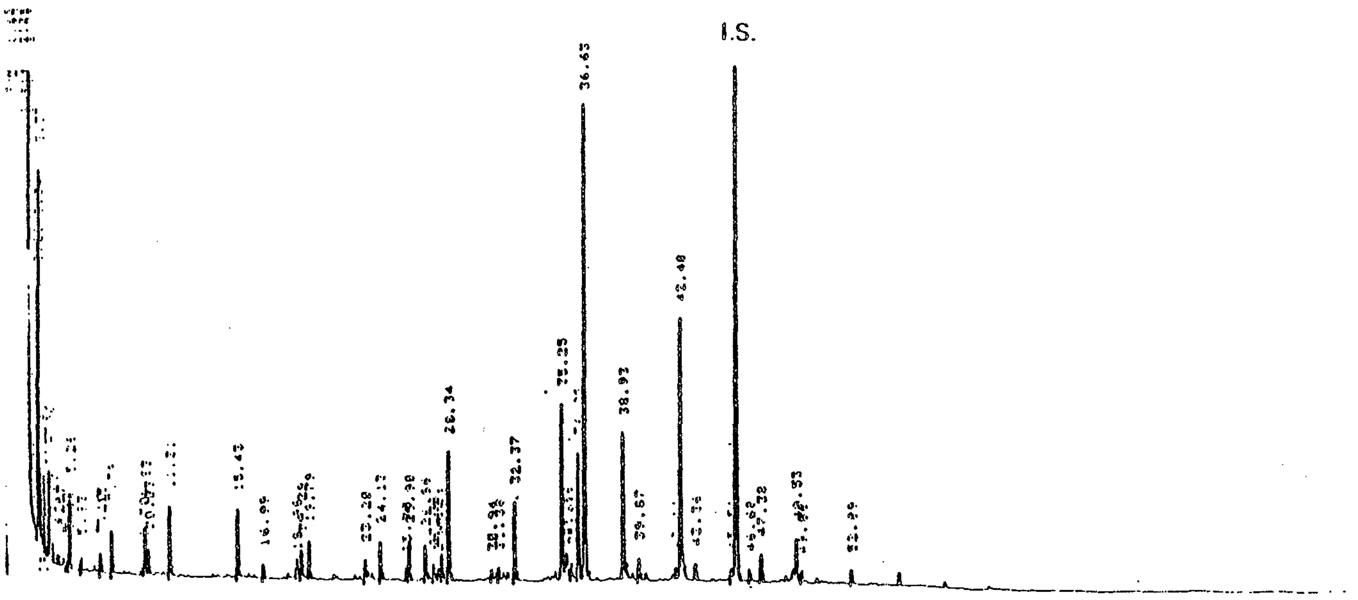
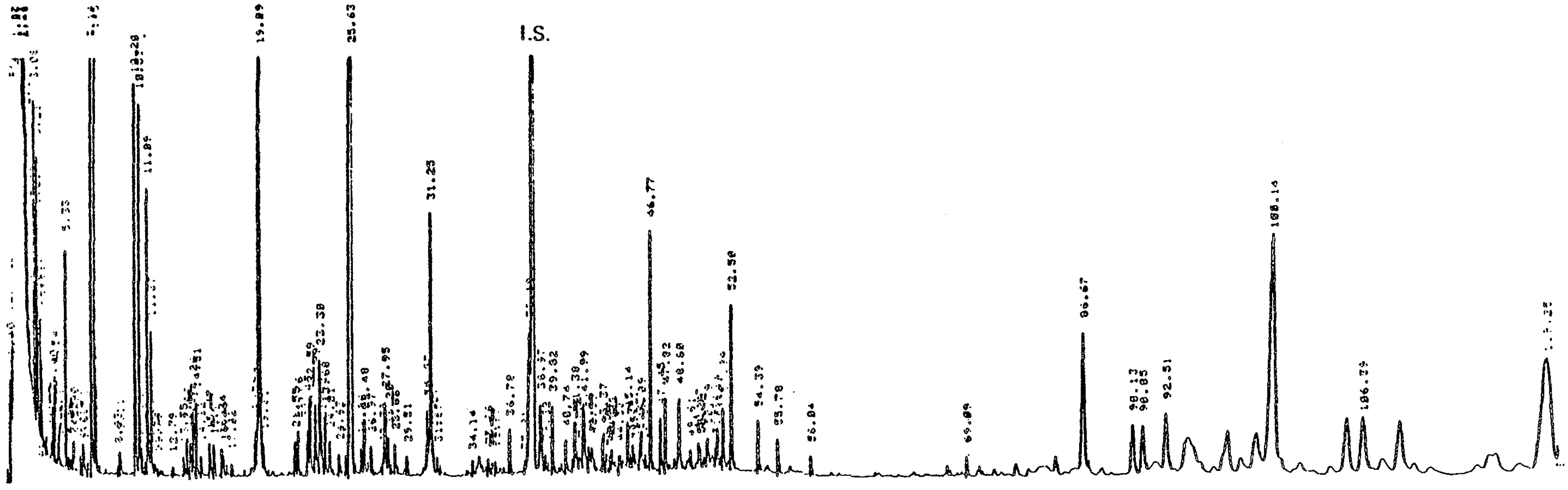


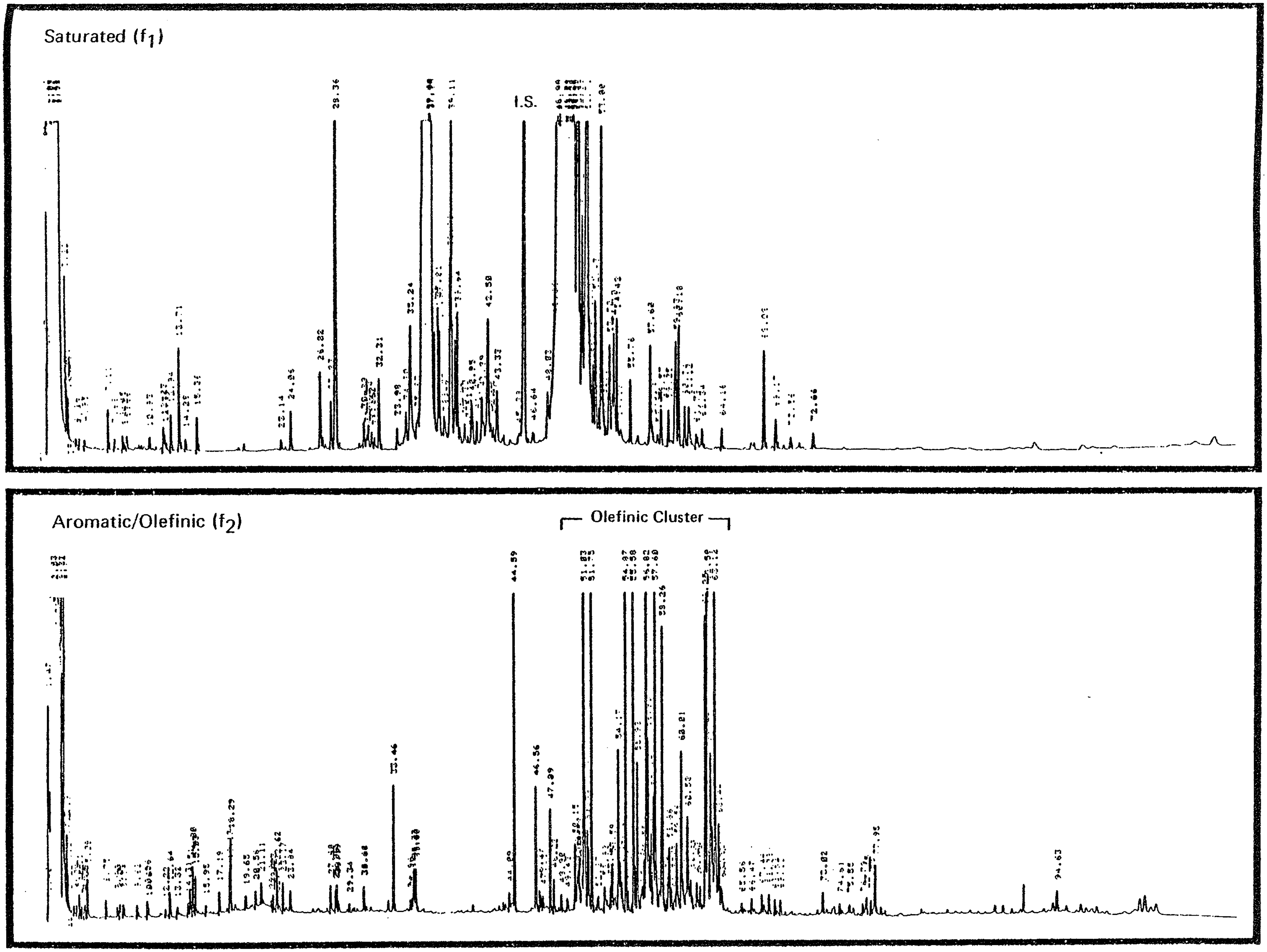
Figure 3.27. GC^2 Traces of *Mya truncata*—Bay 11.



Saturated (f_1)

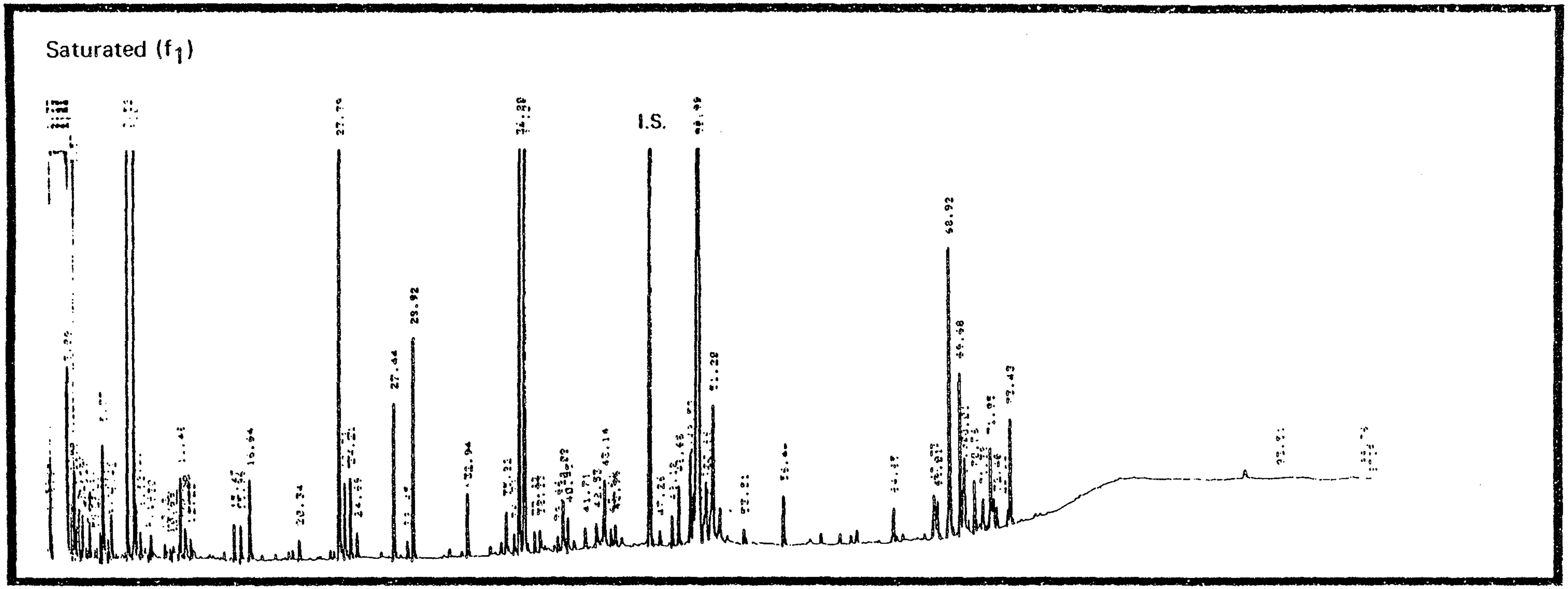


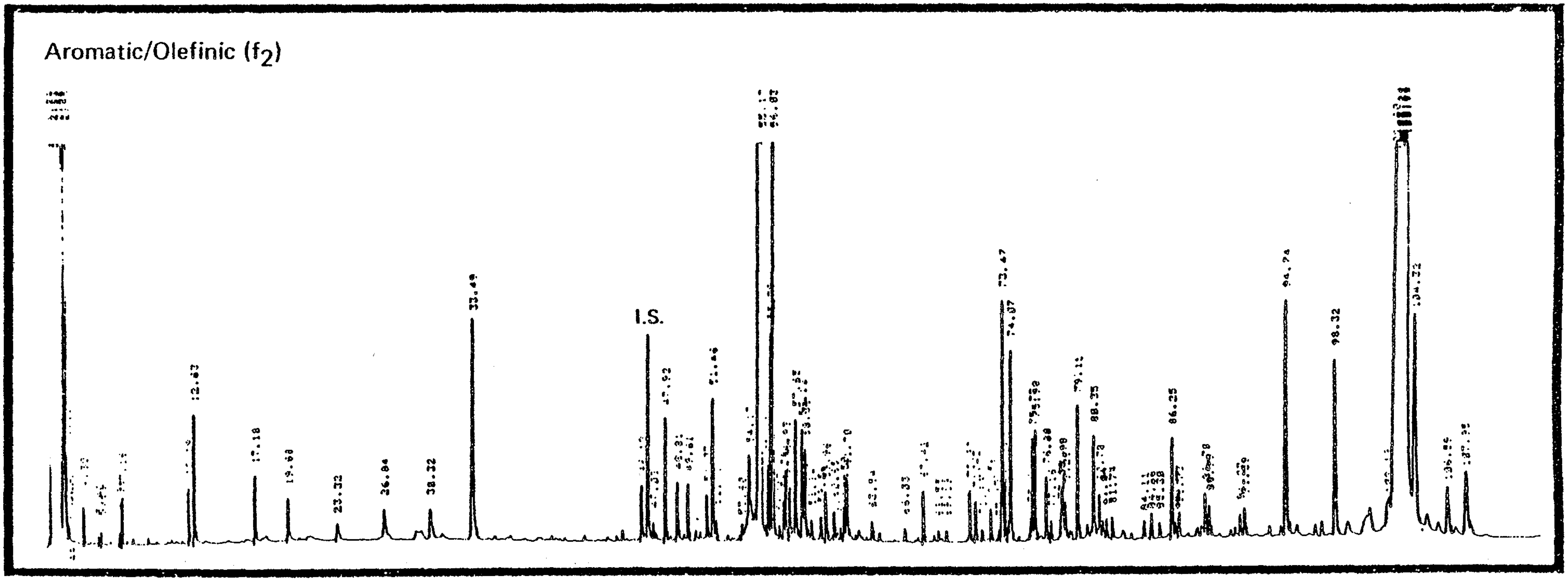
Aromatic/Olefinic (f_2)


Saturated (f_1)

Aromatic/Olefinic (f_2)

Figure 3.29. GC^2 Traces of *Strongylocentrotus droebachiensis*—Bay 9.


Saturated (f_1)
I.S.
27.74
27.44
29.92
32.94
20.34
16.64
68.92
69.68
71.28
72.43

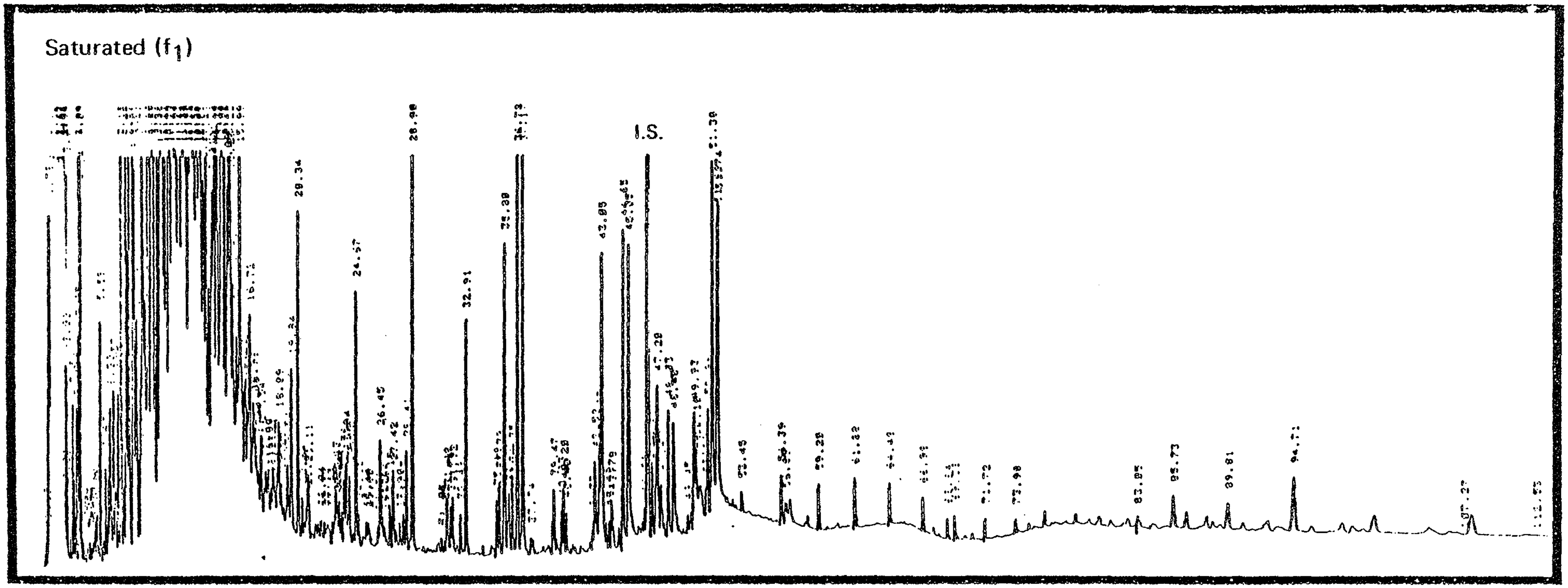

Aromatic/Olefinic (f_2)
I.S.
12.63
17.18
19.68
23.32
26.84
38.32
33.49
47.92
51.46
73.47
74.07
80.35
86.25
94.74
98.32
104.72
106.86
107.96

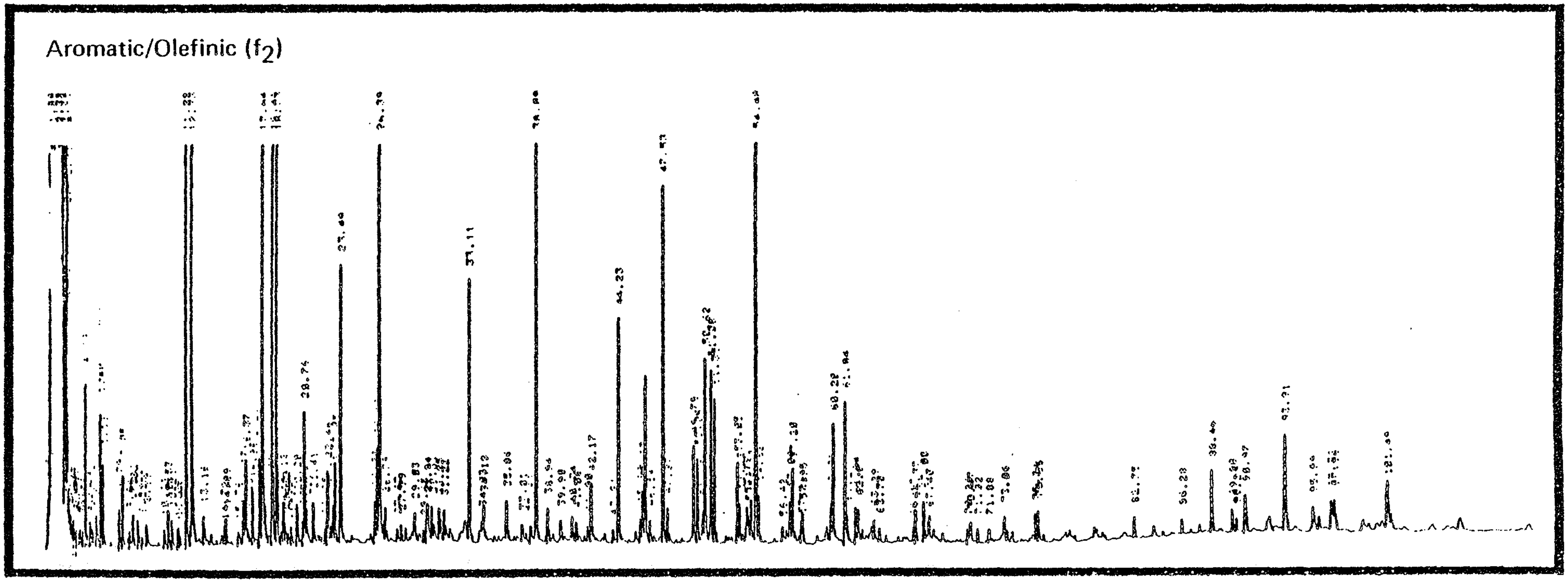
Samples of Leptosterias were comprised of a more complex set of saturated and aromatic/olefinic (f_2) hydrocarbons (Figure 3-31). While no evidence for petroleum hydrocarbon input is seen in the f_1 fraction, GC^2/MS analyses of the f_2 fraction (e.g., Figure 3-29) (see next section) reveal important levels of light aromatic hydrocarbons (alkyl benzenes, naphthalenes) suggestive of low level contaminant input. While most of the samples were comprised of f_1 and f_2 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 f_2 distributions, $G2^C$/MS was used. The GC^2/MS/computer system focused on levels of 1- to 5-ring aromatics in 14 samples chosen on the basis of their GC^2 traces and in an effort to get adequate areal and species coverage.


Saturated (f_1)
I.S.
16.72
20.34
24.57
26.45
28.90
32.91
35.38
36.73
43.85
47.28
51.38
53.45
59.28
61.82
71.72
73.98
83.85
85.73
89.81
94.71
107.27


Aromatic/Olefinic (f_2)
13.18
20.74
23.44
37.11
38.96
42.17
44.23
47.93
60.28
61.94
71.08
80.47
93.21
101.66

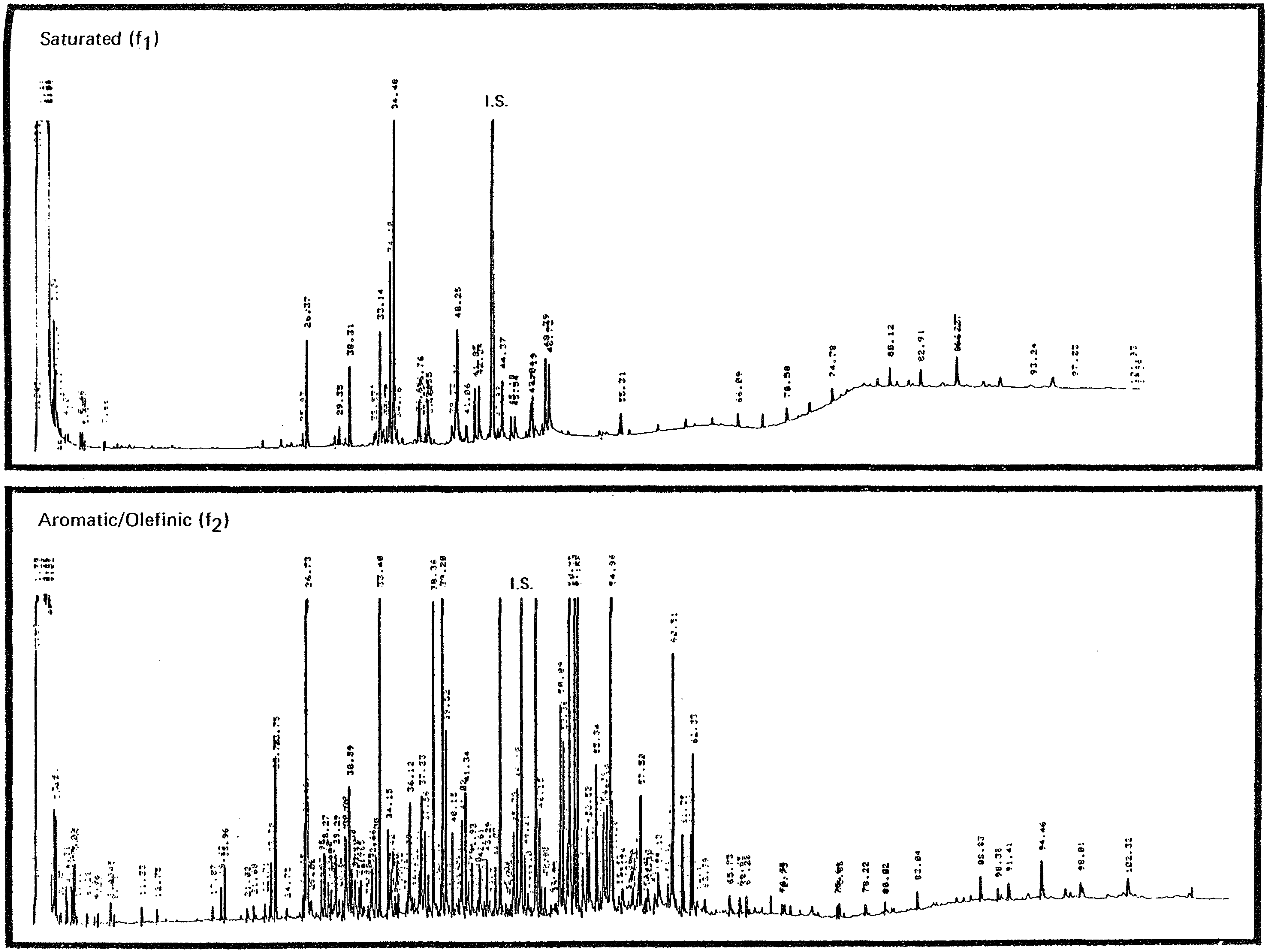
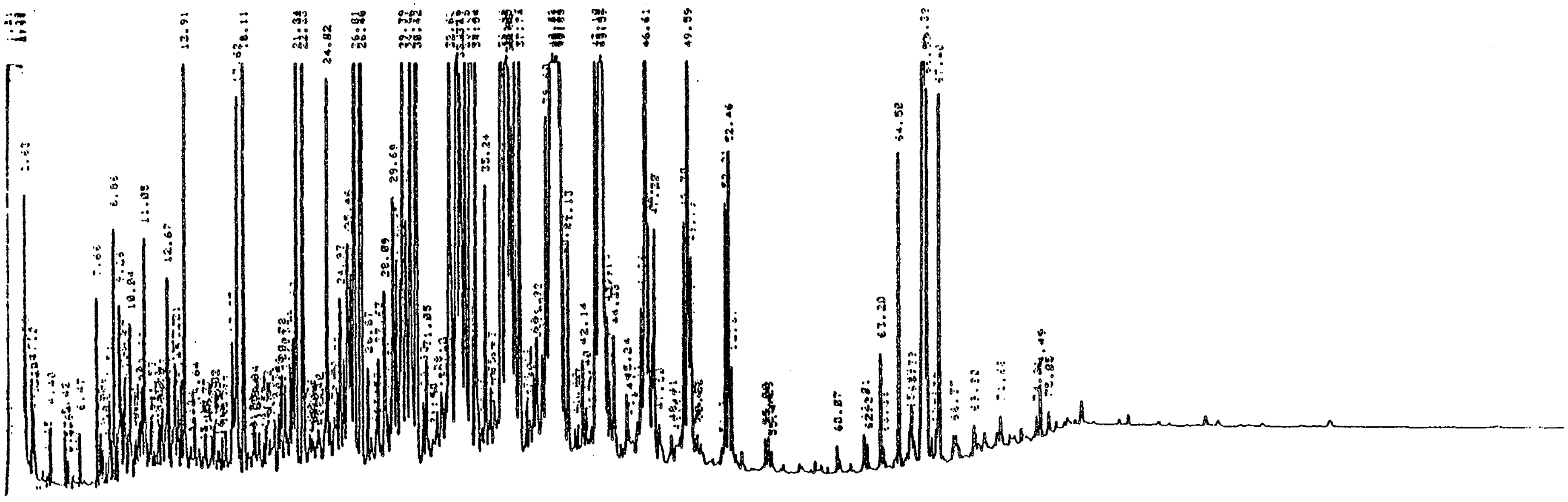
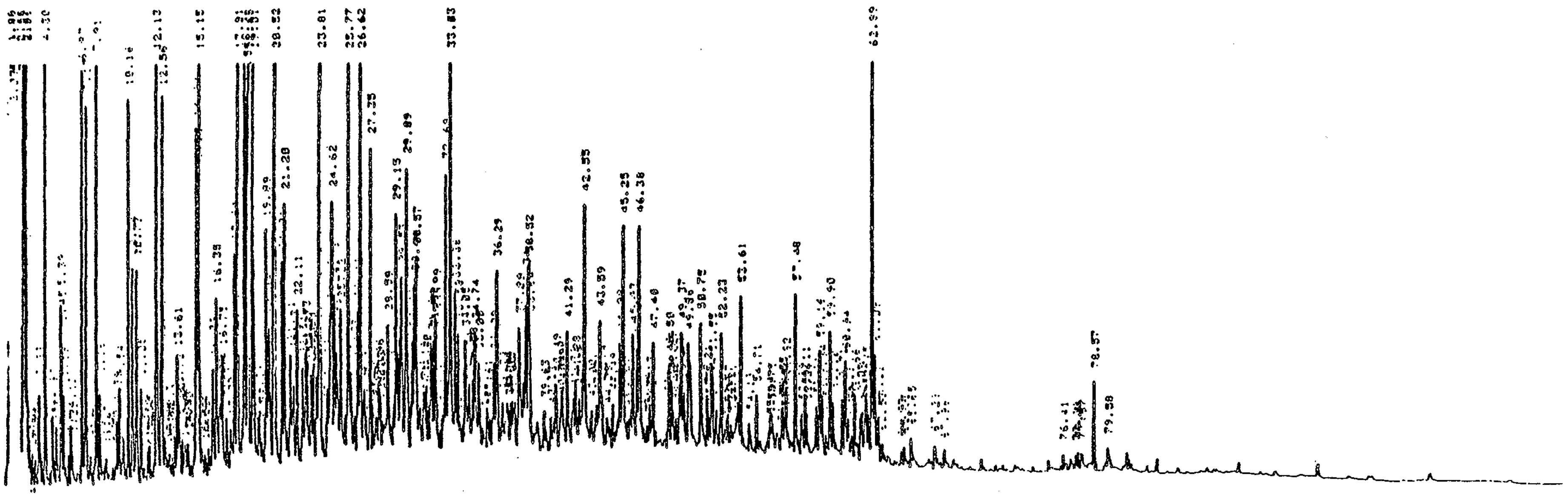


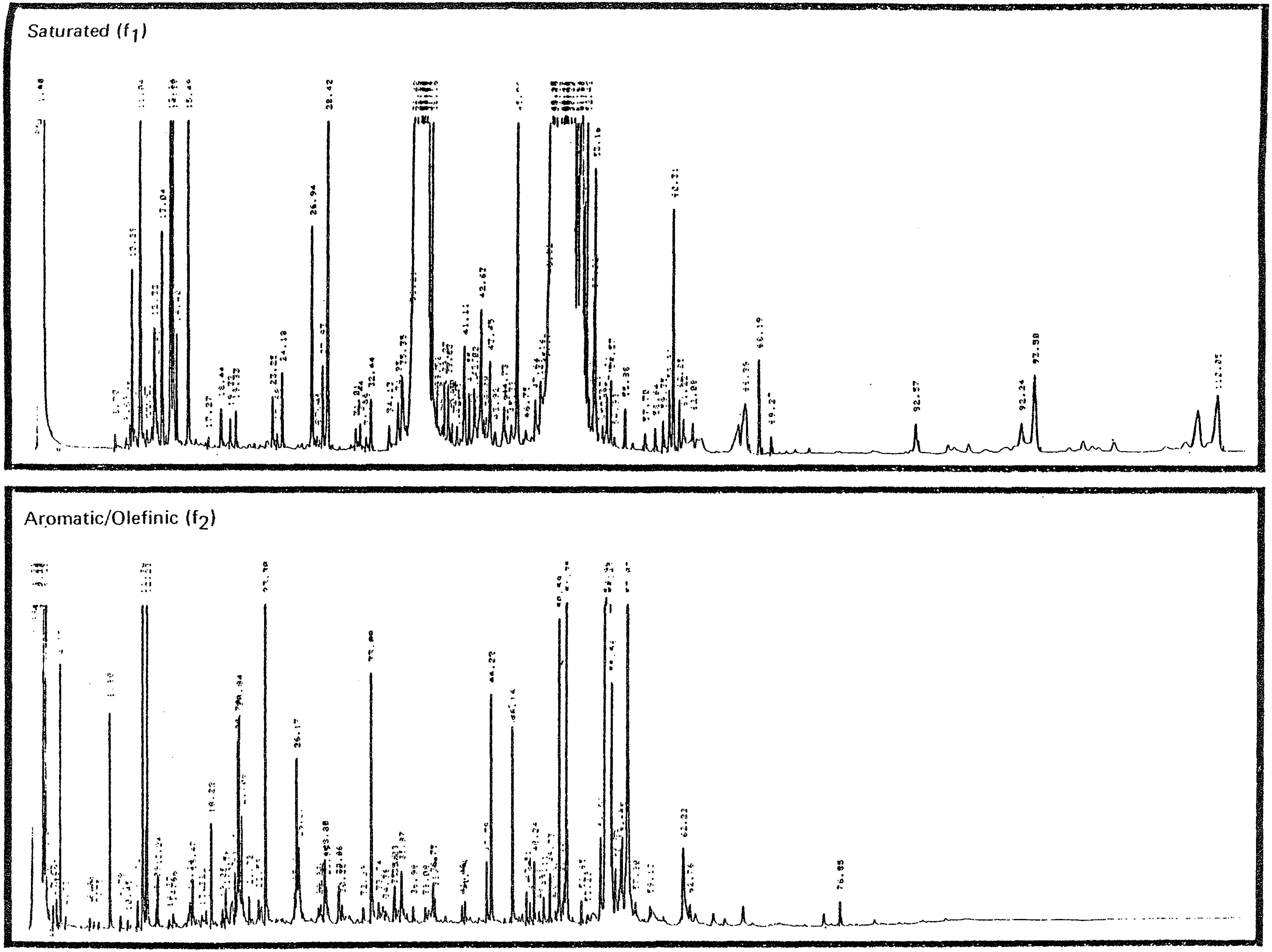
Figure 3.32. GC^2 Traces of *L. polaris*--Bay 9.

Saturated (f1)



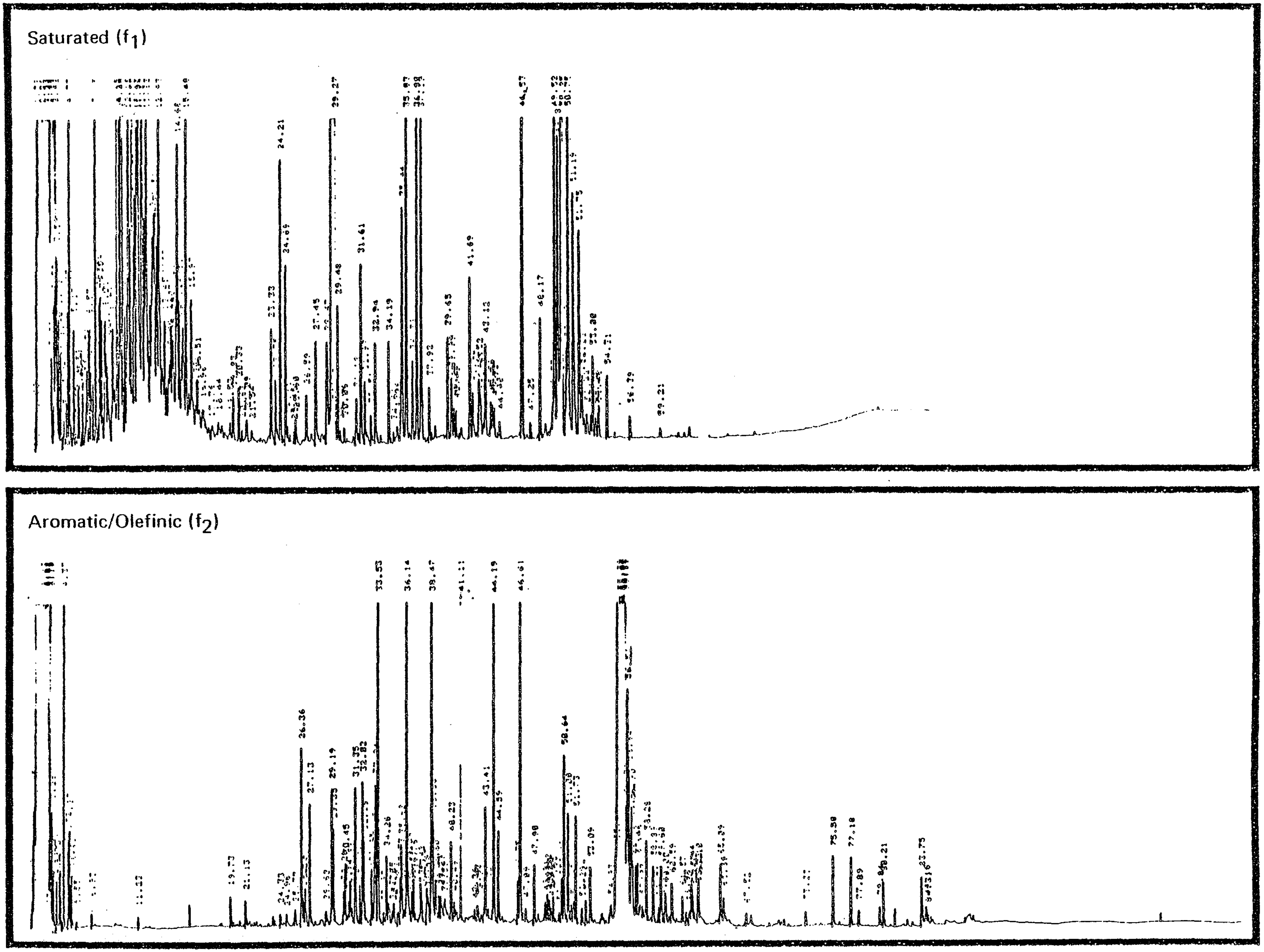
Aromatic/Olefinic (f2)




Saturated (f_1)

Aromatic/Olefinic (f_2)

Figure 3.34. GC^2 Traces of *Laminaria*–Z–Lagoon.


Saturated (f_1)
Aromatic/Olefinic (f_2)

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_0 to C_4) of naphthalene, fluorene, and C_3 to C_5 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^2 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	732[a]	762	753	729	733[a]	750[a]	777	751
SPECIES:[b]	1	1	1	1	2	3	3	3	3	3	3	4	5	6
BAY:	9	Z	10	11	9	9	9	Z	10	9	9	10	11	10
Naphthalenes (m/e 128, 142, 156, 170)	7	5	ND	ND	2	28	1270	140	140	8	5100	6700	150	20
Alkyl Benzenes (m/e 120, 134, 148)	ND	ND	ND	ND	ND	11	1300	220	190	3	3500	1700	10	10
Phenanthrenes (m/e 178, 192, 206, 220, 234)	3	6	8	1	10	ND	ND	10	5	ND	40	490	11	8
Fluorenes (m/e 166, 180, 194, 208)	ND	ND	ND	ND	ND	ND	100	ND	ND	ND	130	70	2	1
Biphenyl (m/e 154)	ND	ND	ND	ND	ND	ND	100	8	11	ND	360	200	8	2
Fluoranthene/Pyrene (m/e 202)	ND	ND	ND	ND	4	ND	ND	ND	19	ND	ND	ND	5	ND
Benzopyrenes (m/e 252)	ND	ND	ND	ND	ND	ND	ND	ND	14	ND	ND	ND	ND	ND

[a] GC^2 trace indicates gross contamination.

[b] Species 1 = *Mya truncata*
2 = *Serripes groenlandica*
3 = *Leptosterioas polaris*
4 = *Fucus*
5 = *Laminaria*

ND = not detected.

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^2) and total (by microgravimetry) 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^2)

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 TOTAL RESOLVED (GC) (µg/g)	SATURATED HYDROCARBONS TOTAL GRAVI-METRIC (µg/g)	AROMATIC HYDROCARBONS TOTAL RESOLVED (GC) (µg/g)	AROMATIC HYDROCARBONS TOTAL GRAVI-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	4,210	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	1,100	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	1,290	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	961	4,400	106	3,720
	8	GC-29	3,920	20,900	487	16,700

TABLE 3-22 (Cont.)

			SATURATED HYDROCARBONS		AROMATIC HYDROCARBONS	
SITE	DAY	SAMPLE ID NO.	TOTAL RESOLVED (GC) (μg/g)	TOTAL GRAVI-METRIC (μg/g)	TOTAL RESOLVED (GC) (μg/g)	TOTAL GRAVI-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	361	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.	GC-11	GC-12	GC-13	GC-14	None
Lab ID No.	06-1060	06-1061	06-1104	06-1062	
Constituent (µg/g)					
n-C_{10}	9.2	4.5	3.6	20.1	
n-C_{11}	13.8	13.9	11.6	36.1	
n-C_{12}	15.9	20.1	17.1	43.9	
n-C_{13}	15.6	22.3	20.0	45.0	
n-C_{14}	15.3	23.1	18.2	43.5	
Farnesane	6.1	9.3	8.5	15.3	
n-C_{15}	14.6	22.7	20.5	42.4	
n-C_{16}	12.9	20.0	18.6	37.9	
n-C_{17}	11.2	18.1	16.7	34.8	
Pristane	4.9	7.3	5.7	15.2	
n-C_{18}	10.1	14.9	13.6	2.8	
Phytane	5.5	9.4	8.2	17.7	
n-C_{19}	9.8	15.8	10.0	31.5	
n-C_{20}	7.6	12.5	10.6	25.3	
n-C_{21}	6.3	10.7	8.3	21.2	
n-C_{22}	5.6	9.7	7.5	21.9	
n-C_{23}	4.4	8.2	6.1	15.0	
n-C_{24}	4.8	7.4	5.3	13.5	
n-C_{25}	3.6	6.0	4.2	11.2	
n-C_{26}	2.9	5.1	3.5	10.9	
n-C_{27}	2.7	4.3	2.8	8.0	
n-C_{28}	2.2	3.7	2.2	5.3	
n-C_{29}	2.2	3.0	1.8	6.0	
n-C_{30}	1.5	2.7	1.4	3.5	
n-C_{31}	1.6	2.1	1.3	4.2	
n-C_{32}	1.0	1.5	1.0	ND[a]	

[a] ND = not detected.

TABLE 3-23 (Cont.)

	DAY				
	1	2	4	8	16
Total Alkanes (GC) (μg/g)	175	288	206	483	None
Total Resolved (GC)(μg/g)	307	421	301	829	
Total Saturates (grav. wt.)(μg/g)	2,650	2,650	4,300	4,210	
ALK/ISO	2.36	2.48	2.64	2.55	
SHWR	2.54	1.89	2.33	2.52	

TABLE 3-24

SHORELINE STUDY - SATURATED HYDROCARBONS (SITE L-2)

	DAY				
	1	2	4	8	16
Sample ID No.	None	GC-17	GC-18	GC-19	None
Lab ID No.		06-1064	06-1065	06-1066	
Constituent (µg/g)					
n-C_{10}		ND[a]	0.26	0.30	
n-C_{11}		0.03	1.5	1.2	
n-C_{12}		0.16	2.9	2.3	
n-C_{13}		0.31	3.6	3.0	
n-C_{14}		0.40	3.7	3.5	
Farnesane		0.15	1.2	1.4	
n-C_{15}		0.44	3.5	3.7	
n-C_{16}		0.40	3.2	3.3	
n-C_{17}		0.38	2.9	3.1	
Pristane		0.14	1.1	1.2	
n-C_{18}		0.35	2.7	2.8	
Phytane		0.20	1.6	1.6	
n-C_{19}		0.35	2.6	1.9	
n-C_{20}		0.29	2.2	2.3	
n-C_{21}		0.25	1.9	1.9	
n-C_{22}		0.22	1.7	1.7	
n-C_{23}		0.18	1.4	1.4	
n-C_{24}		0.15	12.0	1.2	
n-C_{25}		0.12	1.0	1.1	
n-C_{26}		0.10	0.82	0.86	
n-C_{27}		0.07	0.72	0.69	
n-C_{28}		0.05	0.60	0.60	
n-C_{29}		0.05	0.61	0.50	
n-C_{30}		0.04	0.58	0.45	
n-C_{31}		0.03	0.47	0.36	
n-C_{32}		0.02	0.37	0.23	

TABLE 3-24 (Cont.)

	DAY				
	1	2	4	8	16
Total Alkanes (GC)(µg/g)	None	5.1	39.7	38.6	None
Total Resolved (GC)(µg/g)		5.98	57.1	60.8	
Total Saturates (grav. wt.)(µg/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.	GC-1	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_{10}	ND[a]	ND	5.	ND	ND
n-C_{11}	ND	0.8	10.4	0.29	ND
n-C_{12}	ND	2.8	13.2	3.0	0.44
n-C_{13}	ND	4.5	13.1	9.7	2.6
n-C_{14}	0.01	5.5	12.7	15.0	5.4
Farnesane	0.002	2.2	4.4	6.4	2.5
n-C_{15}	0.03	5.6	12.3	16.9	6.7
n-C_{16}	0.05	5.1	11.1	15.0	6.6
n-C_{17}	0.05	4.5	10.2	13.9	6.0
Pristane	0.02	2.0	4.2	5.4	2.6
n-C_{18}	0.05	4.0	9.3	12.5	5.1
Phytane	0.03	2.2	5.5	6.8	2.9
n-C_{19}	0.04	2.4	9.2	7.7	3.8
n-C_{20}	0.04	3.1	7.8	9.5	4.5
n-C_{21}	0.04	2.5	6.6	8.0	3.8
n-C_{22}	0.03	2.2	5.7	7.0	3.3
n-C_{23}	0.03	1.9	4.9	5.9	2.8
n-C_{24}	0.03	1.7	4.3	5.3	2.5
n-C_{25}	0.03	1.4	3.7	4.3	2.3
n-C_{26}	0.02	1.2	3.4	3.8	1.8
n-C_{27}	0.03	1.0	2.8	3.3	1.5
n-C_{28}	0.02	0.89	2.3	2.9	1.3
n-C_{29}	0.02	0.79	2.1	2.6	1.0
n-C_{30}	0.02	0.70	1.7	2.4	0.88
n-C_{31}	0.02	0.64	1.6	2.0	0.73
n-C_{32}	0.01	0.44	1.3	1.6	0.43

[a] ND = not detected.

TABLE 3-25 (Cont.)

	DAY				
	1	2	4	8	16
Total Alkanes (GC)(μg/g)	0.55	54.4	155	145	63.6
Total Resolved (GC)(μg/g)	0.74	84.4	244	236	98.9
Total Saturates (grav. wt.)(μg/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	GC-8	GC-9	GC-10
Lab ID No.	06-1077	06-1078	06-1079	06-1080	06-1081
Constituent (µg/g)					
n-C_{10}	ND[a]	ND	ND	ND	2.5
n-C_{11}	ND	ND	ND	ND	18.0
n-C_{12}	ND	ND	0.04	0.14	38.3
n-C_{13}	ND	ND	0.25	0.47	52.8
n-C_{14}	ND	ND	0.57	0.82	22.0
Farnesane	ND	ND	0.27	0.40	23.5
n-C_{15}	0.5[b]	ND	0.88	0.95	57.6
n-C_{16}	2.0[b]	0.2[b]	0.96	1.1	52.3
n-C_{17}	3.4[b]	1.5[b]	0.99	1.0	46.5
Pristane	4.5[b]	2.2[b]	0.43	0.45	20.8
n-C_{18}	4.8[b]	3.0[b]	0.97	0.88	40.2
Phytane	2.4[b]	1.4[b]	0.58	0.53	24.2
n-C_{19}	1.6[b]	0.2[b]	0.90	0.67	44.5
n-C_{20}	5.4[b]	3.0[b]	0.76	0.76	35.3
n-C_{21}	4.7[b]	2.8[b]	0.62	0.78	30.6
n-C_{22}	5.3[b]	2.4[b]	0.51	0.58	26.4
n-C_{23}	6.2[b]	2.0[b]	0.44	0.51	22.7
n-C_{24}	8.9[b]	1.6[b]	0.38	0.46	19.4
n-C_{25}	11.5[b]	1.6[b]	0.31	0.39	18.1
n-C_{26}	14.0[b]	1.2[b]	0.27	0.35	14.8
n-C_{27}	10.2[b]	1.2[b]	0.25	0.30	13.0
n-C_{28}	8.0[b]	1.0[b]	0.22	0.25	11.0
n-C_{29}	6.1[b]	1.0[b]	0.21	0.24	9.5
n-C_{30}	4.6[b]	0.6[b]	0.20	0.25	11.2
n-C_{31}	3.4[b]	0.6[b]	0.16	0.18	7.7
n-C_{32}	2.2[b]	0.4[b]	0.12	0.17	6.6

[a] ND = not detected.

[b] ng/g.

TABLE 3-26 (Cont.)

	DAY				
	1	2	4	8	16
Total Alkanes (GC)(µg/g)	64[b]	26[b]	11.0	8.7	591
Total Resolved (GC)(µg/g)	141[b]	444[b]	14.8	17.5	1,000
Total Saturates (grav. wt.)(µg/g)	970[b]	810[b]	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

[a] ND = not detected.

[b] ng/g.

TABLE 3-27

SHORELINE STUDY - SATURATED HYDROCARBONS (SITE LT-1)

	DAY				
	1	2	4	8	16
Sample ID No.	GC-21	GC-22	GC-23	GC-24	None
Lab ID No.	06-1067	06-1082	06-1068	06-1084	
Constituent (µg/g)					
n-C_{10}	17.1	23.3	4.3	8.9	
n-C_{11}	28.3	60.8	6.7	36.7	
n-C_{12}	33.5	82.3	7.6	58.2	
n-C_{13}	33.8	86.1	7.5	64.6	
n-C_{14}	34.4	84.2	7.4	68.6	
Farnesane	13.6	28.7	3.0	27.5	
n-C_{15}	33.0	81.4	7.2	68.1	
n-C_{16}	29.8	68.2	6.2	59.9	
n-C_{17}	26.8	76.1	5.6	53.7	
Pristane	11.9	24.8	2.5	23.5	
n-C_{18}	22.7	58.8	4.5	43.9	
Phytane	13.0	34.4	2.8	27.8	
n-C_{19}	22.9	41.3	4.7	33.6	
n-C_{20}	19.5	48.9	4.1	37.9	
n-C_{21}	16.3	41.7	3.4	31.1	
n-C_{22}	14.8	36.9	3.7	27.4	
n-C_{23}	12.5	30.6	2.6	23.1	
n-C_{24}	11.0	26.9	2.3	20.3	
n-C_{25}	9.4	21.5	1.9	19.9	
n-C_{26}	8.1	17.8	1.6	16.7	
n-C_{27}	7.5	14.0	1.4	15.6	
n-C_{28}	6.7	11.6	1.2	13.2	
n-C_{29}	6.6	10.9	1.0	10.9	
n-C_{30}	6.5	7.9	0.91	10.5	
n-C_{31}	5.7	5.2	0.74	8.9	
n-C_{32}	4.2	4.2	0.48	6.3	

TABLE 3-27 (Cont.)

	DAY				
	1	2	4	8	16
Total Alkanes (GC)(μg/g)	411	930	87.2	738	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.	GC-26	GC-27	GC-28	GC-29	None
Lab ID No.	06-1085	06-1086	06-1087	06-1088	
Constituent (µg/g)					
n-C_{10}	9.9	13.7	3.6	47.7	
n-C_{11}	55.6	56.9	17.9	127	
n-C_{12}	114	104	36.4	169	
n-C_{13}	141	119	47.8	199	
n-C_{14}	140	127	41.5	204	
Farnesane	60.9	46.4	17.89	65.9	
n-C_{15}	140	119	43.0	200	
n-C_{16}	139	113	56.5	188	
n-C_{17}	124	126	52.9	172	
Pristane	57.3	48.1	21.8	76.9	
n-C_{18}	115	97.2	47.3	165	
Phytane	61.8	153.7	28.0	91.6	
n-C_{19}	119	67.7	48.8	164	
n-C_{20}	95.1	74.5	39.8	135	
n-C_{21}	86.0	61.7	34.4	121	
n-C_{22}	77.0	49.6	29.3	105	
n-C_{23}	76.2	39.8	25.7	90.6	
n-C_{24}	60.4	33.3	22.9	81.8	
n-C_{25}	52.6	33.4	18.4	68.8	
n-C_{26}	48.3	23.7	16.5	70.3	
n-C_{27}	45.1	22.0	13.5	59.9	
n-C_{28}	42.6	18.5	10.1	52.6	
n-C_{29}	35.0	15.0	8.99	48.9	
n-C_{30}	33.7	14.7	8.97	38.2	
n-C_{31}	35.2	10.6	4.97	23.9	
n-C_{32}	25.9	9.21	4.89	19.9	

TABLE 3-28 (Cont.)

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

TABLE 3-29

SHORELINE STUDY - SATURATED HYDROCARBONS (SITE HT-1)

	DAY			
	1	2	4	8
Sample ID No.	GC-40	GC-42	GC-44	GC-46
Lab ID No.	06-1089	06-1091	06-1093	06-1044
Constituent (µg/g)				
n-C_{10}	4.1	5.0	2.4	26.9
n-C_{11}	18.6	16.7	9.5	78.6
n-C_{12}	30.1	26.5	17.2	122
n-C_{13}	33.0	29.3	20.8	125
n-C_{14}	33.8	29.3	21.4	130
Farnesane	13.4	10.0	7.6	53.1
n-C_{15}	32.8	28.2	21.6	137
n-C_{16}	28.9	24.0	19.4	121
n-C_{17}	25.3	21.5	18.3	112
Pristane	7.1	9.3	8.1	39.9
n-C_{18}	21.3	19.6	16.2	100
Phytane	13.0	10.7	9.5	56.8
n-C_{19}	15.1	19.7	15.7	93.8
n-C_{20}	18.6	15.0	13.4	75.8
n-C_{21}	16.0	13.6	11.9	62.6
n-C_{22}	16.5	11.9	10.4	54.2
n-C_{23}	12.1	9.9	9.0	44.2
n-C_{24}	11.0	8.6	8.0	37.4
n-C_{25}	11.5	7.9	6.3	31.8
n-C_{26}	7.8	6.0	5.3	26.0
n-C_{27}	7.3	4.9	4.1	24.2
n-C_{28}	5.5	3.8	3.6	18.3
n-C_{29}	4.1	3.1	3.2	16.0
n-C_{30}	3.8	2.1	1.9	11.1
n-C_{31}	2.9	2.1	1.9	7.4
n-C_{32}	1.8	1.3	1.1	6.8

TABLE 3-29 (Cont.)

	DAY			
	1	2	4	8
Total Alkanes (GC)(μg/g)	362	310	242	1,460
Total Resolved (GC)(μg/g)	623	490	403	2,270
Total Saturates (grav. wt.)(μg/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.	GC-41	GC-43	GC-45	GC-47	GC-49
Lab ID No.	06-1090	06-1092	06-1105	06-1095	06-1096
Constituent (µg/g)					
n-C_{10}	46.2	2.65	4.0	8.10	6.96
n-C_{11}	139	18.9	67.2	32.0	29.3
n-C_{12}	215	45.0	77.2	62.9	49.8
n-C_{13}	219	63.0	73.2	69.9	69.5
n-C_{14}	215	69.8	68.8	81.0	73.9
Farnesane	90.0	20.5	28.4	35.9	31.0
n-C_{15}	205	70.0	63.6	89.8	75.2
n-C_{16}	198	62.3	63.2	78.4	68.2
n-C_{17}	180	56.6	57.2	70.4	63.2
Pristane	78.5	25.4	24.8	32.5	28.4
n-C_{18}	165	50.9	51.2	63.3	52.8
Phytane	91.1	30.0	26.4	36.3	31.2
n-C_{19}	166	51.4	52.4	54.0	36.6
n-C_{20}	131	41.5	42.4	49.2	43.8
n-C_{21}	114	36.0	36.8	43.8	37.2
n-C_{22}	100	30.7	31.2	36.6	32.5
n-C_{23}	87.1	26.0	26.0	31.2	26.5
n-C_{24}	78.4	24.4	24.0	25.1	22.8
n-C_{25}	80.7	20.7	22.4	22.3	18.2
n-C_{26}	56.5	18.2	18.4	15.3	15.7
n-C_{27}	52.3	15.2	18.4	11.9	10.5
n-C_{28}	41.1	13.9	14.8	11.4	7.53
n-C_{29}	36.6	13.6	15.6	8.75	6.88
n-C_{30}	30.0	13.0	14.4	6.0	5.65
n-C_{31}	21.0	6.56	12.4	4.0	4.12
n-C_{32}	21.7	7.18	9.2	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	1,110	1,350	1,337	1,260
Total Saturates (grav. wt.)(µg/g)	18,300	5,790	13,700	9,120	7,880
ALK/ISO	2.57	2.80	2.98	2.64	2.38
SHWR	2.12	1.96	2.31	2.07	2.12

(C_{10}-C_{32}) 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^2) 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_{14} through n-C_{18} ÷ 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:

	ALK/ISO	SHWR
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_{24}, which is asssumed 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

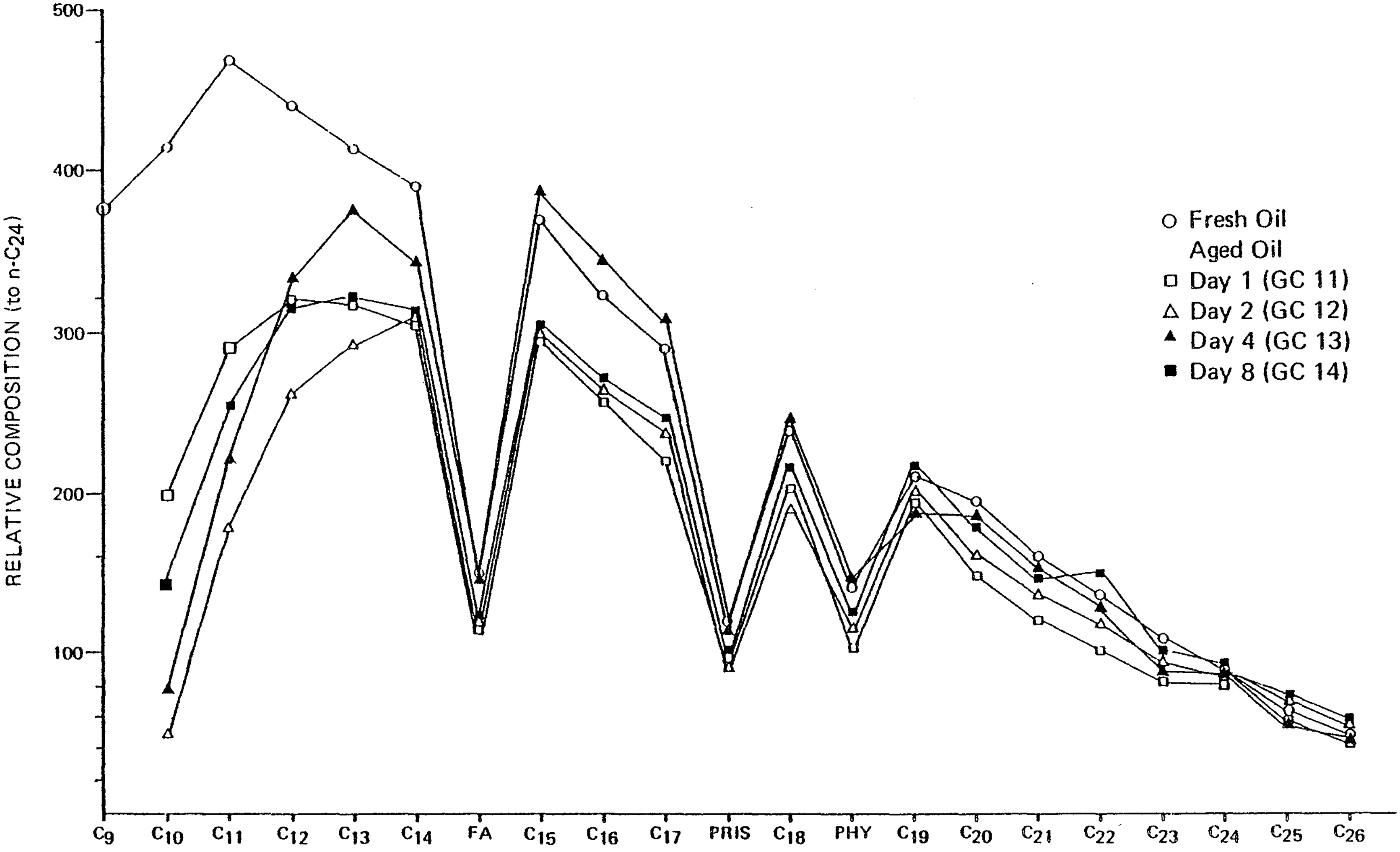


Figure 3.36. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site L–1.

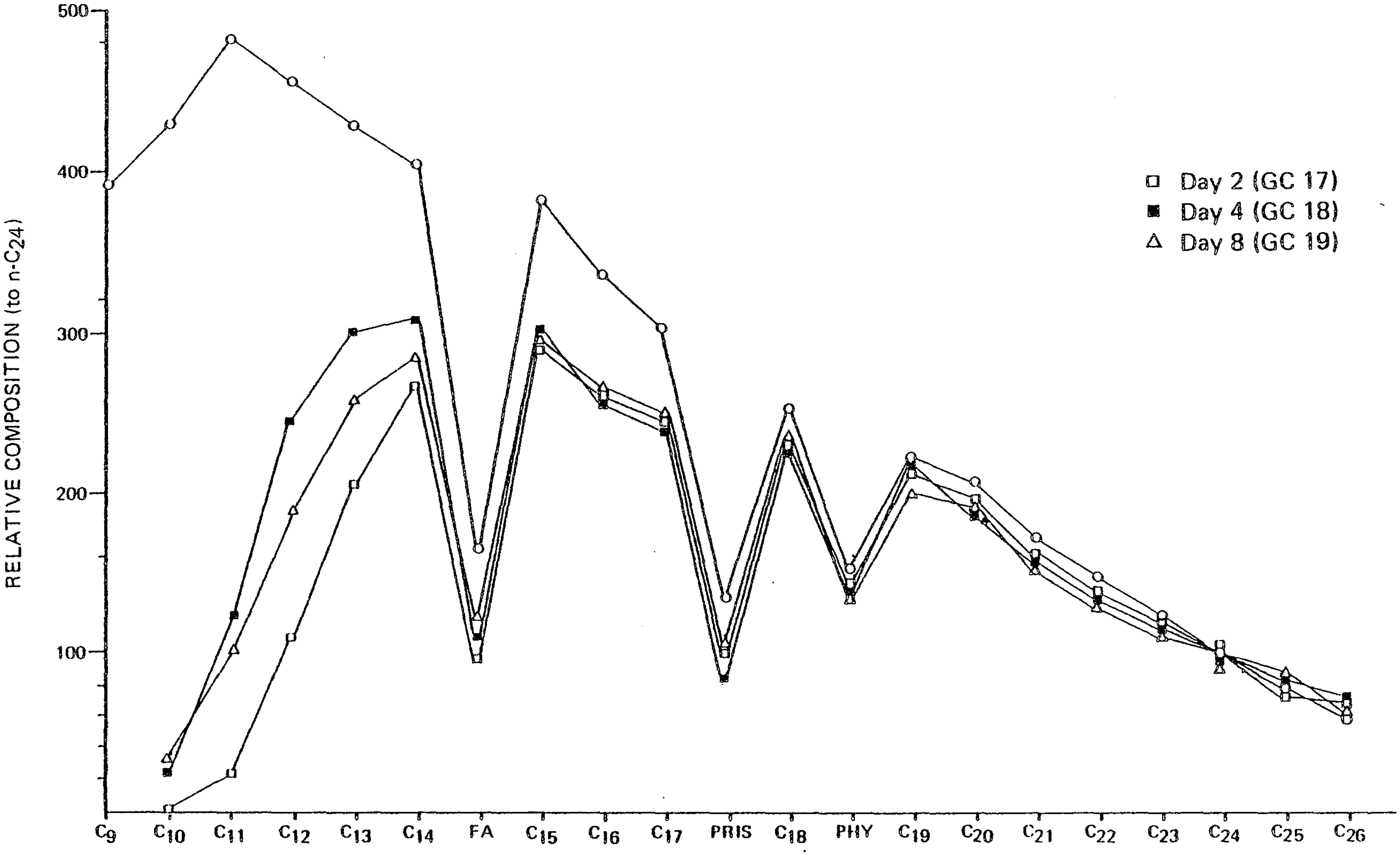


Figure 3.37. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site L–2.

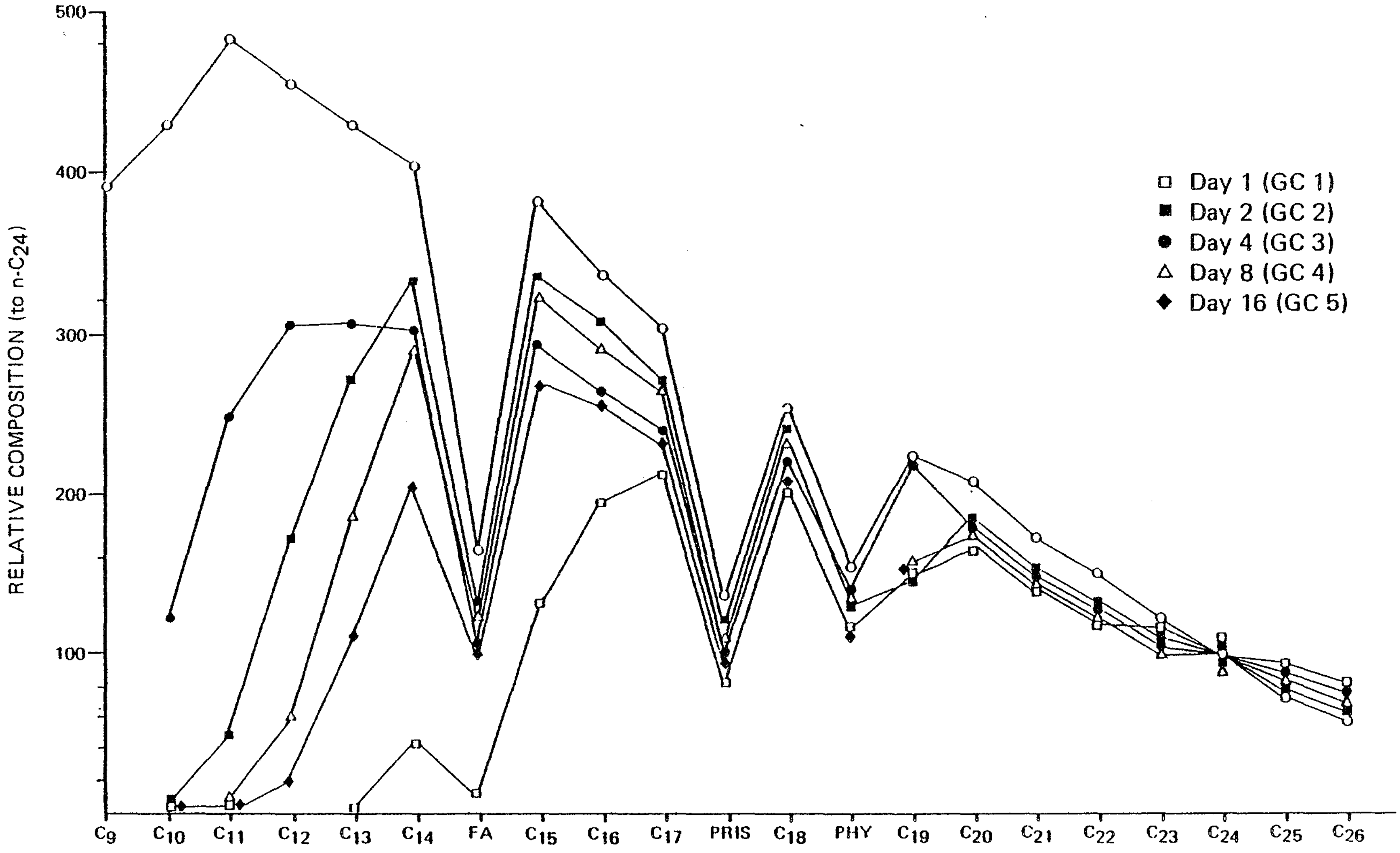


Figure 3.38. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site H–1.

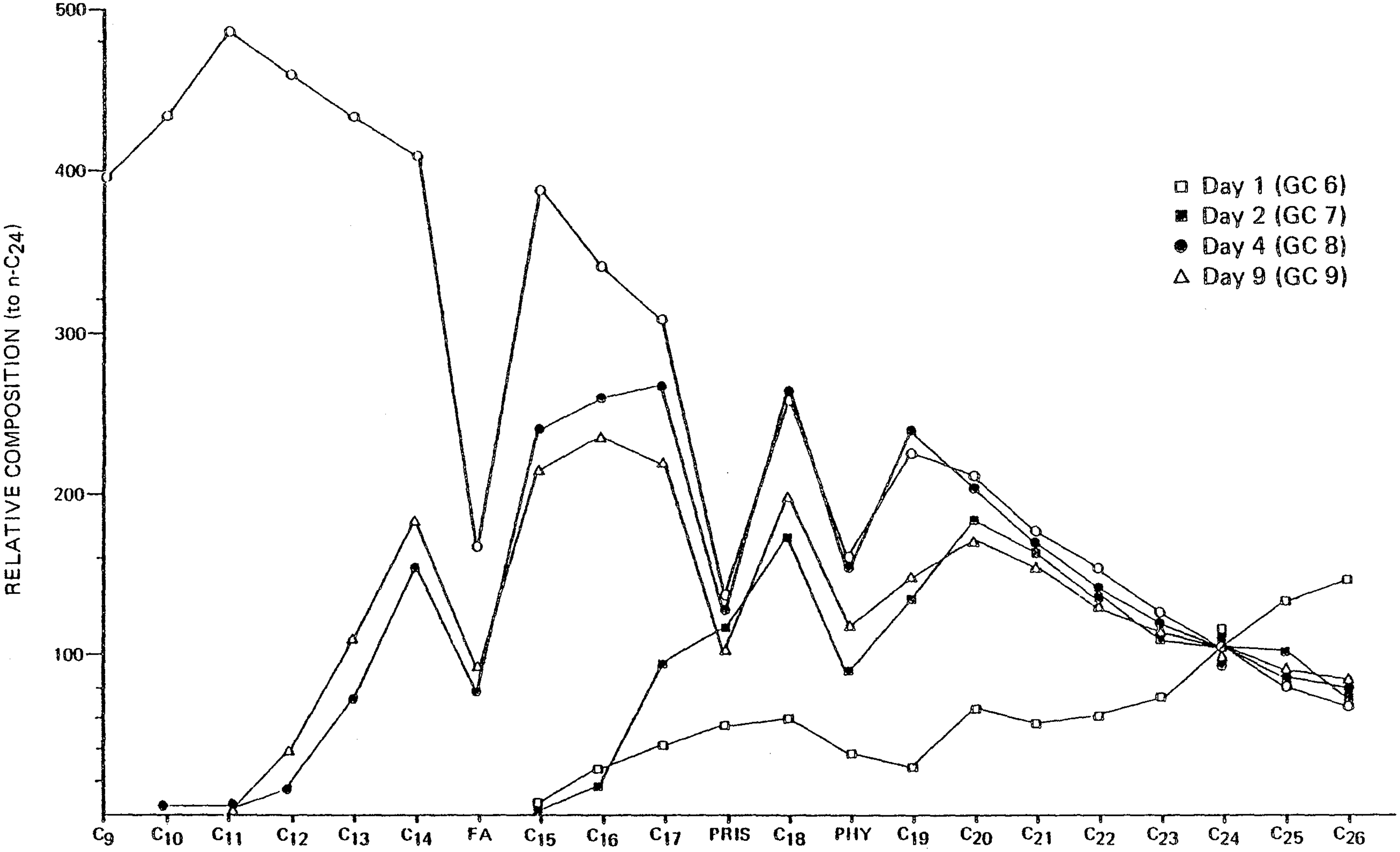


Figure 3.39. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site H–2.

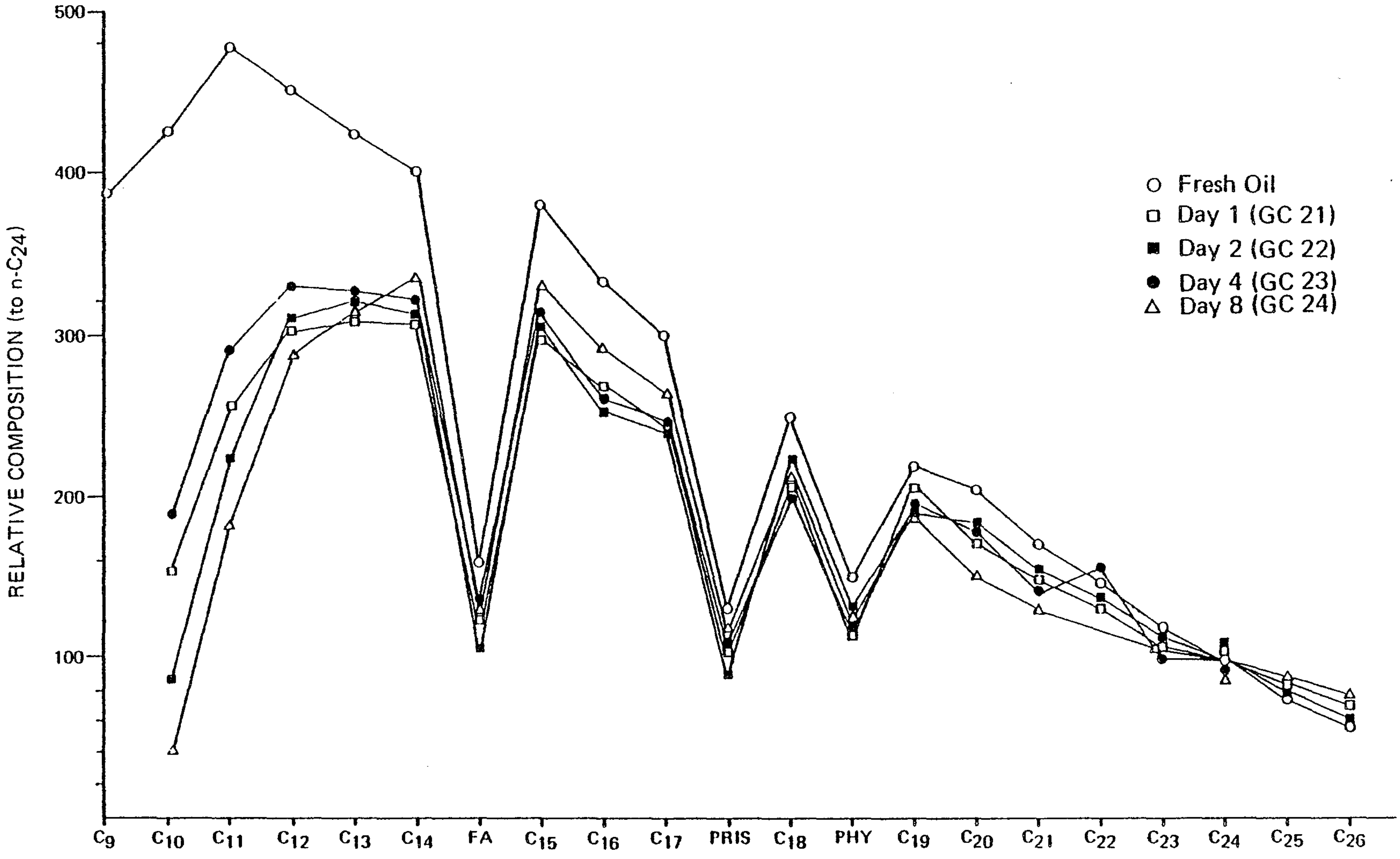


Figure 3.40. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site LT—1.

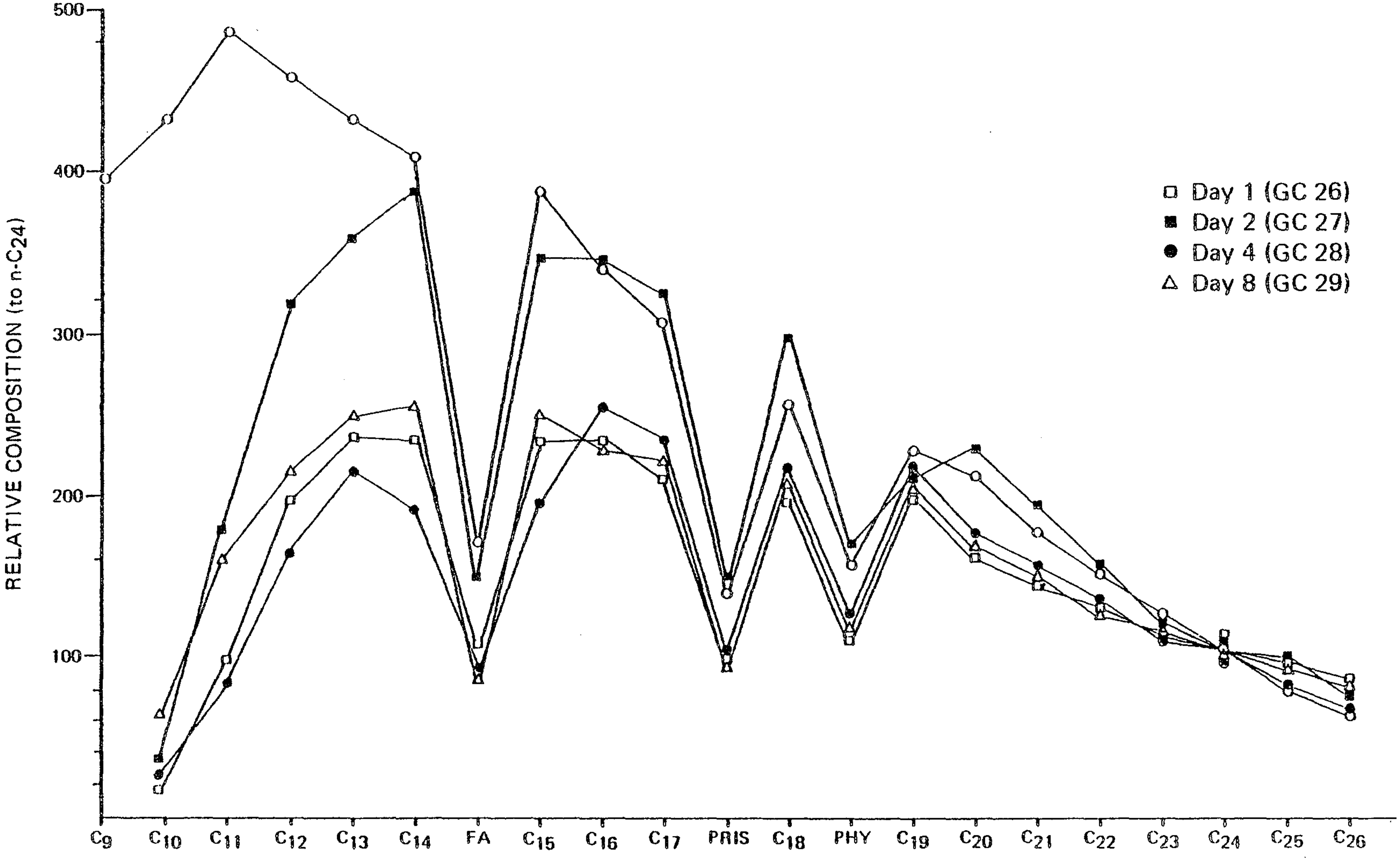


Figure 3.41. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site LT–2.

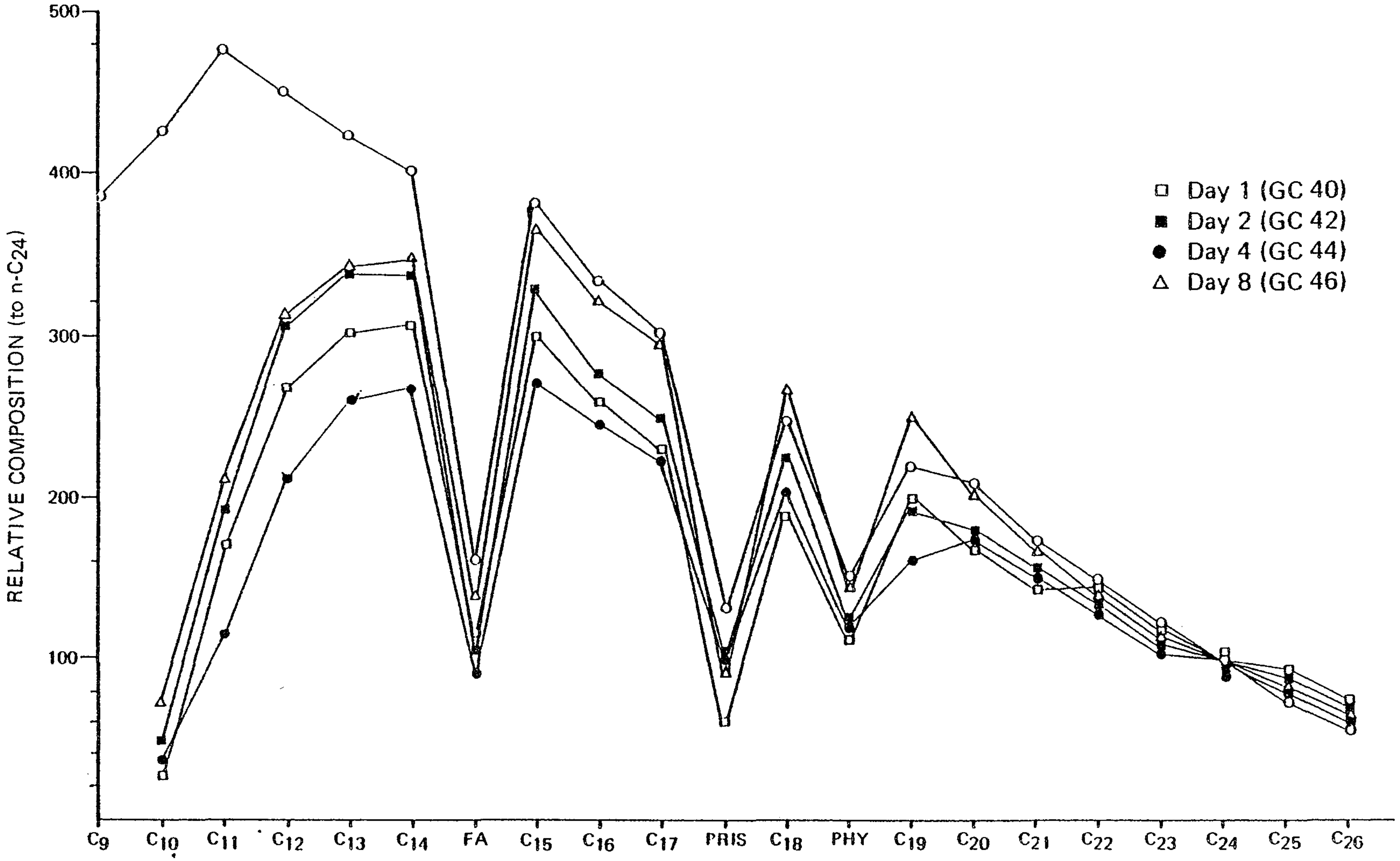


Figure 3.42. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site HT–1.

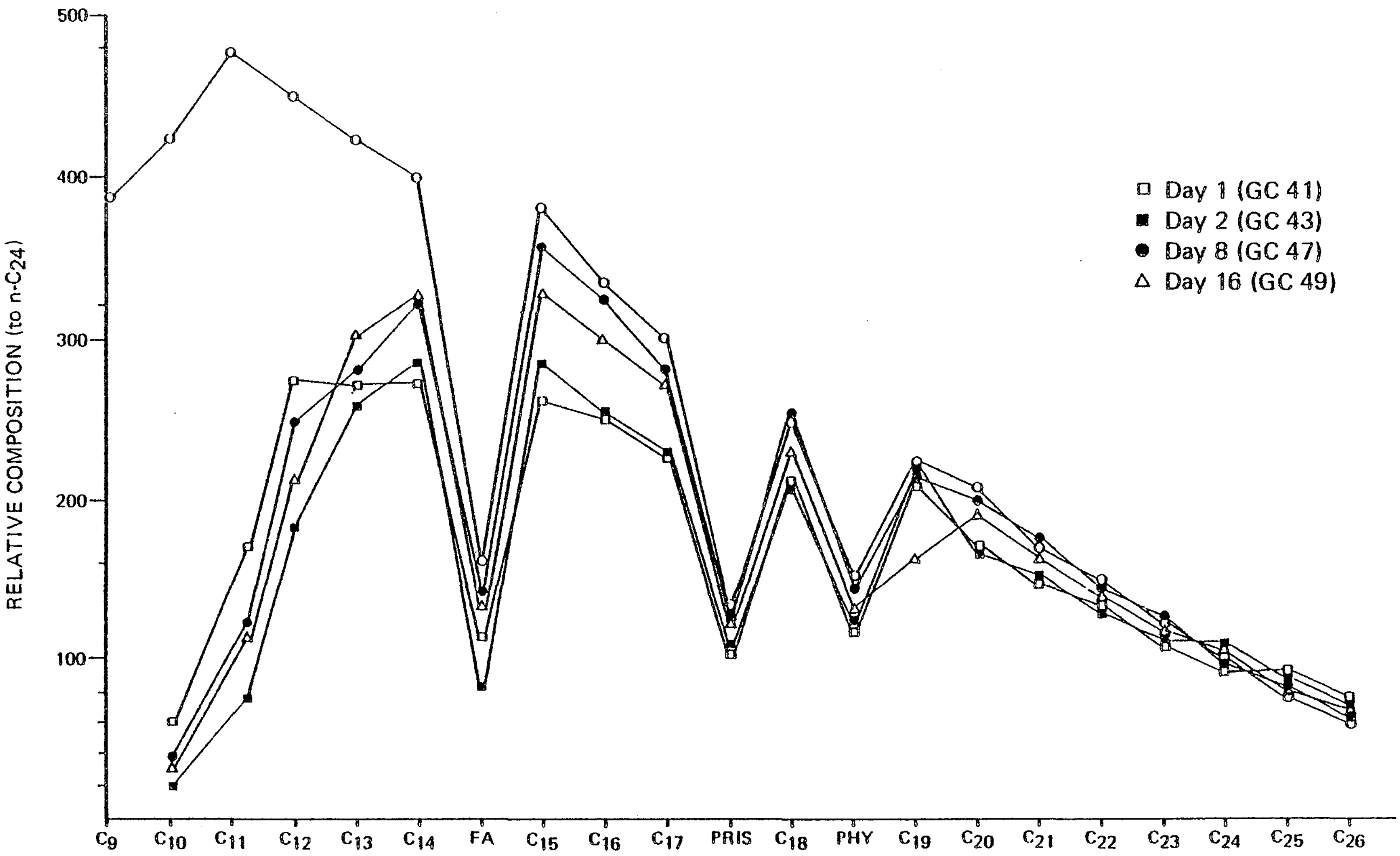


Figure 3.43. Comparative Saturated Hydrocarbon Composition of Lagomedio Crude-Shoreline Experiment, Site HT–2.

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^2/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)

$$AWR = \Sigma\ (\Sigma AB + \Sigma N + \Sigma F + \Sigma P + \Sigma DBT)/\ \Sigma\ (\Sigma P + \Sigma DBT)$$

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 (C_3) 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^2/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	13.0	6.8	2.4	6.9
C_1N	7.1	7.6	15.7	66.0	44.2	12.0	43.4
C_2N	17.7	17.7	38.0	139.0	102.2	28.1	106.0
C_3N	14.7	16.3	30.0	114.0	87.2	22.6	90.5
C_4N	7.7	7.9	15.9	694.0	54.0	13.3	48.3
ΣN	48.4	50.7	102.5	426.0	294.4	78.4	295.1
C_3AB	3.7	3.2	4.1	99.6	21.8	7.3	19.0
C_4AB	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	0.6	2.2
C_1F	1.2	1.3	2.4	8.2	6.2	1.7	6.6
C_2F	1.8	1.9	3.3	16.6	11.2	3.1	12.3
C_3F	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	5.0
C_1P	4.1	3.8	7.2	32.0	18.9	5.1	22.5
C_2P	5.0	5.2	8.6	40.0	25.4	6.6	28.2
C_3P	3.5	3.1	6.0	37.8	22.0	5.8	21.7
C_4P	2.8	2.4	2.1	22.6	13.2	3.4	18.1
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_1DBT	3.8	3.7	6.9	30.8	20.4	5.2	20.2
C_2DBT	6.9	7.2	13.7	62.2	41.4	9.9	38.9
C_3DBT	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_1,C_2,C_3,C_4,C_5 = mono-, di-, tri-, tetra- and penta-methyl homologues.

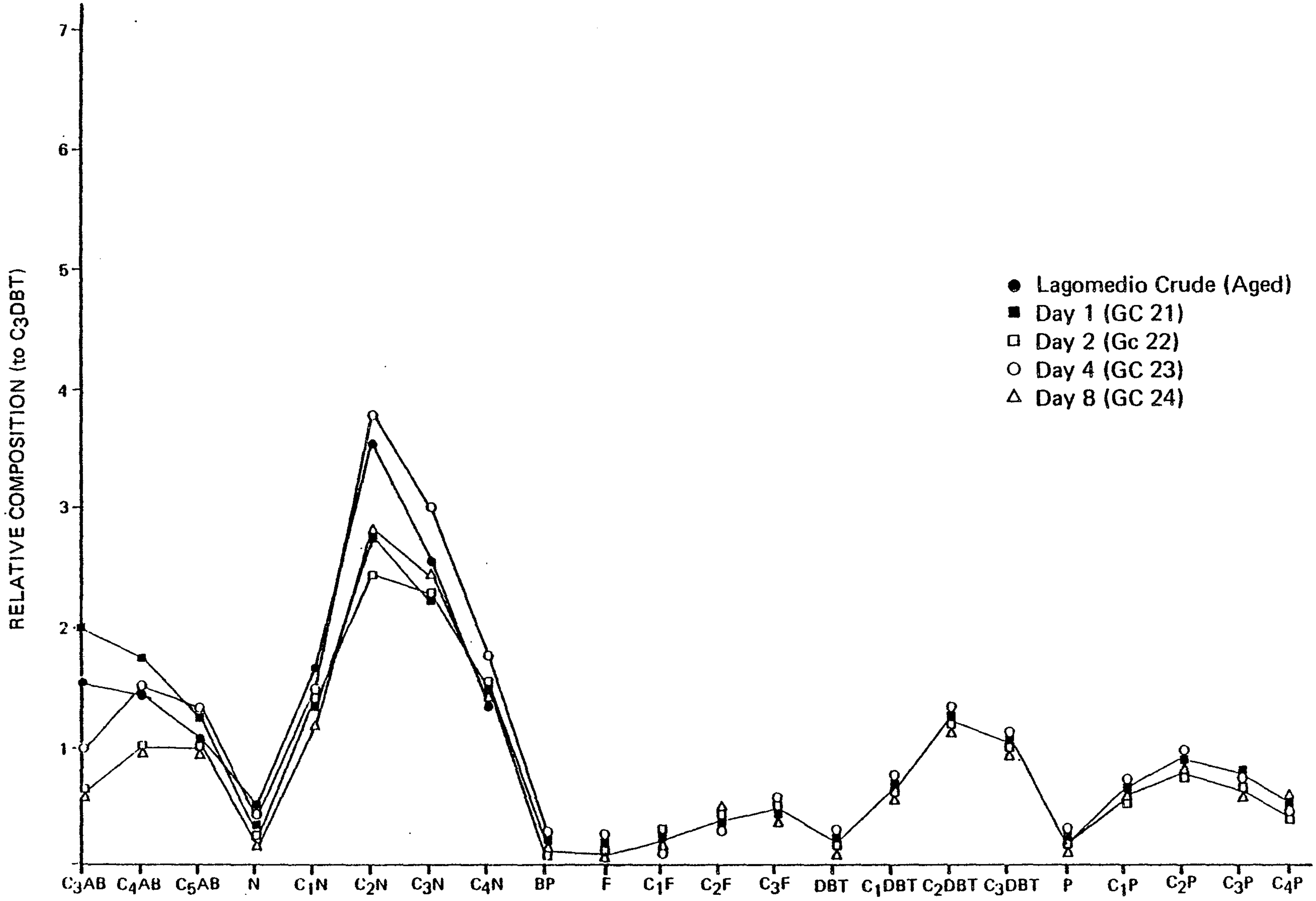


Figure 3.44. Comparative Aromatic Hydrocarbon Compositions, Site L–1: Aged Oil.

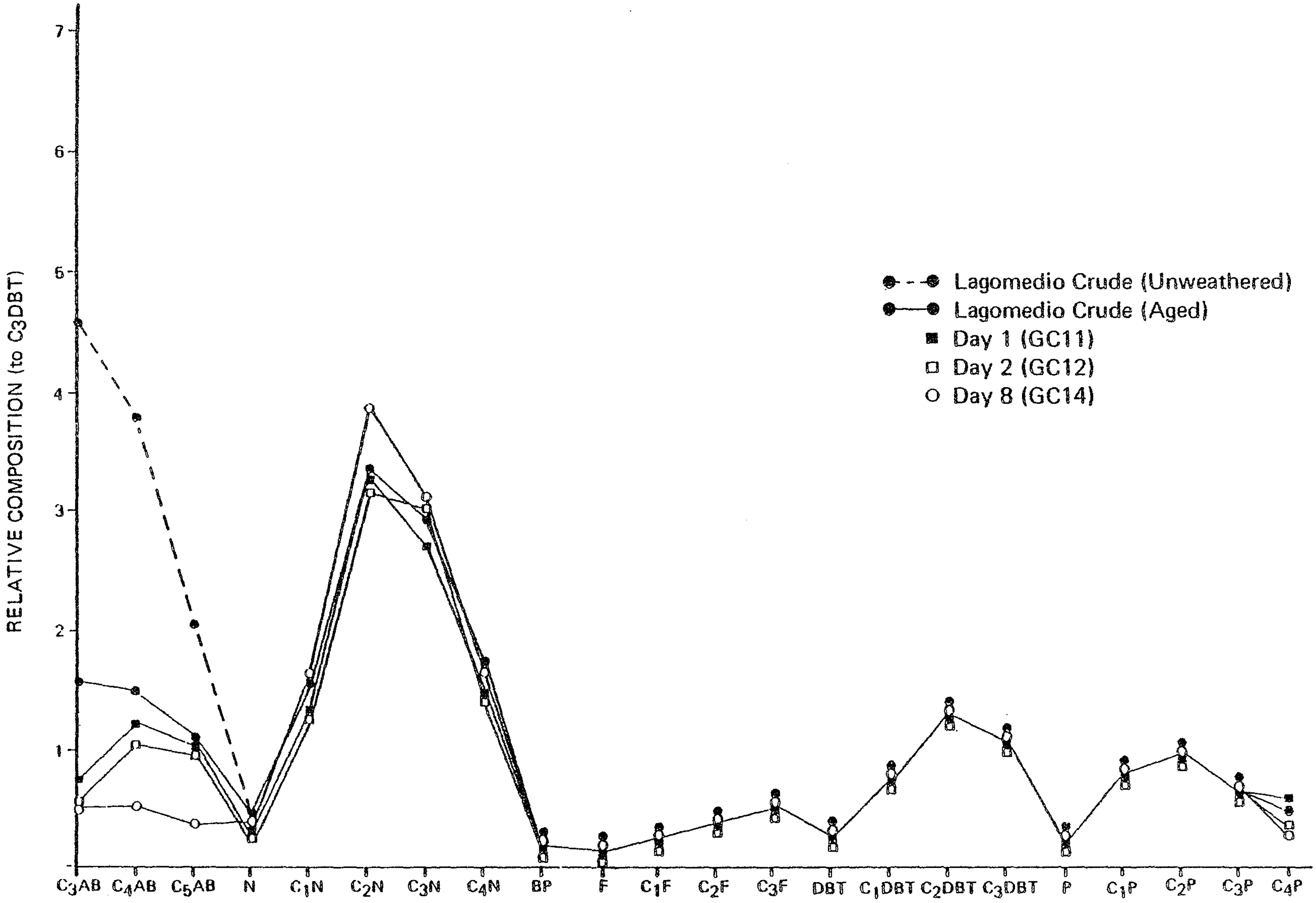


Figure 3.45. Comparative Aromatic Hydrocarbon Compositions, Site LT–1: Aged Oil.

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^2)

Pentacyclic triterpane hydrocarbons (PT) were the subject of a GC^2/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[a]

	SITE L-1		
	DAY 1 GC-11	DAY 2 GC-12	DAY 8 GC-14
M/e			
129 Q	0.8	0.7	--
143 C_1Q	2.2	1.6	1
157 C_2Q	1.9	2.9	1.4
171 C_3Q	7.8	10	15
185 C_4Q	25	31	41
199 C_5Q	21	25	32
213 C_6Q	29	30	30
179A	0.3	0.2	0.5
193 C_1A	8	11	11
207 C_2A	55	51	71
221 C_3A	100	100	100
235 C_4A	54	63	39
249 C_5A	18	22	10
229 BA	0.2	0.3	0.1
243 C_1BA	3	3	1
257 C_2Ba	4	4	2

[a] = Concentrations normalized to C_3A

A = Acridines/phenanthridines
Q = Quinolines
BA = Benzacridines
C_n = Alkyl homologues 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_1Q	6	5	3	1.7
157 C_2Q	5	4	1	2.5
171 C_3Q	15	11	8	11
185 C_4Q	43	33	26	32
199 C_5Q	31	27	23	28
213 C_6Q	30	29	25	28
179A	0.4	0.2	0.3	0.3
193 C_1A	14	10	8	11
207 C_2A	69	58	49	52
221 C_3A	100	100	100	100
235 C_4A	41	53	51	59
249 C_5A	12	19	20	21
229 BA	0.2	0.2	0.3	0.2
243 C_1BA	1	2.4	3	2.5
257 C_2Ba	1	3.0	5	3.4

[a] = Concentrations normalized to C_3A

A = Acridines/phenanthridines
Q = Quinolines
BA = Benzacridines
C_n = Alkyl homologues 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
M/e					
129 Q	0.5	0.3	0.3	0.6	1.0
143 C_1Q	1.1	0.7	1.4	2.3	2.6
157 C_2Q	1.8	2	1	1.5	1.5
171 C_3Q	8	7	8	10	9.5
185 C_4Q	25	22	27	32	30
199 C_5Q	19	16	24	22	23
213 C_6Q	28	22	27	28	27
179A	0.3	0.2	0.2	0.3	0.3
193 C_1A	10	9	9	10	9
207 C_2A	49	47	57	55	47
221 C_3A	100	100	100	100	100
235 C_4A	51	47	56	55	51
249 C_5A	18	15	20	20	0.9
229 BA	0.2	0.2	0.3	0.3	0.1
243 C_1BA	2.1	2	1.5	3.2	3.0
257 C_2Ba	4.3	5	3	5.1	4.6

[a] = Concentrations normalized to C_3A

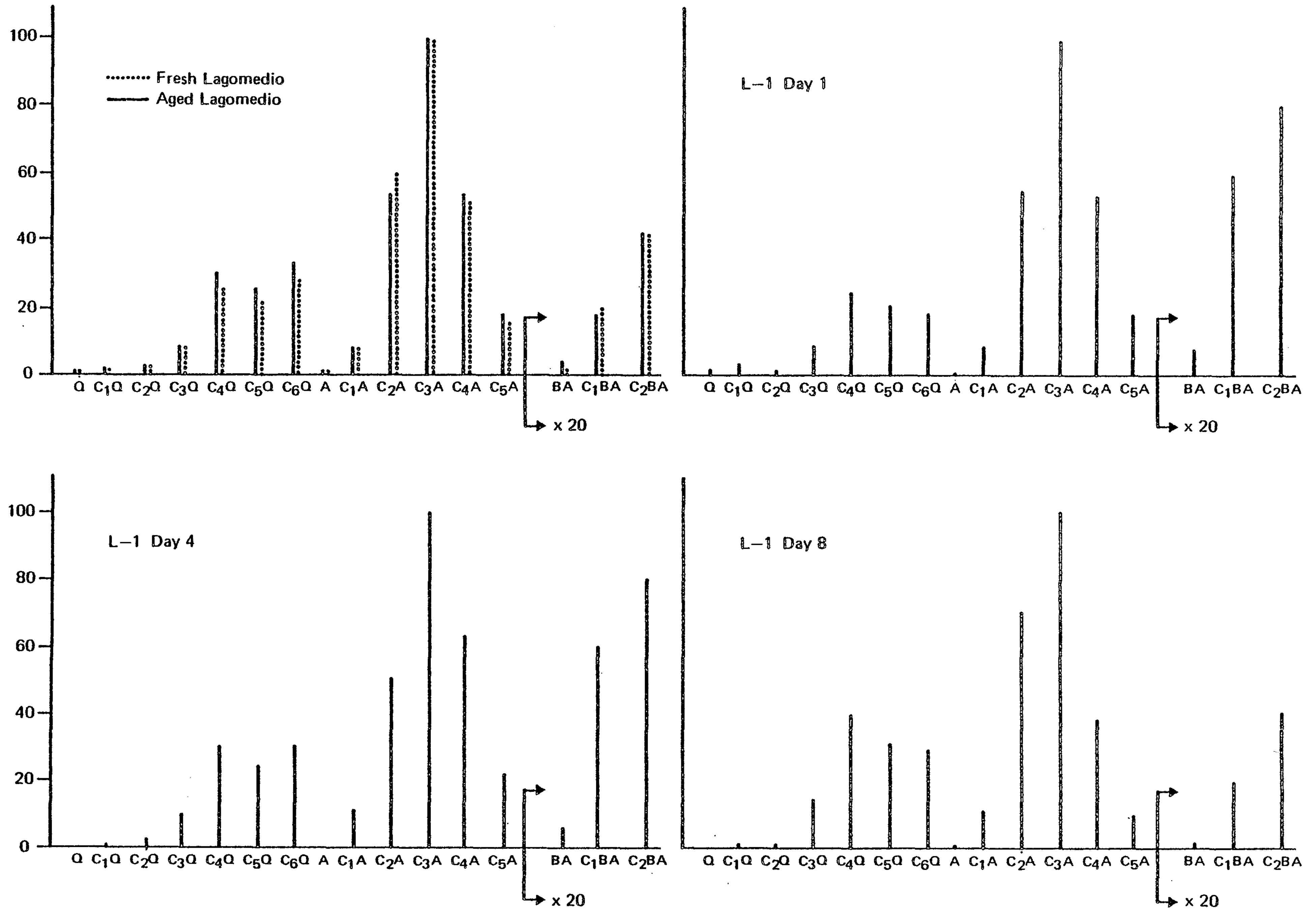
A = Acridines/phenanthridines
Q = Quinolines
BA = Benzacridines
C_n = Alkyl homologues with n-Carbon atoms

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_1Q	1.7	0.7	0.7
157 C_2Q	1.7	1.6	1.1
171 C_3Q	9	9	6.5
185 C_4Q	27	25	20
199 C_5Q	24	22	20
213 C_6Q	29	29	29
179A	0.3	0.2	0.1
193 C_1A	9	10	9
207 C_2A	52	53	50
221 C_3A	100	100	100
235 C_4A	58	58	58
249 C_5A	24	24	24
229 BA	0.2	0.3	0.2
243 C_1BA	3.4	3.1	2.9
257 C_2Ba	5.6	5.4	4.6

[a] = Concentrations normalized to C_3A

A = Acridines/phenanthridines
Q = Quinolines
BA = Benzacridines
C_n = Alkyl homologues with n-Carbon atoms



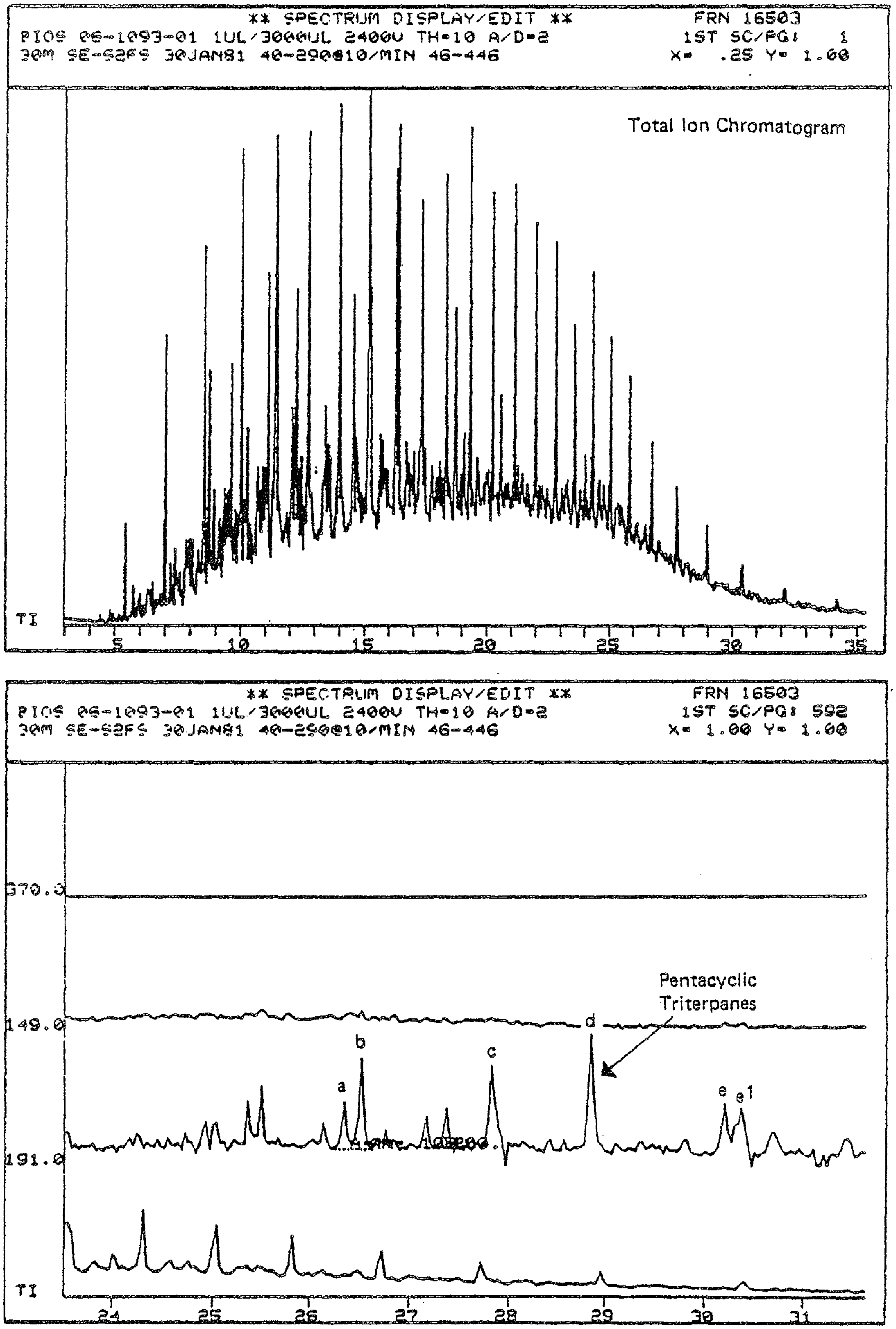
Fresh Lagomedio
Aged Lagomedio
L–1 Day 1
L–1 Day 4
L–1 Day 8
0
20
40
60
80
100
Q
C1Q
C2Q
C3Q
C4Q
C5Q
C6Q
A
C1A
C2A
C3A
C4A
C5A
BA
C1BA
C2BA
x 20

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
COMPOUND[a]										
A	+	+	+	+	+	+	+	+	+	+
B	+	+	+	+	+	+	+	+	+	+
C	+	+	+	+	+	+	+	+	+	+
D	+	+	+	+	+	+	+	+	+	+
E	+	+	+	+	+	+	+	+	+	+
E'	+	+	+	+	+	+	+	+	+	+
F	-	-	-	-	-	-	-	-	-	-
F'	-	-	-	-	-	-	-	-	-	-

[a] See Section 3.2.5(b) for explanation of compound identification.



```
                    ** SPECTRUM DISPLAY/EDIT **              FRN 16503
PIOS 06-1093-01 1UL/3000UL 2400V TH=10 A/D=2               1ST SC/PG:    1
30m SE-52FS 30JAN81 40-290@10/MIN 46-446                   X=  .25 Y= 1.00
```

Total Ion Chromatogram

```
                    ** SPECTRUM DISPLAY/EDIT **              FRN 16503
PIOS 06-1093-01 1UL/3000UL 2400V TH=10 A/D=2               1ST SC/PG: 592
30M SE-52FS 30JAN81 40-290@10/MIN 46-446                   X= 1.00 Y= 1.00
```

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^2 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^2/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^2 analysis must parallel or follow UV/F analysis.

Specified chemical marker compounds (PAH, PAN, PSH) must be analyzed by GC^2/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 artifically 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

REFERENCES

Ackman, R.G., and D. Noble. 1973. Steam distillation: a simple technique for recovery of petroleum hydrocarbons from tainted fish. J. Fish Res. Bd. Canada 30:711-714.

Aizenshtat, A. 1973. Perylene and its geochemical significance. Geochim. Cosmochim. Acta 37:559-567.

Atlas, R.M., P.D. Boehm, and J.A. Calder. 1981. Chemical and biological weathering of oil from the *Amoco Cadiz* oil spillage, within the littoral zone. Est. Coast. Mar. Sci. (in press).

Beslier, A., J.L. Berrien, L. Cabioch, L.J. Douville, C. Larsonneur, and L. LeBorgne. 1981. Distribution et evolution de la pollution des bares de lannion et de morlaix par les hydrocarbures de l'*Amoco Cadiz*. *In* Proceedings, *Amoco Cadiz*: Fates and Effects of the Oil Spill, November 19-22, 1979, Brest France. Centre National pour l'Exploitation des Oceans, COB, Brest, France.

Boehm, P.D. 1980. The decoupling of dissolved, particulate and surface microlayer hydrocarbons in northwestern Atlantic Continental Shelf waters. Marine Chemistry 9: 255-281.

Boehm, P.D., and D.L. Fiest. 1981a. Subsurface water column transport and weathering of petroleum hydrocarbons during the *Ixtoc I* blowout in the Bay of Campeche and their relation to surface oil and microlayer compositions. *In* Proceedings of Symposium on the Preliminary Findings of the *Researcher* Cruise to the *Ixtoc I* Blowout. NOAA/OMPA, Rockville, Md.

Boehm, P.D., and D.L. Fiest. 1981b. Aspects of the transport of petroleum hydrocarbons to the offshore benthos during the *Ixtoc I* blowout in the Bay of Campeche. *In* Proceedings of the Conference on the Preliminary Scientific Results from the *Researcher* Cruise to the *Ixtoc I* Blowout. NOAA, Office of Marine Pollution Assessment, Rockville, Maryland.

Boehm, P.D., J.E. Barak, D.L. Fiest, and A. Elskus. 1981a. A chemical investigati of the transport and fate of petroleum hydrocarbons littoral and benthic environments: the *Tsesis* oil ill. Mar. Environ. Res. (in press).

Boehm, P.D., D.L. Fiest, and A. Elskus. 1981b. Comparative weathering patterns of hydrocarbons from the Amoco Cadiz oil spill observed at a variety of coastal environments. In Proceedings of International Symposium on the Amoco Cadiz: Fates and Effects of the Oil Spill, November 19-22, 1979, Brest, France. CNEXO (in press).

Boehm, P.D., W.G. Steinhauer, D.L. Fiest, N. Mosesman, J.E. Barak, and G.H. Perry. 1979. A chemical assessment of the present levels and sources of hydrocarbon pollutants on Georges Bank. In Proceedings of the 1979 Oil Spill Conference. API, EPA, USCG.

Brown, D.W., L.S. Ramos, A.J. Friedman, and W.D. MacLeod. 1979. Analysis of trace levels of petroleum hydrocarbons in marine sediments using a solvent/slurry extraction procedure. Pages 161-167 in Trace organic analysis: a new frontier in analytical chemistry. National Bureau of Standards Special Publication 519.

Butler, J.N., B.F. Morris, and J. Sass. 1973. Pelagic tar from Bermuda and the Sargasso Sea. Special Publication No. 10, Bermuda Biological Station for Research.

Clark, R.C., Jr. 1974. Methods for establishing levels of petroleum contamination in organisms and sediment as related to marine pollution monitoring. Pages 189-196 in Marine pollution monitoring. National Bureau of Standards Special Publication No. 409.

Clark, R.C., Jr., and D.W. Brown. 1977. Petroleum: properties and analyses in biotic and abiotic systems. In D.C. Malins, ed. Effects of petroleum on arctic and subarctic marine environments and organisms. Vol. 1. Academic Press, New York.

Cram, S.P., and F.J. Yang. 1980. High resolution gas chromatography: an overview. Pages 105-122 in L. Petrakis and F.T. Weiss, eds. Petroleum in the marine environment. Advances in Chemistry Series No. 185. American Chemical Society, Washington, D.C.

Cretney, W.J., C.S. Wong, D.R. Green, and C.A. Bawden. 1978. Long-term fate of heavy fuel oil in a spill - contaminated British Columbia coast bay. Jour. Fish. Res. Bd. Canada 35:521-527.

Dastillung, M., and P. Albrecht. 1976. Molecular test for oil pollution in surface sediments. Mar. Poll. Bull. 7: 13-15.

Ensminger, A., A. Van Dorsselaer, C. Spychkerelle, P. Albrecht, and G. Ourisson. 1974. Pentacyclic triterpanes of the hopane type as ubiquitous geochemical markers: origin and significance. Pages 245-260 in B. Tissot and F. Bienner, eds. Advances in organic geochemistry M73. Paris, Technip.

Farrington, J.W. 1980. An overview of the biogeochemistry of fossil fuel hydrocarbons in the marine environment. Pages 1-23 in L. Petrakis and F.T. Weiss, eds. Petroleum in the marine environment. Advances in Chemistry Series No. 185. American Chemical Society, Washington, D.C.

Farrington, J.W., J.M. Teal, and P.L. Parker. 1976. Petroleum hydrocarbons. Pages 3-34 in E.D. Goldberg, ed. Strategies for marine pollution monitoring. Wiley Interscience, New York.

Fiest, D.L., and P.D. Boehm, 1981. Subsurface distributions of petroleum from an offshore well blowout - the Ixtoc I blowout, Bay of Campeche. Environ. Sci. Technol. (in press).

Gordon, D.C., P.D. Keizer, W.R. Hardstaff, and D.G. Aldous. 1976. Fate of crude oil spilled in seawater contained in outdoor tanks. Env. Sci. Technol. 10:580-585.

Hites, R.A., R.E. Laflamme, and J.G. Windsor, Jr. 1980. Polycyclic aromatic hydrocarbons in marine/aquatic sediment. Pages 289-313 in L. Petrakis and F.T. Weiss, eds. Petroleum in the marine environment. Advances in Chemistry Series No. 185. American Chemical Society, Washington, D.C.

Jewell, D.M. 1980. The role of nonhydrocarbons in the analysis of virgin and biodegraded petroleum. Pages 219-235 in L. Petrakis and F.T. Weiss, eds. Petroleum in the marine environment. Advances in Chemistry Series No. 185. American Chemical Society, Washington, D.C.

Johansen, P., V.B. Jensen, and A. Buchert. 1977. Hydrocarbons in marine organisms and sediments off West Greenland. International Council for the Exploration of the Sea, unpublished manuscript.

John, P., and I. Souter. 1976. Identification of crude oils by synchronous excitation spectrofluorometry. Anal. Chem. 48:520-524.

Keizer, P.D., T.P. Ahern, J. Dale, and J.H. Vandermeulen. 1978. Residues of Bunker C oil in Chedabucto Bay, Nova Scotia, 6 years after the Arrow spill. J. Fish. Res. Bd. Can. 35: 528-535.

Laflamme, R.E., and R.A. Hites. 1978. The global distribution of polyclic aromatic hydrocarbons in recent sediments. Geochim. Cosmochim. Acta 42:289-304.

Lee, M.L., G.P. Prado, J.B. Howard, and R.A. Hites. 1977. Source identification of urban airborne polycyclic aromatic hydrocarbons by gas chromatographic mass spectrometry and high resolution mass spectrometry. Biomed. Mass. Spec. 4:182-186.

Leone, G.M., and T.M. Church. 1976. Trace metals in petroleum: a tool for monitoring estuarine oil spills. NSF-RANN Program Report CMS-RANN-6-76. College of Marine Studies, University of Delaware, Newark, Del.

Lloyd, J.B.F. 1971. The nature and evidential value of the luminescence of automobile engine oils and related materials. J. Forensic Sci. Soc. 11:83-94, 153-10, 235-253.

Lunde, G., and A. Bjorseth. 1977. Polycyclic aromatic hydrocarbons in long-range transported aerosols. Nature 268:518-519.

National Academy of Sciences. 1975. Petroleum in the marine environment. NAS, Washington, D.C. 107 pp.

Overton, E.G., L.W. McCarthy, S.W. Moscarella, M.A. Maberry, S.R. Antoine, J.S. Farrington, and J.L. Laseter. 1981. Detailed chemical analysis of Ixtoc I crude oil and selected environmental samples from the Researcher and Pierce cruises. In Proceedings of the Conference on the Preliminary Scientific Results from the Researcher Cruise to the Ixtoc I Blowout. NOAA Office of Marine Pollution Assessment, Rockville, Md.

Pym, J.G., J.E. Ray, G.W. Smith, and E.V. Whitehead. 1975. Petroleum triterpane fingerprinting of crude oils. Anal. Chem. 47:1617-1622.

Shaw, D.G., D.J. McIntosh, and E.R. Smith. 1979. Arene and alkane hydrocarbons in nearshore Beaufort Sea sediments. Estuar. Coast. Mar. Sci. 9:435-449.

Shaw, D.G., and B.A. Baker. 1978. Hydrocarbons in the marine environment of Port Valdez. Environ. Sci. Technol. 12: 1200-1205.

Simoneit, B.R.T. 1977a. Deterpenoid compounds and other lipids in deep sea sediments and their geochemical significance. Geochim. Cosmochim. Acta 41:463-476.

Simoneit, B.R.T. 1977b. The Black Sea: a sink for terrigenous lipids. Deep-Sea Res. 24:813-830.

Teal, J.M., Burns, K., and J. Farrington. 1978. Analyses of aromatic hydrocarbons in intertidal sediments resulting from two spills of No. 2 fuel oil in Buzzards Bay, Massachusetts. J. Fish. Res. Bd. Can. 35:510-520.

Veith, G.D., and L.M. Kiwus. 1977. An exhaustive steam distillation and solvent extraction unit for pesticides and industrial chemicals. Bull. Environ. Cont. Toxicol. 17:631-636.

Vo-Dinh, T. 1978. Multicomponent analysis by synchronous luminescence spectrometry. Anal. Chem. 50:396-401.

Wakeham, S.G. 1977. Synchronous fluorescence spectroscopy and its application to indigenous and petroleum-derived hydrocarbons in lacustrine sediments. Environ. Sci. Technol. 11:272-276.

Wakeham, S.G., C. Schaffner, and W. Giger. 1980. Polycyclic aromatic hydrocarbons in recent lake sediments II - compounds derived from biogenic precursors during early diagenesis. Geochim. Cosmochim. Acta 44:415-429.

Warner, J.S. 1976. Determination of aliphatic and aromatic hydrocarbons in marine organisms. Anal. Chem. 48:578-583.

Warner, J.S., R.M. Riggin, and T.M. Engel. 1980. Recent advances in the determination of aromatic hydrocarbons in zooplankton and macrofauna. Pages 87-104 in L. Petrakis and F.T. Weiss, eds. Petroleum in the marine environment. Advances in Chemistry Series No. 185. American Chemical Society, Washington, D.C.

Wong, C.S., W.J. Cretney, P. Christensen, and R.W. Macdonald. 1976. Hydrocarbon levels in the marine environment of the Southern Beaufort Sea. Beaufort Sea Tech. Rept. 38. Unpublished manuscript. Environment Canada B.C. 113 pp.

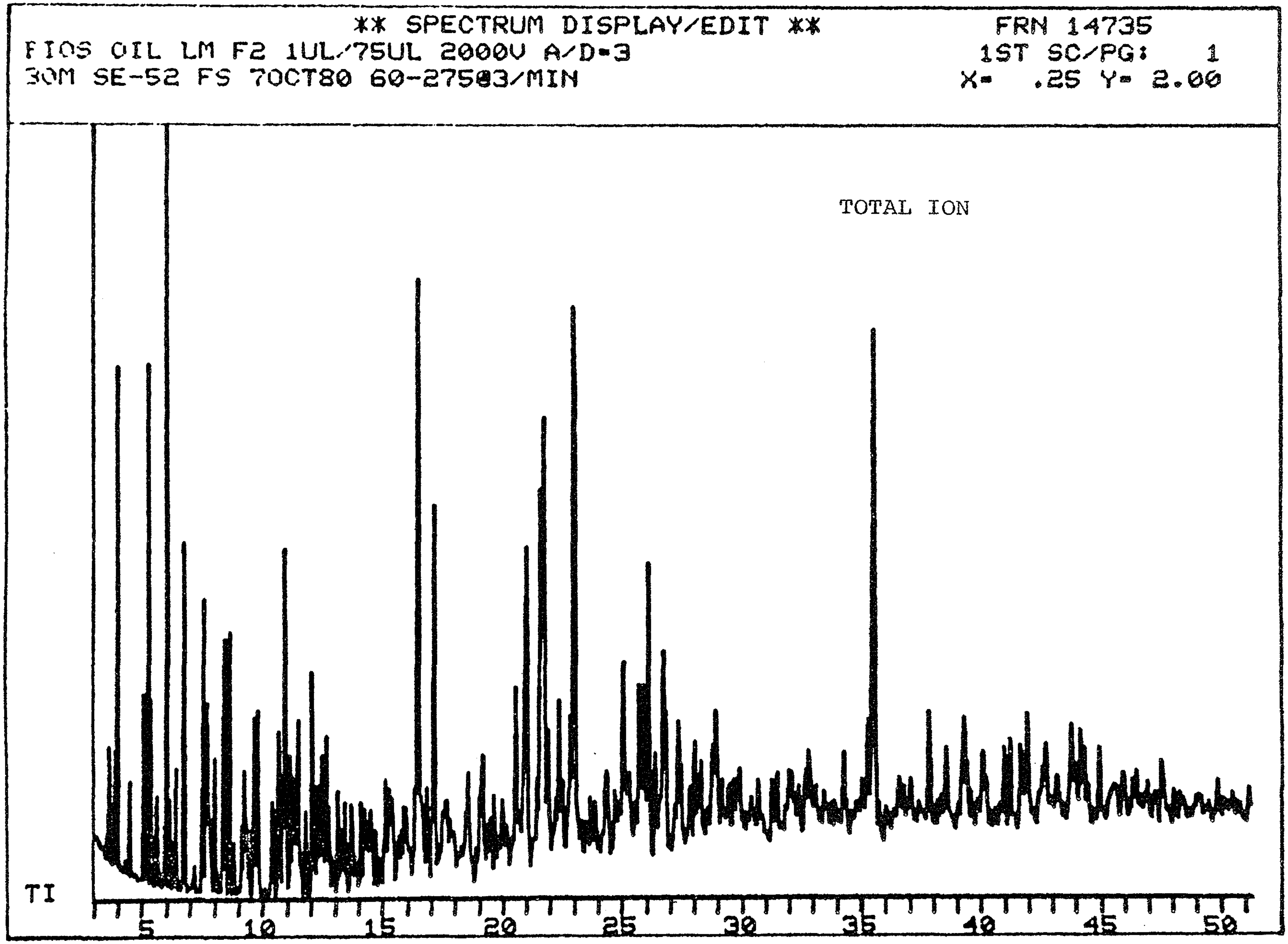
APPENDIX A

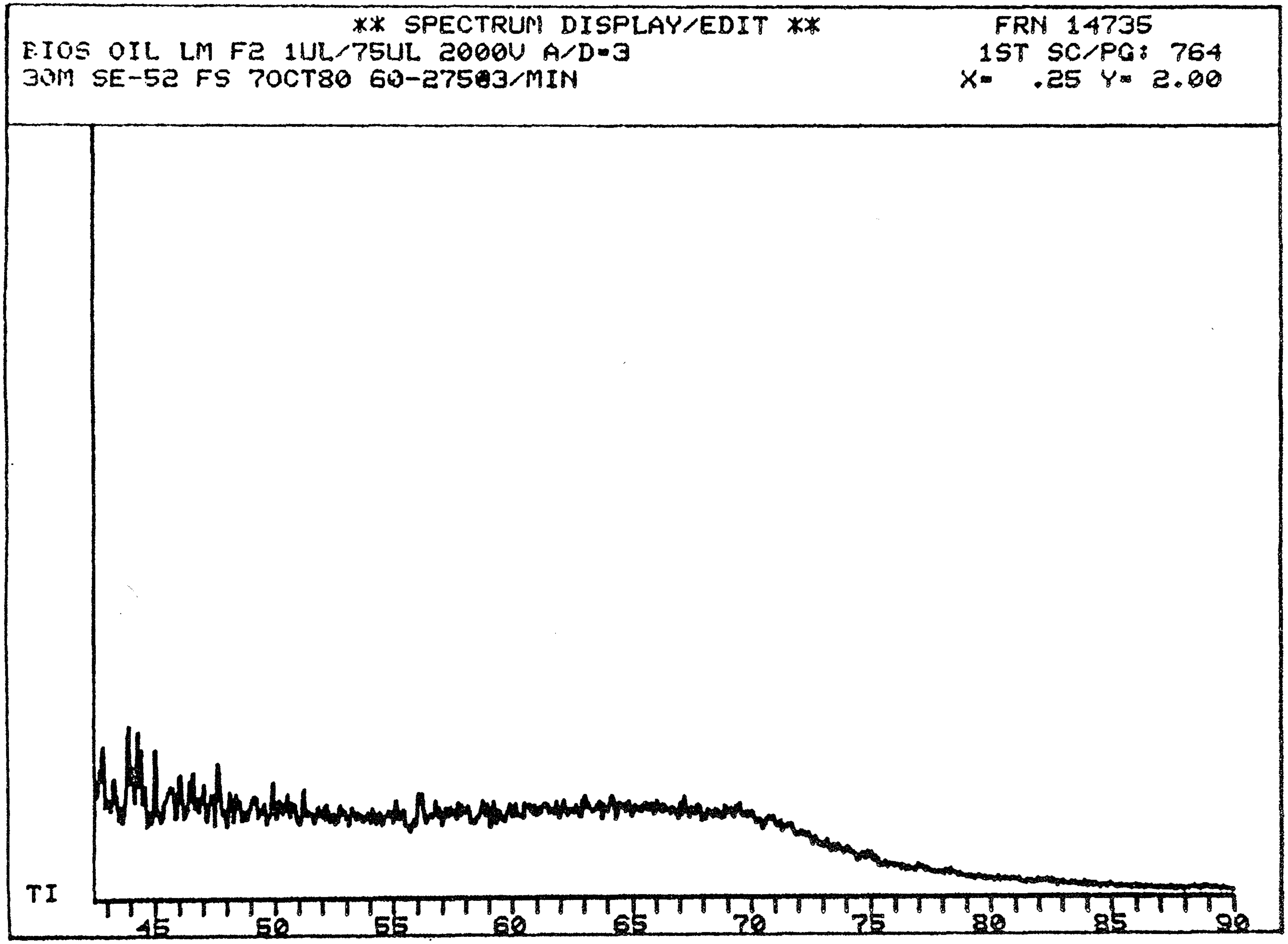
GC^2/MS ANALYSIS OF AROMATIC FRACTION OF LAGOMEDIO CRUDE OIL

Key to mass spectral searches:

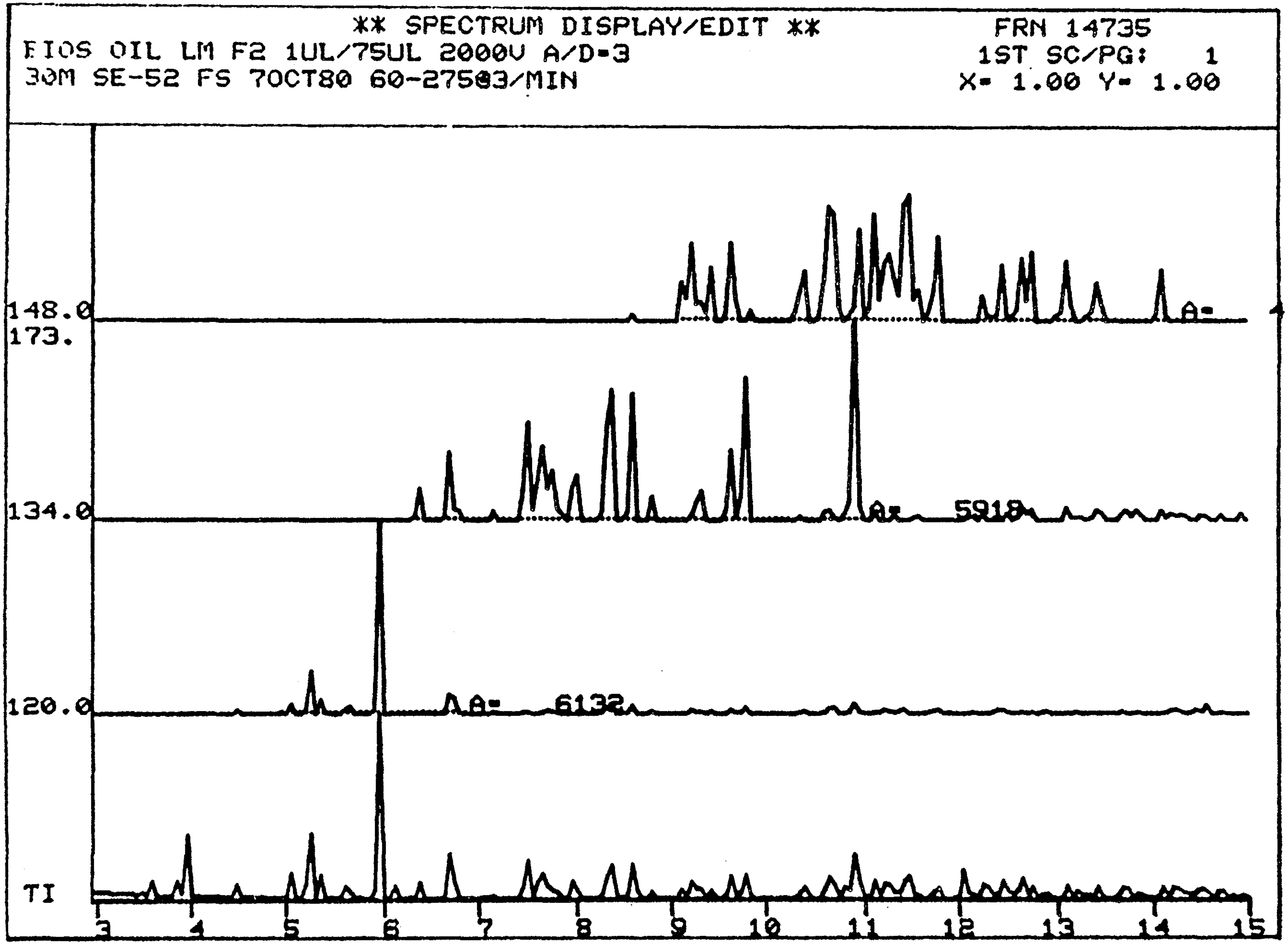
m/e	Compound
120	C_3 alkyl benzenes
134	C_4 alkyl benzenes
148	C_5 alkyl benzenes
128	Naphthalene (N)
142	C_1 N
156	C_2 N
170	C_3 N
184	C_4 N
188	Deuterated anthracene (internal standard)
184	Dibenzothiophene (DBT)
198	C_1 DBT
212	C_2 DBT
226	C_3 DBT
154	Biphenyl
166	Fluorene (F)
180	C_1 F
194	C_2 F
208	C_3 F
202	Fluoranthene/pyrene
178	Phenanthrene (P)
192	C_1 P
206	C_2 P
220	C_3 P
234	C_4 P
228	Benzanthracene/chrysene
252	Benzopyrenes

APPENDIX A: GC/MS OF LAGOMEDIO CRUDE AROMATICS

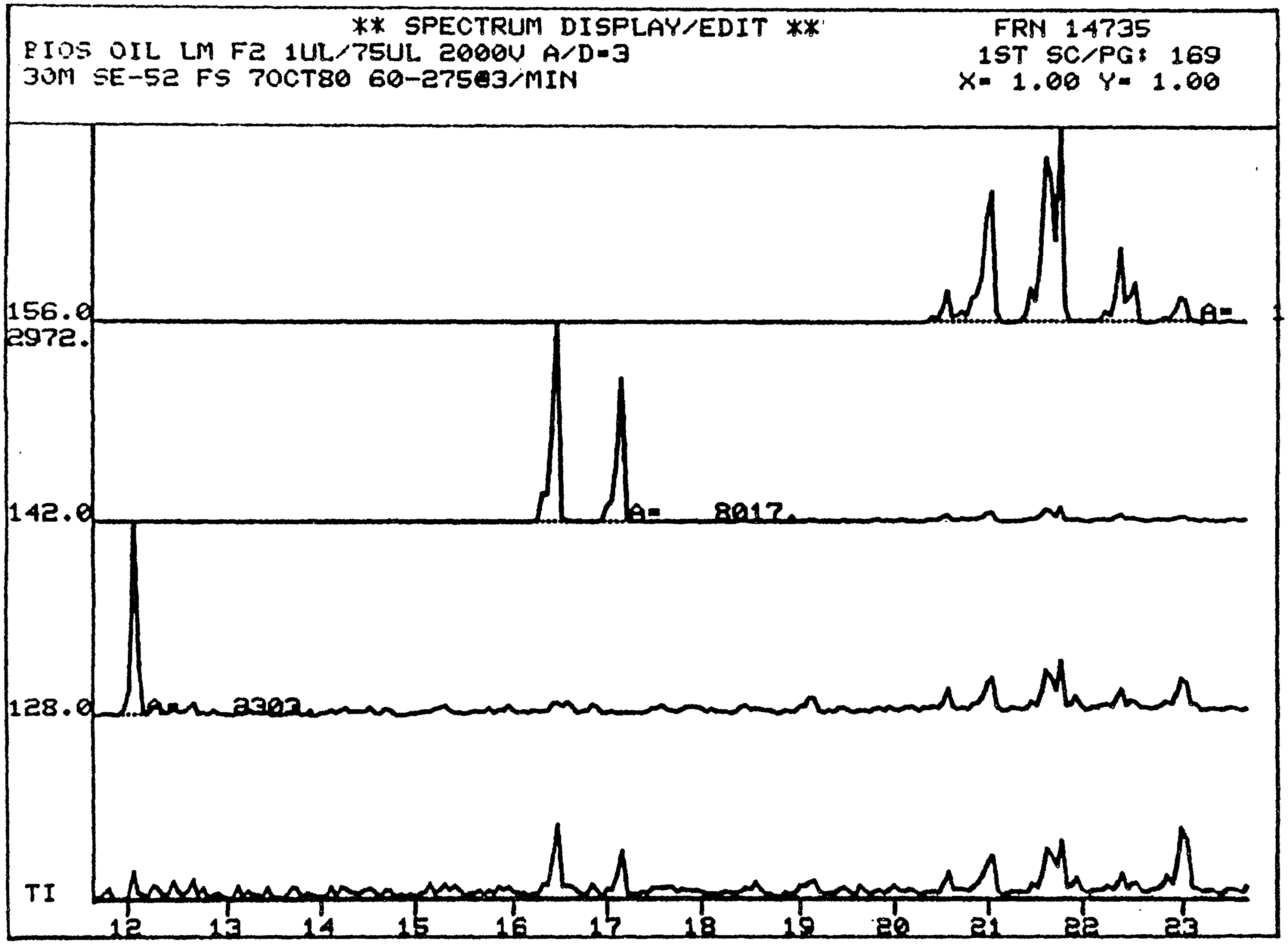




```
               ** SPECTRUM DISPLAY/EDIT **            FRN 14735
BIOS OIL LM F2 1UL/75UL 2000V A/D=3                  1ST SC/PG: 764
30M SE-52 FS 7OCT80 60-275@3/MIN                   X=   .25 Y= 2.00
```

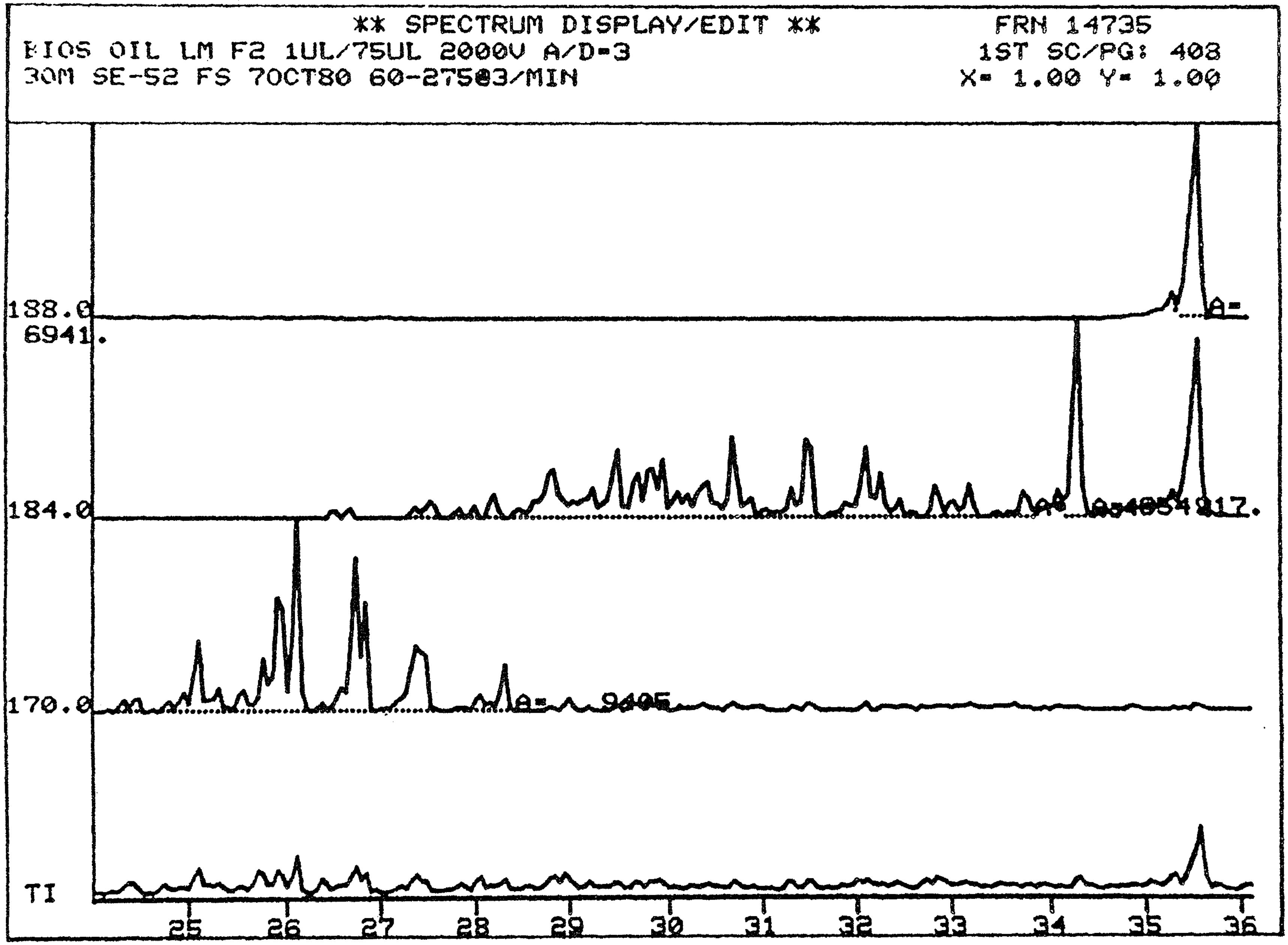


```
                 ** SPECTRUM DISPLAY/EDIT **             FRN 14735
EIOS OIL LM F2 1UL/75UL 2000V A/D=3                     1ST SC/PG:    1
30M SE-52 FS 7OCT80 60-275@3/MIN                       X= 1.00 Y= 1.00
```



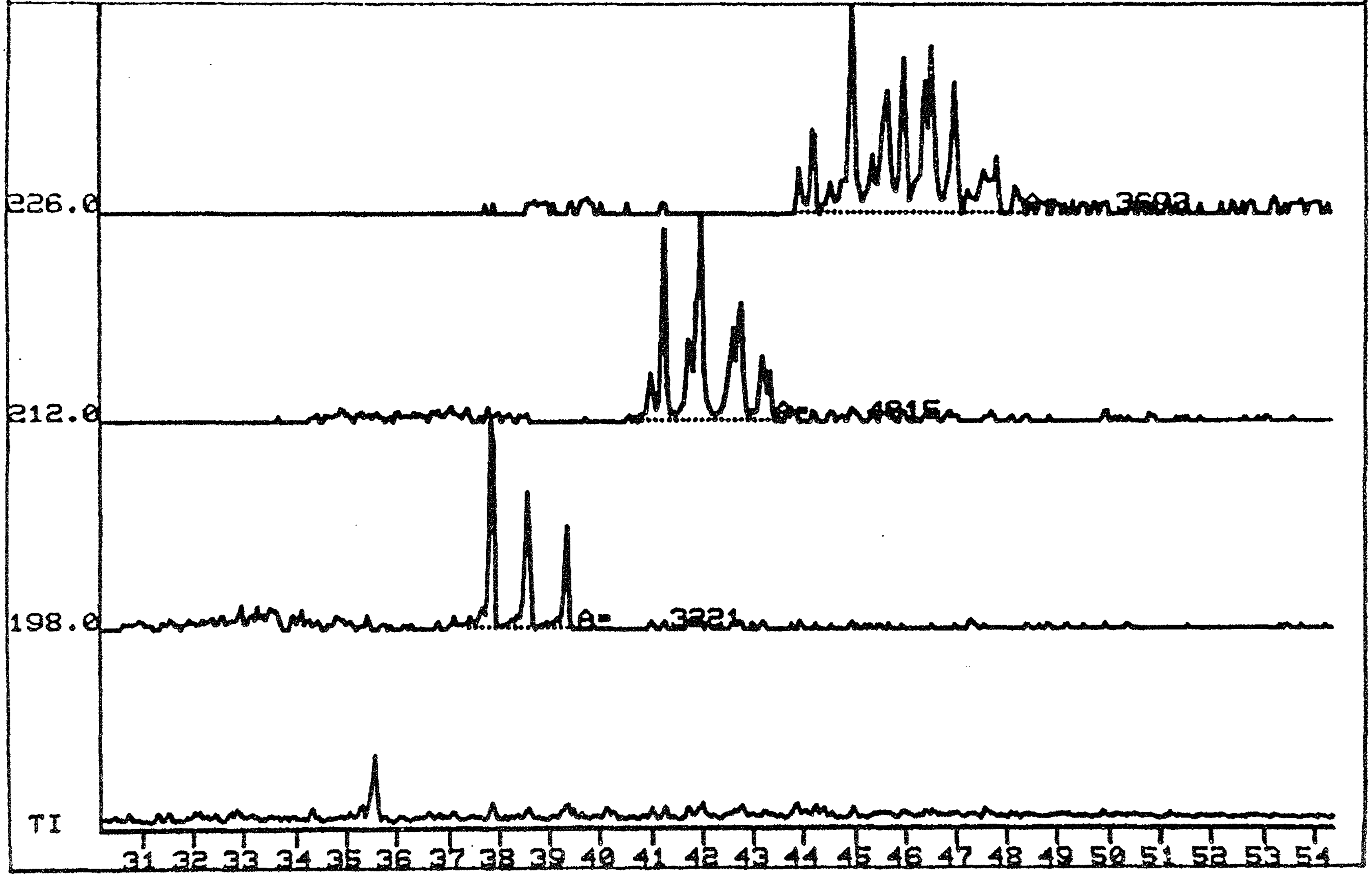
** SPECTRUM DISPLAY/EDIT **
BIOS OIL LM F2 1UL/75UL 2000V A/D=3
30M SE-52 FS 7OCT80 60-275@3/MIN

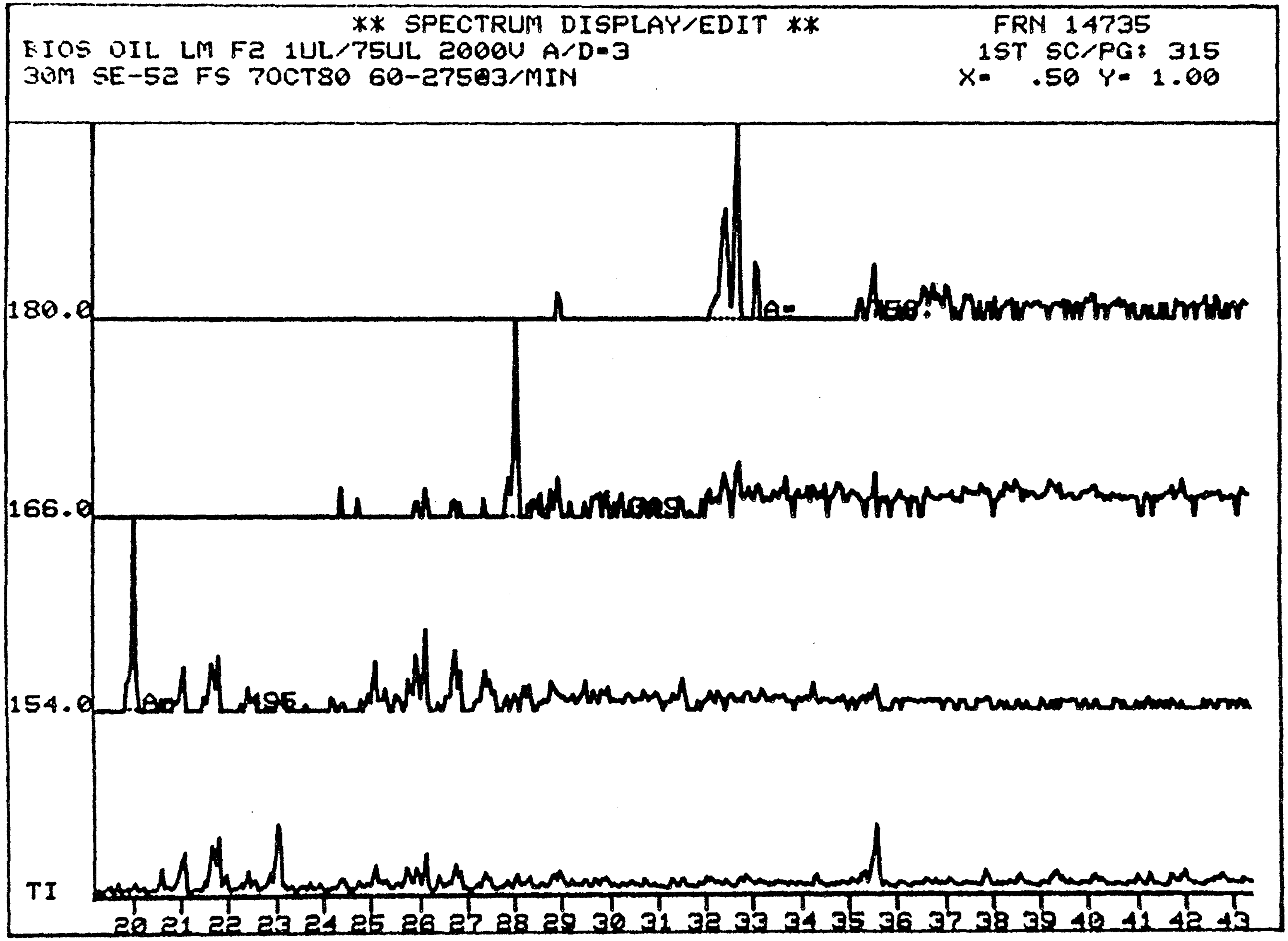
FRN 14735
1ST SC/PG: 169
X= 1.00 Y= 1.00



```
                    ** SPECTRUM DISPLAY/EDIT **              FRN 14735
BIOS OIL LM F2 1UL/75UL 2000V A/D=3                        1ST SC/PG: 408
30M SE-52 FS 7OCT80 60-275@3/MIN                           X= 1.00 Y= 1.00
```

** SPECTRUM DISPLAY/EDIT **
FRN 14735
BIOS OIL LM F2 1UL/75UL 2000V A/D=3
1ST SC/PG: 527
30M SE-52 FS 7OCT80 60-275@3/MIN
X= .50 Y= 1.00

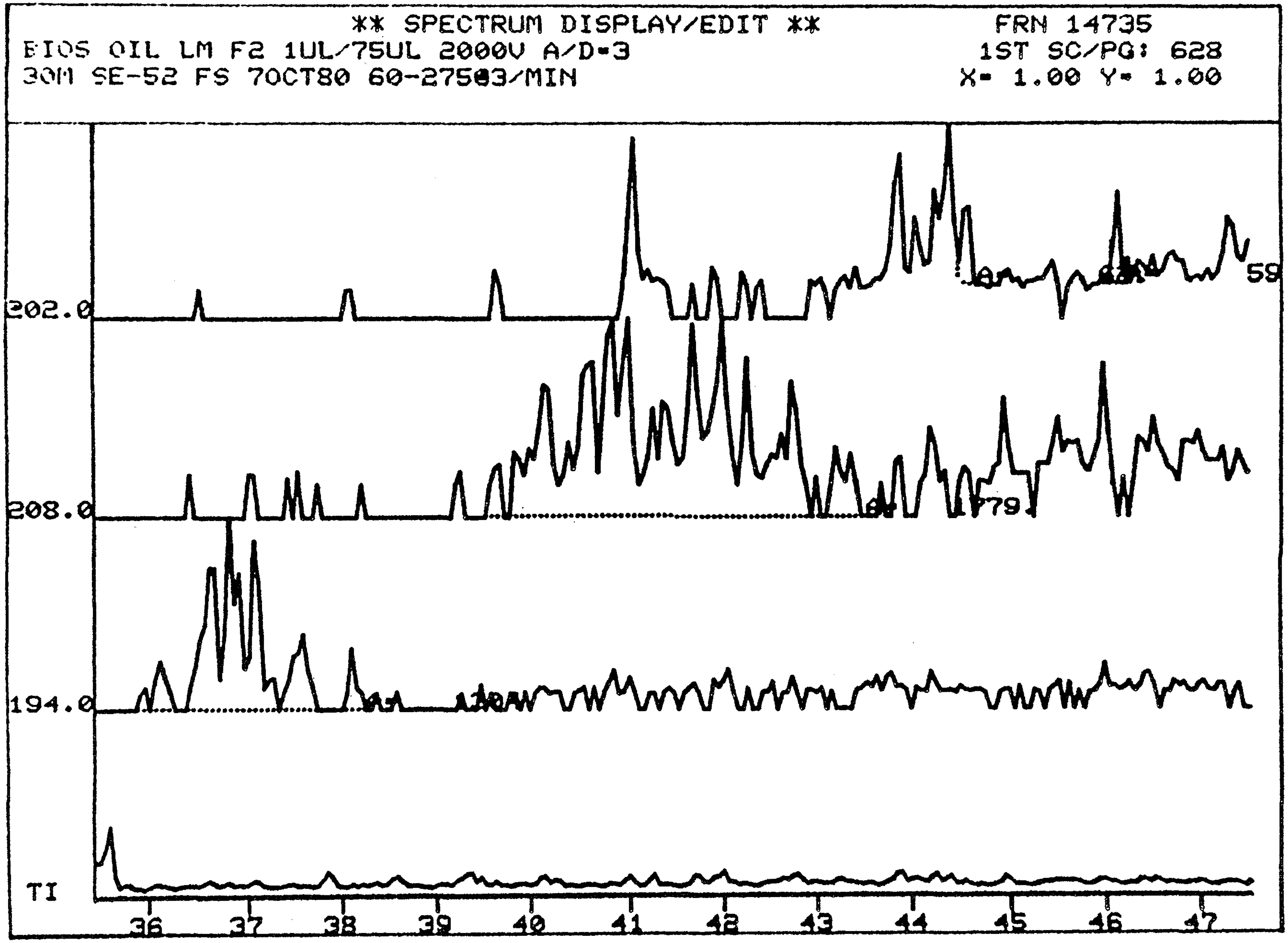




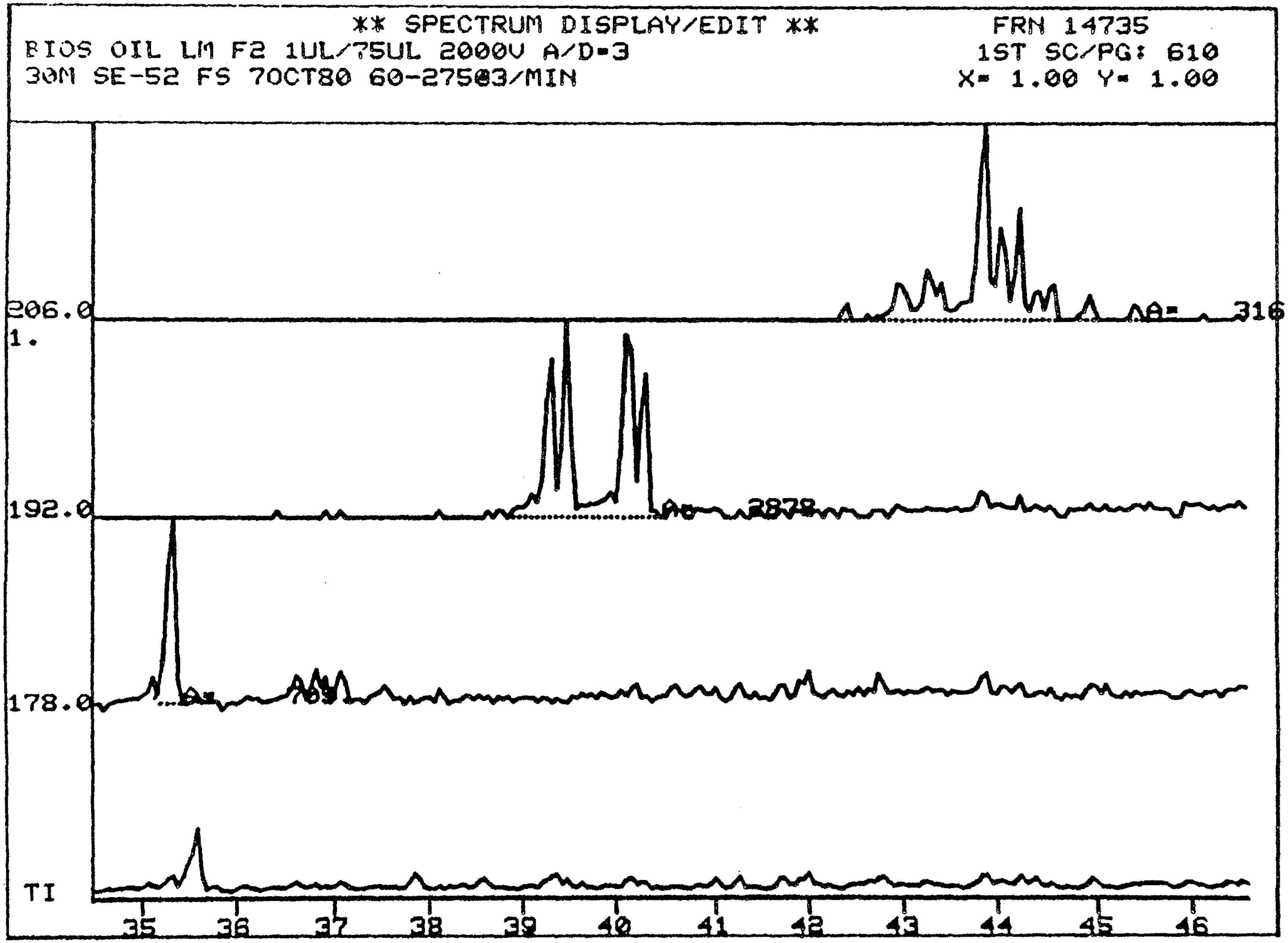
** SPECTRUM DISPLAY/EDIT **　　FRN 14735

BIOS OIL LM F2 1UL/75UL 2000V A/D=3　　1ST SC/PG: 315

30M SE-52 FS 7OCT80 60-275@3/MIN　　X= .50 Y= 1.00

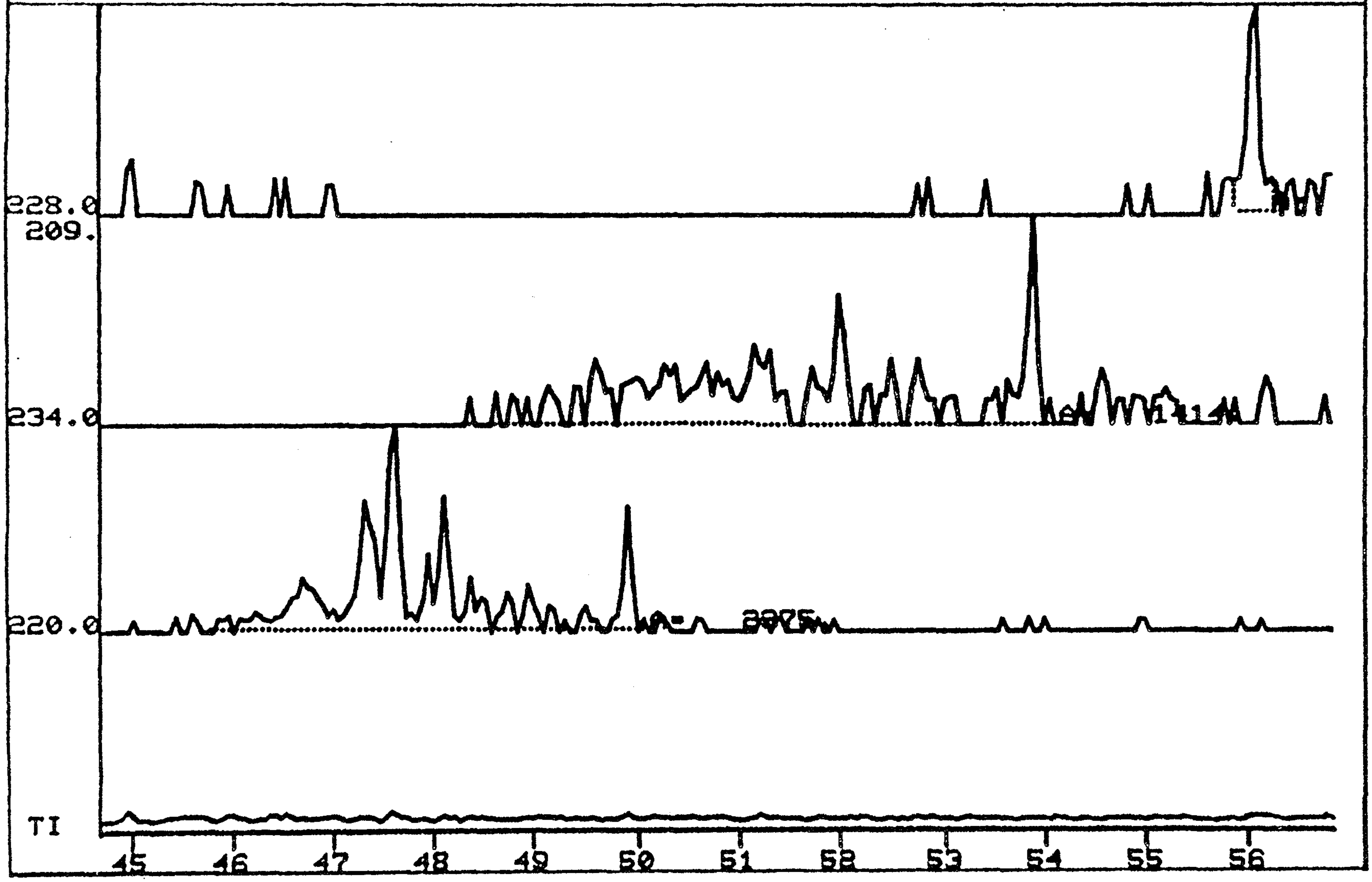


```
               ** SPECTRUM DISPLAY/EDIT **            FRN 14735
BIOS OIL LM F2 1UL/75UL 2000V A/D=3                 1ST SC/PG: 628
30M SE-52 FS 7OCT80 60-275@3/MIN                   X= 1.00 Y= 1.00
```



```
                ** SPECTRUM DISPLAY/EDIT **            FRN 14735
BIOS OIL LM F2 1UL/75UL 2000V A/D=3                   1ST SC/PG: 610
30M SE-52 FS 7OCT80 60-275@3/MIN                     X= 1.00 Y= 1.00
```

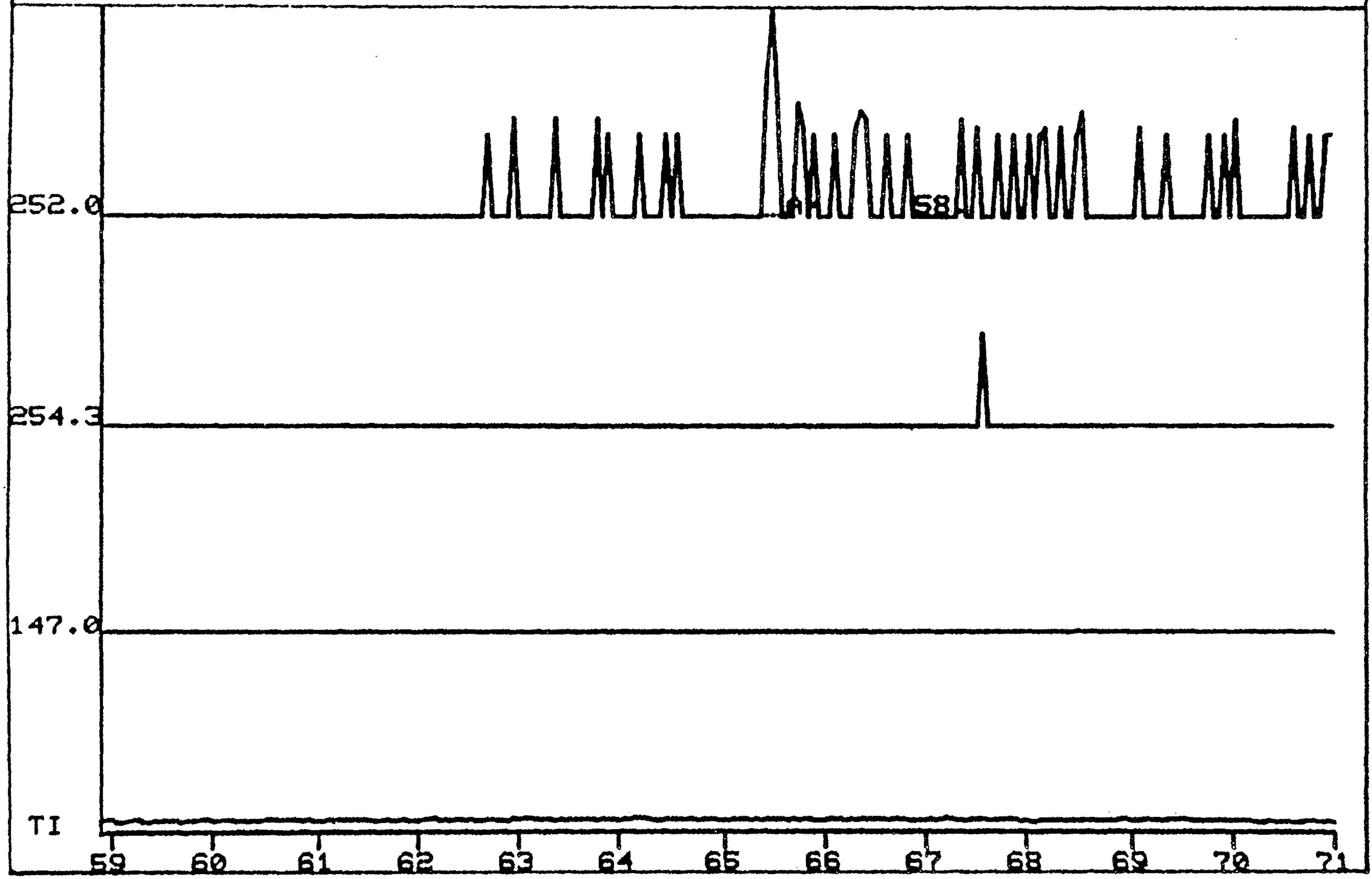
** SPECTRUM DISPLAY/EDIT ** FRN 14735
EIOS OIL LM F2 1UL/75UL 2000V A/D=3 1ST SC/PG: 807
30M SE-52 FS 7OCT80 60-27503/MIN X= 1.00 Y= 1.00



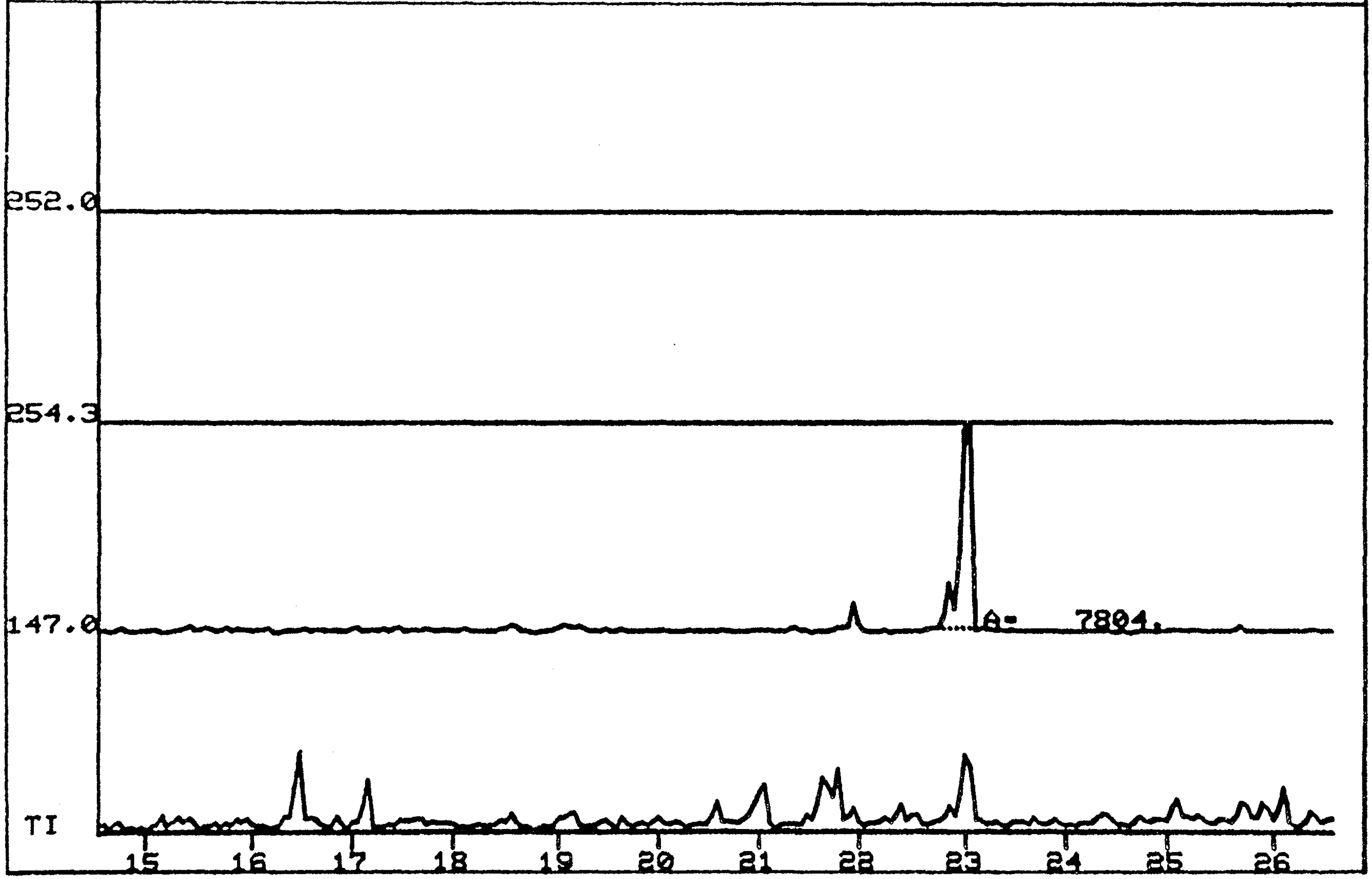
** SPECTRUM DISPLAY/EDIT ** FRN 14735

BIOS OIL LM F2 1UL/75UL 2000V A/D=3 1ST SC/PG:1080

30M SE-52 FS 7OCT80 60-275@3/MIN X= 1.00 Y= 1.00



```
                 ** SPECTRUM DISPLAY/EDIT **          FRN 14735
FIOS OIL LM F2 1UL/75UL 2000V A/D=3                  1ST SC/PG: 225
30M SE-52 FS 7OCT80 60-275@3/MIN                   X= 1.00 Y= 1.00
```



```
FILE NUMBER 14735

ENTRY  TIME    MASS     AREA     %

   1   35.6   188.0     7078.  100.00
   2   30.7   184.0     4780.   67.54
   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   16.5   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   35.3   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   252.0       34.      .48
   3   65.5   252.0       58.      .82
   4   23.1   147.0     7985.   112.82
   5   47.6   220.0     2375.    33.56
   6   53.9   234.0     1414.    19.97
   7   56.1   228.0      209.     2.95
   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    35.6    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?
```

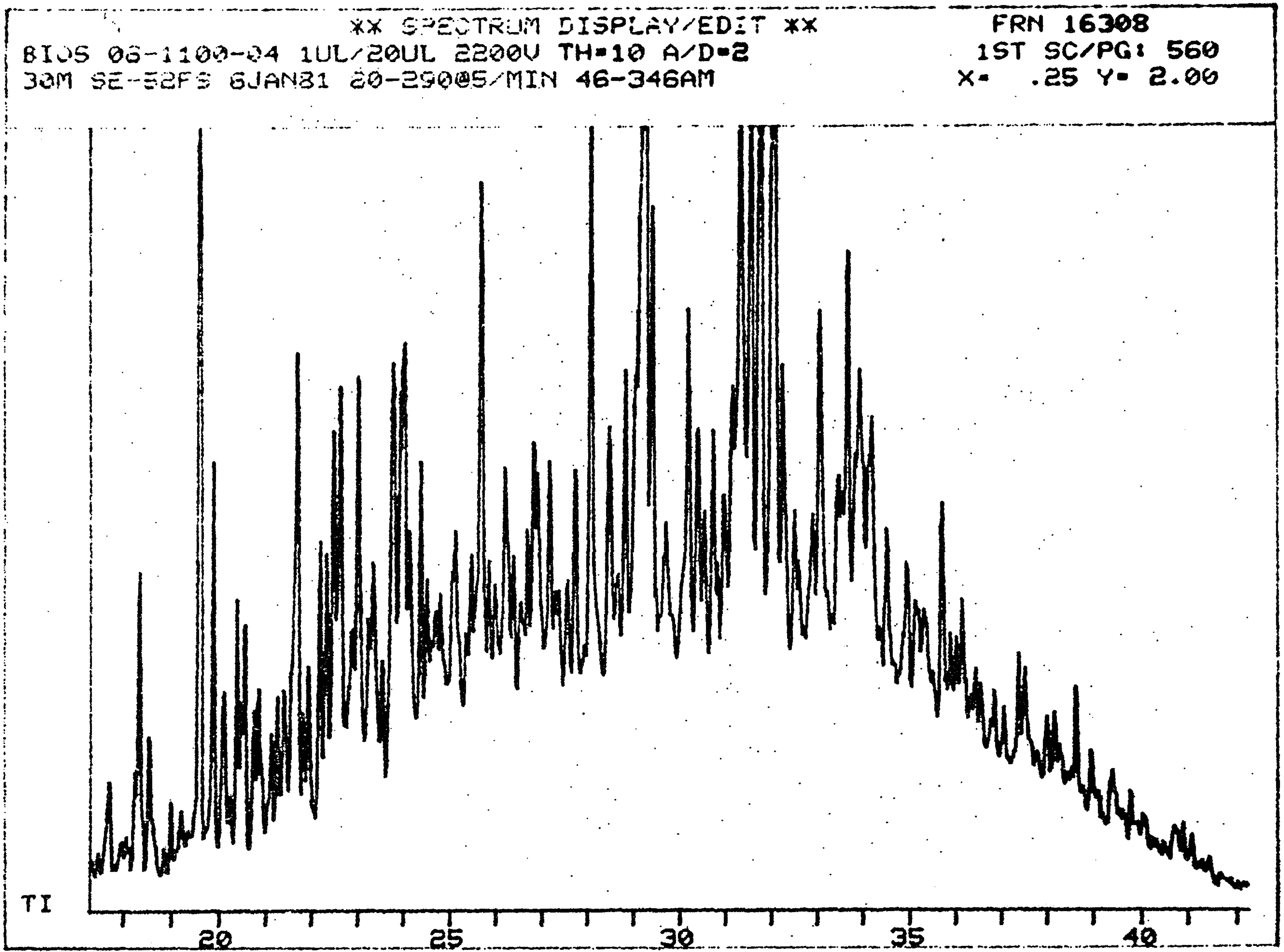
```
FILE NUMBER 14735

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
    5  47.6   220.0      2375.     29.75
    6  53.9   234.0      1414.     17.70
    7  56.1   228.0       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.     88.64

CAL % ON ENTRY?
```

APPENDIX B

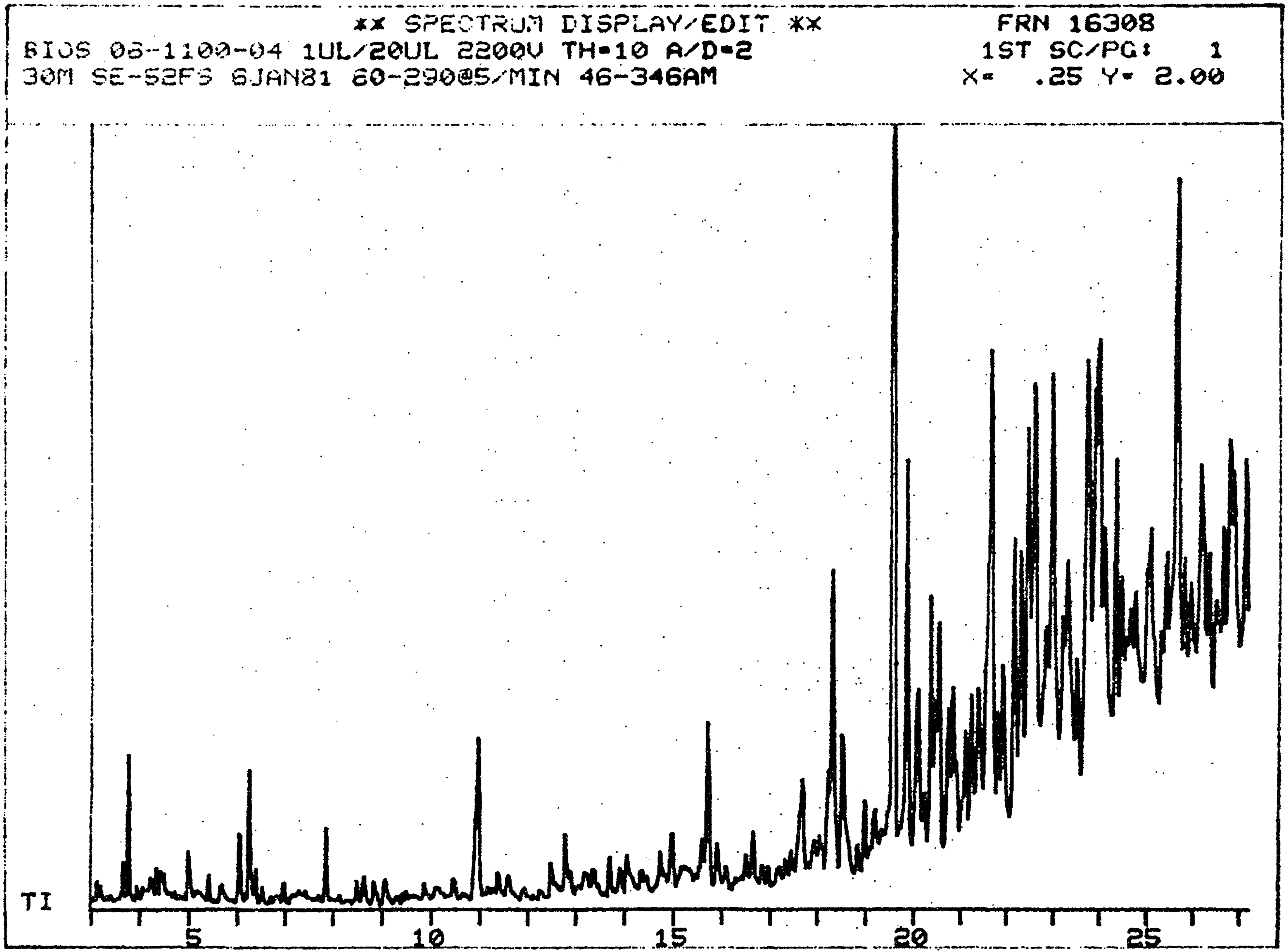
GC^2/MS ANALYSIS OF AZAARENE FRACTION OF LAGOMEDIO CRUDE OIL

Key to mass spectral searches:

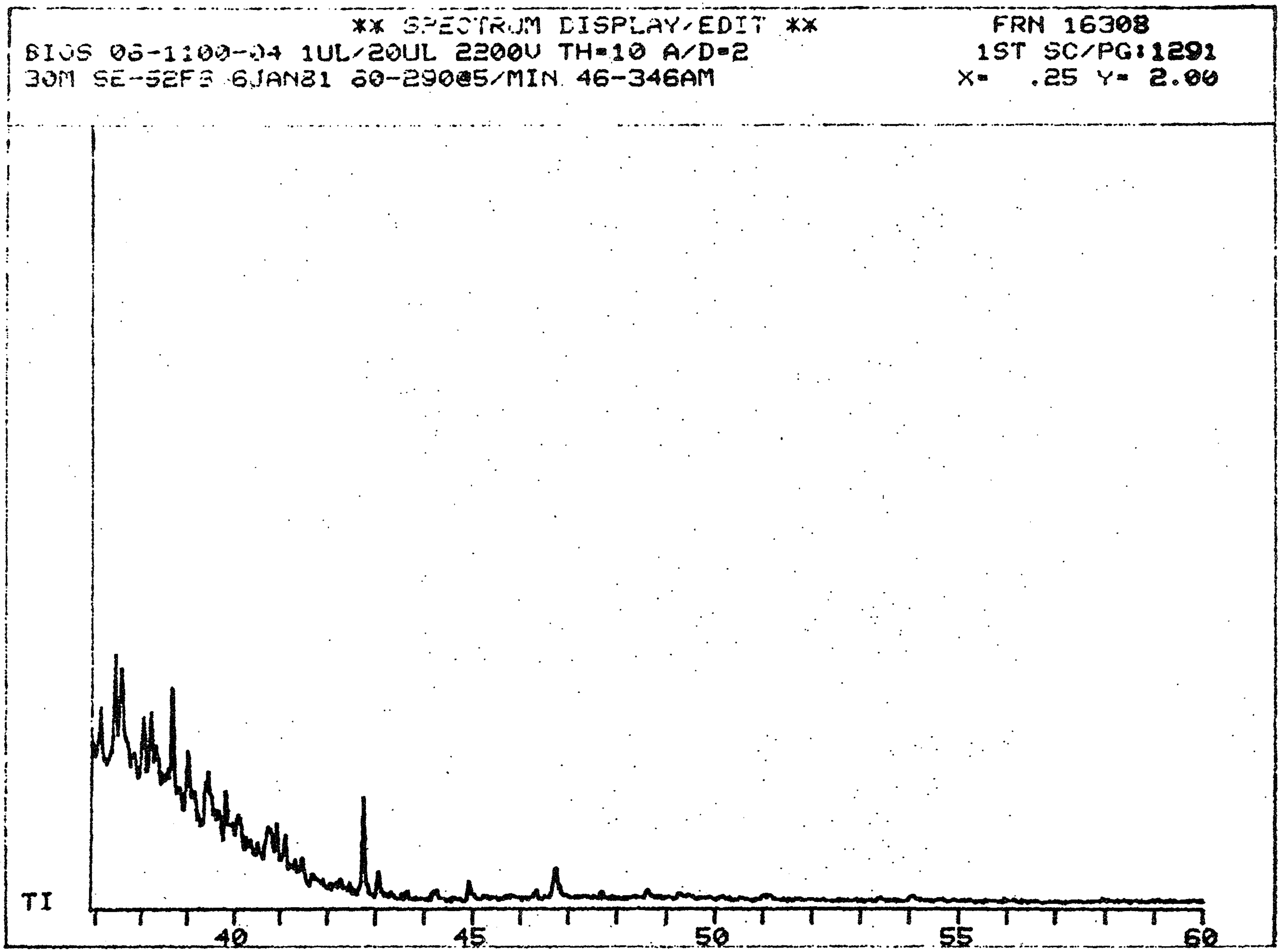
m/e	Compound
129	Quinoline, isoquinoline (Q)
143	C_1 Q
157	C_2 Q
171	C_3 Q
185	C_4 Q
199	C_5 Q
213	C_6 Q
179	Acridine/phenanthridine (AP)
193	C_1 AP
207	C_2 AP
221	C_3 AP
235	C_4 AP
249	C_5 AP
167	Carbazole (C)
181	C_1 C
195	C_2 C
209	C_3 C
223	C_4 C
229	Benzacridine (BA)
243	C_1 BA
257	C_2 BA



```
                 ** SPECTRUM DISPLAY/EDIT **               FRN 16308
BIOS 06-1100-04 1UL/20UL 2200V TH=10 A/D=2                1ST SC/PG: 560
30M SE-52FS 6JAN81 20-290@5/MIN 46-346AM                  X=   .25 Y= 2.00
```



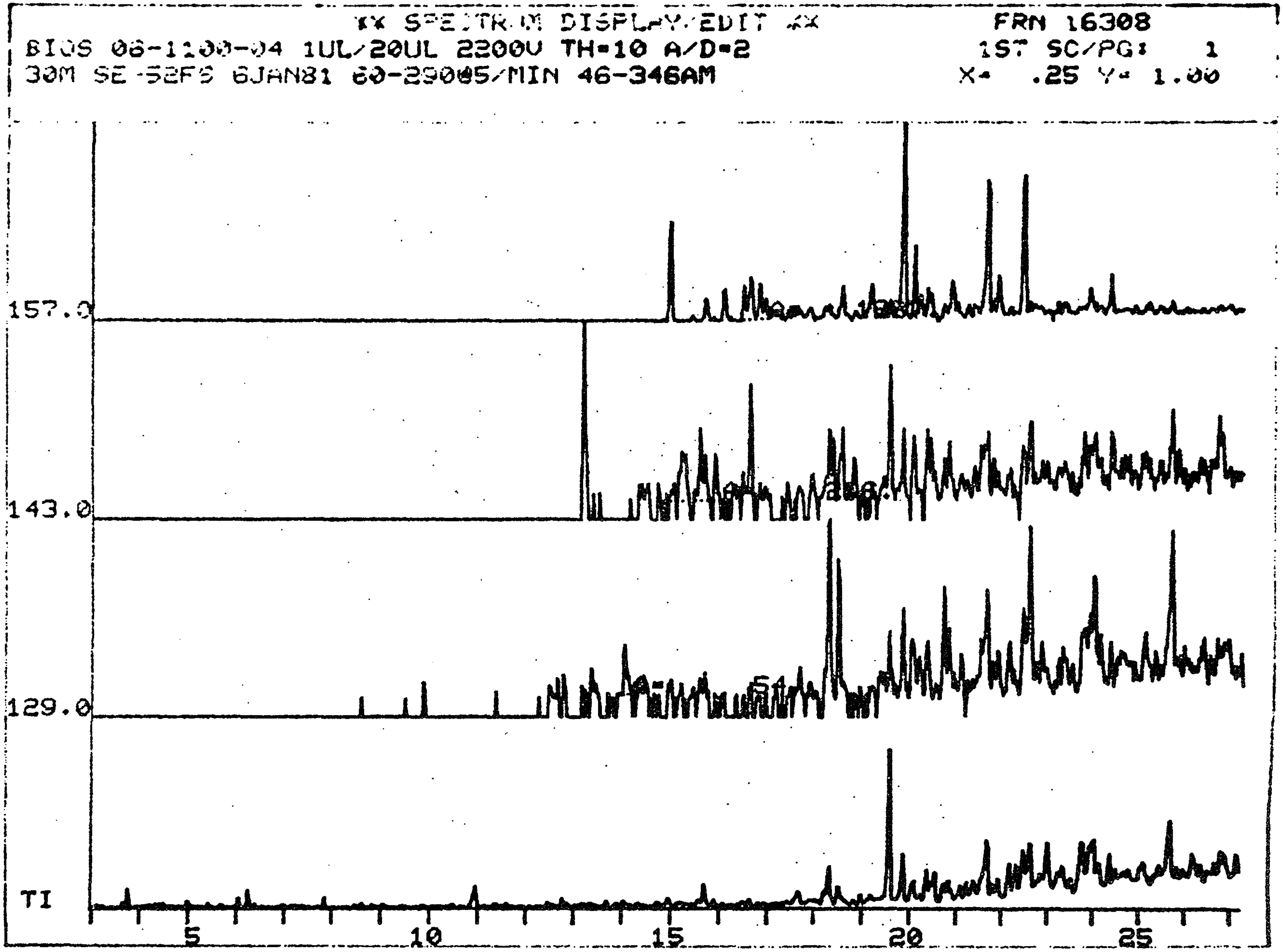
```
                   ** SPECTRUM DISPLAY/EDIT **                FRN 16308
BIOS 06-1100-04 1UL/20UL 2200V TH=10 A/D=2                   1ST SC/PG:   1
30M SE-52FS 6JAN81 60-290@5/MIN 46-346AM                    X=  .25 Y= 2.00
```



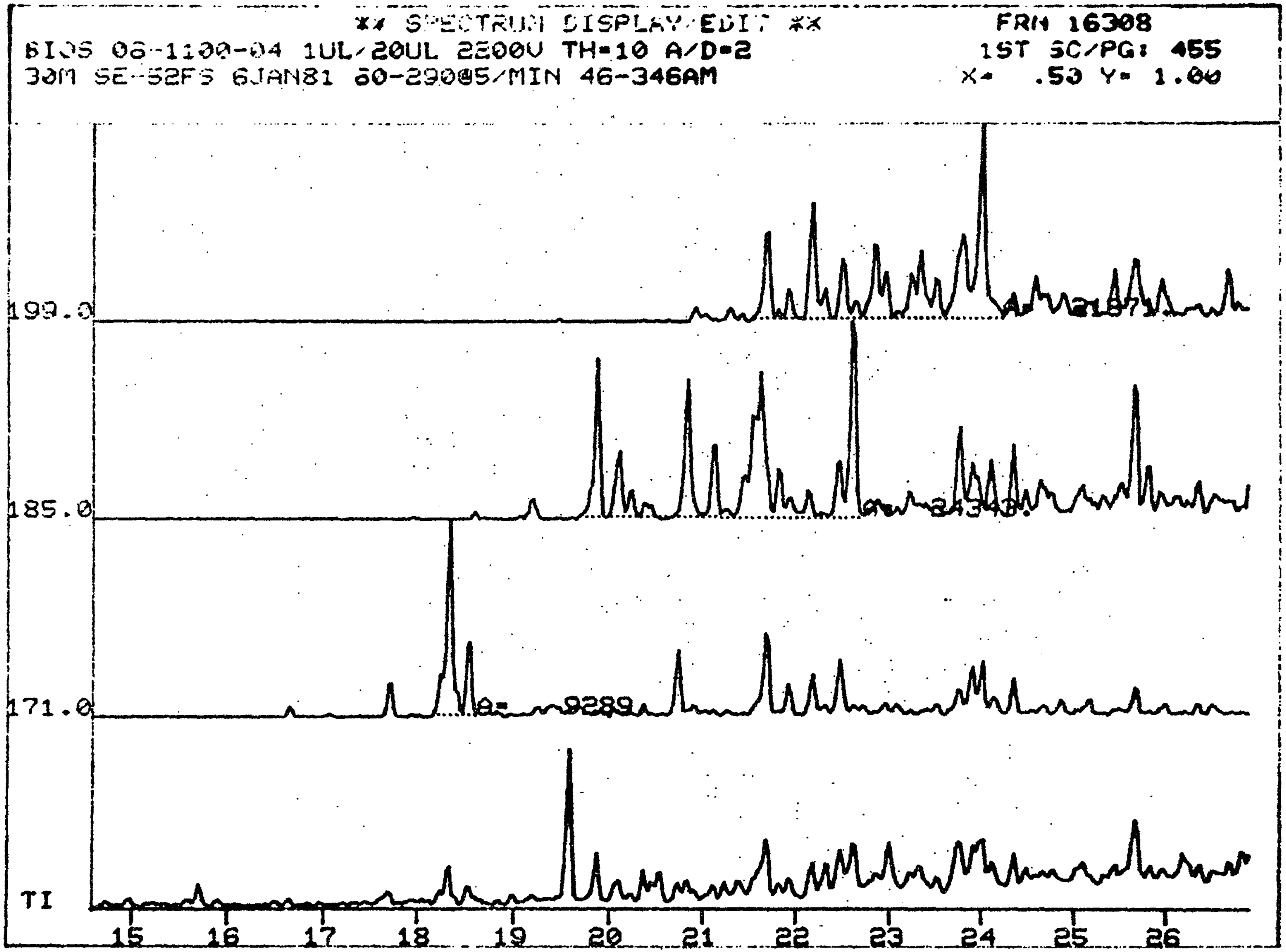
** SPECTRUM DISPLAY/EDIT ** FRN 16308

BIOS 06-1100-04 1UL/20UL 2200V TH=10 A/D=2 1ST SC/PG:1291

30M SE-52FS 6JAN81 60-290@5/MIN 46-346AM X= .25 Y= 2.00



```
                    ** SPECTRUM DISPLAY/EDIT **                FRN 16308
BIOS 06-1100-04 1UL/20UL 2200V TH=10 A/D=2                    1ST SC/PG:   1
30M SE-52FS 6JAN81 60-29005/MIN 46-346AM                     X=  .25 Y= 1.00
```

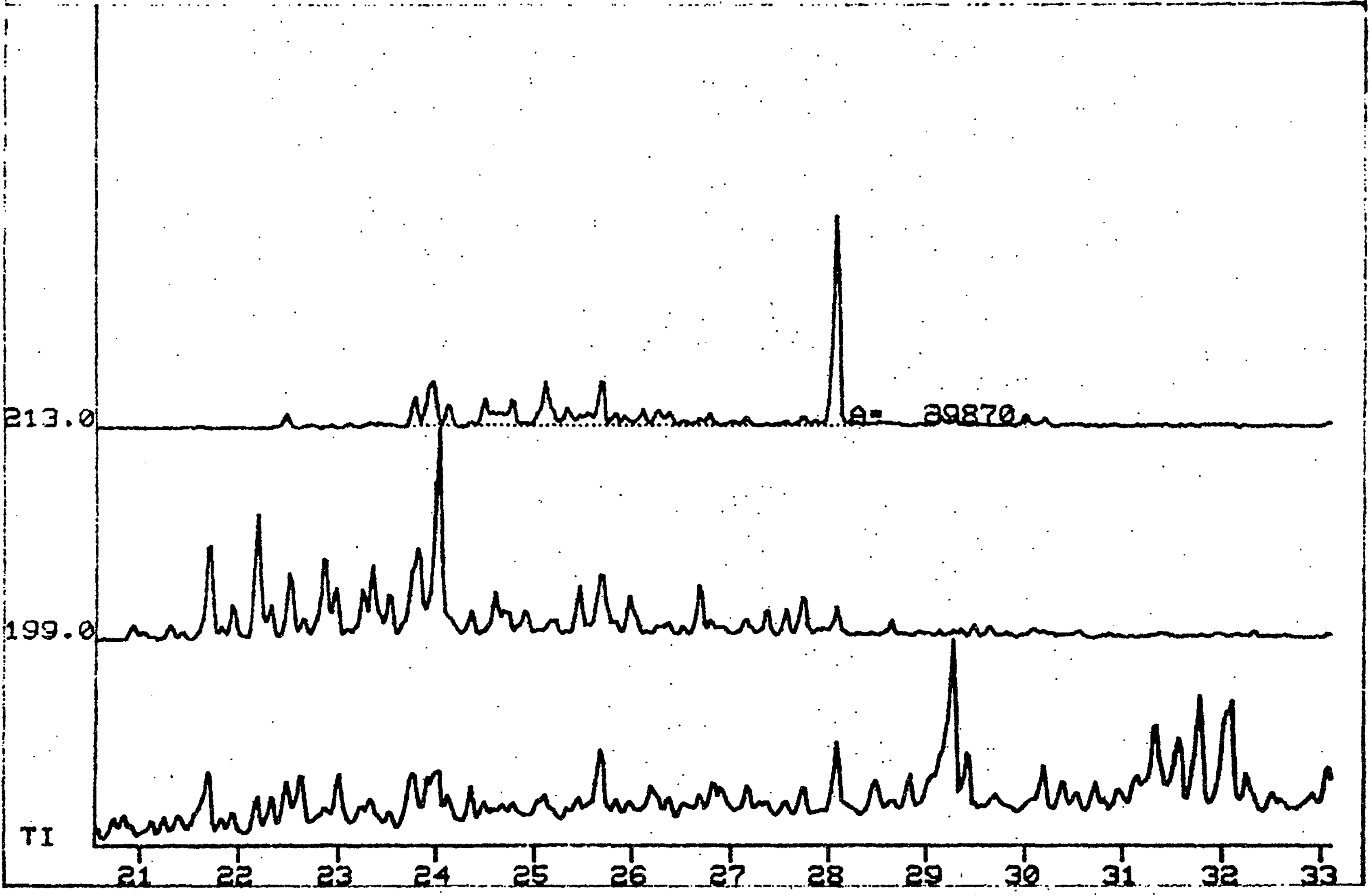


** SPECTRUM DISPLAY/EDIT **
FRN 16308

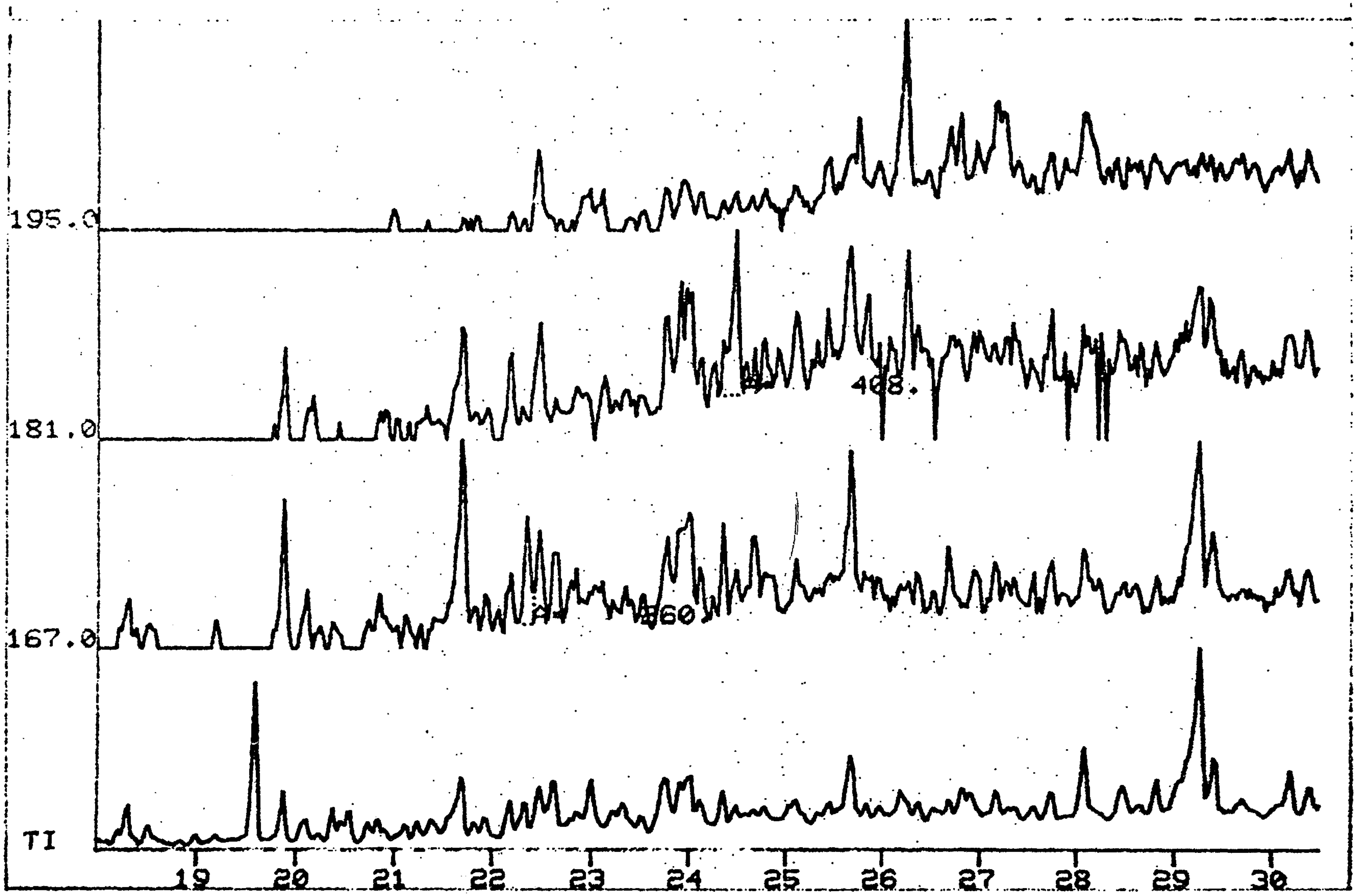
BIOS 06-1100-04 1UL/20UL 2200V TH=10 A/D=2
1ST SC/PG: 455

30M SE-52FS 6JAN81 60-290@5/MIN 46-346AM
X= .53 Y= 1.00

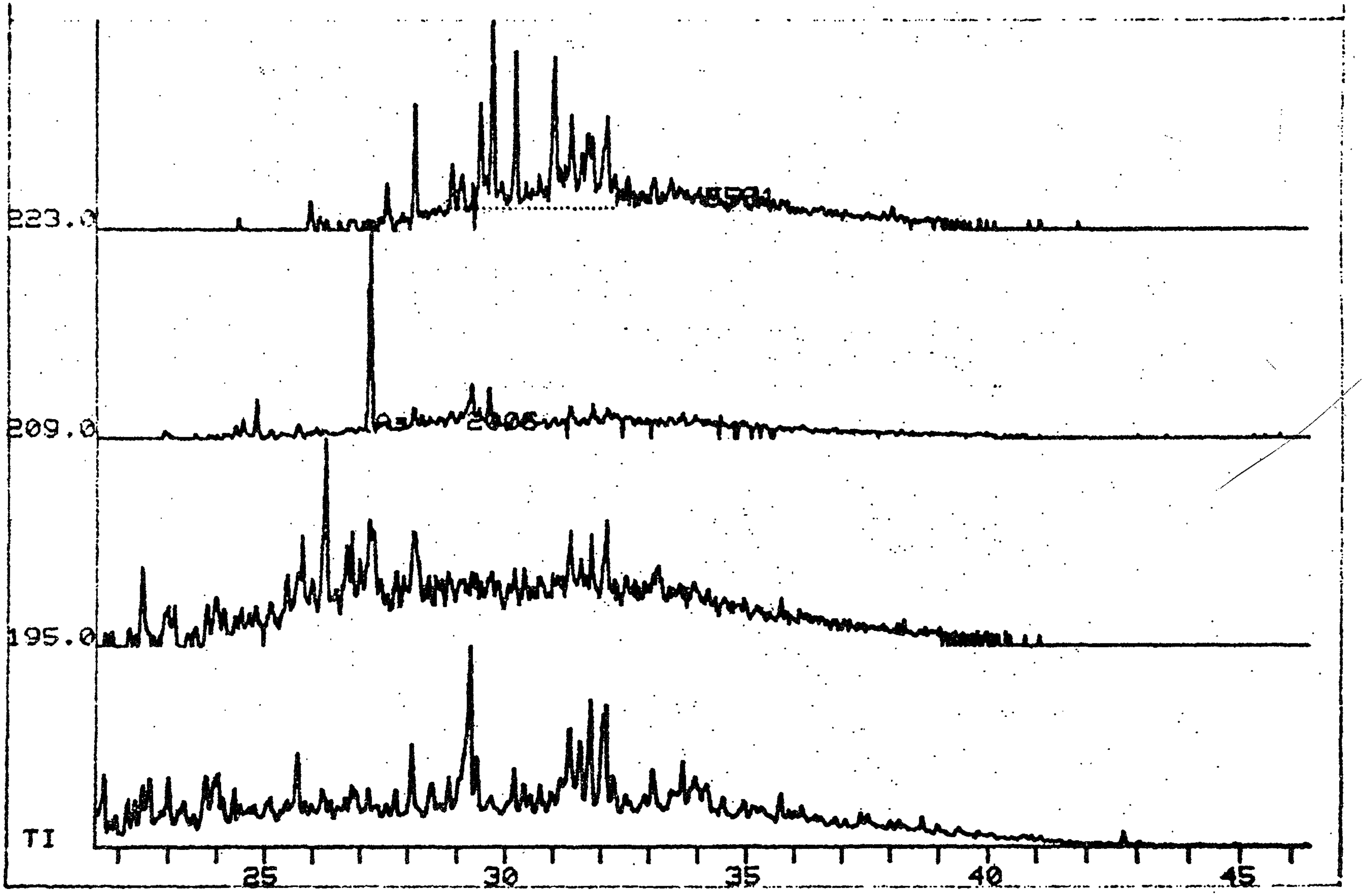
```
              ** SPECTRUM DISPLAY/EDIT **                  FRN 16308
BIOS 06-1100-04 1UL/20UL 2200U TH=10 A/D=2                1ST SC/PG: 685
30M SE-52FS 6JAN81 80-290@5/MIN 46-346AM                 X=   .50 Y= 1.00
```



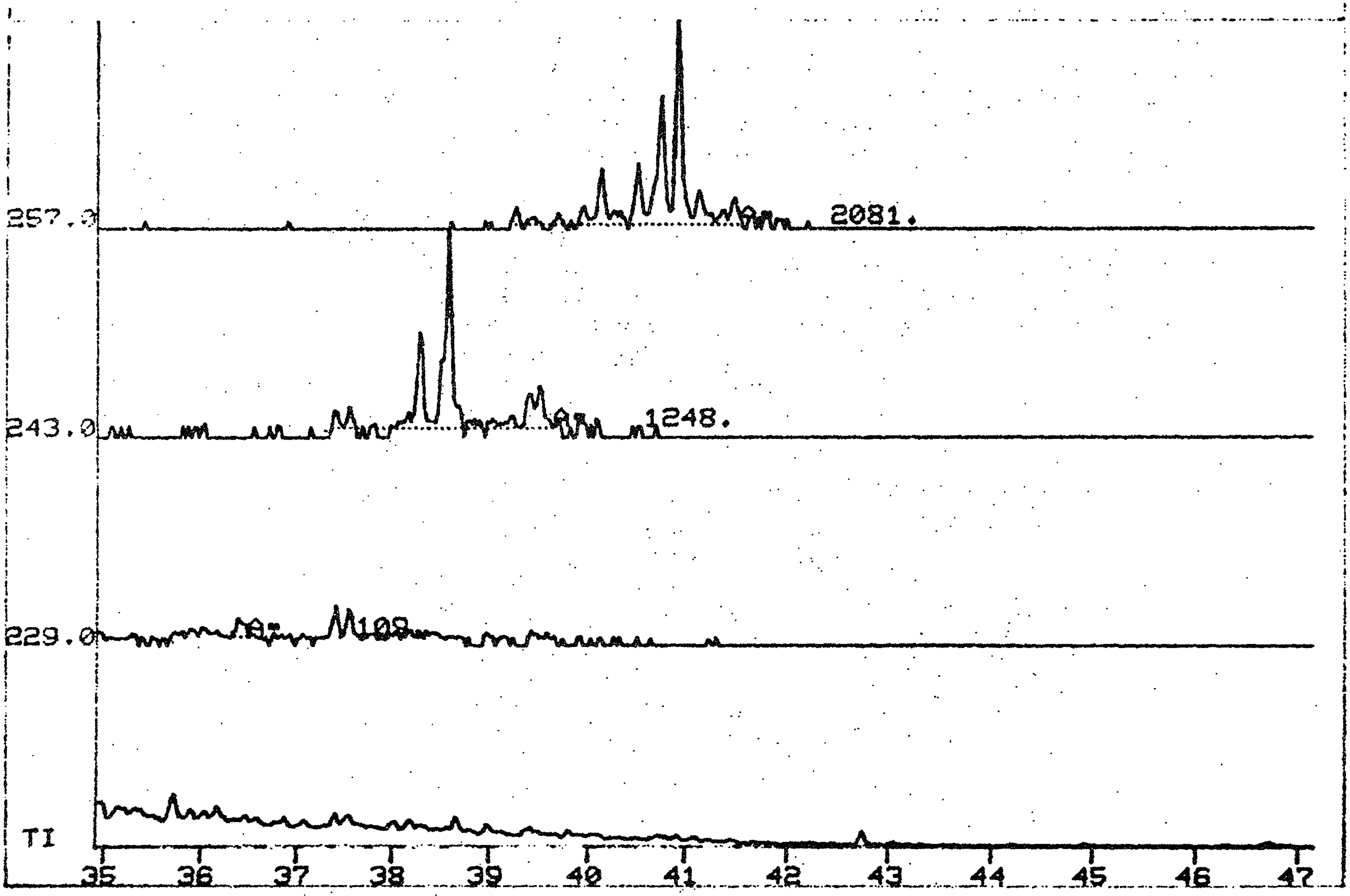
```
            ** SPECTRUM DISPLAY/EDIT **                FRN 16308
BIOS 06-1100-04 1UL/20UL 2200V TH=10 A/D=2             1ST SC/PG: 588
30M SE-52FS 6JAN81 60-250@5/MIN 46-346AM               X=  .50 Y= 1.00
```



** SPECTRUM DISPLAY EDIT ** FRN 16308
BIOS 06-1100-04 1UL/20UL 2200V TH=10 A/D=2 1ST SC/PG: 721
30M SE-52FS 6JAN81 60-290@5/MIN 46-346AM X= .25 Y= 1.00



```
                    ** SPECTRUM DISPLAY/EDIT **                  FRN 16308
BIJS 08-1100-04 1UL/20UL 2200V TH=10 A/D=2                  1ST SC/PG:1218
30M SE-52FS 6JAN81 60-290@5/MIN 46-346AM                   X=  .50 Y= 1.00
```



```
FILE NUMBER 16308

ENTRY  TIME     MASS      AREA       %

   1   14.0    129.0        54.      .05
   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    235.0     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 (?)
   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?
```

JF

DATE DUE

FEB 09 2014			
APR 21 2014			
OCT 13 2014			
FEB 27 2015			