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EFFECT OF BIODEGRADATION ON TAR SAND BITUMEN OF SOUTH WOODFORD AREA, CARTER COUNTY, OKLAHOMA

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A THESIS

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ABSTRACT

Tar-sand bitumens from the South Woodford Area have been analyzed to study effects of biodegradation on oils and to determine their possible sources. The tar-sand deposits, located approximately 1.5 miles south of Woodford, Carter County, Oklahoma, are distributed along the crest of the South Woodford Anticline. Sixteen bitumens from the Rod Club Sandstone (Mississippian) were chosen from a single well (Fitzgerald #5) which was cored near the axis of the anticline.

This study shows that the tar-sand bitumens have been so severely biodegraded that most of the *n*-alkanes, low molecular weight cycloalkanes, isoprenoid alkanes, C_{27}-C_{29} steranes, and light aromatics and sulfur compounds have been removed. In addition, the hopane distributions have been altered to differing degrees with those above C_{30} decreasing prior to the C_{27-29} hopanes. The triaromatic steroid hydrocarbons are also altered with the preferential removal of C_{20-21} and C_{27-28} 20R species. Diasterane and C_{30}-sterane distributions appear to be unaffected by biodegradation. The high resistance of tricyclic terpanes, C_{24}-tetracyclic terpane and monoaromatic steroid hydrocarbons to biodegradation indicate that the distribution of these compounds are well-suited to serve as bitumen-oil correlation parameters.

Geochemical correlation between the tar sand bitumen and oils produced in the Pauls-Valley area was attempted to determine which of these oils was the source for the tar-sand bitumen. The age of the reservoir of these oils range from Ordovician to Pennsylvanian. These oils were divided into two major groups based on biomarker distribution (JONES, 1986). One group appears to be sourced by the Woodford Shale whereas the other appears to be sourced by the Viola Limestone. The tar sand bitumen-oil correlation study, based on biomarker distributions and pyrolysis-gas chromatography of asphaltenes, shows that the tar-sand bitumen is genetically-related to the group of oils derived from the Woodford Shale.

CHAPTER I

INTRODUCTION

Tar sands have been defined by the interstate Oil Compact Commission (1980) as being any consolidated, or unconsolidated, rock containing a crude oil which is too viscous at natural reservoir temperature to be commercially producible by conventional primary recovery techniques. The tar sand deposits of the World have been described as belonging to one of two types: *in situ* deposits (WALTER, 1980) which result from breaching and exposure of an existing oil trap, and migrating oil at an outcrop. Migrated deposits are usually associated with active oil seeps (WALTER, 1980). There are, inevitably, gradations and combinations of these two types of deposits. Heavy oil accumulation and tar sand formation are thought to be created by water washing and bacterial degradation of conventional crude oils (WINTERS and WILLIAMS, 1969; BAILEY *et al.*, 1973; RUBINSTEIN *et al.*, 1977). Water washing removes the more water-soluble, light hydrocarbons, especially aromatics, whereas biodegradation preferentially removes n-alkanes. Both processes result in an increase in density and sulfur content (MILNER *et al.*, 1977). Severe degradation can even remove isoprenoids, and tetracyclic and pentacyclic terpanoids,

making oil-oil correlation and maturity determinations much more difficult. Therefore, a knowledge of compositional changes caused by biodegradation is essential for making accurate assessments of genetic relationships among oils, especially severely degraded heavy oils, seeps, and tar sand bitumens.

In the past two decades, the effect of biodegradation on petroleum composition has been studied extensively. The preferential removal of *n*-alkanes followed by *iso*- and *anteiso*-alkanes and then isoprenoids are well recognized phenomena of biodegradation (WINTERS and WILLIAMS, 1969; BAILEY *et al.*, 1973). Little information was obtained about the biodegradation of steranes and hopanes by gas chromatography alone. The advent of GC-MS techniques made it possible to study the effects of biodegradation on biomarker distributions at the end of 1970's. Reed (1977), Seifert and Moldowan (1979) and Seifert *et al.* (1984) identified many of the changes caused by microbial action on steranes and terpanes in crude oils. Alexander *et al.* (1983) presented a table listing the relative rate of removal of certain components during the biodegradation process. Connan (1984) published a comprehensive review of the biodegradation effects on the composition of petroleum in reservoirs, in which a table of step-by-step alteration of alkanes was proposed, based on data available at that time. Recently, Philp and Lewis (1987) reviewed the biodegradation effects reported in the literature, and summarized those into a table, indicating the changes occurring

with increasing biodegradation (Table 1). They emphasized that the relative extents of biodegradation given in Table 1 is not applicable to all situations. For example, McKirdy *et al.* (1982) showed that steranes and diasteranes were degraded before hopanes, but Volkman *et al.* (1983) showed that hopane degradation immediately followed the initial alteration of 20R-5α(H),14α(H),17α(H)-steranes. The ring A/B demethylated hopanes are another example, and a number of studies have shown that extensive biodegradation of hopanes produces ring A/B demethylated hopanes (SEIFERT and MOLDOWAN, 1979; RULLKOTTER and WENDISCH, 1982; PHILP, 1983; VOLKMAN *et al.*, 1984). Howell *et al.* (1984) observed a series of demethylated hopanes and demethylated tricyclic terpanes in non-biodegraded or less degraded oils. These discrepancies demonstrate that biodegradation is locally controlled by the population of microbes, nutrient supply and oxygen content and probably pH, Eh and temperature of the water in contact with the petroleum in reservoirs (PHILP, 1983).

Over 300 occurrences of heavy oils and bitumen impregnated rocks have been reported in Oklahoma (HARRISON *et al.*, 1981). A total of 45 tar sands occur in Carter and Murray Counties in south-central Oklahoma. The purpose of the present study is to analyze the chemical composition of a series of tar sand bitumens, from a single well, with emphasis being placed on the variation of biomarker distributions as a function of biodegradation of the tar sand bitumens.

Table 1. A summary of the reported effects of biodegradation
(After Philp and Lewis, 1987)

	Progressive Effects of Biodegradation	Reference
1.	Typical paraffinic oil; abundant n-alkanes	
2.	Light end n-alkanes removed	Alexander et al., 1983
3.	Iso- and anteiso-alkanes removed	Alexander et al., 1983
4.	Alteration and removal of pentacyclic hopane carboxylic acids	Behar and Albrecht, 1984
5.	>90% n-alkanes removed	Alexander et al., 1983
6.	Alkylcyclohexanes, alkylcyclopentanes, alkylbenzenes removed. Isoprenoids napnthalene concentration reduced.	Volkman et al., 1984
7.	Isoprenoids and alkylnaphthalenes removed; selective removal of C_2 naphthalenes	Volkman et al., 1984
8.	C_{14}-C_{16} Bicyclic alkanes removed	Alexander et al., 1983
9.	>50% 20R-5α(H),14α(H),17α(H) steranes removed	Alexander et al., 1983
10.	Relative removal rates for 5α(H),14α(H),17α(H) steranes. $C_{27}>C_{28}>C_{29}$	Seifert et al., 1984
11.	Preferential removal of C_{30}-C_{35} hopanes and the 22R configuration	Seifert et al., 1984 Goodwin et al., 1983
12.	Preferential removal of C_{27} diasterane	Alexander et al., 1983
13.	C_{27}-C_{29} Hopanes removed with or without demethylation	Seifert et al., 1984
14.	C_{21}-C_{22} steranes removed	
15.	Tricyclic terpanes removed with or without demethylation	Howell et al., 1984
16.	Alkylated benzenes removed faster than alkylated naphthalenes which in turn are removed faster than alkylated phenanthrenes. Benzo- and dibenzothiophenes also removed at this stage.	Williams et al., 1985
17.	Preferential loss of low molecular weight triaromatic steranes.	Wardroper et al., 1984
18.	Preferential degradation of mono- and triaromatic steranes with 20R configuration.	Wardroper et al., 1984
19.	Low molecular monoaromatic more resistant to biodegradation than high molecular weight monoaromatics.	Wardroper et al., 1984

An attempt has also been made to correlate the tar sand bitumen with oils in the Pauls Valley area, south-east corner of the Anadarko Basin, using biomarkers that survive biodegradation. Flash pyrolysis-GC of the asphaltene fraction has been used to confirm the correlation. Correlation is an important factor for understanding the evolution of petroleum basins. It is hoped that this study will provide some useful information on petroleum geochemistry and serve as an integral part of further studies in the southern Oklahoma petroleum province.

Study Area

The South Woodford Asphalt deposits are located approximately 1.5 mile south of Woodford, Carter County, Oklahoma (Fig. 1). This deposit is in Upper Mississippian-Lower Pennsylvanian strata, and the tar sand deposits are distributed along the crest of the South Woodford Anticline. A geological map of the South Woodford Asphalt deposits (Fig. 1) shows the location of quarry sites and tar sand outcrops. There are some shallow wells (165 to 480 ft.) that produce heavy oil from vertical Pennsylvanian (probably Otterville) sandstone in section 4, T3S, R1W (HARRISON and BURCHFIELD, 1984). Several active oil seeps exist along the axis of the South Woodford Anticline in the Rod Club Sandstone (HARRISON and BURCHFIELD, 1984).

Well OGS-5-Fitzgerald was chosen for this study because it is the deepest well (270 ft.) cored by the Oklahoma Geological Survey

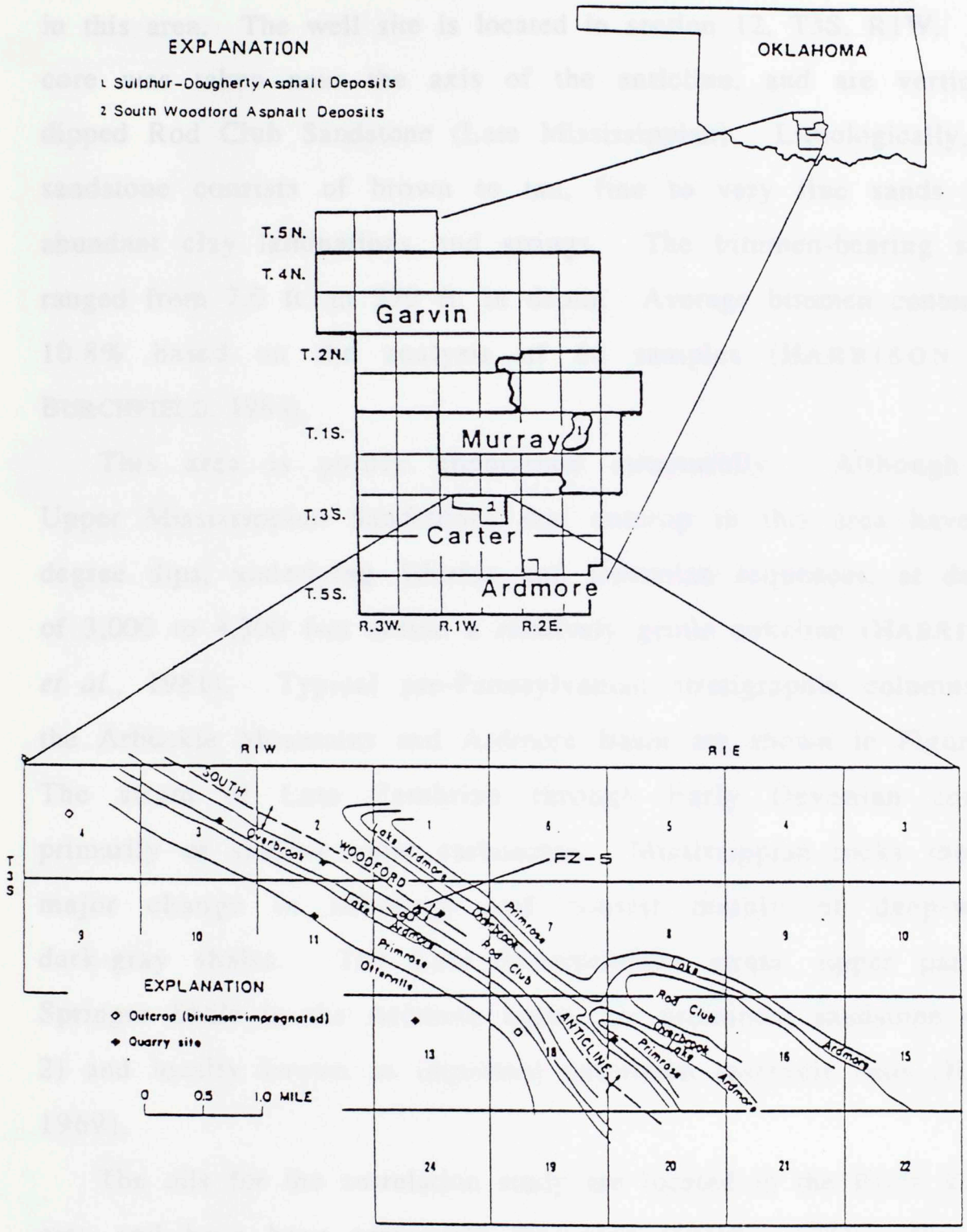


Figure 1. Study area and the structure map of the South Woodford area, Carter County, Oklahoma (After Fay, unpublished).

in this area. The well site is located in section 12, T3S, R1W. The core was taken near the axis of the anticline, and are vertically dipped Rod Club Sandstone (Late Mississippian). Lithologically, the sandstone consists of brown to tan, fine to very fine sands with abundant clay laminations and strings. The bitumen-bearing sands ranged from 7.0 ft. to 270 ft. in depth. Average bitumen content is 10.8% based on the analysis of 66 samples (HARRISON and BURCHFIELD, 1984).

This area is poorly understood structurally. Although the Upper Mississippian Sandstones that outcrop in this area have 90 degree dips, underlying Silurian and Devonian sequences, at depths of 3,000 to 4,300 feet define a relatively gentle anticline (HARRISON *et al.*, 1981). Typical pre-Pennsylvanian stratigraphic columns of the Arbuckle Mountains and Ardmore Basin are shown in Figure 2. The strata of Late Cambrian through Early Devonian consist primarily of shallow-water carbonates. Mississippian rocks show a major change in lithology and consist mainly of deep-water dark-gray shales. The Late Mississippian strata, upper part of Springer Shale in the Ardmore basin, are prominent sandstone (Fig. 2) and locally known as important petroleum reservoir beds (HAM, 1969).

The oils for the correlation study are located in the Pauls Valley area and have been previously discussed (JONES, 1986). Figure 3 shows the tectonic setting of Pauls Valley and adjacent areas, in which sample location of the tar sand and oils studied also shown.

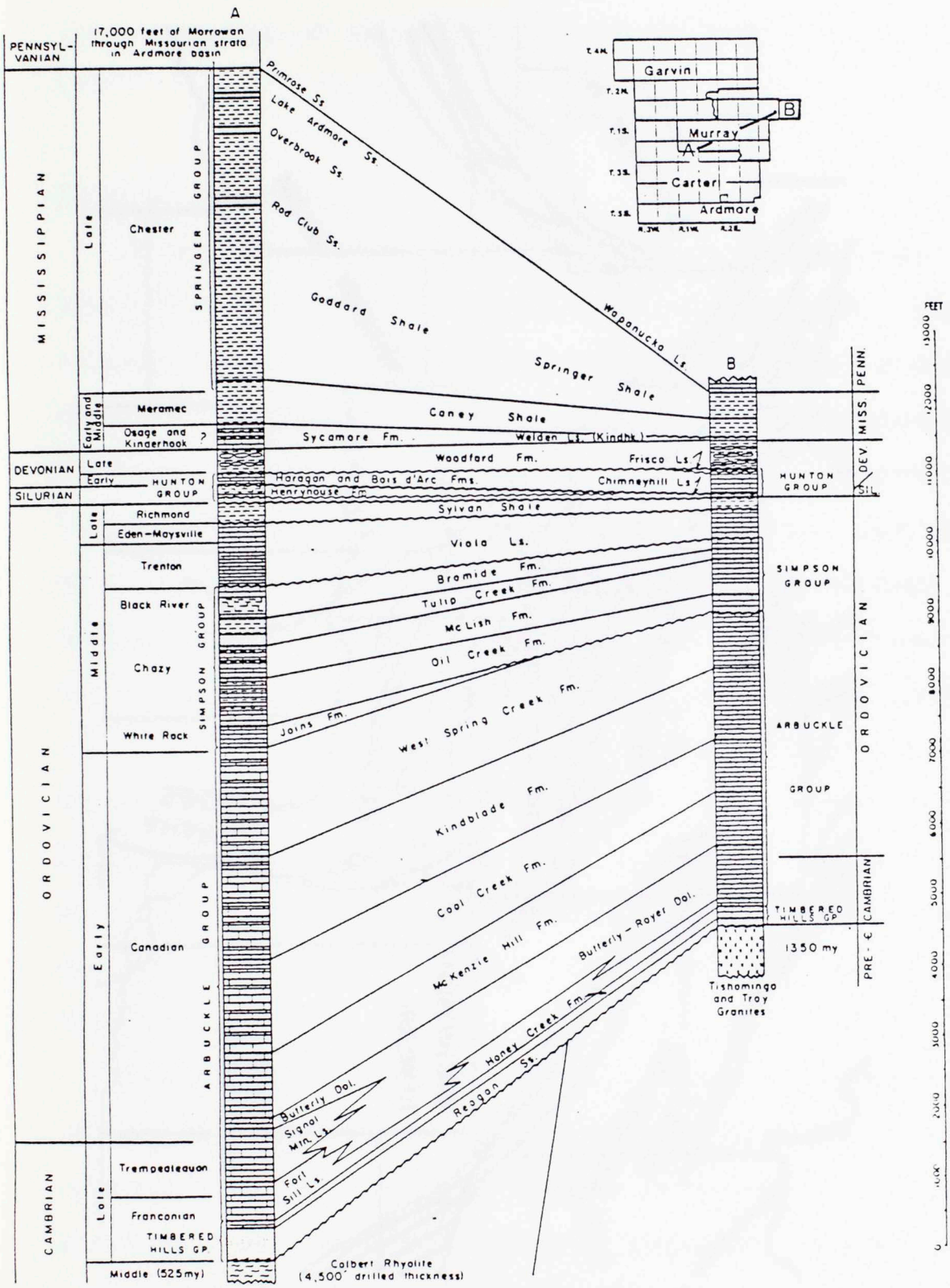


Figure 2. Pre-Pennsylvanian stratigraphic columns of rocks in two areas of the Arbuckle Mountains (After Ham, 1969).

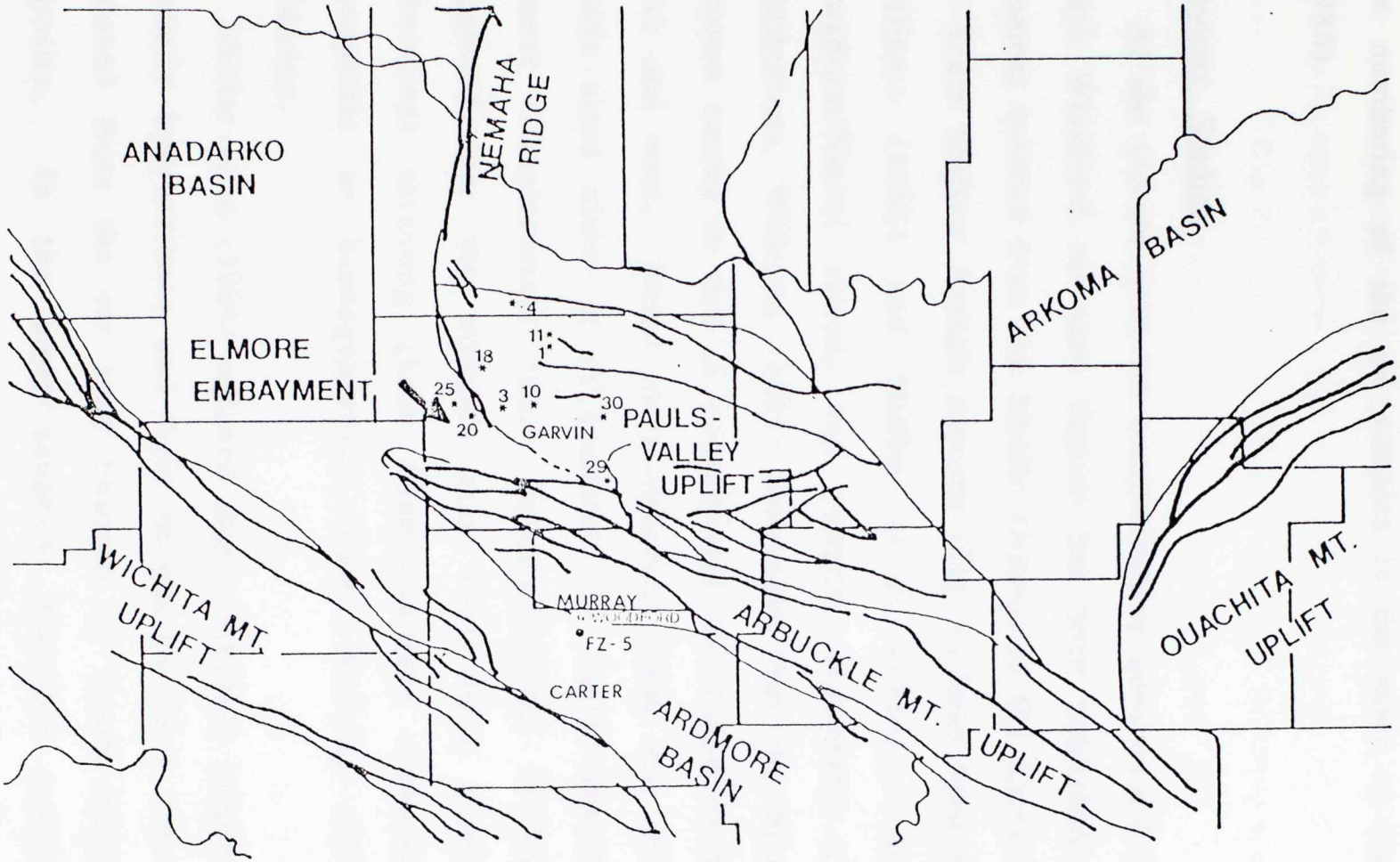


Figure 3. Structure map showing tectonic setting of Pauls Valley and adjacent areas, and sample distribution. Heavy lines represent significant faults.

The numbering of the oil samples is the same as that in Jones (1986).

Previous Studies

At the present time, no comprehensive geochemical study of the South Woodford tar sand deposit has been published. However, bitumens isolated from the Middle Ordovician Oil Creek formation at the South Sulphur Asphalt deposits (Fig. 1) have been examined by Williams (1983) and Miiller *et al.* (1984). According to Vanadium/Nickel ratios, and sterane, diasterane and hopane distributions, Williams (1983) concluded that the bitumen has a common source to that of conventional oils found downdip, to the north and west. Based on a structural study and the finding of cobble sized clasts of oil-saturated Oil Creek Sandstone in the Vanoss Conglomerate (Late Pennsylvanian), Williams (1983) suggested that the bitumen may have been emplaced early. Subsequent thrusting (Late Pennsylvanian) rendered the oils susceptible to biodegradation, water washing and inorganic oxidation.

Miiller *et al.* (1984) reported that *n*-alkanes, isoprenoids, light aromatic hydrocarbons and light thiophenes have been completely removed from the tar sand bitumen of South Sulphur Asphalt deposits. In the most severely degraded samples, sterane distributions were found to be partially altered. The preferential loss of C_{30+} hopanes relative to their C_{27}-C_{29} species was observed

even in the sample with intact sterane distribution. The partial loss of 18α(H)-trisnorhopane, Ts, was also observed in the biodegraded sample. Diasteranes, triaromatic steroid hydrocarbons, tricyclic terpanes, C_{24}-tetracyclic terpanes, C_{29}-hopane and Tm appear to be resistant to biodegradation (MIILLER *et al.*, 1984). Miiller *et al.* (1984) also gave a list of susceptibility toward biodegradation in decreasing order: Thiophenes, naphthalenes, *n*-alkanes, *n*-alkylcyclohexanes, alkylbenzenes, isoprenoids, C_{30+} hopanes, moretanes, 18α(H)-trisnorhopanes, and natural steranes.

Thirty oils from the Pauls Valley area, southeast Anadarko Basin, have been previously analyzed for *n*-alkane, terpane and sterane distributions (JONES, 1986). Six rock extracts from the area were also analyzed in an attempt to perform an oil-source rock correlation. Based on biomarkers, these thirty oils, reservoired in Ordovician to Pennsylvanian rocks, are classified into two major groups. Eighty five percent of the oils have a possible common source, in all probability, the Woodford Shale. Some of the oils reservoired in the Viola Limestone, exhibit distinct geochemical characteristics including an enhanced concentration of the C_{24}-tetracyclic terpane relative to C_{26}-tricyclic terpanes, a reduction of the C_{28-30} tricyclic terpanes relative to Ts and Tm, a reduced concentration of C_{30}-steranes relative to their C_{29} counterparts, a predominance of the C_{35} over the C_{34} extended hopanes and an even/odd predominance of the *n*-alkane distribution (JONES, 1986). The Viola rock extract generally exhibits

the same characteristics as the anomalous Viola oils and was proposed as the probable source rock for them (JONES, 1986).

CHAPTER II

EXPERIMENTAL PROCEDURE

Deasphalting

Tar sand bitumens (0.4 - 0.5g), provided by the Oklahoma Geological Survey, were extracted from the tar sand with dichloromethane (see HARRISON and BURCHFIELD, 1984, p.41 for extraction procedure). Asphaltenes were removed from each sample by addition of *n*-pentane and sonicating (*ca.* 10 min.) to mix the bitumen throughly with the solvent. Samples were placed in a freezer overnight to allow full precipitation of the asphaltenes. The asphaltenes were separated by centrifugation followed by decanting off the pentane soluble fraction into a flask. The *n*-pentane was removed using a rotary evaporator and the concentrated sample was transferred into a tared vial, blown dry using nitrogen, and weighed. The asphaltene fraction was transferred into a tared vial with dichloromethane, blown dry by nitrogen stream, and weighed. Asphaltenes were precipitated from crude oils using the same procedure.

Column Chromatography

Each non-asphaltene fraction obtained from deasphalted

bitumen or oil was separated into saturate, aromatic and NSO fractions by column chromatography. Glass columns (25 or 50ml), with additional solvent reservoirs at the top, were cleaned with soap and water, rinsed with deionized water and finally washed with methanol and dichloromethane prior to use. Glass wool was rinsed with dichloromethane and dried in an oven (150 °C). Silica gel and alumina were activated prior to packing columns by drying in an oven (250 °C for 3 hours).

Columns were slurry packed by first placing a plug of glass wool in the bottom of the column. The column was then filled with *n*-pentane, and silica gel (100-200 mesh) was added slowly and tapped to ensure uniform packing. Alumina (80-200 mesh) was added on top of the silica gel. The proportion of silica to alumina and the total weight of adsorbent was determined by the weight of sample (Guidelines developed by Cities Service Co., Tulsa, OK.). Just prior to use, solvent was removed from the column until *ca.* 0.5ml of solvent was present above the adsorbent. Deasphalted samples were loaded onto the column and washed onto the adsorbent with additional *n*-pentane. Saturate fractions were eluted from the column with pentane (*ca.* 80ml) and aromatics were eluted with toluene (*ca.* 80ml). Finally, NSO fractions were obtained by elution with dichloromethane/methanol (1:1, *ca.* 50ml). Fractions were evaporated either on a rotary evaporator, or by a stream of nitrogen, placed into a tared vial and weighed. All solvents used were Burdick & Jackson, high purity solvent.

Gas Chromatography

Saturate and aromatic fractions were analyzed by gas chromatography using either a Hewlet Packard 5890 or Varian 3300 GC. Both instruments were equipped with a J & W Scientific DB-5 fused silica capillary column (30m x 0.25mm, 0.25μm film thickness). The Varian GC was equipped with a flame ionization detector (FID) and a flame photometric detector (FPD), whilst the HP GC only had a FID. Helium was used as carrier gas with a flow rate of *ca.* 1 ml/min. Injector and detector temperatures were 300 °C. The temperature program was started from 40 °C (1.5 min.) and increased initially to 130 °C at 15 °C/min and then to 300 °C at 4 °C/min (final temperature held for 25 min.). Organic sulfur compounds in the aromatic fraction were analyzed with the FPD of the Varian GC.

Molecular Sieving

Molecular sieving was performed to remove *n*-alkanes from the saturate fraction. Since the tar sand bitumens were so severely biodegraded that no *n*-alkanes were detected by GC, except for the sample at 240 ft., molecular sieving was only applied to the saturate fractions of the conventional oils. Removal of *n*-alkanes increases the concentration of polycyclic compounds in the sample and improves the detection of biomarkers.

The saturate fraction (10-30mg) was placed in a 500 ml flask and Union Carbide-S115 molecular sieve (3-4g), and 150 ml of

iso-octane (Fisher, HPLC grade) was added. After the mixture was refluxed (20 hours), the solvent was decanted from the molecular sieve and was evaporated on a rotary evaporator. The branched and cyclic fraction was finally transferred to a small vial.

Biomarker Analysis

Biomarkers present in the saturate and aromatic fractions were analyzed using a Hewlet Packard 5890A gas chromatograph interfaced to a Finnigan MAT Model 700 Ion Trap Detector (ITD). The GC was equipped with a J & W Scientific DB-5 fused silica capillary column (*ca.* 25m x 0.25mm, 0.25μm film thickness). A split-splitless injection technique was used with helium as the carrier gas and a flow rate of *ca.* 1 ml/min. The injector temperature was 300 °C. The temperature program was started from 40 °C (1.5 min) and increased initially to 140 °C at 10 °C/min and then to 300 °C at 4 °C/min (final temperature held for 20 min.).

The emission current of the ion trap was 80 μA, electron energy 70 eV, multiplier voltage of 1400-2100 V and scan speed of 1 sec/scan. The ITD was used in the multiple ion detection mode monitoring m/z ratios of 191, 217, 231, 253 for di- and triterpanes, steranes, triaromatic and monoaromatic steroids, respectively. Data was collected on an IBM PC-XT using Finnigan MAT ITDS V#3.00 and PCDOS 2.1 software. Component identification was made by comparison with mass chromatograms of samples that had been analyzed previously on the GC-ITD system, and by comparison with

previously published data.

Flash Pyrolysis-GC of Asphaltene

Asphaltenes were disolved in a small amount of dichloromethane and reprecipitated with *n*-pentane three times before being subjected to pyrolysis-GC.

Asphaltenes were analyzed by pyrolysis-GC using a CDS (Chemical Data Systems) 122 extended temperature pyroprobe. Samples were dissolved in dichloromethane and applied to a platinum ribbon. After evaporation of the solvent the sample was pyrolyzed at 800 °C for 20 sec. The pyrolyser was coupled to a Varian 3300 gas chromatograph *via.* a heated interface (300 °C), and connected to the split injection system (split ratio 1:30). The pyrolysis products were transferred directly onto the GC column by helium, (*ca.* 30 ml/min) passing through the interface. Chromatographic separation was performed on a J & W Scientific DB-5 fused silica column (30 m x 0.25 mm, film thickness 1.0 μm). The carrier gas flow rate through the column was *ca.* 1 ml/min. The temperature program was started from -25 °C (2 min.) and increased to 300 °C at 4 °C/min (final temperature held for 30 min.). The column effluent was splited and monitored by FID and FPD mounted in parallel. All data were collected with Nelson Analytical Chromatography Software Model 2600, running on an IBM PC-XT under PCDOS #3.6.

CHAPTER III

RESULTS AND DISCUSSION

Bulk Composition

The ternary diagram of relative weight percentage of saturate, aromatic and asphaltene plus NSO fractions of oils and tar sand bitumens is shown in Figure 4. It is apparent that the conventional oils contain mainly saturated hydrocarbons (71.65-83.19%) whilst the tar sand bitumens contain major amount of aromatic and polar compounds. Table 2 shows the data from fractionation of the tar sand bitumens. Table 3 shows the fractionation data, API gravity, depth and formation for the oils analyzed in this study.

The saturate to aromatic ratio of the tar sand bitumens is generally less than 1 (Table 1) whilst that of the oils is 3.24 to 5.46 (Table 2) except oil #29 and #30 where the values are 0.81 and 1.00, respectively. The *in vitro* study by Rubinstein *et al.* (1977) showed that the tar sand bitumen of Alberta was formed by biodegradation of conventional oils. The aromatics biodegraded at a slower rate than that of the saturates and caused an increase in viscosity and pour point, a decrease in API gravity and a SAT/ARO ratio less than 1.

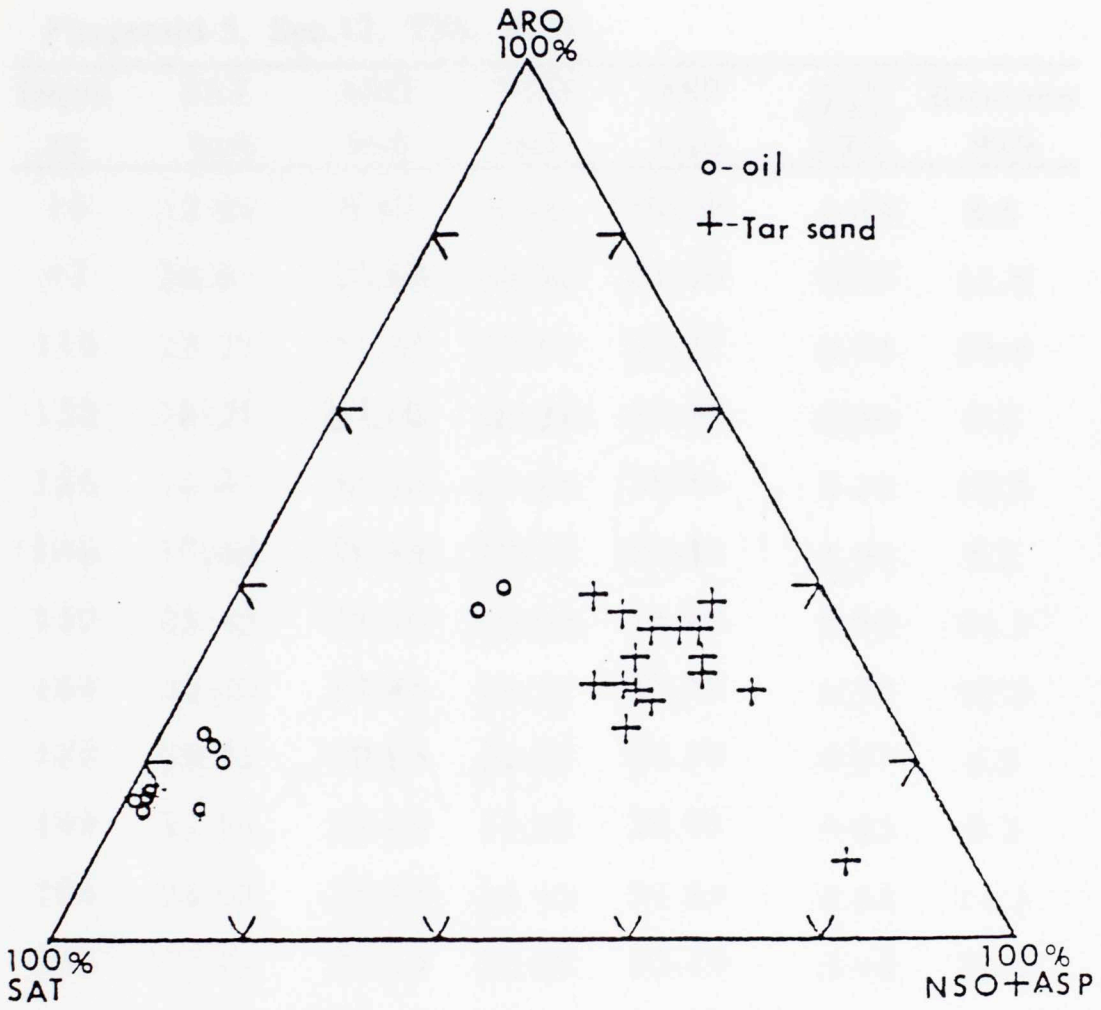


Figure 4. Bulk composition of tar sand bitumens from well Fitzgerald-5 and oils from Pauls Valley area.

Table 2. Fractionation data for the tar sand bitumens.

Fitzgerald-5, Sec.12, T3S, R1W

Depth Ft.	SAT Wt%	ARO Wt%	NSO Wt%	ASP Wt%	SAT / ARO	Bitumen Wt%
16	12.88	8.67	9.10	69.36	1.49	8.6
92	28.81	29.60	19.91	21.69	0.97	11.6
116	23.29	31.66	22.59	22.47	0.74	14.6
128	24.77	27.62	29.22	18.39	0.90	6.2
136	14.77	35.19	21.26	28.41	0.42	13.5
144	17.06	30.19	25.97	26.60	0.56	8.2
152	25.40	28.10	30.00	16.50	0.90	14.1
168	20.00	34.85	22.21	22.93	0.57	10.5
188	25.81	29.63	24.03	20.53	0.87	8.8
196	23.54	27.69	19.83	28.95	0.85	9.2
204	24.05	38.93	15.19	21.83	0.62	11.1
236	17.01	35.14	22.65	25.19	0.48	10.2
240	15.94	32.15	23.12	28.79	0.50	5.4
244	12.44	37.10	27.43	23.03	0.34	10.1
248	13.33	27.50	17.39	41.77	0.48	9.6
256	22.29	36.45	16.50	24.76	0.61	7.8

Table 3. Fractionation data, API gravity, depth and formation of oils in the Pauls Valley area.

Sample No.	Formation	Depth Ft.	API Wt%	SAT Wt%	ARO Wt%	NSO Wt%	ASP Wt%	SAT/ARO
1	Penn. Uncf. Sd.	4570	43.3	81.85	15.97	1.03	1.14	5.13
3	Oil Creek	7940	-	72.14	21.85	4.23	1.78	3.30
4	Penn. Uncf. Sd. +Hunton	6380	40.0	83.19	15.23	0.70	0.90	5.46
10	First Bromide	5230	36.5	76.66	15.02	6.69	1.63	5.10
11	Viola	5430	_	82.82	15.27	0.90	1.03	5.42
18	Oil Creek	8306	_	73.18	22.61	3.93	0.29	3.24
20	Viola	8900	_	71.65	20.54	7.81	_	3.49
25	Viola	9440	_	81.21	16.96	1.83	_	4.79
29	Oil Creek	3925	12	32.86	40.41	10.31	16.42	0.81
30	Oil Creek	4300	10	36.92	36.94	12.15	13.99	1.00

* Oil sample numbles are the same as in Jones (1986).
For well name and well location, see Appendix 2. Jones (1986).

The fluctuation of the SAT/ARO ratio for the tar sand bitumens probably reflects different rates of bacterial degradation and water washing on the saturates and aromatics. Two of the oils (#29 and #30) exhibited low SAT/ARO ratios and also low API gravity (Table 3). Further analysis, by gas chromatography, of saturates, aromatics and sulfur compounds indicate that these two oils have been degraded, probably by bacterial alteration and water washing.

Gas Chromatography. Figure 5 shows gas chromatograms of the saturate fractions of oils #3, #18, #29 and #30. These oils are all reservoired in the Oil Creek Formation and are thought to be sourced from Woodford Shales (JONES, 1986). Figure 5 shows that in the oils, the *n*-alkanes decrease relative to the isoprenoids with decreasing depth of the reservoir. The preferential decrease of *n*-alkanes is a well documented phenomenon of biodegradation (WINTERS and WILLIAMS, 1969; BAILEY *et al.*, 1973; CONNAN *et al.*, 1980; ALEXANDER *et al.*, 1983). This agrees with Price's (1980) study that most heavy oils at shallow depth (2.44 km or 8005 ft.) are formed by bacterial degradation or water washing and not because of the immaturity of the oil.

The gas chromatograms of the aromatic and sulfur compounds of these 4 oils (Figs. 6 and 7) also show a rapid decrease in lower molecular weight components with decreasing depth of the reservoir. The relative susceptibility toward biodegradation of aromatic compounds appears to be: C_1-naphthalene>

C_2-naphthalene > C_3-naphthalene > phenanthrene and C_1-phenanthrene > C_2-phenanthrene. The lower molecular weight aromatics are known to be more water soluble than the saturate hydrocarbons (PRICE 1980), and their biodegradation rate decreases with increasing aromatic ring number and increasing chain length of alkyl substituents (ROWLAND *et al.*, 1986; VOLKMAN *et al.*, 1984; WILLIAMS *et al.*, 1986). At least two major pathways are known for aerobic degradation of alkyl aromatic hydrocarbons: one involves oxidative attack on aromatic ring carbons whilst the other involves oxidation of aromatic alkyl carbons (RAYMOND *et al.*, 1971). Oxidation of aromatic ring carbon is an energy-producing process which often leads to complete degradation of the substrate. Attack on alkyl substituents does not always provide energy but can occur as a cooxidation process when another compound is utilized as the energy source (ROWLAND *et al.*, 1986).

The relative susceptibility of sulfur compounds toward biodegradation, observed from the FPD gas chromatograms, of these four oils, in decreasing order, appears to be: alkylbenzothiophene > dibenzothiophene > methyldibenzothiophene > dimethyldibenzothiophene > trimethyldibenzothiophene (Fig. 7). Compared with the saturate fraction (Fig. 5), the severe degradation of aromatic and sulfur compounds is not coupled with significant alteration of alkanes. This phenomenon has been observed by Connan (1984) who showed that intensive alteration of both aromatics and alkanes is generally encountered only in the surface or at shallow depth, while in deeper reservoirs, highly degraded

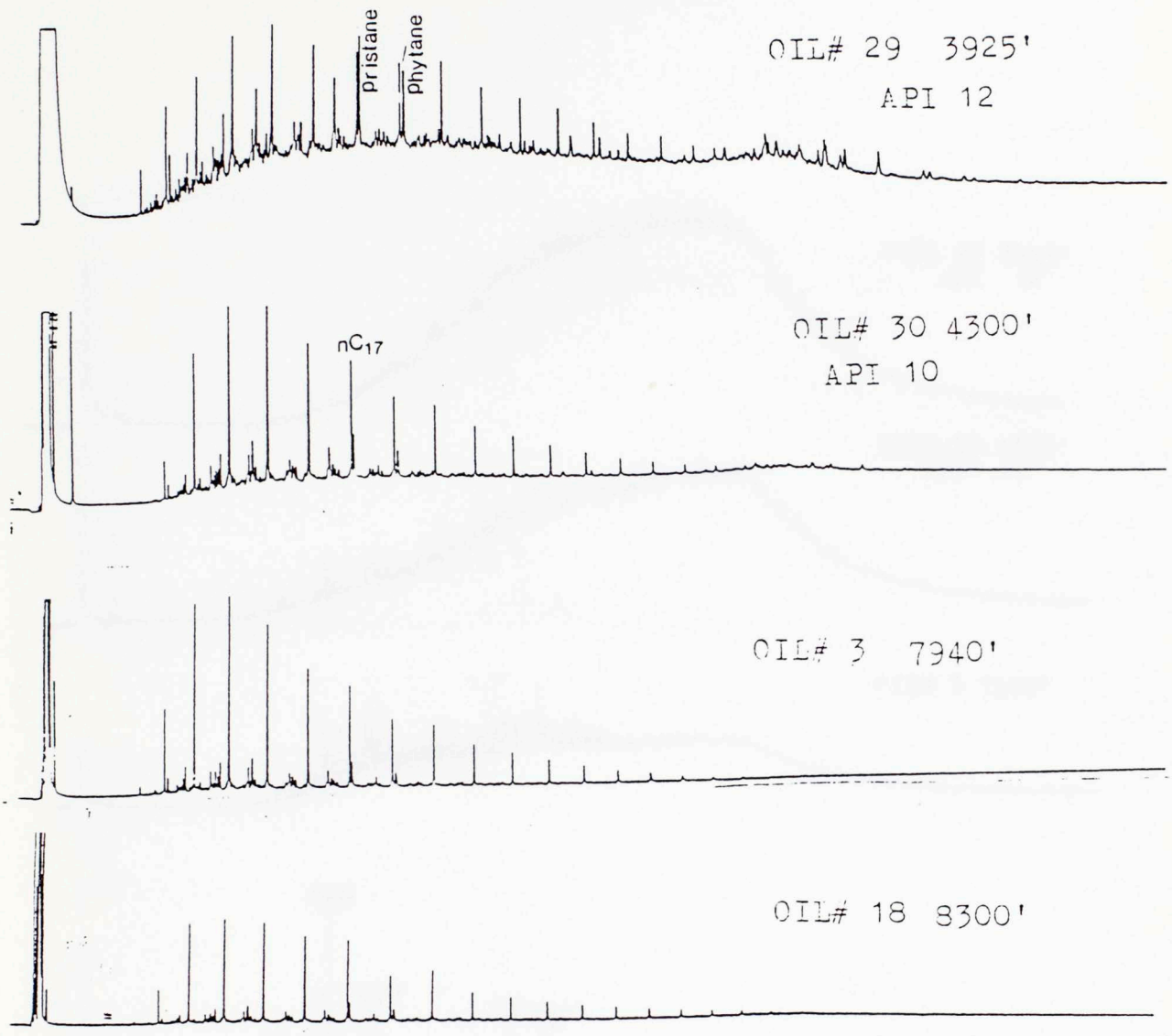


Figure 5. Gas chromatograms of saturate fraction showing increasing biodegradation of 4 oils, that reservoired in Oil Creek Sandstone, with decreasing depth in Pauls Valley area.

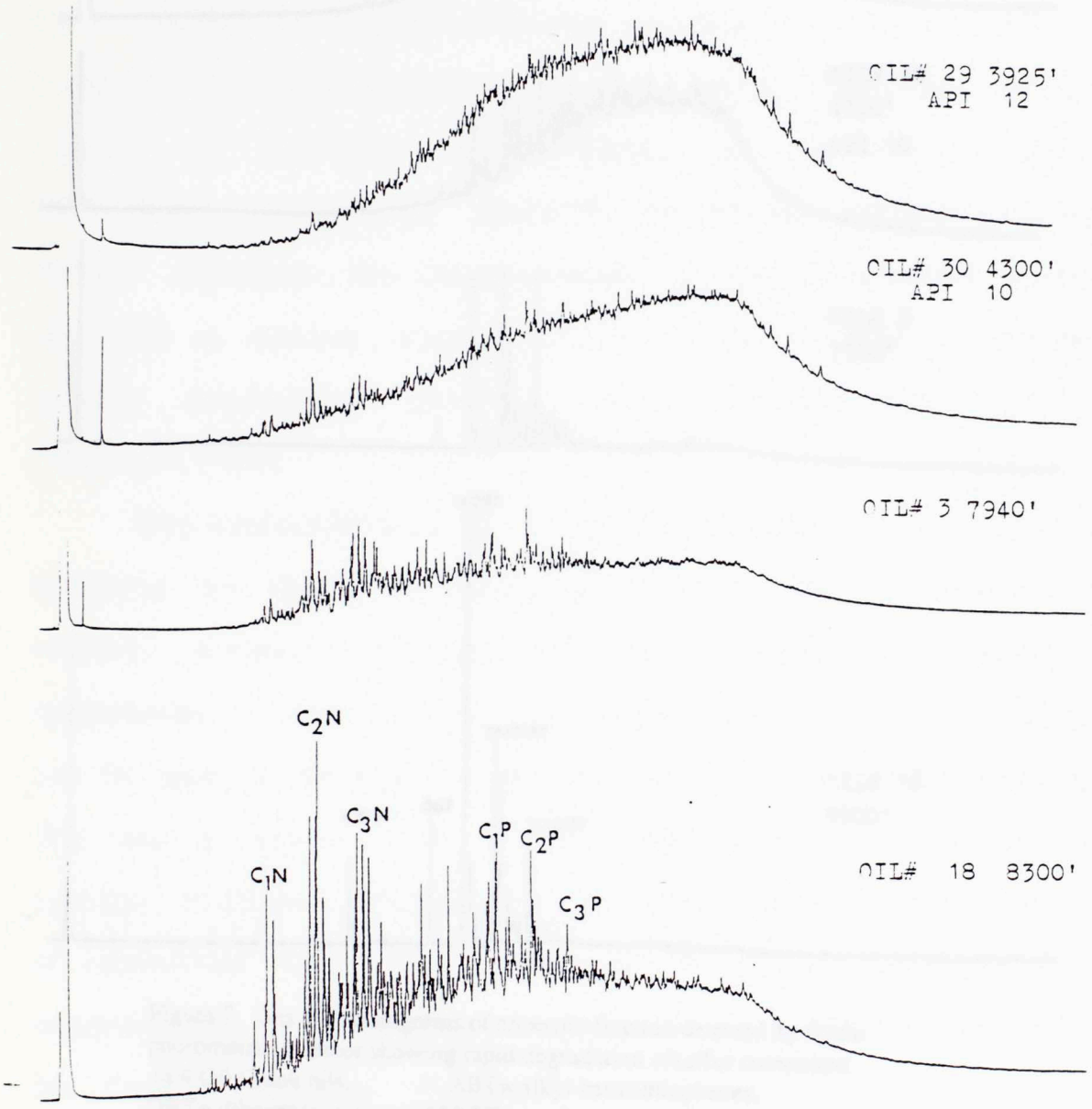


Figure 6. Gas chromatograms of aromatic fraction showing rapid degradation of aromatic compounds in 4 Oil Creek oils. C_1, C_2 and C_3 refer to the number of carbon atoms in ring substuents on naphthalenes (N) and phenanthrenes (P).

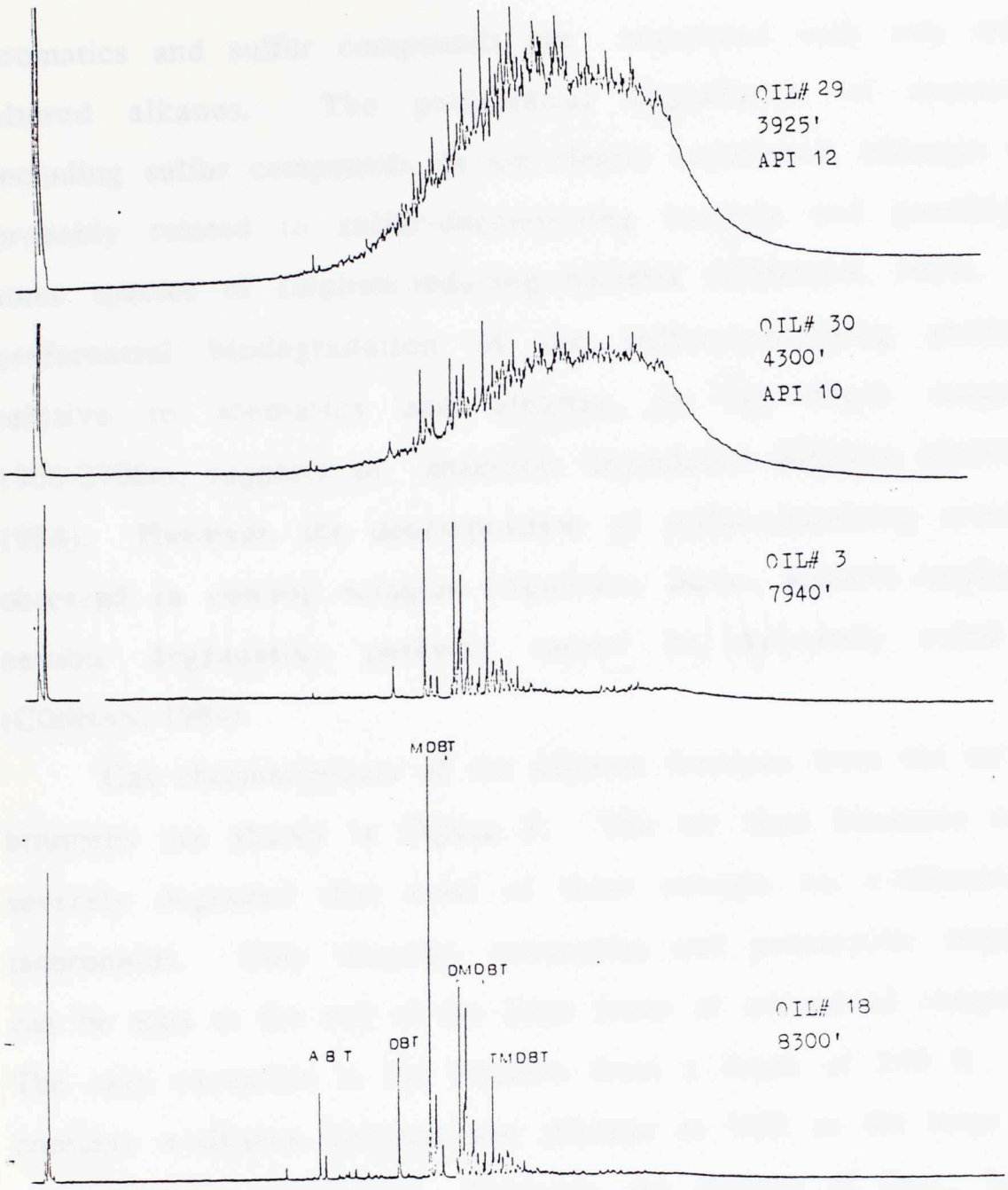


Figure 7. Gas chromatograms of aromatic fraction detected by flame photometric detector showing rapid degradation of sulfur compound in 4 Oil Creek oils. ABT= alkyl benzothiophenes, DBT= dibenzothiophenes, MDBT= methyl dibenzothiophenes, DMDBT= dimethyldibenzothiophenes, TMDBT= trimethyl dibenzothiophenes.

aromatics and sulfur compounds are associated with only mildly altered alkanes. The preferential degradation of aromatics, including sulfur compounds, is not clearly understood, although it is probably related to sulfur-decomposing bacteria and possibly to some species of sulphate-reducing bacteria (CONNAN, 1984). The preferential biodegradation of the sulfur-containing aromatics relative to aromatics and alkanes, in the depth range of 1900-2700m, suggests an anaerobic degradation pathway (CONNAN, 1984). However, the decomposition of sulfur-containing aromatics observed in outcrop samples (Aquitaine Basin, France) implies an aerobic degradation pathway cannot be definitely ruled out (CONNAN, 1984).

Gas chromatograms of the saturate fractions from the tar sand bitumens are shown in Figure 8. The tar sand bitumens are so severely degraded that most of them contain no *n*-alkanes or isoprenoids. Only tricyclic, tetracyclic and pentacyclic terpanoids can be seen at the end of the large hump of unresolved components. The only exception is the bitumen from a depth of 240 ft., which contains *n*-alkanes, pristane and phytane as well as the large hump of unresolved components. However, the absence of C_{30+} hopanes suggests that there has been mixing of an unaltered light oil with the heavily degraded bitumen.

The aromatic fractions also show severe degradation (Fig. 9), such that only a large hump of unresolved components, representing a complex mixture, is present. The peaks visible at the long retention times were subsequently identified by GC-MS, as

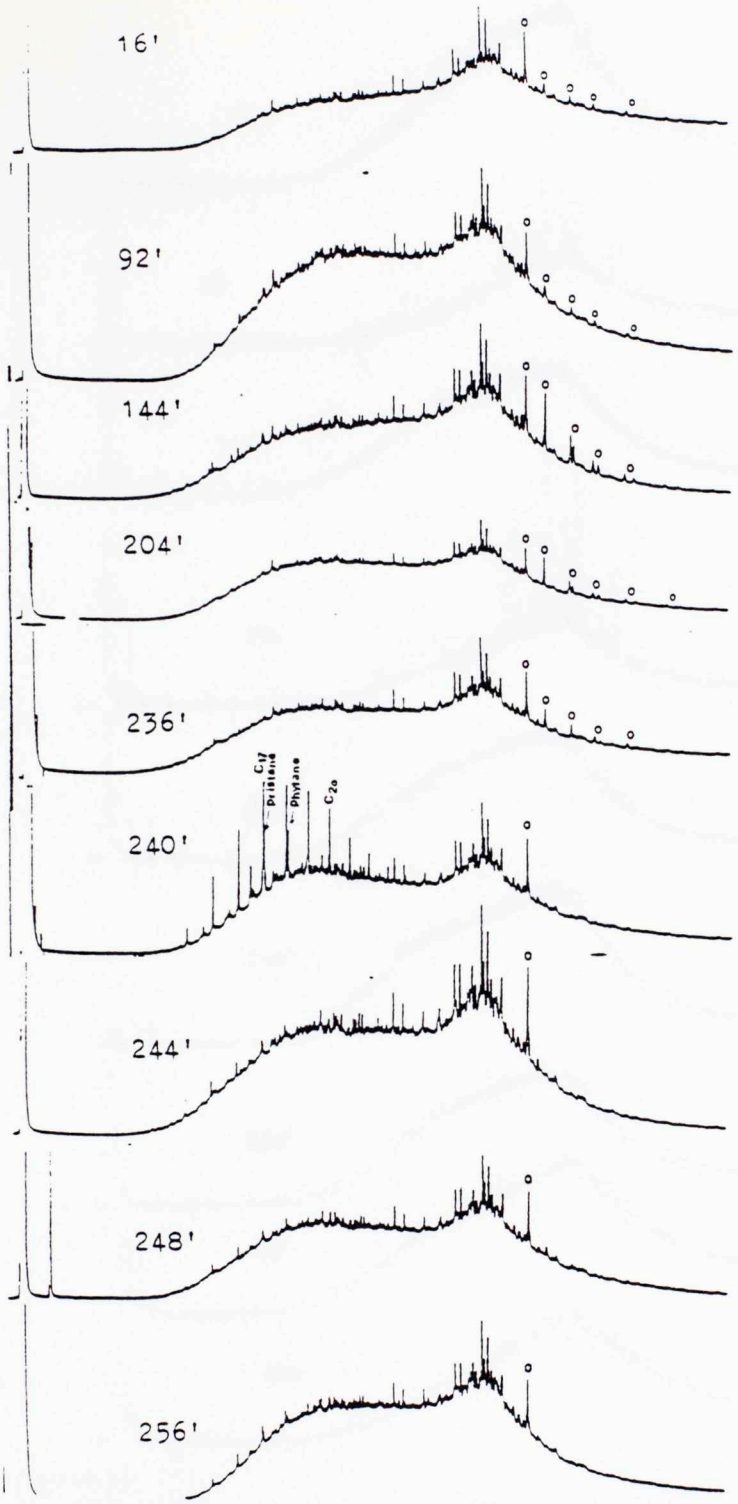


Figure 8. Gas chromatograms of saturate fraction of some representative tar sand bitumens showing the presence of normal alkanes at depth 204 ft. and of abundant biomarkers in the long retention time area. (o: hopane)

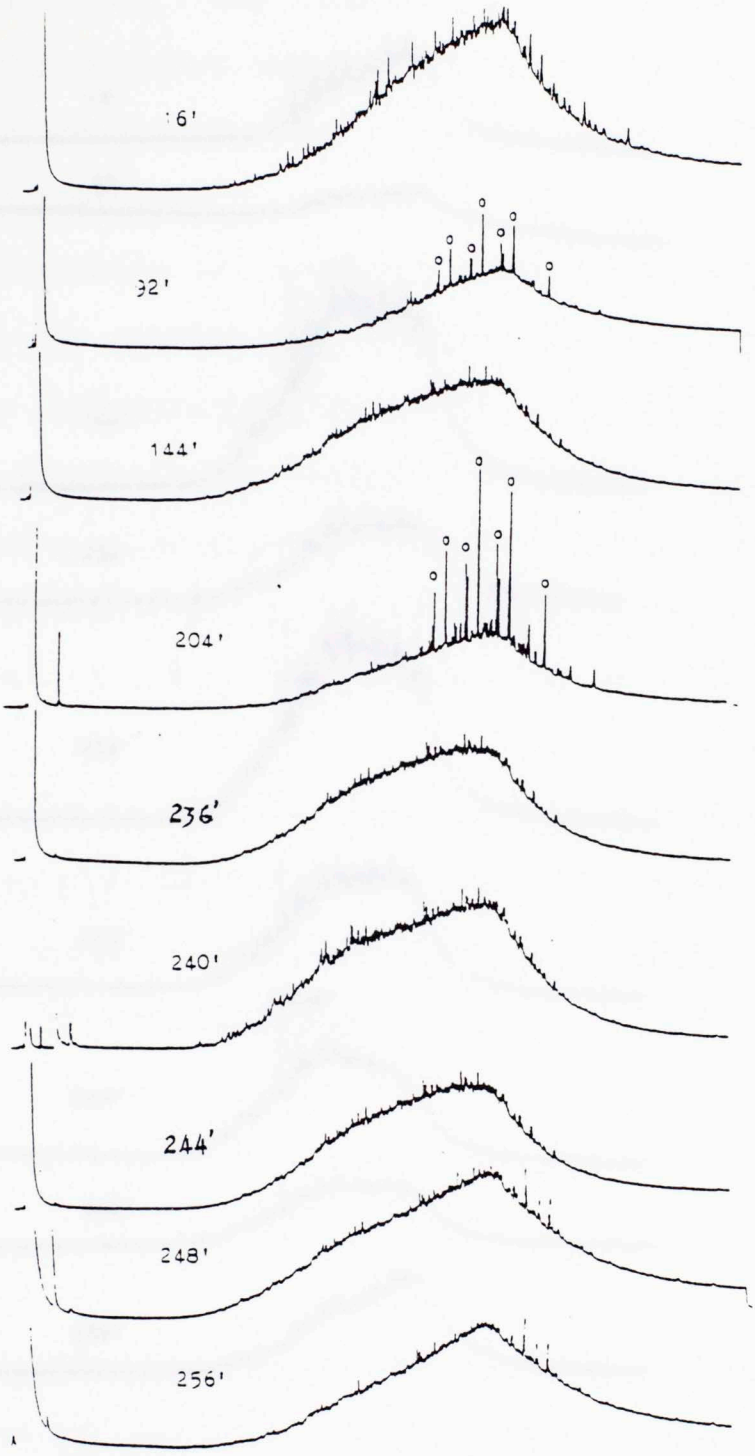


Figure 9. Gas chromatograms of aromatic fraction of tar sand bitumens. (o: phthalate esters. !: triaromatic steroid hydrocarbons)

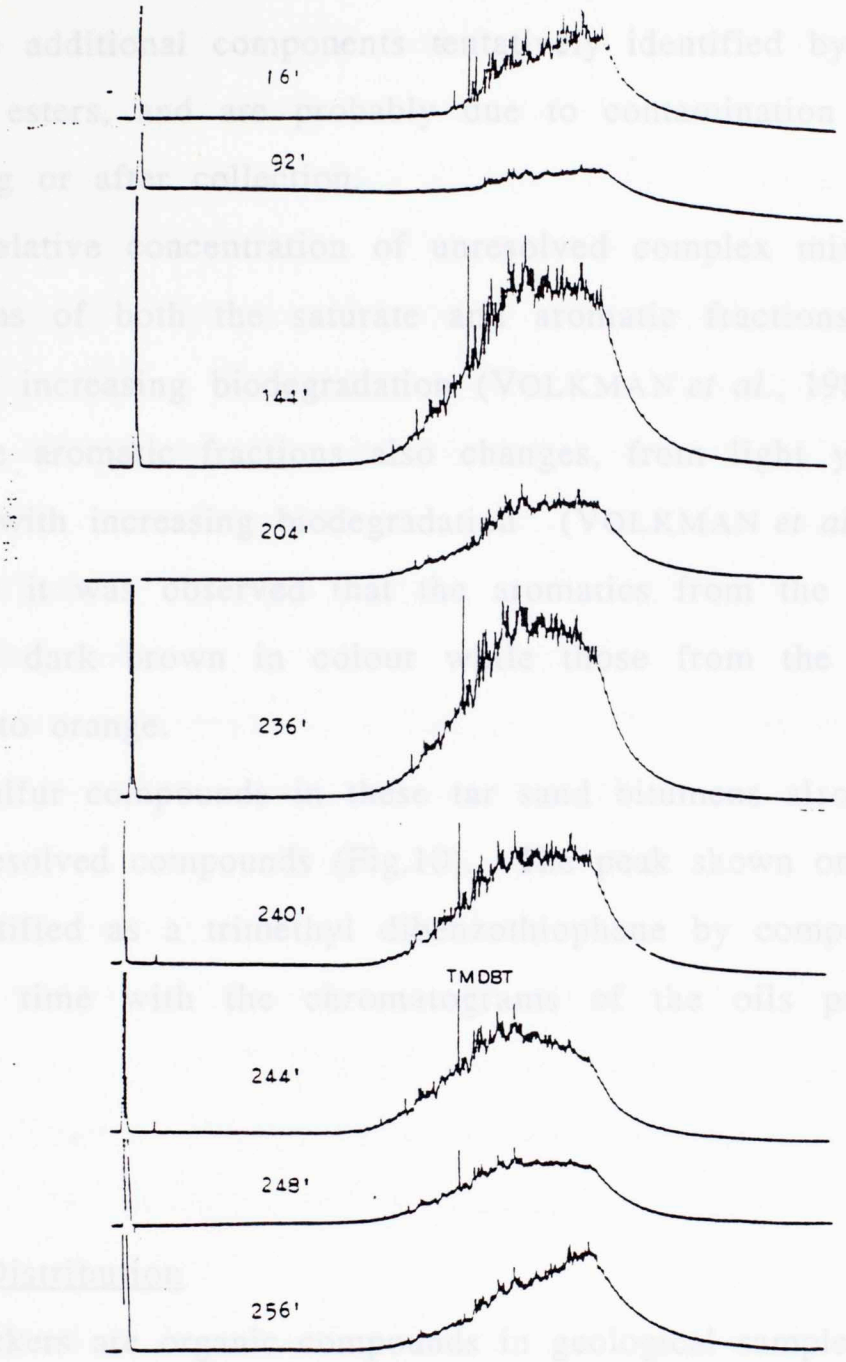


Figure 10. Gas chromatograms of aromatic fraction in tar sand bitumens detected by flame photometric detector. TMDBT= trimethyl dibenzothiophenes.

triaromatic steroid hydrocarbons. The samples from 92 and 204 ft. contain some additional components tentatively identified by GC-MS as phthalate esters, and are probably due to contamination of the sample during or after collection.

The relative concentration of unresolved complex mixtures in chromatograms of both the saturate and aromatic fractions usually increase with increasing biodegradation (VOLKMAN *et al.*, 1984). The colour of the aromatic fractions also changes, from light yellow to dark brown, with increasing biodegradation (VOLKMAN *et al.*, 1984). In this study it was observed that the aromatics from the tar sand bitumens are dark brown in colour while those from the oils are light yellow to orange.

The sulfur compounds in these tar sand bitumens also show a hump of unresolved compounds (Fig.10). The peak shown on the GC trace is identified as a trimethyl dibenzothiophene by comparison of its retention time with the chromatograms of the oils previously discussed.

Biomarker Distribution

"Biomarkers are organic compounds in geological sample that can be structually related to its precursor molecule which occurs as a natural product in a plant, animal, bacteria, spore, fungi or other potential source material" (PHILP and LEWIS, 1987). The distributions of these compounds provide information on the depositional environment (MOLDOWAN *et al.*, 1985), and the type of

organic matter preserved (PHILP and GILBERT, 1984; HUANG and MEINSCHEIN, 1976) and thermal maturity of a sample (MACKENZIE *et al.*, 1983). In the case of oil, the distributions of these biomarkers can provide information of the extent of biodegradation (e.g. SEIFERT and MOLDOWAN, 1979; VOLKMAN *et al.*, 1983) and relative migration distance (SEIFERT and MOLDOWAN, 1978; MACKENZIE, 1984). Biomarkers analyzed in this study include steranes (I), diasteranes (II), monoaromatic steroid hydrocarbons (III), triaromatic steroid hydrocarbons (IV), tricyclic terpanes (V), tetracyclic terpanes (VI), and hopanes (VII) (molecular structures shown in Appendix I). These compounds are not readily biodegraded, as compared to *n*-alkanes and isoprenoids, and therefore, are useful for correlation of biodegraded crude oils (e.g. RUBINSTEIN *et al.*, 1977; SEIFERT *et al.*, 1984). However these compounds may be degraded at very high levels of biodegradation (REED, 1977; SEIFERT and MOLDOWAN, 1979; RULLKOTTER and WENDISCH, 1982; GOODWIN *et al.*, 1983; MCKIRDY *et al.*, 1983; VOLKMAN *et al.*, 1983). The extent of biodegradation of these biomarkers in the tar sand bitumens was examined and is discussed below:

Steranes. There is a general consensus that steranes are degraded much more rapidly than diasteranes (SEIFERT and MOLDOWAN 1979; VOLKMAN *et al.*, 1983; GOODWIN *et al.*, 1983). Within the steranes, the 20R-5α(H),14α(H),17α(H) species are removed faster than their 20S homologues, and the C_{27} steranes are removed prior to the C_{28} and C_{29} species. The mass chromatograms of m/z 217 (Fig. 11)

Table 4

Identification of steranes present in crude oils and tar sand bitumens. Based on Philp (1985) and Moldowan *et al.* (1985).

Peak** No.	Compound
1	13β,17α-diacholestane (20S)
2	13β,17α–diacholestane (20R)
3	13α,17β-diacholestane (20S)
4	13α,17β-diacholestane (20R)
5	24-methyl-13β,17α-diacholestane (20S)
6	24-methyl-13β,17α-diacholestane (20R)
7	24-methyl-13α,17β-diacholestane(20S) +14α-cholestane (20S)
8	24-ethyl-13β,17α-diacholestane (20S)+14β,17β-cholestane (20R)
9	14β,17β-cholestane (20S)+24-methyl-13α,17β-diacholestane (20R)
10	14α,17α-cholestane (20R)
11	24-ethyl-13β,17α-diacholestane (20R)
12	24-ethyl-13α,17β-diacholestane (20S)
13	24-methyl-14α,17α-cholestane (20S)
14	24-ethyl-13α,17β-diacholestane(20R) + 24-methyl-14β,17β-cholestane (20R)
15	24-methyl-14β,17β-cholestane (20S)
16	24-methyl-14α,17α-cholestane (20R)
17	24-ethyl-14α,17α-cholestane (20S)
18	24-ethyl-14β,17β-cholestane (20R)
19	24-ethyl-14β,17β-cholestane (20S)
20	24-ethyl-14α,17α–cholestane (20R)
21	24-propyl-14α,17α-cholestane (20S)*
22	24-propyl-14β,17β-cholestane (20R)*
23	24-propyl-14β,17β-cholestane (20S)*
24	24-propyl-14α,17α-cholestane (20R)*

*Speculative identification based on Moldowan *et al.* (1985)

**Peak numbers correspond to those shown in Figure 11. α and β refer to the stereochemistry at the particular carbon atom that is indicated. β is above the sterane structure; α is below.

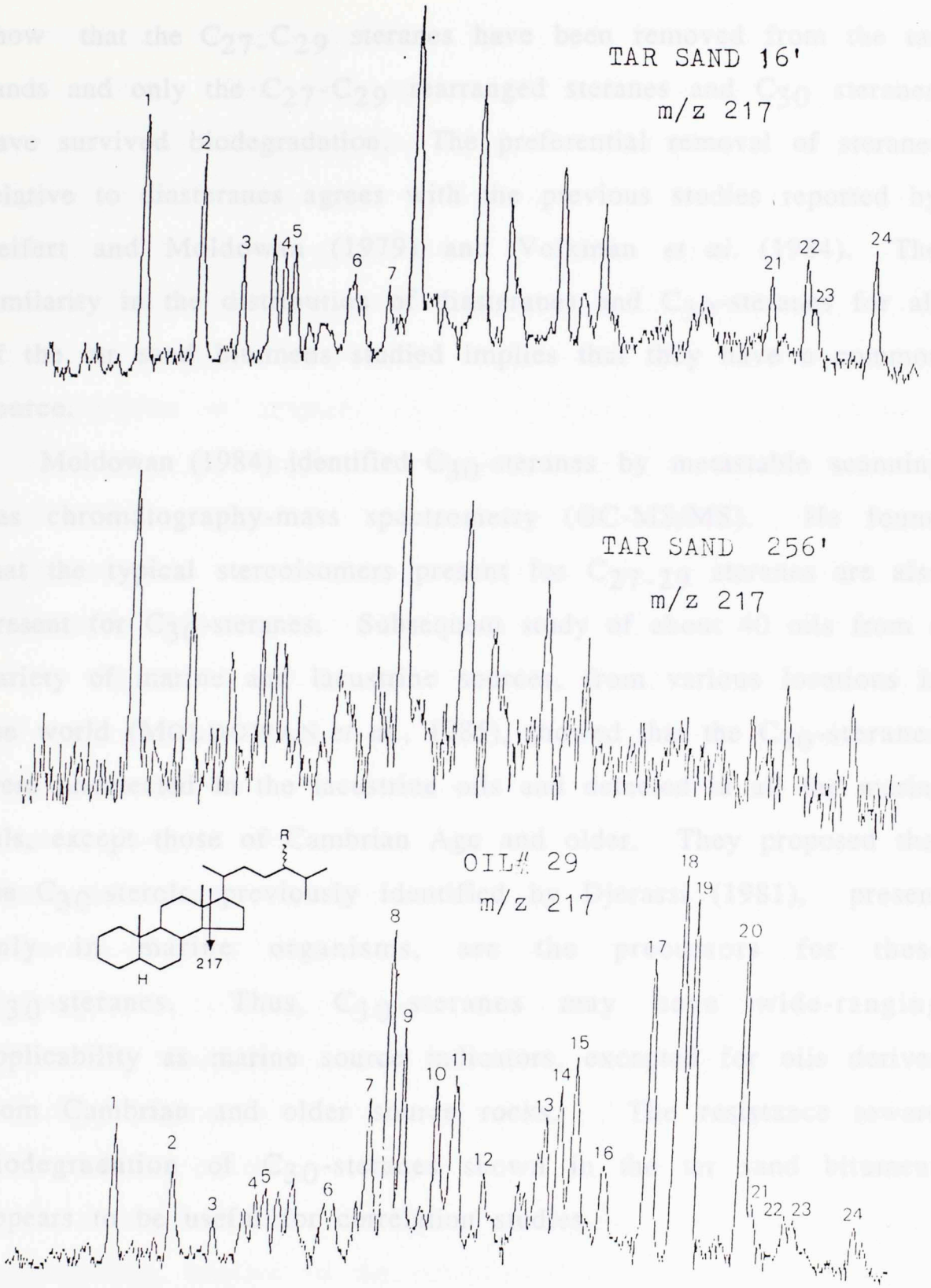


Figure 11. Mass chromatograms of sterane and diasterane (m/z 217) of tar sand bitumens and oil #29.

show that the C_{27}-C_{29} steranes have been removed from the tar sands and only the C_{27}-C_{29} rearranged steranes and C_{30} steranes have survived biodegradation. The preferential removal of steranes relative to diasteranes agrees with the previous studies reported by Seifert and Moldowan (1979) and Volkman *et al.* (1984). The similarity in the distribution of diasteranes and C_{30}-steranes for all of the tar sand bitumens studied implies that they have a common source.

Moldowan (1984) identified C_{30}-steranes by metastable scanning gas chromatography-mass spectrometry (GC-MS/MS). He found that the typical stereoisomers present for C_{27-29} steranes are also present for C_{30}-steranes. Subsequent study of about 40 oils from a variety of marine and lacustrine sources, from various locations in the world (MOLDOWAN *et al.*, 1985), showed that the C_{30}-steranes were undetected in the lacustrine oils and detected in all the marine oils, except those of Cambrian Age and older. They proposed that the C_{30}-sterols, previously identified by Djerassi (1981), present only in marine organisms, are the precursors for these C_{30}-steranes. Thus, C_{30}-steranes may have wide-ranging applicability as marine source indicators, excepted for oils derived from Cambrian and older source rocks. The resistance toward biodegradation of C_{30}-steranes shown in the tar sand bitumens appears to be useful for correlation studies.

Aromatic Steroid Hydrocarbons. The biodegradation of monoaromatic and triaromatic steroid hydrocarbons under

simulated and natural conditions have been studied by Wardroper *et al.* (1984). The major effects observed are: (i) loss of low molecular weight triaromatics (C_{20-21} species); (ii) preferential degradation of mono- and triaromatics with the 20R biological configuration; (iii) resistance of low molecular weight monoaromatics to biodegradation in comparison with their high molecular weight homologues. It was also observed that biodegradation of aromatic steroid hydrocarbons is not apparent until the C_{27-29} steranes, hopanes and C_{27-29} diasteranes have been severely degraded. As a result, the distributions of these compounds are useful for correlation and maturation studies (e.g. MACKENZIE, 1984; SEIFERT and MOLDOWAN, 1978).

Figures 12 and 13 show the monoaromatic steroid (m/z 253) and triaromatic steroid hydrocarbon (m/z 231) distributions, respectively, of the tar sand bitumens. The similarity of these mass chromatograms further shows that these tar sand bitumens are genetically related. The absence of C_{20} and C_{21} triaromatic steroid hydrocarbons is probably due to preferential removal during water washing or biodegradation, as documented by Wardroper *et al.* (1984) and Volkman *et al.* (1984). It is still unclear why the C_{20} and C_{21} triaromatic steroids are degraded in preference to the monoaromatic steroids.

A slight decrease in C_{27}-C_{28} 20R triaromatic steroid hydrocarbons, relative to the corresponding 20S isomers, was also observed (Fig 13). The preferential removal of the 20R species is similar to the preferential decrease of 5α(H),14α(H),17α(H)-20R

Table 5

Structure information relating to mono- (m/z 253) and tri- (m/z 231) aromatic steroid hydrocarbons. Based on Wardroper *et al.* (1984) and Mackenzie (1984).

PEAK	m/z	CARBON NUMBER	STEREO-CHEMISTRY
1	253	21	5βH
2	253	22	5βH
3	253	27	5βH, 20S
4	253	27	- ?
5	253	27	5βH, 20R
6	253	27	5αH, 20S
	253	28	5βH, 20S
	253	27	5αH, 20R
7	253	28	5αH, 20S
	253	28	5βH, 20R
	253	29	5βH, 20S
8	253	29	5αH, 20S
9	253	28	5αH, 20R
	253	29	5βH, 20R
10	253	29	5αH, 20R
11	231	26	20S
12	231	26	20R
	231	27	20S
13	231	28	20S
14	231	27	20R
15	231	28	20R

Peak numbers correspond to those shown in Fig. 12, 13, 17 and 18. α, β refer to the stereochemistry at particular carbon atom that is indicated. α is above the monoaromatic steroid hydrocarbon structure; β is below.

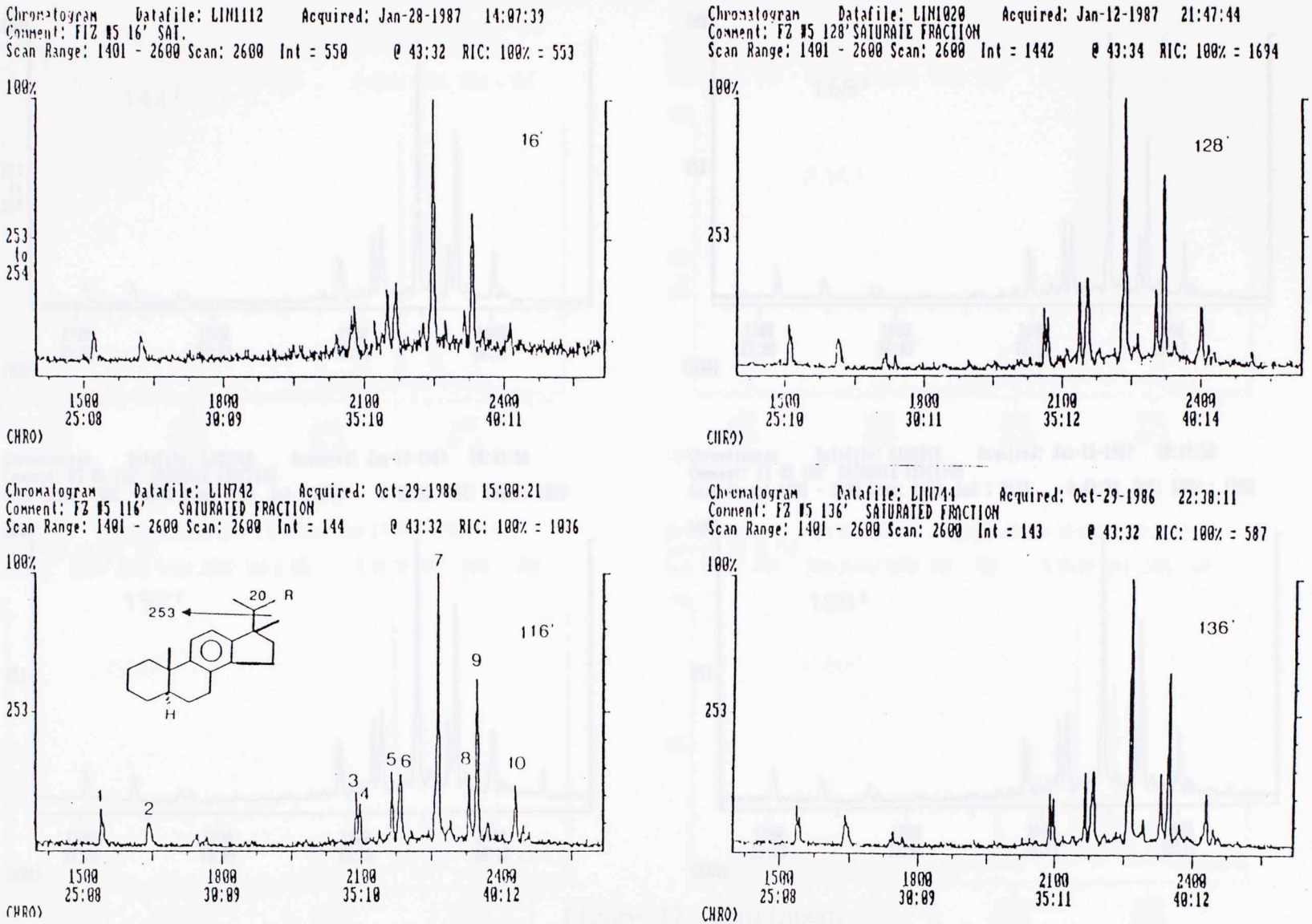
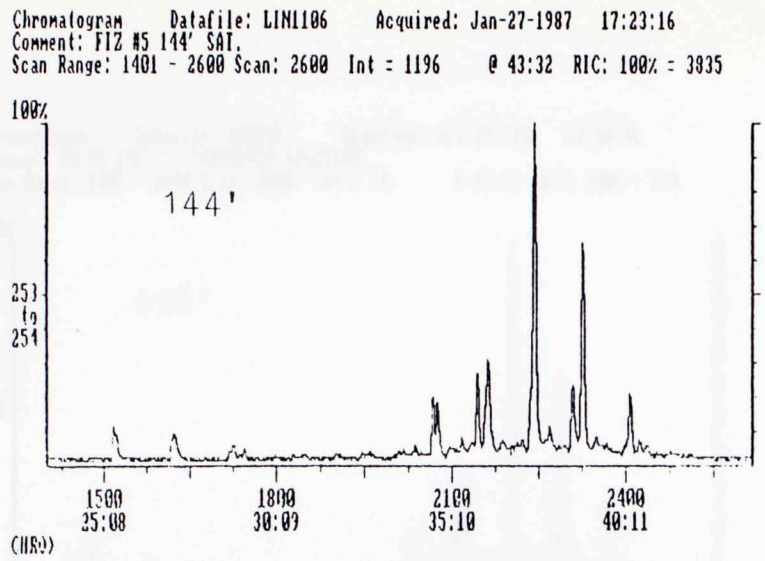
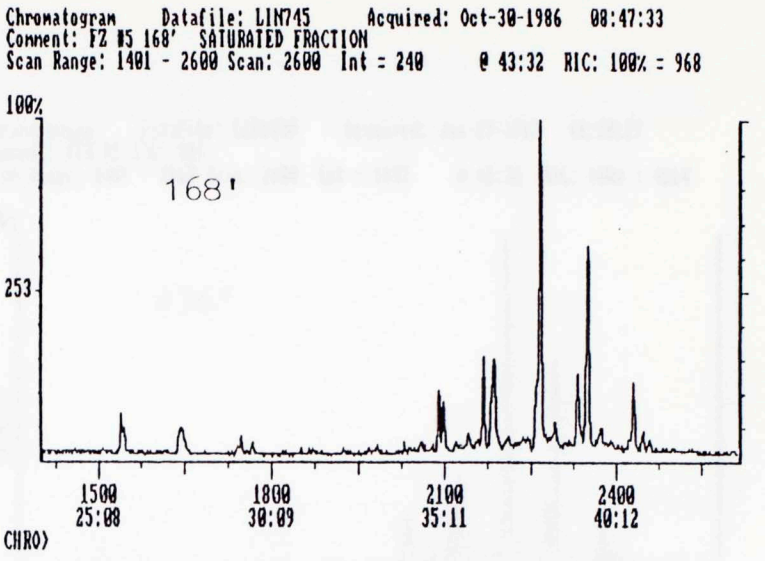
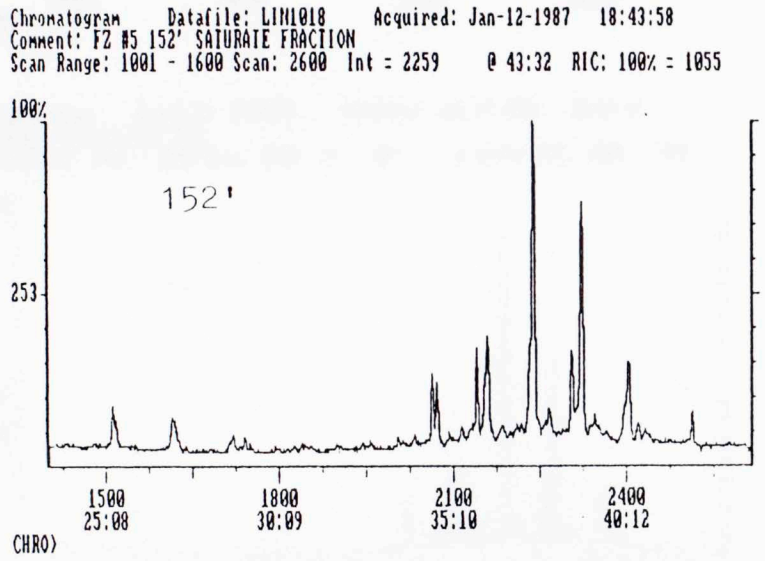


Figure 12. Mass chromatograms of monoaromatic steroid hydrocarbons (m/z 253) in tar sand bitumens.







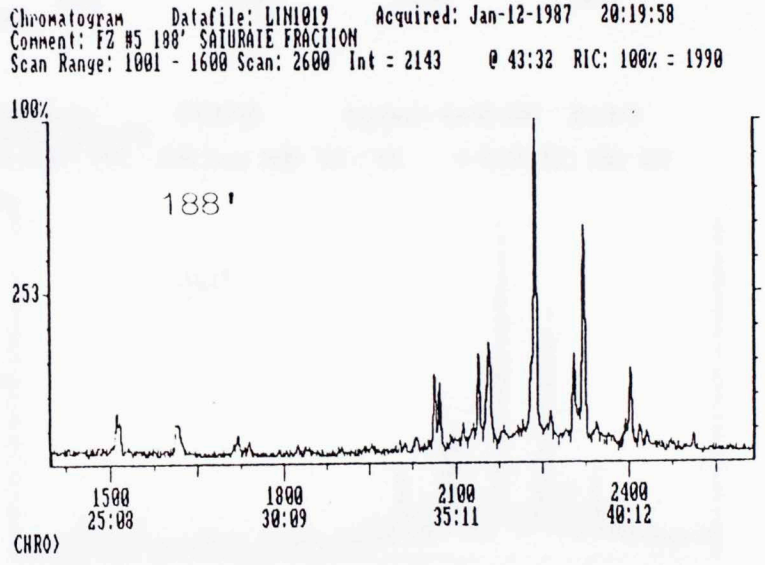
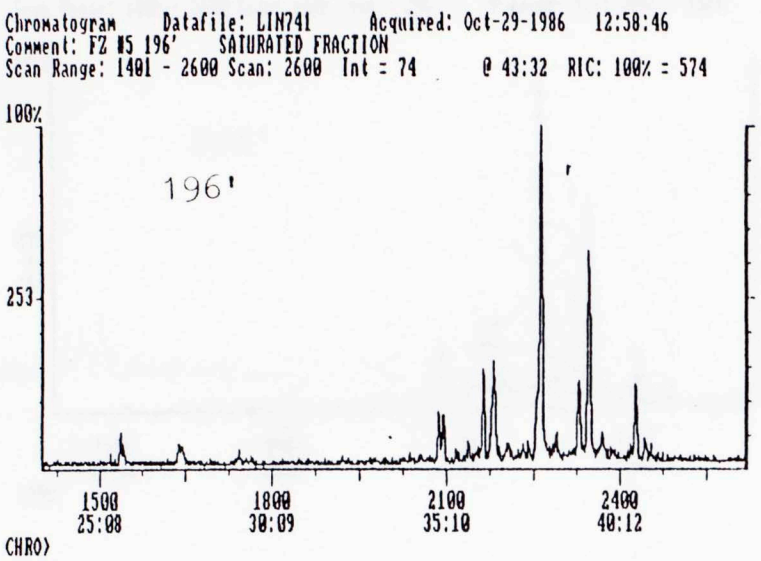
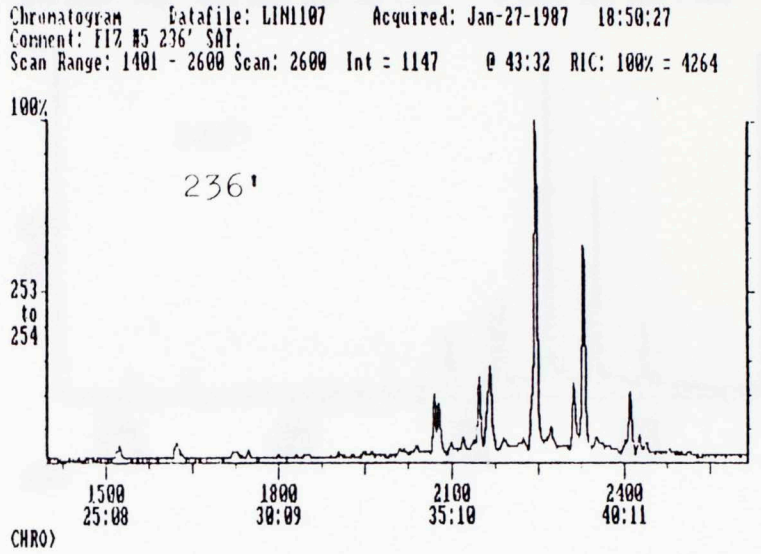
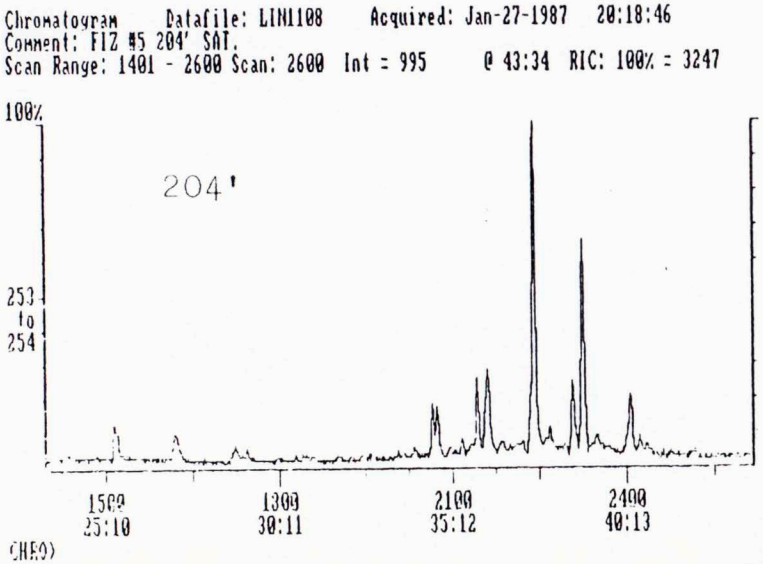


Figure 12. Continued.







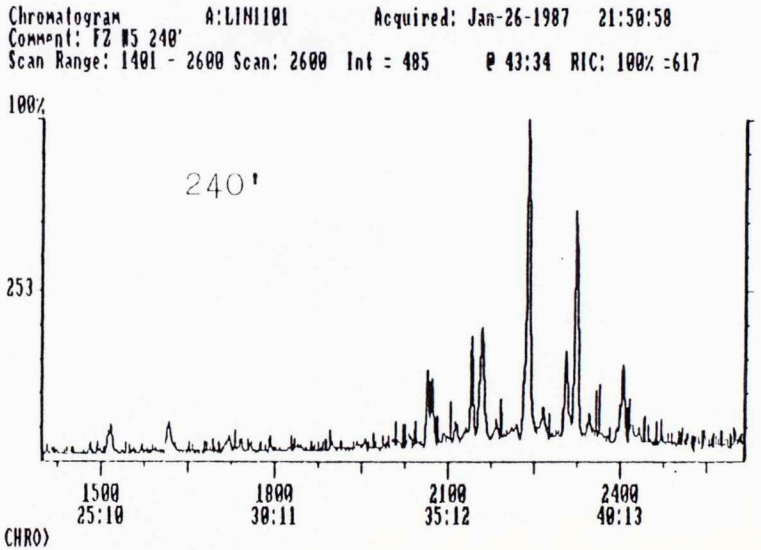
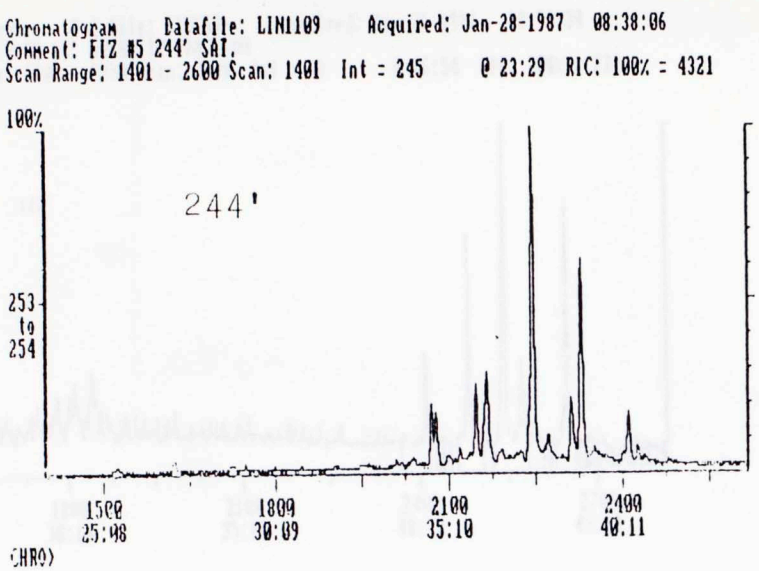
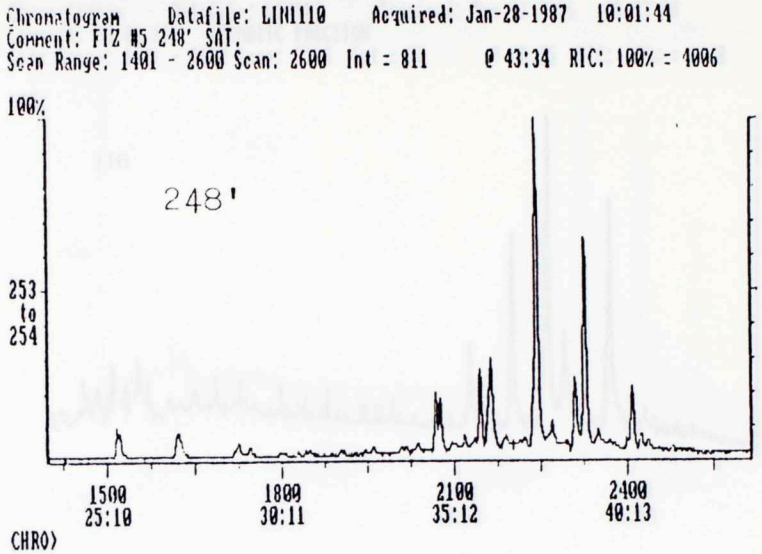


Figure 12. Continued.





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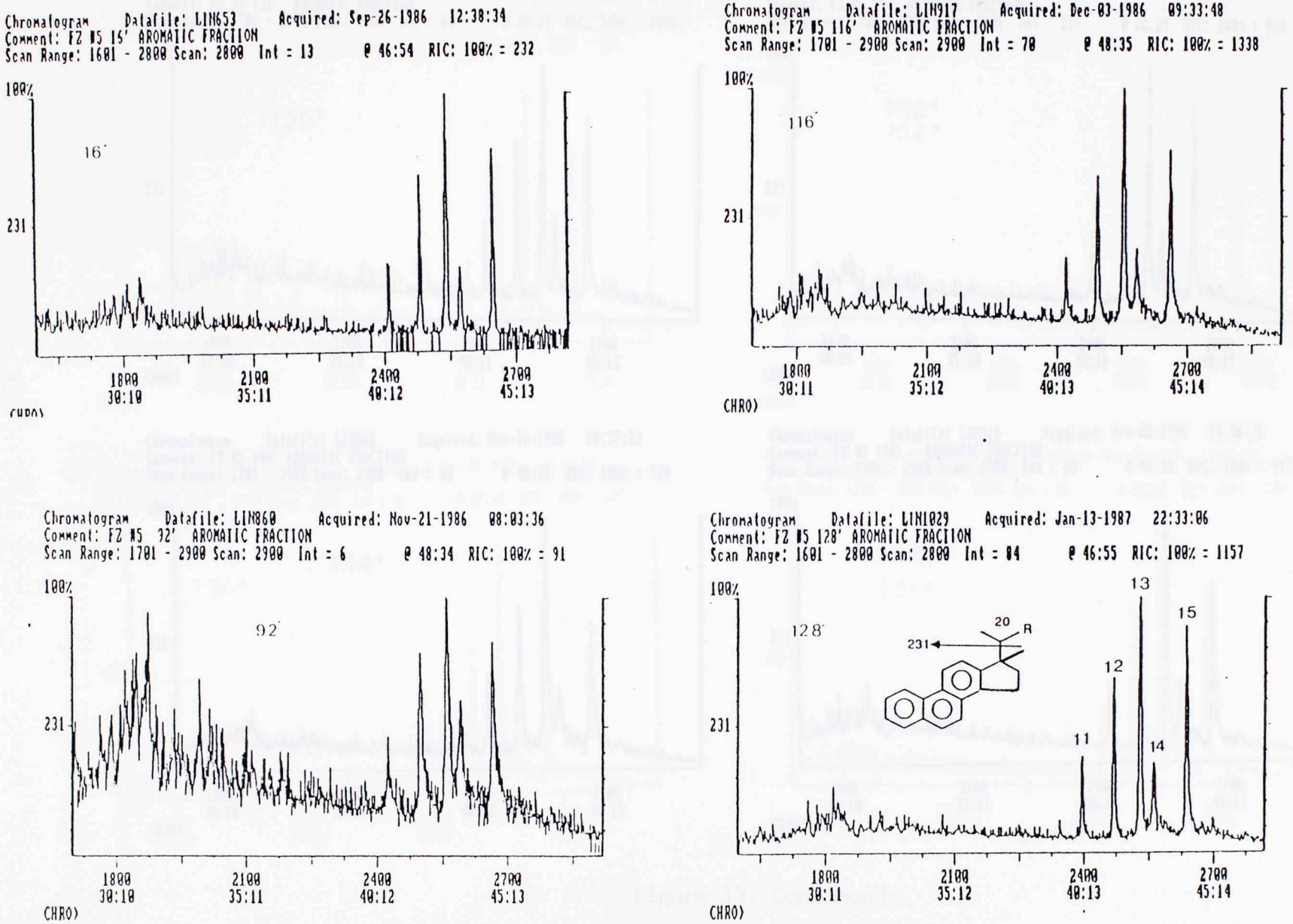
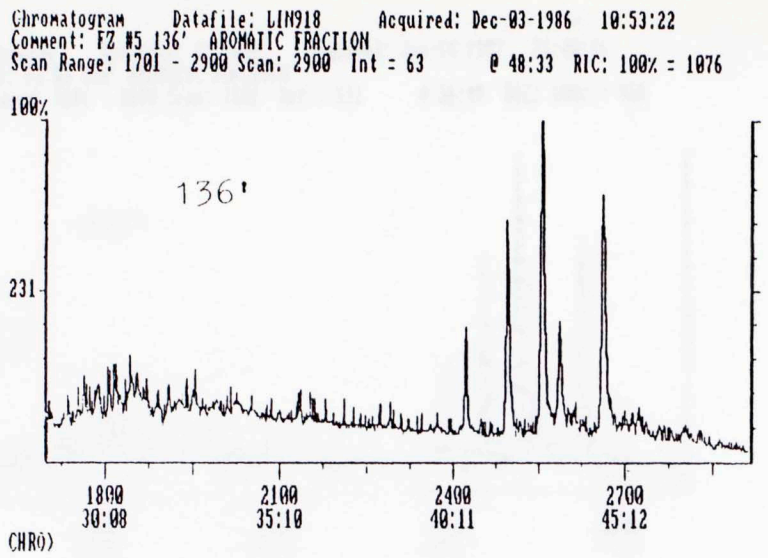
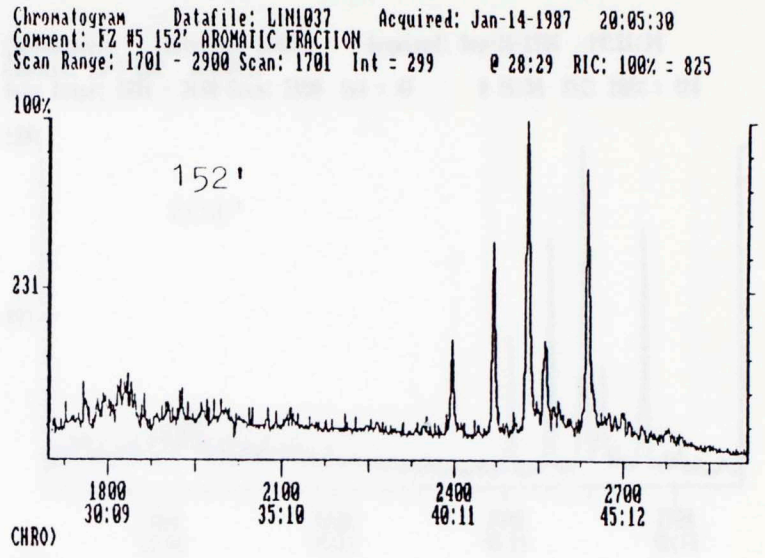
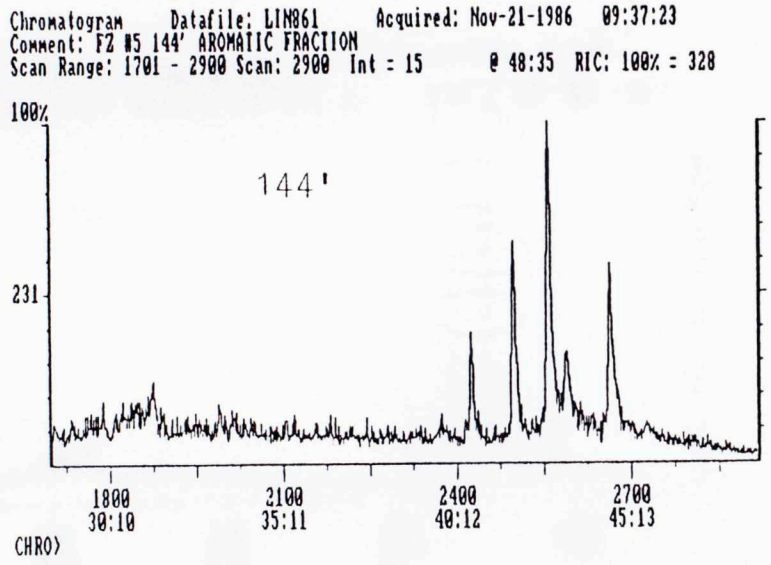


Figure 13. Mass chromatograms of triaromatic steroid hydrocarbons (m/z 231) in tar sand bitumens.







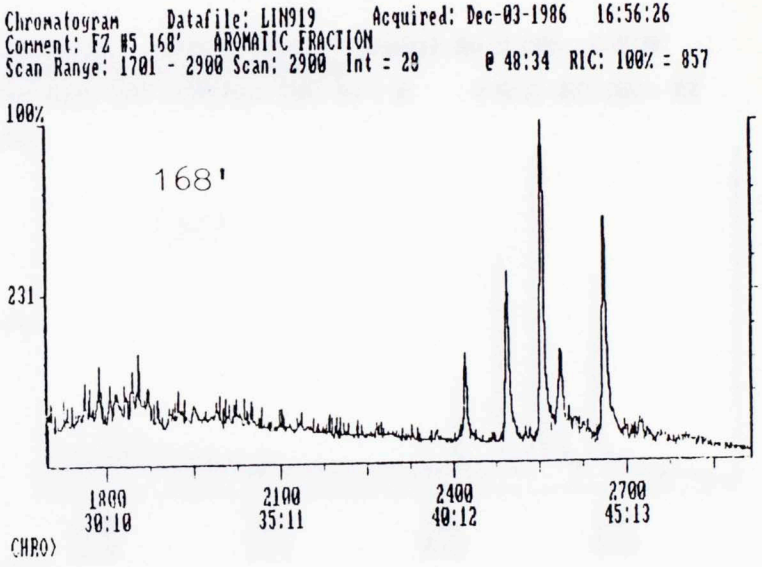
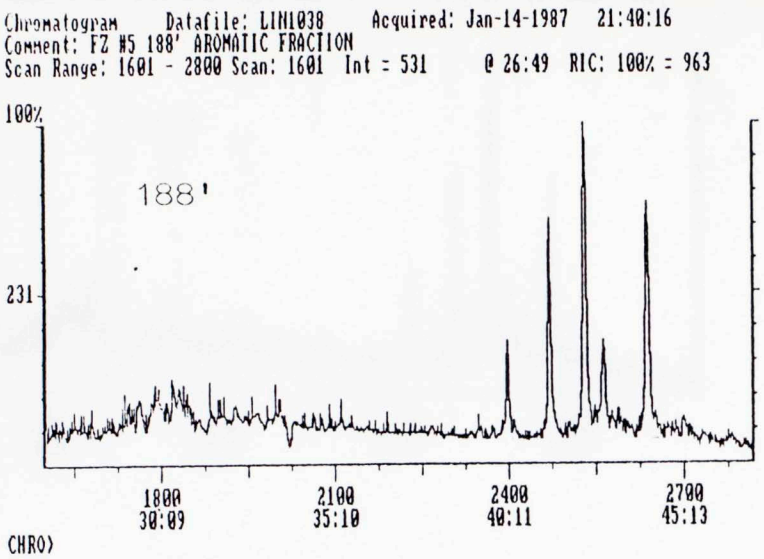
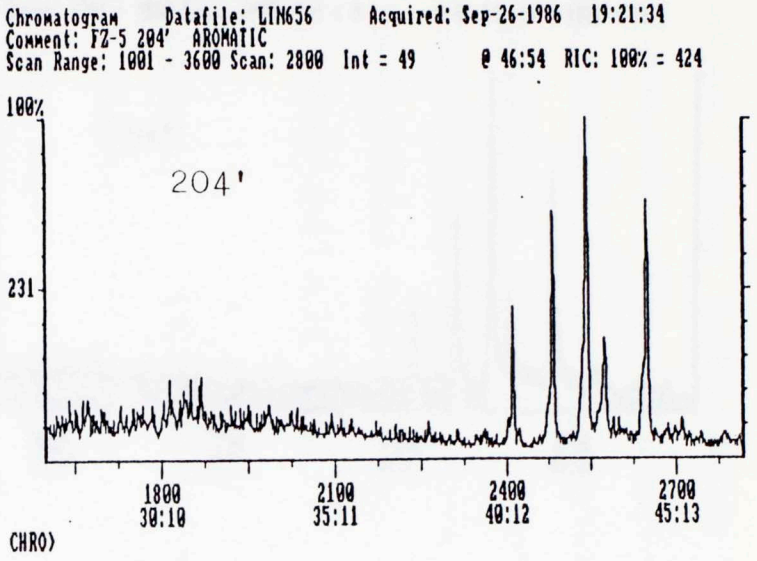
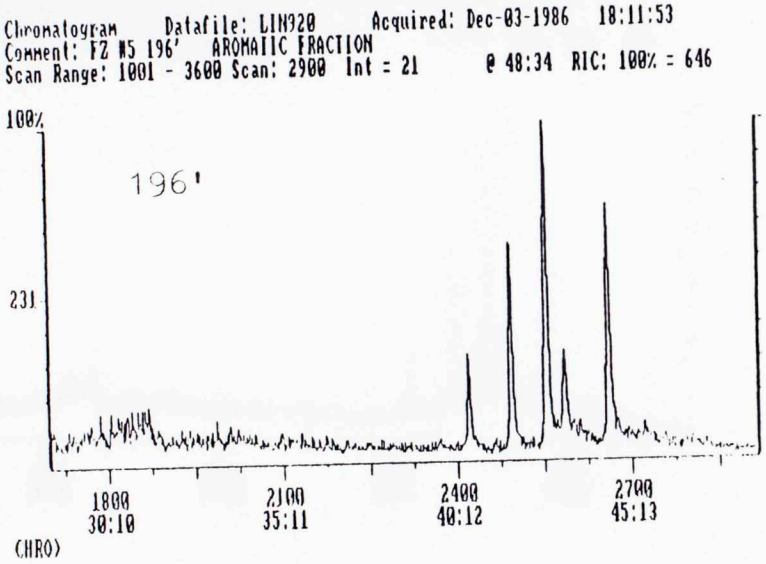


Figure 13. Continued.







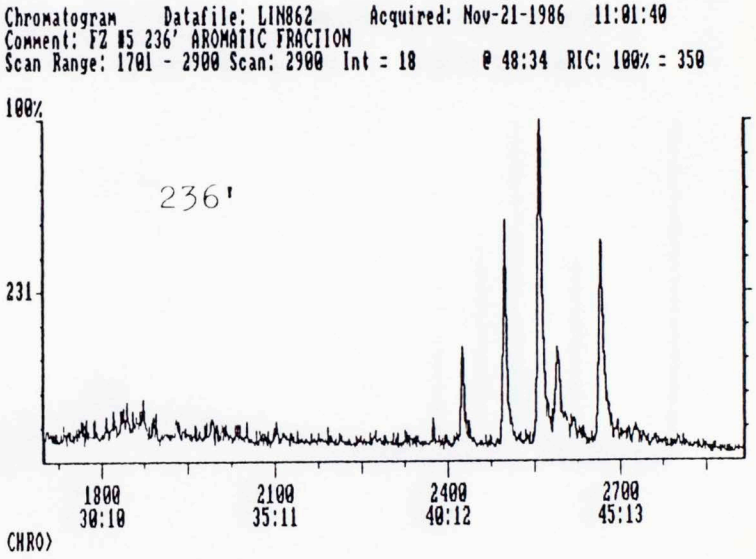
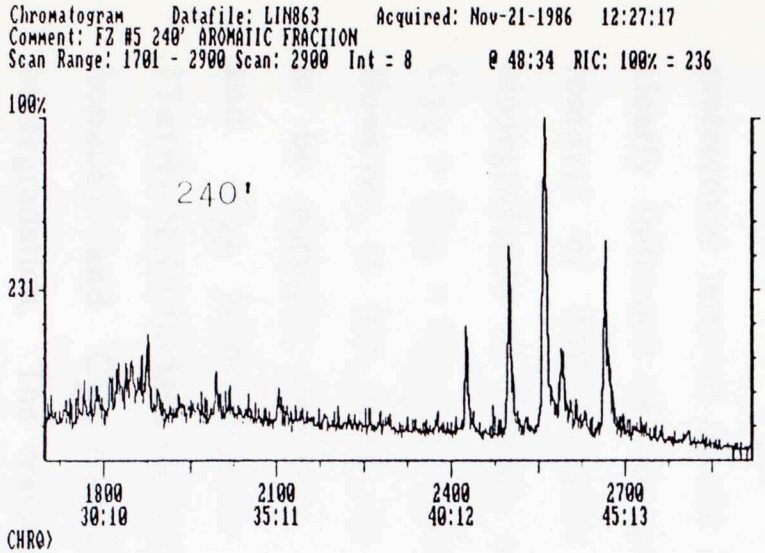
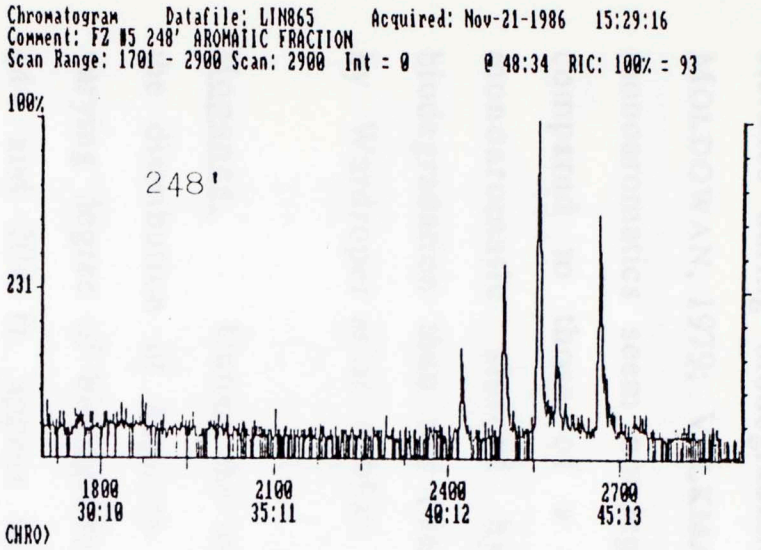
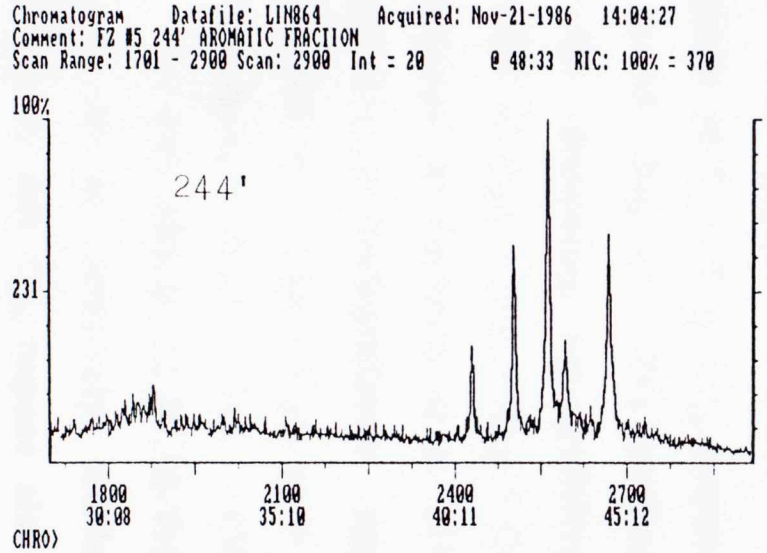


Figure 13. Continued.







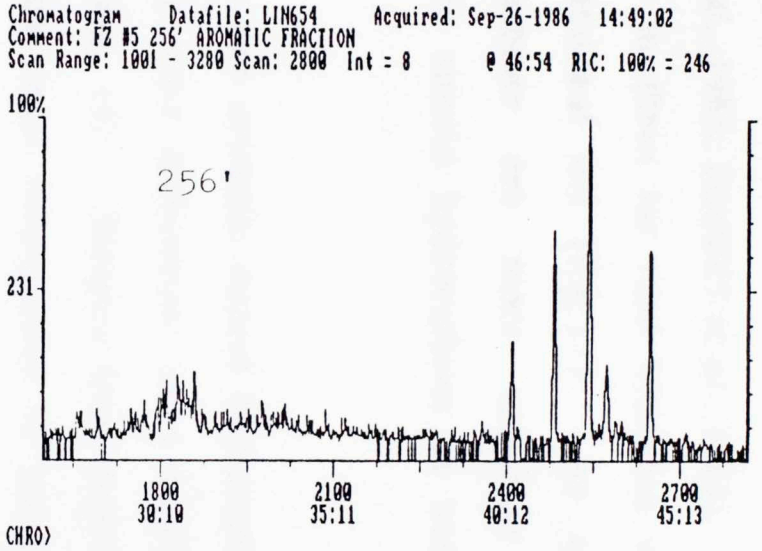


Figure 13. Continued.

steranes during biodegradation (GOODWIN *et al.*, 1983; SEIFERT and MOLDOWAN, 1979; VOLKMAN *et al.*, 1983; SEIFERT *et al.*, 1984). The monoaromatics seem nondegraded in these tar sand bitumens when compared to those of a conventional oil (Fig.17). As such, monoaromatic steroid hydrocarbons are more resistant to biodegradation than the triaromatic steroid hydrocarbons as noticed by Wardroper *et al.* (1984).

Hopanes. Unlike the steranes and aromatic steroid hydrocarbons, the distribution of hopanes shows some differences, as a result of varying degree of biodegradation (Fig. 14). Samples from depths of 144 and 204 ft. appear to be the least biodegraded in terms of hopane distribution (Appendix III). The others show variation in the decrease of C_{30+} hopanes with respect to depth. The preferential removal of the 22R epimer of C_{31}, C_{32}, C_{33} hopanes is clearly indicated in the sample at 16' (Fig.14). The preferential removal of 22R hopanes, and the decreasing susceptibility to biodegradation of hopanes in the order of $C_{35} > C_{34} > C_{33} > C_{32} > C_{31} > C_{30} > C_{29}$ has been documented by Goodwin *et al.* (1983). However, in this study the susceptibility of biodegradation appears to be partially reversed, and the order is $C_{30} > C_{31\text{-}33} > C_{34}$ and C_{35} homologues. Moretanes and Tm (VIII; 17α(H)-22,29,30-Trisnorhopane), Ts (IX; 18α(H)-22,29,30-Trisnor hopane) and C_{29}-hopane appear to be relatively stable to biodegradation. The resistance of Tm, Ts and C_{29}-hopane also had been reported by Seifert *et al.* (1984). However, compared to the

Table 6

Identification of terpanes present in oils and tar sand bitumens. Based on Philp (1985), Ekweozor and Strausz (1983) and Aquino Neto *et al.* (1983).

Peak No.	Symbol	Compund	Formula
1	19*	C_{19}-tricyclic terpane	$C_{19}H_{34}$
2	20*	C_{20}-tricyclic terpane	$C_{20}H_{36}$
3	21*	C_{21}-tricyclic terpane	$C_{21}H_{38}$
4	23*	18,19-bisnor-13βH, 14αH-cheilanthane	$C_{23}H_{42}$
5	24*	C_{24}-tricyclic terpane	$C_{24}H_{44}$
6	25*	C_{25}-22S+22R-tricyclic terpane	$C_{25}H_{46}$
7	24*	C_{24}-17(21) secohopane	$C_{24}H_{42}$
8	26*	C_{26}-22S-tricyclic terpane.	$C_{26}H_{48}$
9	26*	C_{26}-22R-tricyclic terpane	$C_{26}H_{48}$
10	28*	C_{28}-22S-tricyclic terpane	$C_{28}H_{52}$
11	28*	C_{28}-22R-tricyclic terpane	$C_{28}H_{52}$
12	29*	C_{29}-22S-tricyclic terpane	$C_{29}H_{54}$
13	29*	C_{29}-22R-tricyclic terpane	$C_{29}H_{54}$
14	Ts	18αH-22, 29, 30-trisnorhopane	$C_{27}H_{46}$
15	Tm	17αH-22, 29, 30-trisnorhopane	$C_{27}H_{46}$
16	30*	C_{30}-22S-tricyclic terpane	$C_{30}H_{56}$
17	30*	C_{30}-22R-tricyclic terpane	$C_{30}H_{56}$
18	C_{29}	17αH, 21βH-30-norhopane	$C_{29}H_{50}$
M_1	M_1	17βH, 21αH-30-normoretane	$C_{29}H_{50}$
19	C_{30}	17αH, 21βH-hopane	$C_{30}H_{52}$
M_2	M_2	17βH, 21αH-moretane	$C_{30}H_{52}$
20	C_{31}	17αH, 21βH, 22S-30-homohopane	$C_{31}H_{54}$
21	C_{31}	17αH, 21βH, 22R-30-homohopane	$C_{31}H_{54}$
22	C_{32}	17αH, 21βH, 22S-30, 31-bisnomohopane	$C_{32}H_{56}$
23	C_{32}	17αH, 21βH, 22R-30, 31-bisnomohopane	$C_{32}H_{56}$
24	C_{33}	17αH, 21βH, 22S-30, 31, 32-trisnomohopane	$C_{33}H_{58}$
25	C_{33}	17αH, 21βH, 22R-30, 31, 32-trisnomohopane	$C_{33}H_{58}$
26	C_{34}	17αH, 21βH, 22S-C_{34} extended hopane	$C_{34}H_{60}$

27	C_{34}	17αH, 21βH, 22R-C_{34} extended hopane	$C_{34}H_{60}$
28	C_{35}	17αH, 21βH, 22S-C_{35} extended hopane	$C_{35}H_{62}$
29	C_{35}	17αH, 21βH, 22R-C_{35} extended hopane	$C_{35}H_{62}$

Peak symbols correspond to those shown in Figure 14, 15 and 16. α and β refer to the stereochemistry at the particular carbon atom that is indicated. α is below the ring structure, β is above.

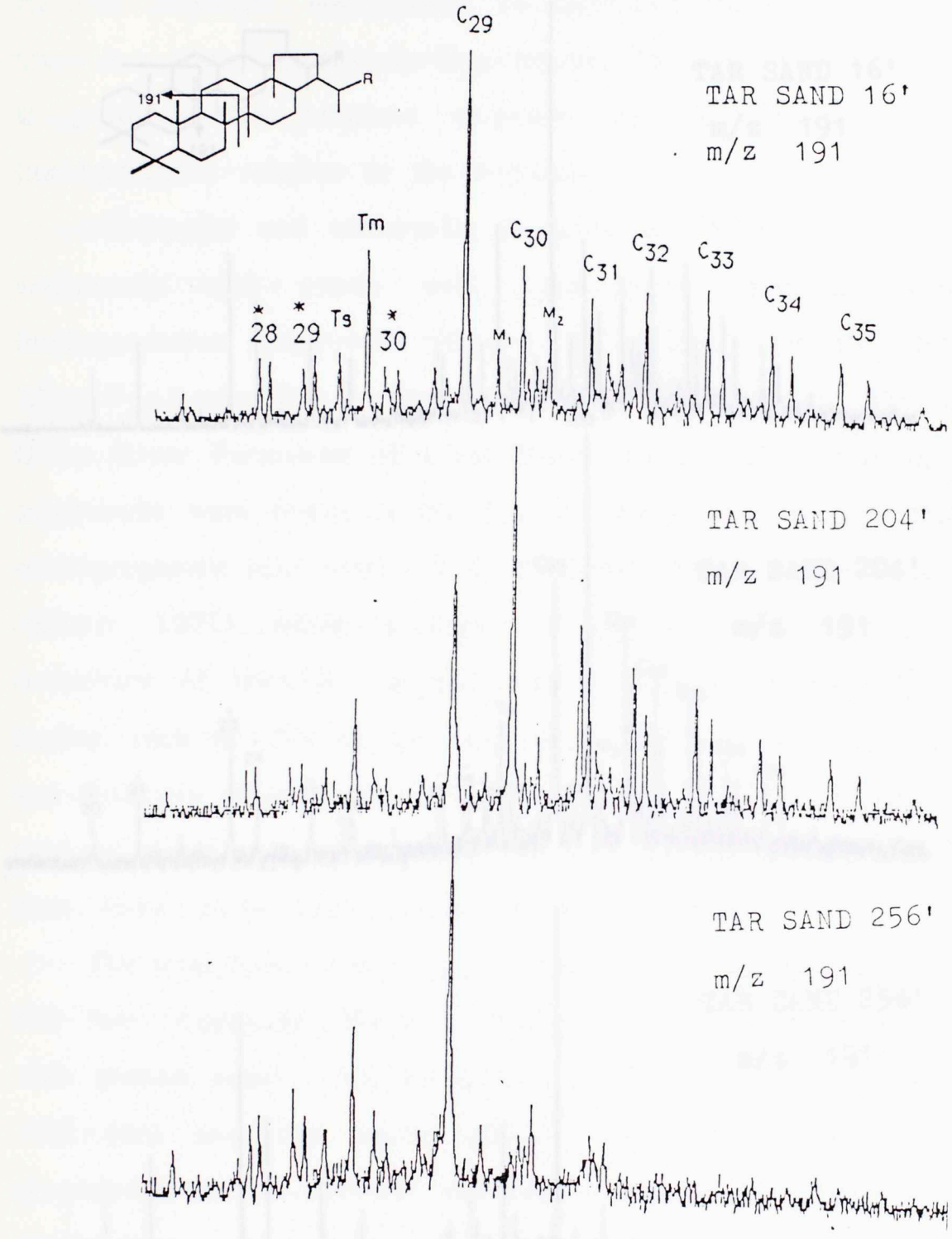


Figure 14. M/z 191 mass chromatograms of tar sand bitumens showing the preferential decrease of C_{30+} hopanes.

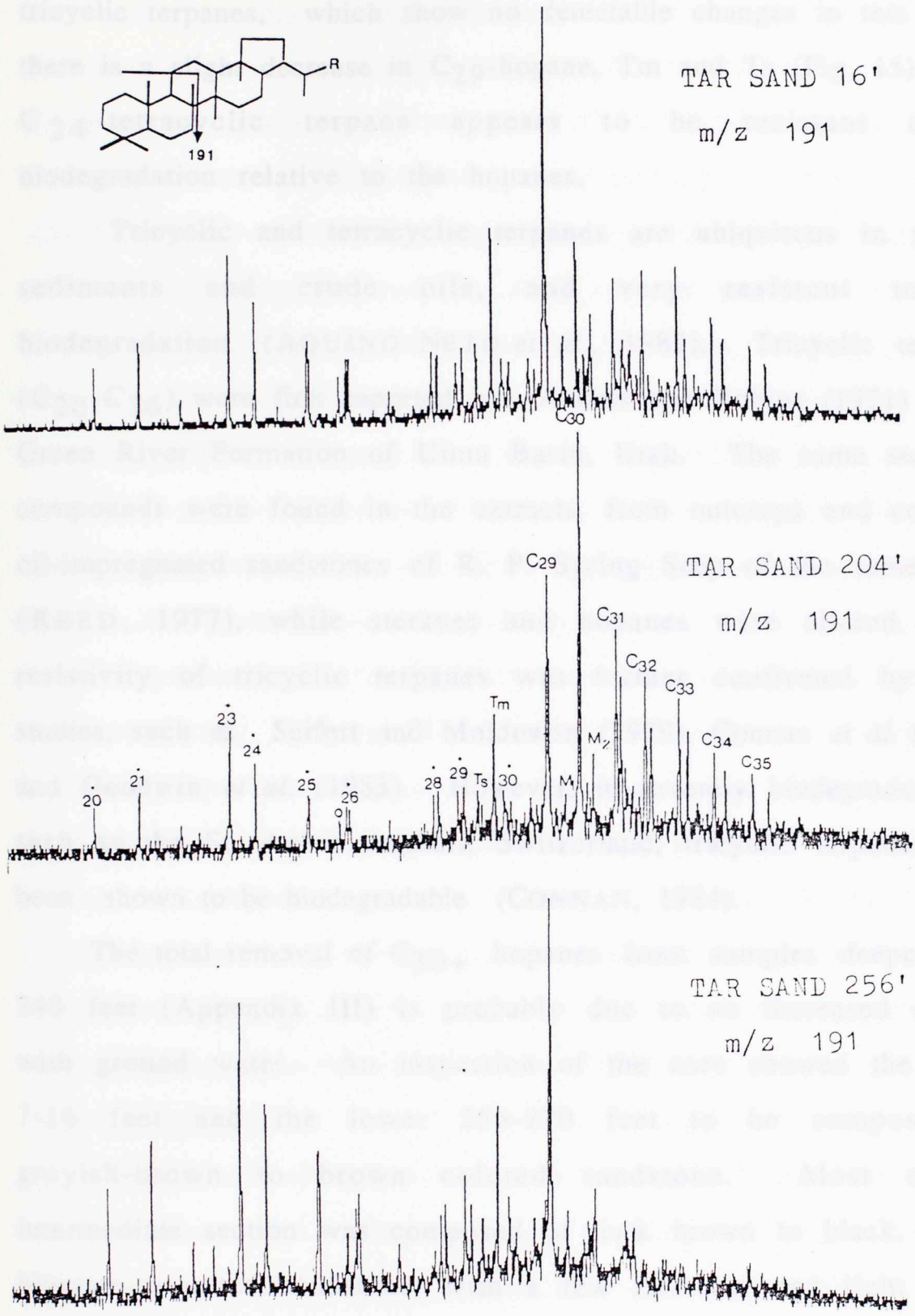


Figure 15. M/z 191 mass chromatograms of tar sand bitumens showing the decrease of hopanes relative to tricyclic terpanes.

tricyclic terpanes, which show no detectable changes in this study, there is a slight decrease in C_{29}-hopane, Tm and Ts (Fig. 15). The C_{24}-tetracyclic terpane appears to be resistant toward biodegradation relative to the hopanes.

Tricyclic and tetracyclic terpanes are ubiquitous in ancient sediments and crude oils, and very resistant towards biodegradation (AQUINO NETO *et al.*, 1983). Tricyclic terpanes (C_{20}-C_{26}) were first reported by Anders and Robins (1971) in the Green River Formation of Uinta Basin, Utah. The same series of compounds were found in the extracts, from outcrops and cores of oil-impregnated sandstones of R. P. Spring Seep of the same basin (REED, 1977), while steranes and hopanes were altered. The resistivity of tricyclic terpanes was further confirmed by other studies, such as Seifert and Moldowan (1979), Connan *et al.* (1980) and Goodwin *et al.* (1983). However, in severely biodegraded oils, such as the St. Aubin Asphalt, Switzerland, tricyclic terpanes have been shown to be biodegradable (CONNAN, 1984).

The total removal of C_{30+} hopanes from samples deeper than 240 feet (Appendix III) is probably due to an increased contact with ground water. An inspection of the core showed the upper 7-16 feet and the lower 256-270 feet to be composed of greyish-brown to brown colored sandstone. Most of the intermediate section was composed of dark brown to black, highly bitumen-saturated sandstone, with a few fractures and light brown sandstone strings. This implies that the upper and lower parts of the tar sand are more accessible to water and, hence, more severely

degraded than the middle section. It is known that bacterial degradation occurs at the oil-water interface, because bacteria live in the aqueous phase and do not thrive in oil (CONNAN, 1984). Some microorganisms can even produce extracellular materials that can adsorb, emusify or wet the hydrocarbon phase of the tar sand, in order to increase the contact area and to produce sub-micron droplets to be phagocytized (ZAJIC and GERSON, 1977). However, more complex mechanisms may be involved. For example, since some heavy oil is seeping out along the crest of the South Woodford Anticline, active migration of heavy oil from a reservoir in the vicinity may be mixing with the tar sand bitumen and causing changes in the distribution of hopanes.

In summary, the tar sand bitumens are so severely biodegraded that *n*-alkanes, isoprenoids, light aromatics, thiophenes, benzothiophene and steranes are removed. The sample from a depth of 240 feet is different since it contains C_{14}-C_{24} *n*-alkanes, pristane and phytane. However, the lack of steranes and severely altered hopanes implies that the *n*-alkanes, pristane and phytane have been recently added to this sample, either by contamination during coring or extraction, or by *in situ* mixing with some migrated light oil.

Hopanes are altered to a variable extent, with the most severely biodegraded samples having depths in the range of 240 to 256 feet. The less degraded samples occurred at depths of 144 and 204 feet. This unsystematic variation in the hopane distributions, as a function of depth, probably reflects the complexity of ground water

saturation or heavy oil migration that causes a variable extent of biodegradation. This variation demonstrates the susceptibility of the hopane series towards biodegradation in the study area. The degradation of hopanes starts with the C_{30}-hopane, at a relatively slow rate, while the 22R C_{31-33} hopanes degrade rapidly after the incipient degradation of the C_{30}-hopane. Moretanes, C_{29}-hopane, Tm and Ts decrease slightly after the C_{30+} hopane have been totally removed.

Ring A/B demethylated hopanes (X) could not be identified and, hence, the degradation of hopanes does not appear to produce demethylated components in this case. The ring A/B demethylated hopanes isolated from a biodegraded asphalt, and identified by Rullkotter and Wendisch (1982), have been proposed to be the biodegradation products of 17α(H)-hopanes. These demethylated hopane series, with a characteristic fragment ion at m/z 177, have a similar retention patern to, but elute slightly earlier than, the corresponding hopane series (ALEXANDER *at al.*, 1983). In severely biodegraded crude oils, it has been proposed that the demethylated hopanes can be used as maturity parameters, in the same way as the regular hopanes are used in nondegraded oils (VOLKMAN *et al.*, 1983). However, the biodegradation of hopanes does not always produce ring A/B demethylated hopanes (CONNAN. 1984). An *in vitro* study carried out by Goodwin *et al.* (1984) also failed to produce demethylated hopanes, though the 17α(H)-hopanes were degraded.

Although the occurrence of demethylated hopanes was first

reported in biodegraded crude oils and asphalt (REED, 1977; SEIFERT and MOLDOWAN, 1979; RULLKOTTER and WENDISCH, 1982; VOLKMAN *et al.*, 1983), these compounds are also present in seemly nonbiodegraded oils (PHILP, 1983; VOLKMAN *et al.*, 1983; HOWELL *et al.*, 1984). As such, the origin of these demethylated hopanes needs to be studied further, although in many cases the proposed mixing of degraded and nondegraded oils can be used to explain their presence.

Diasteranes, C_{30}-steranes, tricyclic terpanes and monoaromatic steroids are rather resistant toward biodegradation and are suitable for correlation studies. Triaromatic steroids are slightly altered with the result that C_{20} and C_{21} species are absent and there is a reduction of C_{27-28} 20R species.

The biodegradation effects summarized from the study of tar sand bitumens of the Fitzgerald core, when compared to that of the tar sand bitumen from the South Sulphur Asphalt deposits, in which the C_{30+} hopanes degraded faster than C_{27}-C_{29} steranes (MIILLER *et al.*, 1984), illustrates the unpredictability of the relative order of degradation of hopanes and steranes.

CHAPTER IV

CORRELATION OF TAR SAND BITUMEN WITH OIL FROM THE PAULS VALLEY AREA

The oils from the Pauls Valley area have been classified into two major groups on the basis of their biomarker distributions (JONES, 1986). Thus, two representative oils, namely Viola oil #20 and Oil Creek oil #29, are used for correlation with the tar sand bitumen. Viola oil #20 is characterized by the high ratio of the C_{24}-tetracyclic terpane to the C_{26}-tricyclic terpanes; diminished concentration of the C_{28-30} tricyclic terpanes relative to Tm and Ts; reduced concentration of C_{30}-steranes relative to their C_{29} counterparts, and a predominance of the C_{35} over the C_{34} extended hopanes. Aquino Neto *et al.* (1983) observed that the C_{26+} tricyclic terpane series may be relatively weak in carbonate samples, compared to their lower molecular weight homologues. The high C_{35}/C_{34} ratio of extended hopanes is one characteristic of carbonate sourced oils (MCKIRDY *et al.*, 1983, RULLKOTTER *et al.*, 1985). Collectively, these parameters indicate that Viola oil #20 is sourced from a carbonate source rock, probably the Viola Limestone

itself (JONES, 1986).

Oil #29 was chosen not only because it is representative of the majority of oils from the Pauls Valley area, but also because it is of similar maturity (Tm/Ts) to that of the tar sand bitumen. It is important to correlate oils at the same stage of maturity because differences in maturity will cause variation in biomarker distributions, making correlations difficult. For example, highly mature oils will contain more tricyclic and tetracyclic terpanes, relative to pentacyclic hopanes, because of the preferential decrease of C_{30+} extended hopanes during thermal maturation (AQUINO NETO *et al.*, 1983). For the aromatic steroid hydrocarbons, the short-chain homologues (C_{20-22}) relative to their C_{26}-C_{29} homologues become concentrated due to their resistance toward thermal cracking (RIOLO *et al.*, 1986). Thus, the ratio of C_{21} to C_{28} triaromatic steroid hydrocarbons has been used as a maturation indicator by Sofer *et al.* (1986).

Biomarkers. Figure 16 shows the m/z 191 mass chromatograms of oil #20, #29 and the tar sand bitumen from a depth of 204 ft. It is apparent from these chromatograms that oil #29 and the tar sand bitumen have almost identical tricyclic, tetracyclic and pentacyclic terpane distributions. Oil #20 differs from the tar sand bitumen by containing a higher C_{24}-tetracyclic terpane and higher C_{35}-hopanes.

Aromatic steroid hydrocarbons are not readily affected by biodegradation until the C_{27}-C_{29} steranes, hopanes and C_{27}-C_{29}

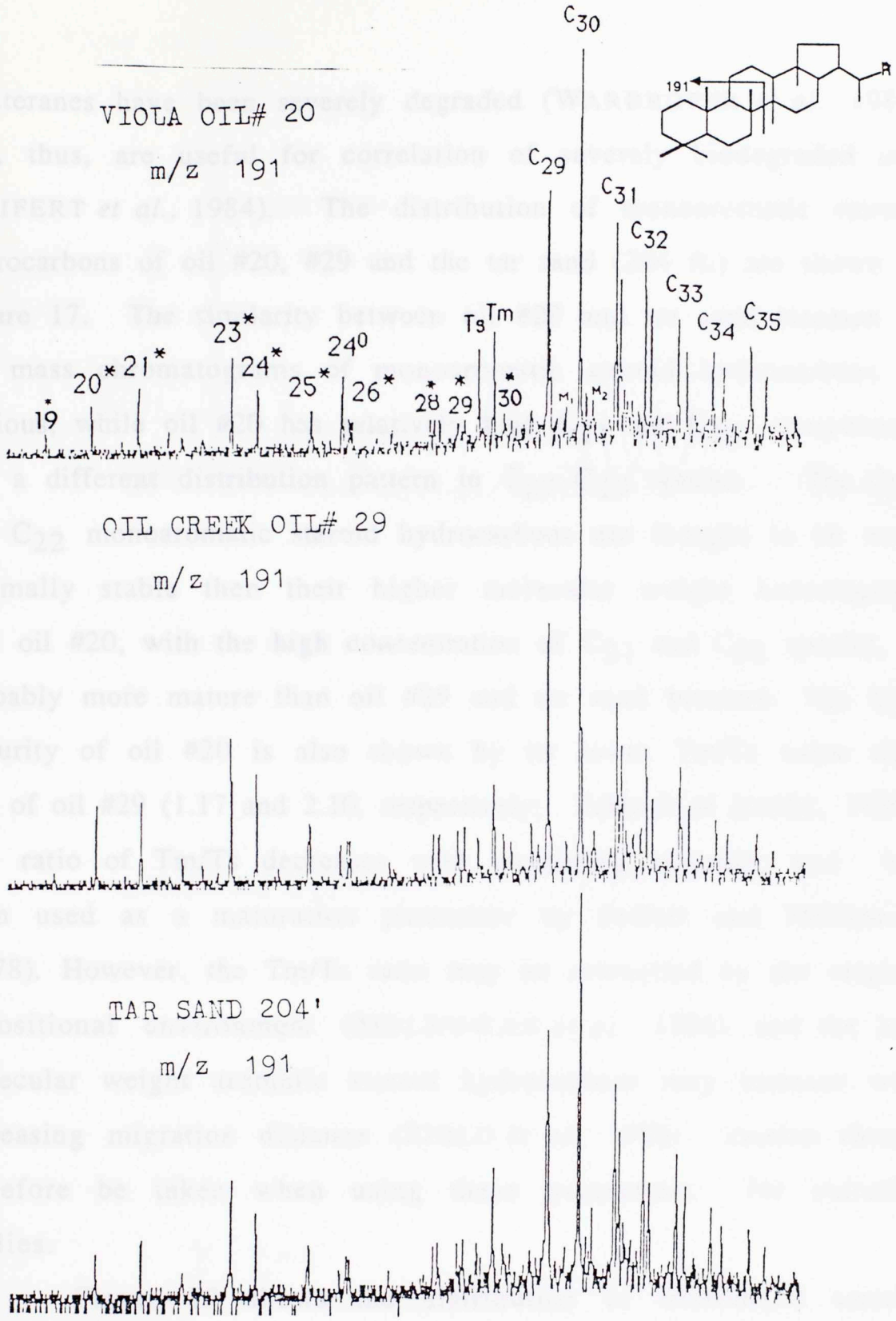


Figure 16 Comparison of m/z 191 mass chromatograms of tar sand bitumen and oils from Pauls Valley area.

diasteranes have been severely degraded (WARDROPER *et al.*, 1984) and, thus, are useful for correlation of severely biodegraded oils (SEIFERT *et al.*, 1984). The distribution of monoaromatic steroid hydrocarbons of oil #20, #29 and the tar sand (204 ft.) are shown in Figure 17. The similarity between oil #29 and tar sand bitumen in the mass chromatograms of monoaromatic steroid hydrocarbons is obvious, while oil #20 has relatively high C_{21} and C_{22} components and a different distribution pattern in C_{27}-C_{29} species. The C_{21} and C_{22} monoaromatic steroid hydrocarbons are thought to be more thermally stable then their higher molecular weight homologues, thus oil #20, with the high concentration of C_{21} and C_{22} species, is probably more mature than oil #29 and tar sand bitumen. The high maturity of oil #20 is also shown by its lower Tm/Ts value than that of oil #29 (1.17 and 2.10, respectively; Table 3 of JONES, 1986). The ratio of Tm/Ts decreases with increasing maturity, and has been used as a maturation parameter by Seifert and Moldowan (1978). However, the Tm/Ts ratio may be controlled by the original depositional environment (MOLDOWAN *et al.*, 1986), and the low molecular weight aromatic steroid hydrocarbons may increase with increasing migration distance (RIOLO *et al.*, 1986), caution should therefore be taken when using these parameters for maturity studies.

Figure 18 shows the distribution of triaromatic steroid hydrocarbons of oil #20, #29 and tar sand bitumen (204 ft.). There is a good similarity in the C_{26}-C_{28} distribution between oil #29 and the tar sand bitume. The absence of C_{20} and C_{21} components and

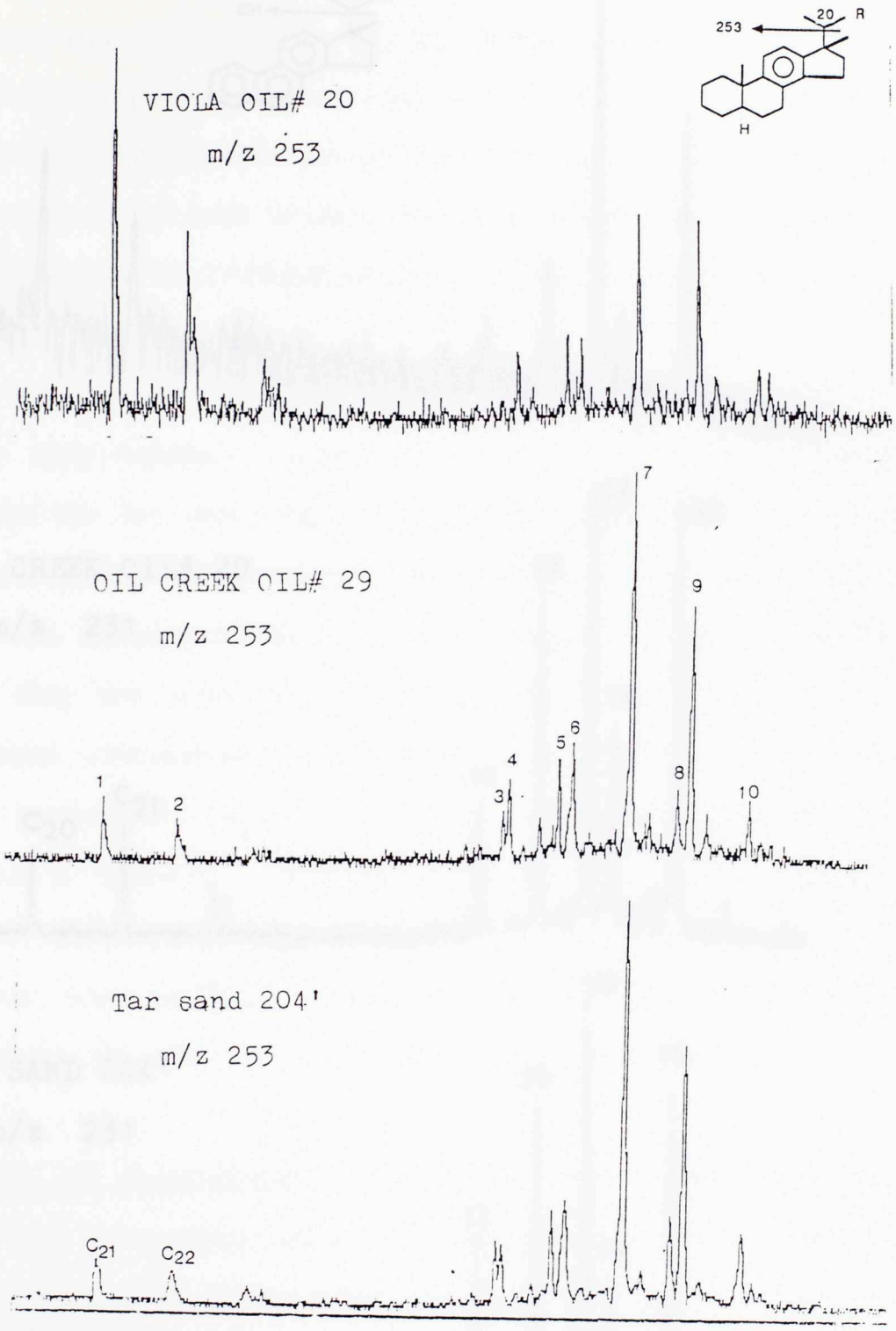


Figure 17. Comparison of m/z 253 mass chromatograms of tar sand bitumen and oils from Pauls Valley area.

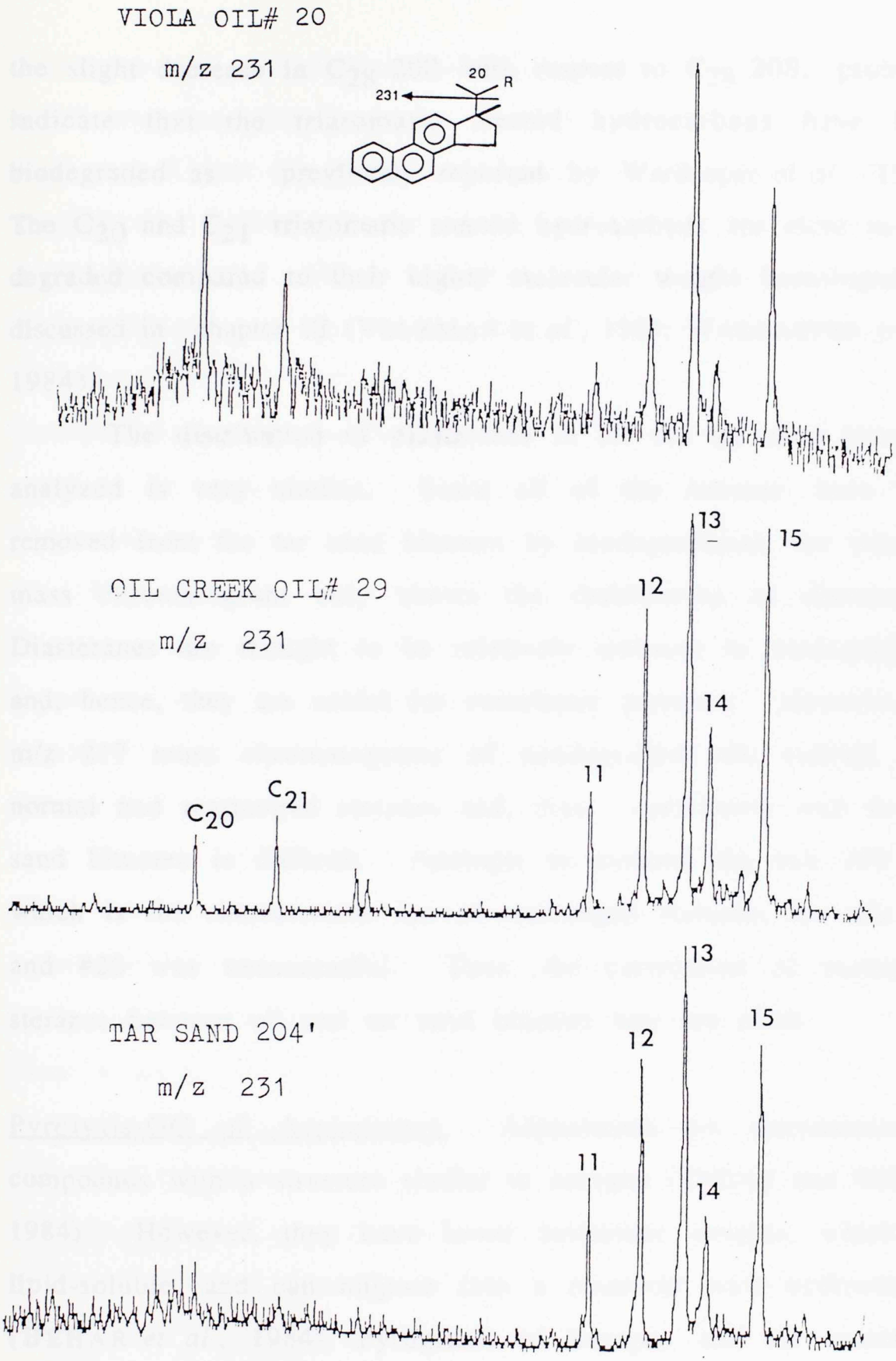


Figure 18. Comparison of m/z 231 mass chromatograms of tar sand bitumen and oils from Pauls Valley area.

the slight decrease in C_{28} 20R with respect to C_{28} 20S, probably indicate that the triaromatic steroid hydrocarbons have been biodegraded as previously reported by Wardroper *et al.* (1984). The C_{20} and C_{21} triaromatic steroid hydrocarbons are more readily degraded compared to their higher molecular weight homologues as discussed in chapter III (VOLKMAN *et al.*, 1984; WARDROPER *et al.*, 1984).

The distribution of diasteranes in all the tar sand bitumens analyzed is very similar. Since all of the steranes have been removed from the tar sand bitumen by biodegradation, the m/z 217 mass chromatogram only shows the distribution of diasteranes. Diasteranes are thought to be relatively resistant to biodegradation and, hence, they are useful for correlation purposes. However, the m/z 217 mass chromatograms of nondegraded oils contain both normal and rearranged steranes and, thus, correlation with the tar sand bitumen is difficult. Attempts to monitor the m/z 259 ion, which is the characteristic ion of rearranged steranes, for oils #29 and #20 was unsuccessful. Thus, the correlation of rearranged steranes between oil and tar sand bitumen was not made.

Pyrolysis-GC of Asphaltenes. Asphaltenes are macromolecular compounds with a structure similar to kerogen (TISSOT and WELTE, 1984). However, they have lower molecular weights, which are lipid-soluble, and can migrate into a reservoir with hydrocarbons (BEHAR *et al.*, 1984). Pyrograms of kerogen and its associated asphaltene show a similar distribution, and therefore are useful for

oil/source-rock correlation (BEHAR *et al.*, 1984). An *in vitro* experiment was carried out by Teschner and Wehner (1985) who demonstrated that the pyrolysis-GC products of asphaltene showed no difference before and after biodegradation of the oil containing that asphaltene. The resistance of asphaltenes towards biodegradation was also demonstrated by Rubinstein *et al.* (1979) and Behar (1984) who compared the asphaltene pyrograms of biodegraded and non-biodegraded oils. The components released by pyrolysis of asphaltenes might have been occluded in a molecular framework which is inaccessible to microorganisms (RUBINSTEIN *et al.*, 1979). Therefore, pyrolysis-GC of asphaltene is a useful tool for correlation of biodegraded oils with non-biodegraded oils. This is especially true for severely biodegraded samples where the commonly used biomarkers have been altered or completely removed.

Figure 19 shows the asphaltene pyrograms of Viola oil #20, Oil Creek oil #29 and tar sand bitumen (204 ft.). The pyrograms show a series of doublets consisting of *n*-alkanes and their corresponding (early-eluting) 1-alkenes, in which the tar sand bitumen and oil #29 show a good correlation in the distribution of both aliphatic and aromatic hydrocarbons. However, the asphaltene pyrogram of oil #20 (Fig. 19) shows a distribution dominated by long chain alkanes extending up to C_{35} and contains less aromatics and no detectable pristene. This is probably related with the difference in organic content and the higher maturity of oil #20. An increase in normal hydrocarbons over isoprenoids, other branched hydrocarbons,

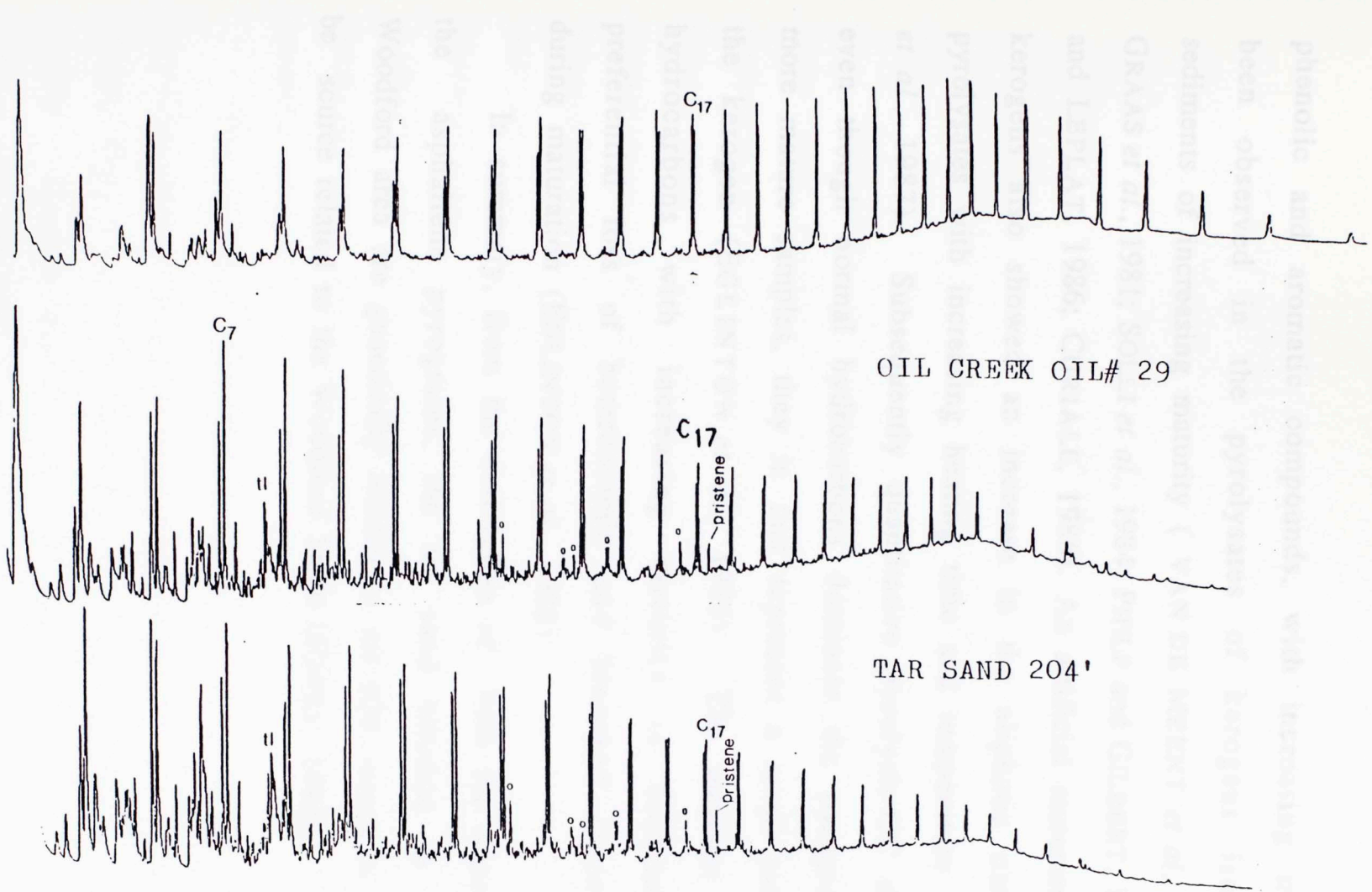


Figure 19. Comparison of asphaltene pyrograms of tar sand bitumen and oils from Pauls Valley area. (C_7, C_{17} etc., are n-alkene/n-alkane of that carbon number with n-alkenes eluting first. o: isoprenoids. tl: toluene.)

phenolic and aromatic compounds, with increasing maturity has been observed in the pyrolysates of kerogens isolated from sediments of increasing maturity (VAN DE MEENT *et al.*, 1980; VAN GRAAS *et al.*, 1981; SOLLI *et al.*, 1984; PHILP and GILBERT, 1985; SOLLI and LEPLAT, 1986; CURIALE, 1986). An artificial maturation study of kerogens also showed an increase in the aliphatic nature of the pyrolysates with increasing heating time and temperature (EGLINTON *et al.*, 1987). Subsequently quantitative pyrolysis-GC showed that even though normal hydrocarbons dominate the pyrograms of the more mature samples, they in fact represent a small percentage of the kerogen (EGLINTON *et al.*, 1986). The increase in normal hydrocarbons with increasing maturity is because of the preferential loss of heteroatomic and branched chain materials during maturation (EGLINTON *et al.*, 1986).

In summary, from the correlation of both the biomarkers and the asphaltene pyrograms, the tar sand bitumen in the South Woodford area are genetically related to oil #29, which is thought to be source related to the Woodford Shale (JONES, 1986).

CHAPTER V

CONCLUSION

The extent of biodegradation of tar sand bitumens extracted from well Fitzgerald-5 have been closely examined by gas chromatography and gas chromatography-mass spectrometry. The results show that *n*-alkanes, isoprenoids, naphthalene, alkyl-naphthalenes, phenanthrene, C_1-, C_2-phenanthrenes, benzo- and dibenzothiophenes have been removed from the tar sand bitumens, and only an unresolved complex mixture is present in the gas chromatograms. The sample at 240 ft., which contains some *n*-alkanes, pristane and phytane, and is thought to be mixed with a nonbiodegraded light oil, since the biomarkers in this sample were severely altered.

The biomarker distributions are also altered to varying degrees. C_{27}-C_{29} steranes and C_{20}-C_{21} triaromatic steroid hydrocarbons are absent, C_{27}-C_{28} 20R triaromatic steroid hydrocarbons decrease slightly. Hopane degradation with preferential removal of C_{30+} hopanes with the 22R configuration was observed. The C_{29}-hopane, Tm, Ts and moretanes are degraded at a slower rate compared to the C_{30+} hopanes. The samples at 144 ft. and 204 ft. seem intact in

terms of hopane distribution, and allow a correlation with oils to be performed. The preferential degradation of C_{27}-C_{29} steranes prior to alteration of hopanes can be observed in these two samples. Comparison with the degradation of tar sand bitumens from the South Sulphur Asphalt deposit, in which the degradation of C_{30+} hopanes occurred prior to steranes, shows the unpredictability in the relative biodegradation rate of hopanes and steranes.

Diasteranes, C_{30}-steranes, tricyclic terpanes, C_{24}-tetracyclic terpane and monoaromatic steroid hydrocarbons appear to be resistant toward biodegradation, and are useful for correlation studies.

The correlation study based on tricyclic terpanes, C_{24}-tetracyclic terpane, hopane, mono- and triaromatic steroid hydrocarbon distributions and asphaltene pyrolysis-GC shows that the tar sand bitumen is source related with oil #29 from the Pauls Valley area. Oil #29, reservoired in Oil Creek Sandstone, was previously studied by Jones (1986), and proposed to be sourced from Woodford Shale.

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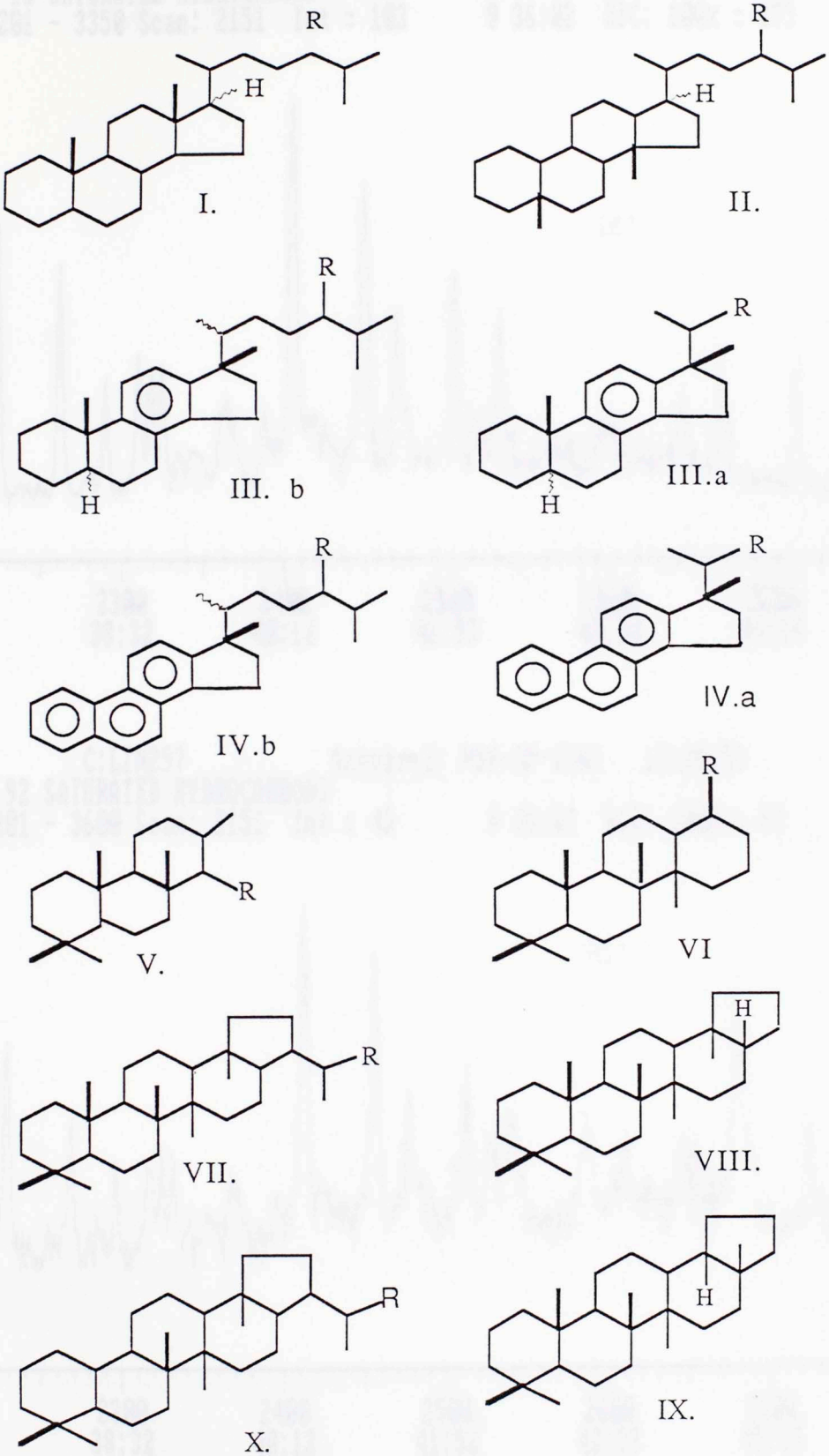
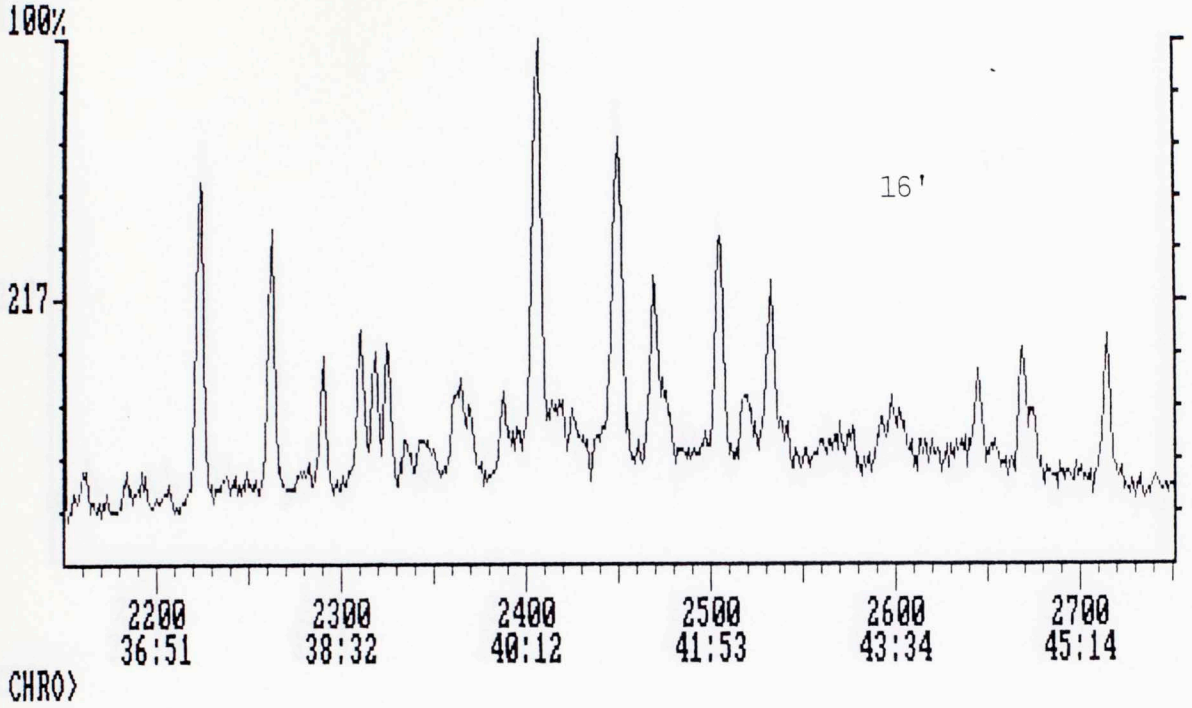
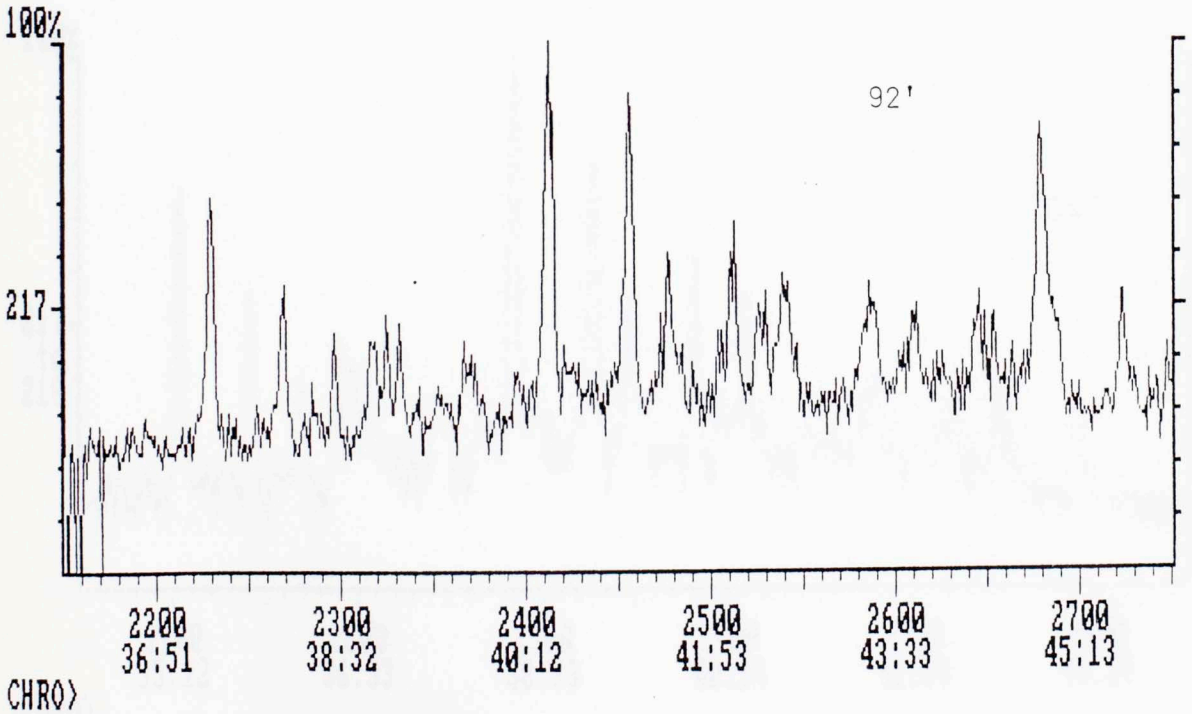


Appendix I. Molecular structure

Chromatogram C:LIN296 Acquired: MAY-23-1986 17:59:38
Comment: FZ-5 16 SATURATED HYDROCABONS
Scan Range: 1201 - 3350 Scan: 2151 Int = 103 @ 36:02 RIC: 100% = 275

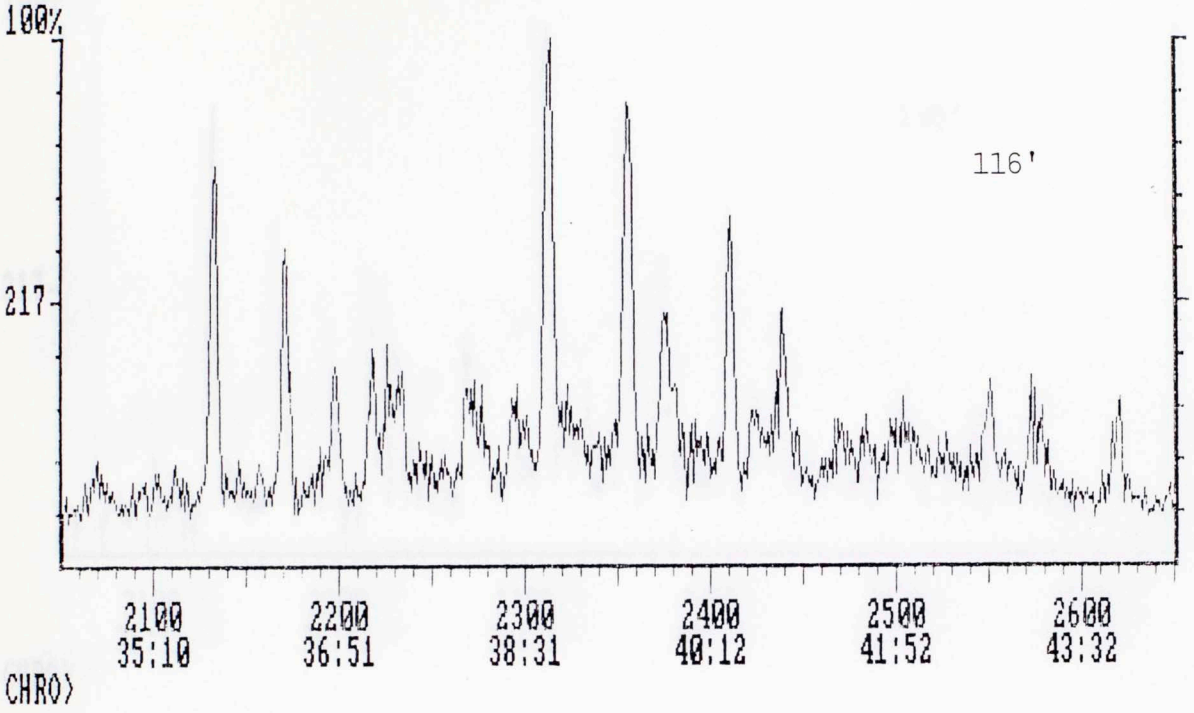


Chromatogram C:LIN297 Acquired: MAY-25-1986 13:29:52
Comment: FZ-5 92 SATURATED HYDROCARBONS
Scan Range: 1201 - 3600 Scan: 2151 Int = 43 @ 36:02 RIC: 100% = 67

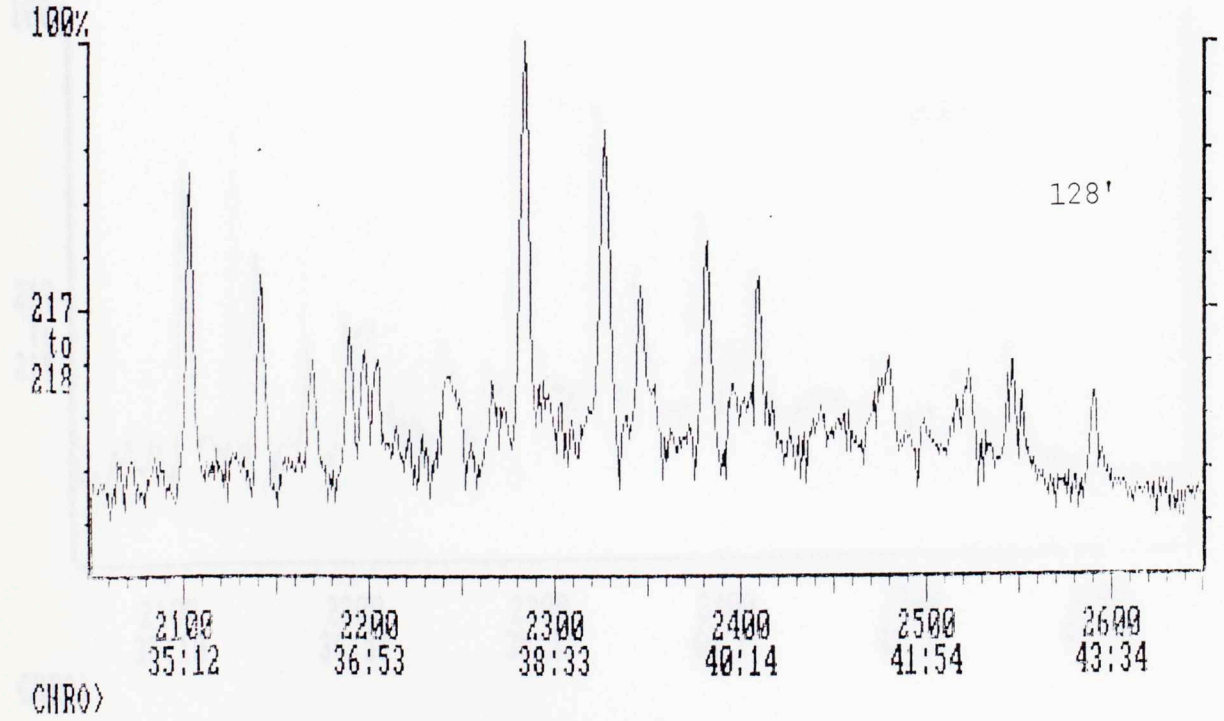


Appendix II. Mass chromatograms of m/z 217

Chromatogram Datafile: LIN742 Acquired: Oct-29-1986 15:00:21
Comment: FZ #5 116' SATURATED FRACTION
Scan Range: 1001 - 3600 Scan: 2650 Int = 172 @ 44:23 RIC: 100% = 212

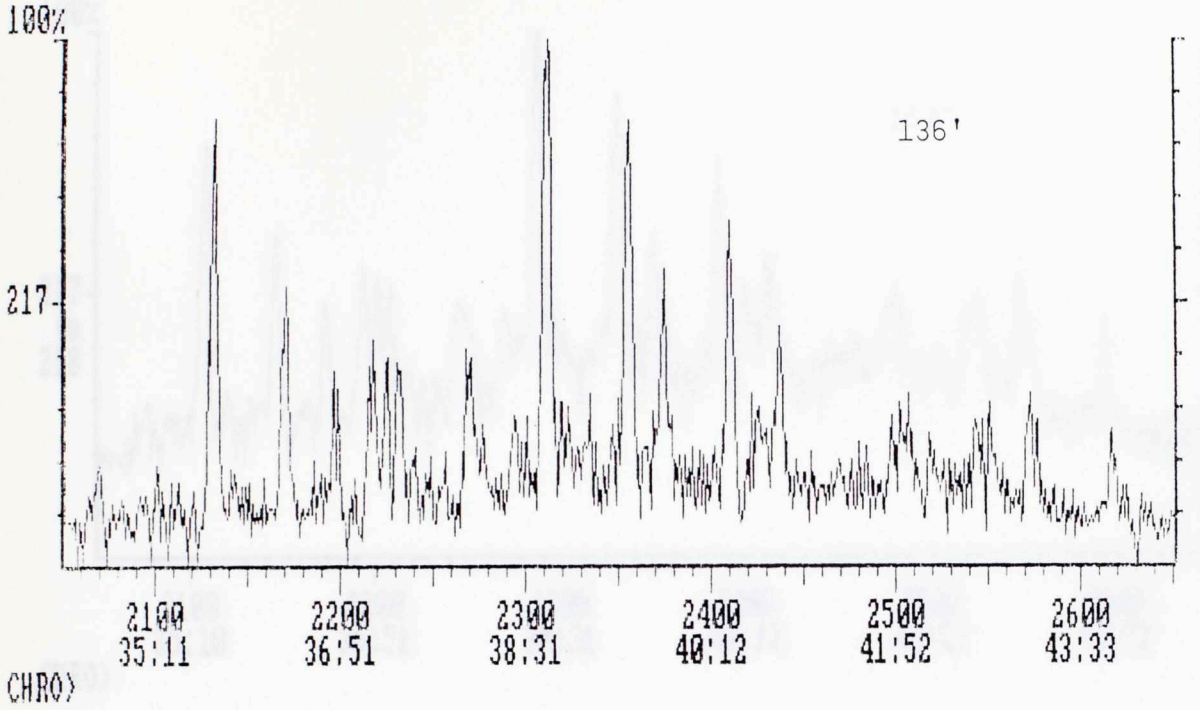


Chromatogram Datafile: LIN1020 Acquired: Jan-12-1987 21:47:44
Comment: FZ #5 128'SATURATE FRACTION
Scan Range: 2101 - 3300 Scan: 2650 Int = 1176 @ 44:25 RIC: 100% = 1204

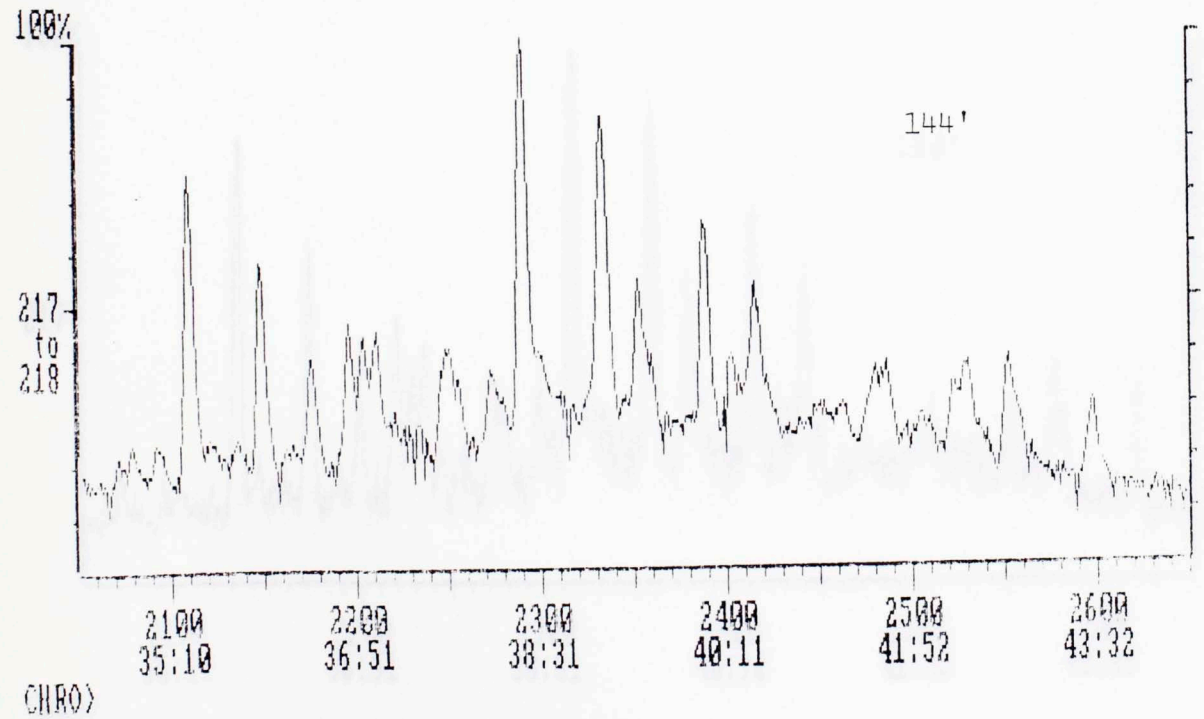


Appendix II. Continued.

Chromatogram Datafile: LIN743 Acquired: Oct-29-1986 18:05:18
Comment: FZ #5 136' SATURATED FRACTION
Scan Range: 1001 - 3600 Scan: 2051 Int = 3555 @ 34:21 RIC: 100% = 223

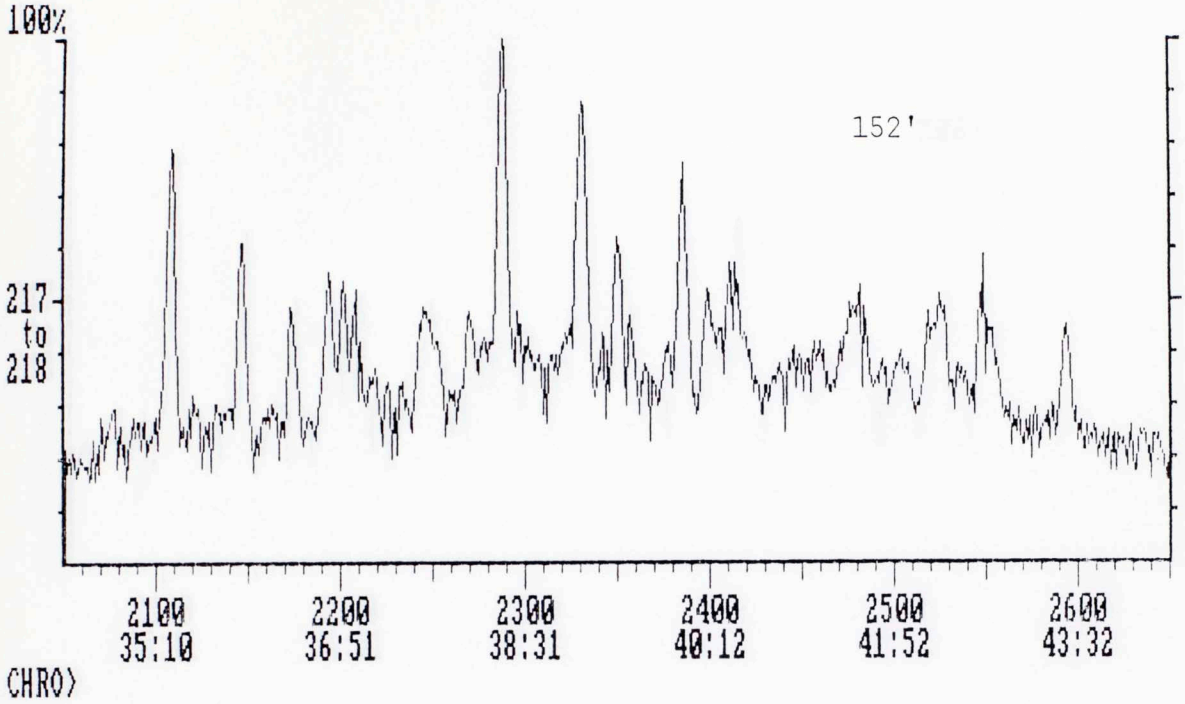


Chromatogram Datafile: LIN1106 Acquired: Jan-27-1987 17:23:16
Comment: FIZ #5 144' SAT.
Scan Range: 2051 - 2650 Scan: 2051 Int = 510 @ 34:21 RIC: 100% = 959

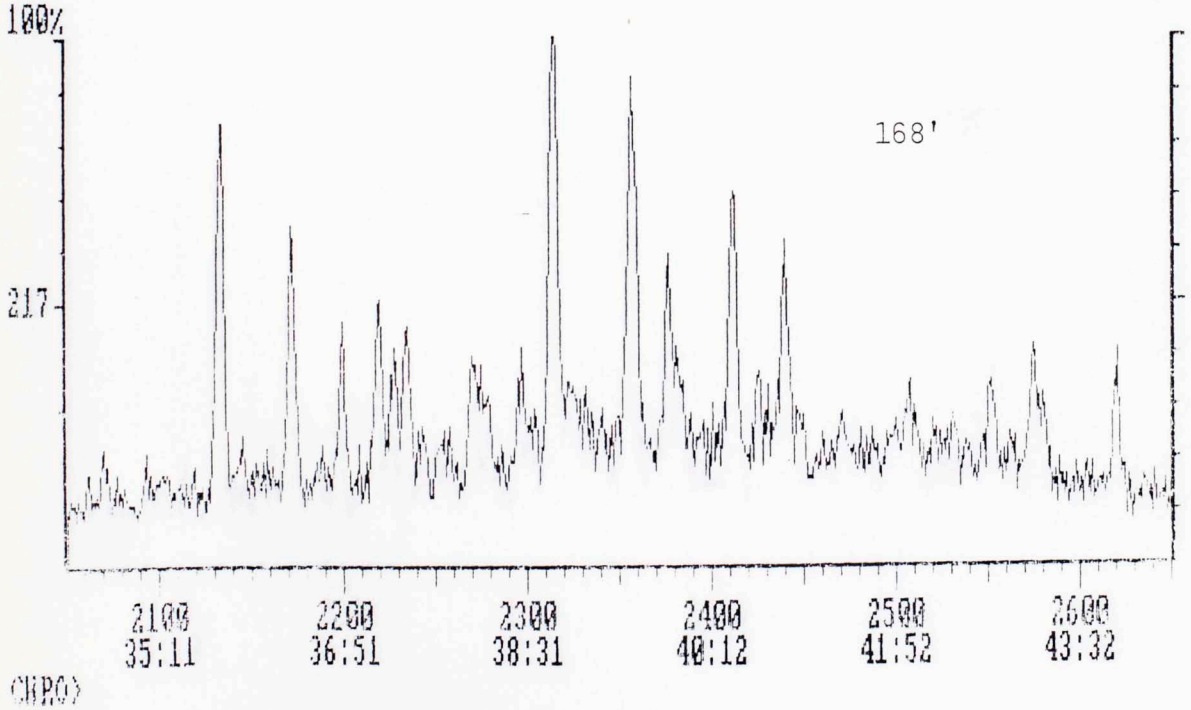


Appendix II. Continued.

Chromatogram Datafile: LIN1018 Acquired: Jan-12-1987 18:43:58
Comment: FZ #5 152' SATURATE FRACTION
Scan Range: 2051 - 2650 Scan: 2650 Int = 1692 @ 44:23 RIC: 100% = 1156

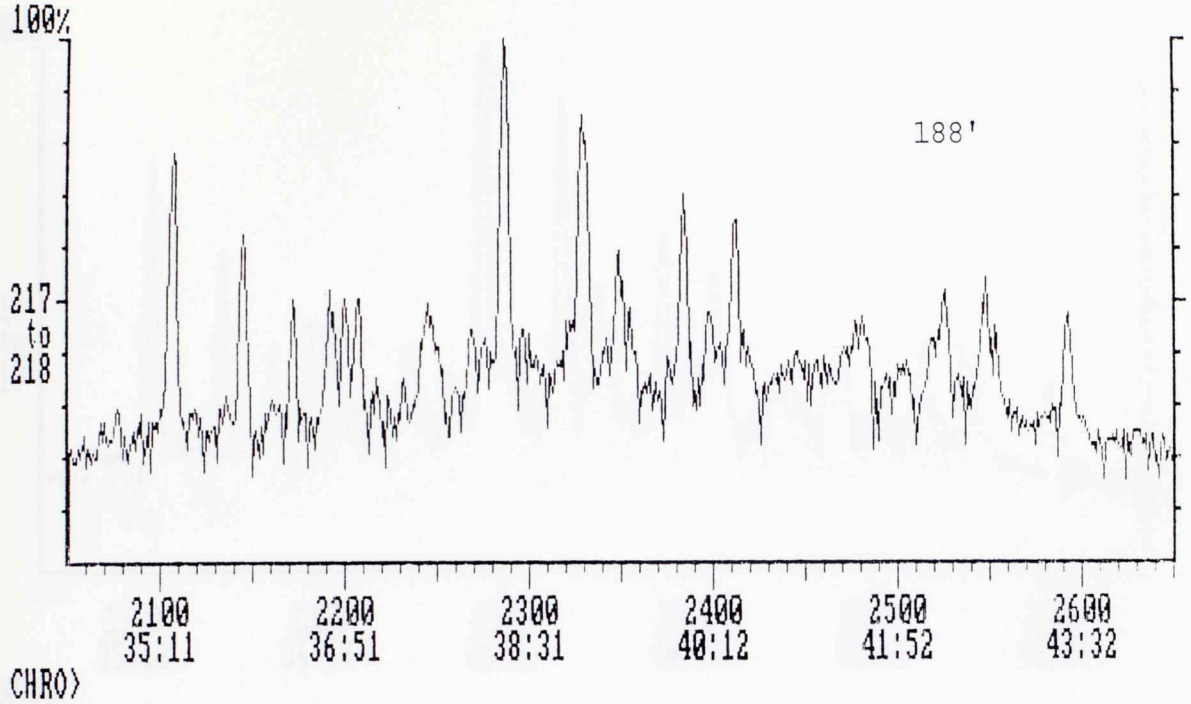


Chromatogram Datafile: LIN745 Acquired: Oct-30-1986 08:47:33
Comment: FZ #5 168' SATURATED FRACTION
Scan Range: 1001 - 3600 Scan: 2650 Int = 267 @ 44:23 RIC: 100% = 286

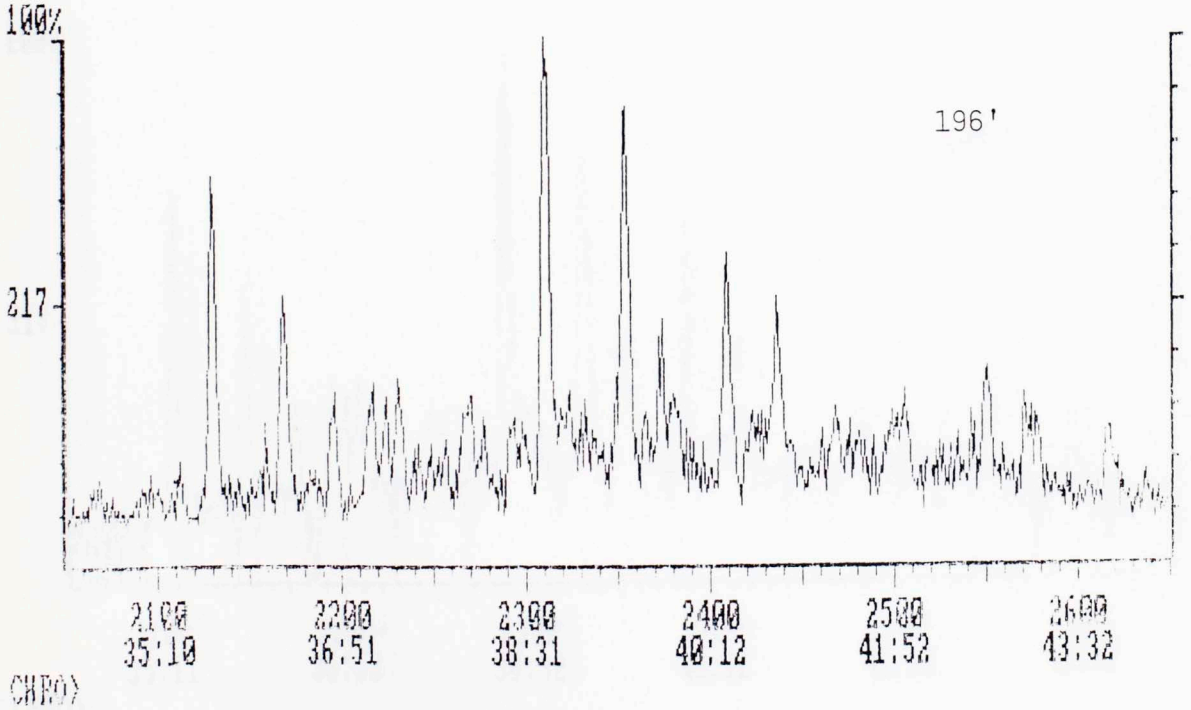


Appendix II. Continued.

Chromatogram Datafile: LIN1019 Acquired: Jan-12-1987 20:19:58
Comment: FZ #5 188' SATURATE FRACTION
Scan Range: 2051 - 2650 Scan: 2650 Int = 1730 @ 44:23 RIC: 100% = 1177

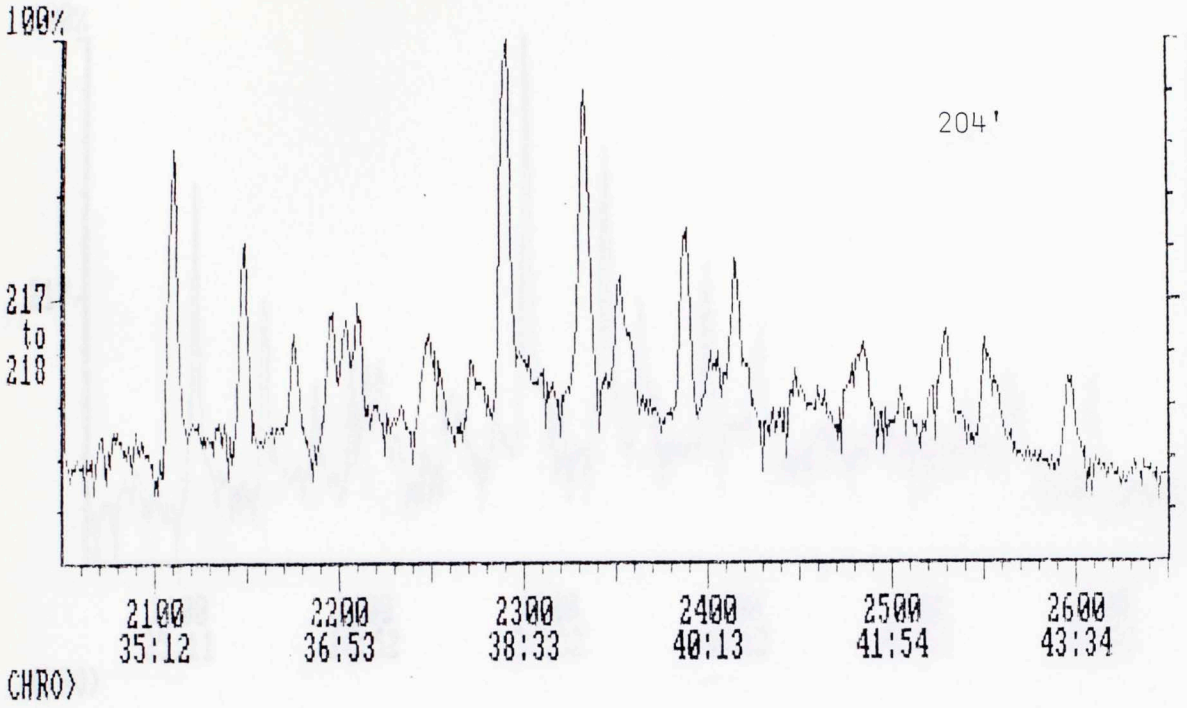


Chromatogram Datafile: LIN741 Acquired: Oct-29-1986 12:58:46
Comment: FZ #5 196' SATURATED FRACTION
Scan Range: 1001 - 3600 Scan: 2051 Int = 55 @ 34:21 RIC: 100% = 142

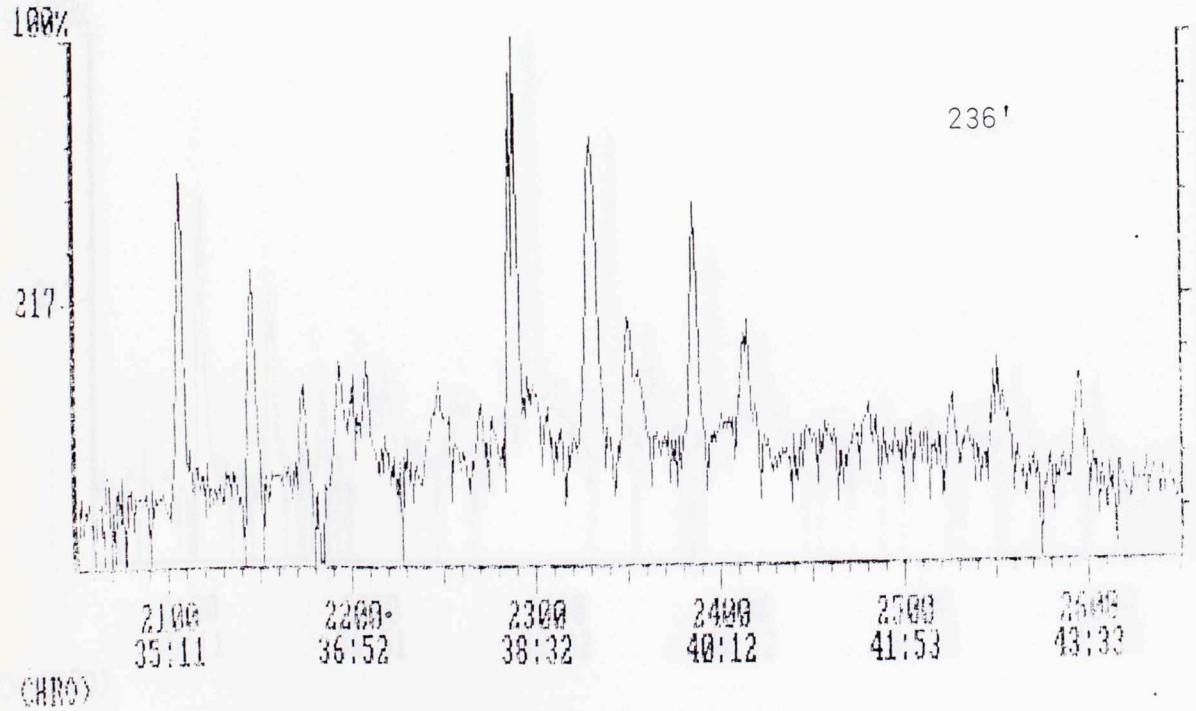


Appendix II. Continued.

Chromatogram Datafile: LIN1108 Acquired: Jan-27-1987 20:18:46
Comment: FIZ #5 204' SAT.
Scan Range: 2051 - 2650 Scan: 2051 Int = 432 @ 34:23 RIC: 100% = 788

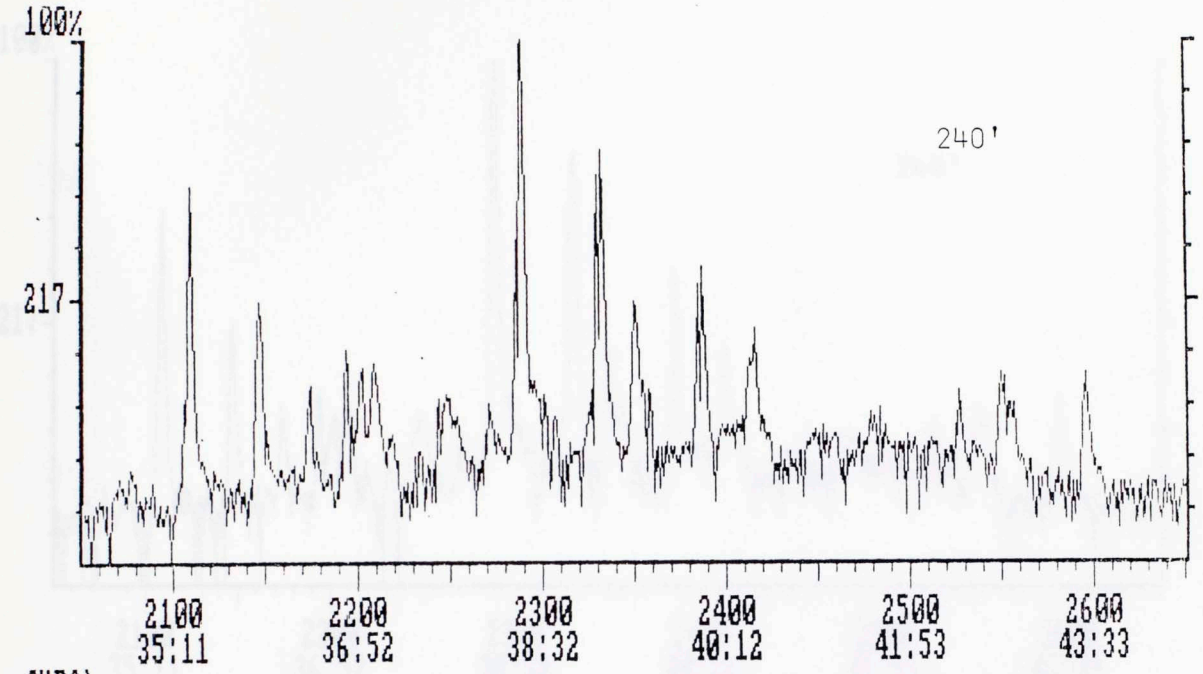


Chromatogram Datafile: LIN467 Acquired: Jul-29-1986 13:41:14
Comment: FZ-5 236'
Scan Range: 1001 - 3600 Scan: 2051 Int = 31 @ 34:22 RIC: 100% = 114

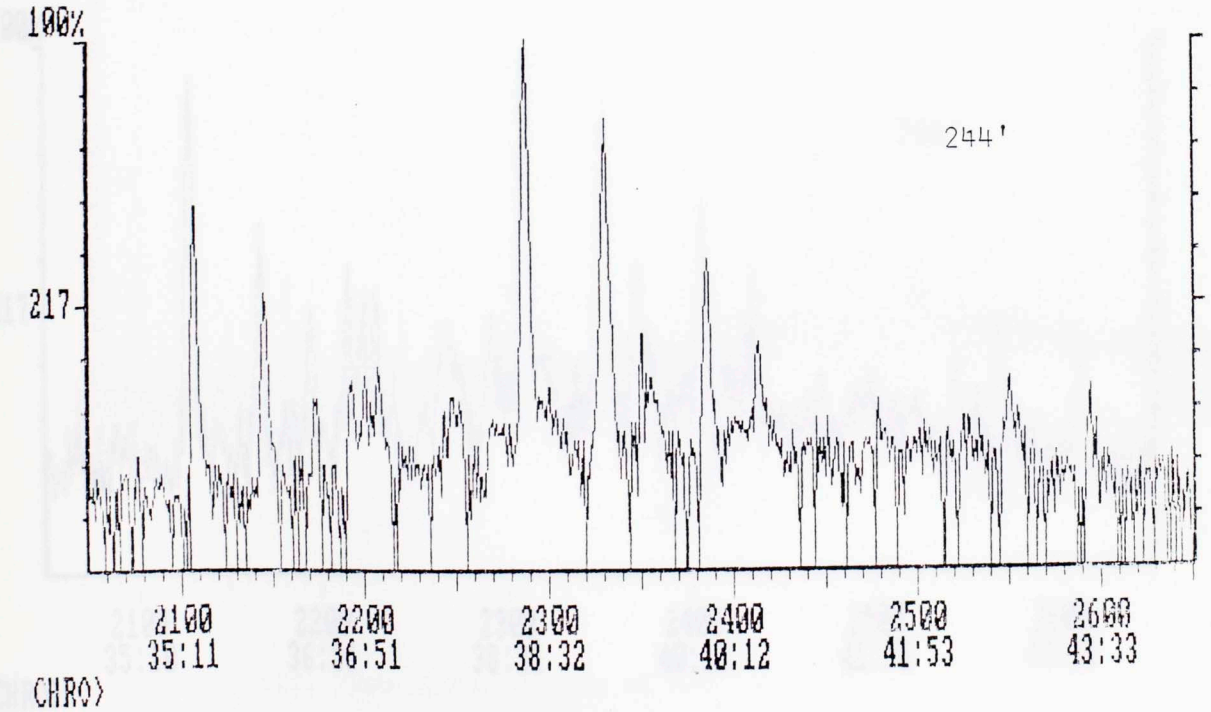


Appendix II. Continued.

Chromatogram Datafile: LIN468 Acquired: Jul-29-1986 14:57:51
Comment: FZ-5 240'
Scan Range: 1001 - 3600 Scan: 2051 Int = 76 @ 34:22 RIC: 100% = 210

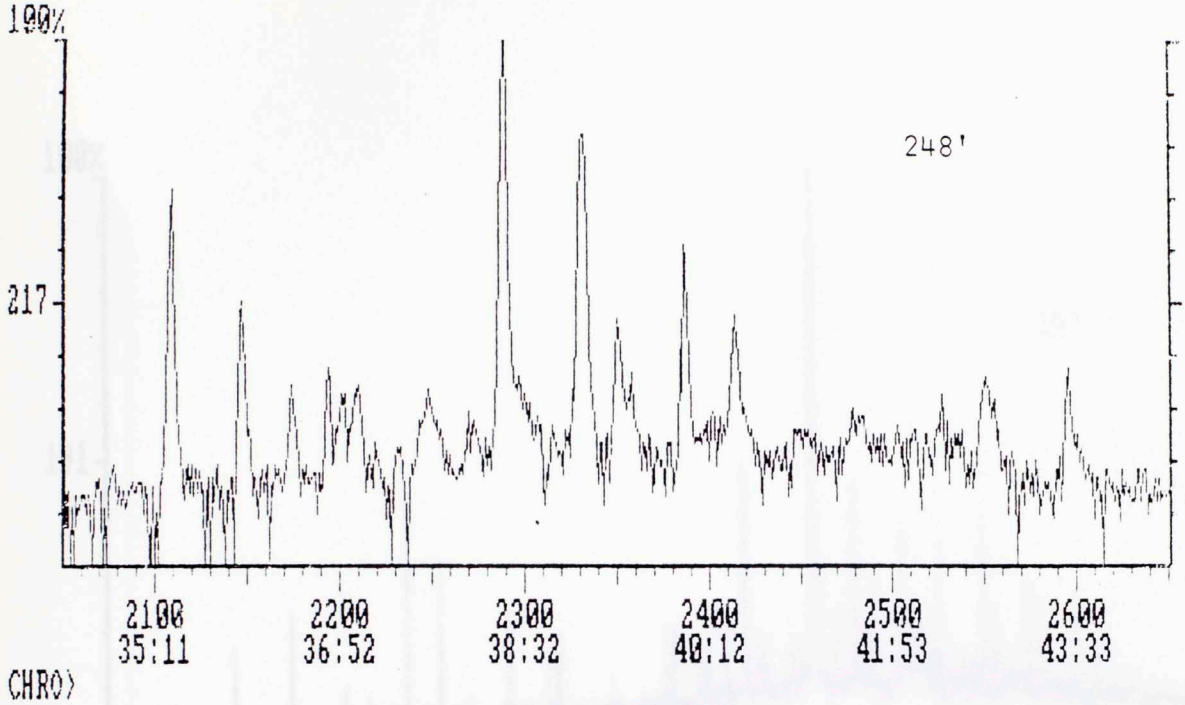


Chromatogram Datafile: LIN466 Acquired: Jul-29-1986 12:11:05
Comment: FZ-5 244'
Scan Range: 1001 - 3600 Scan: 2051 Int = 9 @ 34:22 RIC: 100% = 71

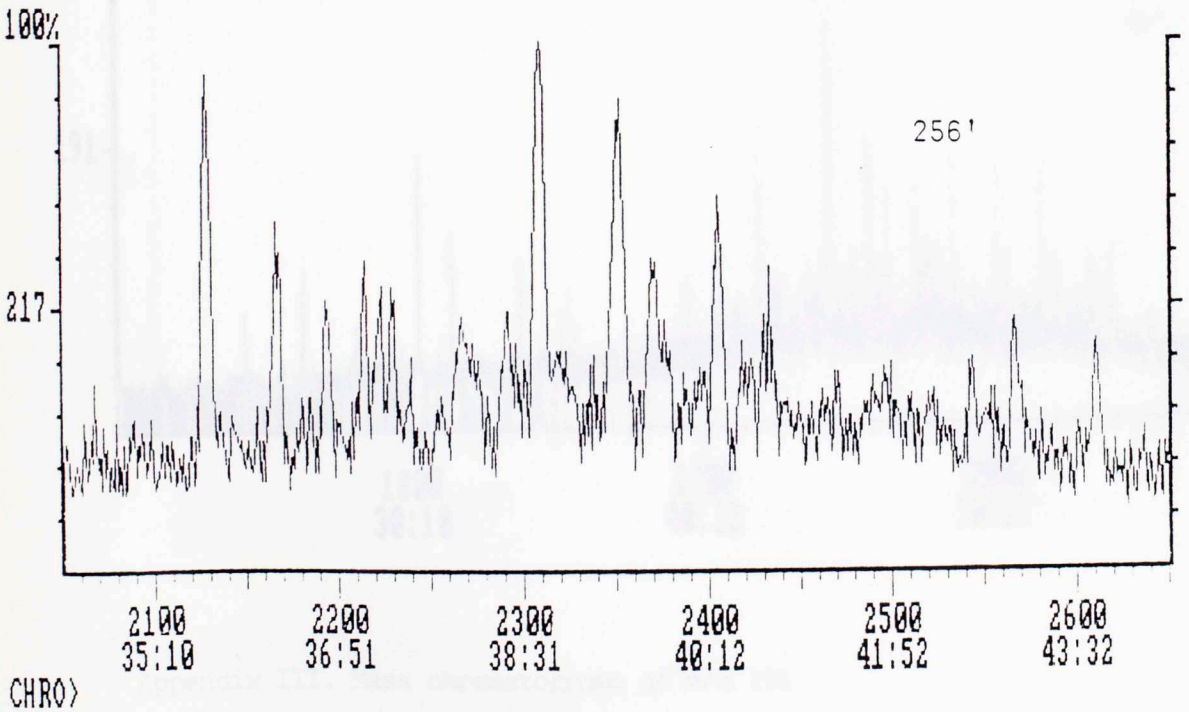


Appendix II. Continued.

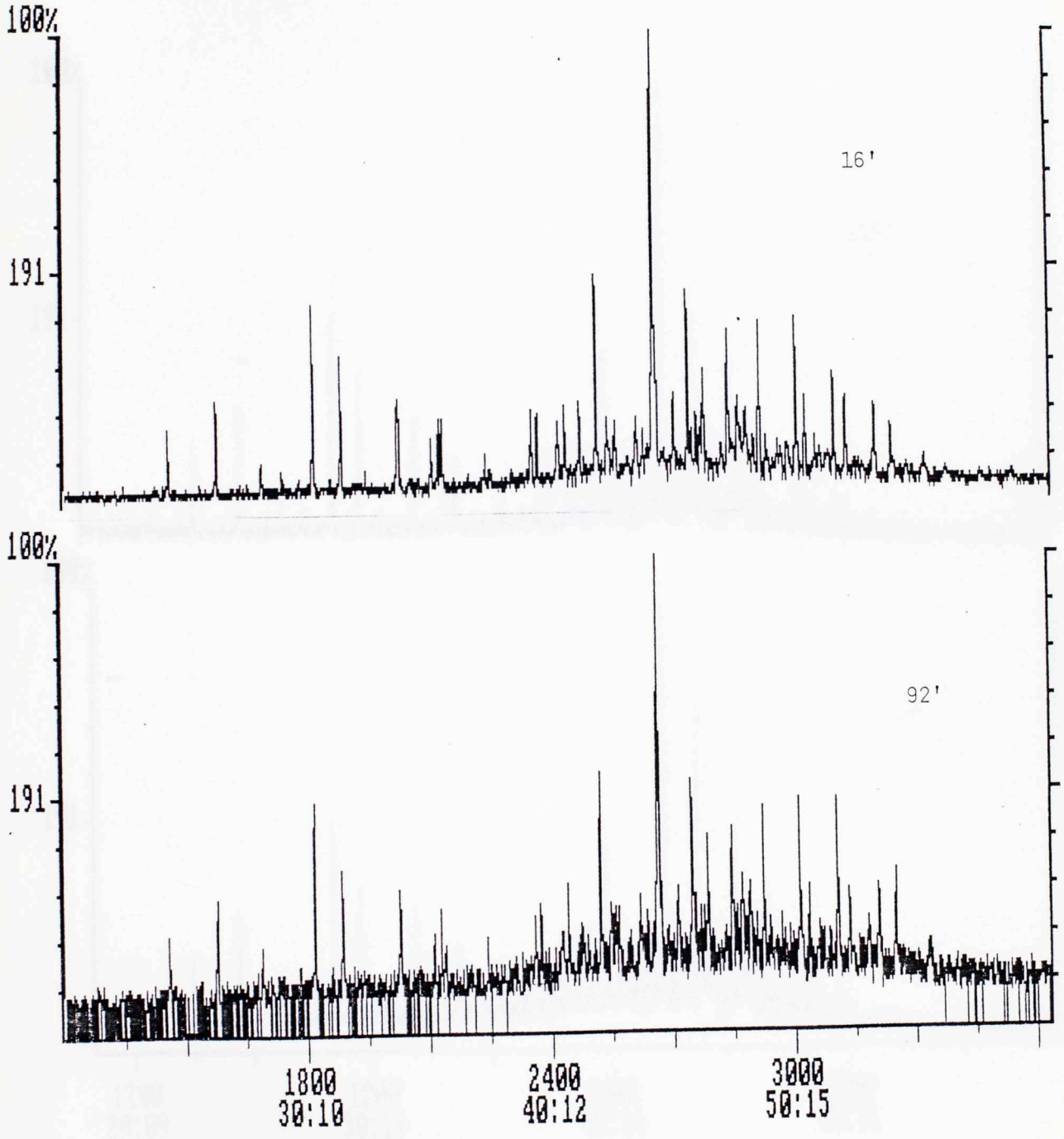
Chromatogram Datafile: LIN469 Acquired: Jul-29-1986 16:15:11
Comment: FZ-5 248'
Scan Range: 1001 - 3600 Scan: 2051 Int = 39 @ 34:22 RIC: 100% = 124



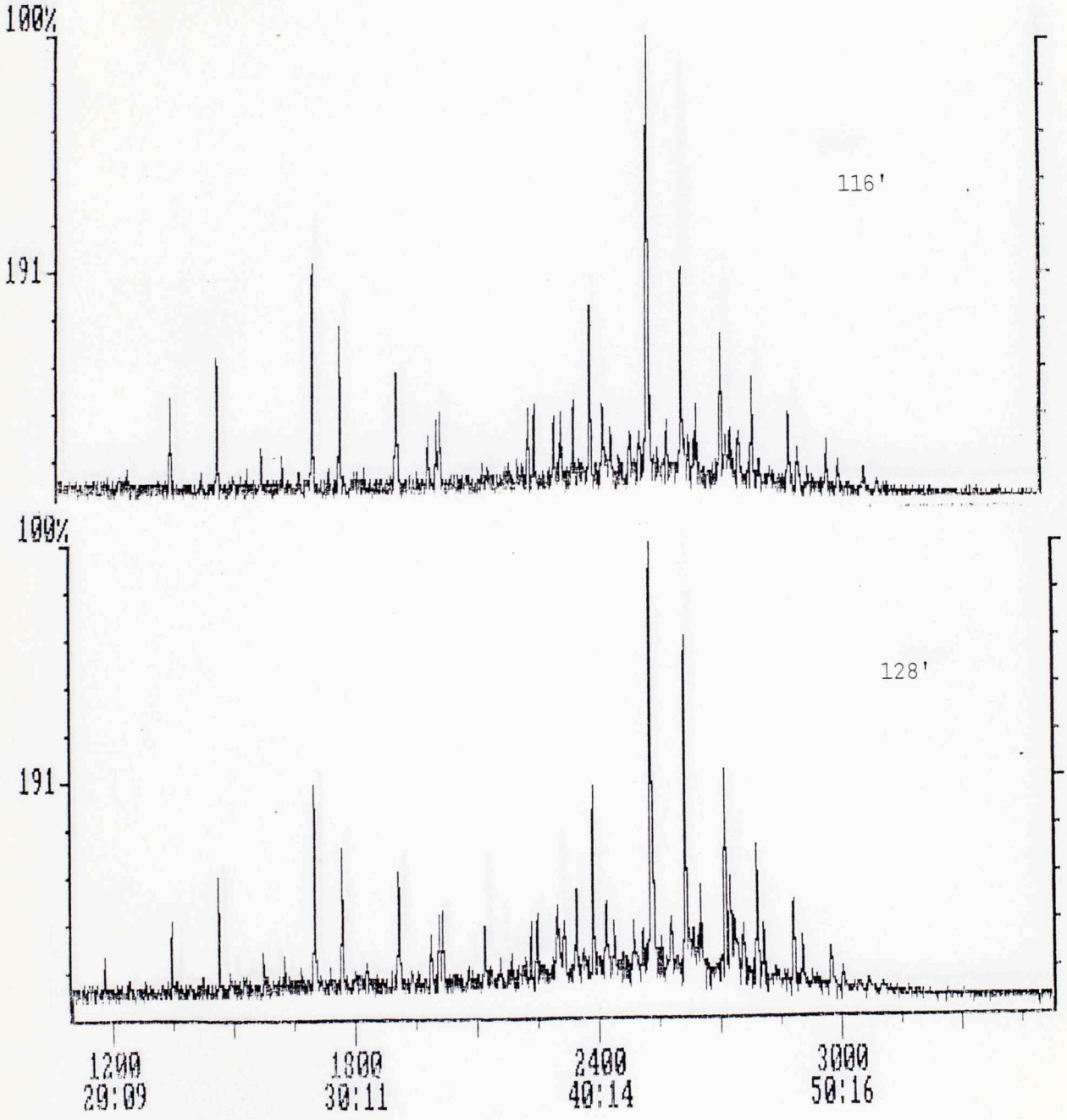
Chromatogram Datafile: LIN646 Acquired: Sep-24-1986 22:15:24
Comment: FZ-5 256' SATURATED FRACTION OF TARSAND
Scan Range: 1001 - 3600 Scan: 2650 Int = 487 @ 44:23 RIC: 100% = 291



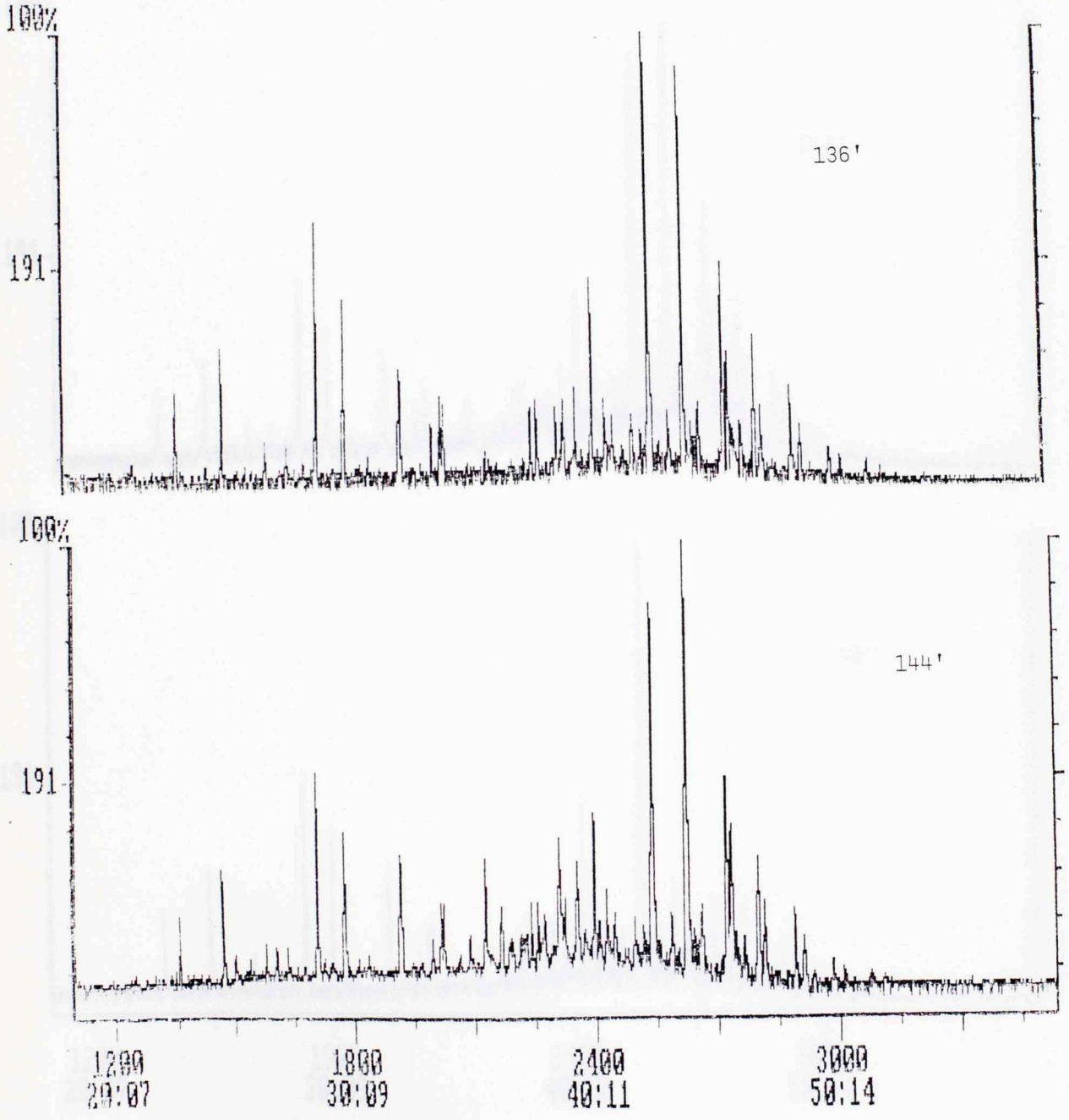
Appendix II. Continued.



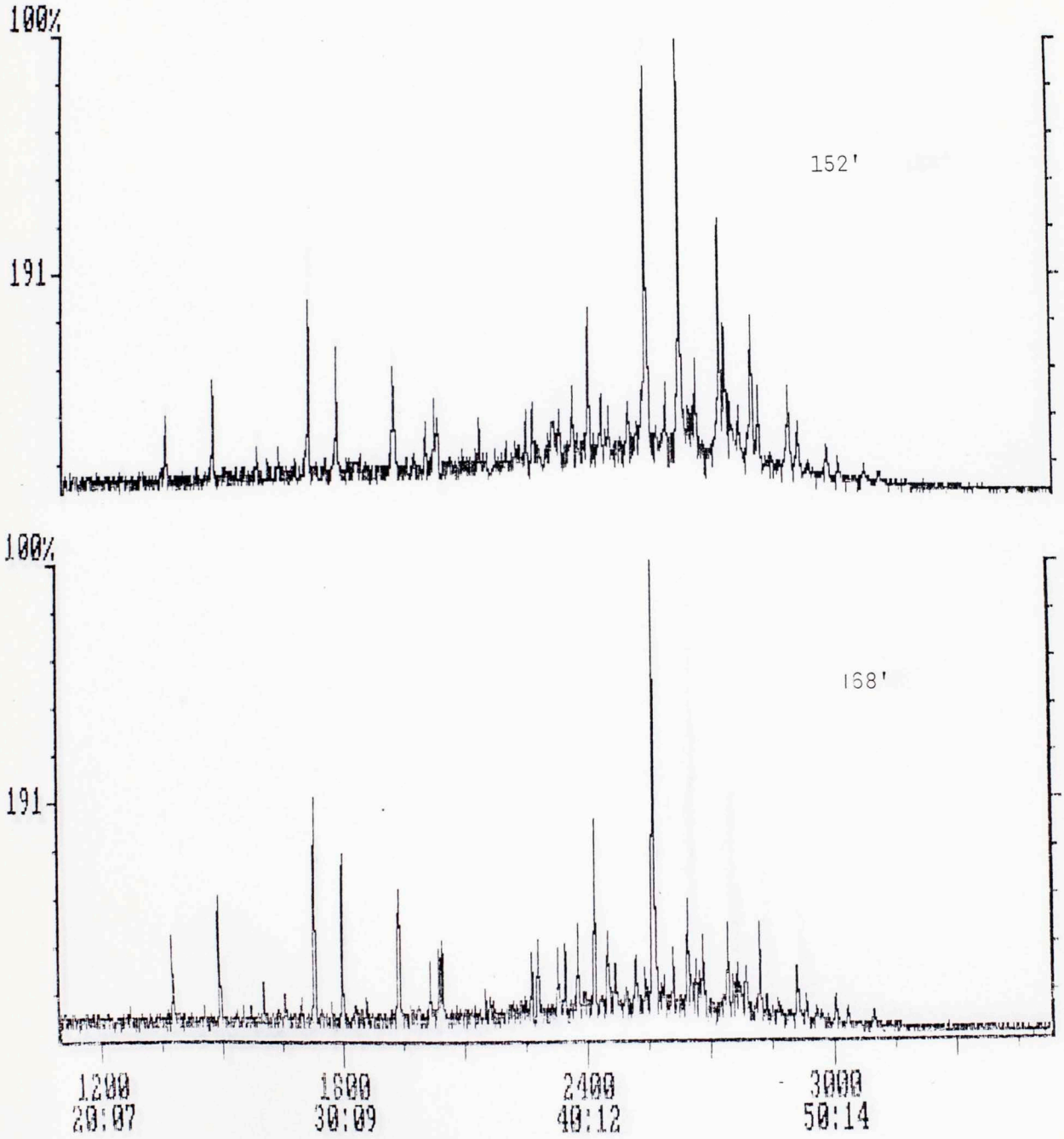
Appendix III. Mass chromatograms of m/z 191



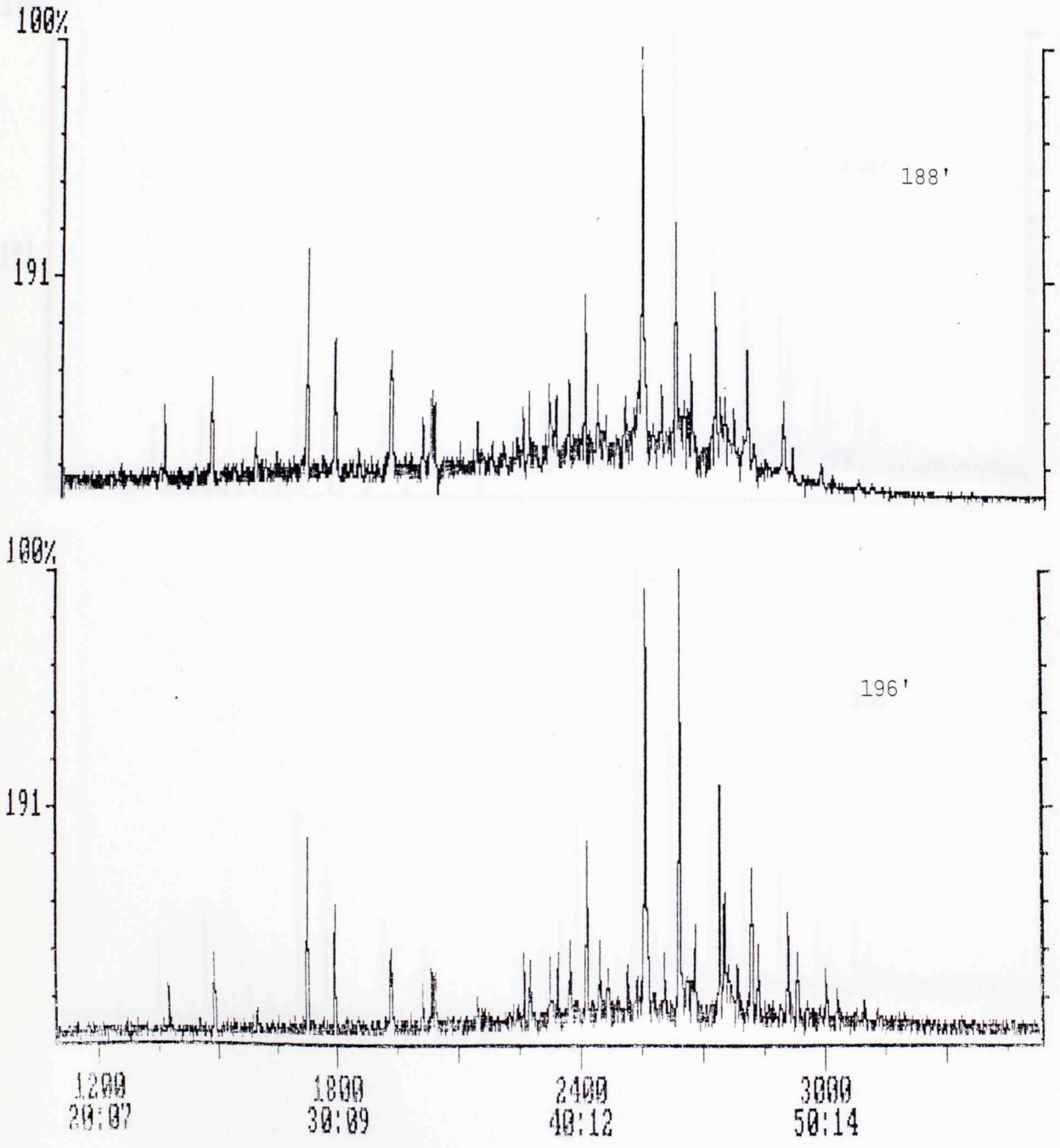
Appendix III. Continued.



Appendix III. Continued.



Appendix III. Continued.



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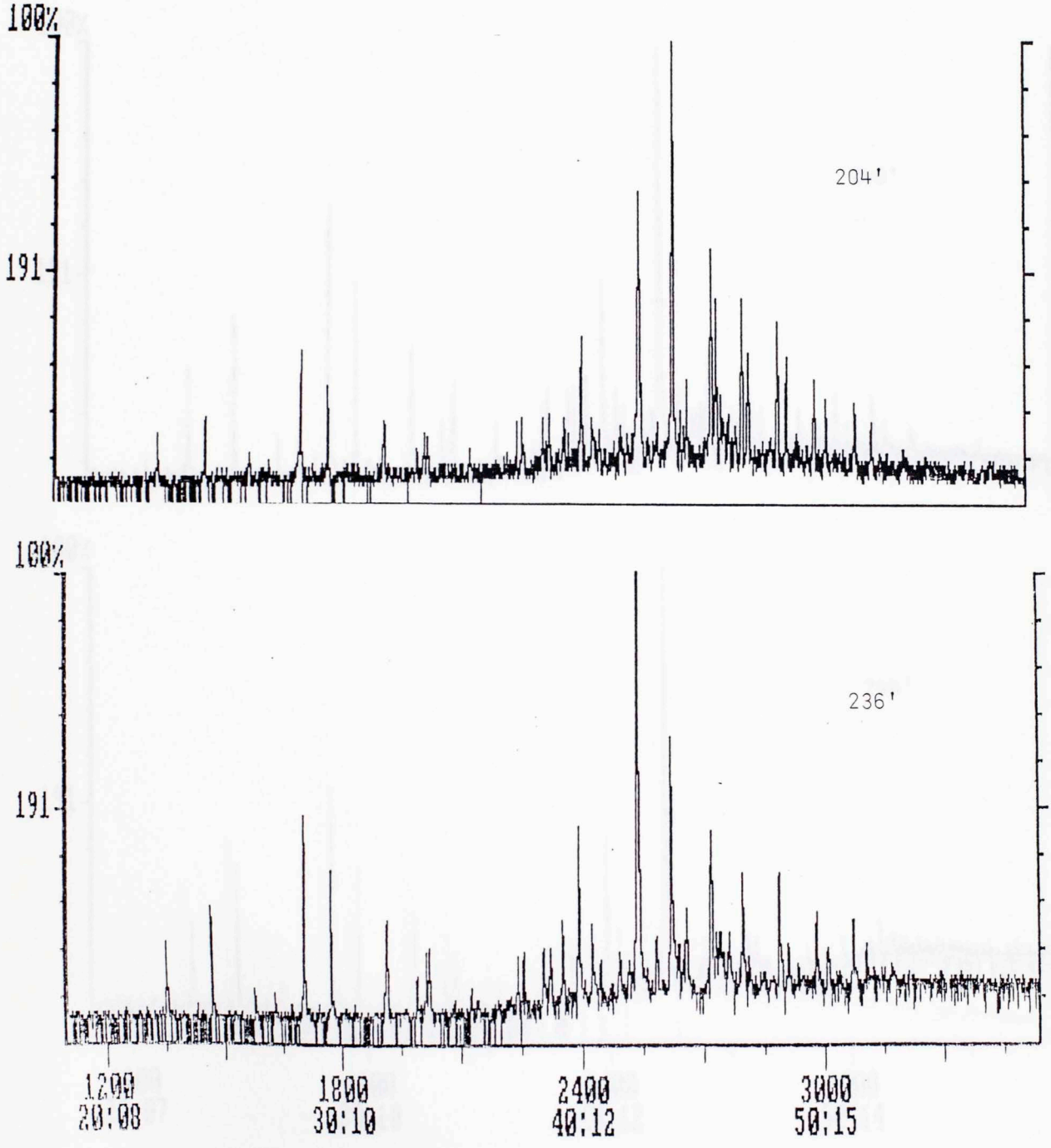

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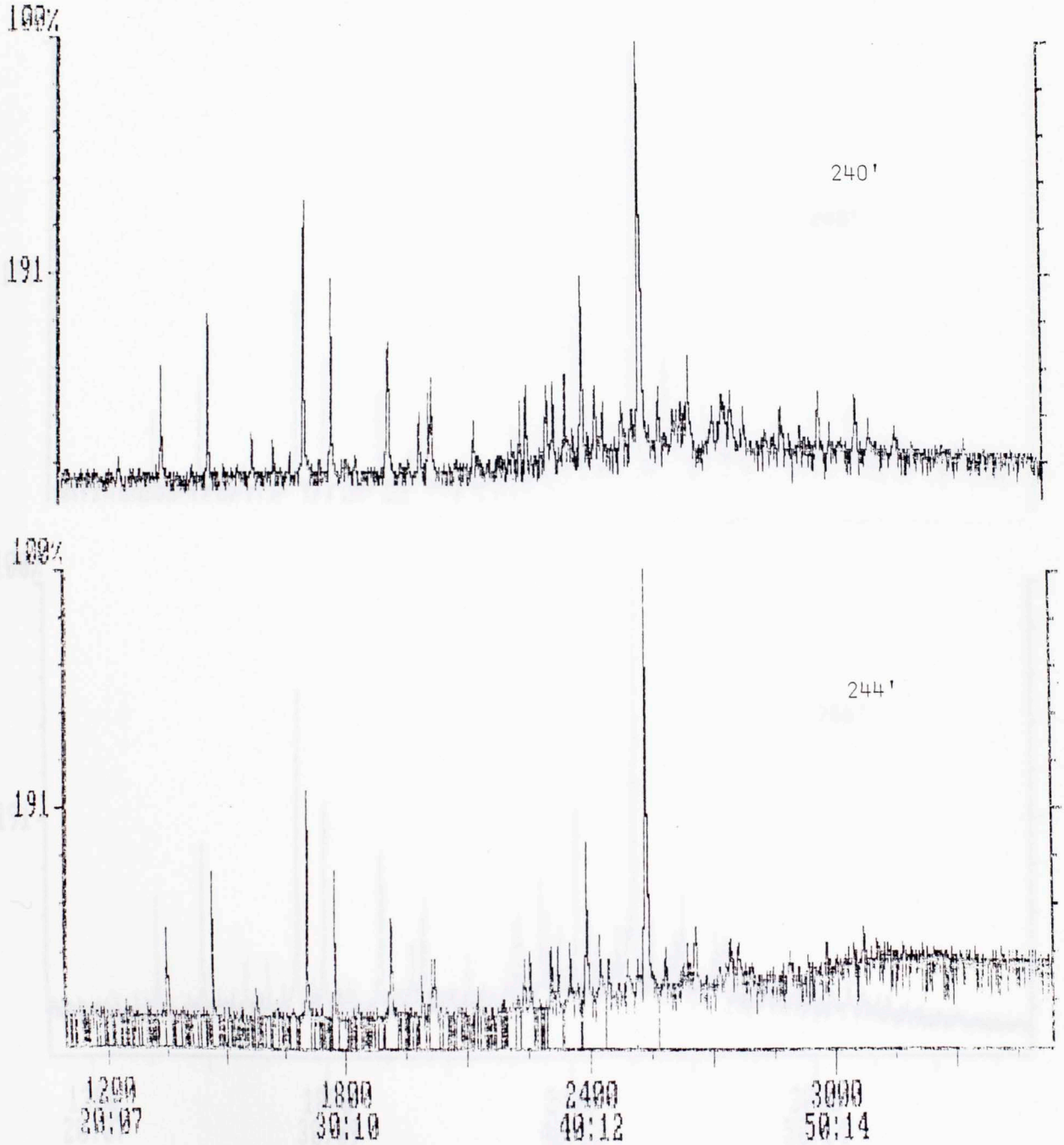

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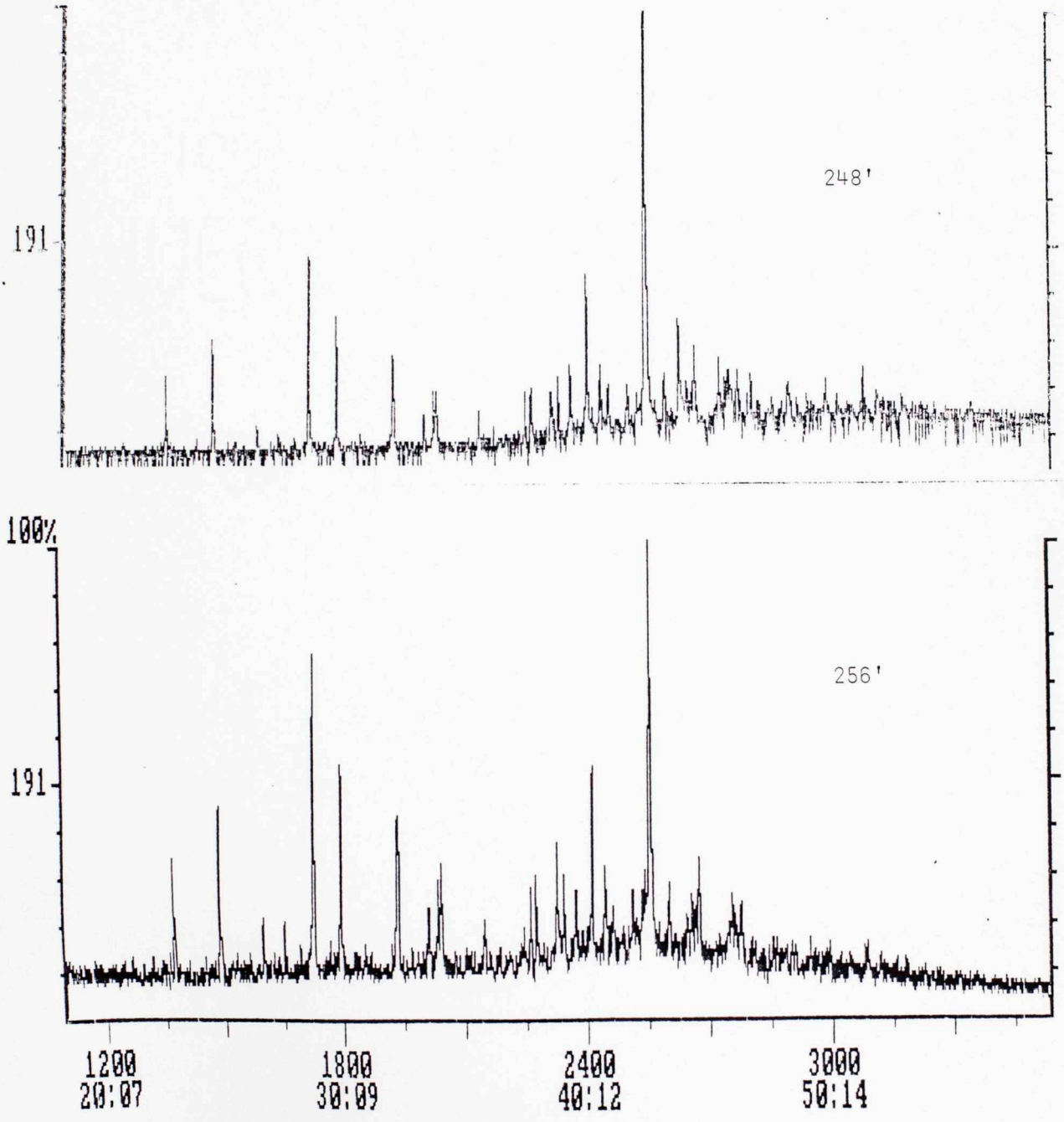

Appendix III. Continued.