PETROLEUM GEOCHEMISTRY OF A SOURCE ROCK--RESERVOIR CONTACT

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BY

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ABSTRACT

In order to shed light on the mechanism of primary oil migration, a core from the Upper Jurassic Kimmeridge Clay Formation overlying an oil-filled reservoir in the North Sea was sampled and studied. In the study area, this is the only effective source rock and aims of the study were to detect and quantify source rock depletion approaching the reservoir and compare this, chemically, to the reservoir oil. Such depletion should be characteristic of the migration mechanism in operation. Previously published studies of this nature have been few, and often in settings where limited migration and no oil accumulation has taken place and source rock maturity was low.

Source rock samples from the 92 m core were crushed and analyzed for total organic carbon and kerogen carbon isotope ratio. Crushed samples were solvent extracted and, along with the reservoir oil, these extracts were separated into compound type fractions and subsequently analyzed by gas chromatography (GC) and mass spectrometry; the latter for both carbon isotope ratio and compound class breakdown. Selected rock samples were also subjected to Rock-Eval pyrolysis and visual kerogen inspection.

Lithologically, the section consisted of variably calcareous siltstone ($9.8\% < CaCO_3 < 51.5\%$) with total organic carbon ranging from 1.3 to 5.6%, and generally lower in the bottom 30m. Hydrocarbon content ranged from 623 to 3704 ppm (46.6 to 159.6 mg/g TOC) and source rock quality rated, generally, as good to very good using three classifications.

Source rock maturity was estimated using vitrinite reflectance, thermal alteration index, pyrolysis T_{max}, odd-even predominance (OEP), methyl phenanthrene index and comparison with regional Kimmeridge Clay Formation data. A concensus of early oil window maturity resulted. Organic matter type was determined as Type II from Rock-Eval Hydrogen Index, hydrocarbon yield, and low OEP at this early maturity. Isotopically, the organic matter and oil had a marine signature. Three samples showed exceptionally abundant acyclic isoprenoids. The reservoir oil, from GC data, was typical for the North Sea and correlated well with regional data for Kimmeridge Clay bitumens at *peak* oil generation maturity. Isotope ratios were the only parameter which correlated well with the studied section.

The only depletion detected was molecular weight dependent depletion characteristic of diffusion. This was found at the second of three siltstone/sandstone contacts and composition of bitumen components expelled did not match the reservoir crude. Maximum extent of such depletion was 1.9m. The presence of such diffusional loss in pre-expulsion source rocks indicates that diffusion will impair subsequent source rock performance in interbedded sections.

Based on the maturity difference and the lack of depletion phenomena observed, it is concluded that the oil migrated from a more mature section of the same formation and that no primary migration had taken place in the section studied. The fact that expulsion had not taken place in source rocks rated as good to very good suggests that source rock classifications in general may be over optimistic and actual source rocks for some Tertiary delta provinces such as the Mississippi and Niger may be as yet undiscovered.

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Chapter 1

INTRODUCTION

1.1. Background

Oil occurrences result from generation, migration, and accumulation of petroleum, and each of these processes has been elucidated separately in the course of understanding of petroleum geology and geochemistry.

The first oil well in North America was hand dug (successfully) beneath an oil seep in 1858 and the anticlinal theory of oil accumulation was advanced three years later (Hunt, 1861) after a geological examination of this discovery and a larger nearby field in a salt solution induced anticline at Petrolia, Ontario. With refinements to include stratigraphic traps, this theory is equally valid today. Although slow in gaining acceptance in the industry after such an early start, the anticlinal theory has been the basis for the discovery of most of the world's oil and most modern detailed exploration is based on increasingly refined methods for locating underground situations which function, as the original anticline of Hunt, to trap oil.

The origin of oil, speculated on since at least 1781 (Mattavelli *et al*. 1983), has always been believed to be biological by most geologists. Development of improved techniques of geochemical analysis in the last three decades has enabled great progress to be made in demonstrating oil generation to be a function of thermal maturation (temperature and time) both for basins (Phillipi, 1965) and individual source rocks (Tissot *et al*. 1971). Oils can now be routinely correlated to individual source rocks (Williams, 1974), and the generation of oil from such rocks can be duplicated with difficulty in the laboratory (Lewan *et al*. 1979). Regions where effective source rocks have reached a level of maturity sufficient for oil generation can be delineated for intensive exploration effort, and in the absence of extensive lateral migration, these areas correlate well with proven reserves (Barnard and Cooper, 1980).

1.2. Oil migration

Oil migration remains the least understood aspect of oilfield evolution and can be split into:

- Primary migration:
  - migration of oil from source rock into reservoir rock or carrier.
- Secondary migration:
  - migration of oil in reservoir rock to trap or surface.

Secondary migration, to some extent intuitively understood by Hunt (1861), has long been the object of intensive study (Darcy, 1856) by reservoir engineers and others. The principles governing two-phase flow, phase behaviour, and pressure distribution in water-wet porous reservoirs are understood with sufficient accuracy to allow mathematical reservoir modelling and accurate estimation of reserves and recoveries. Poor understanding of oil migration is due to poor understanding of primary migration.

Primary migration might at first seem to be, like secondary migration, a problem in fluid mechanics and thus not an ideal topic for a geochemical study such as the title of this thesis suggests. However, consistent major differences in composition between crude oils and source rock bitumens together with uniform compositions of crude oils in single accumulations and among accumulations from the same reservoir-source combination indicate that primary migration is accompanied by significant chemical fractionation. The nature of this fractionation is among the best clues for deciphering the migration mechanism.

1.3. Constraints on oil migration mechanisms

Although many migration mechanisms have been suggested and discussed, to be valid, a mechanism must satisfy constraints imposed by the knowledge already gained of petroleum generation, accumulation, secondary migration, and source-rock geology.

1.3.1. Generation

Petroleum generation studies have shown that petroleum source rocks are organic carbon rich and deposited in low-energy environments (shales, siltstones, and lime mudstones). Marine and lacustrine rocks from anoxic, non-bioturbated environments are especially favorable, characterized by high hydrocarbon/total organic carbon ratios. These high ratios are developed only within the 'Oil Generation Window' where time and temperature history has been adequate for an intermediate degree of thermal maturation (Waples, 1980). Immature and overmature sediments have much lower ratios and their hydrocarbon composition does not match that of crude oils. Primary migration must occur via a mechanism which is operative at oil generation depths and which is capable of migrating hydrocarbons to reservoirs with only minor changes in their composition.

1.3.2. Accumulation

Oil accumulations are reasonably common features of most sedimentary basins. Except for dry synclines (Landes, 1959), accumulations occur where oil is trapped in a reservoir rock above water by an impermeable surface which is concave downward. This seal may be a different rock type of lower permeability than the reservoir, such as shale or anhydrite, a fault surface blocked with gouge, or a permeability decrease in the reservoir rock itself. Oil migration ceases (in the long term temporarily) at the accumulation and migration mechanisms must be incapable of transporting oil through seals and out of traps. In addition, conditions for primary migration must be common enough to exist in most sedimentary basins and be adequately extensive to account for, at minimum, the amount of accumulated oil discovered to date.

1.3.3. Secondary migration

Two-phase fluid flow and pressure distribution in porous reservoir rocks has been intensively studied (Schowalter, 1979) and has some bearing on a discussion of primary migration. Permeability of reservoir rocks may be measured with various fluids, but of importance in water-wet oil reservoirs is the relative permeability or the fraction of the single-phase permeability (K) available to each of the two phases in the accumulation. This is measurable in the laboratory and the symbols K_{rw} and K_{ro} indicate relative permeability to water and oil respectively. Since the presence of each phase interferes with the other, relative permeabilities total less than 1.0, and each reaches a value of zero while pore space saturation with the corresponding fluid is still significant.

Oil accumulations follow closely these principles of secondary migration. When fully developed they consist of (in descending order):

- a gas cap (optional)
- a zone of irreducible water saturation
- an oil-water transition zone and
- an aquifer of 100% water saturation

The pressure exerted on the water in the reservoir by the oil is referred to as the *capillary pressure* and is due to the buoyancy resulting from the density difference between the two fluids. This pressure increases linearly with height above the *free water level* (a reference level where both fluid pressures are equal and capillary pressure is zero), and the zone of irreducible water saturation occurs where the capillary pressure is sufficient to displace water from the pores to the minimum level where K_{rw} equals zero. Wells completed in this zone produce only oil, but this zone can be missing in accumulations of limited vertical extent.

The oil-water transition zone marks the range where capillary pressures are sufficient to displace some water from the pores, but not to irreducible water saturation. K_{rw} is finite and increases with depth, and wells completed in this zone produce both oil and water. The zone may be absent in very high porosity reservoirs, or where reservoirs are completely oil-filled such as sandstone lenses. The lower boundary of this zone is the *oil-water contact*, below which wells produce only water and oil saturation is zero. Only in spilled accumulations is a zone of residual oil saturation present. Oil-water contacts are sharp, and in the absence of rare hydrodynamic gradients in the aquifer, are level within the accuracy of depth measuring equipment. The oil-water contact is not found at the free water level, but lies above it by a height corresponding to the capillary pressure necessary to displace water from the largest pores (Schowalter, 1979) and this has major implications for primary migration.

Since oil is only found in pores that it has sufficient capillary pressure to displace water from, and since residual oil saturation is not found below the oil-water contact, the conclusion is unavoidable that the displacing oil has come from above and that oil-water contacts have reached their present positions by a discrete oil phase moving downward. This can be accomplished by having the source rock above the reservoir or, in the more usual opposite situation, by having the accumulation fed laterally by feeder streams along the upper reservoir contact. These would follow topographic highs on the contact, analogous to an upside-down surface drainage pattern, and need only have a small cross-sectional area, rendering negligible their probability of being intersected by drilling. Coalescence of oil droplets from below (Cartmill, 1976), or appearance of a hydrocarbon phase by some process of exsolution in the aquifer beneath the accumulation cannot account for oil accumulations as they are found to occur.

In addition, Chapman (1982) has pointed out that accumulations of sufficient thickness to possess a zone of irreducible water saturation have sufficient capillary pressure to induce a downward potential gradient in the water phase strong enough to have expelled water until hydraulic continuity is lost. Such accumulations, although water-wet, are impermeable to water (more so than the cap rock in many cases) and thus migration processes requiring cross-stratal flow of water through the oil accumulation (Roberts, 1980) are not possible.

1.3.4. Source rock geology

Source rocks are defined as those having provided oil in sufficient quantity for commercial accumulations and, as mentioned earlier, are found to be organic carbon-rich shales, siltstones, and lime mudstones in which the total organic carbon contents are generally greater than 1.5%. These, when mature, have high hydrocarbon/total organic carbon ratios. These ratios are low in coals, even though these are richest in hydrocarbons and total organic carbon, (Baker, 1962), and thus coals are at best a source for minor oil or, at high maturities, gas.

Carbonate source rocks (lime mudstones) often have very low or negligible clay content such as the Hanifa Formation of Saudi Arabia (Meyer and Nederlof, 1984) which has sourced some of the largest accumulations in the world, so the presence of clay is obviously not a requirement for primary migration (or generation). Carbonate source rocks typically have similar total organic carbon contents as source shales (Jones, 1984) and are most often hydrostatically pressured as in the Persian Gulf (Cousteau *et al*. 1975) indicating that super-normal pressures need not be present for migration. Although carbonates do show a general loss of porosity with depth (Schmoker and Halley, 1982) this is much less regular than for shales, and due to early cementation, many mudstones experience negligible additional water loss after shallow burial. This may mean that a supply of compaction-released water may not be available in some carbonate-dominated basins as a potential agent of primary migration.

1.4. Chemical fractionation during primary migration

Both crude oils and bitumens (organic compounds soluble in organic solvents) from potential source rocks consist of hydrocarbons (compounds containing only hydrogen and carbon), and hetero-compounds which in addition may contain nitrogen, oxygen, and sulfur. Traces of metals, principally nickel and vanadium are also present, in specific hetero-compounds. All these are members of the compound classes herein defined (following Jewell *et al*. 1972) as:

- Saturates:
    - Hydrocarbon compounds containing no double bonds.
- Aromatics:
    - Hydrocarbon compounds containing one or more aromatic rings.
- Resins:
    - Hetero-compounds soluble in n-pentane (generally of high molecular weight).
- Asphaltenes:
    - Hetero-compounds insoluble in n-pentane (always of high molecular weight).

Resins have been defined as being n-pentane soluble and propane insoluble, but have been found to be equivalent to the above definition (Jewell *et al.* 1972). Olefins (hydrocarbons containing one or more double bonds outside of aromatic rings) are normally absent or present only in trace amounts in crude oils and bitumens.

Compositions of oils and bitumens can conveniently be plotted on a triangular diagram by grouping resins and asphaltenes together, and this also allows comparison with data from sources where solvents other than n-pentane are used to distinguish between these two.

Tissot and Welte (1984) have analyzed and thus plotted the C15+ compositions of 517 non-degraded crude oils, and 87% of these are found to lie within the zone marked 'normal crude oils' on Fig. 1-1. The remaining 13% lie very close to this zone. Overall the distribution is weakly bimodal, with the major mode at approximately the position

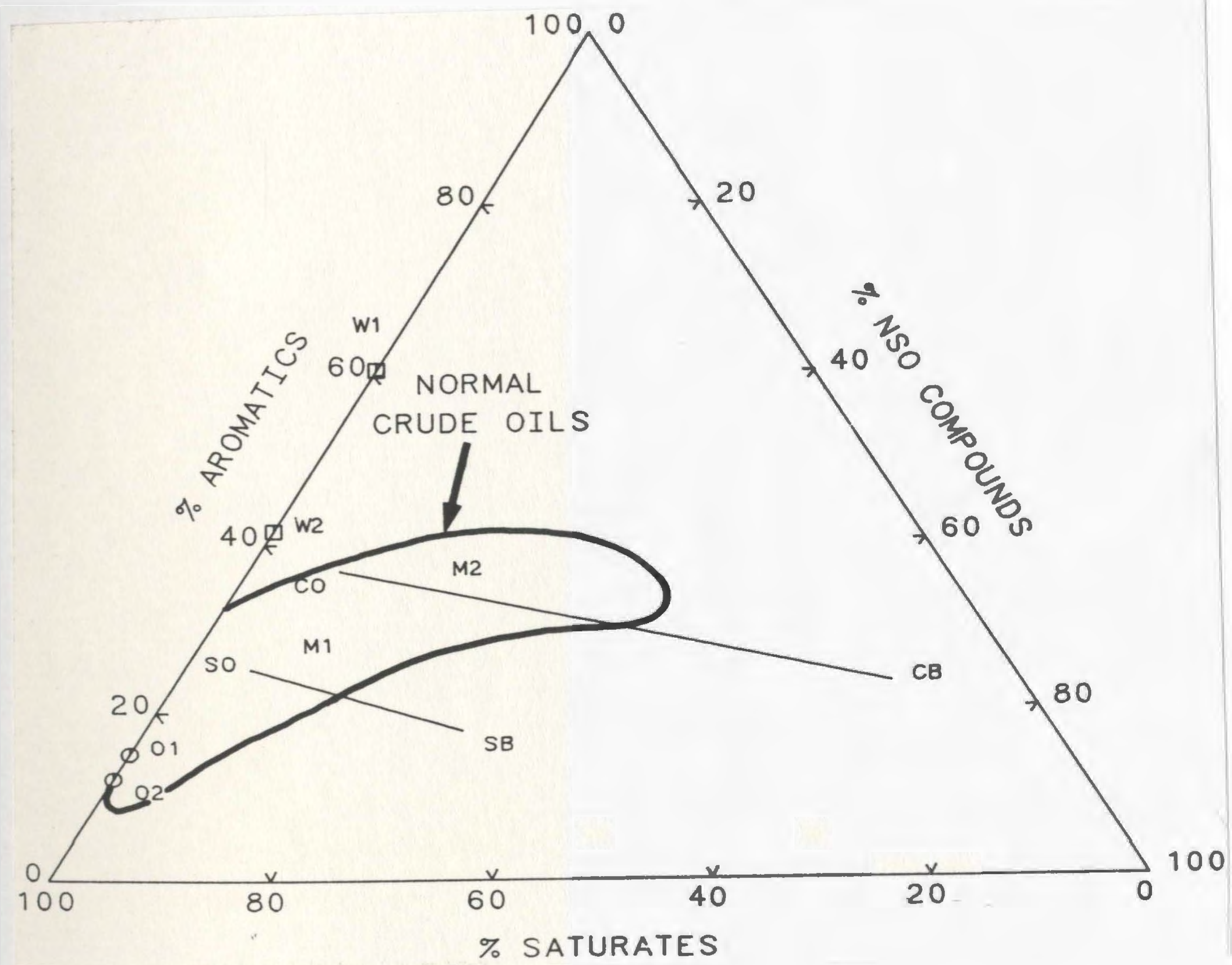


Figure 1-1: Composition of crude oils and bitumens

'M1' and a smaller mode at 'M2'. The latter corresponds to 'aromatic-intermediate oils', high in sulfur compounds and characteristic of oils from some carbonate sources such as in Venezuela and the Persian Gulf (Tissot and Welte, 1978). The overall distribution is a regular one characterized by increasing hetero-compound content with decreasing saturate/aromatic ratio. This regularity, together with the dependence of the two poorly separated modes on source rock lithology and not depth, organic matter type, hydraulic, or stratigraphic criteria; or migration distance, suggest that differing primary migration mechanisms are operating with similar chemical fractionation, or that a single mechanism is dominant.

The study of source rock bitumens has shown that when these are of oil-generating maturity, they are much enriched in hetero-compounds and poorer in hydrocarbons than reservoired oils they have given rise to (Hunt, 1979). Tissot and Pelet (1971) have presented 'average' bitumen(B) and oil(O) compositions for carbonate(C) and shale(S) source rocks and these are plotted on Fig. 1-1 as points and joined with lines CB-CO and SB-SO respectively. Although the hetero-compound content can vary somewhat with solvent used for bitumen extraction (Ferguson, 1962), this enrichment appears to be universally present. Additionally, the compositions of the saturate and aromatic fractions of bitumens are found to be very close to those of the derived crude oils, enough to be commonly used as a definitive correlation parameter (Williams, 1974; Powell et al. 1984). Thus migration takes place such that compound class proportions are changed with little or no change in individual hydrocarbon class compositions (the detailed composition of resins and asphaltenes is much more difficult to study). The regularity of crude oil compositions noted previously, independent of secondary migration distance, indicates that this fractionation takes place during primary migration.

1.5. Possible mechanisms of primary migration

Primary migration has been attributed by various workers at different times to aqueous phase processes, organic liquid phase processes, gas phase processes, and molecular diffusion.

1.5.1. Primary migration by diffusion

Diffusion is the transfer of matter, as individual molecules, driven by activity gradients from zones of high concentration to those of lower concentration, to ultimately give uniform activity. As such, diffusion can act only in decreasing concentrations and thus cannot be effective to any extent during oil accumulation.

Since relatively large organic molecules can move only with great difficulty through crystal lattices of clays or carbonates, it is probable that molecular diffusion of organics in source rocks takes place through the pore water.

Leythaeuser *et al*. (1982), have estimated diffusion coefficients for light hydrocarbons by measuring the decrease of their concentrations in a vertical shale core. They found diffusion coefficients to decrease rapidly with increasing molecular weight and concluded that diffusion is insignificant for primary migration except for gas and some gasoline range hydrocarbons. The core was however taken from a region of present-day permafrost, and may also have been weathered, so diffusion coefficients at actual oil generation depths may be much higher. Their dependence on molecular weight would remain. Although this could account for the higher retention in the source rock of high molecular weight resins and asphaltenes, it does not explain the similarity in molecular weight distributions of saturates and aromatics between crude oils and source rock bitumens. Diffusion is unable to account for migration to accumulations in contact with source rocks, where migration is counter to the concentration gradient, such as the present study.

Since accumulations are zones of maximum concentration of organics, diffusion in the subsurface should be much more active as an agent of dispersal, particularly of gas accumulations. Although this must take place to some extent, the failure of surface geochemical prospecting (Hunt, 1979) indicates that it is rarely of major significance.

If conditions are such that diffusion is able to transfer significant quantities of oil to reservoir rocks, these will be at a concentration equal to, at most, their aqueous solubility (limited by back-diffusion from exsolved oil). This presents major problems for secondary migration as will be outlined in the following section.

1.5.2. Primary migration in aqueous phase

1.5.2.1. Solution in water

Water, not surprisingly, receives extensive consideration as an agent of primary migration due to its ubiquity in the subsurface and its expulsion in large quantities from compacting shales. Water moves with relative ease through tight rocks without the relative permeability problems of oil and gas, and since generated oil must first move through a tight source rock to the reservoir and then be trapped therein by its inability to pass through a similarly tight caprock, primary migration in aqueous phase followed by accumulation as a separate organic phase seems an attractive explanation. Tertiary deltas such as the Mississippi, Niger, and Mackenzie contain thick, undercompacted shales of low organic carbon content but abundant retained water, and the many oil and gas accumulations in these settings are difficult to account for with other migration mechanisms.

Solubilities in water of individual petroleum hydrocarbons at 25°C have been determined (McAuliffe, 1978) and are, with the exception of gas constituents, low. For normal alkanes concentrations decrease exponentially from about 8000 ppm for methane to .01 ppm for C_{12}, and are approximately an order of magnitude higher at 150°C, a temperature seldom reached before gas generation from thermal cracking of oil begins. From C_{12} to C_{36}, solubilities at 25°C are below .01 ppm, where accurate solubilities become difficult to measure. Aromatics show a similar decrease but, for equivalent carbon number, are higher by approximately 2 orders of magnitude. These higher *relative* solubilities increase with temperature (Price, 1976). Cyclo-alkanes are intermediate between the two other classes, but nearer the n-alkanes (McAuliffe,1978). Data were not found on the solubilities of hetero-compounds typical of crude oils and bitumens, likely due to the largely unknown chemistry of these fractions. Although water soluble organics used in laboratory chemistry are hetero-compounds, those in oils and bitumens are of considerably higher molecular weight (500-1200 for resins, Tissot and Welte, 1978) and probably of low solubility. Water-washed crude oils are enriched in these components (Palmer, 1984) and any having significant solubility would risk being dispersed by water during and following migration. Price (1976) also measured solubilities of whole crude oils without regard to differing solubilities of individual compounds, and found a maximum of approximately 120 ppm at 150°C for the oils studied.

In light of findings about the generation of oil (Phillipi, 1965) at depths where shales have already expelled much of their pore water (and carbonates may never have had much), these solubilities are too low, assuming bitumens to have solubilities comparable to crude oils. Jones (1980) has calculated the whole-oil solubilities necessary to account for known oil in place in basins where source rocks are well studied (Williston and Los Angeles) and arrives at figures of 50,000 and 100,000 ppm respectively, assuming trapping efficiencies of 20-30%. Goff(1983) makes a similar calculation for the Kimmeridge Clay of the northern North Sea (assuming 30% expulsion efficiency) and concludes that oil content in expelled pore fluids must have been 130,000-170,000 ppm. These figures are not compatible with migration in aqueous solution. Even in the Gulf Coast Tertiary (where source rocks have not been conclusively identified), 230 ppm of oil in water are required under the most optimistic assumptions (Jones, 1980), and all the above figures assume complete exsolution by an unspecified mechanism.

Geochemically, fractionation due to solution in water has been measured by McAuliffe (1978), but only for gasoline-range hydrocarbons in waters equilibrated with crude oils. Nevertheless, these show effects expected from known hydrocarbon solubilities, namely enrichment in aromatics. The compositions of the gasoline-range hydrocarbons from two of the oils(O) and the corresponding hydrocarbons dissolved in water(W) are plotted as O1-W1 and O2-W2 in Fig. 1-1. The effect of hetero-compounds is not shown by this experiment, but if of negligible solubility as suggested above, solution in water of oils or bitumens should produce a fractionation similar to that shown, i.e. movement toward the 100% aromatics apex. This is at right angles to the observed migration fractionations, and in addition should include pronounced molecular weight fractionation, at least below C_{12} for hydrocarbons. In the examples of McAuliffe 70% of the dissolved aromatics consist of benzene and toluene, which make up 62% of the total dissolved gasoline-range hydrocarbons, in contrast to concentrations of approximately 3% in the gasoline fractions of the oils used.

Additional problems with aqueous phase migration arise when secondary migration to traps is considered, and as mentioned earlier, this also applies to migration by diffusion where the end product should at best be hydrocarbon-saturated water entering the reservoir.

To form an accumulation, oil dissolved in water must be exsolved, and chemically this can be carried out by an increase in salinity, decrease in temperature, or decrease in pressure, the latter probably effective for gaseous hydrocarbons only. Since oil accumulations are often found within the oil generation window, or nearby, extensive vertical migration necessary for significant pressure or temperature reduction often does not take place. In addition, Bonham (1980) has shown that although water released from compaction generally moves stratigraphically upward, basins are locations where water, as well as sediments, is buried. The net flux of water in the absence of uplift is thus downward with respect to sea level and the majority of pore water in sedimentary basins may never experience significant decreases of temperature or pressure other than those due to changes in heat flow from the basement, or uplift. This leaves salinity as the most feasible means of exsolution.

Shale (but not necessarily carbonate mudstone) pore waters are typically fresher than those in neighboring reservoir rocks (Hunt, 1979), and Price (1976) found that salinity greatly decreased the solubilities of hydrocarbons. This salinity though, should be relatively uniform, due to diffusion, throughout large volumes of the reservoir thus exsolution should occur over the source-reservoir contact and spread, rather than in a trap. Oil saturation in the reservoir would then have to rise to residual oil saturation (where $K_{ro}>0$) before oil flow could occur, with the result that most of the reservoir outside the trap would contain this amount of oil. As mentioned under 'Secondary Migration' above, this is normally found not to be the case (but see du Rouchet, 1984), and would in any event be, volumetrically, extremely wasteful (McAuliffe, 1978). Exsolution from temperature decrease, although as outlined above unlikely, would show the same effect to a greater degree, since temperature change and therefore exsolution would take place gradually as the water rose, exsolving oil to be trapped as residual throughout the dipping reservoir.

Due to the above implications and other difficulties, simple migration of oil dissolved in water appears extremely unlikely, if not impossible. To overcome some of these difficulties, some modifications have been proposed to the simple pore-water solution mechanism. These include changes to increase solubility of hydrocarbons, and those which strive for the same effect by increasing availability of water.

Price (1976) advocated migration in super-hot (>300°C) waters from great depths in sedimentary basins, thus vastly increasing solubilities. This mechanism requires temperatures that are never reached in many petroliferous basins, and a mechanism to bring such hot waters up to oil generation depths to dissolve hydrocarbons from source rocks. Problems of chemical fractionation and residual oil saturation will remain, even if such a fortuitous mechanism could be found.

1.5.2.2. Micellar solution

Cordell (1973) and others have proposed surfactants to solubilize oil as 'micelles', much like household detergents, thus enabling migration of important quantities of oil in water. This mechanism, as reviewed by McAuliffe (1978), requires large amounts of surfactant (approximately equal to the oil dissolved), and the origin and fate of this surfactant cannot be accounted for. Surfactants are used in some tertiary recovery projects in depleted reservoirs (Herbeck *et al*. 1976) where only an advancing front of solubilized oil is established, not dissolution of the entire reservoir contents. Even this is not feasible in carbonate reservoirs due to adsorption of surfactant onto mineral surfaces, and McAuliffe (1978) indicates that water-in-oil micellar solutions are preferentially formed. The chemical fractionation effect of micellar solution would likely be similar to that of pure water, if solubility is increased uniformly for all compound classes, and upon breakdown of micelles into oil droplets, (mechanism unspecified); secondary migration problems similar to those for simple water solution should remain. If, somehow, droplets smaller than reservoir pore sizes could be stabilized by some remaining surfactant, and rise by buoyancy, they could not establish normal oil-water contacts as explained earlier under 'Secondary Migration'.

1.5.2.3. 'Protopetroleum'

A similar mechanism involving 'in-transit conversion' of a soluble protopetroleum has been proposed by Hodgson(1980), but consists of actual generation during migration rather than solubilization of pre-existing compounds. In such a case, oil precursors or incompletely generated oils should be found in reservoir rocks, and being water soluble, should have a composition very unlike 'normal crude oils' in Fig. 1-1. Breakdown products should also be evident. Petroleum generation in source rocks has been shown to result from thermal breakdown of insoluble, high molecular weight kerogen, and it would be a strong coincidence if oil of near-identical hydrocarbon composition could be generated from water-soluble molecules. Problems of secondary migration of such generated oil should be of equal difficulty to those resulting from micellar solution.

1.5.2.4. Solution in CO_2-saturated water

Bray and Foster (1980) have reported CO_2-saturated water to be much more effective than distilled water for transporting oil through sediments, and propose that oil migration may take place by this mechanism. Whether subsurface waters approach CO_2-saturation is doubtful because:

1. most organic CO_2 generation is complete before the onset of oil generation in oil-prone source rocks.
2. inorganic CO_2 generation takes place at temperatures well above those of oil generation.
3. CO_2 in water can react to form secondary carbonate minerals, and
4. natural gases in contact with pore water for long periods typically contain only traces of CO_2.

CO_2 is used in tertiary recovery projects where its high solubility in both water and oil lowers interfacial tensions and makes possible miscible flooding of reservoirs (Momper, 1978). This may account for the report of Bray and Foster (1980).

1.5.2.5. Additional water source

In addition to seeking means of greater oil solubility in water, aqueous phase migration could conceivably be achieved by acquiring a larger volume of water available for transportation. Toth (1980) has analyzed the flow of meteoric water from topographically high to low regions in a basin, and shows that with large surface areas compensating for low permeabilities, such flow can penetrate to great depths and cycle large volumes of water through source and reservoir rocks alike. Even if this flow were sufficient to successfully transport significant quantities of oil, with attendant fractionation and secondary migration problems, it would leave unexplained the migration and accumulation of offshore oil. Here the water table is level and constant (excluding tides) and yet oil is seen to originate and accumulate exactly as in onshore basins, the only difference being the present day surface geography. Similarly, Powers (1967) and many others have proposed the conversion at depth of montmorillonite to illite to provide the extra water necessary for aqueous migration. This mechanism would leave unexplained the migration of oil from montmorillonite-free (and practically clay-free) carbonate source rocks such as those feeding the richest producing areas of the world in the Persian Gulf.

1.5.3. Primary migration in oil phase

Primary migration in a separate oil phase was suggested as early as 1935 (Hoots *et al.* 1935) but received little consideration until much later (Dickey, 1975) due to the lack of modern techniques of detailed hydrocarbon analysis, and a concentration of attention on aqueous phase migration thought to be more likely for the Gulf Coast Tertiary. Oil phase migration is becoming increasingly favored as an explanation for oil occurrences (Durand, 1981), largely due to increasing recognition that other proposed mechanisms fail to account satisfactorily for geochemical observations and material balance calculations for known oil-source rock combinations. Problems, however, remain and if, as many believe, oil undergoes primary migration as a separate phase, it is by a process or processes as yet poorly understood.

Geochemically, the similarity in composition of saturate and aromatic hydrocarbon fractions between oils and source rocks, mentioned earlier, is one of the observations most strongly favoring migration in oil phase. As was seen in the case of diffusion (molecular weight dependent), and aqueous phase migration (solubility dependent), and as will be outlined for gas phase migration (vapor pressure dependent), migration by any of these mechanisms will result in more or less severe fractionation of hydrocarbons. They are, however, totally miscible in a liquid hydrocarbon phase with the possible exception of some very high molecular weight polycyclic aromatics. The observed depletion in hetero-compounds of oils relative to their sources indicated on Fig. 1-1 has been attributed to adsorption on mineral surfaces (Tissot and Welte, 1978) or their limited solubility in a liquid hydrocarbon phase (Tissot, 1981). If either of these processes is active, migration in oil phase can explain observed geochemical fractionation better than other mechanisms considered herein.

Other evidence favoring oil phase migration includes direct and indirect observations. Liquid oil has been observed in source rock fractures (Hoots *et al.* 1935) and produced therefrom in particularly rich source rocks (Meissner, 1984), the production being water-free. Oil has also been observed in fractures in rocks between oil reservoirs and underlying source rocks (all being carbonates) in the Persian Gulf area (Murris, 1984). Surface oil seeps, although common, are equivocal and in many cases are instances of secondary migration from underlying accumulations. Meissner (1984) and Goff (1983) have documented large increases in deep resistivity on wireline logs in mature source rock intervals. In the North Sea Kimmeridge Clay example given by Goff (1983) this decreases to normal levels below the oil generation window, and thus cannot be due to compaction-related porosity loss. Such resistivity increases independent of porosity indicate increasing hydrocarbon saturation in the pore space (Archie, 1942) and increasing discontinuity of the conducting water phase. The decrease after termination of oil generation must indicate expulsion of oil generated, or expulsion of gas generated from thermal cracking of oil.

The observation that source rocks generating commercial oil generally contain large amounts of organic matter (>2.5% TOC- Jones, 1980) seems intuitively obvious, but is inconsistent with migration in water solution. Jones (1980) shows that rocks with total organic carbon as low as 0.2% still have enough hydrocarbons at peak maturity to saturate their pore water. This implies that virtually all fine-grained rocks can expel equal amounts of oil in solution, and that for many rocks, peak expulsion could thus occur well above oil generation depths. This is not consistent with either the distribution or composition of reservoired oil, but if migration in oil phase is possible, this difficulty is overcome.

1.5.3.1. Flow through pores

Difficulties encountered in explaining primary migration in oil phase are principally of a mechanical nature and some also arise from field observations. Migration in oil phase in a source rock must proceed by increasing the oil saturation in the pore space to a point where the relative permeability to oil becomes appreciable (considered to be 20-30%), to establish a continuous oil phase in finely porous shales. This involves injecting oil into water-filled pores much smaller in diameter (10^{-5} to 10^{-6}mm, Momper, 1978) than those in reservoir rocks. Due to the greatly decreased radius of curvature of the oil-water interface upon penetrating such pores, the capillary pressure (pressure differential between oil and water) necessary becomes enormous. Tissot and Welte (1978) calculate that for pores of 10^{-5}mm and viscosity and interfacial tension for typical oil generation conditions, a capillary pressure of approximately 240 kg/cm^2 would be required to force entry. There is no reasonable source for such pressures. Buoyancy alone, for an oil SG of 0.8, would require an oil column of 12 km, and the pressure of the oil phase (water pore pressure + capillary pressure) would equal overburden pressure at a depth of 1900 m under hydrostatic conditions. It is impossible to approach such pressures without hydraulic fracturing (Eaton, 1969), and since the capillary pressure is an increment added to the pore pressure, undercompacted overpressured shales only compound the problem. Dickey (1975) suggested that permanently adsorbed water layers on pore walls in shale rendered much of the water functionally solid, thus greatly increasing the hydrocarbon saturation in the remaining effective porosity. This, however, adds to the capillary pressure problem by decreasing pore diameters and is likely not applicable to carbonates where both pore diameter and porosity may be much less than shales (Ayres *et al*. 1982).

If oil does migrate from source rock to reservoir in oil phase, subsequent secondary migration by buoyancy through the reservoir should leave residual oil saturation along the migration path. If the entire contact surface between source and reservoir transmits oil, as would be expected for migration through pores, this residual saturation should be easily detected during drilling, logging, and coring and should tie up a sizeable fraction of migrated oil, increasing with area of contact and distance of migration. This residual oil is seldom, if ever, encountered and Sluijk and Nederlof (1984), after analyzing several hundred oil accumulations from 37 basins, found no correlation between migration efficiency and migration distance (over 100 km in some cases). They concluded that 'no appreciable oil loss takes place during migration'. This is difficult to reconcile with oil phase migration through source rock pores.

Coals, having low porosity and high hydrocarbon content, should be the best of source rocks, if migration is in oil phase through pores. Coal measures generally have abundant clean channel sandstones and sealing shales and thus should contain major oil reserves in stratigraphic traps. In fact, they are only marginally prospective, usually for gas at high maturities. On the opposite end of the source-rock scale, thick Tertiary deltas such as the Mississippi and Niger are characterized by very thick organically poor (<1% TOC) shales featuring gas prone terrestrial and oxidized organic matter. These should be very unfavorable for oil phase migration, yet such deltas contain abundant oil reserves. This fact has directed much study toward aqueous phase migration as noted earlier.

1.5.3.2. Flow through fractures

In an effort to explain oil phase migration, in spite of the enormous capillary pressures required in shale pores, Tissot and Pelet (1971) have proposed migration through micro-fractures. If present, these would presumably have dimensions sufficiently great to alleviate the capillary pressure problem, and if distributed densely enough, could contact sufficient kerogen to attain appropriate oil saturation and conduct adequate volumes of oil to reservoir rocks. The formation of such fractures is more problematic. Du Rochet (1981), using an analysis based on effective stresses (maximum downward) shows that hydraulic fracturing occurs in a source rock when pore pressure (P_s) exceeds the least principle stress (S_3) by the tensile strength of the rock (T), normally low.

$$S_3 - P_s = -T$$

Further increases in pore pressure are bled off by reopening or extending such fractures. Injection of fluid from fractures to reservoir rocks encountered during fracture extension can only take place if the reservoir pore pressure (P_r) is sufficiently less than that of the source rock such that the least principle stress (S_3) now exceeds it by an amount equal to the capillary pressure necessary to force entry into the largest pores in the reservoir (P_c).

$$S_3 - P_r = P_c$$

This implies that water cannot enter a reservoir from a tensional fracture ($S_3 - P_r = 0$), and that pore pressures greater than hydrostatic are needed for any hydraulic fracturing. However, with oil, if sufficient vertical oil column can be established in a fracture system to achieve sufficient capillary pressure by buoyancy, a reservoir may be entered through any fractures, even ones predating oil generation or produced by tension. Thus supernormal pressures may be required only to initiate and propagate microfractures until they encounter any pre-existing permeable conduits. Those conduits first encountered which are capable of transmitting enough oil and/or water to prevent further pressure increases, will stop further fracturing and propagation, and transmit all of the produced fluids in the fracture system. Thus entry to a reservoir rock would be at distinct localities and not uniformly across the contact, if this scheme applies.

Such a mechanism of migration by microfractures, although not restricted by high capillary pressures or secondary migration losses, still leaves unexplained the problem of coals, because these have very low tensile strengths and should fracture easily. Similarly, thick Tertiary deltas (the other problem area) are characterized by much higher supernormal pressures than most other geological environments and these pressures could not be sustained if hydraulic fracturing was occurring. This is therefore likely due to high values of least principal stress, indicating a more plastic rock behaviour, and should apply to other shale lithologies.

Oil phase migration through pores and fractures would involve bitumen contact with water-wet mineral surfaces. Adsorption on such surfaces increases in the order: saturates < aromatics < hetero-compounds (Van Cangh and Fripiat, 1973) and the fractionation observed from primary migration has been attributed to such adsorption by Tissot and Welte (1978). Seifert and Moldowan (1981) have used the term 'geochromatography' to describe such fractionation, due to effects analogous to conventional liquid chromatography. Some differences from laboratory chromatography exist, however, and are important. Bitumen entry into the migration path can take place anywhere in the source rock and no carrier liquid or gas is present. This is analogous to simultaneous sample injection at many points along a chromatographic column, with no carrier flow. A two-component mixture normally eluting as two peaks in conventional chromatography would, under these conditions, elute as a single broad peak containing a small percentage of the more strongly adsorbed component. The remainder of this component would remain permanently adsorbed on the substrate. Final composition of the oil migrated under these conditions, for a given generated bitumen and mineral composition, would depend on the bitumen/mineral ratio, a high ratio resulting in an aromatic and hetero-compound rich oil. Low ratios in the source rock should produce a more saturate-rich oil and any lean rocks subsequently passed through should produce the same effect, increasing with primary migration distance.

1.5.3.3. Flow through kerogen

McAuliffe (1978) has suggested that oil phase migration routes should in fact be along strands of kerogen in the source rock. He argues that because oil is generated from the kerogen, it is automatically oil-wet and no capillary pressure or relative permeability problems will be encountered if a three-dimensional kerogen network exists. He also shows examples of isolated uncrushed kerogens which are both porous and interconnected in three dimensions.

Source rocks, both shales and carbonates, are commonly laminated, with alternating kerogen-rich and kerogen-poor layers undisrupted since deposition due to anoxic conditions toxic to bottom-dwelling burrowers. Continuous kerogen connections in two dimensions are easily visualized in such rocks, but connections between laminae must be much less abundant, and if present, would likely be caused by rare burrows or very low-angle cross-bedding. Permeability to oil flowing through kerogen would thus likely be much lower across bedding than along it, and oil entering a reservoir rock would likely be at discrete localities rather than continuous over the contact. This avoids the secondary migration problems mentioned previously by minimizing the cross-sectional area of oil migration pathways through the reservoir rock.

Some other difficulties with oil phase migration are also avoided by assuming flow along kerogen, thus making this an attractive scheme. Minimum TOC values for oil expulsion, often assumed as 0.5% (Momper, 1978) or 2.5% (Jones, 1980- observed from known accumulations) may represent minimum values for achieving three-dimensional continuity. Oil expelled from source rocks by migration along kerogen should be oil surplus to that required to saturate the kerogen itself, thus the HC/TOC ratio should determine source potential. This, as mentioned previously, has often been documented or is implicit in reporting of data normalized to organic carbon, and accounts well for the poor source potential of coals.

1.5.3.4. Oil phase migration - summary

It appears extremely difficult for oil phase primary migration to take place through source rock pores, but alternative mechanisms of fracturing or flow along kerogen appear feasible. Since any compaction-expelled water should be free to move through pores, oil phase primary migration may be independent of water movement altogether. The driving force responsible would then be limited to compaction from overburden or volume expansion from oil generation. The latter has been shown to be negligible during oil generation (Ungerer *et al.* 1981), and many examples are known of source rocks which have successfully sourced many accumulations without achieving the higher volume expansion attendant upon incipient gas generation (Meissner, 1984; Ayres *et al.* 1982).

Compaction as a driving force for expulsion can act only when oil is subjected to overburden stress if, as in the majority of rocks, pore pressure is hydrostatic. Dispersed fragments of kerogen may well be effectively pore space, under hydrostatic pressure with the effective overburden stress supported by surrounding mineral grains. Continuous kerogen laminae on the other hand, must be subjected to overburden stresses, and this style of kerogen distribution may thus lead to improved expulsion of generated oil. The kerogen is, in effect, partly converted to liquid (particularly oil-prone kerogen) which must move under overburden stress until solid-solid contact is again established. Because capillary pressures for pore entry are unattainably high, migration should take place along kerogen laminae, with pressure in the oil phase building to fracture limits without affecting water pore pressure when escape is blocked. This would ultimately lead to migration by a combination of the two mechanisms suggested above: along kerogen where possible and through fractures when necessary, linking semi-continuous kerogen pathways. Any abnormally large pores could also be invaded. This would account for observations of oil in microfractures (Murris, 1984; Hoots *et al.* 1935) without requiring supernormal pore pressures or pervasive hydraulic fracturing. Such a combination would also retain the advantages of the mechanism of McAuliffe (1978) in explaining coals and minimum TOC values of oil-expelling source rocks.

Regardless of the predominance of microfracturing or kerogen 'wicking' in the final expulsion system, the first effective connection with lower pressured reservoir rocks or other permeable conduits would prevent further pressure increases in any isolated hydraulically continuous oil-wet system. This would prevent establishment of a large number of 'outlets', and the few functional outlets could expel semi-continuously low cross-section feeder streams for volumetrically efficient secondary migration to traps or surface seeps. Geochemical fractionation on the other hand may differ between microfracturing and kerogen wicking. In the former, oil flow would contact mineral surfaces and adsorption of organic compounds could be a factor, but kerogen wicking should avoid this and fractionation should depend on solubility only. As such, it should be independent of the length of the migration path.

Neither microfracturing, wicking, nor a combination of the two appears to be a good explanation for oil migration in Tertiary deltas. These are almost certainly too low in TOC for a three-dimensional kerogen network and too highly overpressured to have any significant microfracture permeability. This is in addition to their unfavorable organic matter type. However, as well as the above characteristics, the Mississippi and Niger deltas also share a lack of published oil-source rock correlations. The depths at which oil generation maturities are presently reached have been located for the Mississippi (Laplante, 1974) and for the Niger (Ekweozor and Okoye, 1980) but the reservoired oils in these respective regions have not been shown to be expelled from these mature, but lean, rocks, or indeed that any oil has been expelled from them at all. A lack of drilling to deep pre-Tertiary rocks is also a feature of such sequences, and a rich lower Tertiary or Mesozoic conventional source rock could do much to explain the many problems of generation and migration in the Tertiary deltas. In areas of such rapid deposition, efficient seals such as anhydrite would lead to thermal destruction of trapped oil, and in areas of slow deposition inefficient seals would lead to surface loss. However, *rapid* deposition of *inefficient* seals could lead to vertical secondary migration and remigration roughly keeping pace with sedimentation, even after source rocks are deeply buried below oil generation maturities. This would result in multiple-pay fields, stacked reservoirs at wide-ranging depths, and gas relatively high in the section due to inefficient sealing, all hallmarks of Tertiary deltas. Also, in the resulting absence of major surface loss or thermal destruction, trapping efficiency may be quite high and the actual source rock not outstandingly rich. The entire situation may be comparable to the North Sea, where a lean, rapidly deposited Tertiary sequence, lithologically similar but much thinner than the two deltas mentioned, hosts numerous accumulations from shallow degraded oil to gas and condensate, all sourced by the underlying Jurassic. Oil-source rock comparisons between delta oils and landward, older potential source rocks could possibly resolve this long-standing problem. Isotopically, at least, some Tertiary and Cretaceous Louisiana crudes are similar (Sofer, 1984), and a rich Cretaceous source has been correlated to several Mackenzie delta crudes (Bruce and Parker, 1975).

1.5.4. Primary migration in gas phase

Hedberg (1974, 1980) has proposed primary migration of oil in gas phase. At oil generation maturities, CO_2 and biogenic methane generation have largely ceased for oil-prone kerogen and H_2S generation has not yet become significant (Le Tran, 1973), thus any gas phase present should be dominated by thermally generated methane, as Hedberg (1980) proposes.

Solubility in gas phase of compounds normally present in crude oil depends on temperature, pressure, and the overall composition of the system. Although it is not possible to measure the effects of each variable, solubilities of several whole oils in 'natural gas' as a function of temperature and pressure are given by Zhuze *et al*. (1962, 1963) and in methane (with water present) for one crude oil and two distillation fractions by Price *et al*. (1983). The data are broadly similar and show increasing solubility with temperature and especially pressure, the solubilities being higher overall in the hydrous system.

Theoretically, assuming Raoult's law is broadly applicable, solubility of individual compounds in the gas phase should be a function of vapor pressure and concentration in the liquid phase. Primary migration in gas phase would thus favor compounds of high vapor pressure (generally low molecular weight) and the resulting fractionation should produce a gas phase enriched in these components relative to the remaining liquid. This is shown by the data of Price *et al*. (1983) at temperatures of 150°C or lower. In terms of compound types, this would in general show up as an enrichment in saturates relative to aromatics due to the minimum aromatic molecular weight of 78, and an enrichment of aromatics relative to hetero-compounds due to the very high molecular weight of asphaltenes and most resins. In practice, however, analysis of $C_{15}+$ fractions of oils would largely miss the low molecular weight fractionation effect, and any saturate/aromatic fractionation observed would depend largely on the molecular weight distributions of these compound types above C_{15}.

Asphaltenes and resins were previously defined herein as being 'n-pentane insoluble' and 'n-pentane soluble, propane insoluble' respectively and it is difficult to see how such high molecular weight compounds can be dissolved in much greater weight dilution by methane, which according to Mitchell and Speight (1972) should have a much reduced capacity to retain these in solution than propane or n-pentane. Notwithstanding, Price *et al.* (1983) have found a measurable solubility of vacuum distillation residue in methane at 250°C, in addition to hetero-compound enrichment in gas equilibrated with heavy distillate at various temperatures. $C_{25}+/(C_1-C_{15})$ ratios for crude oil dissolved in methane were also found to exceed those for the initial crude oil at various temperatures and pressures in the study of Price *et al.* (1983). This is the opposite of expected fractionation and was left unexplained. Price *et al.* (1983) used crude oils of very low hetero-compound content to begin with (3.25%), and dissolved oil in the gas phase was measured by taking two differences, so possibly small systematic errors were magnified. Also it is clear that for at least some of the liquid-gas equilibrations, new crude oil (or fraction thereof) was not added to the system, the changes made being only increasing temperature or pressure after sampling gas from a previous run. With pure liquid (such as the water present) or solid, no activity change would result from this, but for a liquid mixture, concentration and thus activity would decrease for those compounds depleted by the first sample withdrawal. Concentrations subsequently measured would not be at equilibrium with the original starting material. Another possibly pertinent factor would be the limited *volume* dilution by methane in the gas phase at high pressures.

Assuming that the quantities of 'liquid' dissolved in gas phase measured by Price *et al.* (1983) are accurate, any fractionation of individual compounds may mean that some are effectively insoluble in methane under experimental conditions and thus gas/liquid ratios calculated for oil migration are only minimum, similar to water/oil ratios calculated from 'whole oil' water solubility. However they are still useful for comparison to gas/liquid ratios measured at various stages of source rock maturation. Data presented by Rumeau and Sourisse (1973) and Zhuze *et al.* (1962) on initial conditions in natural condensate reservoirs show gas/oil ratios greater than or equal to those determined by Price *et al.* (1983). The weight ratios presented by Price *et al.* (1983) reach a minimum of 0.71 (gas/liquid) at 150°C and 845 kg/cm^2, considered to be maximum temperature and pressure for oil generation and preservation, and reach a value of 3.57 at 100°C and 422 kg/cm^2, conditions corresponding closely to the reservoir in this study and more normal for oil generation conditions.

Studies of gas content of source rocks are rare due to the specialized equipment required and uncertain extent of loss from core recovery and storage. Tissot *et al.* (1971) have carried this out for source rocks of the Paris basin and report a maximum weight ratio of .028 $(C_1-C_5)/(C_6+ HC)$. This corresponds to near peak oil generation, the maximum maturity reached by the type II kerogen in this basin.

Several efforts to duplicate oil generation in the laboratory have also quantified gas/oil ratios. Using hydrous pyrolysis, considered to be the most authentic laboratory duplication of natural maturation (Winters *et al.* 1981), Tannenbaum *et al.* (1986), working with a type I kerogen, measured a weight ratio of .011 (C_1-C_6)/(total bitumen) at peak bitumen generation maturity. With dry pyrolysis this ratio reached .289 (same kerogen and maturity) and .467 (different kerogen, same maturity). Rohrback *et al.* (1984), using dry pyrolysis of immature recent sediments, measured ratios of $C_1/(C_{15+}$ HC) of .379 and .787 for types II and III kerogen respectively, at peak liquid hydrocarbon generation maturity. All of these pyrolysis results, free from the loss hazards of core studies, show in general a decrease in the gas/oil ratio (in the units chosen) as the pyrolysis experiments approach natural maturation, i.e. in the order: Recent sediment dry pyrolysis > Ancient sediment dry pyrolysis > Ancient sediment hydrous pyrolysis. Not even in the recent sediment dry pyrolysis does this ratio approach the value of Price *et al.* (1983) for oil generation conditions.

Under natural maturation conditions, where generation is much slower, more time is available for methane loss by diffusion and water solution, as evidenced by the lack of CO_2 in gas accumulations relative to that generated by kerogen maturation. Sluijk and Nederlof (1984) in a statistical analysis of known source-migration path-accumulation situations, estimate that in contrast to oil as previously cited, an average of 75% of gas is lost during migration, probably by diffusion and solution. Finally, although in many respects not an accurate simulation of natural maturation, Ungerer *et al.* (1981) used dry pyrolysis to calculate that at maturities of 1.3% Ro vitrinite reflectance equivalent (approximate oil deadline), both types II and III kerogen will generate liquid phase products only. It appears from all the above evidence that sufficient gas is not available at peak oil generation for gas phase oil migration. Hedberg (1980) indicates otherwise, but his diagram of generation products vs. depth is taken largely from composition data of accumulations, which have undergone varying degrees of vertical secondary migration.

The conclusion of insufficient gas for gas phase primary migration is supported by field evidence from regions where key source rocks have not matured beyond peak oil generation. In the central and northern North Sea, the main source rock, the Kimmeridge Clay Formation, has for the most part not exceeded peak oil generation maturity (Cooper and Barnard, 1984). Oil accumulations here with few exceptions are unsaturated (lack gas caps) but due to continuing present day subsidence, most are probably still accumulating or spilling oil.

Although discussion so far has centred on peak oil generation maturities, gas/oil ratios in the source rock can rise to near infinite values with increasing temperature and pressure while ratios required for gas phase migration fall. There thus appears to be no valid reason why gas phase migration cannot take place at advanced maturities where wet gas, dry gas, and condensate are the main products. Greatly increased volume expansion at such maturities (Ungerer *et al*. 1981) should greatly assist such expulsion, and indeed migration may become possible for gas and condensate under such conditions for source rocks (for example coals) which were unable to expel oil at lesser maturities.

In cases where migration has proceeded in gas phase, migration direction should be dominantly upward due to buoyancy, and exsolution of oil will be by retrograde condensation under conditions of decreasing pressure and temperature. This should lead to an increase in gas and light hydrocarbon content in an upward direction where vertically stacked accumulations are available for sampling. Such a pattern, the opposite of normal maturity-depth trends, has been observed by Illich *et al*. (1981) and Ungerer *et al*. (1984) and attributed by the latter to gas phase migration. Such migration, however, need not be primary, and in at least one of the cases mentioned (Ungerer *et al*. 1984), mature gas-prone source rocks are present in great quantity below the accumulations. This would allow gas, if migrating from below in gas phase, to dissolve hydrocarbons from accumulations passed through and condense them higher in the sequence, producing the observed effect. Unlike water, as previously explained, gas is able to enter and pass through oil accumulations (although probably not able to enter source rocks) and thus the scheme outlined is one of secondary migration, a form of segregation-migration as described by Silverman (1965). The presence therefore of such a sequence as observed, where a possible underlying gas source exists, cannot be accepted as a case of gas phase primary migration (or even principally gas phase secondary migration) without further detailed study.

1.6. Aims of the present study

A study of primary oil migration to determine which, if any, of the mechanisms, or combinations of mechanisms, outlined above has been operative is best carried out where source rock, migration path, and resulting oil composition are accurately known. The ideal location would be a source rock-reservoir contact where the reservoir is oil-bearing, and still being filled, minimizing the possibility of post-accumulation alteration. The present study comprises an organic-rich shale overlying an oil-bearing reservoir in the North Sea, a region where only one oil source rock appears to be present (Cornford, 1984). As previously stated, Tertiary-Recent subsidence has been rapid and is continuing, such that in most areas oil generation and thus presumably migration are ongoing, without any special pressure and temperature conditions as postulated by Cartmill (1976). Due to the shale overlying the reservoir, oil-bearing sandstone is adjacent to the shale rendering impossible any post-accumulation hydrocarbon diffusion from source to reservoir. Like most North Sea accumulations, the reservoir is unsaturated, making gas phase primary migration unlikely and certainly impossible by buoyancy alone. Geochemical analysis of source rock bitumens and reservoir oil in this situation should reveal chemical fractionation and depletion characteristic of the migration mechanism operating as follows:

Primary migration by diffusion or gas-phase flow, although seemingly impossible in the situation under study, should be made evident by a preferential depletion in low molecular weight compounds in the shale bitumens as the reservoir is approached. If the gas phase is able to flow through fractures or other permeable conduits, depletion should increase toward these in addition to the reservoir contact. Reservoired oil should show a concentration of low molecular weight compounds together with a large gas cap in the case of gas phase migration.

Primary migration in aqueous phase should result in depletion in aromatics as the reservoir or permeable conduits are approached. Reservoir oil, in the case of near-total exsolution, should be greatly enriched in aromatics, the enrichment increasing with efficiency of exsolution.

Depletion and fractionation due to oil phase migration should depend also on the specific flow mechanism. 'Wick' flow of bitumen through a continuous kerogen network should involve minimum contact with mineral surfaces and thus minimum adsorption of compounds thereon. Geochemical fractionation should be entirely due to solubility in the liquid organic phase and thus independent of primary migration distance. Asphaltenes would likely be more abundant in bitumens than in oils due to such fractionation if saturation is reached. For a given kerogen type, bitumen generation per unit kerogen should be constant and since the migration path is along kerogen and this, being under compaction pressure, constitutes a poor reservoir site, any depletion should be observed along the kerogen flow path and thus show up as a depletion per unit TOC, independent of mineral composition, as the reservoir or other permeable conduit is approached.

Oil phase migration through pores and fractures on the other hand, would involve bitumen contact with water-wet mineral surfaces. Adsorption on such surfaces increases in the order: saturates < aromatics < hetero-compounds (Van Cangh and Fripiat, 1973) and the fractionation observed from primary migration has been attributed to such adsorption by Tissot and Welte (1978). Seifert and Moldowan (1981) have used the term "geochromatography" to describe such fractionation, due to effects analogous to conventional liquid chromatography. Some differences from laboratory chromatography exist, however, and are important. Bitumen entry into the migration path can take place anywhere in the source rock and no carrier liquid or gas is present. This is analogous to simultaneous sample injection at many points along a chromatographic column, with no carrier flow. A two-component mixture normally eluting as two peaks in conventional chromatography would, under these conditions, elute as a single broad peak containing a small percentage of the more strongly adsorbed component. The remainder of this component would remain permemantly adsorbed on the substrate. Final composition of the oil migrated under these conditions, for a given generated bitumen and mineral composition, would depend on the bitumen/mineral ratio, a high ratio resulting in a aromatic and hetero-compound rich. Low ratios in the source rock should produce a more saturated-rich oil and any lean rocks subsequently passed through should produce the same effect, increasing with primary migration distance.

Depletion due to primary migration under these conditions should be observed per unit porosity as the reservoir is approached (or per unit rock in a fairly homogeneous lithology), independent of kerogen content. Mineralogically, calcite has been shown to be a weaker adsorbent (wet or dry) for bitumen compounds than most clay minerals by pyrolysis experiments (Tannenbaum *et al.* 1986; Espitalié *et al.* 1980). Limestones or calcareous shales should thus show less geochemical fractionation from primary migration than normal shales if flow is primarily through pores and fractures, and in a mature heterogeneous source rock, clay-rich intervals should show increased aromatic and hetero-compound content in bitumen.

If geochemical analyses are carried out with a sufficient sampling density approaching a source rock-reservoir contact, observed fractionation and depletion should make it possible to deduce the nature of the governing mechanism, or combination of mechanisms, as outlined above. In addition, if depletion shows enough regularity to be quantified and confidently extrapolated, this could be compared with known oil reserves in the same drainage area, allowing more accurate estimation of trapping efficiencies, and regional contouring of expelled oil in ideal cases. Tissot and Welte (1978) state that:

> **'Very little data are available on detailed investigations of source rocks in actual contact with an oil-filled reservoir rock.......it is this kind of information that is needed to solve the problems of primary migration.'**

This study is an attempt to fill some of this need.

Chapter 2

PREVIOUS INVESTIGATIONS OF SOURCE ROCK-RESERVOIR CONTACTS

In comparison to studies of reservoir rock properties or source rock generation potential, case studies of primary migration are very limited. Migration case studies require sampling at controlled and closely spaced depths, ruling out drill cuttings, and thus require coring of non-reservoir lithologies, often mature only in off-structure synclinal locations. This can seldom be justified economically, and the resulting shortage of cores has contributed to the lack of published contact migration studies. Five such studies found in the literature are outlined below in chronological order, and original data is presented as far as possible in a consistent manner and plotted on similar horizontal scales to facilitate comparison. Emphasis will be placed on evaluating herein migration-depletion on the basis of molecular weight, TOC, and total rock to seek insight into migration mechanisms operating.

2.1. Middle Devonian, USSR

Neruchev and Kovacheva(1965) have presented elemental analyses of shale bitumens in the vicinity of Middle Devonian reservoirs in the Shkapovo district, USSR. These are taken from the depth range 1900-2100 m and represent averages of up to 13 samples with rather wide scatter, from more than one core and more than one well. Whether these represent lower and/or upper reservoir contacts is not specified, nor is whether the adjacent reservoirs are oil-bearing. Bitumen contents per unit TOC are also given, permitting the data to be plotted against distance from reservoir (Fig.2-1). This is plotted as an upper contact to facilitate comparison with the present study.

Neither organic matter type(s) nor maturity were specified. From the amounts of $CHCl_3$ extractible bitumen, it can be seen that the organic matter type, if undepleted at 7.5 m from the contact, must be type III if mature, or in the case of oil-prone types I or II, must be immature or overmature for oil generation. The quantities of extractible hydrocarbons do not approach the values (approximately 100 mg/g TOC) reached and exceeded by oil-prone source rocks at near-peak oil-generating maturity and thus presumably peak oil

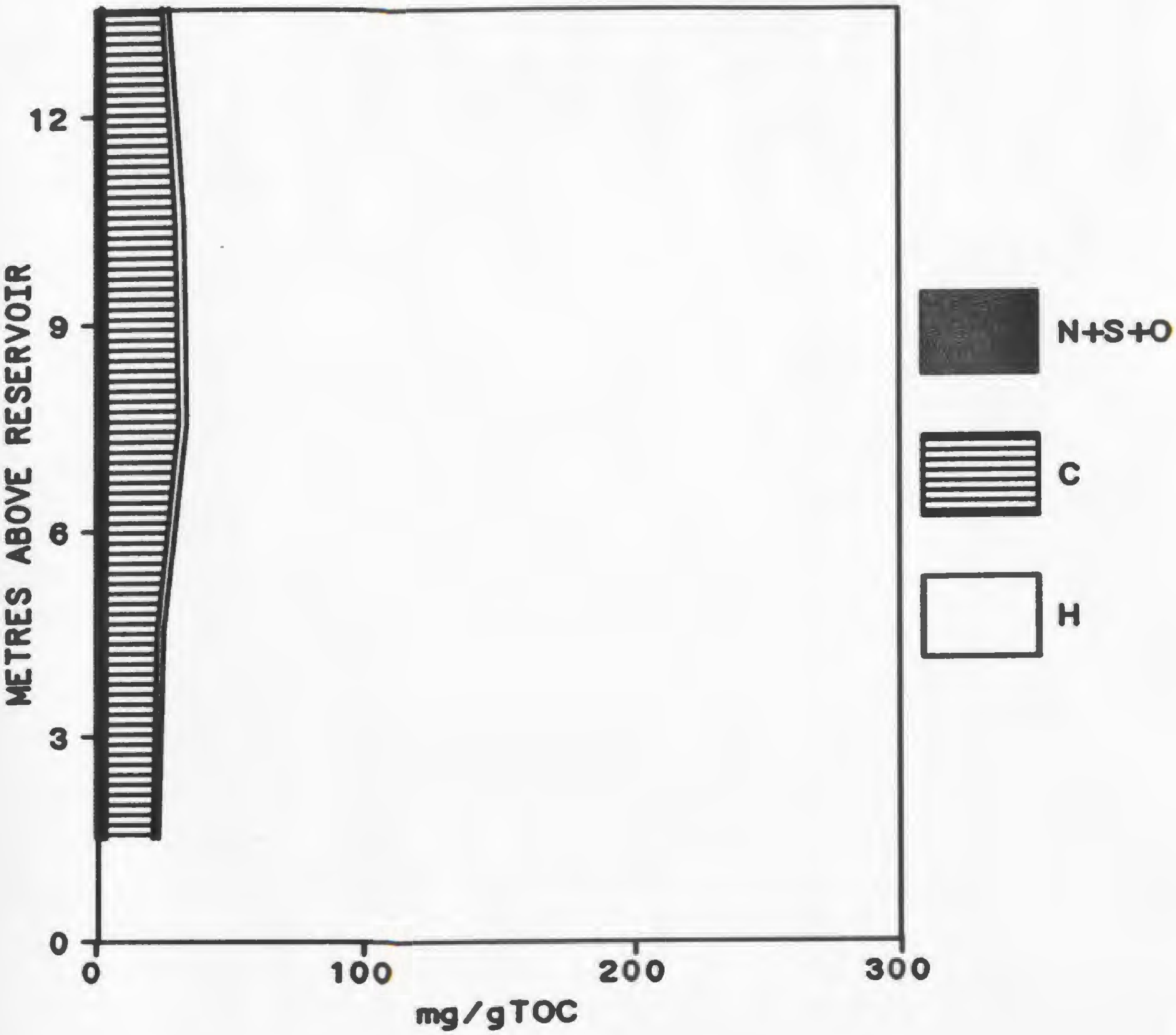


Figure 2-1: Carbon-normalized bitumen profile, M. Devonian, USSR

(after Neruchev and Kovacheva, 1965)

expulsion (Tissot and Welte, 1978). Assuming constant organic matter type, it can be seen that soluble heteroelement (N+S+O) content of the total organic matter remains fairly constant upon approaching a reservoir, indicating no significant migration of resins and asphaltenes (Fig.2-1). From a distance of 7.5 m from the contact, a decrease in C and H can be seen, pointing to increasing hydrocarbon depletion, to a maximum of approximately 11 mg/g TOC as the reservoir is approached. No analyses by molecular weight or compound type were presented.

Although oil is found in Middle Devonian reservoirs, oil-source correlations were not shown to demonstrate that the oil had in fact originated in the adjacent shales. The case(s) studied could thus equally well be that of minimal primary migration from type III or immature types I or II organic matter coupled with secondary migration of oil to the reservoirs from another source, or pervasive primary migration (beyond 13.5 m) from the rocks under study. The lack of liquid and gas chromatographic data on compound types and molecular weights, TOC percentages to calculate whole rock data, and maturities of the organic matter analyzed make it impossible to elucidate the migration mechanism from the information given.

2.2. Upper Devonian, Algeria

Tissot and Pelet (1971) have published the results of source rock analyses from a shale core underlying a sandstone reservoir rock from the Illizi basin of eastern Algeria. This sandstone is a productive reservoir elsewhere in the basin, but is not specified as oil-bearing adjacent to the section sampled.

Geochemical data consist of compound-type abundances per unit TOC down to 14 m below the reservoir. Saturates and aromatics are grouped together. Values given are 'averages of 3 or 4 measurements' of unknown scatter. It is not specified whether these measurements are replicates from the same depth or whether the values are averages of several closely spaced depths. The data are plotted as if the shale overlies the reservoir, once again for ease of comparison (Fig.2-2). The lack of TOC data prevents plotting of values as ppm of total rock. Organic matter type and maturity have not been reported in this study, but the shale is described as 'homogeneous' so the assumption of uniform organic matter type and TOC content is made. A plot of compound type abundances as ppm of total rock should thus be similar to Fig.2-2. Peak oil generation for the shale in question is about 140 mg bitumen/g TOC at a depth of approximately 2000 m (Tissot *et al.* 1973) and thus the maximum of 118 mg/g TOC found in the core furthest from the reservoir represents near-peak generation. This same sample contains 75 mg HC/g TOC, making organic matter type I or II likely, this value seldom being reached for type III organic matter. Oil-source correlations based on monoaromatic steroids (Tissot *et al.* 1973) indicate that this shale formation has sourced many oil accumulations in U. Devonian and Carboniferous reservoirs.

Depletion, assuming uniform organic matter type, appears to extend systematically throughout the entire core, diminishing somewhat from 10.5 to 14 m below the reservoir contact. The maximum bitumen and hydrocarbon generation therefore, for this level of maturity, may well be greater than the figures cited above, and an undepleted end-member unavailable for comparison. Asphaltenes show slight, possibly significant, enrichment toward the contact, but resins and hydrocarbons are continuously depleted. Hydrocarbon/non-hydrocarbon ratios are constant beyond 7 m indicating that depletion beyond this point is without notable fractionation, or that an undepleted end-member, richer in hydrocarbons, lies beyond 14 m. From 2 to 7 m from the contact, hydrocarbons are preferentially expelled. No saturate/aromatic breakdown is available. Maximum measured depletion is 46 mg bitumen/g TOC of which 80% is hydrocarbon.

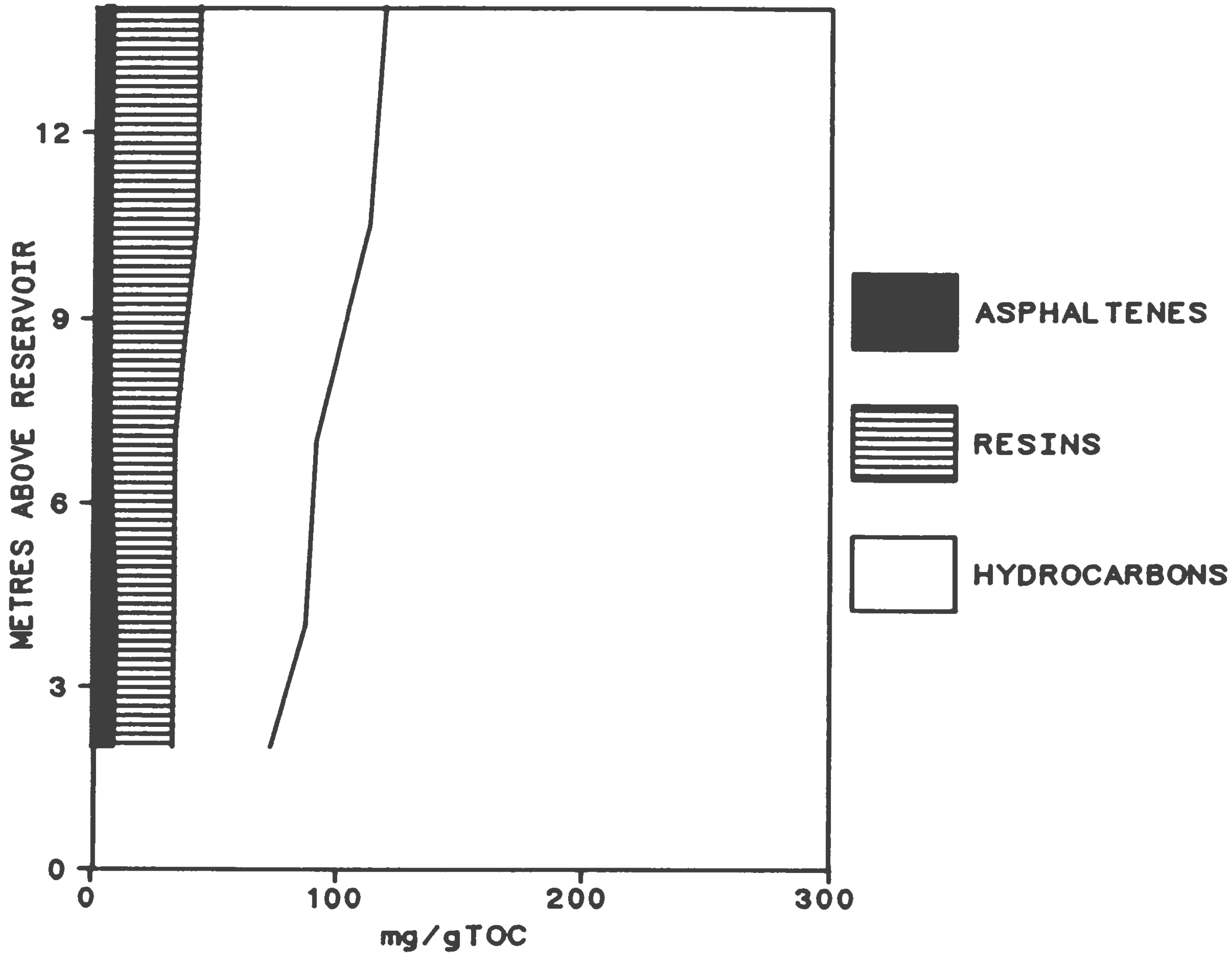


Figure 2-2: Carbon-normalized bitumen profile, U. Devonian, Algeria

(after Tissot and Pelet, 1971)

The lack of gas chromatographic data on molecular weight distributions, saturate/aromatic ratios, and TOC values makes it impossible to determine whether migration was carried out via diffusion, gas phase, aqueous solution, oil flow through kerogen, or oil flow through pores and fractures, but the observed depletion is far greater than that documented by Neruchev and Kovacheva (1965) and thus more likely to be representative of the large scale migration necessary to produce significant oil accumulations.

2.3. Lower Jurassic, France

The 'schistes cartons' of the Paris basin, made famous through use as a petroleum generation laboratory for pioneering geochemical studies (Louis, 1964), and the type locality for type II organic matter, have also been the subject of a detailed and thorough primary migration study at a shale-limestone contact. Twelve metres of this formation overlying a limestone were continuously cored and geochemically analyzed (Vandenbroucke, 1972) as follows:

- Light hydrocarbon extraction (C_6-C_{20})
- Mineralogical breakdown (Qtz, Clay, total Carbonates)
- TOC
- Solvent extraction
- Liquid chromatography
- Gas chromatography (2 samples:saturates)
- Mass spectrometry (6 samples:4 saturates, 2 aromatics)

Lithologically, (Fig.2-3), the core consists of calcareous shale overlying a tight clean limestone. For the lower 4m of the core, carbonate appears to act as a diluent to clay and organic matter, but in the upper half organic matter decreases upward despite decreasing carbonate content, reflecting changes in conditions of deposition and preservation. Two stringers of argillaceous limestone and very calcareous shale at 0.9m and 1.7m respectively above the limestone contact are associated with lower values of TOC and higher values of bitumen/unit TOC than adjacent shale, as is the underlying limestone, and these two zones appear to have functioned to a limited extent as reservoir rocks for migrating hydrocarbons.

Organic matter for this formation is type II (Tissot and Welte, 1978) and although maturity was not measured directly in this study, the presence of a sterane 'hump' of tetracyclic alkanes in all of the saturate MS data indicate that peak oil generation maturity has not been obtained. The core comes from a depth of approximately 2040m in a basin where oil generation increases steadily from 1500m to maximum burial depth of approximately 2400m (Louis and Tissot, 1967), reaffirming the conclusion drawn above from the MS results and possibly primary migration, which must lag behind oil generation, may not yet have begun at the depth in question. Hydrocarbon generation reaches a maximum of 96.5 mg/g TOC in this core.

No oil accumulation was found in the limestone 'reservoir' below the shale, although a show was observed at its upper contact. This was found to total 16.5 ppm bitumen, a value lower than any in the overlying shale. Any significant migration from the shale to the limestone must thus have been accompanied by lateral migration away from the zone sampled. Reservoir properties reported of the limestone are very poor. The compound

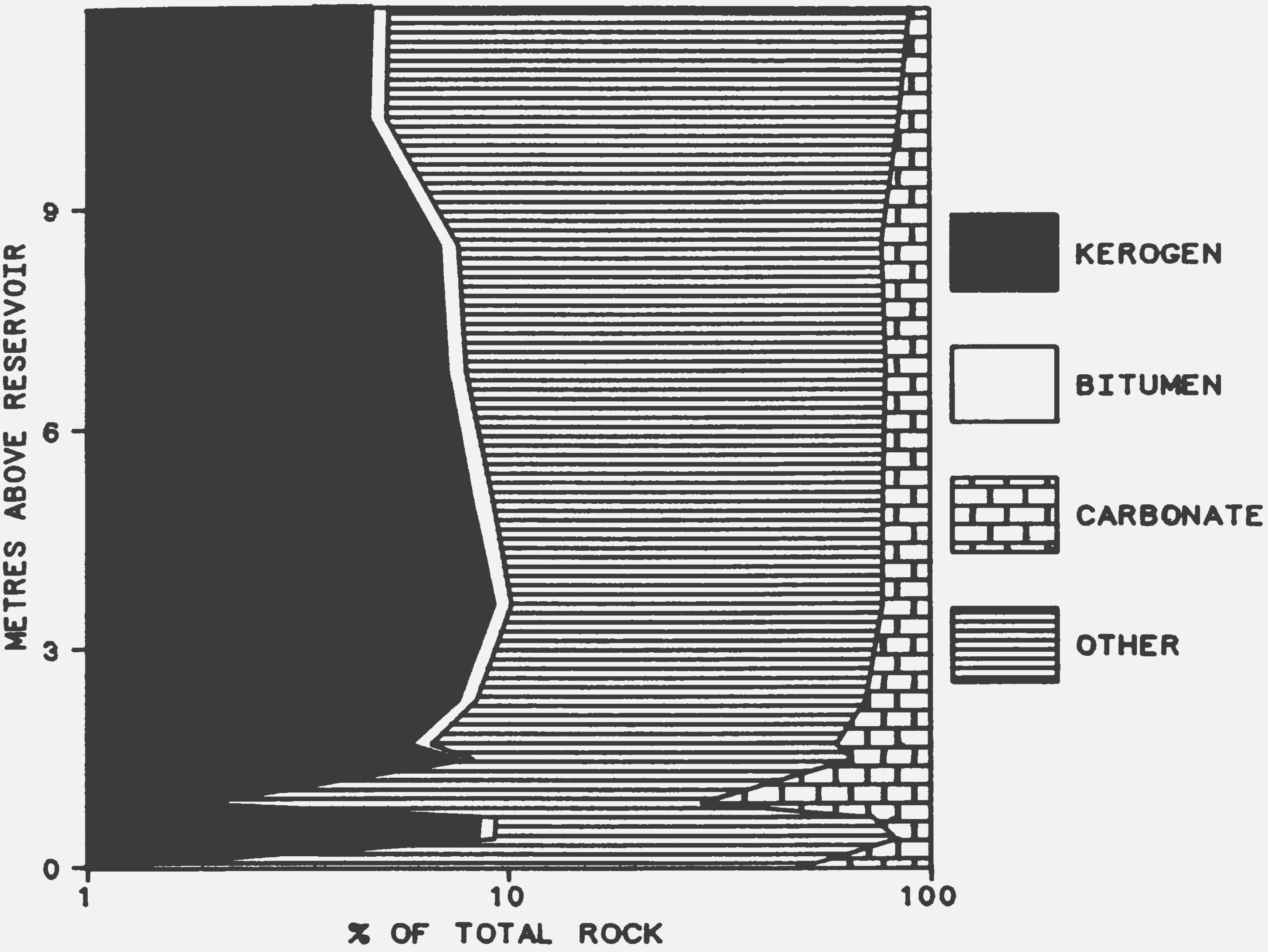


Figure 2-3: Litho-facies profile,
L. Jurassic, France

(after Vandenbroucke, 1972)

type data from the solvent extracts are plotted as mg/g TOC (Fig.2-4) and since TOC data are available, the data are also shown as ppm total rock in Fig.2-5. It can immediately be seen that the data normalized per unit TOC are much more constant with depth than as ppm total rock, indicating that bitumen has failed to redistribute itself evenly into shale porosity. The two calcareous stringers at 0.9 m and 1.7 m from the contact are apparent in Fig.2-4 as being relatively enriched compared to adjacent shales. The underlying limestone (not plotted) shows this to a much greater degree, to 185.1 mg/g TOC. Although the uppermost, at 1.7 m, is enriched in all four compound types, the lower stringer at 0.9 m is enriched only in hydrocarbons, principally saturates. The same is true for the underlying limestone, where enrichment is almost entirely saturates.

Vandenbroucke (1972), citing mainly data of compound type per unit TOC (Fig.2-4), suggests that the lower values below 5.1 m, excluding the calcareous stringers, represent shales depleted by migration, while the stringers, the underlying limestone, and to a

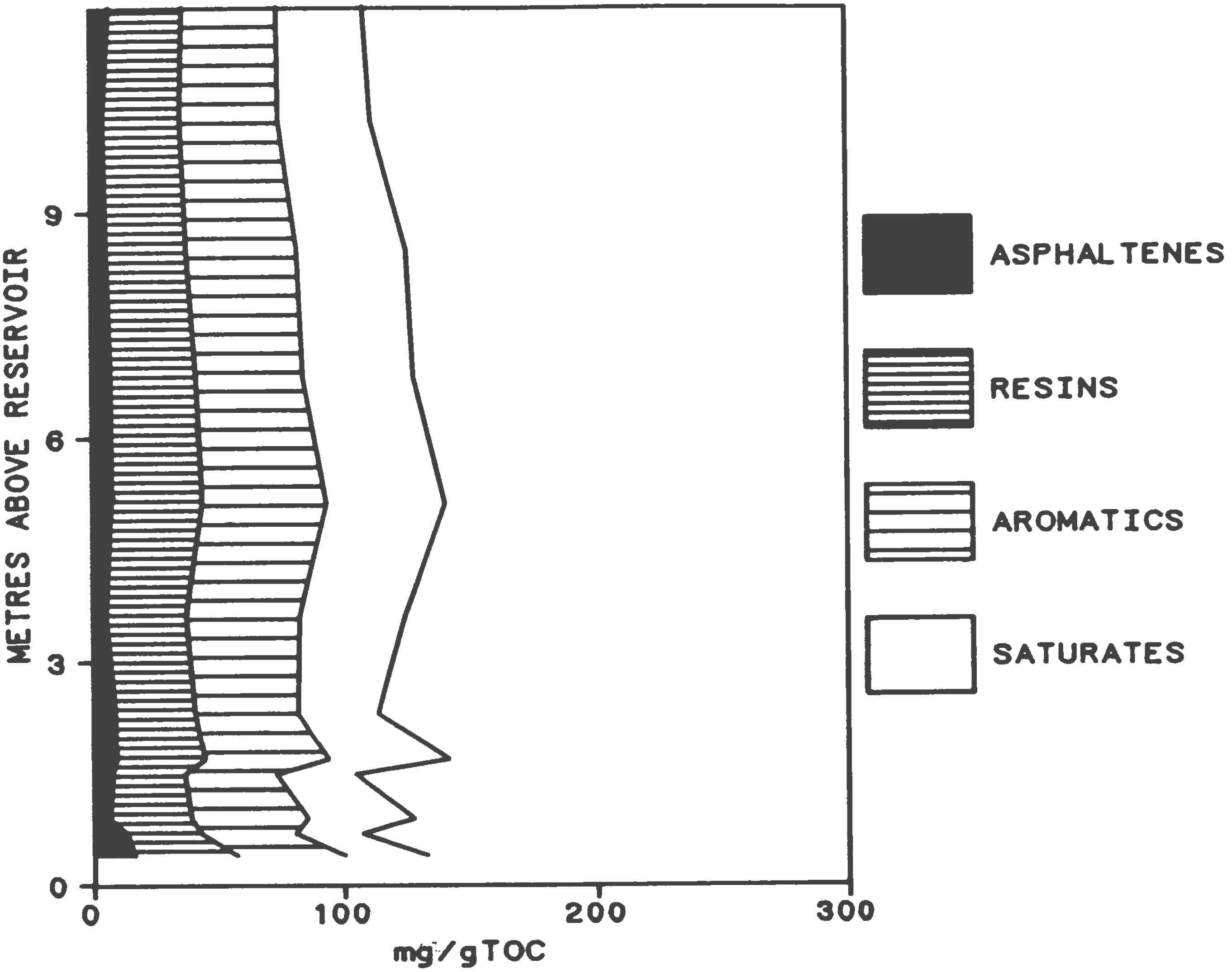


Figure 2-4: Carbon-normalized bitumen profile, L. Jurassic, France

(after Vandenbroucke, 1972)

limited extent the lowest shale sample (0.4 m) represent enrichment by migrated oil. Maximum depletion is thus 35.7 mg bitumen/g TOC. Decreasing bitumen/unit TOC from 5.1 m toward the top of the core is not associated with any known reservoir rock and is attributed to changing conditions of deposition and preservation of organic matter. Why this explanation cannot hold equally well for the zone below 5.1 m is not outlined. Bitumen in both zones consists of hydrocarbons and heterocompounds in relatively constant proportions except for the lowest 2.3 m. This would indicate (for the zone above 2.3 m) migration of bitumen without fractionation, or equally well, reduced bitumen generation due to environmental conditions as suggested.

The lowest 2.3 m of core feature decreased hydrocarbons relative to heterocompounds, and from MS, depletion of saturates of 0 and 1 ring relative to those of 2-5 rings. These findings could be indicative of migration with fractionation. This zone also contains the relatively enriched calcareous stringers and contacts the underlying limestone. However,

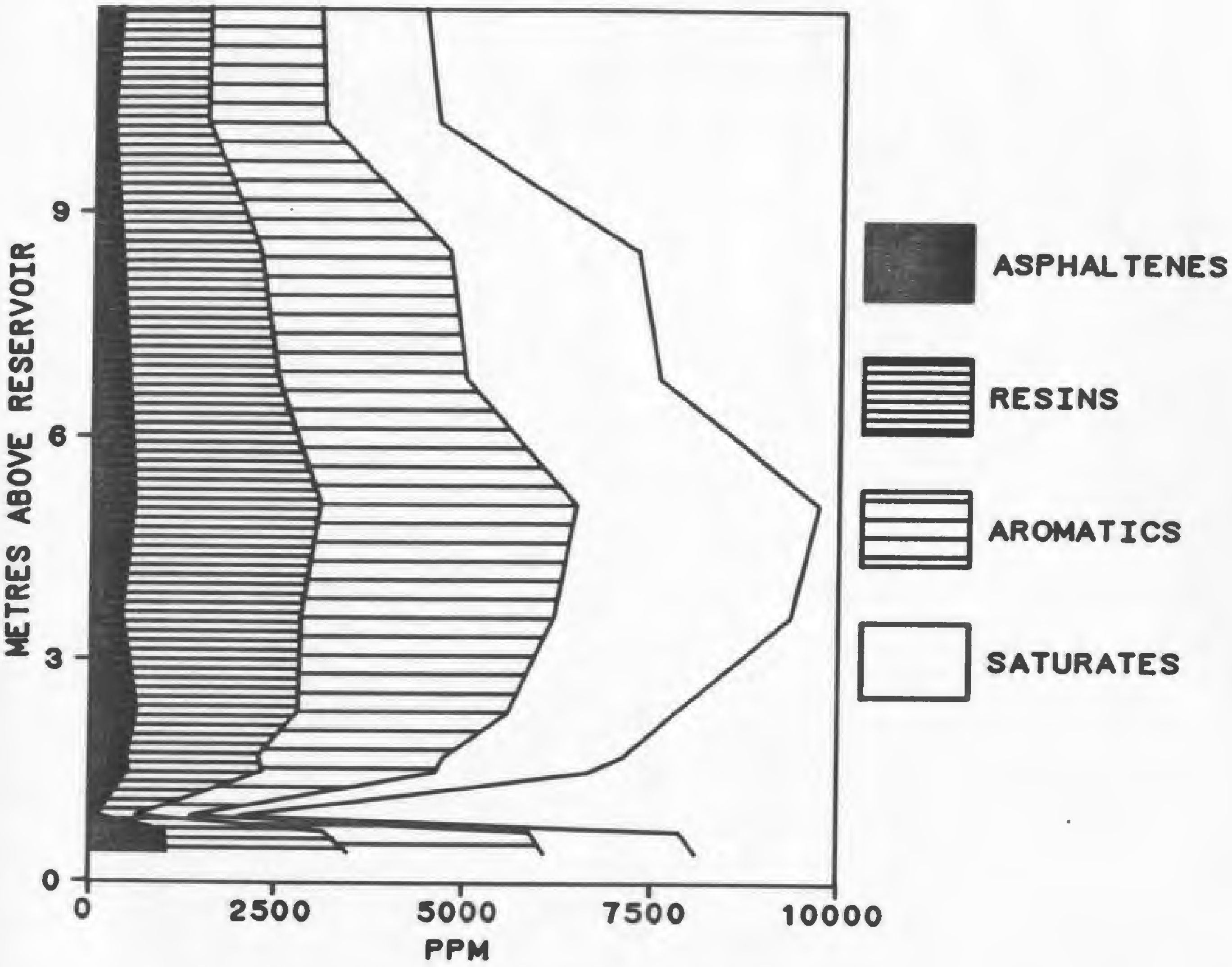


Figure 2-5: Bitumen profile,
L. Jurassic, France

(after Vandenbroucke, 1972)

if the undepleted end- member is no longer the shale at 5.1 m ,but rather that at 2.3 m, overall maximum depletion is only 9.2 mg/g TOC. Both the lower calcareous stringer and the underlying limestone, although enriched per unit TOC, actually contain much less bitumen, as ppm of total rock, than the shales (Fig.2-5), and thus represent negligible accumulation. This is in keeping with a negligible depletion of the shale, assuming only the lower 2.3 m of core are involved.

GC data for the underlying limestone and a shale at 0.7 m show no differences and thus migration by diffusion or gas phase, each with molecular weight fractionation, seems unlikely. No enrichment or depletion of aromatics relative to saturates in limestones or shales is present to give credence to migration in aqueous solution. Since bitumen redistribution into shale porosity appears not to have occurred, oil phase migration along kerogen may be the most likely mechanism.

However, it is herein felt also possible that the case studied here is one where oil migration has been negligible and has not led to accumulations, thus evidence for or against any particular migration mechanism is weak. Conditions responsible for decreasing bitumen content above 5.1 m could well be responsible for most of the 'depletion' in the lower core.

2.4. Paleocene, Spitzbergen

Two coal exploration boreholes drilled in 1979 in Spitzbergen recovered continuous cores of sandstone/shale contacts of Lower Cretaceous and Paleocene age, and these were studied for evidence of primary oil migration (Leythaeuser *et al.* 1984a). Since findings are similar for both cores, and more detailed observations are available for the Paleocene, this core only will be discussed here.

The sequence consists of a shale unit (45 m) enclosing a thin conglomeratic sandstone, underlain by sandstone with thin interbedded shales (65 m), which is in turn underlain by shale with thin coal seams. The core comes from a region of continuous permafrost, with a lower boundary estimated to approximately coincide with the lower contact of the 65m thick sandstone (Leythaeuser *et al.* 1983)

Organic matter type, as determined by Rock-Eval pyrolysis, is type III and has been carefully subdivided for comparison into types III-A, III-B, and III-C based on GC-MS measured distributions of biological marker compounds. Mean vitrinite reflectance was 0.71% in shales and 0.82% in coals, the latter value assumed by Leythaeuser *et al.* (1983) to indicate a maturity close to peak hydrocarbon generation for the sequence. Price and Barker (1985) have documented that frequently lower vitrinite reflectance values are found where vitrinite is diluted by other maceral types, as compared to more nearly pure vitrinite in nearby rocks. This may not be a major problem, contrary to what Price and Barker suggest, since vitrinite reflectance scales for oil generation have been calibrated, for the most part, with oil source rocks where vitrinite is normally subordinate or rare. However this does mean that the reflectance measured in shales rather than pure coals is likely to be more reliable when used against a commonly accepted reflectance scale, and thus the sequence studied may be only at the beginning of oil generation. This is in keeping with the very small amounts of hydrocarbon found, even for type III kerogen.

Bitumen content per unit TOC and hydrocarbon content of bitumen are presented for the upper shale interval (Leythaeuser *et al.* 1983) and allow comparison with other studies (Fig.2-6). TOC data were incomplete such that data could not be plotted as ppm of total rock. In addition to the above Rock-Eval pyrolysis, TOC, and gas chromatograms of total saturates were presented for selected samples.

No oil shows or production were encountered throughout the cored interval, but a residual accumulation was believed to be present at the top of the sandstone interval.

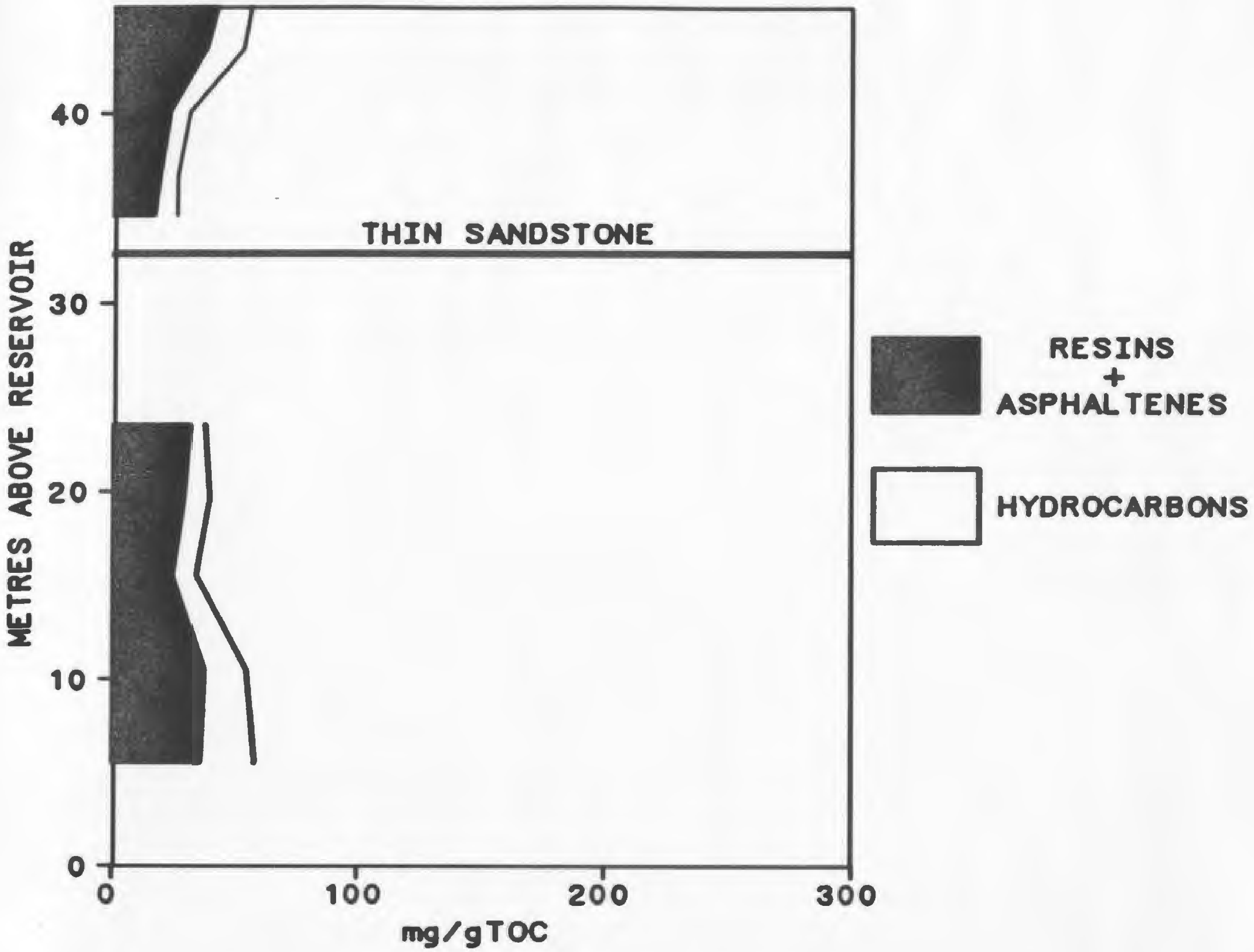


Figure 2-6: Carbon-normalized bitumen profile, Paleocene, Spitzbergen

(after Leythaeuser *et al.* 1983)

2.4.1. Upper shale interval

Fig.2-6 illustrates the compound type abundances in shale bitumens analyzed above and below the thin conglomeratic sandstone from 32.4 m to 32.6 m above the main sandstone contact (0 m). Above the thin sandstone, depletion appears to extend 12.8 m into the shale, and to reach a maximum of 30 mg bitumen/g TOC, of which 15% is hydrocarbons, contrary to the fractionation observed in the previous studies, and between source rocks and crude oils in general. Below the thin sandstone, apparent depletion extends 26.9 m into the shale, reaching a maximum of 20.4 mg bitumen/g TOC, of which 79% is hydrocarbons. The thin sandstone itself contains more bitumen per unit TOC (105.8 mg/g TOC) than any of the adjacent shales, but this amounts to only 106 ppm of total rock (minimum 112 ppm in lower adjacent shale) of which 17% is hydrocarbons.

No depletion at all is shown by the given data above the top of the lower sandstone at 0 m. The top 4.5 m of this rock type, together with 0.5 m of the overlying shale are believed by the authors (Leythaeuser *et al*, 1984a) to be a former oil accumulation together with an impregnated cap rock. This is shown by much larger values of mg bitumen/g TOC for this interval compared to adjacent samples. However maximum ppm bitumen is only 345, a value only slightly exceeding 308 ppm for the depleted shale at 34.5 m, and much less than that used as a 'depleted' shale (1524 ppm) for subsequent expulsion efficiency calculations. Even assuming a low 5% sandstone porosity, 345 ppm only amounts to an oil saturation of 1.7%, an unrealistically low value for residual oil saturation. Sandstone analyses in general quoted for this core are lower in ppm bitumen/total rock and higher in mg bitumen/g TOC than shales, and the two sandstones targeted here as incipient or former reservoirs are not noticeably different. The entire sequence, featuring low hydrocarbon generation, low depletion with inconsistent compound type fractionation, no oil accumulation, and low TOC values inducing scatter in TOC-normalized data, may be one where significant migration has not occurred, and variations noted could be due to natural variability (noise) in the parameters measured.

On a molecular level, no depletion was noted in the biological marker compounds measured, but GC results showed consistent differences in normal alkane distributions which appear to be due to migration. Shale bitumens from thin shale beds within the thick sandstone and from the edges of thick shales were found to be preferentially depleted in low molecular weight normal alkanes relative to those from the center of thick shales. On the other hand, many sandstone bitumens were enriched in normal alkanes of the same low molecular weight range. For example, the thin sandstone from 32.4 to 32.6 m shows a mode at nC_{17} with a steady decrease toward higher molecular weights, whereas the two closest shales show an additional mode at nC_{21}, with a much more even n-alkane distribution in the nC_{17}-nC_{23} range. Some limited odd-carbon predominance is also apparent in these samples.

2.4.2. Expulsion efficiencies

The n-alkane fractionation thus made evident was quantified by calculation of 'expulsion efficiencies'. These are ratios, different for each alkane, of the amount of alkane expelled per unit of alkane originally in place, expressed as a percentage (Leythaeuser *et al*. 1984a).

2.4.2.1. Using two rich shales

In the first determination presented, a thin 'depleted' shale within the thick sandstone member is compared to an 'unmodified' sample within the lower massive shale below the sandstone. These samples are not shown on Fig. 2-6. The two samples, although 64m apart, are of roughly similar high TOC content and organic matter subtype, but are not on the same primary migration path. Expulsion efficiencies are calculated using alkane abundances *per unit rock*. Absolute amounts of $nC_{27}+$ alkanes from the two shales are very close, resulting in expulsion efficiencies of near 90% for nC_{15}, decreasing steadily to near zero for $nC_{27}+$. Both pristane and phytane are shown to be 'expelled' to a markedly lesser degree than n-alkanes of equivalent carbon number.

2.4.2.2. Using one rich and two lean shales

Expulsion efficiencies are next determined for another thin shale within the sandstone, and a sample from the upper contact of the lower massive shale. Both have considerably lower TOC contents than the 'unmodified' shale considered, the same one as for the previous determination. The thin shale is 20 m distant from the unmodified, whereas the contact sample, 7m from the unmodified, could in this case very likely lie on the same primary migration path (upward into the sandstone). Efficiencies calculated as before, on a total rock basis, are now approximately 80% for nC_{15}, decreasing uniformly to approximately 60% for nC_{27}. Mass expulsion of all alkanes considered is thus indicated, although greater for those of low molecular weight, and attributed to possible differences in pore size distributions by these authors (Leythaeuser *et al*. 1984a). However, accepting such 'expulsion efficiencies' as accurate requires assuming that, for example, in the case of the contact sample, a shale of 1.19% TOC and 704 ppm bitumen originally contained a quantity of n-alkanes equal to that of the 'unmodified' shale of 5.7% TOC and 2310 ppm bitumen (same organic matter subtype). This may not be a reasonable assumption since the dependence on TOC content of the calculated efficiencies is obvious. This, as in the French example, demonstrates a lack of bitumen redistribution into shale porosity. The approach of these authors (Leythaeuser *et al*. 1984a), has been to use absolute amounts of hydrocarbons per unit rock to measure source rock depletion, and, as reviewed earlier, bitumen per unit TOC to delineate residual reservoir accumulation. This is opposite to the overall trend of oil migration and accumulation, which is broadly *from* source rock organic carbon *to* reservoir porosity and assuming constant reservoir porosity for want of better data, the search for and quantification of effects as documented in this paper should be best carried out with an approach opposite to that presented.

2.4.2.3. Using a shale and a sandstone

In the same paper comparison is next made between the same 'depleted' shale (1524 ppm bitumen) as used in the first expulsion efficiency determination and an 'impregnated' sandstone (273 ppm bitumen) 21.5m distant and of a differing organic matter subtype, not shown on Fig. 2-6. Assuming the n-alkanes in the sandstone to be derived from the thin shale interbeds, the authors reconstruct an 'unmodified' shale by adding the amounts of each n-alkane *per unit rock* in the sandstone to those in the shale.

Expulsion efficiencies are now calculated as before and are found to decrease steadily from near 90% for nC_{15} to approximately 20% for nC_{27}, this time with phytane, unlike pristane, being expelled as readily as its straight chain isomer.

Such efficiencies, although somewhat similar to those obtained in the first instance with two rich shales, are in addition dependant on a material balance. Not only are all n-alkanes in the sandstone assumed to be non-indigenous, it is also implicit that for the expulsion calculations to be meaningful, the n-alkane amounts and distributions of the depleted shale and impregnated sandstone samples must be representative for their respective rock types throughout the core and the ratio of these rock types in the core must be 50:50. Inspection of gas chromatograms of saturate fractions presented and the overall sand/shale ratio shows this not to be the case, with one sandstone from near the lower massive shale (Leythaeuser *et al.* 1983, Fig. 7) appearing to be as depleted in light n-alkanes as the 'depleted' shale selected. The resemblance of the expulsion efficiencies for the shale-sandstone pair to those for the two rich shales reviewed earlier may be due mainly to a fortunate choice of samples for comparison.

2.4.2.4. Using an unmodified and an impregnated shale

The same approach as used for the calculation of the expulsion efficiencies above was also used to calculate 'enrichment factors' by comparing the 'impregnated' cap rock of the residual oil accumulation with an immediately overlying shale sample. Enrichment factors, calculated separately for each alkane, are each the ratio of the difference of the alkane concentrations per unit rock in impregnated and unmodified shales, divided by the concentration in the unmodified shale. They were found, for the case studied, to equal approximately 5.0 for all nC_{15}-nC_{32} alkanes and the two isoprenoids, pristane and phytane. This lack of molecular weight fractionation was suggested by Leythaeuser *et al.* to indicate bulk oil invasion, but this would require identical alkane compositions for invading and indigenous hydrocarbons. It could with equal validity be interpreted as indicating no invasion at all. Both 'impregnated' and 'unmodified' shales for this calculation had n-alkane distributions unimodal at nC_{17} and decreasing steadily in concentration to near zero for nC_{33}. This is in contrast to the bimodal distributions considered 'unmodified' for expulsion calculations.

2.4.2.5. Discussion

It is clear from all the above expulsion and enrichment data that in spite of the mathematical treatment of GC data questioned above, some low-molecular-weight alkane depletion does occur in thin shales and near shale edges as Leythaeuser *et al.* suggest. The first expulsion example, with two rich shales, is straight forward and shows the increasing depletion of low molecular weight n-alkanes, with virtually no depletion of nC_{25}+ alkanes including tetra- and pentacyclic biomarkers. Such migration alone cannot, therefore, lead to accumulations of normal crude oils, or to the similarity of their saturate fractions to those of their corresponding source rock bitumens. Also no preferential expulsion of saturates relative to aromatics was found for this case (Mackenzie *et al.* 1983) making adsorption on mineral surfaces an unlikely factor in the alkane fractionation. The second pair of expulsion calculations illustrated the dependence of the efficiencies as calculated on TOC content, thus indicating, as did the previously reviewed L. Jurassic study, that bitumen had not been redistributed into shale porosity. Finally, the investigation of 'impregnation' of the shale overlying the main sandstone, together with many saturate fraction gas chromatograms in the references cited show that a variety of n-alkane distributions, isoprenoid abundances, and bitumen contents are present in both sandstone and shale and are not always easy to explain, by expulsion or otherwise. A plot of pristane/nC_{17}, phytane/nC_{18}, and pristane/phytane against depth, for all rock types in this core may have been revealing, by illustrating the amount of natural variation to be expected in these parameters.

Taken together, the above observations of depletion varying with molecular weight rather than compound type are indicative of migration by molecular diffusion or gas phase. The latter is herein considered unlikely due to the low maturity of the section investigated, generally low TOC contents (average 1.7%) and lean organic matter type of the shales under study. If diffusion is the process responsible, it agrees well with migration into the upper thin sandstone (Fig. 2-6), where bitumen per unit TOC is higher, but bitumen as ppm total rock is lower than surrounding shales. The more difficult apparent expulsion of isoprenoids relative to their n-alkane isomers may be due to initially different isoprenoid/n-alkane ratios in the shales chosen for comparison, or to a lower water solubility for the isoprenoids. This would be approached sooner than the corresponding n-alkanes and thereafter diffusion rate would become dependent on water expulsion. Migration by diffusion can also be expected to affect the aromatic fraction of bitumens, be present at all source rock-reservoir contacts regardless of maturity, and will likely result in very minor amounts, at most, of bitumen migrated. Although this would have a composition differing from the parent bitumen, it would, of necessity, end up in a less concentrated state and not as an oil accumulation.

Leythaeuser *et al.* (1984a) account for the observed fractionations by proposing a migration mechanism based on oil droplets in shale pores, moved by compaction water flux. Fractionation attributed to mineral adsorption or alternatively, more rapid flow of droplets containing a larger proportion of low viscosity low molecular weight hydrocarbons. An analogy is made to frontal analysis chromatography, where injection is continuous in time, varying amounts of alkane fractionation at contacts being attributed in part to permeability barriers, said to allow higher retention compounds to catch up to those of lower retention. However, bitumen generation in shales is, in addition to being continuous in time, also continuous in space i.e. along the migration path, thus an advancing front will not occur. The analogy is also flawed with respect to permeability effects, which will slow down both carrier and compounds of all degrees of relative retention, the latter having no independent mobility of their own in a system where expelled water is the carrier phase.

2.5. Upper Carboniferous, W. Germany

A borehole drilled for coal exploration in the Ruhr district of Germany provided core subsequently used to study primary oil migration (Leythaeuser and Schaefer, 1984). Approximately 50 m of core was studied and the data presented include:

- TOC
- Bitumen Content
- Rock-Eval Pyrolysis
- Compound-Type Distribution
- Gas Chromatograms for Selected Saturate Fractions

The section consists of a thin shaley sandstone overlying approximately 30m of shale, which in turn overlies a thin coal. Compound-type data for the shale is plotted per unit TOC in Fig. 2-7 and as ppm of total rock in Fig. 2-8 with distance above the coal as the ordinate. Organic matter type, based on pyrolysis hydrogen indices, is type III from 10-30 m, type II in a transgressive marine shale from 1-4 m, a mixture of types II and III at 7 m, and type II with reworked coal (up to 60%) for the lowest two samples from 0-0.7 m. Maturity was estimated to be at or near the oil floor from a mean vitrinite reflectance measured to be 1.20% in the underlying coal. However, significant $C_{15}+$ hydrocarbon content is still present in all samples, and $C_{25}+$ saturates are prominent in all gas chromatograms shown, thus the findings of Price and Barker(1985) referred to earlier (page 33) may be equally applicable to this section, and the actual maturity may be less than the coal would indicate. In keeping with most coal samples, the coal in this study features the highest TOC content and the highest ppm bitumen value, but is the lowest in mg bitumen/g TOC of all the samples analyzed. In addition, hydrogen index for this coal is the second highest of any of the samples analyzed, higher than most of the type II shales, indicating that rock-eval pyrolysis results for coals may give misleading data with regard to their hydrocarbon source potential. This could be due to a lack of dry mineral matrix adsorption of pyrolyzate. A small non-commercial oil accumulation is present 220 m above the studied interval, but its source, maturity, and reservoir age are not given. Depletion, attributed to migration by Leythaeuser *et al.* was described and quantified as before (Leythaeuser *et al.* 1984b) by calculation of expulsion efficiencies. This was done for thin shales in the sandstone, shales immediately below the sandstone, and the marine shale unit above the coal.

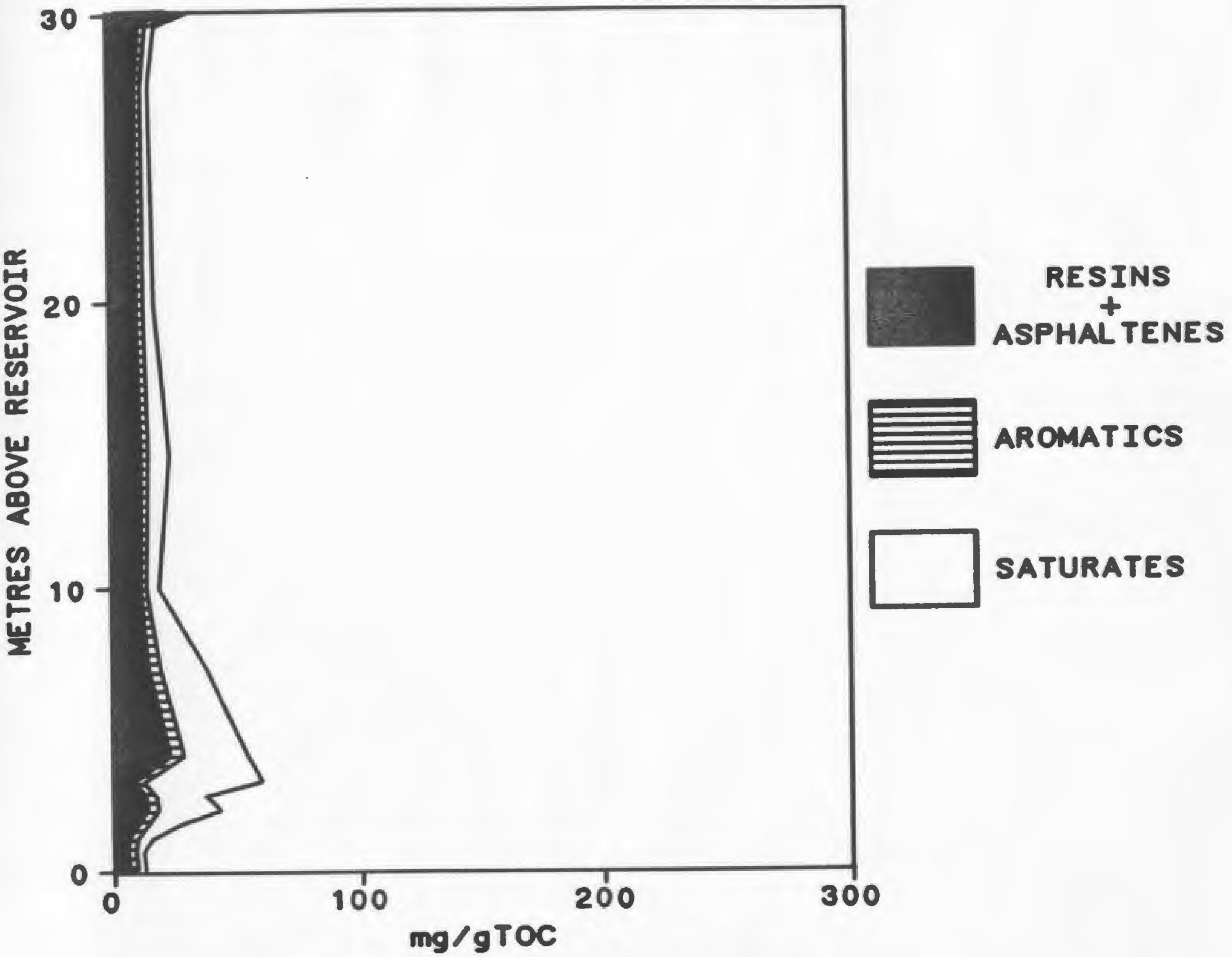


Figure 2-7: Carbon-normalized bitumen profile, U. Carboniferous, Germany
(after Leythaeuser and Schaefer, 1984)

2.5.1. Thin shales

Two thin shales were analyzed from within the sandstone above 30 m and one of these was compared to the shale at 14.56 m for expulsion efficiency calculations. The two shales have similar TOC content, thus this will only marginally affect the results unlike in the Spitzbergen study reviewed above. Bitumen content is also similar for both samples, which would itself suggest limited migration, but the proportion of saturates is much higher in the 14.56 m sample. This in turn suggests a different type of organic matter despite both appearing as type III from pyrolysis hydrogen indices. No differentiation based on biomarkers was used in this study.

Calculated expulsion efficiencies are approximately 80% from nC_{15} to nC_{25}, declining to near zero for nC_{35}, with no conspicuous front end loss as was obvious in the 'depleted'

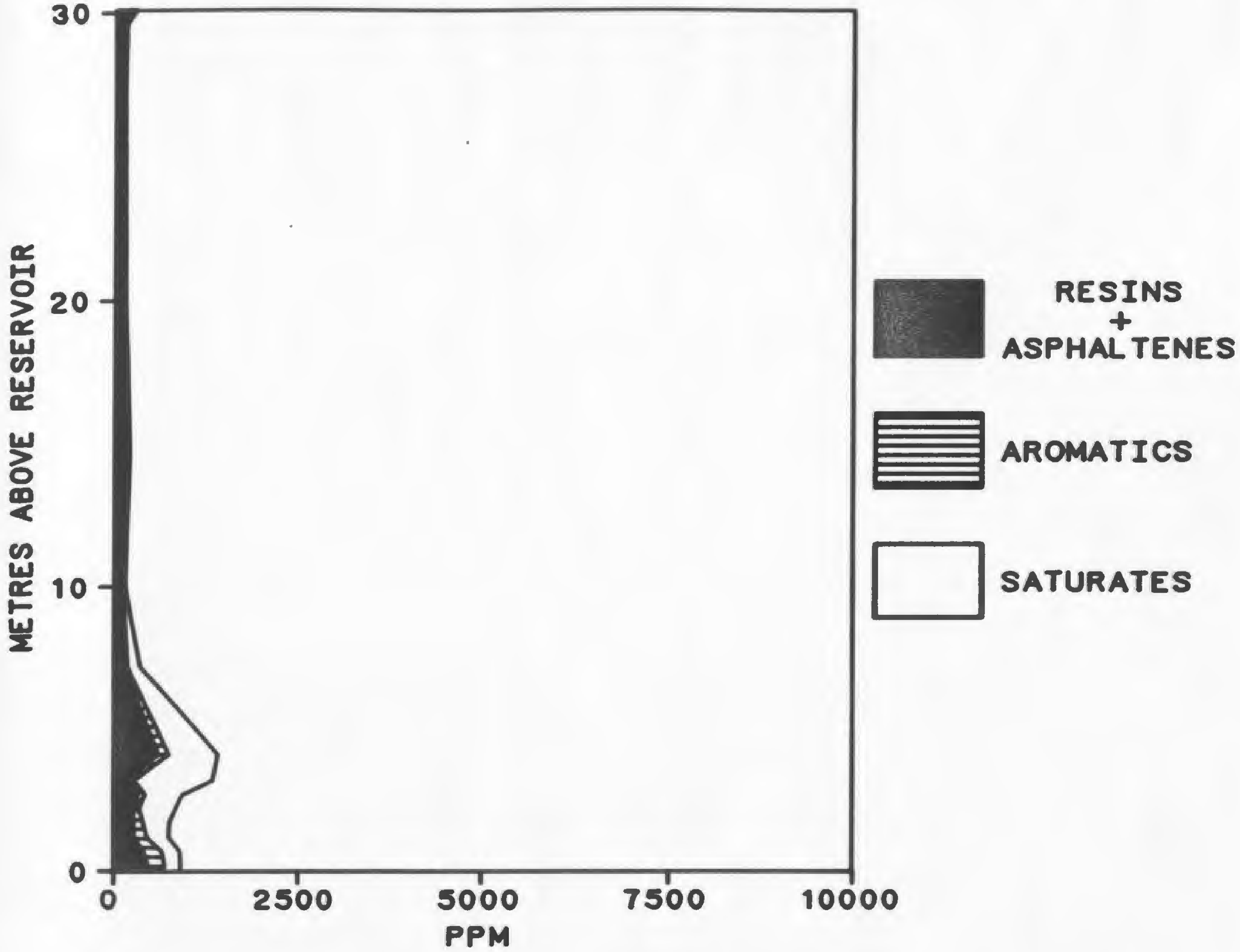


Figure 2-8: Bitumen profile,
U. Carboniferous, Germany
(after Leythaeuser & Schaefer, 1984)

Spitzbergen samples. Isoprenoids were again expelled less readily than their n-alkane isomers with expulsion efficiencies of 8.5% for pristane (nC_{19} 82.2%) and 54.9% for phytane (nC_{20} 81.3%). Steric or solubility factors as suggested earlier may be responsible for the difference between isoprenoid and n-alkane expulsion, but it is not apparent how a terminal methyl group, in the case of phytane, should enhance its expulsion so much relative to pristane. More likely this is due to a much lower pristane/phytane ratio in the 'undepleted' shale at 14.56 m compared to all the overlying shales. This sample, in addition, has much higher n-alkane/isoprenoid ratios and saturates content than any of the overlying shales, suggesting again that it may, in spite of its hydrogen index, be a different organic matter subtype. An altrnetive choice, instead, of the shale at 19.86 m as 'undepleted' would likely have resulted in more realistic measures of expulsion, or its absence. The measured expulsion was attributed by the authors to an advanced stage of chromatographic migration, with expelled water or generated gas as a carrier phase, the lower carbon numbers ($<nC_{25}$) presumably close to terminal concentrations

2.5.2. Upper shale

The shale unit above the marine shale and below the overlying sandstone, from 10.01-30.06 m on Fig. 2-7, was also found to be depleted and the expulsion was quantified. Similarity of TOC values once again results in similar patterns for bitumen composition on both Figs. 2-7 and 2-8. Bitumen concentrations are highest at 14.56 m and 30.06 m, and lowest at 27.36 m, not the expected distribution due to depletion due to migration into the sandstone. However, no core was recovered for 20cm from 27.46 - 27.66 m and this has been interpreted to be a fracture zone acting as a sink for migrating hydrocarbons (Leythaeuser and Schaefer, 1984). Core was also not recovered from a thicker zone near 7.16 m, where no depletion was observed; and the sample at 10.01 m appears depleted, but no fracturing was reported from the core at this depth. Many factors, geological and mechanical, affect core recovery, and this assumption of fractures is questionable.

Accepting the fracture 'sink' proposed, maximum depletion extends 2.4 m above, totalling 135 ppm bitumen (14.5mg/g TOC), 24% of which is hydrocarbons. Maximum depletion below extends 12.9 m and totals 88 ppm bitumen (7.4 mg/g TOC), 81% of which is hydrocarbons, mostly saturates. Only this lower interval (14.56-27.46 m) is examined further here. Organic matter is type III and amounts of bitumen generated per unit TOC are very low, indicating low maturity, or thermal cracking of bitumen beyond peak oil maturity. Overall expulsion efficiency for bitumen reached 30%. Individual alkane expulsion efficiencies were not calculated, but appear similar from gas chromatograms. Pristane is expelled less readily than nC_{19}, but phytane appears to have an expulsion efficiency near that of nC_{20}. The situation is similar to that of the thin shales discussed above. Leythaeuser *et al.* (1984b) believe a trend of increasing pristane/nC_{17} and pristane/phytane to be indicative of increasing expulsion but offer no explanation for the variability of the latter ratio. If the fractured 'sink' is in fact not present and expulsion into the sandstone is assumed, this trend is destroyed by the overlying shales and a cause of the variability is not apparent, unless it reflects subtle changes in organic matter subtypes.

2.5.3. Lower marine shale

Hydrogen index values for the lower marine shale (0.66-4.06 m on Figures 2-8 and 2-7) indicate this unit to be one of type II kerogen, with the sample at 7.16 m gradational into the overlying type III-containing shale just discussed. The two lowest samples at 0.1 and 0.66 m contain some reworked coal (up to 60%) from the underlying seam, and have hydrogen indices typical of type III organic matter. Maximum hydrocarbon generation for the marine shale of 52.31 mg/g TOC indicates low maturity for this organic matter type, or thermal cracking as suggested for the shale above. Depletion was observed by

Leythaeuser *et al.* (1984b) for the marine shale as the coal was approached. This is unusual, coal being invariably a very poor reservoir rock, and even if migration has been to some lower reservoir, as the authors suggest (Leythaeuser *et al.* 1984b), migration to or through a coal does little to support the idea (Durand and Paratte, 1983) that coals can function as effective oil source rocks. If, on the other hand, migration takes place along a 3-dimensional kerogen network (McAuliffe, 1978), coal should be able to serve as a 'sink' or even a conduit if a high enough hydrocarbon saturation is achieved.

Considering bitumen concentrations as ppm of total rock (Fig. 2-8), maximum apparent depletion in the shale extends 2.9 m reaching 666 ppm bitumen (52% hydrocarbon). In this case, the underlying coal is not reservoir but source, and depletion is both upward and downward toward the shale at 1.16 m, an unlikely sink. Taken as mg bitumen/g TOC (Fig. 2-7), depletion extends 3.16 m into the shale and reaches a maximum of 48.5 mg/g TOC, of which 95% is hydrocarbons. These latter figures are certainly influenced by the reworked organic matter at the coal contact. GC results from samples in the marine shale show lower pristane and phytane compared to n-alkanes and lower pristane/phytane ratios than samples in the overlying shale. These are the same trends attributed to lack of depletion in the previous two expulsion calculations from this core, suggesting the possibility that small admixtures of this or a similar organic matter type may reproduce the effects observed in the overlying shales without any expulsion. No front-end loss of low molecular weight alkanes was observed for any of the samples in the marine shale.

Expulsion of whole bitumen reached approximately 80% on a per unit TOC basis, and individual alkane expulsion efficiencies were calculated, unlike previous examples, also on this basis. These were nearly equal for nC_{15}-nC_{30} for samples near the coal, but as the 'undepleted' sample at 3.16 m was approached, the efficiencies became markedly lower at low carbon numbers until for 2.66 m, they varied linearly from 30% at nC_{15} to 65% at nC_{30}. The authors (Leythaeuser *et al*, 1984b) suggest this to be due to subsequent light hydrocarbon generation in the depleted shales but the 3.16 m sample gas chromatogram shows an abrupt decrease in n-alkane abundances below nC_{25} and this is likely responsible. Pristane and phytane appear to be expelled as readily as their n-alkane isomers.

Comparison of apparent depletion in this richer shale (TOC 1.87-7.48%) to that of the overlying lean shale (TOC 0.68-0.94%) shows that although amount of maximum depletion and bulk expulsion efficiency as calculated are greater for the marine shale, apparent depletion extends much further into the leaner rock, and is associated therein with increases of pristane/nC_{17} and pristane/phytane. The authors (Leythaeuser *et al.* 1984b) recognize the fundamental difference between the two, not only implicitly when expulsion efficiencies are calculated on a per unit TOC basis for the lower shale, but also in a discussion related to mode of migration.

Recognizing the much greater maximum apparent expulsion from the marine shale, an oil saturation of 40% is assumed in the shale since relative permeability (K_{ro}) is 'believed to increase drastically' beyond this value. Because 40% is well beyond the solution capacity of water, the necessity of oil phase migration is concluded (Leythaeuser *et al*, 1984b). This argument appears flawed in two respects:

1. No attempt is made to calculate what relative permeability (K_{ro}) and absolute permeability (K) are actually needed to account for the apparent depletion, and
2. The richest shale in bitumen/unit rock, 1392 ppm at 4.06 m, would have 40% S_o only if total porosity equalled 1.0%, which is much too low for a shale at this stage of compaction (Magara, 1980)

Although the conclusion of oil-phase migration may be correct for the lower shale, it cannot be supported by the argument given. The differences in extent of expulsion between the upper and lower shales, together with the unexplained difference in pristane and phytane expulsion in the upper shale, herein seem best explained by slight differences in organic matter type in the upper shale not apparent in Rock-Eval hydrogen indices, together with no significant expulsion. The lower shale may have expelled some oil, but the presence of up to 60% reworked coal in the lowest two samples (most depleted) means that apparent depletion per unit TOC has been enhanced. However, if migration is via a 3-dimensional kerogen network (McAuliffe, 1978), permeability to oil being expelled has also been enhanced. The uniformity of n-alkane and isoprenoid expulsion efficiencies (calculated on a TOC basis) indicates no molecular weight fractionation, and the authors (Leythaeuser *et al*. 1984b) show saturates to be 'expelled' much more readily than aromatics. These observations are characteristic of oil phase migration. If so, this is likely via a kerogen network, the reworked coal facilitating this somewhat, and alleviating the need for a 'sink' in the shale at 1.16 m, necessary if migration takes place through the rock as a whole.

2.6. Summary and conclusions

Table 2-1 summarizes the data from these contact studies. It can be seen that only the case studies from Algeria, France, and the lower marine shale from the German core combine significant hydrocarbon generation with significant apparent depletion. Of these, only the example from Algeria may have been in contact with an oil-filled reservoir, and this one shows much greater depth of depletion than the other two. Cores such as those from Spitzbergen may show deep depletion but only of limited magnitude, due to the inability to distinguish actual depletion from natural variations ('noise') in bitumen or hydrocarbon content.

As a result of the low maturity, lack of accumulation, and unexplained upper apparent 'depletion' interval in the French example, and the very limited depth of depletion

Table 2-1: Summary of contact migration studies

LOCATION	MAXIMUM GENERATION (mgHC/gTOC)	EXTENT OF DEPLETION (m)	MAXIMUM DEPLETION (mgHC/gTOC)
USSR	<34.0	7.5	<10.7
Algeria	75.5	14.0	36.6
France	96.5	5.1	27.9
Spitzbergen (above SST)	13.8	12.8	4.6
Spitzbergen (below SST)	22.0	26.9	16.1
Germany (upper SH)	11.5	12.9	6.0
Germany (marine SH)	52.3	3.2	45.9
This Study	107.4	<1.9	48.5

together with lack of accumulation in the German marine shale, it appears that the study of the core from the Upper Devonian of Algeria may be the only one representative of the extensive primary migration necessary for significant oil accumulations. As such, its lack of GC, TOC, and reservoir oil (if any) data render it less than definitive for elucidating a migration mechanism.

None of the examples contain evidence for migration in water solution and diffusion, which appears to be present in the Spitzbergen study, results in very minor depletion at low maturity, perhaps due to greater shale porosity at this stage. The reduced variation in TOC-normalized, as compared to whole rock, bitumen data for the French and Spitzbergen studies indicate that at the maturities in question, bitumen redistribution into rock pores or fractures has been, at most, minor. At the higher maturity of the marine shale in the German study, a bitumen distribution not explained by depletion or generation on a whole rock basis becomes, as TOC-normalized data, exactly the compound type distribution expected for oil-phase expulsion. This constitutes evidence for migration along a kerogen network, particularly the role of reworked coal as a conduit and a coal seam as the effective 'reservoir' for the limited quantities of oil expelled. Whether or not this mechanism can account for large scale oil migration could become evident from a study of a contact where significant oil migration is known to have occurred, and variations in TOC content are sufficient to cause measurable differences between whole rock and TOC-normalized data. As can be appreciated from the published studies reviewed herein, the first requirement of known large scale migration is the more difficult to fill.

Chapter 3
ANALYTICAL PROCEDURES

The source rock section studied herein consists of 92 m of Kimmeridge Clay Formation siltstone overlying a sandstone reservoir rock. A 3.4 m thick sandstone is also present in the siltstone 12.4 m above the reservoir, and both sandstones are oil-bearing. The entire section was cored and sampled at intervals of 5-7 m for the upper part of the core, decreasing to 1-3 m for the last 30 m above the reservoir. Attention was given while sampling to avoid fractures and possible porous zones with drilling mud invasion. All rock samples (19-162 g.) were obtained from 4" diameter conventional drill core, wrapped in aluminum foil, and stored in plastic bags prior to the study. The sample of reservoir oil was obtained from the operating company and was stored in a brown glass bottle in darkness.

3.1. Crushing and grinding

After removing core edges contaminated with diesel oil (see Appendix A, page 146), samples were crushed to approximately 0.5 cm in a Braun 'Chipmunk' jaw crusher (steel jaws), which was brushed and washed with methanol between samples. Crushed samples were then ground for 5 minutes in a Siebtechnik agate disk mill (10.6-9 cm.), again brushed and washed with methanol between samples. The steel and agate crushing and grinding surfaces prevented contamination by tungsten carbide.

Most source rock studies in the literature leave the crushing and grinding procedures and results unreported. Ferguson (1962) found a median size of approximately 10 μ (ball milling) necessary for complete extraction of hydrocarbons, finer grinding increasing only the yield of non-hydrocarbon organic compounds. The size distribution of Ferguson showed approximately 85%<75 μ, and 95%<150 μ. Powell (1978) specifies grinding to 100%<149 μ. To evaluate the grinding of samples in the present study, a 74 μ sieve was used. After 2 minutes of grinding in the agate mill, 37% was found to be <74 μ. After 5 minutes of grinding, visible aggregates began forming on the sieve, and only 19% passed through. Wet sieving was not attempted due to the swelling nature of the powdered shale. It was decided that further size analysis would be difficult, and that a substantial fraction should be <74 μ, aggregates possibly having already formed and contributed to the results after 2 minutes of grinding. Overgrinding, leading to oxidation and pyrolysis of contained organic matter (Peters, 1986) was undesirable, therefore all samples were ground for 5 minutes and stored in glass jars.

3.2. Solvent extraction

After the removal of aliquots for organic carbon analysis, all the remaining samples were solvent extracted for isolation and quantification of soluble organics (bitumens). Organic solvents for this and all subsequent analyses, with the exception of diethyl ether for liquid chromatography, were purified by glass distillation.

3.2.0.1. Glass distillation

Glass distillation of solvents was done in 4 litre batches in a 3000 ml round-bottom flask with glass bead reflux column, pre-washed with distilled solvent remaining from the previous distillation. Initially 2 litres of reagent grade solvent, as received, was charged to the flask along with half a dozen or so boiling chips. This was distilled at a rate sufficient to give a reflux flow about equal to that of the distillate without overloading the column. The first 100 ml of distillate were discarded and the rest collected in a 4 litre brown glass bottle, prewashed like the flask. Distillation was stopped when about 100 ml of solvent remained in the flask. The second 2 litres of solvent were then charged along with additional boiling chips, and distilled at the same rate, discarding the first 100 ml of distillate and stopping when about 200 ml remained in the flask. This final 200 ml residue was discarded. Distilled solvents were kept in darkness.

3.2.0.2. Procedure

Although many methods of solvent extraction are used, the most popular appears to be the Soxhlet extractor (Dembicki, 1984) which allows continuous extraction by fresh solvent. Solvents employed for extraction also vary widely, and the choice of solvent and method greatly affect the results obtained making interlaboratory comparison uncertain. On advisor's recommendation, samples in this study were extracted by reflux with a benzene-methanol mixture.

Crushed and ground samples (19-162g) were extracted without drying or acid treatment. Each sample was weighed and added to a 500 ml round-bottom flask along with 200 ml of a 70/30 vol/vol benzene/methanol mixture. This corresponds to the minimum boiling azeotrope at 10 mm Hg total pressure and allowed subsequent evaporation to be carried out at room temperature. Sample and solvent were then hand swirled sufficiently to ensure good wetting, which also imparted a deep brown color to the solvent. A condenser was next added to each flask and the mixture gently boiled for 24 hr under total reflux.

Refluxed sample-solvent mixtures were next filtered on 11 μ (nominal pore size) paper filters (Whatman #1 Qualitative, 15 cm). These were the only type available sufficiently large for the sample sizes used, and due to their organic composition, were thoroughly prewashed before use, with the azeotropic mixture, as was all glassware used in the solvent extraction procedure. Filter cake and used extraction flasks were also thoroughly washed with the mixture, these washings being added to the filtrate. This was then reduced to about 30 ml in a rotary evaporator at 25°C. Evaporation revealed the presence of fine clay still remaining in the bitumen-solvent mixtures, so these were re-filtered on prewashed 1.5 μ (nominal pore size) glass fibre filters (prefired at 900°C, 1hr) and then evaporated to dryness in preweighed vials in a vacuum oven at 10 mm Hg and 25°C for 24 hr. Initially, evaporation to near dryness of the azeotropic mixture resulted in phase separation into 2 layers, but this was alleviated by washing the filter cake from the second step with benzene instead of azeotrope, and including the washings with the filtrate. Dry bitumens with visible salt were redissolved in pure benzene, filtered again, and dried. After weighing, bitumens were ready for fractionation into compound classes.

Extracted samples (filter cakes from the initial filtration step) were stored in glass jars for organic carbon analysis and Rock-Eval pyrolysis. One of these was re-extracted and yielded 2.1% of the original bitumen yield, thus it was assumed that near-total removal of bitumen was achieved.

3.3. Organic carbon analysis

All rock samples, before and after solvent extraction, were analyzed for organic carbon. Because carbon analysis is usually done by measuring CO_2 produced by high temperature combustion, distinction cannot be made between organic and inorganic carbon. It is thus necessary to determine carbonate carbon independently and subtract from total carbon, or to remove carbonate completely before combustion. The latter option was adopted because the former can lead to large errors when carbonate carbon >> organic carbon (Baker,1962).

3.3.0.1. Procedure

Samples of ground rock (100-900mg) were weighed, dried for 24 hr at 45°C, and reweighed. Water content was determined and used to correct weights of undried rock used for solvent extraction. Dried rock was then soaked for 24 hr in 30% HCl and filtered on pre-fired (500°C, 1 hr), dried (45°C, 24 hr), and pre-weighed 1.5 μ (nominal pore size) glass fibre filters, followed by several rinses with distilled H_2O. Filters plus filter cake were then dried (45°C, 24 hr) and weighed. This allowed calculation of % acid solubles (approximating total carbonate) and samples were now ready for combustion.

Samples thus prepared had lost all acid soluble organic carbon. Although this loss can be avoided by drying instead of filtering excess acid solution, such acid soluble organics should be rare at this level of maturity. In addition, drying of excess acid solution leaves hygroscopic chlorides which may complicate subsequent weighing (Hedges and Stern, 1984). Samples so tested gained 17-39% of their original dry weight while in the oven (45°C), rapidly increasing thereafter to as high as 86% and fluctuating with ambient humidity.

Combustion of organic carbon was done in 10 mm O.D. quartz tubes, prefired at 550°C for 1 hr. Due to the difficulty of cleanly separating cake from the filters, the entire filter plus cake for each sample was torn (over weighing paper) into approximately 3 mm pieces and loaded into the tube, mixed with approximately 15 g ground (mortar and pestle) CuO (BDH wire, prefired at 900°C, 1hr), a tedious and time-consuming procedure. Approximately 5 g of granular Cu metal (Alpha Resources) were then added and the tube evacuated and sealed with a flame. Tubes were heated at 850°C for 1 hr, then cooled to approximately 300°C very nearly linearly over a 16 hr period. After combustion, each tube was broken while sealed in an evacuated glass manifold and CO_2 purified and collected cryogenically. The isolated CO_2 was then measured by expansion against a calibrated Hg manometer. The manometer had been calibrated using nC_{24} combusted by the same method, and organic carbon was calculated on a dry rock basis. The CO_2 from each sample was collected and kept for carbon isotopic analysis.

3.4. Fractionation of bitumens and oils

Dried bitumens and oils from the above procedure were opaque, dark brown, and very viscous liquids. Analysis of bitumens, oils, and other complex multi-component mixtures normally requires separation into compound classes, followed by analysis of individual compounds when these are sufficiently abundant and free of interfering molecules. In this study, distinction between compound classes is by type of accommodation in solution between resins and asphaltenes and by molecular type among saturates, aromatics, and resins.

3.4.1. Precipitation of asphaltenes

Although subsequent column chromatography for separation of saturates, aromatics, and resins can be carried out without prior removal of asphaltenes, this results in possible loss of saturates (Radke *et al.* 1980), possible on-column alteration of asphaltenes, and some carryover of asphaltenes into the aromatic fraction (Palacas *et al.* 1984). In addition, subsequent separation of resins and asphaltenes, if defined by retention on the column after elution with polar solvents, becomes dependent on properties other than n-pentane solubility.

Although 'n-pentane solubility' is used herein to define asphaltenes, Koots and Speight (1975) have shown that asphaltenes are insoluble in the hydrocarbon fraction of their own oils without any n-pentane addition, indicating that resins are necessary for accommodation of asphaltenes in crude oils, probably as a colloidal dispersion (Hunt, 1979). Viscosity and density of crude oils are a function of resin and asphaltene content (Tissot and Welte, 1978), and resins by weight equal or exceed asphaltenes in crude oils (Hunt, 1979). Mitchell and Speight (1973) show that the ability of a solvent to precipitate asphaltenes is a function of the ratio of the surface tension to the cube root of the molar volume, a measure of the ability of a solvent to prevent association and consequent precipitation of asphaltenes after resins are dispersed by dilution. The work of Mitchell and Speight (1973) also showed that asphalt precipitation was much reduced by using cyclo-alkanes rather than normal- or iso-alkanes or terminal olefins, all of the same carbon number. For n-alkanes, precipitation increased sharply with decreasing carbon number below n-octane.

Although other workers have used n-hexane (Jonathan *et al.* 1976), n-heptane (Palacas *et al.* 1984), or petroleum ether, it was decided to use n-pentane for asphaltene precipitation because pure n-hexane and n-heptane were not readily available and the extra asphaltene obtained with n-pentane would result in a smaller amount of resins in resultant liquid chromatography feed, improving recovery therein. A simple trial with the reservoir crude oil yielded 32% more asphaltenes by using n-pentane than with 'hexanes' available in bulk. According to the findings of Mitchell and Speight (1973) this difference should be about 25% in the case of pure n-hexane.

Ratios of solvent to sample in the literature (V/V) were found to vary from 10/1 (ASTM D2007) to 100/1 (ASTM D4055), but were often unreported. Trials were carried out with a readily available crude oil, using approximately 0.5 ml of dried oil redissolved in 0.5 ml of benzene (Mitchell and Speight, 1973), and varying quantities of n-pentane. Results are shown in Fig. 3-1.

Solvent ratios are expressed as vol n-pentane/vol oil and asphalt percentages are on a dried oil basis. Although scatter obviously exists and reproducibility limits on such data may be large, no maximum appears to be reached beyond which further increases in solvent ratio produce no changes. It was therefore decided to use a solvent ratio of approximately 60/1, the largest practicable when processing many samples with existing space and equipment limitations.

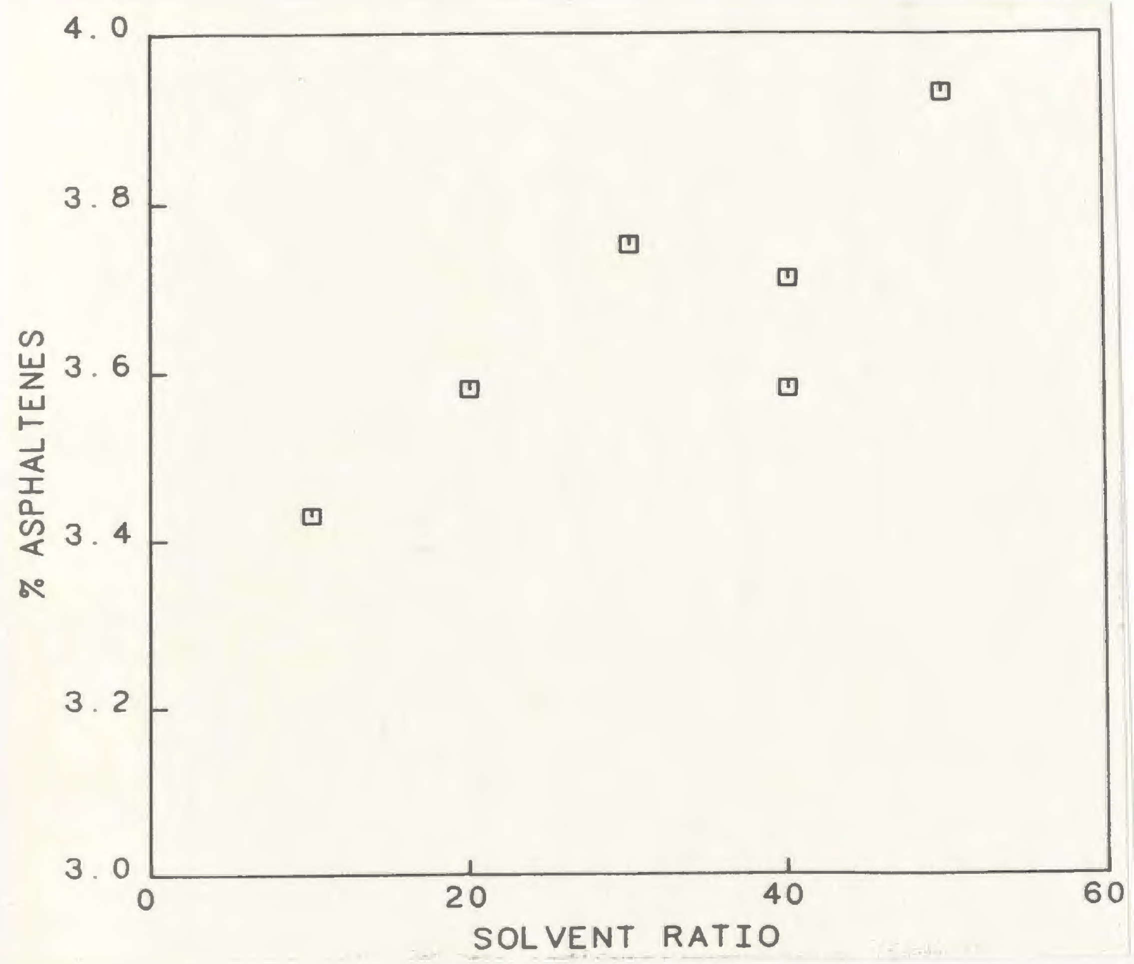


Figure 3-1: Asphaltene precipitation trials

3.4.1.1. Procedure

Dried bitumens and oils were redissolved in 0.5 ml benzene, diluted with 30 ml n-pentane, sealed, shaken vigorously, and stored for 24 hr at 0°C, in darkness. Although refrigeration is not necessary for asphaltene precipitation this was done to ensure constant conditions for all samples during a period when ambient laboratory air temperature was variable. Asphaltenes were then filtered on pre-fired (500°C, 1 hr), pre-weighed, 1.5 μ (nominal pore size) glass-fibre filters, and washed several times with n-pentane. Filters plus asphaltenes were then dried at 45°C for 24 hr and weighed, and the asphaltenes redissolved in benzene. All asphaltenes appeared to be 100 % benzene soluble. Pentane soluble filtrate was dried, redissolved in hexane, and stored for subsequent liquid chromatography.

3.4.2. Liquid chromatography

Liquid chromatography, either high pressure or in columns under atmospheric pressure, is most commonly used to separate de-asphalted bitumens, although thin layer chromatography is also sometimes employed. Liquid chromatography separates compounds according to their degree of adsorption on selected substrates in selected liquid phases. In general, polarity increases in the order: saturates < aromatics < resins, although some overlap occurs, notably between the two latter types.

Most liquid chromatography applied to bitumens utilizes a substrate which adsorbs resins and allows hydrocarbons to pass, followed by a more active substrate which adsorbs aromatics and allows saturates to pass. Saturates are thus collected and more polar solvents are then used to elute aromatics and resins. This sequence is outlined by Oudin (1970) for a two stage procedure, and by Jonathan *et al*. (1976), for a dual-packed column. It is also implicit in ASTM standard method D2007(1984) where the two substrates are physically separated after saturate elution for independent recovery of resins.

Some form of silica gel was used for adsorption of aromatics in all documented methods reviewed in the literature, but adsorption of resins was variously carried out with alumina, bauxite, Attapulgus clay, and combinations of ion-exchange resins with $FeCl_3$-coated clay. Radke *et al*. (1980), have successfully used wide-pore (63-200 μ) silica gel for resin adsorption (thermally de-activated to allow elution of polyaromatics), indicating that pore size and not substrate chemistry may be the controlling factor for high molecular weight resins.

Little standardization exists with regard to chromatographic separation of bitumens and most studies leave this procedure poorly documented, particularly for purity of products. The adsorption of aromatics on silica gel is not 100% irreversible in the presence of non-polar solvents, and exhaustive elution will include monoaromatics in the saturate fraction (Jewell *et al*. 1972). Similarly, a solvent of too high polarity will introduce resins into the aromatic fraction (Durand *et al*. 1970). Insufficient quantities of either adsorbent can result in 'breakthrough' with the same effects. The extent of these overlaps, always present to some degree, are rarely stated in descriptions of procedures. For this study, a method was sought which used existing equipment (ruling out HPLC), was applicable to source rock bitumens, and was well documented with respect to product purity, elution volumes, and column loading.

Of well documented methods studied, several required HPLC equipment, e.g. Radke *et al*. (1980), one gave no aromatic-resin separation (ASTM D2549,1984), the USBM/API 60 method required prior ion-exchange resin treatment and did not effect a complete resin-polyaromatic separation (Hirsch *et al*. 1972), and ASTM standard method

D2007(1984) was developed for rubber extender and processing oils. Although this latter method uses high gel/sample ratios and was used by Aczel and Lumpkin (1972) for gas oils, it was found by Radke *et al.* (1980) and Suatoni and Swab (1976) to allow excessive amounts of monoaromatics (up to 47%) into the saturate fraction. The method of Durand, Espitalié, and Oudin (1970) was developed for source rock bitumens, uses simple lab equipment, is well documented, and has been used widely with success by the Institut Français du Pétrole. This method, with minor modifications, was used in this study.

3.4.2.1. Procedure

The original procedure as outlined by Durand *et al.* (1970), was modified as follows to use available materials and accommodate larger sample sizes:

- 11 mm I.D. burettes were used as columns in place of 6 mm in the original procedure,
- BDH silica gel (124-250 μ) was used in place of Davison 923 (74-149 μ),
- bulk 'hexane' was used instead of n-heptane as eluent. Density measurement ($\rho = 0.66$) and GCMS examination indicated this to be free of cyclohexane, methyl cyclopentane, and benzene, and
- elution volumes and adsorbent weights were scaled up by a factor of 1.37 from the original

The original procedure (Oudin, 1970) calls for 30g alumina for 1g column feed, and 40g silica gel for 500mg hydrocarbon feed. Thus the streamlined procedure (Durand *et al.* 1970) is designed for 233mg of total feed (59% hydrocarbon) although it has been used successfully for up to 525mg. A combination of 9.6g alumina and 15g silica gel was therefore employed for this study (Fig. 3-2). Both adsorbents were activated at 180°C for 4 hr in small batches every 2 days to maintain activity, and stored in tightly sealed jars.

To verify the effectiveness of the method with the above modifications, standard pure compounds at a concentration of approximately 1mg/ml were eluted through the column as dummy samples. They included:

- Saturates:
    - 2 n-alkanes, C_{16} and C_{30}
    - 1 iso-alkane, pristane(2,6,10,14 tetra-methyl pentadecane)
    - 2 cyclo-alkanes, decalin and cholestane
- Aromatics:
    - 2 mono-aromatics, n-decyl benzene and tetralin
    - 1 polyaromatic, 3,4 benzopyrene
- Resins:
    - 7,8 benzo-quinoline and 1,2,7,8 dibenzo-carbazole

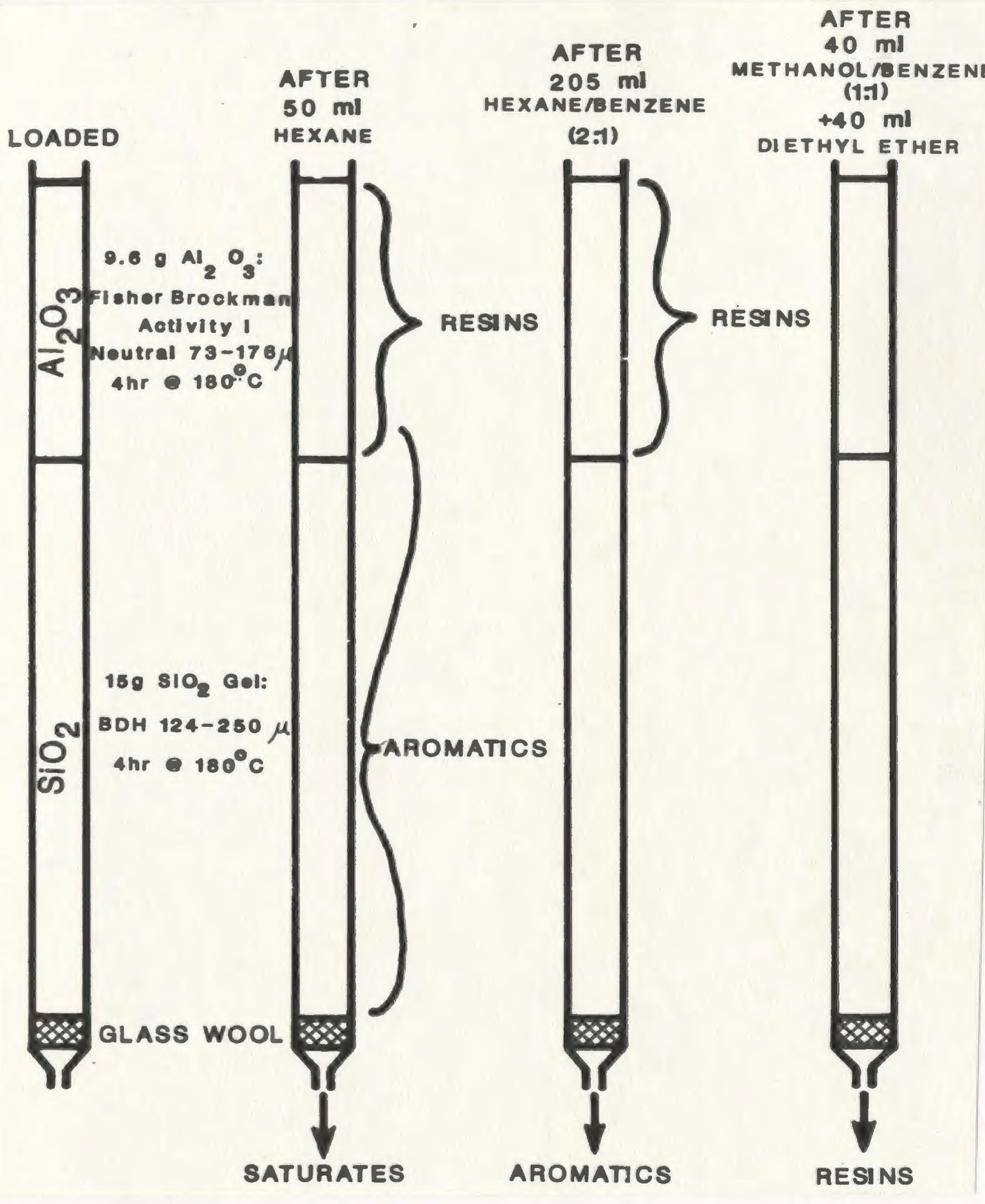
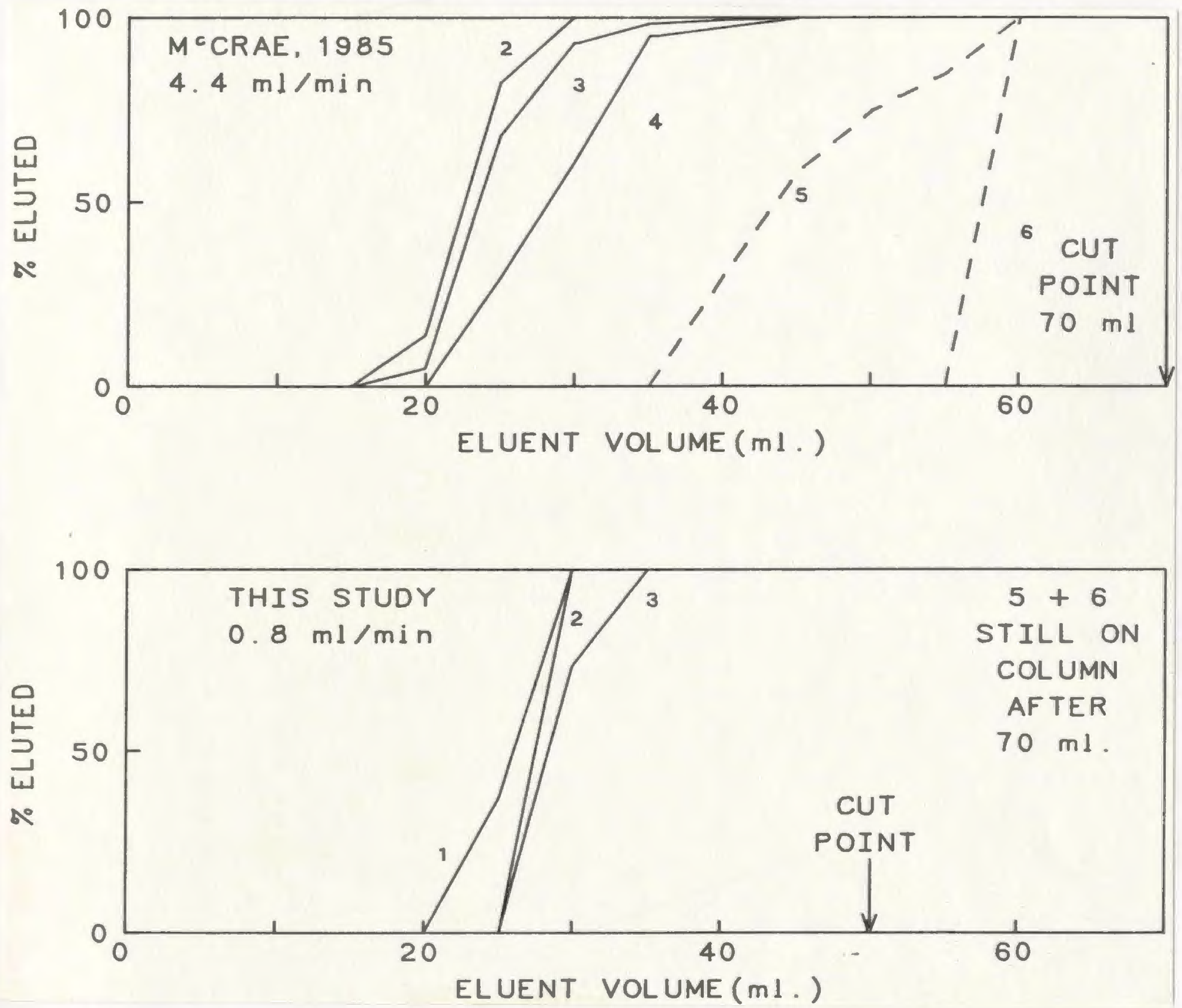


Figure 3-2: Liquid chromatography - schematic

Saturates and monoaromatics were exhaustively eluted with hexane (analyzed by GC in 5 ml subfractions) to verify the saturate/mono-aromatic cut-off point. All elution volumes referred to herein are volumes entering the column, no attempt being made to save solvent by taking into account the column pore volume. Oudin (1970) found that cut-off at the first appearance of mono-aromatics leaves approximately 7% saturates in the aromatic fraction, but these are probably heavily substituted very high molecular weight mono-aromatics as found by Aczel and Lumpkin (1972) to be included in saturate fractions. The mono-aromatics chosen here were the most heavily substituted available, and were not eluted after 70 ml hexane. All saturates studied were eluted by 35 ml hexane, and all except cholestane by 30 ml (Fig. 3-3). It was thus decided to retain the cut point at 50 ml as in the scaled original method (2.5 x column pore volume of 20 ml approximately), the substitution of hexane for n-heptane having no apparent effect on the separation. Radke *et al.* (1980), regard baseline separation of n-octyl benzene and nC_{30} as the minimum acceptable for column operation and this standard was easily met, n-octyl benzene having a similar elution pattern to n-decyl benzene (McRae, 1985). Speed of elution was kept at 50 ml/hr (not scaled from original) and the results of McRae (1985) using a similar column indicate that this factor may be critical (Fig. 3-3). The method used should give less than 1% mono-aromatics in the saturate fraction (Oudin, 1970), well below the maximum 5% for subsequent type analysis by mass spectrometry (ASTM D2786,1984).

The poly-aromatic and resins were next charged to a similar column and eluted as before at 50 ml/hr The eluent used was 33% benzene in hexane (vol/vol), under the assumption that the substitution of hexane for n-heptane would have even less effect on aromatics elution than for saturates. Durand *et al.* (1970), found that 45% benzene was sufficient to elute some resins, and Palacas *et al.* (1984), were able to elute some asphaltenes, thus probably resins as well, with 100% benzene, so the specified 33% was adhered to. The benzopyrene was completely eluted by 190 ml and both resin compounds were still on the column after 270 ml. As with the saturates endpoint, it was decided to retain the aromatics cut-off point at 205 ml as in the scaled original method based on these findings and the fact that during an actual run, the 50 ml hexane elution would advance the aromatics. The standard compounds chosen represented the hydrocarbon and resins with the maximum number of aromatic rings, available at the time, but findings by Aczel and Lumpkin (1972) and Robinson and Cook (1969) indicate that oxygen compounds are more likely to overlap with aromatics than are nitrogen compounds, so an endpoint minimizing the overlap between a highly condensed poly-aromatic such as coronene and substituted dibenzofurans may result in purer fractions. All methods reviewed found that substituted thiophene sulfur compounds were inseparable from aromatics by liquid chromatography.

Columns used were 11 mm I.D. burettes with teflon stopcocks, washed with methanol, and plugged at the bottom with glass wool. Columns and wool plugs were then washed



- Saturates:
  - nC_{30}- - - - - - - - - - 1
  - Decalin - - - - - - - - 2
  - Cholestane- - - - - - 3
  - nC_{25}- - - - - - - - - - 4
- Aromatics:
  - n-Decyl Benzene - 5
  - Tetralin- - - - - - - - 6

Figure 3-3: Pure compound elution

with benzene followed by hexane. Silica gel and later alumina were measured volumetrically, slurried in hexane to remove air, and charged to the column by pipette. Filled columns were then washed with 40 ml hexane (2 pore volumes approximately) and compacted with vigorous tapping. This was much more effective with solvent flowing than in a static fluid column. At no time was the liquid level allowed to fall below the top of the alumina. Burette tips were rinsed with benzene, and columns were ready for use.

Asphalt-free bitumens and oils were dried at 25°C and 10 mm Hg overnight, redissolved in 1 ml hexane, and charged to the column, letting the liquid level drop again to the alumina surface. A charge of 50 ml hexane was measured out, and bitumen vials were then rinsed twice with 1 ml of this hexane, each time charged to the column as before. Vials were weighed before and after to evaluate loss from asphalt removal. Column walls were washed with another 1 ml of the hexane as before, and then saturates were eluted at 50 ml/hr with the hexane remaining into a 500 ml round bottom flask, rinsing off the burette tip with hexane. The brown color of the bitumen was observed to remain on the upper half of the alumina. All saturate fractions were clear and colorless.

Aromatics were then similarly eluted with 205 ml of 33% benzene in hexane, the first 3 ml introduced in 1 ml quantities, allowing the liquid level to reach the alumina after each. Elution was at 50 ml/hr as before, into a 500 ml round bottom flask, rinsing off the burette tip with benzene. During the elution, the brown color was seen to advance further into the alumina (but not to the silica gel), and a light greenish-yellow color to advance from the alumina through the silica gel and into the eluate. All aromatic fractions were transparent light greenish-yellow, similar to concentrated hexane solutions of coronene or perylene, and the advance of this color from the alumina possibly indicates that the heavier poly-aromatics are not advanced to the silica gel by the hexane elution, as shown in Fig. 3-2.

Resins were eluted with 40 ml 50/50 benzene-methanol followed by 40 ml diethyl ether, introducing each new solvent in 3 x 1 ml quantities as before. Diethyl ether (Fisher Anhydrous, .001% res. after evap.) was used as received, with 1 ml distilled H_2O added per 500g can to inhibit peroxide formation. Elution of resins was done with the stopcock wide open into a 500 ml round bottom flask and the burette tip washed with benzene. All but traces of brown color were swept from the column, mainly by the benzene-methanol, and all resin fractions were opaque to transparent dark brown.

Collected fractions were transferred directly to a rotary evaporator and evaporated to dryness at 25°C. These were then transferred to pre-weighed vials by pipette with 5 x 1 ml quantities of solvent and dried overnight at 25°C and 10 mm Hg. Hexane was suitable for saturates and aromatics, but resins, after collection, were found to be only partially hexane soluble (except those from crude oils) and were transferred with benzene. This is possibly due to on-column alteration as documented by Durand *et al* (1970). All fractions were redissolved in 5 ml solvent after weighing.

By this method one run could be completed in 8 hr and 4 samples could be run simultaneously in 12 hr, including evaporation, cleanup, and weighing and redissolving fractions of the previous day.

3.5. Gas chromatography

Saturate and aromatic fractions from liquid chromatography were analyzed by capillary gas chromatography (GC). For the saturates, this allows calculation of odd-even predominance, a maturity parameter (Scalan and Smith, 1970), and of relative proportions of n-alkanes and acyclic isoprenoids. Accurate proportions relative to the total fraction can only be determined by duplicate injections with an internal standard (Powell, 1978), which was not carried out in this study. Hilpert *et al.* (1978), have found variability of up to 300% when quantitation was attempted using GC alone, due to integrator sensitivity and resolvability of mixtures. Aromatics in general are much less well-resolved than saturates and abundant overlap between alkyl-substituted aromatic and thiophenic series largely prevents determination of relative proportions by GC alone, except for unusual oils with an abundance of specific compound types such as dibenzothiophenes (Palmer, 1984) or alkylbenzenes (Powell *et al.* 1984). For both saturates and aromatics GC shows qualitatively the molecular weight distribution in the fraction, helpful in recognizing biodegradation (Winters and Williams, 1969), molecular weight selective depletion by migration (Leythaeuser *et al.* 1984), and organic contamination (Powell, 1978).

3.5.0.1. Procedure

All saturate and aromatic fractions except the system blank were diluted or evaporated (as required) to a concentration of 6 mg/ml, approximately half the concentration at which peak saturation just began to appear for the most abundant compound, usually pristane. A Varian 3700 gas chromatograph was used with a 30m DB-1 capillary column, programmed from 80°C to 320°C at 3°C/min with a 1 min hold at 80°C and 10 min hold at 320°C. Detector (FID) temperature was 360°C. Injector temperatures from 280 to 360°C were tried, but discrimination against nC_{30} in the calibration standard still persisted slightly, even at the higher temperature, so the problem was circumvented as recommended by Grob and Grob (1981) with on-column injection (0.8μl). Calibration was done with a standard mixture of nC_{16}, pristane, nC_{24}, and nC_{30} for the saturates; and fluorene, 1-M phenanthrene, 2,3 benzofluorene, and coronene for the aromatics. These were all at a concentration of approximately 1 mg/ml and were injected after every fifth sample. Chromatogram peaks were integrated with an HP 3390A integrator and all determinations were based on peak areas, measured valley-to-valley over unresolved humps.

3.6. Carbon isotopic analysis

All crude oil and bitumen fractions as well as total organic carbon from extracted and unextracted rock samples were analyzed for carbon isotope ratio. Because this is only done for CO_2 gas, all samples must be combusted completely and the resulting CO_2 isolated before analysis.

3.6.0.1. Procedure

For each crude oil and bitumen fraction, approximately 3g CuO (BDH wire, prefired at 900°C, 1 hr) was ground lightly with mortar and pestle and spread evenly over the bottom of a thoroughly clean 100 ml beaker. The beaker was then placed on a hotplate at approximately 45°C and allowed to equilibrate. A volume of the redissolved fraction containing 2 mg of the solvent-free eluate was then withdrawn from the fraction vial by pipette and lightly distributed drop by drop over the warm CuO, ensuring quick solvent evaporation and near-uniform coating of the fraction on the CuO surface. The coated CuO was then loaded along with approximately 2g Cu metal (Alpha Resources, granular) into a prefired (900°C, 1 hr) 6 mm O.D. quartz tube, which was then evacuated and sealed with a flame. All tubes were then combusted and resulting CO_2 from each fraction was purified and isolated as outlined under **Organic Carbon Analysis**, page 49, omitting only the vaporization and volume measurement step.

The CO_2 from all fractions and rock samples, thus purified and isolated, was analyzed for carbon isotope ratio on a Micromass 903E mass spectrometer using an internal standard. All results were recalculated and reported relative to PDB, corrected following Craig(1957).

3.7. Mass spectrometric analysis

Selected oil and bitumen fractions were analyzed for compound class abundances by batch inlet mass spectrometry, conditions as follows:

- Sample size: 1.5 μl.
- Inlet:
    - Brunfeldt all glass
    - Temperature: 350°C
    - Expansion Volume: 1 l.
    - Transfer Line: 350°C
- Detection:
    - HP Mass Selective Detector

Chapter 4
GEOLOGICAL BACKGROUND

4.1. Introduction

The central and northern North Sea, where only a single source rock, the Kimmeridge Clay Formation, has the necessary source rock characteristics and areal distribution to have sourced the numerous accumulations, is an ideal locality for oil migration studies. Oil migration routes should be more readily pinpointed and more often vertical than in basins with multiple sources and effective continuous horizontal permeability.

The present study is of a 92m core of Kimmeridge Clay Formation siltstone, overlying a sandstone oil reservoir. A 3.4m sandstone bed is present in the lower part of the siltstone but this gives way to mm scale lamination and generally higher TOC contents in the upper 64m. These observations are consistent with a transgressive, upward deepening depositional history with anoxic bottom water, predominantly marine organic matter, and waning influence of sea floor topography and terrestrial inputs. Organic carbon content is moderate (1.3 - 5.6%). Oil and rock samples were obtained from the operating company with the agreement that the well identity and depths would be treated as confidential.

With adequate maturity the section should function as a good oil source, with the underlying sandstone favorably positioned to accumulate migrating oil.

4.2. Setting

The North Sea basin is a continental rift basin (Perrodon, 1983) being situated entirely on the European continental shelf. Characteristically, such basins develope sequentially in the following way:

1. Tensional faulting and graben formation during crustal extension and thinning, with upwelling of underlying mantle
2. Continuous subsidence, decreasing with time, during thermal contraction of cooling crust and underlying upwelled mantle material

They are often referred to as 'failed spreading axes' (Pegrum *et al*, 1975), since sea-floor spreading axes begin their development the same way, but continuous extension replaces the thermal contraction step. Geothermal gradients in such basins are high and

- Scan: 20 to 800 amu.
- Scan Time: 2.4 sec.

Analysis of data was done for saturates using summed total spectra and ASTM D-2786 revised matrices (without typos and errors in published matrices). Aromatics were quantified using averaged composite spectra and ASTM D-3239 as published.

decreasing with time, favorable for source rock maturation. In the North Sea, rifting began in the Triassic and culminated in the Upper Jurassic. The post-rifting subsidence phase began in the Lower Cretaceous and continues to the present, such that with the exception of a few salt piercements and inversion troughs, sediments are presently at their maximum depths and temperatures.

Oil occurrence is limited almost entirely to the central and northern North Sea and further discussion will be limited to areas north of approximately 55°N. General outlines of North Sea basin geological and tectonic development are presented by Zieglar (1981) and Sclater & Christie (1980).

4.3. Source rocks

The presence of both a thick Permian proto-rift evaporite sequence and a thick Triassic syn-rift continental redbed sequence restricts oil generation in the North Sea to the overlying Jurassic, Cretaceous, and Tertiary.

Both Oudin (1976) and Barnard and Cooper (1981) have found the Cretaceous and Tertiary shales, although moderately high in organic carbon, to have kerogen dominated by vitrinite and inertinite and thus, at best, gas-prone. Their low oil source capability is demonstrated by the observation that Tertiary and Cretaceous-reservoired oils can be correlated to the underlying Upper Jurassic (e.g. Van den Bark and Thomas, 1981) even in locations most favorable for Tertiary and Cretaceous thickness and maturity (Byrd, 1975).

4.3.1. Jurassic

The syn-rifting Jurassic sequence is, in general, rich in organic carbon and buried to oil generation maturities. Basically it consists of, in order of increasing areal distribution:

- a marine, shale-dominated Lower Jurassic
- a sand-dominated deltaic Middle Jurassic with volcanics and coal
- a marine, anoxic, shale-dominated Upper Jurassic

4.3.1.1. Lower Jurassic

Fuller (1975) and Oudin(1976) have found Lower Jurassic shales in the northern North Sea to contain dominantly gas-prone kerogen types. In addition, oils from the central and northern North Sea are very similar (Mackenzie & Maxwell, 1983; Oudin, 1976; Brooks & Thusu, 1977) and the central North Sea lacks Lower Jurassic sediments (Brooks & Chesher, 1975). These observations make Lower Jurassic shales very unlikely as a significant oil source rock in the North Sea oil- producing sectors.

4.3.1.2. Middle Jurassic

Middle Jurassic rocks in the North Sea consist predominantly of deltaic deposits rich in sandy delta top facies with little source potential except for thin coals and coaly shales. These have been found to be gas-prone by Fuller (1975) and Oudin (1976), the latter finding poor correlation by GC between saturate fractions from these rocks and North Sea oils. Ungerer *et al* (1984) assign a high oil generating potential to these coals, but their oil expulsion model is based on oil content as ppm of total rock and not per unit TOC. Also much work is based on pyrolysis results (Durand and Paratte, 1983) which can be misleading for coals as previously shown in the literature review chapter, page 39. Most North Sea oil is reservoired in Middle Jurassic sandstones, yet does not correlate with the shale and coal interbeds therefrom. Also, like the Lower Jurassic, Middle Jurassic sediments are missing from much of the central North Sea, where oils similar to those in northern North Sea Middle Jurassic reservoirs are abundant (Brooks and Thusu, 1977, Oudin, 1976). This argues against Middle Jurassic rocks acting as effective sources.

4.3.1.3. Upper Jurassic

The Upper Jurassic of the central and northern North Sea consists of a lower marine shale unit grading to sandstone near the paleoshoreline, and a much more widespread upper marine shale with rare sandstone intercalations. The former, the Heather Formation in its shale facies (Deegan and Scull, 1977), was found by Fuller (1975) to contain predominantly gas-prone kerogen, but Oudin (1976) found moderate oil-generating potential in the same rocks, but much less, however, than in the overlying Kimmeridge Clay Formation.

4.3.1.4. Kimmeridge Clay Formation

The highest unit in the North Sea Upper Jurassic (locally extending into the lowest Cretaceous) is the Kimmeridge Clay Formation. It covers larger areas than the underlying Jurassic formations and is one of the most widespread formations in the North Sea (Deegan and Scull, 1977). It is invariably organic-rich and oil-prone, and numerous investigations of North Sea oil source rocks have found it to be the principal, if not only, source of North Sea oil. Oil-source correlations between this formation and North Sea oils are generally definitive (Reitsema, 1983; Fuller, 1975; Mackenzie and Maxwell, 1983; Bissada, 1981), even with biodegraded oils in shallow Tertiary reservoirs (Oudin, 1976). Cooper and Barnard (1984) have presented a map showing excellent correlation between location of North Sea oilfields and areal distribution of oil-mature Kimmeridge Clay . A distribution such as mapped by Cooper and Barnard (1984) indicates, at least for the North Sea, limited lateral, but extensive vertical, secondary migration. However, large areas with mature Kimmeridge Clay and little discovered oil suggest that the availability of migration routes and/or traps is also an important factor.

Organic matter type in the Kimmeridge Clay Formation appears to be variable, with type III generally occurring nearer the paleoshoreline (Mackenzie and Maxwell, 1983), types I & II in the most distal and presently oil-mature facies, and type IV (inertinite) in minor amounts throughout. Barnard *et al.* (1981) find an upward increase in TOC as well as in the proportion of types I & II kerogen in thick sections, consistent with transgressive deposition and a marine origin for the greater part of the organic matter.

Regional mapping coupled with maturation studies shows that the Kimmeridge Clay Formation is mature for oil generation in oil-producing sectors of the central and northern North Sea (Cooper and Barnard, 1984) and has reached this maturity level in the Tertiary (Hansen and Mikkelson, 1982; Rönnevik, 1983). Continuous and ongoing subsidence since the Lower Cretaceous means that oil generation is actively continuing in most of the producing areas today, and sandstone reservoirs here are commonly full and spilling.

4.4. Lithology of studied section

The section studied is shown in Fig. 4-3. Macroscopically, the core is a monotonously uniform sequence of blocky, olive black to brownish black (Goddard *et al.* 1980) very silty shale, grading to siltstone. Carbonate and organic contents are variable, and discrete thin, hard, calcareous stringers were present. These appeared to be secondary features, as fracture filling and were very similar to features reported by Lindgreen (1985) and became more frequent with depth. Very thin (approximately 10 cm) organic-poor calcareous siltstone bands were also observed above 33 m, locally with bioturbation near the upper contacts.

Beyond 28 m from the reservoir top, undisturbed, millimeter scale lamination was observed throughout, and this type of bedding, typical of anoxic shales, was also locally present below 28m. Bioturbation was very rare and observed fossils consisted of belemnites, fish bones, and rare small valves. These observations are consistent with deposition in an anoxic bottom water layer toxic to burrowers, overlain by oxic water supporting pelagic life. Below 12m, angular clasts of very fine, tight sandstone are locally present, possibly indicative of deposition near an active fault. Megascopically visible pyrite was rare.

4.4.1. Geochemical analysis

Analysis for total organic carbon and soluble bitumen allows a crude mineralogical breakdown of the rock, and this is shown plotted as a depth profile on Fig. 4-3, page 68.

Total organic carbon (TOC) was measured on both extracted and unextracted rock samples. Some samples were checked for repeatability, both intentionally and as a side benefit from repeat isotope analyses, and all repeated to within 0.20% TOC of the mean, the value reported herein, with a pooled standard deviation of 0.09% TOC (N=42). As a percentage of the mean, this standard deviation is 3.12%, based on the number average TOC from the repeat analyses. The method used does not allow for water-soluble organic carbon, but Roberts *et al.* (1973) report that this occurs only in minor amounts in mature rocks, amounting to approximately 0.45% of the total organic carbon in the Kimmeridge Clay. Blank filter papers (ashed) were also found to register organic carbon, about 0.2% of the total, and this, although miniscule, was subtracted from each sample.

TOC of extracted samples showed better repeatability, within 0.08% TOC of the mean, and with a pooled standard deviation of 0.04% TOC (N=31). As a percentage of the mean, standard deviation of the extracted samples was 1.46%, which compares more favorably with values of 1.26% and 1.43% reported by Dembicki (1984) for source rocks of similar TOC content. Some of these same extracted samples were independently analyzed for TOC in conjunction with pyrolysis studies, and those results were systematically higher by a factor of 1.16 - 1.20 than those presented here. Thus although the results of the extracted rocks are considered more accurate than those of the unextracted samples, both may contain systematic error due to incomplete combustion or some other cause. In Fig. 4-1, bitumen weight is plotted against organic carbon loss on extraction for all samples. A best-fit straight line of the type Y=KX is shown fitted to the data and has a slope of 1.13 g bitumen/g TOC. In view of the scatter, this compares favorably with similar values in the literature, *i.e.*: 1.22 (Hunt and Jamieson, 1956), 1.25 (Vandenbroucke, 1972), 1.25 (immature) and 1.16 (mature)(Tissot and Welte, 1978, p 164), and 1.22 (Espitalié *et al.* 1984). Due to the suspected inaccuracies outlined above in the results from this study and the greater experience and data base of the quoted authors, a value of 1.2 was selected and used to convert TOC of extracted rock to kerogen for plotting on Fig. 4-3. The value of 1.13 was however used to estimate bitumen weight for the sample at 0 m which was partially lost before separation.

Acid treatment for removal of carbonate carbon prior to TOC analysis enabled an estimate of carbonate content to be made. Although this is in fact total acid solubles including pore water salts and possibly some clay mineral components, a trial with a sample using distilled water in place of acid yielded 1.16% loss as compared to 13.53% loss with acid, suggesting that salts make up only a small percentage of reported carbonate, likely decreasing in less porous carbonate-rich samples. Blank filter papers registered 0.14% acid loss and this has been corrected for in the reported carbonate contents. Results showed a pooled standard deviation of 0.40% carbonate (N=48) and repeated to within 0.93% carbonate of the mean, the value reported herein. In Fig. 4-2, TOC (unextracted) is plotted against carbonate content. The plot shows no clear relationship between TOC and carbonate, but a clear decrease of maximum TOC as percent carbonate increases. This is consistent with the findings of Lindgreen (1985) and observations herein which suggest that the carbonate is largely diagenetic in origin and is

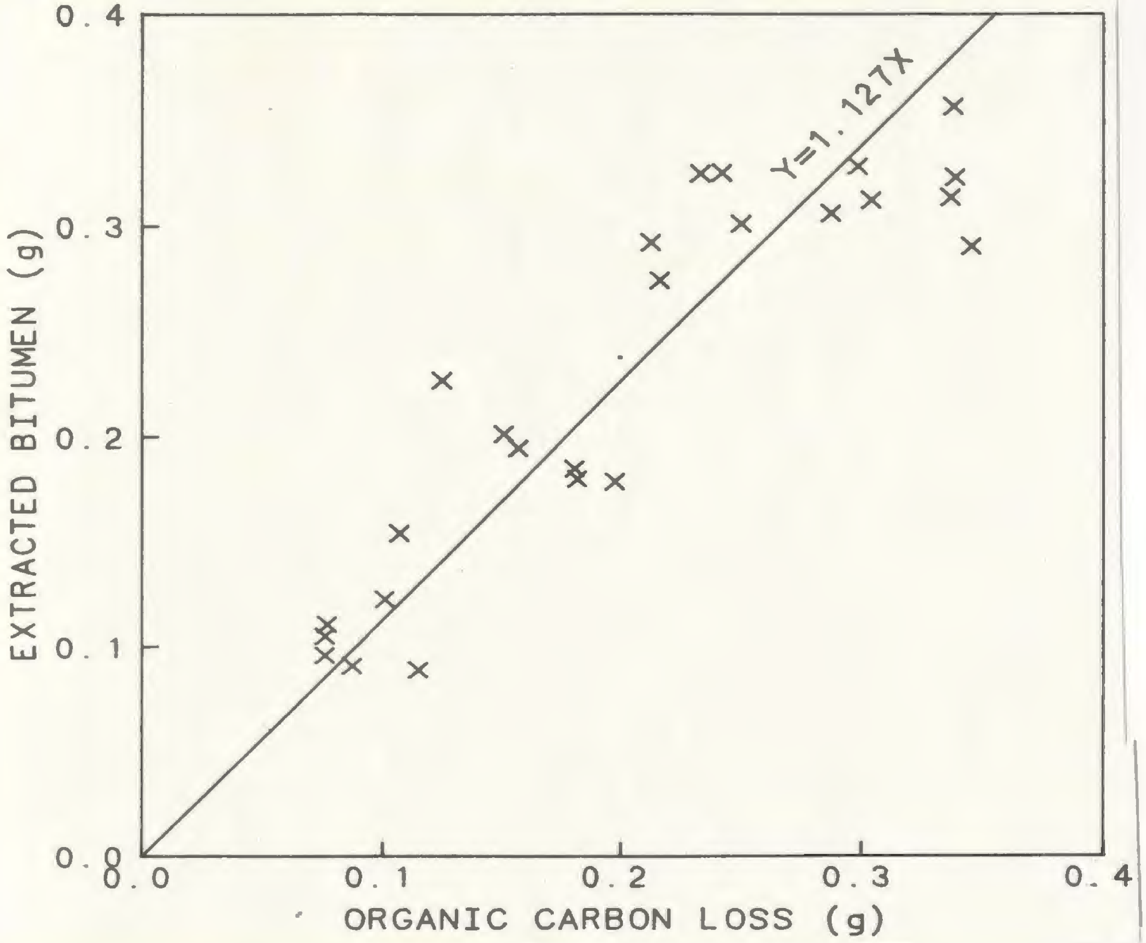


Figure 4-1: Bitumen wt. vs. carbon loss

thus a diluent to organic carbon. Variation in organic carbon content of the non-carbonate fraction could be due to other factors such as variable organic productivity and preservation, or clastic supply, both of which should show greatest influence in more proximal facies. Primary carbonate deposition due to clastic starvation should lead, in the case of predominantly marine organic matter, to an increase of TOC with increasing carbonate content. Fig. 4-3 attempts to show this dilution effect by illustrating composition on a log scale. The variation of TOC content with carbonate content is most evident above 25m, and TOC content is consistently higher above 30m. This is roughly the same depth above which mm scale lamination (anoxia) becomes ubiquitous. The upward increase in TOC is similar to that observed by Barnard *et al*. (1981) and the overall sequence is that expected of transgression and water deepening, with decreasing influence of terrestrial clastic and organic input, and thus increasing relative influence of carbonate content on TOC. The presence of the thin sandstone and the sandstone clasts below 12m are likely indicative of proximity to the paleoshoreline, shelf edge, or a submarine fault scarp, all of which show diminishing influence with increasing water depth and the gradual burial of submarine topographic relief which is characteristic of the

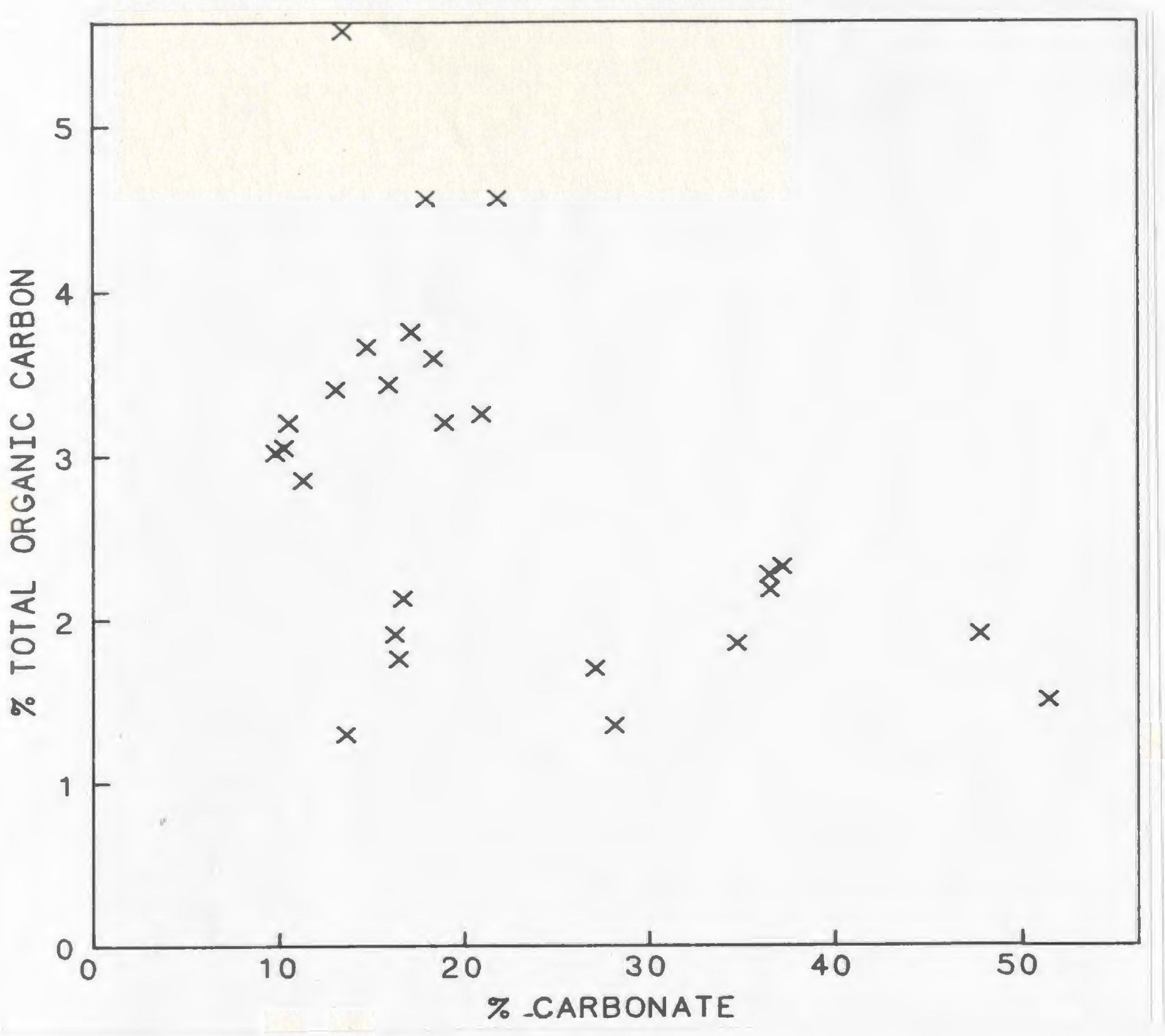


Figure 4-2: TOC vs. CO_3

Kimmeridge Clay. Experimental data used to construct the plots in this chapter is tabulated in Appendix B, Table B-1.

4.4.2. Petrographic observations

Portions of the core samples removed to avoid diesel contamination (see Appendix A) were made into thin sections for microscopic examination. In general, these were monotonously uniform, and in keeping with many 'shales' in general and 'oil shales' in particular, they appear to be surprisingly poor in clay content and must be classified as variably calcareous siltstones. All photographs herein are in plain light.

A laminated siltstone typical of the organic rich upper part of the core is shown in Fig. 4-4. Lamination is defined by mm scale dark organic-rich, and light organic-lean layers, which are more easily seen in hand specimen. Carbonate content, 17.2%, is concentrated in the light layers. Bedding is also defined by parallelism of fine mica flakes. The siltstone appears to be effectively grain-supported in the light laminae, but less so in

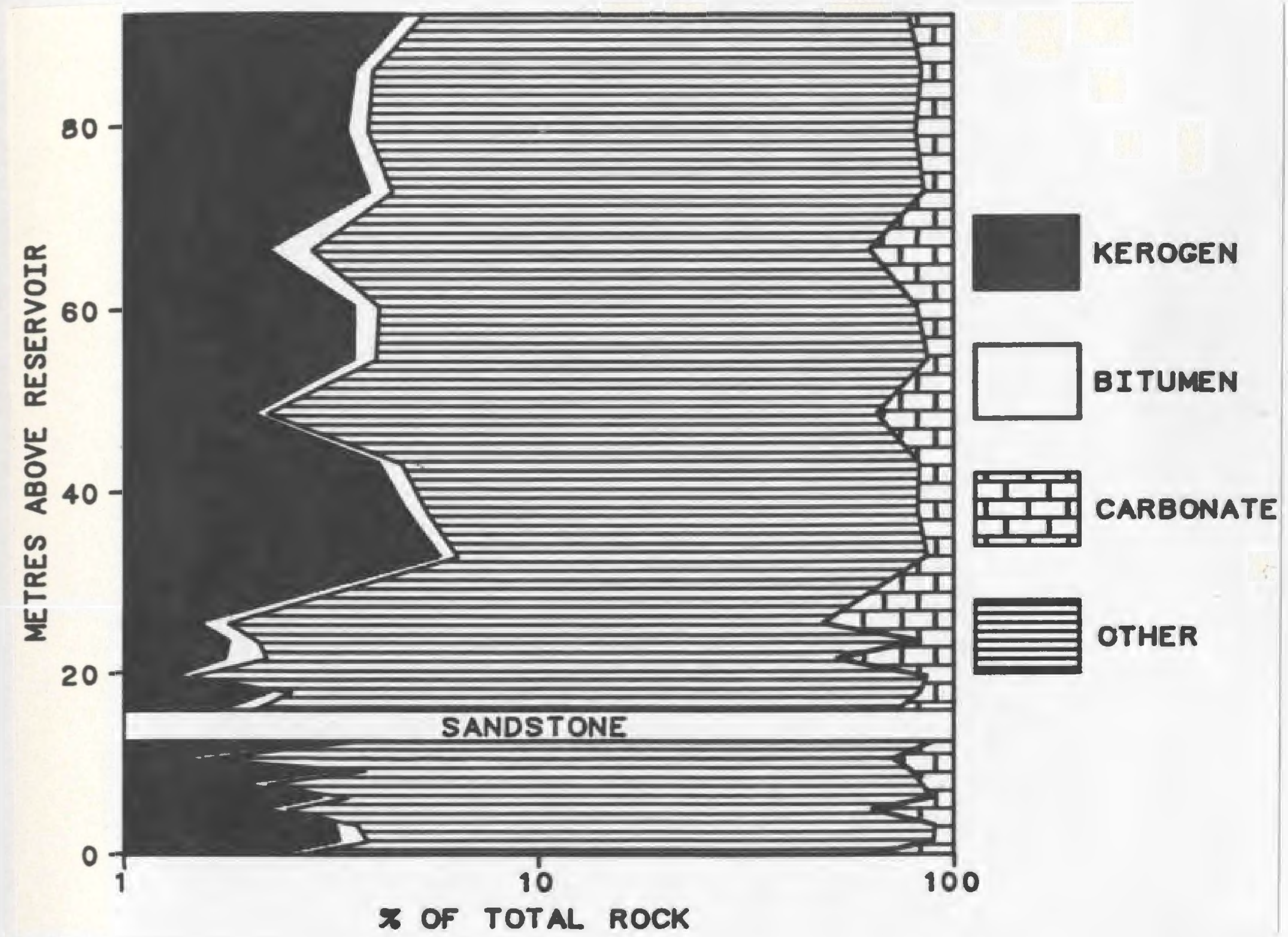


Figure 4-3: Lithological breakdown of section

organic-rich layers which may thus be subject to overburden stress, favoring oil expulsion. Kerogen continuity appears good horizontally, but the presence of vertical connections to form a three-dimensional kerogen network capable of conducting migrating oil is less evident. A definite lack of silt grain-support is shown in the darkest laminations in Fig. 4-5. Vertical kerogen connections through the light laminae are more evident than in the previous example. A siltstone of slightly coarser grainsize and weaker lamination than the previous two is shown in Fig. 4-6. Less horizontal kerogen continuity appears than higher in the core, and vertical continuity questionable. Carbonate makes up 51.5%, probably less in the section viewed, effectively cementing the lighter colored portions of the slide. Because of this, rigid-matrix grain-support is probably higher than in the previous example, but may be more susceptible to pressure solution. The fossil, a

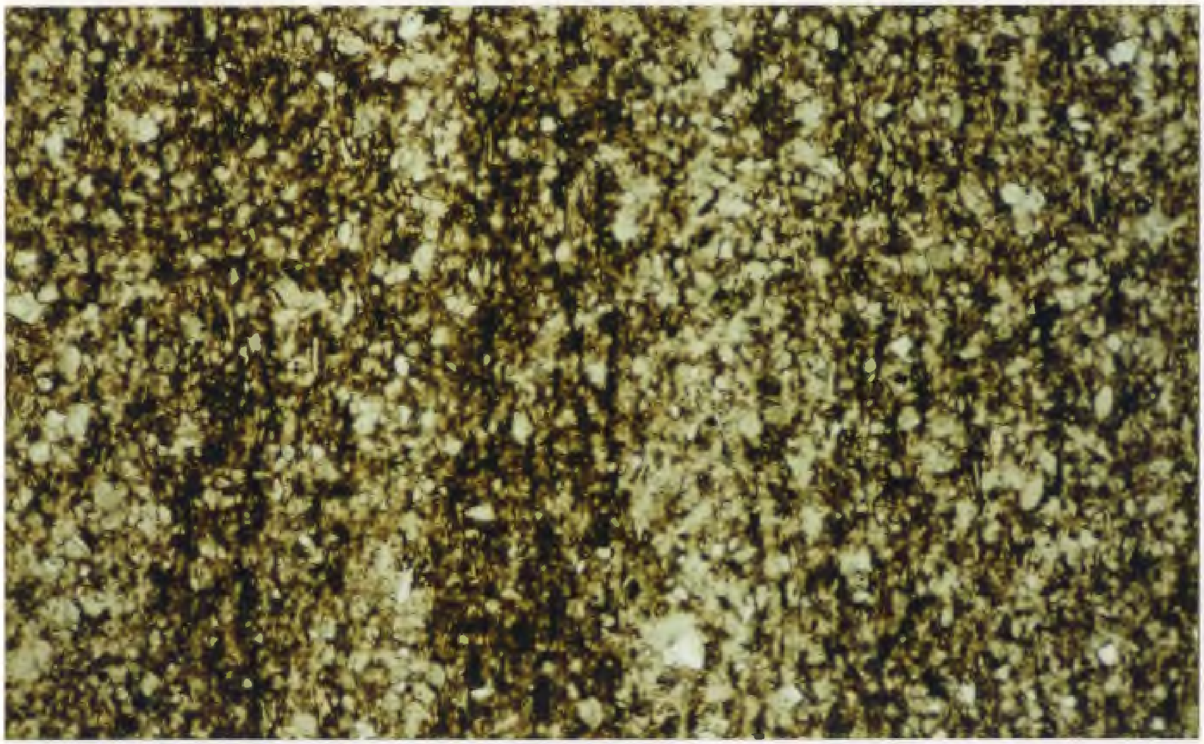


Figure 4-4: Laminated siltstone, 43.1m (x30)

fish bone, is pelagic. The lowest 12m of core were found to contain angular sandstone clasts, mostly larger than the granules shown in Fig. 4-7. The sandstone is very fine grained, organic-lean, and pyritic, possibly due to redeposition in a reducing environment. It is likely tightly cemented, since larger such clasts are angular and hard. Sand content of the siltstone matrix is no higher than previous examples and matrix is non-laminated. This is consistent with transportation of the clasts into a low energy environment. Non-laminated siltstones in the lower 25m of the core were frequently lean in TOC, but where rich as in Fig. 4-8 (3.02%), grain support appears to be only partial and a three-dimensional kerogen network may be present. These conditions should be ideal for oil migration along kerogen. The non-segregated nature of the organic matter may have helped restrict development of secondary carbonate cement by reducing permeability.

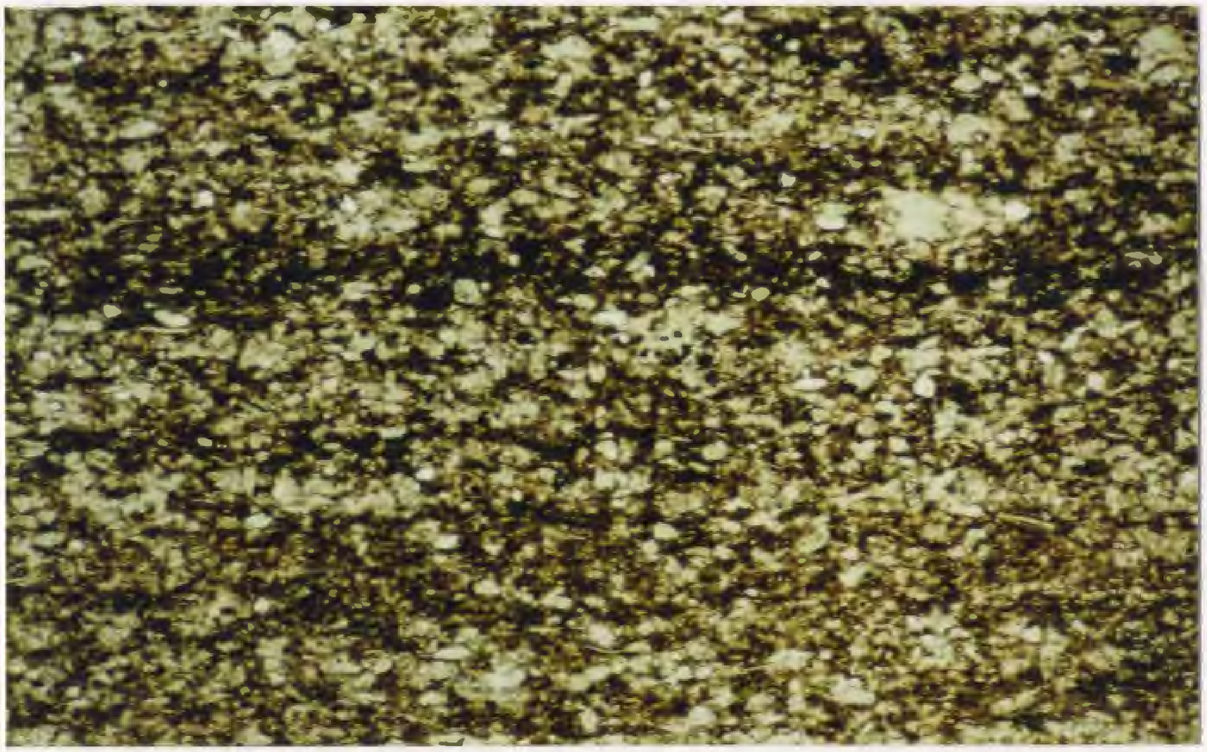


Figure 4-5: Laminated siltstone, 43.1m (x30)

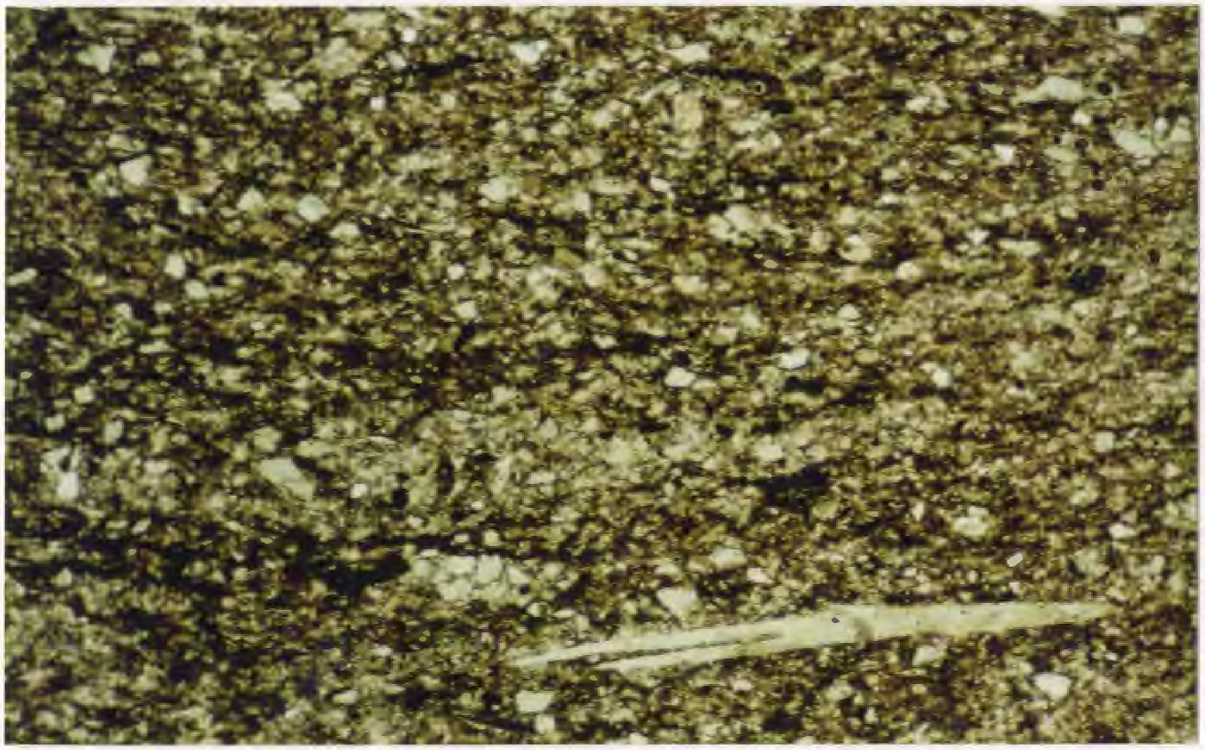


Figure 4-6: Weakly laminated siltstone, 25.5m (x30)

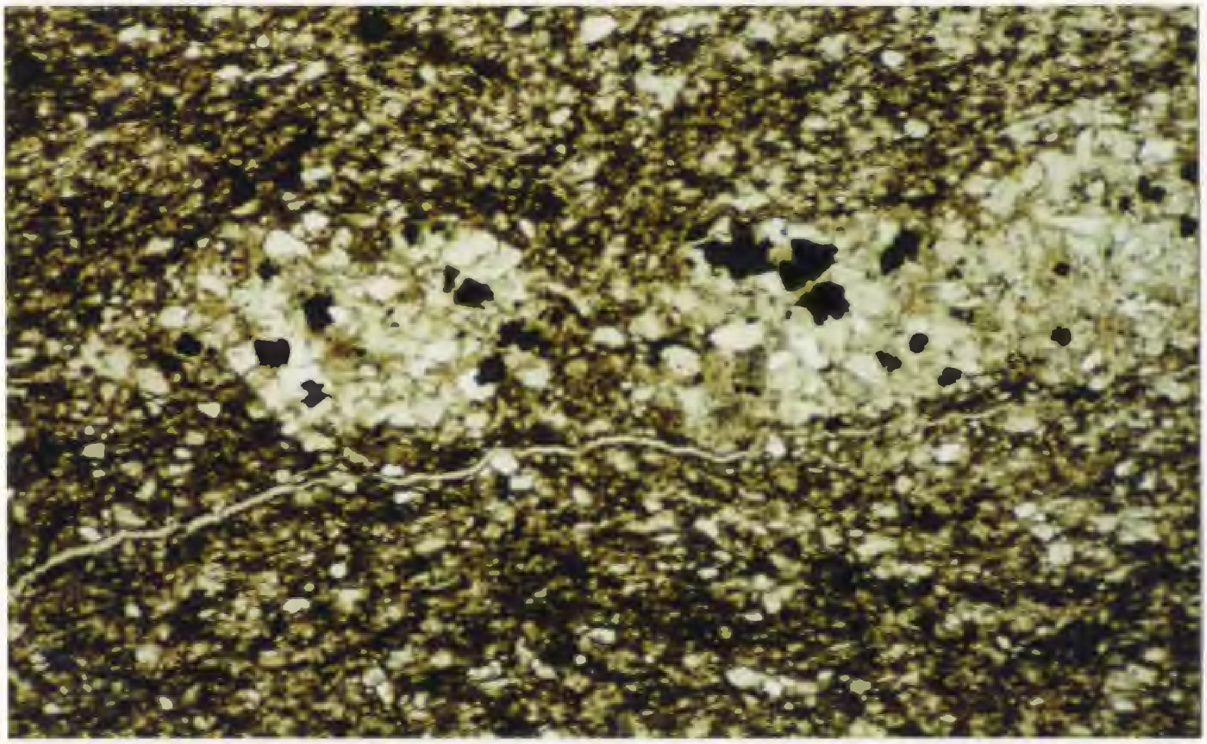


Figure 4-7: Siltstone with sandstone clasts, 7.7m (x30)

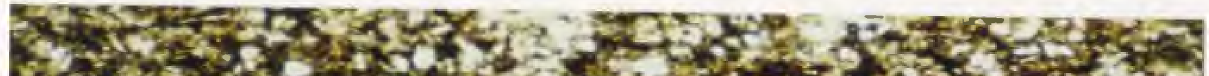


Figure 4-8: Massive siltstone, 3.2m (x30)

Chapter 5
SOURCE ROCK BITUMENS

5.1. Analysis by compound type

5.1.1. Allocation of losses

Separation of bitumens by compound type was carried out by asphaltene precipitation and liquid chromatography as described in the chapter 'ANALYTICAL PROCEDURES'. Weighing of bitumens at intermediate steps allowed for the evaluation of losses, which were corrected for in the results as outlined below.

Sample loss on asphaltene removal (Initial Bitumen - (Asphaltenes + Asphalt-free Bitumen)) ranged from 2.7 to 13.8% of initial bitumen, averaging 7.5%. Such losses were not likely the result of filtration of asphaltenes, the asphaltenes adhering well to the filter and not at all to the glassware. The most likely source of sample loss of this magnitude was felt to be volatiles removal under vacuum from the asphaltene-free bitumens, these having been dried only once previously. Accordingly, amounts recorded are based on recovered weights only.

Sample loss during liquid chromatography (asphalt-free bitumen - recovered fractions) ranged up to 9.3%, averaging 3.4% of the asphalt-free bitumen. This is likely a combination of evaporation loss and retention of polar resins on the alumina. The former was expected to be much less than in the previous step, being the third drying operation, and resins could readily be observed on the alumina after final elution, so these smaller losses were allocated to the resin fraction.

Finally, a procedure blank initially run through the solvent extraction, asphaltene removal, and liquid chromatography steps was found to weigh 0.9mg, probably leached from the filter papers employed after extraction, and this was subtracted on a compound-type basis from all the shale bitumens (but not the reservoir oil). This data is tabulated in Appendix B, Table B-2.

The sample from the lowest shale contact (0.0m) was partially lost before asphaltene removal. Proportions of the compound types were determined as above for the remaining sample, and the original bitumen weight was estimated from organic carbon loss on extraction. Also, the weight of asphalt-free bitumen was not determined for the sample from 1.4m, and an average 3.4% resin loss on the column was assumed. This introduced negligible error.

5.1.2. Reproducibility

As outlined under 'Precipitation of Asphaltenes', page 51, a readily available crude oil was used for asphalt precipitation trials. Asphaltenes were precipitated using a range of solvent ratios from 10 to 50 ml solvent/ml dried oil and standard deviation for percent asphaltenes was 0.17% (or 4.7% of the mean). Since a constant solvent ratio was used for samples in this study, the above figure should be regarded as a maximum and the reproducibility of percent asphaltenes in this study will be somewhat better.

The same crude oil samples, when asphalt-free, were fractionated by an identical method as used for the other samples. Standard deviations were for saturates: 1.95% (3.8% of mean); for aromatics: 1.61% (5.3% of mean); and for resins: 0.66% (4.4% of mean). Reproducibilities should be similar for the fractions in this study, the effect on other fractions of the variable asphaltene removal in the trials being negligible.

5.1.3. Bitumen profiles

Using the results of compound-type analysis presented in Table B-4, bitumen composition in units of ppm dry rock is plotted against depth in Figure 5-1. Wide variation can be seen between samples from differing depths, but in general the lower portion of the core, below 30 m from the reservoir, contains less bitumen, as would be expected if primary migration into the thin sandstone and the underlying reservoir resulted in significant depletion. However, TOC content also decreases below this point, and a plot of bitumen composition in units of mg/gTOC against depth, Figure 5-2, shows much less variation between samples and no large apparent depletion zone. Although apparent depletion may be present immediately below the thin sandstone or immediately above the reservoir, the lowest sample has had total bitumen weight estimated from carbon loss data, and is thus much less reliable in terms of total quantity than the others. Slightly higher values are generally found for samples below 30m, possibly part of an inverse trend of increasing hydrocarbon/ TOC with decreasing TOC, noted by Jones(1984).

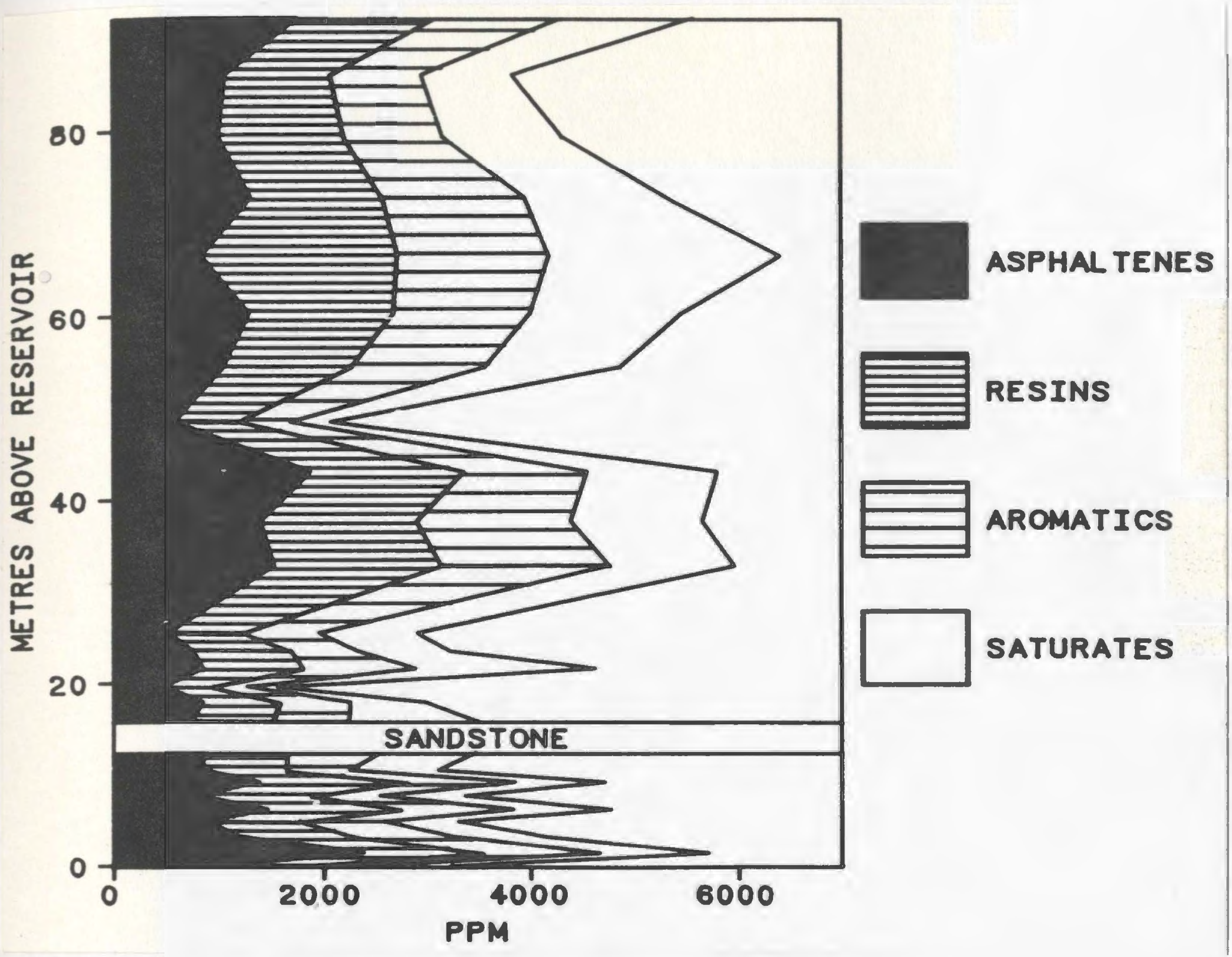


Figure 5-1: Rock-normalized bitumen profile

5.2. Analysis by gas chromatography

Gas chromatographic analysis was carried out on all saturate and aromatic fractions, and chromatograms are included in Appendix C.

5.2.1. Quantification

Quantification was done by using peak areas calibrated versus a solution containing 4 external standard compounds (nC_{16}, Pristane, nC_{24}, & nC_{30} for saturates; Fluorene, 1-methyl Phenanthrene, 2,3 Benzofluorene, & Coronene for aromatics). Peak identification was done using the above standard compounds together with comparison of relative retention times from the literature e.g. Palmer (1984). All n-alkane and isoprenoid abundances are normalized to the total of nC_{15} to nC_{35} n-alkanes and plots of the resulting distributions are shown with the respective gas chromatograms in Appendix C.

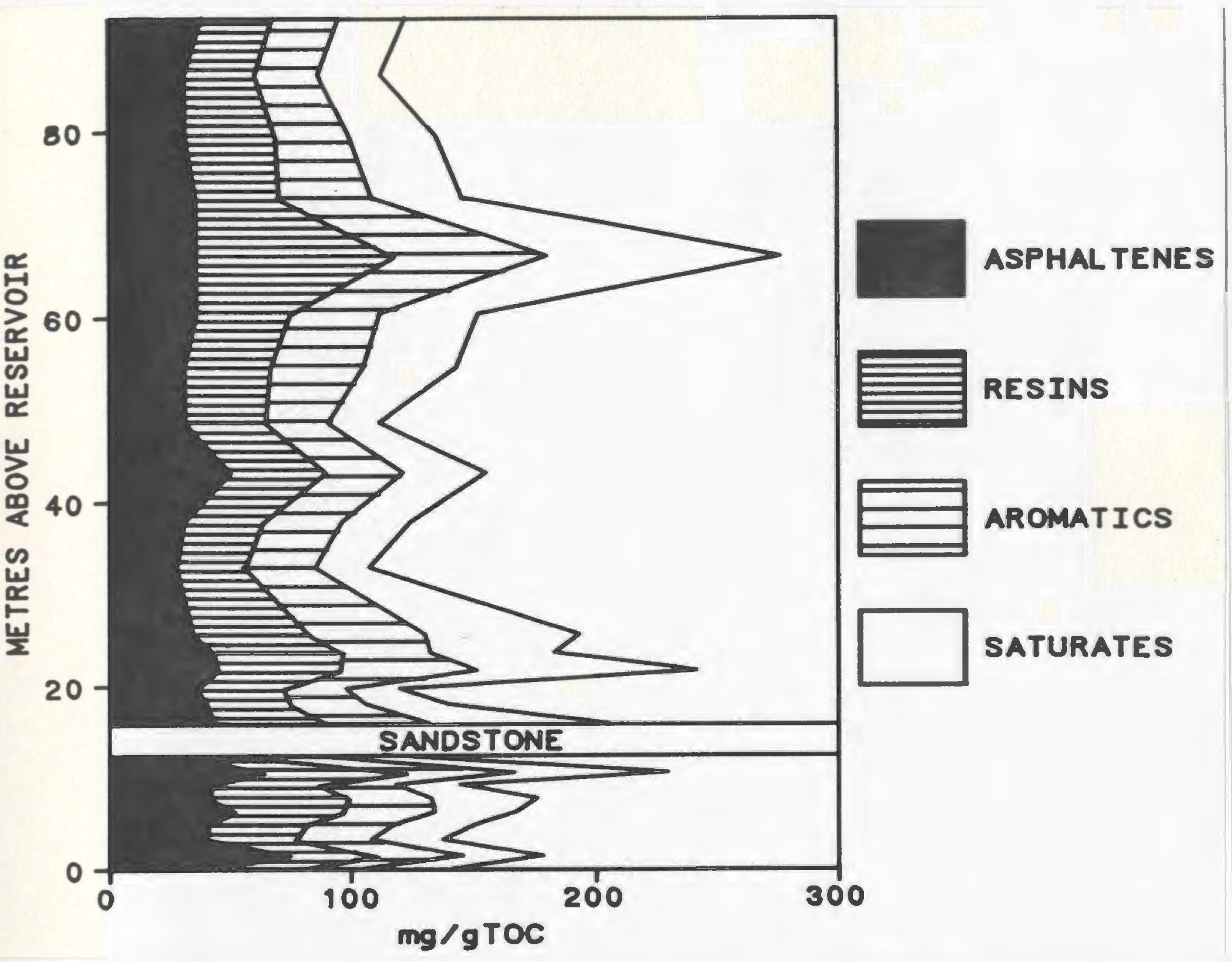


Figure 5-2: Carbon-normalized bitumen profile

For calculation of methylphenanthrene indices from the aromatic fractions, integration was carried out between major valleys on the chromatograms, and sensitivities were assumed equal for phenanthrene and methyl phenanthrenes.

5.3. Analysis by mass spectrometry

Eight saturate and eight aromatic fractions from the same depths were analysed by mass spectrometry for compound class breakdown. Results are tabulated for samples from 66.4m, 25.5m, 17.9m, 15.8m, 12.4m, 10.5m, 0.0m, and the reservoir oil in Appendix B, (Table B-8 for saturates and Table B-9 for aromatics). Breakdown by compound classes is plotted for saturate and aromatic fractions from the above depths with their respective gas chromatograms in Appendix C.

The standard matrices and computer program used for data processing raw mass spectra from this study (ASTM 2786-81, and 3239-81 respectively) were developed for a CEC

21-103 mass spectrometer and the fact that spectra herein were obtained with an HP mass selective detector may introduce errors in the resulting compound type abundances. If so, these errors will likely be greater for saturates fractions because their abundances are calculated from fragment ions rather than parent and M-1 ions as for the aromatics. Differences in fragmentation due to mass spectrometer type will have less effect on the more stable aromatics.

5.4. Detection of contamination

Gas chromatograms for both saturate and aromatic fractions of the procedure blank (Appendix C, pages 160 and 189) indicate barely detectable contamination, in the aromatic fraction only as expected from fraction weights, and quantifiable and identifiable contamination in neither. Contamination in hydrocarbon fractions can thus be expected from:

- diesel oil from drilling mud introduced into samples during coring
- cross-contamination between fractions

5.4.1. Diesel contamination

Although an attempt was made to eliminate diesel-contaminated rock before solvent extraction (Appendix A), its effectiveness could not be verified for all samples, particularly those lacking exposed core edges. However, knowing some chemical characteristics of diesel oil such as:

- very low to zero resin + asphaltene content
- predominance of C_{14} to C_{18} molecules, and
- abundance of normal alkanes (Appendix A),

gas chromatographic analysis of the hydrocarbon fractions aided in the identification of those samples with potential diesel contamination. Contamination by straight-run diesel oil, whose saturate fraction chromatogram is broadly similar to those of bitumens, should result in increased 'unresolved mixture' and alkane peak heights in the C_{14} to C_{18} range. Ratios of isoprenoids to n-alkanes of similar boiling point will change only if such ratios differ between the bitumens and the diesel used.

Although the actual amount of unresolved mixture ('humptane') shown on the chromatograms varies with amount injected and attenuation setting, source rock bitumens (but not reservoir oil) from this study generally show a bimodal distribution: the first from approximately nC_{12} to nC_{24}, well illustrated in the chromatogram from 0.0m and another from nC_{26} to nC_{31} possibly consisting of abundant steranes and triterpanes characteristic of bitumens of less than peak oil generating maturity. This second hump, best illustrated in the chromatogram from 12.4m , is beyond the range of possible diesel contamination and thus the relative proportions of the 2 humps can be used as a diesel indicator. Although subjective, visual inspection shows significant enhancement of the first hump in samples from 60.2m, 43.1m, 23.5m, 21.6m, 15.8m, and 0.0m.

Diesel contamination should be made evident in aromatic fractions by an enrichment of all aromatics in its boiling range, corresponding roughly to oven temperatures of 80 to 200°C on the chromatograms where, unlike saturates, carbon numbers cannot be clearly delineated. Such enrichment can be seen, as above, in bitumens from 60.2m, 43.1m, 23.5m, 21.6m, 15.8m, and 0.0m, best typified by the chromatogram from 0.0m and less pronounced at 15.8m. As for the saturate fractions, such evidence is subjective with perhaps some other bitumens being less clear cut.

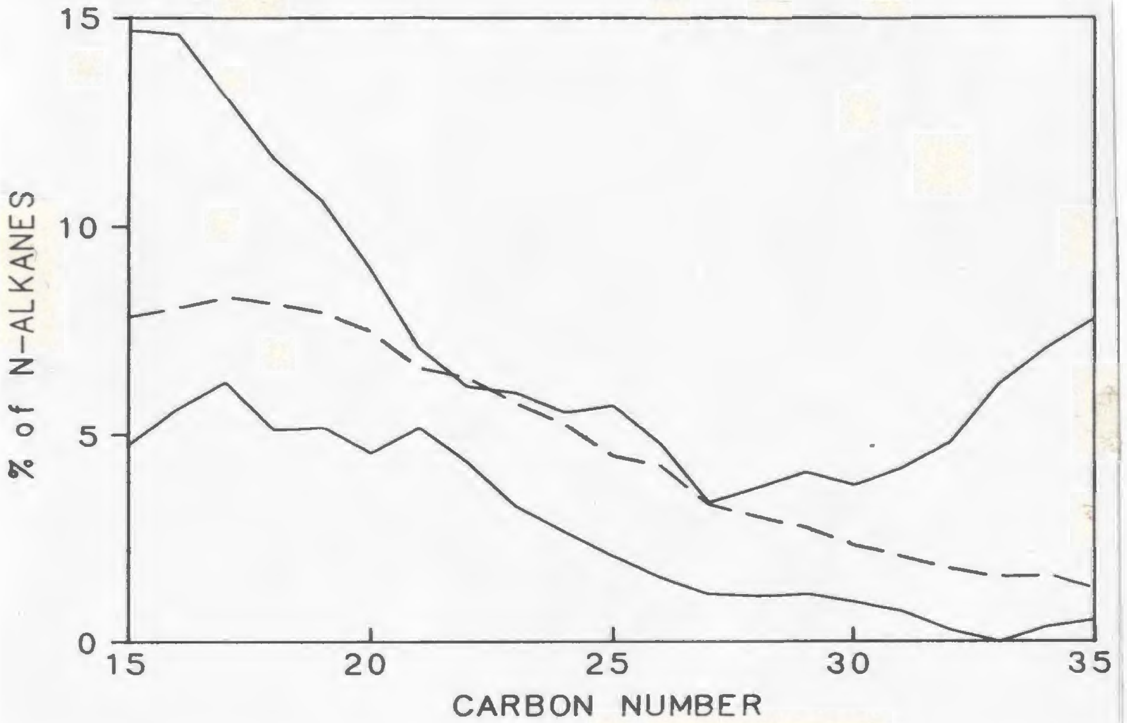


Figure 5-3: Composite n-alkane envelope - all bitumens (dashed line is reservoir oil)

As well as 'humptane', contaminated saturate fractions should be enriched in n-alkanes in the diesel range. Figure 5-3 shows a composite 'envelope' of all bitumen n-alkane distributions, plotted as maximum and minimum values for each carbon number, with the actual reservoir oil for comparison. Since all curves must delimit an area of 100%, deviations to higher values at low carbon numbers possibly due to diesel contamination will be compensated for by lower values at high carbon numbers, thus limiting separation of individual curves. However, if all curves are normalized to a constant value for a normal alkane beyond the diesel range, any diesel contamination should be clearly shown by a departure of the curve in question to markedly higher values at low carbon numbers. All bitumen n-alkane distribution curves are shown normalized to nC_{30} in Figure 5-4 and

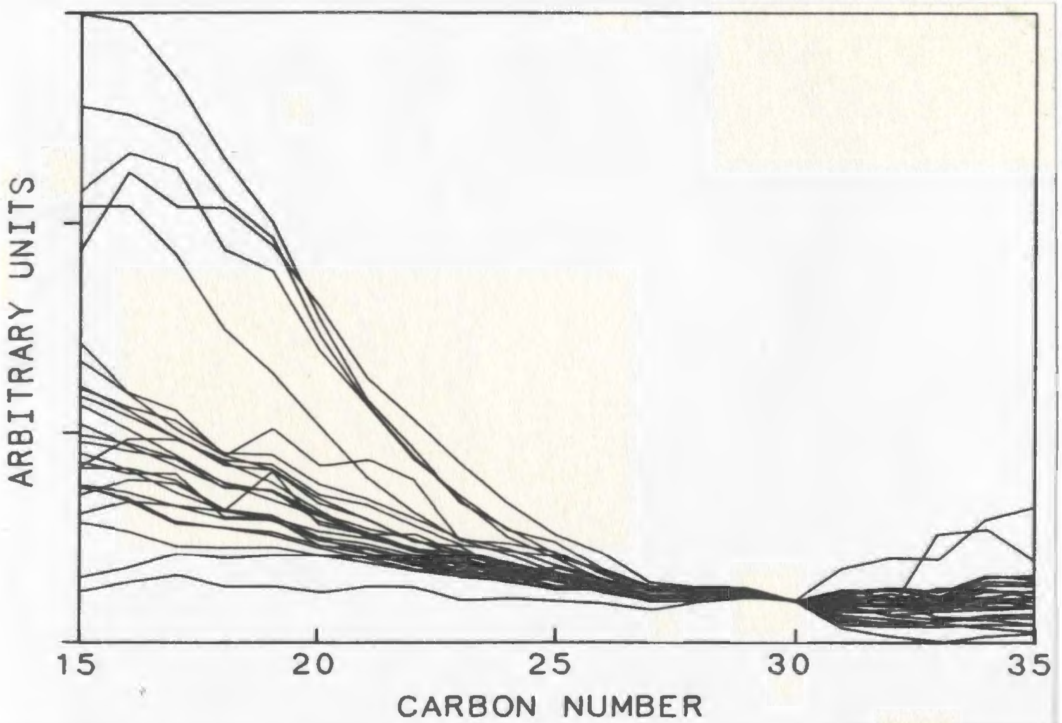


Figure 5-4: nC_{30}-normalized n-alkane distributions

it can be seen that 5 of the curves are cleanly separated from the others in the diesel molecular weight range. In addition these 5 curves are clustered reasonably closely suggesting that contamination has been of a similar extent in these bitumens or that it has been sufficient to mask original differences in the alkane distributions. Figure 5-5 shows the alkane distribution envelope of these 5 bitumens. They can be seen to occupy a narrow range and form a distinct mismatch-match to the reservoir oil. The 5 bitumens are from 60.2m, 43.1m, 23.5m, 21.6m, and 0.0m, all samples suspected as being contaminated from the previous chromatogram inspections. The sample from 15.8m did not demonstrate an anomalous n-alkane distribution. Using a similar approach, mass spectrometry data for individual fractions, when plotted as volume percent against compound class, can also be normalized to a compound class beyond the diesel range and used to detect contamination. This is shown for aromatic fractions in Figure 5-6, normalized to a constant volume percent of pentaaromatics. Although, in keeping with most crude oils and source rock bitumens, monoaromatics are the most abundant class in all samples analysed, one sample clearly stands above the rest in content of mono-, di-, and triaromatics when normalized, and this is from 0.0m, previously suspected of contamination from gas chromatogram inspection. The only other 'suspect' sample analysed by mass spectrometry, that from 15.8m, shows no apparent contamination on this plot.

For saturate fractions, normalization to constant 4 or 5 ring naphthene content showed no anomalous behaviour, with all curves grouped together. This could indicate no contamination, proportional contamination in all ring classes, or inaccurate mass spectrometry results, as suggested earlier.

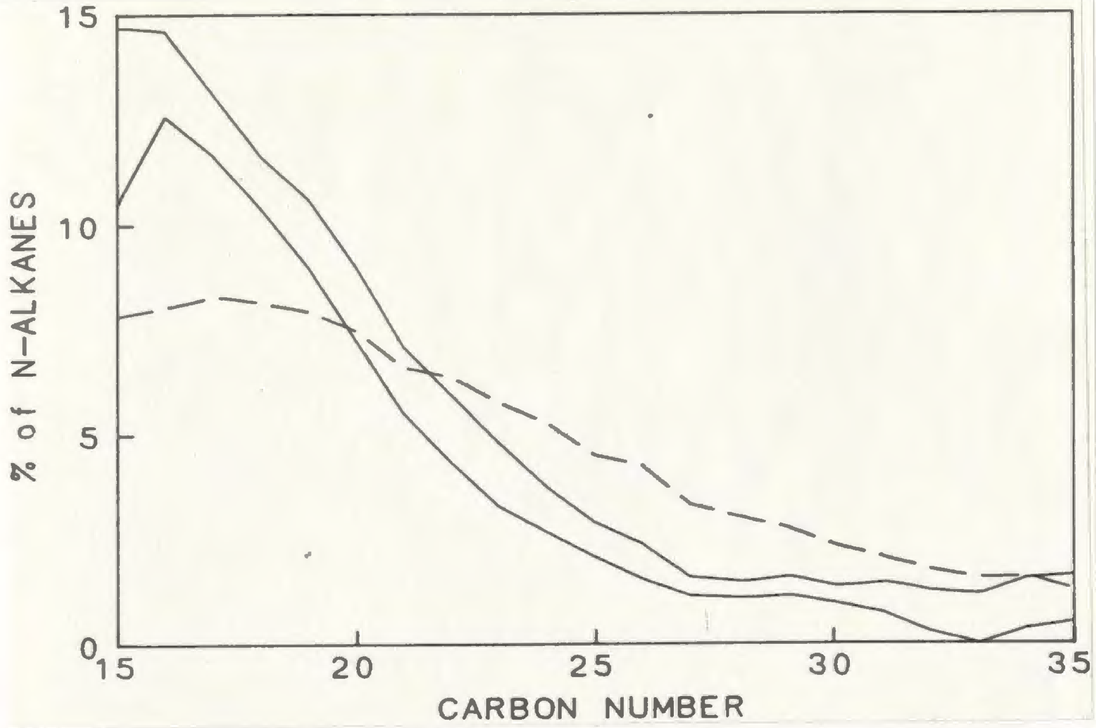


Figure 5-5: Composite n-alkane envelope - contaminated bitumens (dashed line is reservoir oil)

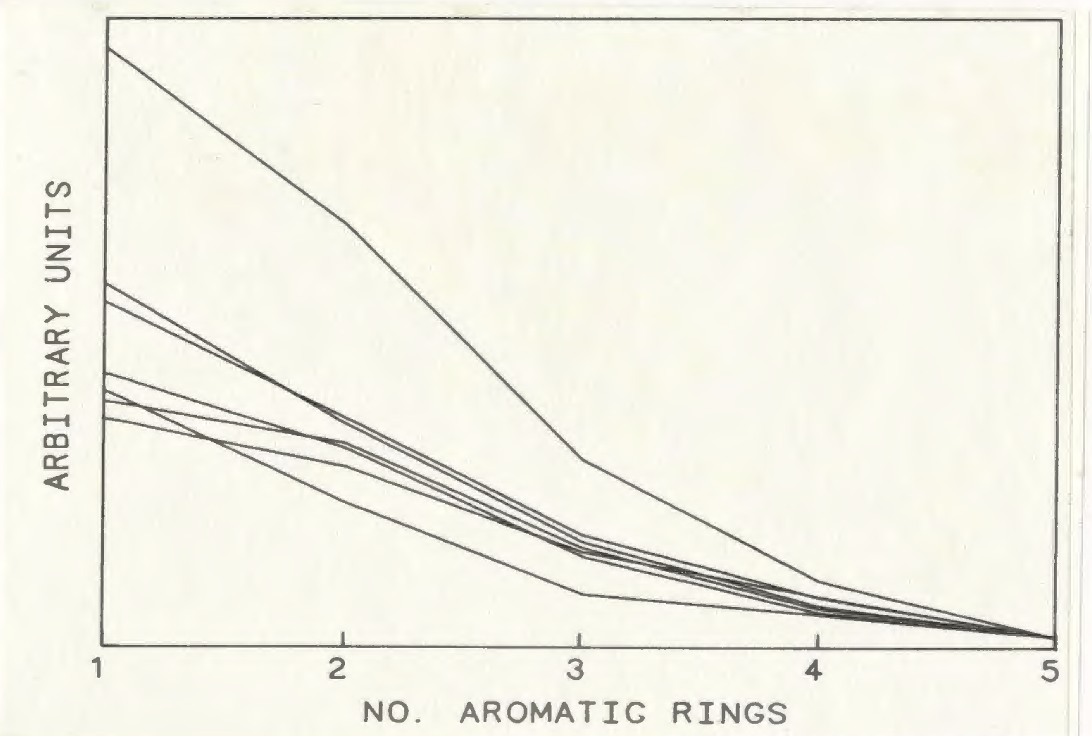


Figure 5-6: Pentaaromatic-normalized aromatic distributions

The shape of an individual n-alkane distribution curve can be quantified by the 'Quadratic Coefficient', QC. Quadratic Coefficients for this study were calculated for comparison with the correlations of Sofer(1984) in the chapter 'CARBON ISOTOPES' .

QC becomes higher for more concave up alkane distributions and this parameter thus also becomes useful for identifying contamination in bitumen saturate fractions, although choice of a cut-off value may not be clear cut.

In Appendix A, study of a core edge for diesel contamination revealed that invading diesel oil had lower Pr/nC_{17} and Ph/nC_{18} ratios than the shale bitumen. Greatest differences were seen in the Pr/nC_{17} ratio as expected, since these compounds are more abundant in diesel than those in the nC_{18} boiling range. This parameter, like the QC, is thus also potentially useful for identifying contamination, and choice of cut-off values for both can be aided by crossplotting. Figure 5-7 shows QC plotted against Pr/nC_{17} and contaminated bitumens (high QC, low Pr/nC_{17}) are clearly separated from the bulk of the others and plotted with the marker 'c' on this and subsequent plots. These 6 bitumens are from the depths previously determined from inspection of chromatograms and normalization of n-alkane distribution curves, the bitumen from 15.8m being somewhat transitional between the other contaminated and uncontaminated bitumens. Values of QC and Pr/nC_{17} ratio are tabulated in Appendix B, Table B-6, page 155.

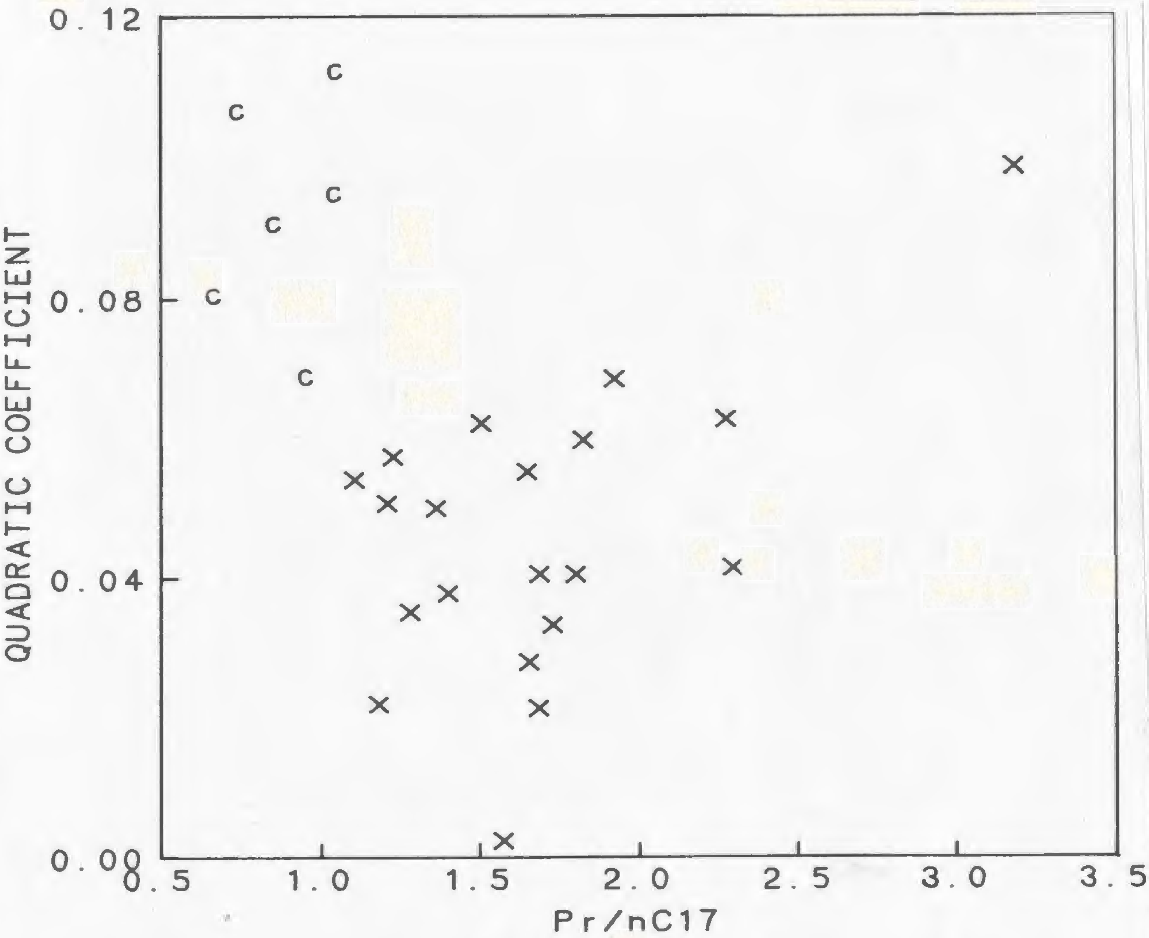


Figure 5-7: QC vs. Pr/nC_{17}

The consistency of the bitumens judged 'contaminated' using visual inspection of saturates and aromatics chromatograms, normalization of n-alkane and aromatics distributions, and the crossplot lends confidence to this interpretation, particularly the last 2 approaches which are objective and show a clean separation from 'uncontaminated' bitumens. The sample from 15.8m, not separable with n-alkane or aromatics distribution data, is adjacent to a sandstone contact as is that from 12.4m which shows extensive depletion. A combination, in the bitumen from 15.8m, of similar depletion followed by contamination may account for the final n-alkane and aromatics distributions being similar to uncontaminated bitumens.

5.4.2. Cross-contamination

Cross-contamination is herein used to refer to contamination between compound type fractions due to less than perfect separation procedures. Separations between resins and asphaltenes, and between aromatics and resins were not verified after the liquid chromatography step, reliance for the latter being placed on the total separation of the standard compounds employed. Aromatics of high aromaticity constitute a diminishing proportion of total aromatics (Appendix B, Table B-9,), and loss of some of these to the resin fraction should change the relative proportions very little. The separation between saturates and aromatics however is vulnerable to considerable error.

Inspection of gas chromatograms of aromatic fractions (Appendix C) reveals that many contain heavy n-alkanes at the maximum temperature end of the chromatogram, identifiable by their even spacing and individual retention times. Assuming a constant quantity of fraction injected, accurate but not precise, estimates can be made. Because external standards in this molecular weight range were not employed for the aromatic fractions, an average sensitivity (mg/unit peak area) for nC_{30} in the saturate fraction calibration runs was used. Results, tabulated in AENDIX B, Table B-6, vary from 0.07 to 1.84% of the aromatic fraction, averaging 0.61%.

No such n-alkanes were present in the aromatic fraction of the procedure blank and their source appears clearly to be holdover from the elution of saturates during liquid chromatography. Bitumens with large amounts of heavy n-alkanes in the aromatic fraction are also those with truncated n-alkane distributions in the saturate fraction, the lightest in the aromatic fraction corresponding well with the heaviest in the saturate fraction. This is best illustrated by referring to the chromatograms of saturate and aromatic fractions of bitumens from 19.6m and 85.9m. The cause of this holdover is not clear, but appears to be related to the quantity of asphalt-free bitumen separated during liquid chromatography. Figure 5-8 is a plot of n-alkanes in the aromatic fraction against liquid chromatography sample size and a clear inverse relation can be observed. Such a relation would be expected from external contamination, smaller samples being relatively more contaminated, but calculation of absolute amounts of n-alkane contaminants shows

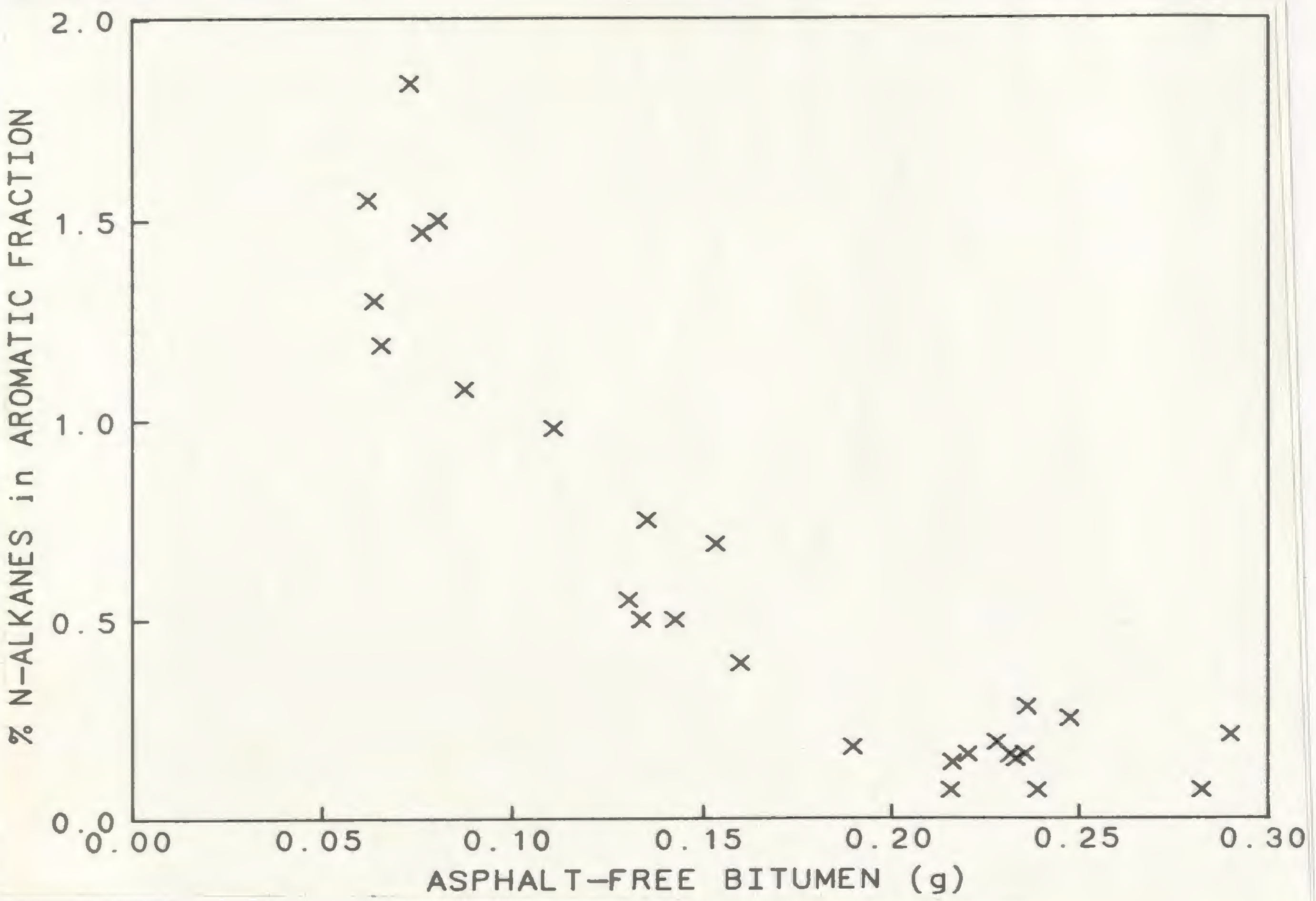


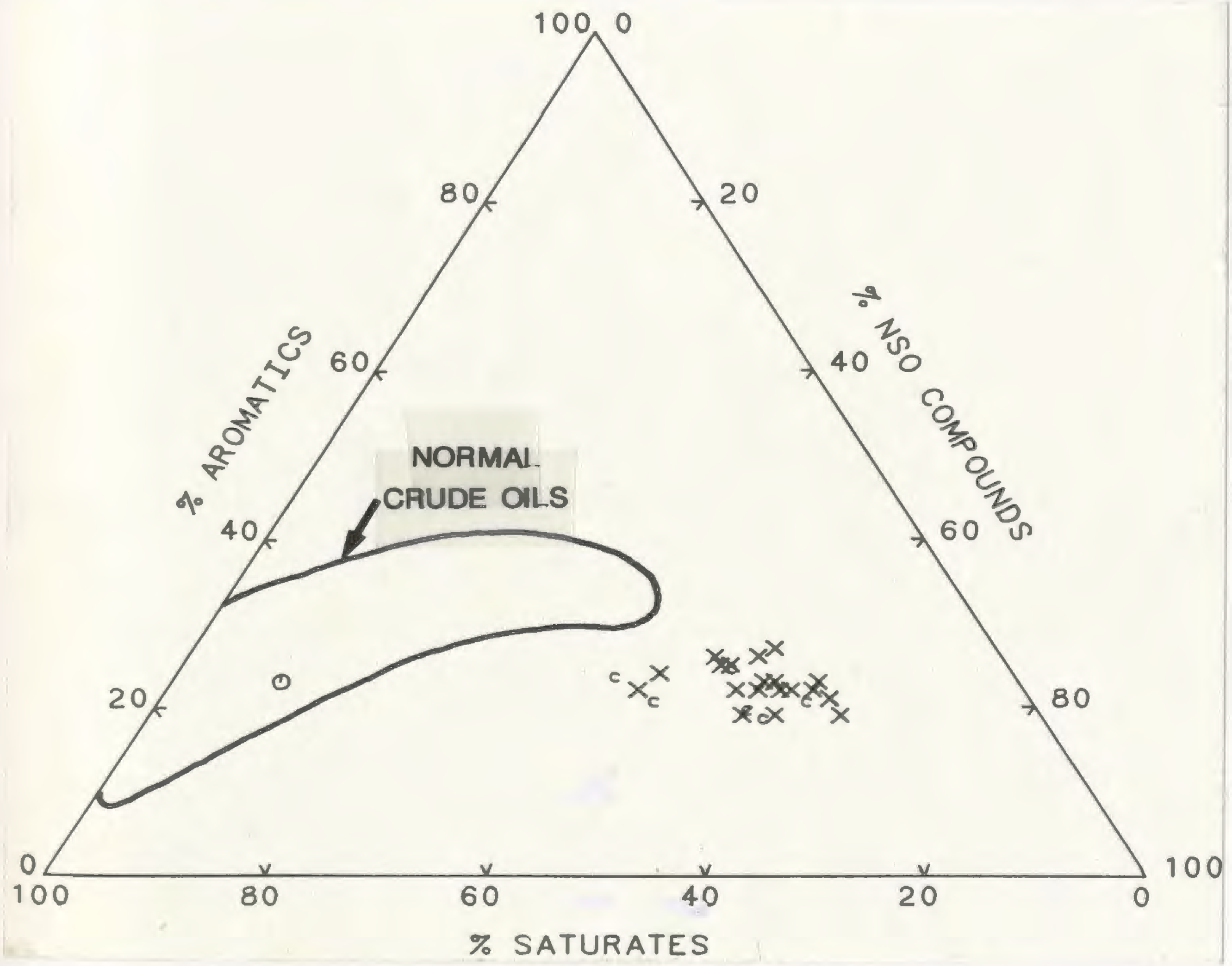
Figure 5-8: Cross-contamination vs. column feed

the same rise with decreasing sample size. In addition, contamination cannot account for the good correspondence between heaviest alkanes in saturates and lightest in aromatics. Intuitively, one would expect larger samples with larger saturate fractions to take longer to elute and thus show greater holdover, particularly crude oils with a much higher percent saturates than the shale bitumens. The opposite, however, is the case and trial analyses (for reproducibility) of a crude oil external to this study showed no n-alkanes in 6 aromatic fractions despite column feeds of 0.28 to 0.36g. Obviously column overload was not contributing to the problem. The cause of this cross-contamination of smaller samples is not clear, but the obvious remedy is to use an appropriately smaller column size for smaller samples. Reports of similar cross-contamination are scarce in the literature, but Tissot *et al.*(1977) report $nC_{40}+$ n-alkanes eluting with resins during normal column chromatography, and Radke *et al.*(1980) suggest that long chain alkanes tend to remain on alumina. Final gas chromatograph oven temperatures reached in this study were higher than most, and the phenomenon may be more general, similar effects beyond nC_{30} having gone undetected (or unreported) in other work.

Monoaromatics content in saturate fractions was measured by mass spectrometric analysis and ranged from 1.4 to 4.6 volume percent (Appendix B, Table B-8 . These amounts show no relationship to sample size or to saturates contamination in the aromatic fraction and are all below the 5% level considered maximum for acceptable mass spectrometric results (ASTM 2786). The fact that these are higher than the saturates contamination in aromatic fractions would seem to indicate a poor choice of endpoint in the column chromatography procedure, but the estimated saturates-in-aromatics contamination is for n-alkanes only, thus a minimum. Other questions surrounding the mass spectrometry of saturate fractions, discussed later, may mean that these monoaromatics percentages in saturates fractions are inaccurate.

5.5. Source rock quality

5.5.1. Overall composition



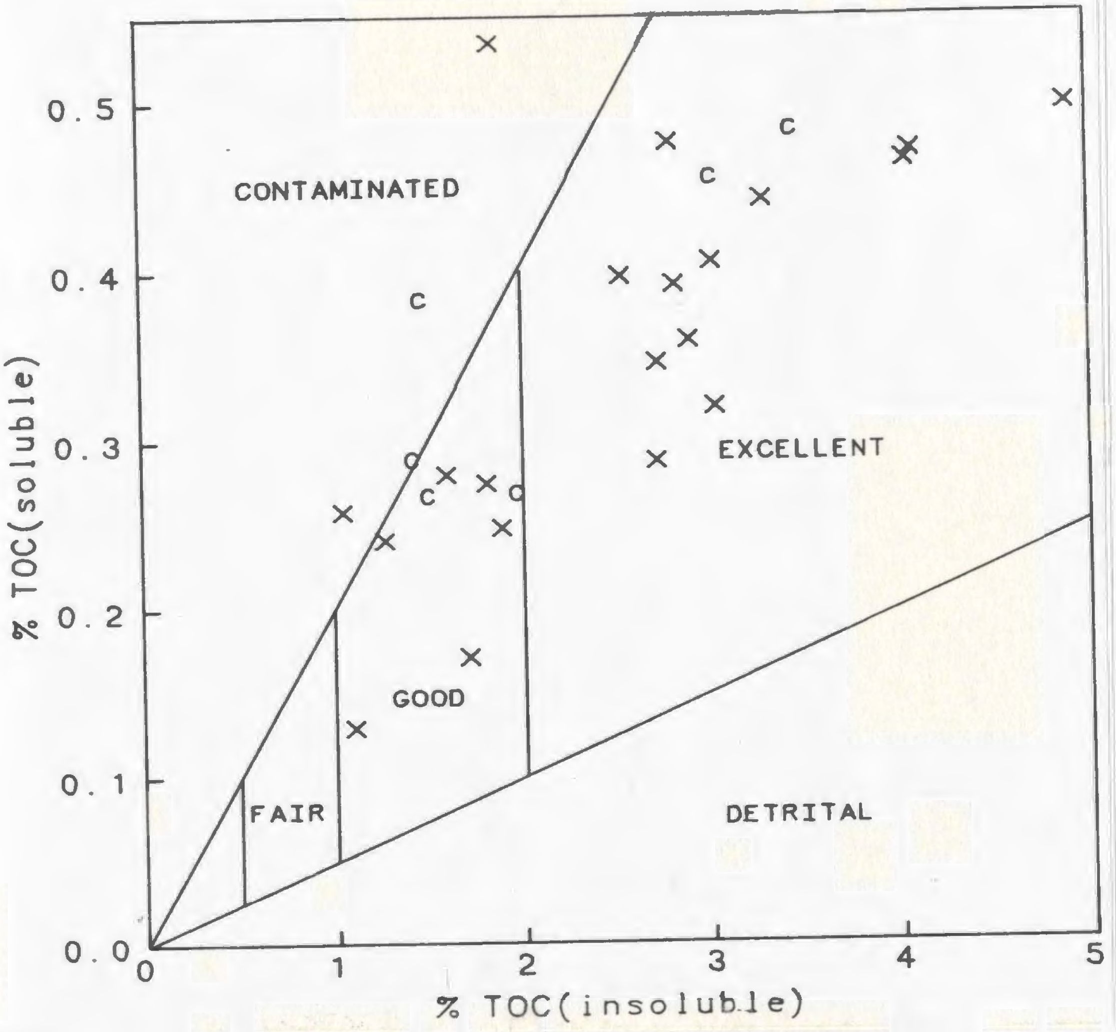
(x=clean bitumen,c=contaminated bitumen,o=reservoir oil)

Figure 5-9: Bitumen composition by compound type

Determination of composition by compound type allows plotting of bitumens and crude oil on a triangular diagram as introduced in the chapter 'INTRODUCTION'. This plot is shown in Figure 5-9, with the zone of 'Normal Crude Oils' roughly outlined after Tissot & Welte(1978). The reservoir crude oil from this study is thus not unusual. Bitumens plot as a fairly tight cluster in the zone of the triangle typical for source rock bitumens. Although diesel contaminated bitumens appear in general to be slightly more hydrocarbon-rich than average, they are by no means separable by such a diagram, meaning that either the amount of contamination is small as a percentage of total bitumen or that most of the other bitumens are contaminated more or less equally and have escaped detection. The clean separation of contaminated bitumens noted in the previous section makes the first alternative seem the more likely, in which case the separation based on n-alkanes and not evident on the triangular plot indicates that the percentage of n-alkanes in the bitumens is low, as also indicated by the mass spectrometry results (Appendix B, Table B-8).

Interestingly, the sample from 15.8m, thought in the previous section to be less contaminated than the 5 others and possibly suffering from the combined effects of depletion and contamination, plots as the contaminated sample second highest in % saturates. This makes the depletion + contamination situation appear more likely, whereby a higher degree of contamination (% Hydrocarbons, Pr/nC_{17}) can be tolerated without obvious effects on the alkane distribution (QC, nC_{30}-normalized distribution). Oudin (1976) has evaluated oil source rocks using a plot of soluble against insoluble organic carbon and this is shown for the present study in Figure 5-10. Soluble organic carbon was approximated by using the factor 1.2 explained previously and insoluble organic carbon was taken to mean TOC of extracted rock. Oudin (1976) considered rocks containing >200mg bitumen/gTOC (approximate maximum bitumen generation in Paris Basin type II kerogen) as contaminated and those with <57mg/g TOC (approximate onset of oil generation in Paris Basin type II kerogen) as detrital (type III organic matter). Between the above limits, source rocks are graded as fair, good, or excellent if exceeding insoluble organic carbon contents of 0.5%, 1%, or 2% respectively. No allowance is made for hydrocarbon content of bitumen.

Using this plot, samples rate as good to excellent source rocks, with 4 exceeding the contamination limit. Of the bitumens previously judged to be contaminated, 2 appear so on this diagram and the remaining 4 plot with the good and excellent source rocks. This method of source rock classification assumes source potential to be dependent on carbon-normalized bitumen content, not ppm, and that minimum TOC contents must be exceeded for varying degrees of oil expulsion performance. A disadvantage is that distinction is not made between hydrocarbons and heterocompounds in the bitumen, and rocks with high hydrocarbon content in their bitumens may be classified with those high in heterocompounds, most of which will not be incorporated in expelled oil. Also choice of extraction solvent, affecting the hydrocarbon/heterocompound ratio (Ferguson, 1962) will affect such a plot. Hunt(1979) has classified source rocks by plotting hydrocarbon

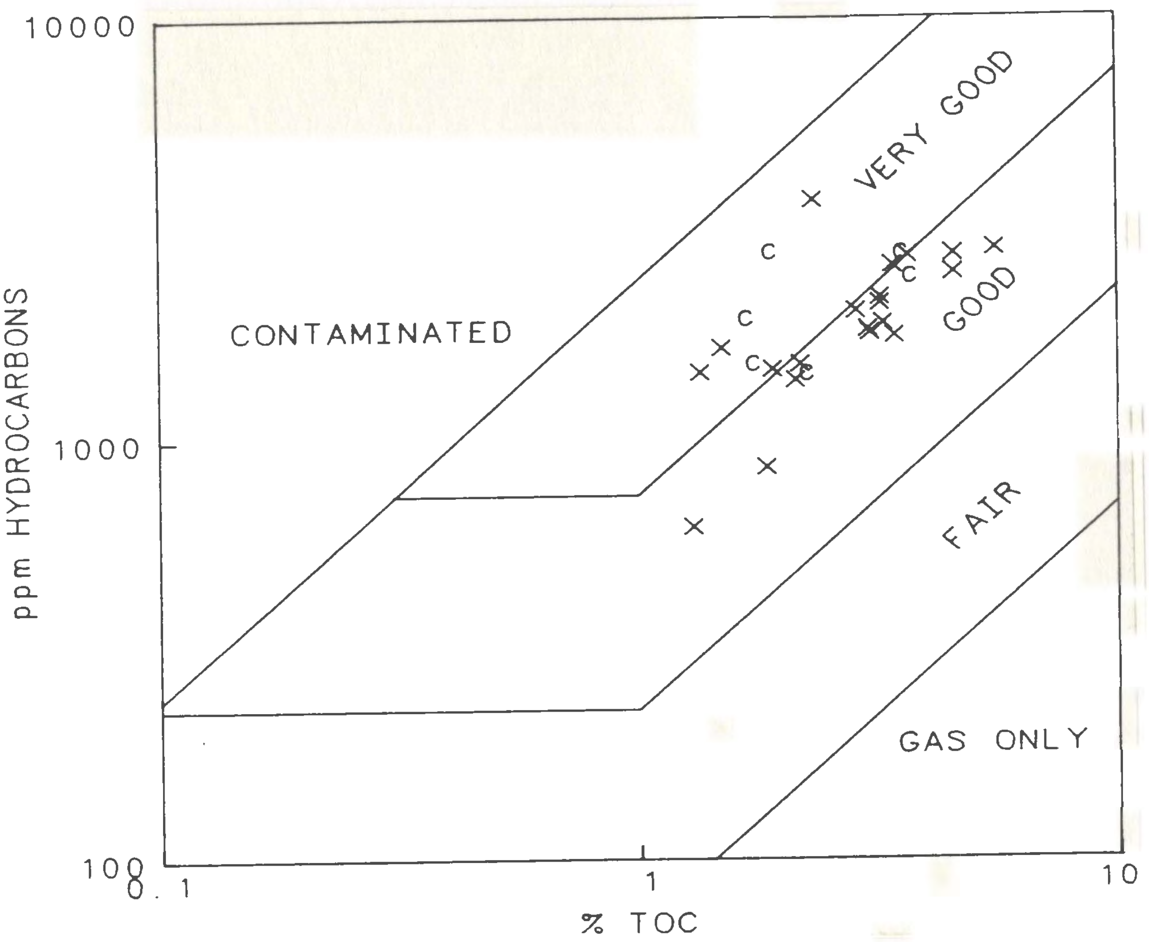


(x=clean bitumen;c=contaminated bitumen)

Figure 5-10: Soluble vs. insoluble organic carbon

content (ppm) against TOC on logarithmic scales. Rocks are classified as contaminated if above 240 mg HC/gTOC, and as non-source rocks if containing less than 7 mg HC/gTOC, or less than 70 ppm hydrocarbons. Reasons for this choice of limits are not given. Variations on this diagram appear in the literature which incorporate lower contamination thresholds and threefold division into fair, good, and very good categories (Landais, 1980; Leenheer, 1984) based on geometrically intermediate values of mgHC/gTOC. Data from this study are shown plotted in this manner in Figure 5-11.

On this plot, all bitumens are classified as good to very good, and none exceed or closely approach the contamination threshold. Neither do any of the potential source rocks shown by Hunt(1979) except organically very lean carbonates, which may have acted as local reservoirs, and this appears to be the reason for the lower thresholds preferred by other authors. Hydrocarbons, expressed as mg/gTOC, only slightly exceed 150 at peak generation for the classic Uinta Basin type I kerogens (Tissot & Welte, 1978).

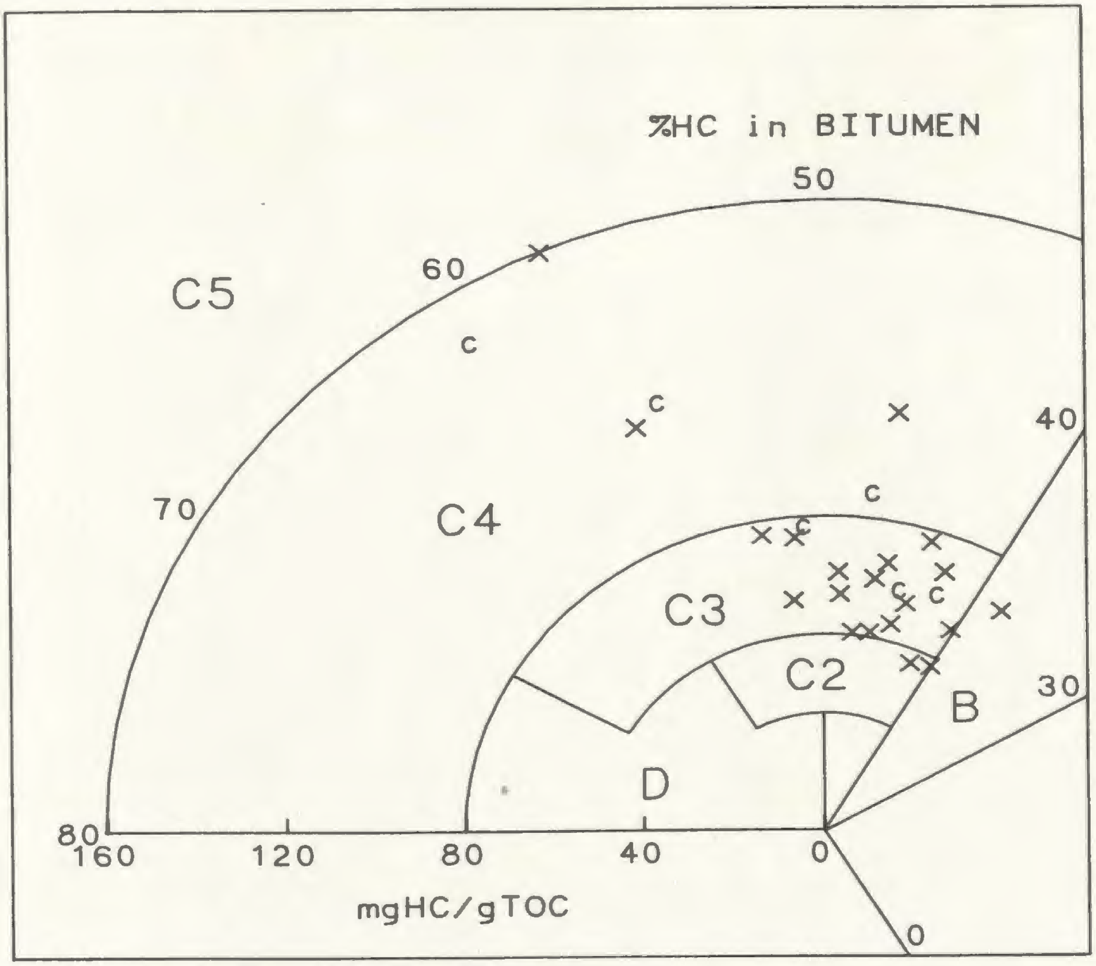


(x=clean bitumen;c=contaminated bitumen)

Figure 5-11: ppm Hydrocarbons vs. TOC

A classification such as this implies dependence of source quality on carbon-normalized hydrocarbons only, with no dependence on, or minimum value of, TOC. The minimum value of 70 ppm for source potential (or higher values for fair-good-very good subdivisions) appears to reflect that a certain minimum saturation in the rock is believed necessary for expulsion. Rocks with a high content of heterocompounds or those extracted with a variety of solvents will not be misleadingly interpreted on such a diagram. Hydrocarbon yield in mg/g TOC plotted against % of hydrocarbons in bitumens has been used to evaluate oil source rocks by Powell(1978). Such a plot, shown in Figure 5-12 with data from the present study, is done with polar coordinates using R=mg HC/g TOC and Θ=%HC in bitumen. Although the latter will be affected by solvent type, the diagram has been intended for use with benzene-methanol or $CHCl_3$-methanol solvent mixtures, so should be applicable to the present study.

Using this classification, bitumens are classed as marginally mature (B) if between 30 and 40% hydrocarbon, and mature to overmature for higher values. Source potential at peak and pre-peak maturity is rated as minor (C2) from 30 to 50 mgHC/g TOC, based on a maximum yield from coals of about 25, and the assumed existence of some good oil



B=marginally mature;C=mature;D=overmature

(x=clean bitumen;c=contaminated bitumen)

Figure 5-12: mgHC/gTOC(R) vs %HC in bitumen(Θ)

potential in the classic Douala Basin type III kerogens which peak at about 70 mgHC/g TOC (Tissot and Welte, 1978). Rocks with hydrocarbon contents between 50 and 80 mgHC/g TOC are rated as intermediate sources (C3) with the upper limit that determined by Philippi (1957). Prolific oil sources (C4) are those containing between 80 and 160 mgHC/g TOC, the upper limit again from Philippi (1957), but corresponding well to the maximum obtained at peak generation from classic Uinta Basin type I kerogens (Tissot and Welte, 1978). Rocks with over 160 mgHC/g TOC are considered contaminated (C5).

Maturation paths on such a diagram, from initial oil generation, are in general:

- for type III organic matter: C2-D, or C2-C3-D.
- for types I & II organic matter: C2-C3-C4-D.

Bitumens from the present study plot from marginally mature to prolific on the path: b-C2-C3-C4, none exceeding the contamination limit (Figure 5-12). The bulk plot as intermediate oil sources, but at lower values of % hydrocarbon than those of the type II examples presented by Powell (1978), which pass through C3 at 60 to 70% hydrocarbon.

These bitumens thus appear to be of an organic matter type with high oil source potential (type I or II) but at less than peak maturity. This is information not supplied by the previous evaluation schemes and suggests that oil migration, which must lag oil generation, may not yet have begun in these rocks. Organic carbon content is not taken into account by this plot, but is not unimportant and must be taken into consideration separately (Powell, 1978).

5.5.2. Summary

Although the rocks evaluated above rate from marginally mature to possibly contaminated, depending on the classification chosen, the method of Powell (1978), although not taking TOC into account, also allows an estimate of maturity to be made. The designation of 'intermediate oil source' for the bulk of the samples may thus be more realistic than the good to excellent ratings of the other methods. If, in fact, maturity is somewhat less than peak oil generation, expulsion and primary migration should still depend on the hydrocarbon saturation of the organic matter or rock porosity, regardless of how much future generation potential may remain.

5.6. Source rock maturity

In many oil source rocks, particularly with little terrestrial organic matter, thermal maturity cannot be unequivocally determined by any one maturity indicator and best results are obtained by using as many indicators as feasible and looking for a consensus among a large number of these, disregarding those giving apparently anomalous estimates. This approach is taken herein and maturation indicators employed can be broadly grouped as those derived from kerogens, those derived from comparison with regional data for the source rock in question, and those derived from bitumens. Although data from kerogens do not strictly belong in a chapter on source rock bitumens, they are included here so that all maturity indicators can be evaluated together.

5.6.1. Maturity indicators from kerogens

5.6.1.1. Vitrinite reflectance

Mean vitrinite reflectance (R_0) was measured on 4 rock samples using edges removed from the core to avoid diesel contamination (Appendix A). Measured means varied from 0.70 to 0.82%, indicative of early to peak oil generation, but organic matter in all samples appeared to be extensively reworked by anaerobic bacteria, and vitrinite was scarce. The reflectance results were thus judged to be invalid by the analyst.

5.6.1.2. Thermal alteration index

Thermal alteration index (TAI) was determined using kerogen concentrates from 5 samples selected as those for R_0. Visually, the kerogens were indistinguishable and showed signs of severe anaerobic biodegradation indicating anoxic conditions of deposition. However, indications of oxidation suggest an oxic water column above the deeper anoxic zone. These interpretations agree well with those taken from petrographic examination of the core in the chapter:'GEOLOGICAL BACKGROUND'.

The thermal maturity was very difficult to determine due to the oxidation and biodegradation, but samples were mostly bimodal with modes at TAI 2.3-2.5 (R_0=0.5-0.6%) and TAI 3.2 (R_0=1.2%). The latter mode, at post-peak oil generation maturity was judged by the analyst to be the best estimate, but presence of any reworked organic matter would make the lower mode more likely (conversions from Waples, 1985).

5.6.1.3. Pyrolysis T_{max}

Pyrolysis was carried out on 13 extracted samples using a Rock-Eval II pyrolysis instrument. Pyrolysis is normally carried out on unextracted samples and the bitumen in these does contribute somewhat to the S2 peak (Peters, 1986). S2 will thus be lower for extracted samples, but this is not necessarily so for hydrogen index (HI), since the TOC denominator is also lower for extracted rocks and the two effects may largely compensate for each other. Pyrolysis HI is plotted against T_{max} (following Espitalié *et al.*, 1984) for the 13 samples in Figure 5-13 and these can be seen to cluster about a maturity of R_0=0.5%, marginally mature for oil generation. Any effect of bitumen on T_{max} seen on pyrolysis of unextracted samples should be to lower T_{max}, thus the value of R_0=0.5% may represent a maximum. In the HI range shown for these samples, any potential errors in HI will have no noticeable effect on apparent maturity.

5.6.2. Maturity from regional comparison

Whereas all the bitumens studied come from a 92m interval with no apparent unconformities, all samples should have similar maturity and no definition of the upper or lower limits of the oil generation window will be possible. Using data from these bitumens alone, maturity may be estimated as early, following the method of Powell (1978) as illustrated in Figure 5-12, but comparison with bitumens from the same source rock formation at various maturities can better place the studied section within the regional oil generation sequence.

Cornford *et al.* (1983) have presented data on 34 source rock bitumens from the North Sea Kimmeridge Clay Formation and this section consists of comparison of this data with

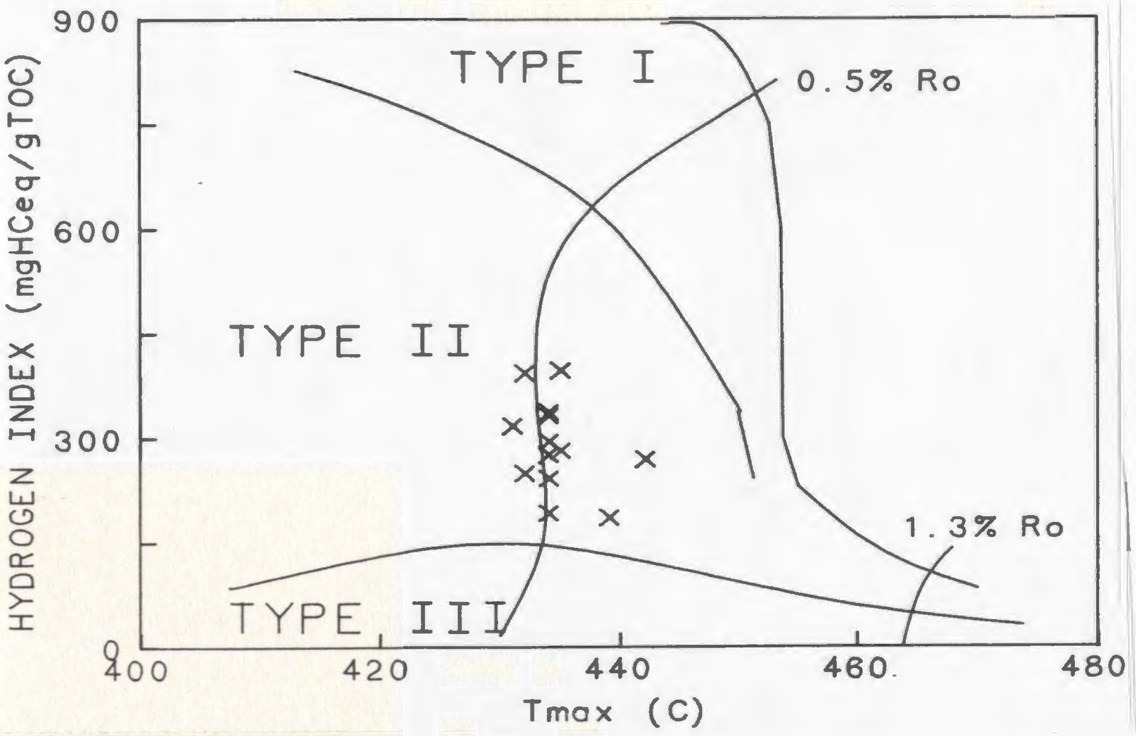


Figure 5-13: Rock-Eval HI vs. T_{max}

that of the present study. Although opinions may vary over the stages of oil generation corresponding to various values of, for example, vitrinite reflectance, or how reliably it may correspond to actual oil generation in a given situation (Price and Barker, 1985), direct comparison of bitumen parameters with the regional generation sequence should produce reliable maturity information even in situations where indirect methods encounter pitfalls. This is obviously contingent upon analytical results being directly comparable with outside data and internal consistency alone in no way guarantees this.

5.6.2.1. Carbon-normalized hydrocarbon yield

Because actual depth to the oil generation window in the North Sea varies according to subsidence history and geothermal gradient, the data of Cornford *et al.* (1983) are plotted against formation temperature determined from wireline logs, which although not itself a maturity indicator, is in this case more consistent than depth.

Hydrocarbon yield, as mgHC/g TOC, was found for the North Sea Kimmeridge Clay Formation to rise from about 50 to a peak of approximately 200, although the latter maximum is poorly defined (Cornford *et al.*, 1983, Figure 6). The stages of Immature, Early Mature, Mid Mature, and Late Mature are distinguished, the last 3 corresponding to minimum formation temperatures of 80, 107, and 130°C respectively, with the Early Mature stage marking the top of the oil generation window and peak generation occurring in the Late Mature stage. Regional data (Evans and Coleman, 1974) suggest a subsurface temperature of about 110°C for the core under study, corresponding to Early to Mid Maturity. Hydrocarbon yield for the uncontaminated samples herein ranges from 46.6 to

159.6 mgHC/g TOC, averaging 71.8. This spans the boundary between Immature and Early Mature stages, with the mean suggesting Early Maturity.

5.6.2.2. Ph/nC$_{18}$ ratio

In keeping with decreasing isoprenoid/n-alkane ratios with increasing maturity due to increasing n-alkane generation documented for other areas (Tissot *et al.*, 1971), the data of Cornford *et al.* (1983) show the Ph/nC$_{18}$ ratio decreasing steadily from approximately 3.0 in the Immature stage to approximately 0.4 in the Late Mature stage. The same ratio in bitumens from this study uncontaminated by diesel oil ranges from 0.61 to 3.27 and is tabulated in Appendix B, Table B-6. Due to extremely abundant isoprenoids in 3 of these bitumens, these are believed to be of an uncommon and unusual organic matter subtype discussed in a following section. The Ph/nC$_{18}$ ratios for these 3 bitumens are thus not considered for maturity estimation and it appears that Cornford *et al.* (1983) have disregarded 2 similarly high values in the Immature stage. Remaining bitumens now show ratios ranging from 0.61 to 1.24, averaging 0.84. This corresponds to the Early and Mid Mature stages with the average in the early mature stage. Estimated maturity would be slightly less if the isoprenoid-rich bitumens were included.

5.6.2.3. Pr/Ph ratio

Cornford *et al.*(1983) found Pr/Ph ratios from the Kimmeridge Clay Formation to vary from 0.5 to 1.8 and to show no relation to thermal maturity. The same ratio in uncontaminated bitumens from the present study ranges from 1.20 to 2.80, averaging 2.03 and is tabulated in Appendix B, Table B-6.

5.6.2.4. Saturate/aromatic ratio

Saturate/aromatic (S/A) ratios in North Sea Kimmeridge Clay Formation bitumens were found to vary from approximately 0.2 to 3.0 by Cornford *et al.* and to show an increase with maturity, accelerating in the oil generation window, although scatter is considerable. S/A ratios for uncontaminated bitumens in this study are tabulated in Appendix B, Table B-2, and range from 0.75 to 1.54, averaging 1.03. The corresponding maturity range is from Immature to Late Mature, with the average in the Mid Mature stage near the boundary with Early Mature. This estimate, due to scatter in both sets of data, is considered less reliable than the earlier Ph/nC$_{18}$ and hydrocarbon yield comparisons.

5.6.3. Maturity from bitumen data

5.6.3.1. Odd-even predominance

Although high values of Odd-Even Predominance (OEP) indicate low maturity for the bitumen in question, values close to 1.0 such as those from this study may indicate peak oil generation maturity in rocks of originally high OEP or any maturity in rocks of originally low OEP. Thus, in the present case, low OEP values in a set of bitumens of equal maturity give by themselves no indication of actual maturity.

5.6.3.2. Methylphenanthrene index

Radke *et al.* (1982) have developed the Methylphenanthrene Index (MPI 1), a numerical parameter calculated from the gas chromatographic analysis of aromatic fractions, which correlates well with vitrinite reflectance and may be used as a maturity parameter. MPI 1 is the ratio of [1.5 x (2-methylphenanthrene + 3-methylphenanthrene)] to [phenanthrene + 1-methylphenanthrene + 9-methylphenanthrene]. Although pure standards were not available for all these compounds, retention times were established for phenanthrene and 1-methylphenanthrene, and identification of others was based on comparison of relative retention times with those of Palmer (1984) and Radke *et al.* (1984). Accurate separation of 2- and 3-methylphenanthrene and 1- and 9-methylphenanthrene was not always achieved by the integrator, but since these 2 pairs of peaks are both summed in the calculation, this had no effect on the result. An FPD detector was not available to quantify 1-methyl dibenzothiophene, which partially co-elutes with 3-methylphenanthrene, but since this compound is normally greatly subordinate to 2-, 3-, and 4-methyl dibenzothiophene, and these were not apparent in any of the chromatograms of aromatic fractions, the contribution of 1-methyl dibenzothiophene is judged to be negligible. This is also suggested by the mass spectrometry results of aromatic fractions which all feature dibenzothiophenes much less abundant than phenanthrenes (Appendix B, Table B-9). Since this compound, if present, would increase the numerator of the MPI, the ratios can in any event be considered as maximums. Phenanthrene and methylphenanthrene peaks are labelled in the gas chromatograms of the aromatic fractions in Appendix C. Phenanthrenes appear on gas chromatograms to become much more abundant below 21.6m, but this has little effect on the MPI which is only slightly diminished. This increased phenanthrenes content is not supported by mass spectrometry results, possibly indicating that methyl- and dimethylphenanthrenes make up only a small proportion of this class (Appendix B, Table B-9). MPI 1 is tabulated for all bitumens and the reservoir oil in Appendix B, Table B-6.

Radke *et al.* (1982) and Radke & Welte (1983) have shown the MPI to rise from approximately 0.5 to a maximum of 1.8 at a vitrinite reflectance of R_0=1.3%, before falling again with increasing maturity. Taken alone, therefore, MPI can indicate 2 maturities, 1 preceeding and 1 following peak maturity. MPI values for uncontaminated source rock bitumens in this study range from 0.39 to 0.66, averaging 0.53. These indices can be converted to equivalent vitrinite reflectance values using the formulae determined by Radke and Welte (1983) for type III organic matter, assuming these also hold true for the organic matter type(s) in this study. The resulting maturities are: R_0=0.63 to 0.79%, averaging 0.72% assuming less than peak maturity; or R_0=1.91 to 2.07%, averaging 1.98% assuming post peak maturity.

5.6.3.3. Unresolved steranes and triterpanes

The gas chromatograms of all bitumen saturate fractions except that from 0.0m feature an unresolved hump eluting between nC_{26} and nC_{31}. Such humps are a feature prominent in immature bitumens, particularly those of marine origin, and generally diminish as peak oil generation maturity is approached. Although not easily quantified, those in the bitumens studied herein appear greater than for the reservoir oil from below the studied section. The bitumen from 0.0m may not show this feature merely due to excessive contamination in the diesel oil molecular weight range.

Mass spectrometry results for saturate fractions, plots of which accompany the respective gas chromatograms in Appendix C, all show very pronounced 'humps' of 4 and 5 ring naphthenes, including that of the reservoir oil and the highly contaminated bitumen from 0.0m. These are typical of bitumens at the earliest stage of oil generation in the classic Paris Basin source rocks (Tissot *et al*., 1971), but no non-biodegraded crude oil could be found in the literature with such high polycyclic naphthene content, particularly one of 40°API as in the present study. The near equivalence of 4 and 5 ring naphthene content in the contaminated bitumen at 0.0m and the depleted one at 12.4m is also inconsistent with the observed 'humps' on the respective chromatograms, and due to these observations the mass spectrometry results for saturates are viewed as anomalous. Possible contaminants are not obvious, and monoaromatic cross-contamination appearing as 4 and 5 ring naphthenes would consist of alkyl benzenes and indanes/tetralins, both of which are taken into account in the fragment ions summed for monoaromatics determination.

5.6.4. Summary

Table 5-1 summarizes the maturity estimates outlined above and it can be seen that a general consensus of Early oil generation maturity is present with several estimates also falling in the Immature or Middle mature categories. In hindsight it appears probable that the vitrinite reflectance measurements were an accurate if unreliable indicator and that the indicators giving 2 estimates, i.e. MPI and the bimodal TAI, were correct in their common early mature alternative. Whether early oil generation maturity is sufficient for

Table 5-1: Comparison of source rock maturity indicators

MATURITY INDICATOR	INDICATED MATURITY	ESTIMATED RELIABILIT
Powell Diagram	Early to Middle	Fair
Vitrinite Reflectance	Early to Middle	Poor
TAI	Early or Late	Poor
T_{max}	Immature to Early	Good
Subsurface Temperature	Early to Middle	Fair
HC Yield	Immature to Early	Good
Ph/nC_{18}	Early to Middle	Good
S/A Ratio	Immature to Late	Poor
MPI	Early or Overmature	Fair
Terpanes	Early to Middle	Good

oil expulsion in these rocks is by no means certain and will be given detailed consideration in the section 'OIL-SOURCE COMPARISON'

5.7. Organic matter type

As well as an adequate quantity of organic matter and sufficient maturity, an oil source rock must contain oil-prone organic matter to generate and expel significant quantities of oil. In addition, comparison of bitumen yields for recognition and quantification of depletion due to migration must be between rocks of similar organic matter type. Although not a property of source rock bitumens alone, organic matter type is reviewed in this chapter owing to its direct bearing on interpretation of source rock bitumen composition and abundance.

5.7.1. Pyrolysis HI data

Organic matter types are defined in terms of elemental analysis (Tissot and Welte, 1978), which was not carried out in this study, but correlation of elemental analysis with pyrolysis data enables determination of organic matter type for rocks with TOC > 0.5% approximately (Peters, 1986). The pyrolysis results of 13 extracted samples from the section studied are shown in Figure 5-13. All of these plot together within the field of Type II organic matter, although as mentioned earlier, the same analyses carried out on unextracted rocks may have resulted in slightly different hydrogen indices. Using S2 as measured and TOC of unextracted rocks, minimum values of HI can be calculated, and these differ only slightly from those plotted, all lying as before in the Type II field. In the area of the plot concerned, errors in T_{max} will have minimal effect on organic matter type. Also, a plot of HI vs. TOC yielded no discernable correlation, indicating that samples were not sufficiently lean to suffer from excessive matrix adsorption (Peters, 1986). Organic matter thus appears to be Type II, or possibly mixtures of Type III with Type II or Type I, and is probably similar for all samples. This agrees well with a marine origin for the bulk of the organic matter indicated by the increase in TOC moving up the core to more distal facies (see chapter 'GEOLOGICAL BACKGROUND').

5.7.2. Hydrocarbon and bitumen yields

Previously presented plots of bitumen data have been used to eliminate detrital organic matter (Type III) for the rocks in question and shown yields of carbon-normalized hydrocarbon beyond those reached for Type III organic matter, especially at the early maturity of these rocks (Figs. 5-10 and 5-12). These two classifications of source rocks thus support the organic matter type suggested by Rock-Eval pyrolysis data.

5.7.3. Gas chromatographic evidence

5.7.3.1. Isoprenoids

The acyclic isoprenoids, phytane and pristane, are considered by many to be derived from the phytol chain of chlorophyll by reduction or oxidation-decarboxylation respectively. In addition to indicating a major input from phytoplankton or terrestrial plants to oil generating organic matter, such an origin would mean that the Pr/Ph ratio could be used as an indicator of the relative oxidizing potential of the depositional environment. Powell and McKirdy (1973) have proposed this and suggested that Pr/Ph ratios > 1 indicate oxidizing environments, which probably contain in large part terrestrial organic matter. Using this criterion, all source rock bitumens analysed in this study are indicated to have been generated from oxidized organic matter, and similarly, from the data of Cornford *et al.*(1983), about half of the Kimmeridge Clay Formation bitumens in their data set (36).

The assumption of a phytol origin, though, for all or even a major part, of bitumen isoprenoids is increasingly uncertain. Moldowan and Seifert (1979) have identified a periodic distribution of head to tail acyclic isoprenoids in a crude oil, with maxima at 19, 24, 29, and 34 carbon atoms. Also detected was a C_{40} head to head biphytane and several cracking products therefrom, suggested to have a bacterial origin and to act as a precursor to some of the lower molecular weight series. Chappe *et al.* (1982) have detected phytane in diethers from shale bitumens and head to head biphytane in glycerol tetraethers from shale bitumens and a North Sea crude oil and suggested an origin from methanogenic bacteria for acyclic isoprenoids.

Using a more empirical approach, Illich (1983) plotted C_{19} and lighter isoprenoids percentage against phytane percentage for oils of various families and found these, when fitted with a straight line, to have positive y-intercepts, indicating an additional source for the lighter isoprenoids other than cracking of phytane. However, percentages of the isoprenoids were calculated using the respective peak areas as a percentage of total whole oil resolvable peak area, after passage through a precolumn to remove NSO compounds. Because the heterocompound content and percent resolvables will vary from oil to oil, the calculated percentages are not for whole oil and thus may not be compared. Although the conclusions may be correct, they are not supported by the data which, as presented, contain only isoprenoid ratios.

In an effort to characterize crude oils isotopically, Sofer(1984) divided a set of 339 oils into waxy and nonwaxy categories, based on visual inspection of n-alkane distributions. Assuming these to be derived from terrestrial and marine sources respectively, an effort was then made to define criteria to efficiently distinguish between these groups of oils. Although a clear correspondence between waxy oils and terrestrial sources has not been demonstrated (1 of the 85 waxy oils has a Silurian source), the bulk of these oils likely have a terrestrial origin. When plotted against Pr/Ph, no clean separation was observed between the two, although waxy oils were found to have a slightly higher average ratio with Pr/Ph > 5 being found only in waxy oils. Ratios ranging from 0.5 to 2.8, encompassing those from this study and that of Cornford *et al.* (1983), were found for both waxy and nonwaxy oils, indicating that in this range, and up to about 5, Pr/Ph ratios cannot be used as a reliable indicator of source depositional environment. The large spread in the data of Cornford *et al.* (1983) also attest to the variability of this ratio in a single source formation and thus its additional lack of utility in oil-source correlation.

Three of the bitumens in this study, from 66.4, 60.2, and 54.4 m above the reservoir sandstone, contain abundant C_{15}-C_{22} acyclic isoprenoids, although possibly masked by diesel contamination at 60.2 m. These were identified by injection of pure pristane and comparison of relative retention times with those of McKirdy *et al.*(1984). Isoprenoids of carbon number < 17 are somewhat affected by evaporation.

The cause for isoprenoid abundances is not clear. Assuming an origin from phytol, a temporarily high phytoplankton population could be invoked, but TOC percentages at these depths are not abnormally high, and the abundances of C_{21} and C_{22} isoprenoids (phytane=C_{20}) are also enhanced. In addition, an origin from cracking of phytol would likely lead to a regular distribution of isoprenoids of lower molecular weight, not the ubiquitous minimum at C_{17}. The distribution observed is much closer to that observed by Moldowan and Seifert (1979), which was periodic, with minima at every 5th carbon number, including C_{17}. This suggests an origin from a series of precursors separated by 5 carbon atoms. The gas chromatogram of the sample from 66.4m also clearly shows a series of 5 peaks in the nC_{32}-nC_{36} region which may represent long chain precursors of the lower molecular weight isoprenoids. Mass spectrometry data for this sample show no increase in high molecular weight polycyclic naphthenes.

If, as suspected by Chappe *et al.* (1982), such isoprenoids originate in methanogenic bacteria, this would tie in well with evidence of severe anaerobic biodegradation noted from visual kerogen examination and would be consistent with anoxic conditions deduced from petrography and original core examination in the chapter 'GEOLOGICAL BACKGROUND'. Why the isoprenoids are abundant in these three samples only is not clear. Only the 66.4m sample shows anomalously high bitumen and hydrocarbon (but not asphaltene) yield (Figure 5-2), but even this is still rated as Type II organic matter by pyrolysis, with an HI only slightly higher than for other samples. Oils and source rock bitumens enriched in isoprenoids are described by McKirdy *et al.* (1984) from the Cambrian of Australia where source rocks are both marine and lacustrine, but it is not clear how many of these may be biodegraded and/or stained. Similarly Han and Calvin (1969) found abundant isoprenoids in a Bell Creek, Montana crude oil, but this was from a field used as a classic study of biodegradation in reservoirs (Winters and Williams, 1969), thus the isoprenoid abundance is likely only relative and not reflected in the original source rock bitumen.

Tissot *et al.* (1977) have found high concentrations of isoprenoids up to C_{25} with Pr > Ph, in bitumens with high odd or even predominance in the nC_{15} to nC_{18} range and attribute such n-alkane distributions to an origin from phyto- and zooplankton, and benthic algae. Although such a predominance is not present in the bitumens considered herein, masking of a weak predominance in this range by limited catagenesis or diesel contamination could have taken place. Obviously, C_{25} isoprenoids cannot originate from cracking of phytane, but an origin from bacteria, as suggested by Chappe *et al.* (1982), which are associated with an anoxic depositional environment and algal and planktonic-derived organic matter would seem to be a reasonable explanation for the isoprenoid abundances found. This in turn would suggest a type II organic matter for the isoprenoid-rich bitumens, consistent with pyrolysis results. The unreliability of Pr/Ph ratios for organic matter determination and the possible origin of these isoprenoids from methanogenic bacteria would not rule out a type II organic matter for the remaining bitumens, but would make their origin in an oxidizing depositional environment less likely.

5.7.3.2. n-alkane distributions

Disregarding diesel contaminated bitumens (60.2 m, 43.1 m, 23.5 m, 21.6 m, 15.8 m, and 0.0 m) and that from 12.4 m where important depletion appears to have taken place, n-alkane distributions from saturate fractions (Appendix C) all show maxima at nC_{15} to nC_{17} and a steady decrease to low values at nC_{35} (the distribution for 66.4 m is affected by coelution of possible isoprenoids at nC_{33} to nC_{35}). Such distributions are of the type

'Poor in Heavy n-Alkanes' following the classification of Tissot *et al.* (1977) and their origin is attributed to either catagenesis - doubtful at this early maturity stage - or organic matter from predominantly phytoplankton in detrital sequences (Figure 3b of Tissot *et al.* (1977)), also characterized by high naphthene content (see Appendix B, Table B-8). Values of Odd-Even Predominance (Scalan and Smith, 1970) in the region of nC_{29} are only slightly in excess of 1.0, indicating at early maturity only minor input from terrestrial plants. These observations are consistent with marine algal type II organic matter for the section studied.

5.7.4. Summary

Type II organic matter is, in addition to n-alkane distributions, also in agreement with other organic matter type indicators considered. Type III organic matter hydrocarbon yields are below those found for samples in this study according to Oudin (1976) and Powell (1978) and such organic matter should result in lower pyrolysis HI. Similarly, Type I organic matter should show high HI and characteristic flat n-alkane distributions not seen in the study. It thus appears that the organic matter from source rocks of this section is all Type II, oil-prone, of marine origin, and the bitumens may be compared directly without qualification. Differences in bitumen yield of non-contaminated samples are thus likely due to gains and losses from migration or merely represent the variability that can be expected within this organic matter type (Figure 5-2). Similarly, changes in bitumen composition of uncontaminated samples not attributable to migration, for example the increased abundance of phenanthrenes below 21.6 m (Appendix C), also probably represent variations neither affecting overall oil generation performance nor reflecting significant changes in depositional environment.

5.8. Oil-source comparison

The advantages of an oil migration study conducted at a source rock-reservoir contact hinge on the ability to establish that significant oil migration has actually taken place over the section in question, and this was seen to be a shortcoming of some previous studies of this nature. While the organic matter type of the section studied here is oil-prone and TOC contents are moderately high, maturity has only reached the early oil generation stage, and whether or not oil expulsion is possible at this maturity has not been established. Under these circumstances, only the reservoir oil sample can be said with certainty to represent the end member of the oil migration process and as such must be regarded as the most important sample in the study.

5.8.1. Characterization of reservoir oil

5.8.1.1. By compound type

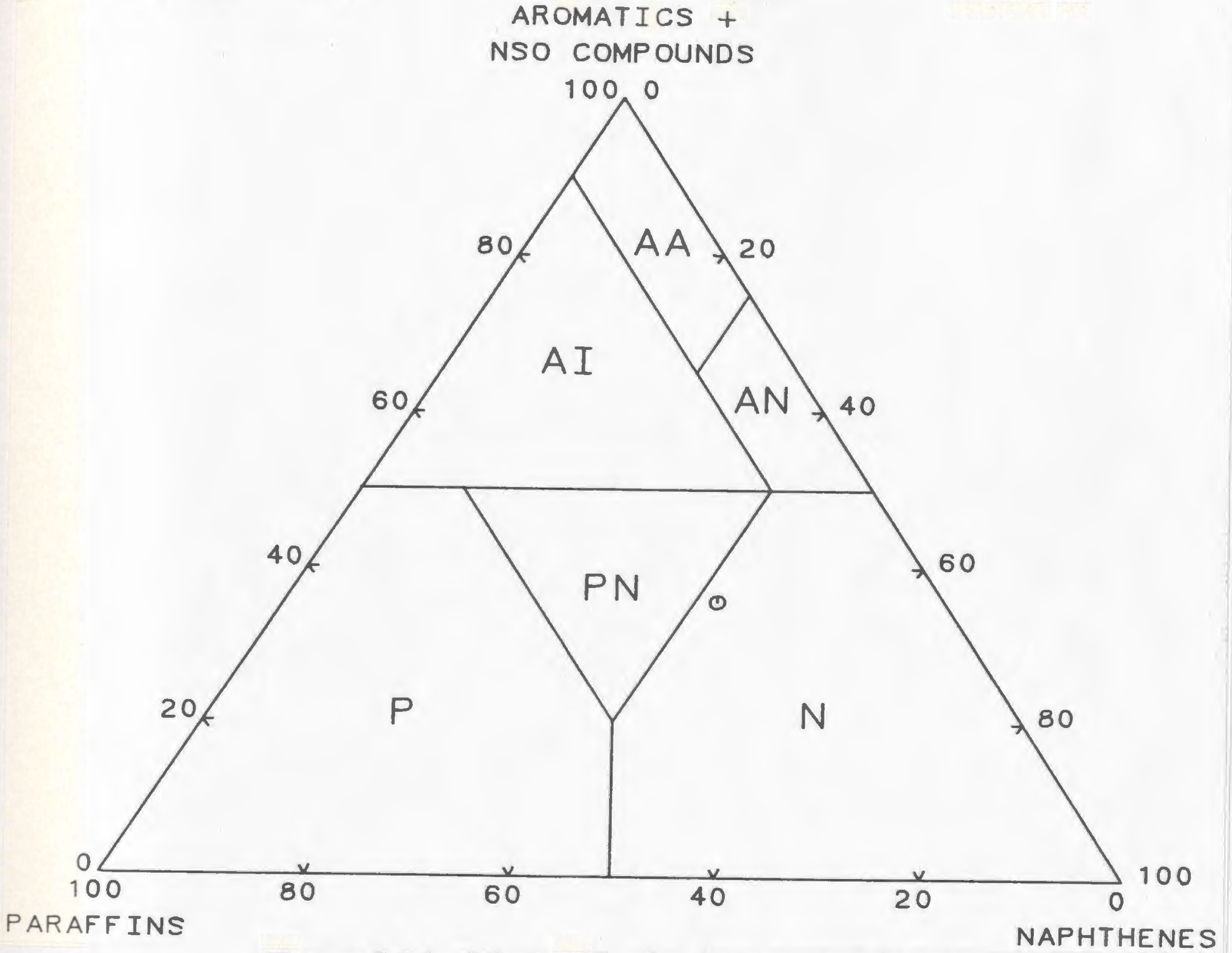


Figure 5-14: Oil classification by compound type
AA=Aromatic Asphaltic, AI=Aromatic Intermediate,
AN=Aromatic Naphthenic, PN=Paraffinic-Naphthenic,
P=Paraffinic, N=Naphthenic, (o=reservoir oil)

Figure 5-14 shows the reservoir oil classified according to Tissot and Welte (1978), after correction for monoaromatics in the saturate fraction. This plots with naphthenic oils, a rare category occupied largely by biodegraded low sulfur oils (Tissot and Welte, 1978). Since the reservoir oil shows no signs of biodegradation, but features the large 'hump' of 4 and 5 ring naphthenes in the mass spectrometry results (Appendix C) which is not evident on the gas chromatogram, it appears that suspected inaccuracy in the mass spectrometry results discussed earlier is responsible for the misclassification as shown. North Sea oils plot typically in the Paraffinic-Naphthenic class (Tissot & Welte, 1978), and an increase in the proportion of paraffins relative to naphthenes would shift the oil of this study into this category, typical of shale source rocks containing marine organic matter.

5.8.1.2. By regional comparison

In addition to Kimmeridge Clay Formation source rock bitumens, Cornford *et al.* (1983) have presented data on 100 North Sea oils which can, by itself, shed light on how typical the studied oil is on a regional scale and, in conjunction with bitumen data, can indicate the maturity level of source rocks expelling such oils.

Asphaltenes content for the 100 oils was determined using nC_7 as solvent, unlike nC_5 for the reservoir oil. According to Mitchell & Speight (1973), nC_7 should precipitate approximately 0.58 times the asphaltenes of nC_5, thus the reservoir oil from this study contains an estimated 1.2% nC_7 asphaltenes. This is also the average for the 100 oils analysed by Cornford *et al.*, although their modal class is 0-1%.

The reservoir oil has a density of 40°API, near the mean for the 100 oils (36°). The frequency distribution is symmetric unimodal and the reservoir is in the modal 35-40°API class.

Saturate/aromatic ratio of the reservoir oil, 2.83, is well above the mean, 2.02, for the 100 oils and higher than the 1.5-2.0 modal class. However, some of the oils are biodegraded and the reservoir oil in this study will be somewhat nearer the mean for unaltered oils. Cornford *et al.* plot S/A against API gravity and from this it can be seen that the reservoir oil is within the positive trend defined by their data.

With regard to isoprenoids, the Pr/Ph of the reservoir oil, 1.00 + or - .05, is less than the mean of the 100 oils (1.24), and below the modal class of 1.2-1.4. Pr/nC_{17}, 0.52 + or - .01, in the reservoir oil, averages 0.63 for the 100 oils and no distribution or mode is given. Ph/nC_{18} is 0.53 for the reservoir oil; less than the mean (0.56) but within the modal class 0.4-0.8.

For all parameters compared except Pr/Ph and possibly S/A ratio, the reservoir oil seems to be a typical North Sea oil and the higher than average value of the latter ratio, typical for a 40°API North Sea oil, may indicate that it is close to average for unaltered oils.

5.8.2. Comparison with source rock bitumens

5.8.2.1. From regional data

The plot of S/A against formation temperature for Kimmeridge Clay Formation bitumens (Cornford *et al.*, 1983), referred to above to estimate source rock maturity, indicates that an S/A of 2.83 (reservoir oil) should be reached by bitumens from this source rock in the Late Mature stage, very near peak hydrocarbon generation. This is also true for the modal class for the 100 oils. This is in contrast to an Early to Mid maturity indicated by the average S/A ratio for the source rock bitumens in this study.

The Ph/nC_{18} ratio is also plotted against sediment temperature for the 34 Kimmeridge Clay Formation bitumens, and the ratio from the reservoir oil, 0.53, is reached in source rock bitumens at the beginning of the Late Mature stage, once again near peak hydrocarbon generation. North Sea oils of the modal class, 0.4-0.8, correspond to Mid-Late maturity. The same ratio from bitumens of this study indicated Early to Mid maturity. Finally, as mentioned earlier, Pr/Ph ratio, although lower in the oil than any of the bitumens, appears to bear no relationship to maturity.

5.8.2.2. By gas chromatographic analysis

The gas chromatogram of the reservoir oil saturates (Appendix C) shows a barely visible terpane hump (nC_{26}-nC_{31}) in contrast to the shale bitumens. This indicates greater maturity and a more advanced degree of catagenesis for the oil relative to the overlying Kimmeridge Clay. This lower content of polycyclic naphthenes, as previously discussed, is not apparent in mass spectrometry results. The reservoir oil n-alkane distribution, like those of the bitumens, is of the type 'Poor in heavy n-alkanes' (Tissot *et al.*, 1977), but in the absence of maturity indications this could be a function of the source rock organic matter type as in the bitumens, or due to extensive catagenesis regardless of the original organic matter type (Tissot *et al.*, 1977, Figure 3a). Figure 5-15 shows the composite n-alkane envelope of uncontaminated bitumens minus the depleted distribution from 12.4m and that richest in isoprenoids from 66.4m. The last was left out because co-elution of nC_{33}+ n-alkanes with unidentified, possibly isoprenoid, compounds distorted the n-alkane distribution. The resulting envelope as shown gives a good match to the reservoir oil with the wide span at nC_{15}-nC_{17} probably due to variable evaporation losses. The good match would indicate a similar maturity (degree of catagenesis) for both bitumens and oil, or alternatively a higher degree of catagenesis for the oil with alkanes in the later stages having been generated in approximately the same proportions as those already present in the bitumens. A stage of catagenesis sufficient for cracking of C-C bonds would result in an n-alkane distribution for the oil with abundances surpassing those of the bitumens at low carbon numbers and falling short of them at higher carbon numbers, much like the diesel-contaminated samples in Figure 5-5. Figure 5-16 shows the composite envelope of compound classes for undepleted and uncontaminated aromatic fractions, normalized to exclude thiophenes and unidentified aromatics. A good

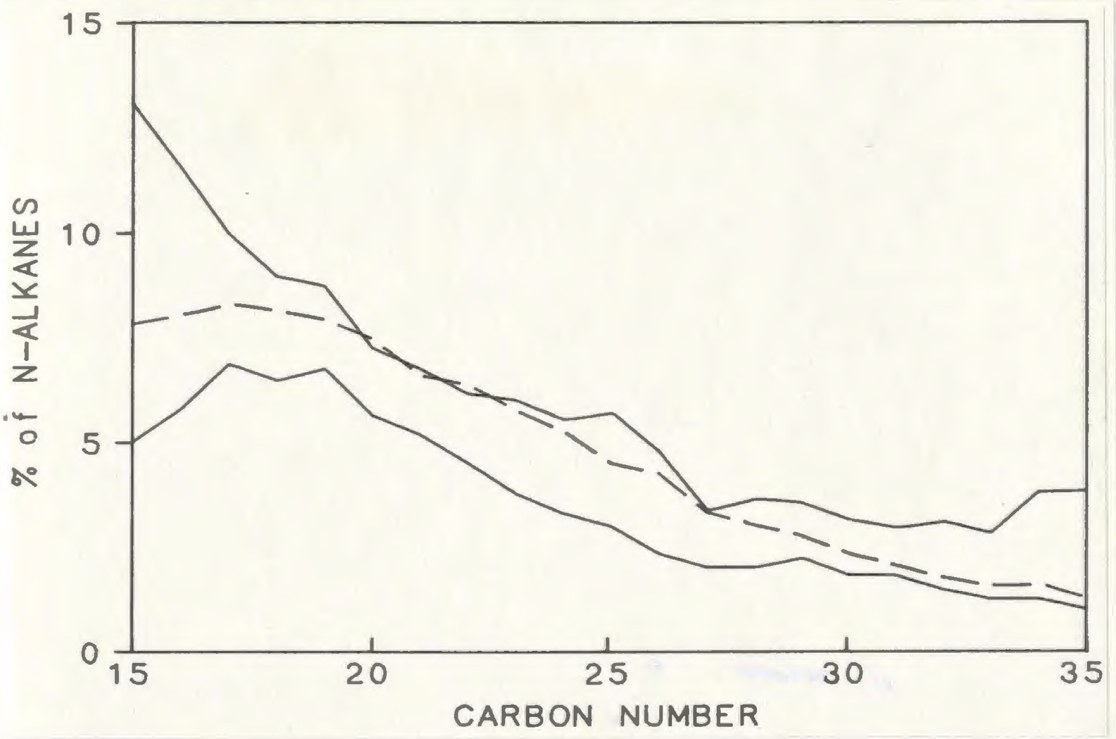


Figure 5-15: Composite n-alkane envelope: all unaltered bitumens (dashed line is reservoir oil)

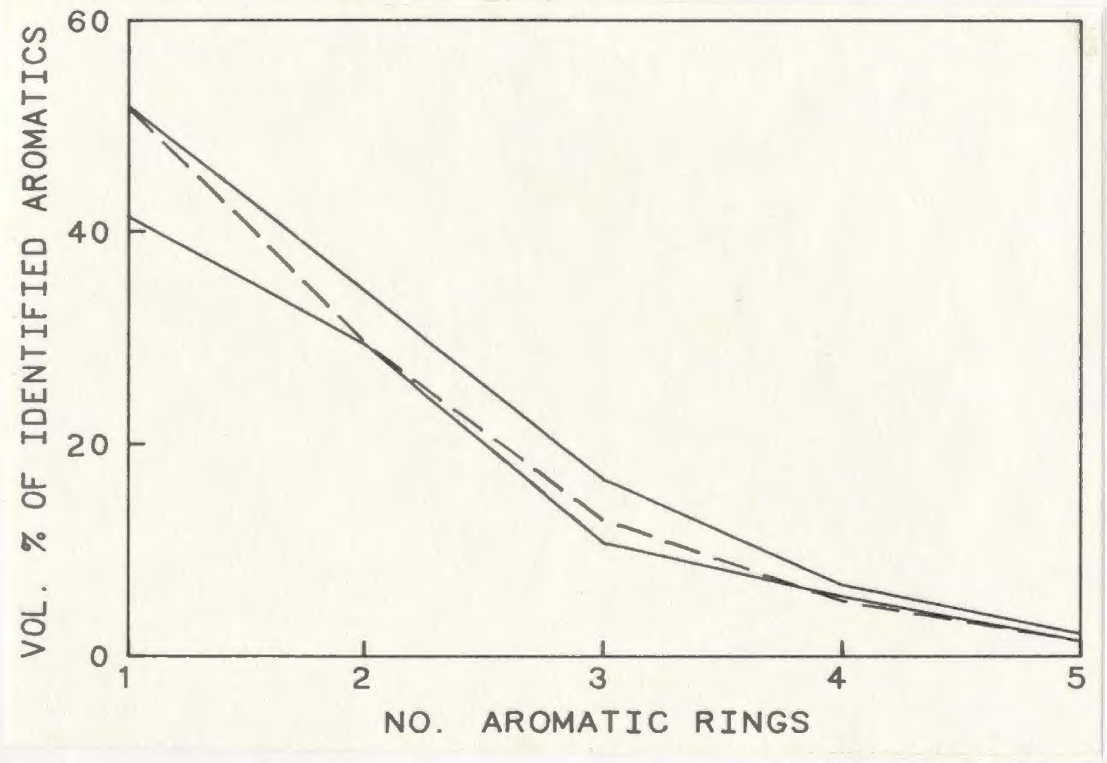


Figure 5-16: Composite aromatic envelope: unaltered bitumens (dashed line is reservoir oil)

fit is obtained to the reservoir crude oil, although the latter is somewhat enriched in monoaromatics, but it must be borne in mind that the distribution is only partially

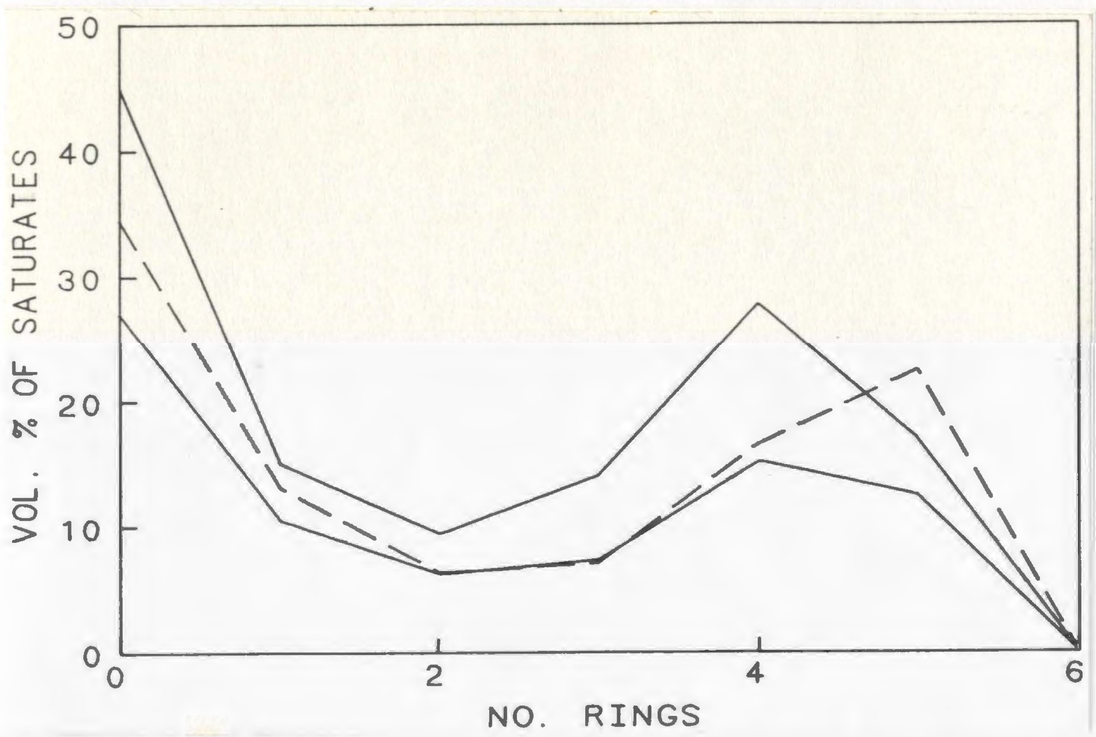


Figure 5-17: Composite saturate envelope: unaltered bitumens (dashed lLine is reservoir oil)

dependent on molecular weight. Similarly, Figure 5-17 shows a reasonable fit from 0 to 4 naphthene rings, but the reservoir oil has an anomalously high pentacyclic component. Reservations expressed earlier concerning this mass spectrometric data should be borne in mind. Figure 5-18 shows the composite envelope of all OEP curves (Scalan and Smith, 1970) compared with the reservoir oil. High values resulted in the isoprenoid-rich bitumens due to partial co-elution at $nC_{33}+$ as outlined above and at nC_{19} with the C_{21} isoprenoid. Removing these bitumens and those 6 as before with diesel contamination results in the envelope shown in Figure 5-19. Although all values are close to 1.0, those of the bitumens generally differ from this more than the reservoir oil and show 3 maxima at nC_{17}, nC_{24}, and nC_{30} as well as some even predominance around nC_{27}. The first two maxima and the nC_{27} minimum are exhibited by only a few bitumens, but the nC_{30} maximum is evident in all, including the reservoir oil. Odd-carbon predominance in the nC_{15}-nC_{19} range is fairly common, notably in some early Paleozoic oils, and is attributed by Tissot *et al.* (1977) to organic matter with a high input from phytoplankton and benthic algae, often rich in acyclic isoprenoids. The origin of the odd predominance at nC_{24} and the even at nC_{27} are not clear, but these along with that at nC_{17} are subtly reflected in the reservoir oil as well.

The odd predominance at nC_{30} is shared by all bitumens and the oil and is commonly associated with input from terrestrial plants. It is more pronounced in the bitumens than in the oil, suggesting a greater maturity for the latter. Values of OEP around nC_{30} in general often exceed 2.0 and at the early maturity of the bitumens studied here the low

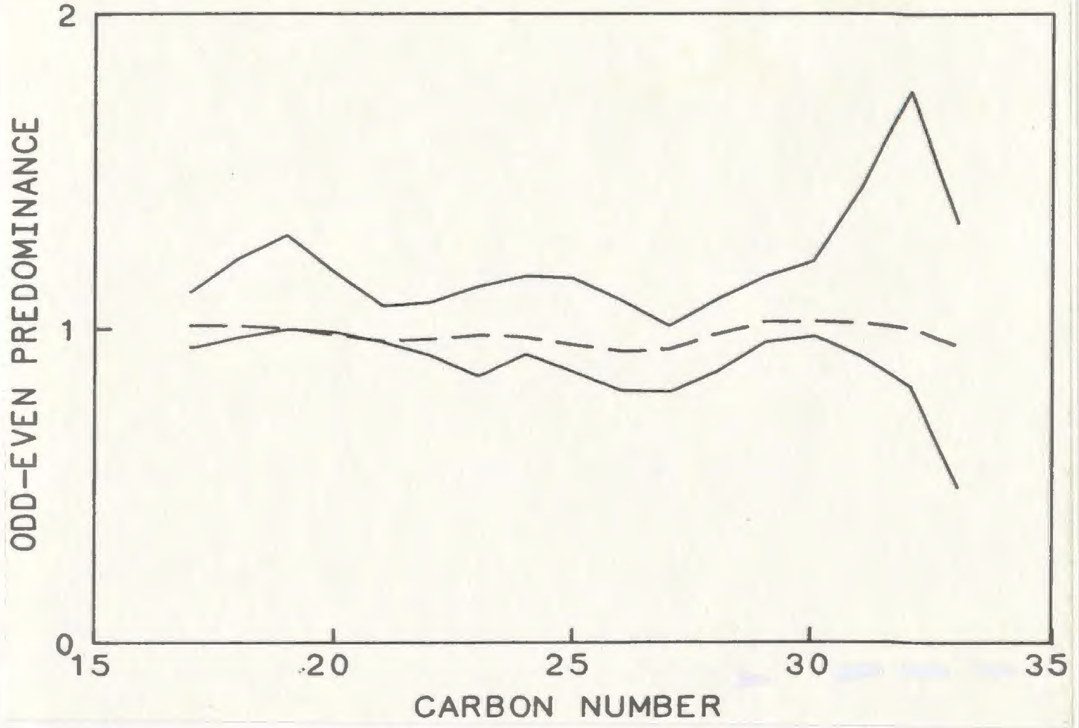


Figure 5-18: Composite OEP envelope: all bitumens
(dashed line is reservoir oil)

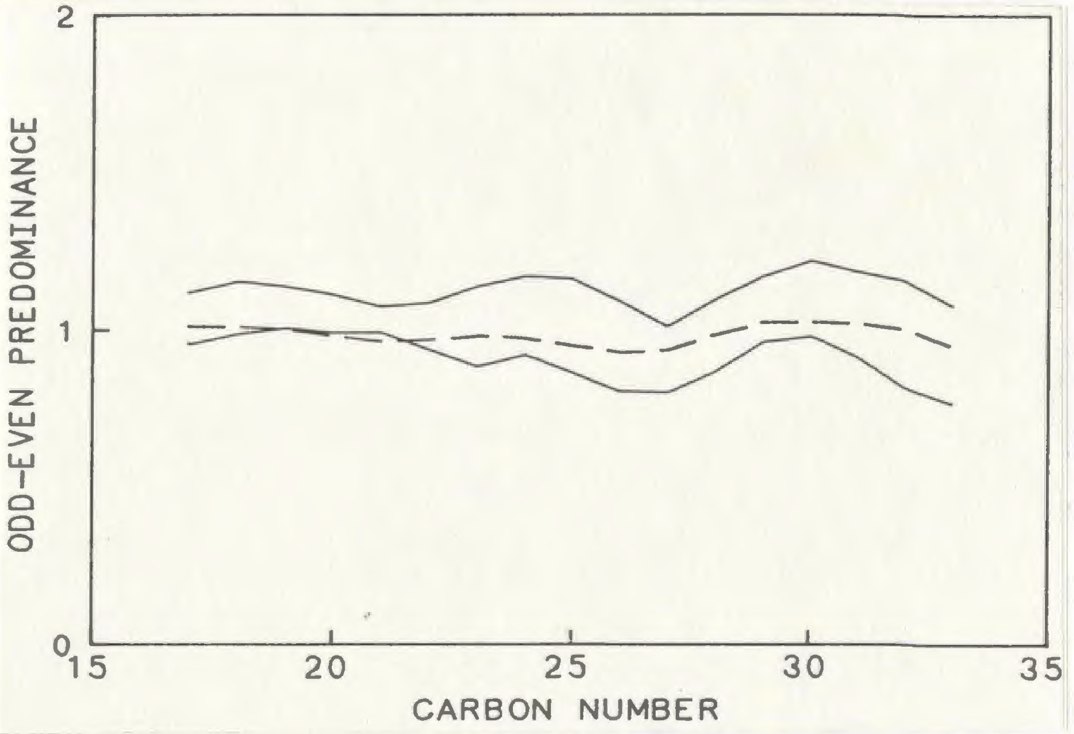


Figure 5-19: Composite OEP envelope: all unaltered bitumens
(dashed line is reservoir oil)

OEP values indicate a very minor terrestrial input. For comparison, Figure 5-20 shows the OEP envelope of the 6 contaminated bitumens and these can be seen to show a similar odd-predominance at nC_{30}, beyond the range of the diesel oil contaminant, but are very similar to the reservoir oil at lower carbon numbers, reflecting the origin of the diesel from a crude of similarly high maturity. Gas chromatograms of aromatic fractions of uncontaminated and undepleted bitumens (Appendix C) consist of peaks representing identifiable di- and triaromatics superposed on an unresolved hump, which begins to decrease at an oven temperature of about 250°C. The reservoir oil, although showing essentially the same peak distribution except for the relative proportions of C_1 fluorenes and C_3 biphenyls (Palmer, 1984), features a steadily decreasing unresolved hump indicating much less high molecular weight material. Color of this fraction was also considerably paler yellow than that of the bitumens. Like the terpane hump in saturate fractions, this 'hump' gives an indication of higher maturity in the reservoir oil than in the shale bitumens (Tissot *et al.*, 1971).

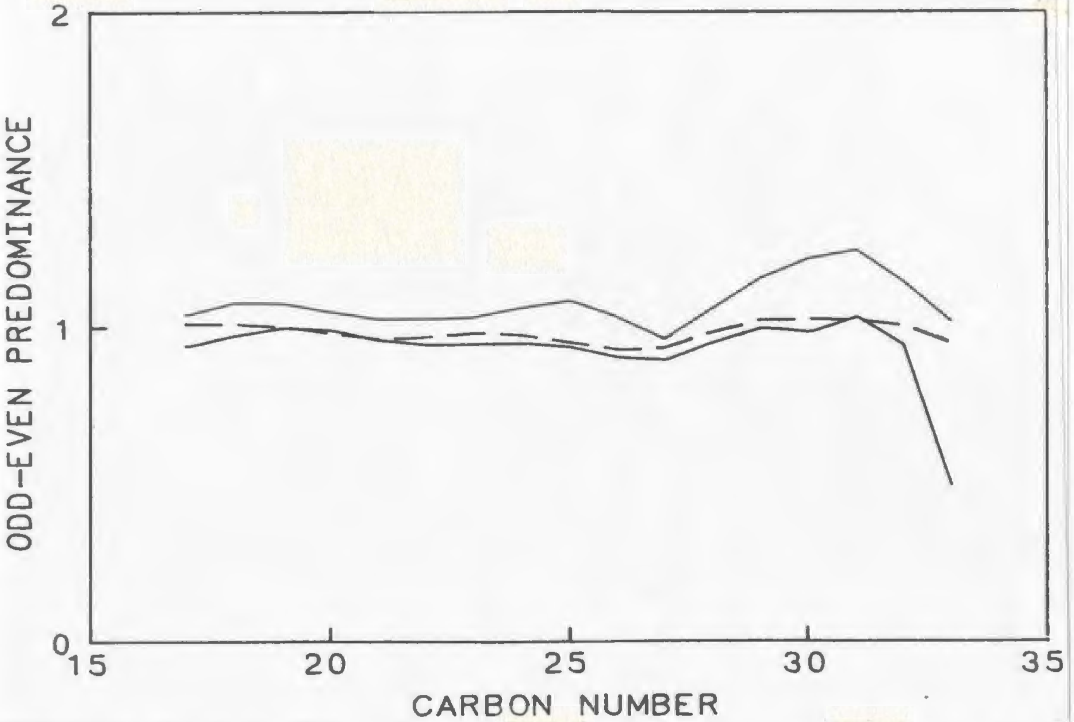


Figure 5-20: Composite OEP envelope: contaminated bitumens
(dashed line is reservoir oil)

This difference is not reflected in mass spectrometry results by a corresponding increased abundance of polyaromatics. Although a similar explanation to that advanced for saturates may apply, many aromatics give more abundant parent and (m-1) fragment ions than saturates, so differences in their abundance may be relatively less significant, and in any case the abundance of polycyclics with respect to gas chromatographic evidence is the opposite of the saturate fractions. Because the number of aromatic rings is in itself not a measure of molecular weight, and ignores alkyl substitution, breakdown by aromatic rings may be somewhat similar over a large molecular weight range and thus give no evidence for the observed chromatographic differences.

Methylphenanthrene Index (MPI 1) of the reservoir oil (0.59) calculates to an equivalent vitrinite reflectance of 0.75 or 1.95% (Radke and Welte, 1983) depending on whether or not peak maturity has been passed, assuming correlations for type III organic matter are also applicable to type II. This would indicate early to middle or post-peak maturity, respectively, for the oil.

5.8.3. Summary

The reservoir oil appears from regional comparisons to be a typical unaltered North Sea oil as expelled from the Kimmeridge Clay Formation. Comparison with source rock bitumens indicates a greater maturity for the oil, and Kimmeridge Clay Formation bitumens with similar attributes are found in the Late mature stage near peak hydrocarbon generation. Although fractionation during migration could be called upon to account for the differences in hydrocarbon fractions between bitumens and oil in this study, the simplest and most direct explanation consistent with the observations detailed above is that the oil was generated and expelled from the Kimmeridge Clay in a more deeply buried location near peak oil generation maturity, where bitumens with similar hydrocarbon fractions (Reitsema, 1983) are available in greater quantities. Furthermore, since the oil appears to be typical for the North Sea, it appears that rocks of the quality and maturity of those in the studied section have not yet reached oil expulsion capability.

5.9. Depletion at source rock-reservoir contacts

The source rock section under study contains three shale-sandstone contacts and the possibility of detecting and quantifying depletion approaching these contacts was the major objective of this study. The evaluation of diesel contamination, outlined earlier, concluded that the bitumen from 0.0m was highly contaminated and that from 15.8m less so, possibly affected by both depletion and contamination. This latter possibility is also supported by mass spectrometry data which show low tri-, tetra-, and pentaaromatics content and attendant very abundant mono- and diaromatics relative to other bitumens (Appendix C). This leaves the bitumen from 12.4m as the only possible uncontaminated depleted contact.

5.9.1. Liquid chromatographic evidence

Analysis by compound type and subsequent normalization to total rock indicates that the contact sample at 12.4m is actually richer in ppm hydrocarbons than the adjacent one at 10.5m, but in terms of mg/g TOC, is depleted in all four compound types (Tables B-4 and B-5, Appendix B). This is consistent with the data of Leythaeuser *et al* (1984a), which gives more realistic expulsion efficiencies when normalized to a TOC basis as previously pointed out in the chapter 'PREVIOUS INVESTIGATIONS...'.

Assuming the same organic matter type at 12.4 and 10.5m, gross expulsion efficiencies are calculated to be:

- Saturates : 52.7%
- Aromatics : 34.7%
- Resins : 55.2%
- Asphaltenes : 55.8%

However, accurate determination of organic matter subtypes was not carried out in this study, unlike those of Leythaeuser and co-workers, and admixture of inert organic matter at either depth would also greatly alter the above figures. These should therefore be regarded as rough estimates with estimated error + or - 22% expulsion for aromatics and 14% for the other 3 fractions.

5.9.2. Gas chromatographic evidence

Inspection of gas chromatograms of both saturate and aromatic fractions from 12.4 and 10.5m (Appendix C) shows clearly that depletion has taken place in both fractions, preferentially at low molecular weights, of both resolved peaks and background 'hump'. Isoprenoids are also depleted while n-alkanes are still present, ruling out biodegradation as a cause.

Since the absolute concentration of n-alkanes per unit TOC or total rock was not measured, in order to quantify expulsion it was assumed that depletion did not extend beyond nC_{35} (the heaviest n-alkane quantifiable) and that before depletion, both bitumens (12.4 and 10.5m) had identical n-alkane contents and distributions. The most and least abundant n-alkane at the depths of 12.4 and 10.5m respectively is nC_{35}, and is beyond the range of fraction cross-contamination for these 2 samples. The resulting n-alkane and isoprenoid distributions, normalized to an equal value for nC_{35} are shown in Figure 5-21. From such normalized distributions, expulsion efficiencies can be calculated for n-alkanes and isoprenoids, and these are plotted against carbon number in Figure 5-22. From this it can be seen that expulsion has been very efficient at low molecular weights, approximately 85%, and diminishes to about 50% at nC_{32}. The method of calculation forces the expulsion efficiency to 0% for nC_{35}, but in the event of actual expulsion of $nC_{35}+$ n-alkanes the calculated efficiencies will be too low, thus they can be regarded as minimums. Differences will be slight, however, except at the high molecular weight end. Interestingly, expulsion efficiencies for isoprenoids are similar to those of n-alkanes of the same molecular weight unlike the findings of Leythaeuser *et al* (1984a) for type III organic matter. This suggests that, as recognized in the chapter 'PREVIOUS INVESTIGATIONS...', original differences in isoprenoid/alkane ratios may have accounted for these findings and are fortunately not present in this study. Based on the given assumptions, overall n-alkane expulsion efficiency is 74%, which will be little

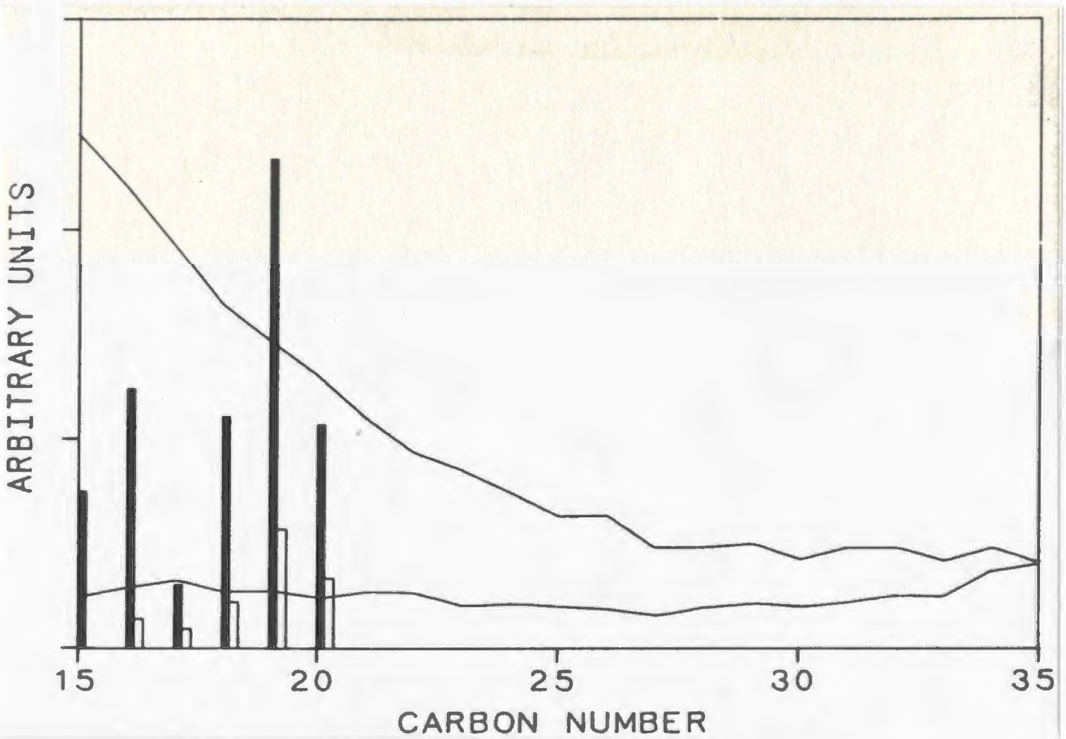


Figure 5-21: nC_{35}-normalized alkane distributions
10.5m is upper line and solid bars(isoprenoids)

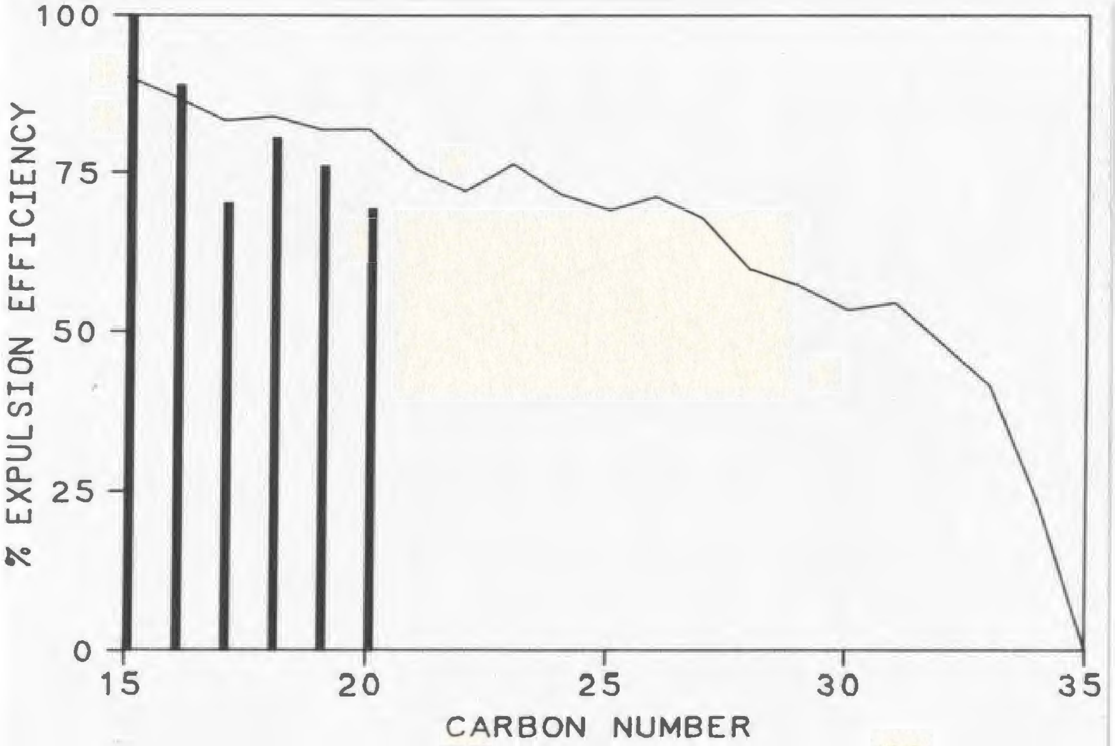


Figure 5-22: N-alkane expulsion efficiencies, 12.4m
(solid bars = isoprenoids)

affected if minor nC_{35}+ expulsion has occurred. Assuming, once again, that nC_{35} is the depletion limit and that the two samples contain similar organic matter, the normalized distribution of the expelled n-alkanes may be plotted and compared to the reservoir oil. This is presented in Figure 5-23 and it is apparent that this forms a mismatch, with the expelled distribution skewed to lower molecular weight than the oil, and considerably richer in isoprenoids, whose relative abundance is more reminiscent of the source rock bitumens. Gas chromatographic analysis of aromatics also shows loss of both 'hump' and resolved peaks at low retention times. The ratio of phenanthrene to adjacent diaromatics remains constant, indicating that depletion is molecular weight dependent rather than a function of aromaticity as in liquid chromatographic separations.

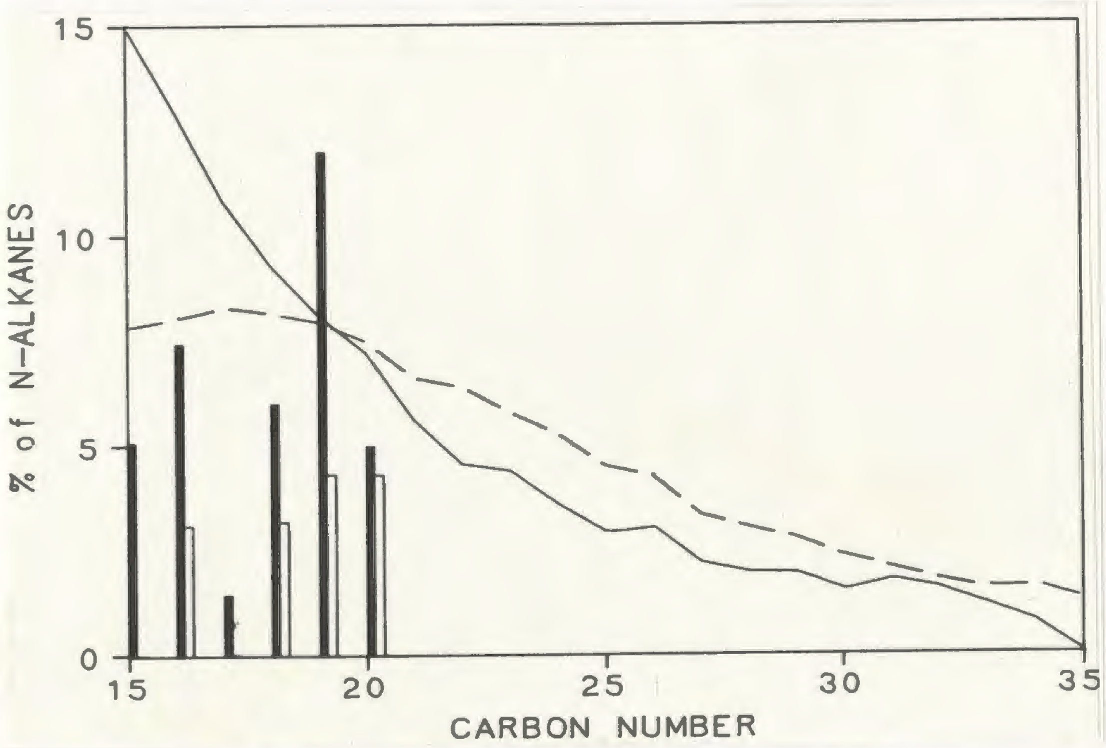


Figure 5-23: Distribution of expelled n-alkanes, 12.4m
(dashed line, open bars = reservoir oil)

5.9.3. Mass spectrometric evidence

5.9.3.1. Aromatics

Unlike n-alkanes, aromatic compound class abundances can be estimated with fair accuracy per unit TOC or as ppm by assuming volume percent equal to weight percent. Whereas the depleted sample (12.4 m) is actually greater as ppm aromatics than the undepleted (10.5 m), normalization of the aromatic hydrocarbon class abundances to TOC content produces the plot shown in Figure 5-24. Here it can be seen that depletion is very small for tetra- and pentaaromatics , approaching the experimental error and supporting the assumption of similar organic matter type. Depletion becomes progressively greater for lower aromaticity. Expulsion efficiencies, now calculated per

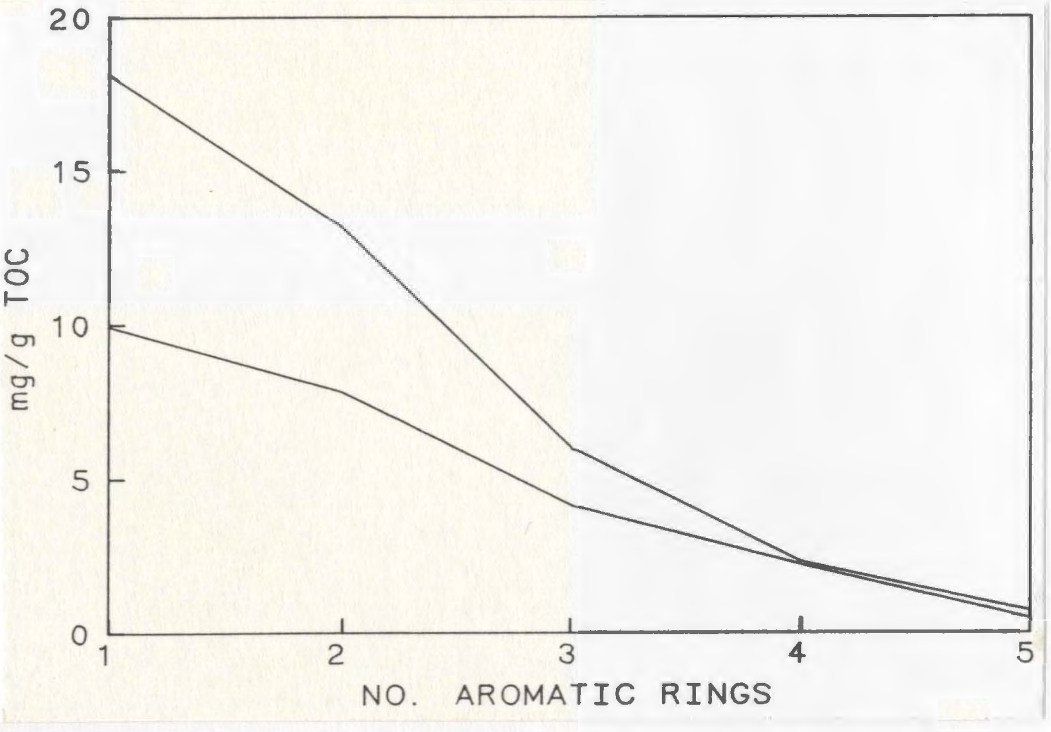


Figure 5-24: Carbon-normalized aromatics distributions (upper curve = 10.5m)

unit TOC, are plotted vs. aromaticity in Figure 5-25 and can be seen to fall from near 45% for monoaromatics to near zero for tetraaromatics. The values for tetra- and pentaaromatics may be inaccurate due to the large effects of small errors at these low abundances. Composition of expelled aromatics can be calculated from the TOC-normalized distributions, and is plotted for comparison with the reservoir oil in Figure 5-26, normalized to exclude differences in thiophene derivatives and unidentified aromatics. Correspondence is close except for tetraaromatics, but distribution by aromaticity can mask considerable differences in molecular weight which, as mentioned above, appears to be the controlling factor.

5.9.3.2. Saturates

In a manner similar to the aromatics and with the same assumptions, compound class distributions from mass spectrometry for saturate fractions are plotted in mg/g TOC in Figure 5-27. The presence of 6 ring naphthenes in the bitumen from 12.4m (lower curve) is due to choice of calibration matrix, which is dependent on average carbon number (ASTM 2786), thus this compound class is not directly comparable between the two depths. Neglecting the 6 ring naphthenes, expulsion efficiencies were calculated as for the aromatics and are plotted on Figure 5-28. They can be seen to be approximately equal, at about 55%, from 0 to 4 rings, decreasing slightly at 5 rings and forced to 0% for 6 ring naphthenes. The low value (60.7%) for acyclic paraffins is much lower than the 74% minimum calculated for bulk n-alkanes from GC data. This difference could be due

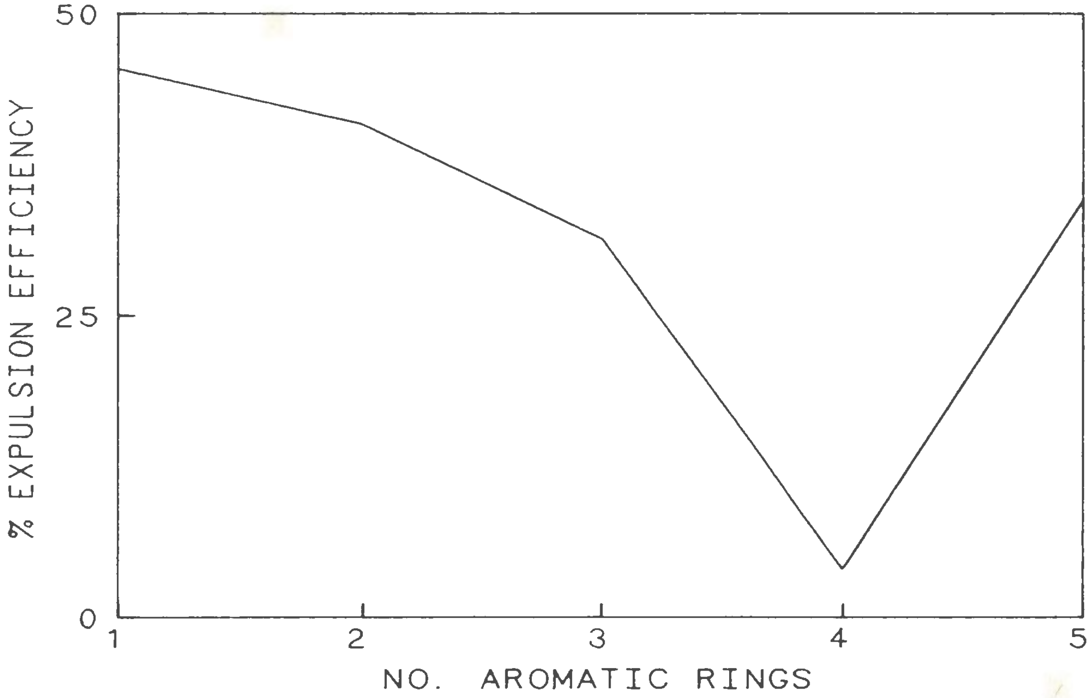


Figure 5-25: Expulsion efficiencies, aromatics fraction, 12.4m

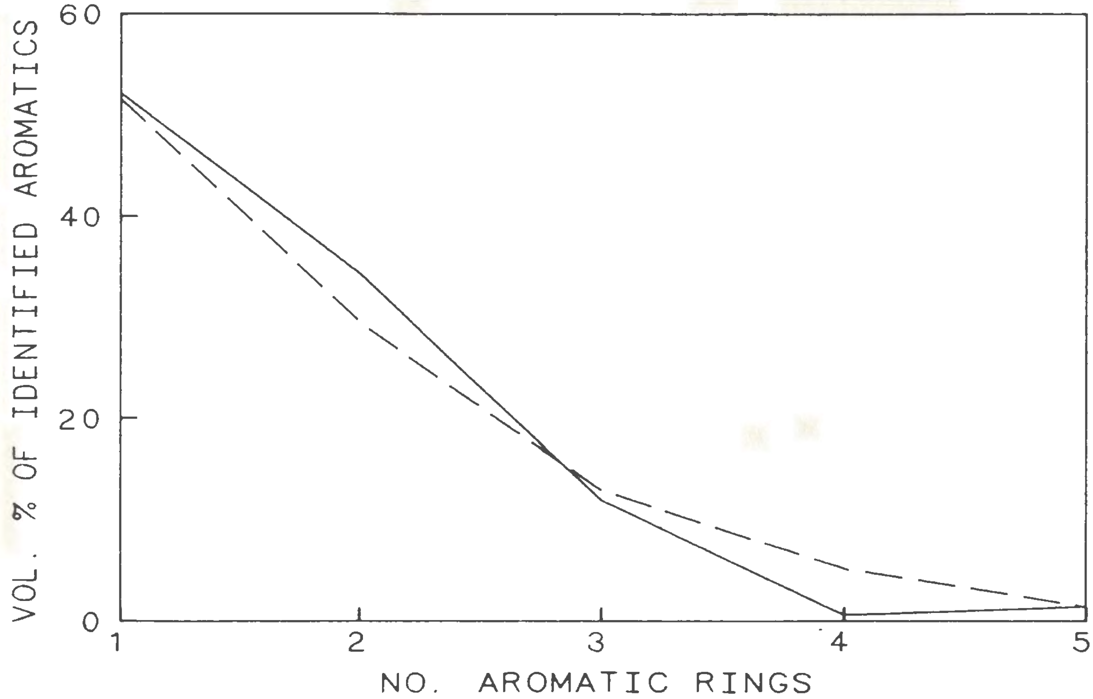


Figure 5-26: Distribution of expelled aromatics, 12.4m
(dashed line is reservoir oil)

to lower expulsion efficiency of isoalkanes, but since isoprenoids appear to be expelled as easily as n-alkanes of similar molecular weight, this explanation can only hold if isoalkanes as a group are both less expellable and of higher average molecular weight

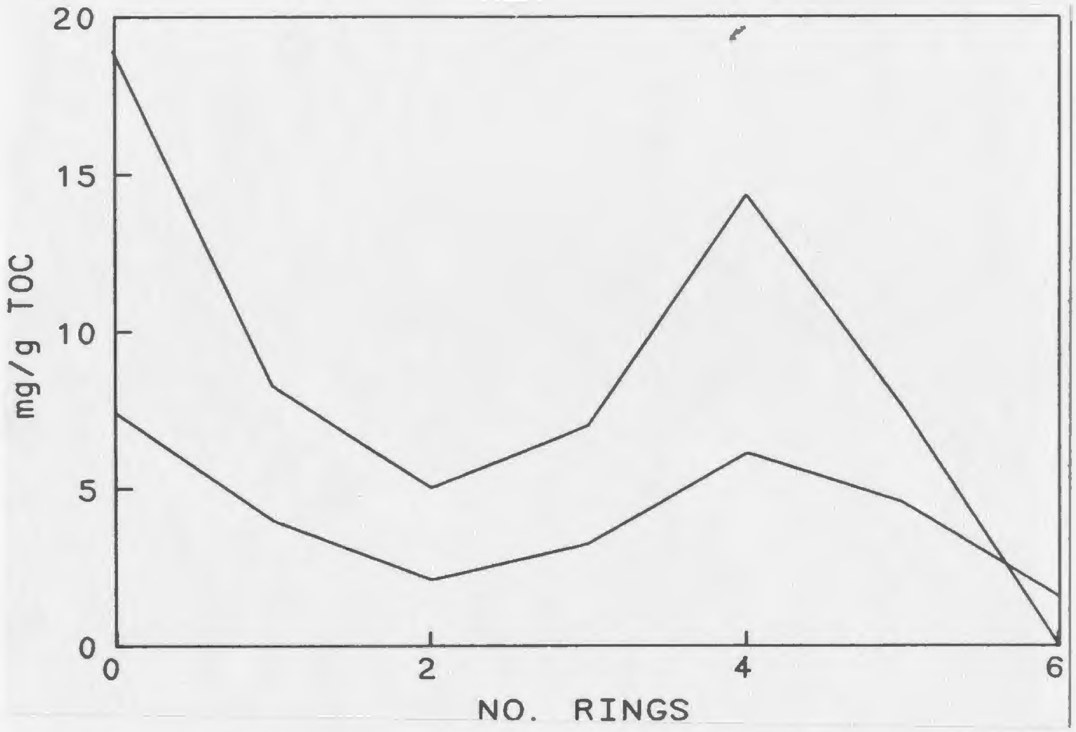


Figure 5-27: Carbon-normalized saturates distributions (Upper curve = 10.5m)

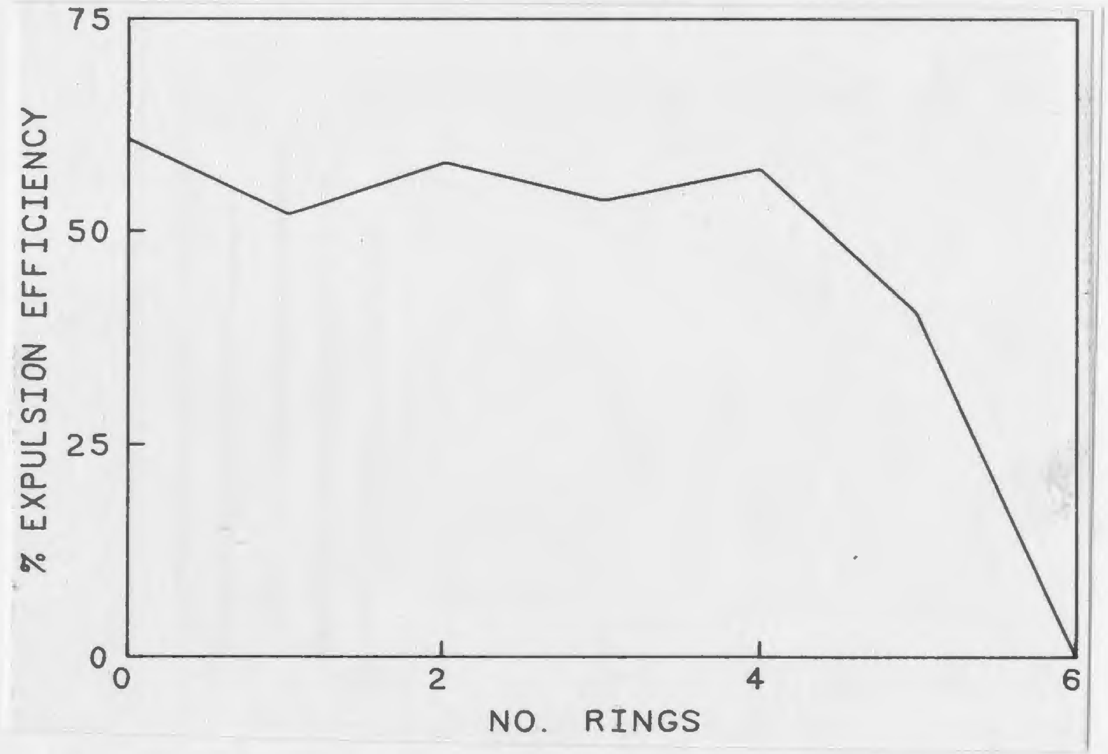


Figure 5-28: Expulsion efficiencies, saturates fraction, 12.4m

than n-alkanes. This possibility is untested, but certainly not true for identifiable isoprenoids. The calculated compound class composition of the expelled saturates is plotted along with the reservoir oil in Figure 5-29. The same discrepancy as previously

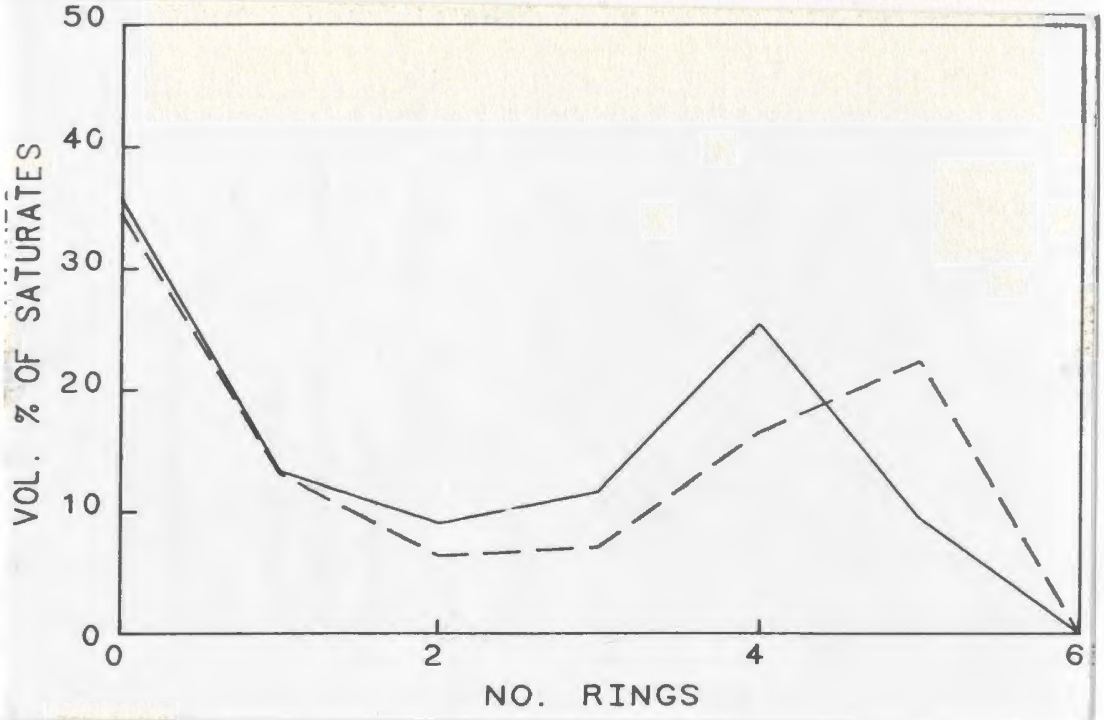


Figure 5-29: Distribution of expelled saturates, 12.4m (dashed line is reservoir oil)

noted between bitumens and oil, namely the 5 ring mode in the latter, is also present here, suggesting that the expelled saturates, like the n-alkanes, are more similar to other bitumens than to the oil. However, the discrepancy between the acyclic paraffin expulsion efficiency calculated from the mass spectrometry results and that from the gas chromatography of n-alkanes and isoprenoids can now be added to the evidence previously presented which suggests that the saturate fraction mass spectrometry data are in error, and thus conclusions regarding depletion drawn from these results are considered suspect.

5.9.4. Discussion

The bitumen depletion at source rock-reservoir contacts sought in this study was found at one of three such contacts, the remaining two being contaminated by diesel oil, possibly obscuring similar effects. This appears likely from gas chromatography and aromatics mass spectrometry data for the contact at 15.8m. Depletion at 12.4m extends less than 1.9m from the contact and is estimated to total 48.5 mgHC/g TOC, from a source rock having generated 107.4 mgHC/g TOC. Comparison with previous contact migration studies in Table 2-1 places this studied section highest in hydrocarbon generation, highest in maximum depletion, and lowest in extent of depletion.

As estimated from compound type abundances, aromatics are expelled less readily than saturates. That this is not due to polarity from aromatic rings is shown by similar phenanthrene/(C3 biphenyl + C1 fluorene) ratios in depleted and undepleted aromatic fractions. A dependence of expulsion on molecular weight could account for this reduced depletion if aromatics are of higher average molecular weight than saturates, but resins and asphaltenes also show greater depletion than aromatics. However, as can be seen in Table B-5, carbon-normalized yields of bitumen fractions are quite variable, even for constant organic matter type, and this greatly influences expulsion calculations through the choice of 'undepleted' end member. Use of an average uncontaminated bitumen composition instead of that from 10.5m results in similar expulsion efficiencies for saturates and aromatics, but with resins and asphaltenes much more depleted.

Inspection of gas chromatograms of saturate and aromatic fractions from 12.4 and 10.5 m (Appendix C) shows depletion increasing with decreasing molecular weight for both fractions. This is similar to depletion observed by Leythaeuser *et al* (1984a) and is in rocks of similar low maturity. Also, like this previous study, realistic depletion is observed on a carbon-normalized rather than a rock-normalized basis, indicating lack of bitumen redistribution into source rock porosity. Dependence of depletion on molecular weight is characteristic of migration by diffusion or gas phase solution, as reviewed in the chapter 'INTRODUCTION', and its presence at low maturities, masked by bitumen formation near peak oil generation (Leythaeuser *et al* (1984b), and its situation at source rock-reservoir contacts indicates the former mechanism to be operative.

Diffusion should be most active where concentration gradients are highest (contacts) and when reservoir water flux is highest, since reservoir pore water is the most effective sink for diffusing organic compounds. This will be at very shallow depths where compaction dewatering is most active. On the other hand, *extent* of diffusion should increase with time and water loss, thus depth, until masked by thermal generation of bitumen. Depletion from diffusion should thus be evident at all uncontaminated source rock-reservoir contacts above oil generation depths.

The gas chromatograms of the fractions from 12.4m suggest depletion of low molecular weight compounds still present at 10.5m and possibly generated in the early stages of oil generation reached relatively recently by these rocks. This suggests a recent age for the diffusion. However, this may only apply to the evidence of diffusion, pre-existing low molecular weight compounds being largely diluted. Also, diffusion related loss, at a much earlier stage, of more water soluble precursors of the hydrocarbons studied may produce the observed effects and account for losses of resins and asphaltenes too, if these are not merely artifacts of sample variability as discussed above. In addition, back diffusion of reservoir oil into the source rock was not observed, also suggesting a lack of relatively recent diffusion.

Implications for primary oil migration of such diffusive expulsion are minimal. Composition of 'expelled oil' back-calculated from GC and MS data as previously carried out has only a superficial resemblance to actual crude oil, and fails to duplicate the close similarities observed between crude oil hydrocarbon fractions and those of their source rock bitumens at peak maturity. Since diffusion will result in bitumen concentrations in reservoir rocks below those of source rocks, diffuse bitumen will be more difficult to accumulate than source rock bitumen and hence diffusion hinders effective primary migration. However, the amount of oil, or potential oil, lost is very small, extending less than (and possibly much less than) 1.9m in the studied section. This can only become significant in a source rock finely interbedded with reservoir lithologies, as few are, having been deposited in what must be the last word in low-energy environments. Any such rocks can be expected to lose their effectiveness as oil sources rather than have it enhanced by the permeable interbeds.

5.10. Conclusions

Study of the bitumens (and kerogens) from shale samples from throughout the cored section reveal that:

- Source rock quality rates from minor to prolific, depending on the classification, but that of Powell (1978), which uses less arbitrary limits, rates the bulk as intermediate oil sources at less than peak maturity.
- A strong concensus of maturity indicators indicates the section to be in the early stages of oil generation, just within the oil generation 'window'.
- Organic matter is of type II, originating mainly from planktonic sources and deposited in an anoxic marine environment with subsequent anaerobic biodegradation.
- Compound type bitumen composition is more constant on a carbon-normalized than on a rock-normalized basis, indicating lack of bitumen redistribution into porosity.

Study of the reservoir oil using the same techniques concludes that:

- The oil is a very typical North Sea oil, classed as Paraffinic-Naphthenic or possibly Paraffinic, typical of clastic source rocks containing low sulfur marine organic matter.
- Chemical properties of the oil match those of Kimmeridge Clay Formation bitumens at peak oil generation maturity, not those of the overlying section. It is concluded that the oil has been generated from the same source rock, but at higher maturity, and has accumulated in its present location after secondary migration.
- N-alkane envelopes of the bitumens and oil correspond well, indicating that alkanes generated between early and peak maturity levels have essentially the same distribution, and extensive cracking of C-C bonds in straight chains thus takes place primarily beyond peak maturity.

Depletion characteristic of extensive primary migration was not found in the section studied. Since unaltered North Sea oils, in general, resemble source rock bitumens at peak oil generation maturity, it is concluded that at least for the Kimmeridge Clay Formation and possibly for most other source rocks, oil migration lags considerably the onset of oil generation, and has not begun at the maturity levels of the source rocks in the section studied.

Molecular weight-dependent depletion was detected at the single uncontaminated source rock-reservoir contact and resembles that expected from molecular diffusion, either of presently existing compounds or their earlier precursors. It appears to play no part in primary migration, but rather lowers source rock potential in the immediate vicinity of reservoir contacts.

Chapter 6
STABLE CARBON ISOTOPES

Stable carbon isotope ratios($\delta^{13}C$ vs PDB standard) were measured on all rock samples, extracted and unextracted, and on all oil and bitumen fractions as outlined in the chapter 'ANALYTICAL METHODS', and these are tabulated in Appendix B, Table B-7

For oil and bitumen fractions, standard deviations averaged 0.11 per mil for samples repeated and worst case repeatability difference was 0.29 $^{o}/_{oo}$.

6.1. Environmental interpretation

Organic carbon in recent sediments has isotope ratios clustering about and varying between approximately -18 $^{o}/_{oo}$ and -23 $^{o}/_{oo}$ for marine and terrestrial end members, respectively (Sackett and Thompson, 1963) and this relationship has frequently been used simplistically to deduce ancient environments. Although isotope ratios of land plants and coals cluster around -25 $^{o}/_{oo}$ since the Carboniferous (Degens, 1969), secular variations are apparent in those of kerogens and crude oils (Degens, 1969, and Stahl, 1977) with most of these in the pre-Tertiary being isotopically lighter than contemporaneous land plants. Pre-Devonian kerogens and crude oils are among the lightest and are exclusively of marine origin owing to the non-existence of terrestrial life in this period. All of this has been noted by Arthur *et al* (1985) who suggest that the present terrestrial-marine carbon isotope ratios and their order of lightness are only a post Oligocene phenomenon. They attribute this to, among other causes, a CO_2 source largely from bacterial oxidation of organic matter rather than atmospheric CO_2, encouraged by the relative abundance of shallow seas pprior to the Tertiary. However as Schoell (1984) states:'There is no current concept to explain the isotopic variability in kerogens'.

Sofer (1984), in an isotopic study of 339 crude oils, came to a similar conclusion, namely that isotopic differences between whole oils cannot distinguish terrestrial from marine sources. His study went further, however, and isotope ratios of isolated saturate and aromatic fractions were measured and related to oil source. Source was assumed as terrestrial for 'waxy' oils and marine for non-waxy oils based on saturate fraction gas chromatograms, and thus the resulting discrimination based on isotopic data alone can only be as good as the chromatogram interpretation. In addition, the existence of marine waxy oils, such as in the Silurian of the Michigan basin (Powell *et al*, 1984) will also hinder accurate source determination using this approach.

According to Sofer (1984) discrimination between waxy and non-waxy crude oils isotopically is best using a 'canonical variable'(CV in Table B-7) calculated as:

$$CV=-2.53\delta^{13}C_{sat}+2.22\delta^{13}C_{aro}-11.65$$

where waxy oils generally have a CV larger than and non-waxy oils less than 0.47. Even using this discriminant, approximately 12% of the oils were misclassified. This was improved by crossplotting CV against 'Quadratic Coefficient' (QC in Table B-6), a parameter calculated from alkane distribution data, independent of isotope ratios, following the method of Sofer (1984).

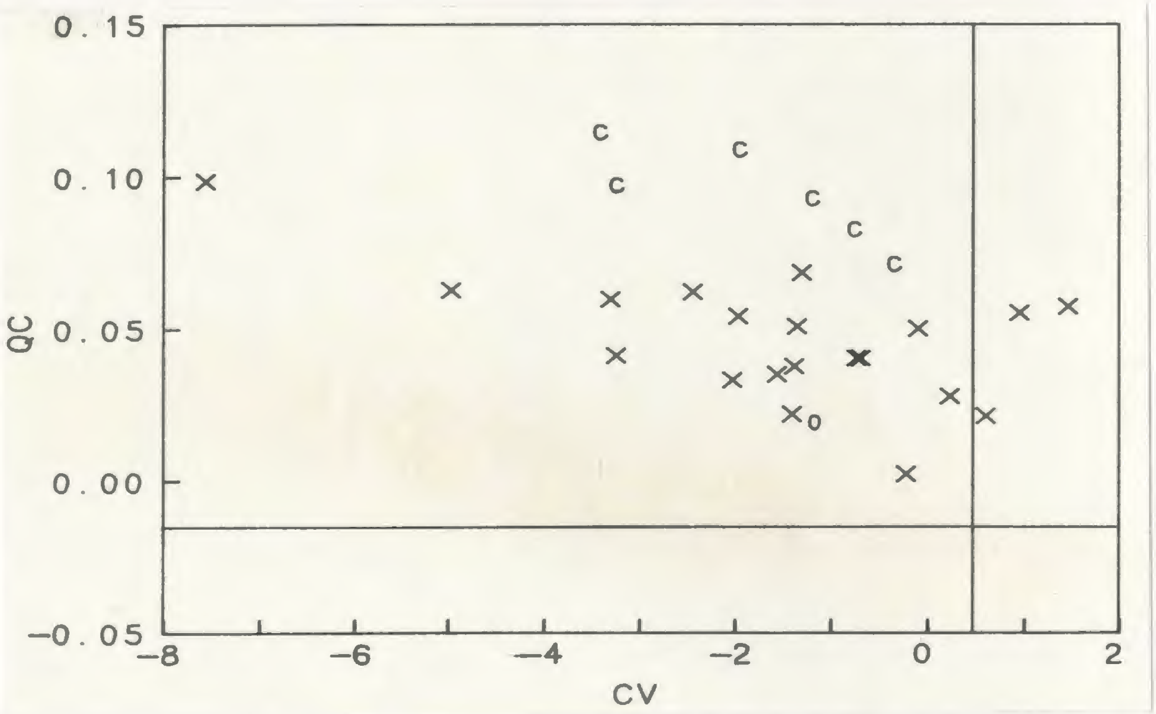


Figure 6-1: QC vs CV (after Sofer,1984)

Figure 6-1 shows a crossplot of QC vs CV for the oil(O), contaminated bitumens(C) and uncontaminated bitumens(X) from this study. A CV of 0.47 and QC of -0.015 are used to divide the plot into 4 quadrants following Sofer (1984) and it can be seen that the reservoir oil lies in the northwest quadrant corresponding to oils of marine source (non-waxy). Although the study of Sofer (1984) involved only crude oils, the assumption that saturate and aromatic fractions of bitumens migrate to help form reservoir oils without isotopic fractionation allows the same relationship to be used to assess source rock organic matter type from bitumens alone. Bitumens from this study plot mostly within the same quadrant as the oil, with 3 in the northeast quadrant representing, according to Sofer, very mature terrestrial sources. Since all the bitumens must have similar maturity, and this was determined to be immature as discussed in the chapter 'SOURCE ROCK BITUMENS', the interpretation of very mature terrestrial is doubtful, and mature and marginally mature terrestrial sources should plot in the southeast quadrant. These 3 bitumens are thus isotopically similar to terrestrial sources, but have alkane distributions of marine sources. This situation could arise from an unusual type of terrestrial organic matter, from marine organic matter isotopically outside the range of those investigated by Sofer, or simply from the fact that these relationships were developed for crude oils rather than immature bitumens. However, the fractions investigated (saturate and aromatic) should, for these relationships to apply strictly, be isolated using the method of Sofer, which was not that used in this study. A crude oil used for procedure trials prior to this study gave CVs ranging from -1.02 to 2.25 using identical isotope ratio measurement procedures and 3 different liquid chromatographic separation procedures, illustrating the sensitivity of this variable to the isolation method employed (Table 6-1).

Table 6-1: Sensitivity of CV calculation to LC method

LC METHOD	$\delta^{13}C$ Sat.	$\delta^{13}C$ Aro.	CV
A	-26.9	-24.4	2.25
B	-25.7	-24.5	-1.02
C	-26.3	-24.2	1.165

The 6 bitumens believed to be contaminated by diesel oil as outlined in the chapter 'SOURCE ROCK BITUMENS' plot in the same quadrant as the bulk of the other bitumens, with similar CVs and higher QCs due to enrichment in light n-alkanes. This indicates contamination by diesel oil isotopically similar to the bitumens themselves.

Isotope ratios of bitumen fractions and kerogen show no apparent relationship with depth or TOC content in this study, but a general increase in Rock-Eval Hydrogen Index (HI) with increasing $\delta^{13}C$ of kerogen (Figure 6-2) for the limited number of samples so analyzed may indicate a more prolific organic matter type with less negative isotope ratio. Cooper and Barnard (1984) subdivide Kimmeridge Clay kerogens into macerals with isotope ratios varying from -22 to -31 $^{o}/_{oo}$, all from marine environments, but details of how these ratios are obtained are not given. They find this formation to be dominated by anoxic marine 'Algal Sapropel' and open marine 'Waxy Sapropel' with isotope ratios of -26 and -31 $^{o}/_{oo}$ respectively. This interpretation suggests that kerogens from this study may be intermediate between these end members, with the algal sapropel having a greater generation potential.

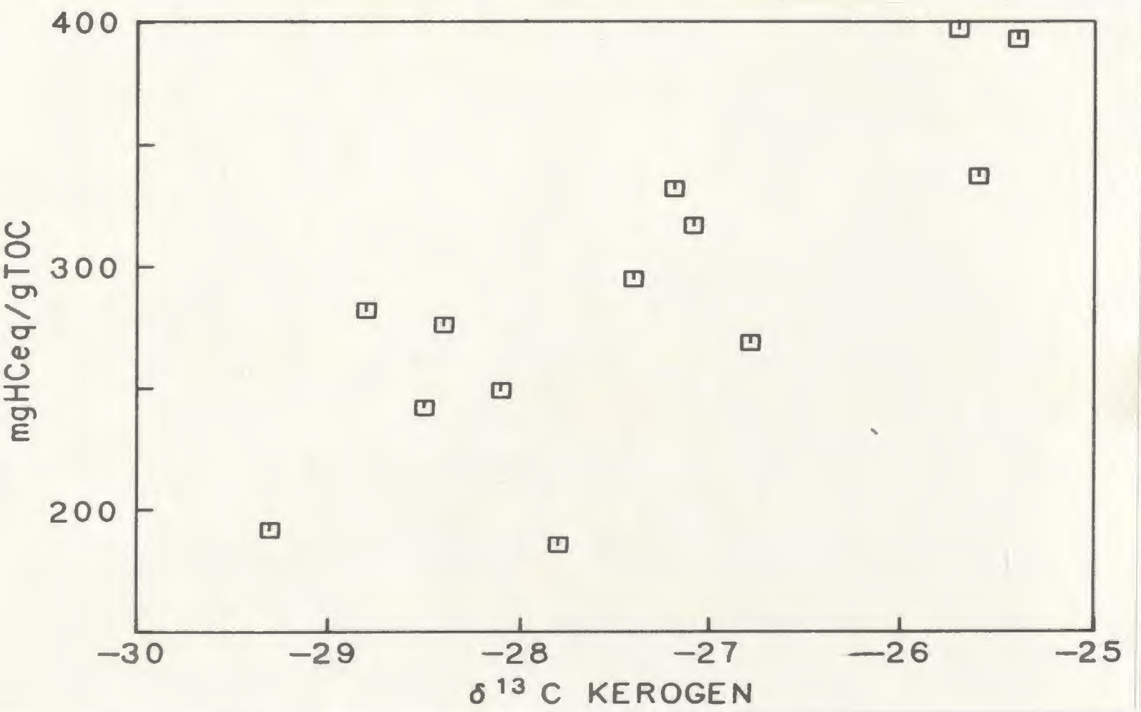


Figure 6-2: HI vs δ^{13}C kerogen

6.2. Oil-source correlation

The lack of a good explanation of isotopic variability in oils and kerogens mentioned previously has led to much isotopic data being used for oil-source correlation only, and a widely used method of this nature is that presented by Stahl (1978). Using this approach, isotope ratios are measured for saturate, aromatic, resin, and asphaltene fractions of a crude oil and plotted as in Figures 6-3, 6-4, and 6-5. A line is then fitted to this data (dashed in Figures 6-3 to 6-5) and extrapolated (downward in Figures 6-3 to 6-5) to give an estimate of the isotope ratio of the parent 'kerogen' (X). Since Stahl (1978) worked with unextracted rocks, δ^{13}C TOC values from Appendix B, Table B-7 are used herein.

Following Stahl (1978), a least squares straight line fit is made to the oil fraction data. However, in making such a fit, one variable must be selected as independent, for the resulting X vs Y or Y vs X straight lines differ greatly owing to deviations from the lines being minimized in either of 2 perpendicular directions. For isotopic measurements it must be assumed that uncertainty in isotope ratio is greater than that due to incorrect choice of the discrete fraction to be analyzed, for which the latter cannot be compensated for statistically. Thus δ^{13}C must be taken as the Y variable for fitting of a straight line regardless of it having been plotted on the horizontal axis by Stahl. This has been done for all plots in Figures 6-3, 6-4, and 6-5.

Stahl (1978) has found, using a calibration set of 6 corresponding oils and source rocks,

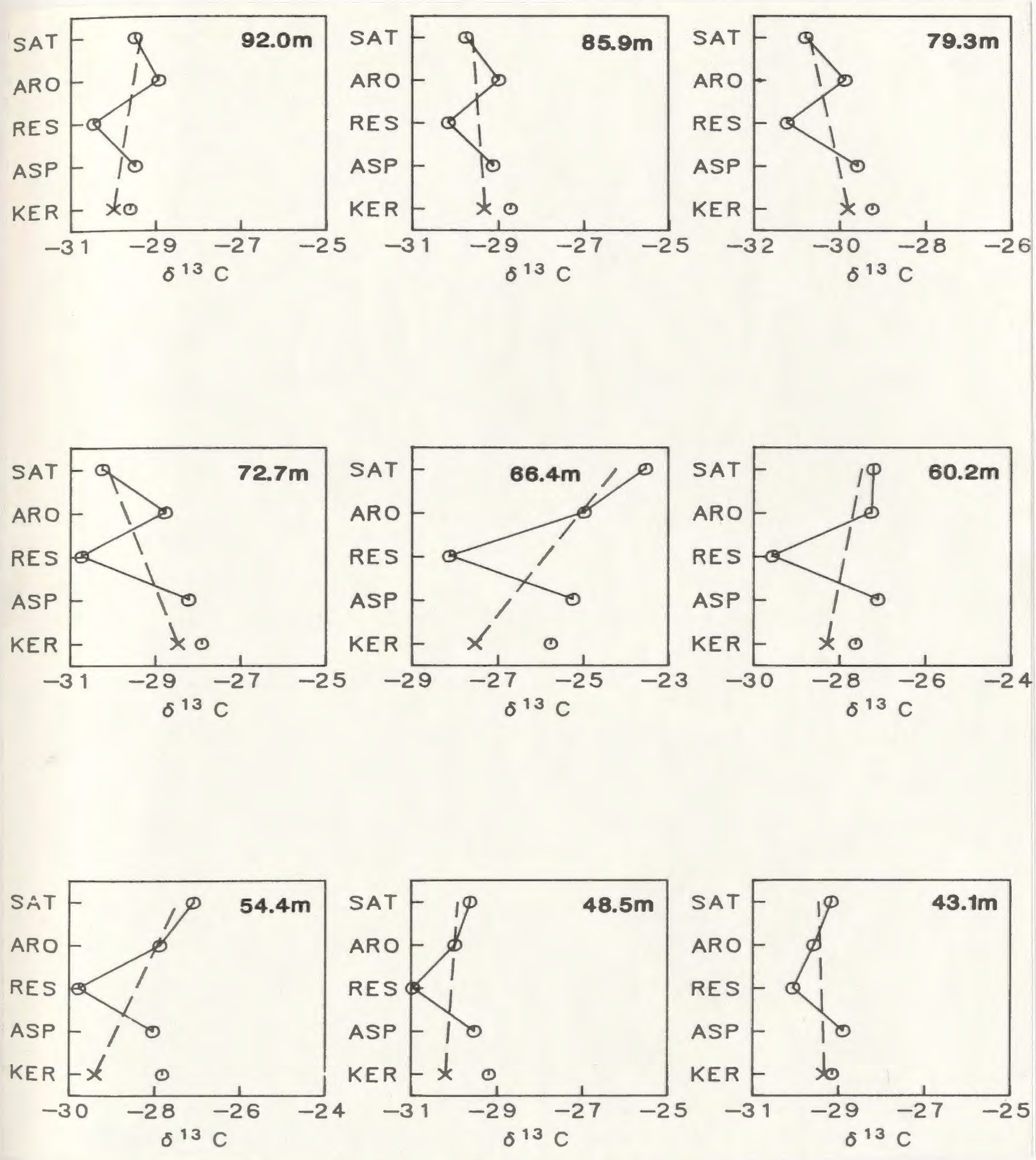


Figure 6-3: Isotopic type-curves
(after Stahl, 1978)

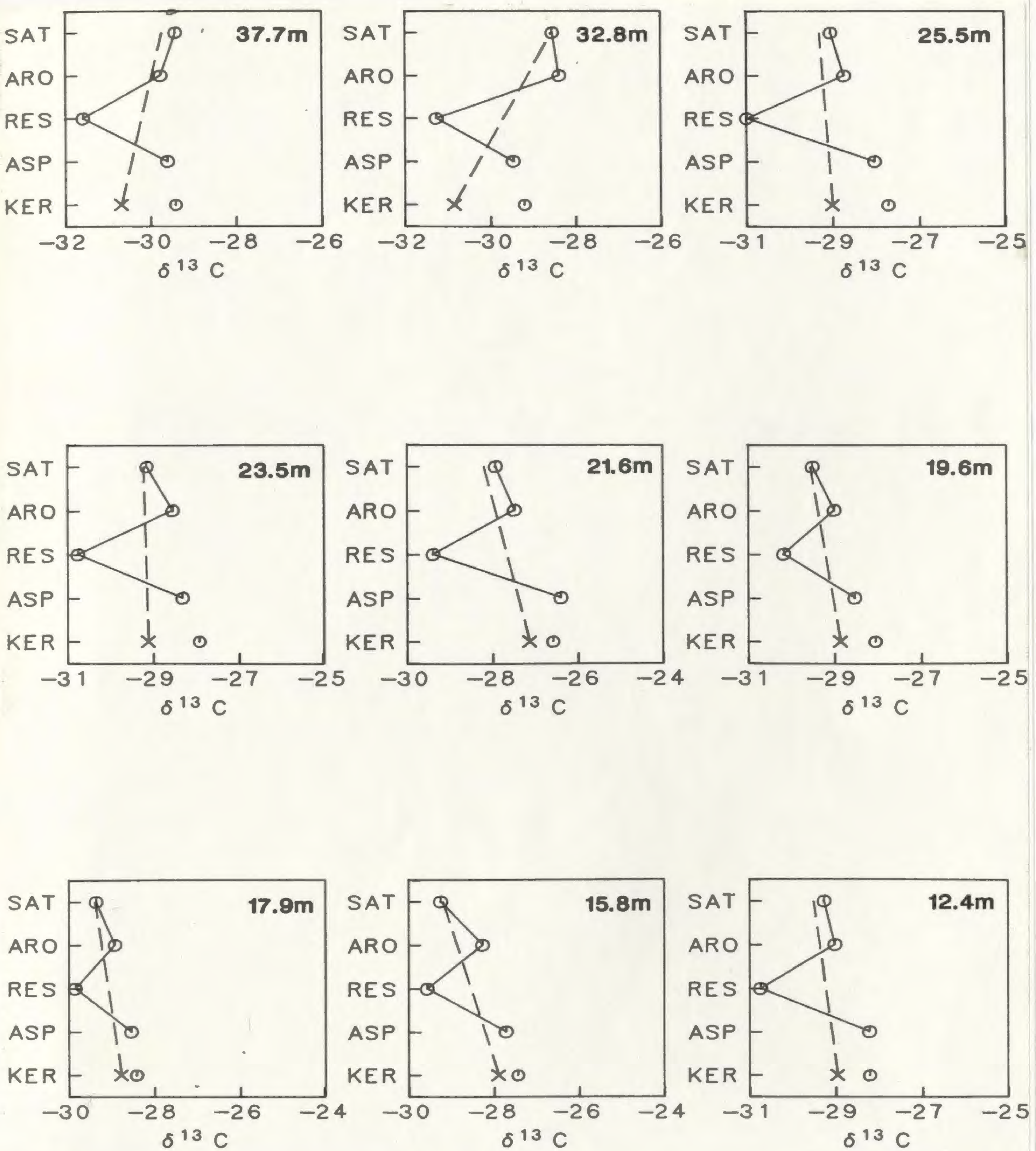


Figure 6-4: Isotopic type-curves
(after Stahl, 1978)

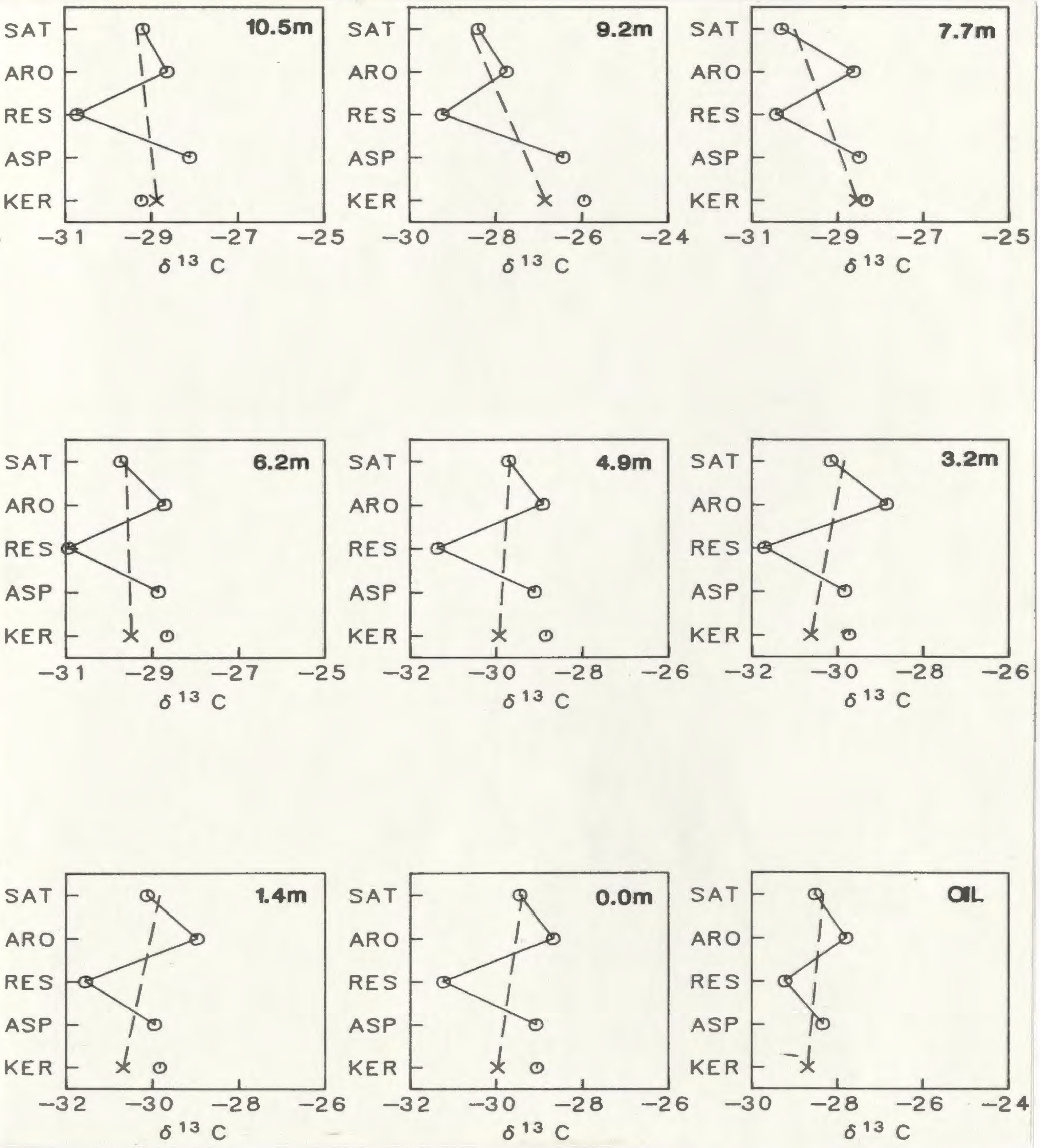


Figure 6-5: Isotopic type-curves
(after Stahl, 1978)

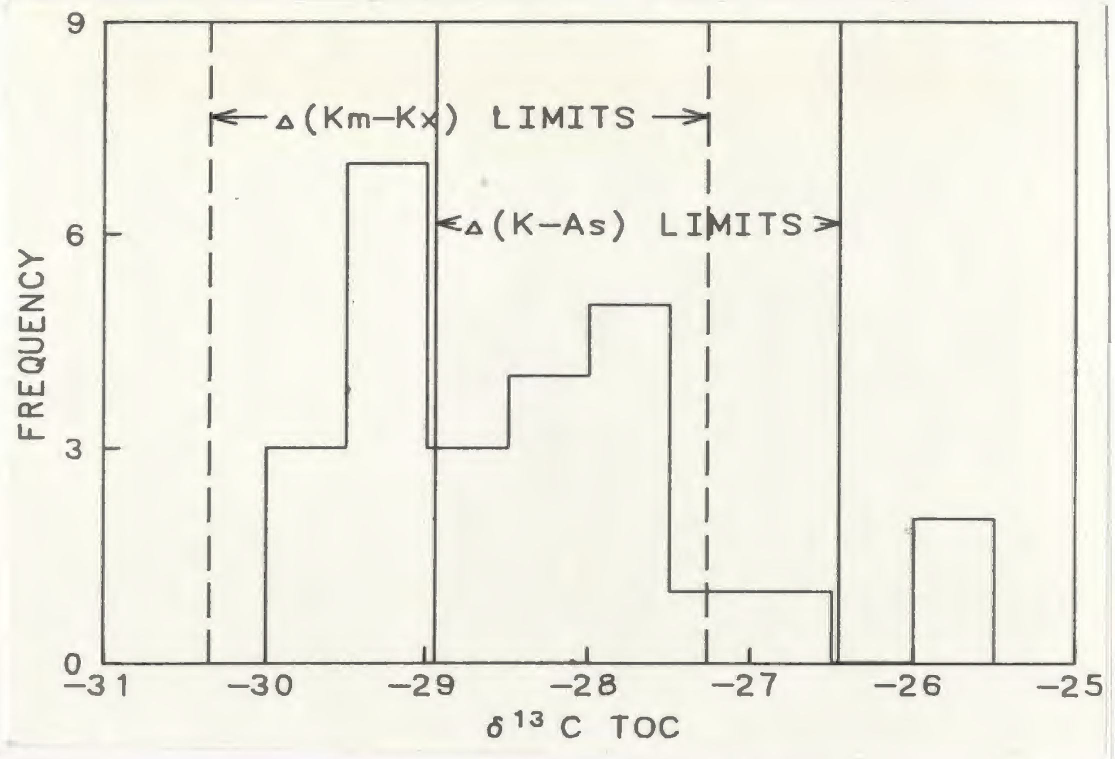


Figure 6-6: Isotopic oil-source correlation

that the extrapolated 'kerogen' (in Stahl's terminology) isotope ratio obtained as above (Kx) exceeded the actual source rock value (Km) by an average of 0.5 °/$_{oo}$, with a standard deviation of 0.7 °/$_{oo}$, and then suggested that this average, plus or minus 2σ, can be used as a range of possible source 'kerogens' for the oil in question. Using $\delta^{13}C$ as the dependent variable as outlined above, but the same set of 6 calibration pairs results in a range of 0.12 plus or minus 1.54 °/$_{oo}$ (σ=0.77). Thus the reservoir oil for this study (Figure 6-5) gives an extrapolated 'kerogen' isotope ratio of -28.7 °/$_{oo}$ (Table B-7) and a corresponding range of possible source 'kerogen' isotope ratios of -30.35 to -27.27 °/$_{oo}$. This range is that between the 2 vertical dashed lines in Figure 6-6 and the histogram shows that the bulk (88%) of the measured 'kerogens' lie between these 2 limits, indicating a positive oil-source correlation. The fact that the organic matter in this study was determined as immature to perhaps marginally mature, in spite of the isotopic correlation, may indicate that the same formation at higher oil expulsion maturity may not differ significantly isotopically. Also, as previously, it must be stressed that a correlation such as this should ideally be carried out using the same liquid chromatographic procedure as Stahl (1978) and this was not the case in this study. In general, for crude oil fractions, $\delta^{13}C$ increases from saturates to asphaltenes in the order plotted by Stahl, and the very light isotope ratios obtained for resins in this study may be due to the separation procedure selected.

In addition to extrapolated 'kerogen' values, Stahl (1978) also found from his calibration set that $\delta^{13}C$ of source rock 'kerogen' exceeded that of the asphaltenes of expelled crude oils by an average of 0.64 °/$_{oo}$ with a standard deviation of 0.62 °/$_{oo}$. For the crude oil of this study, this would correspond to a range of -28.94 to -26.46 $^{o}/_{oo}$ for potential source 'kerogens', lying between the solid vertical lines in Figure 6-6. In this instance, a significant portion (46%) of the 'kerogens' lie outside this range, and the correlation is much more uncertain than with extrapolated values as above. This could be due to differences in asphaltene separation between this study and Stahl (1978), differences between these immature 'kerogens' and those expelling oil, inadequacy of the calibration set of Stahl, or possibly oil expulsion from selected levels in source rocks. The last alternative seems unlikely in light of the much better isotopic correlation using extrapolated 'kerogen' values above.

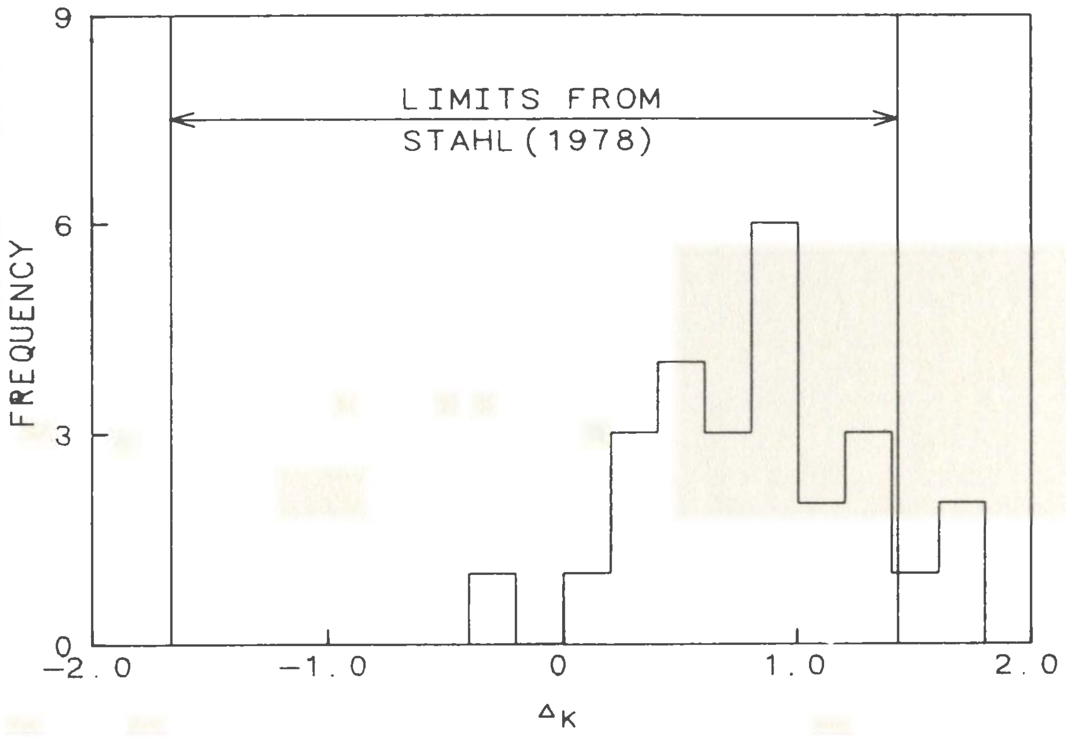


Figure 6-7: Isotopic bitumen-source correlation (using Km-Kx)

As with the method of Sofer (1984), bitumens from this study can be assumed to be similar isotopically to oils expelled from similar kerogens at expulsion maturity, and this allows use of the present study as a calibration set to check the validity of the 6 oil-source rock pairs of Stahl (1978). Plots of all bitumen fraction isotope ratios similar to those of the crude oils of Stahl and that of this study, are shown in Figures 6-3 to 6-5, with extrapolated 'kerogen' ratios plotted as Xs and actual measured ratios of TOC as circles. Figure 6-7 shows the Km-Kx differences as a histogram along with the limits of this ΔK from Stahl (1978) for a positive correlation (after re-determination with alternative least squares fit). The bulk of the bitumens (88%) can be seen to lie within the limits, lending support to the values of Stahl. The 3 bitumens outside the limits (66.4m, 54.4m, and 32.8m) are all ones with anomalously light resin fractions. Similarly in Figure 6-8,

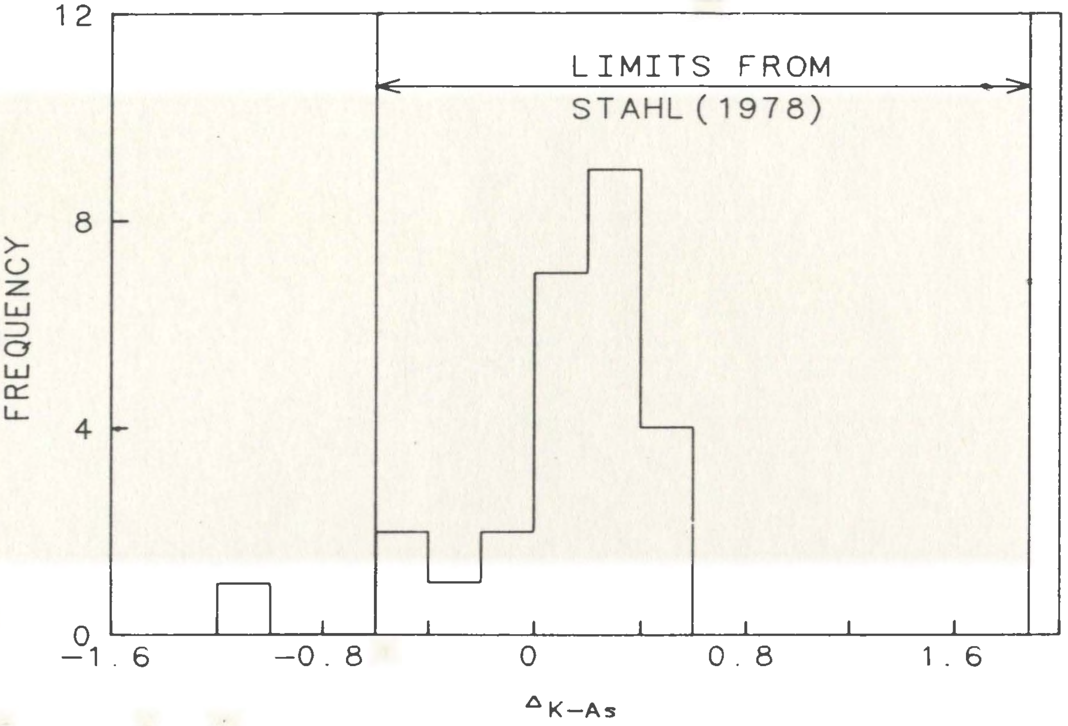


Figure 6-8: Isotopic bitumen-source correlation
(using Km-As)

'kerogen'-asphaltene isotope ratio differences for the bitumens are plotted as a histogram and again the bulk (96%) plot within the limits of Stahl.

Both of these 'Bitumen-Source Rock Correlations' suggest that the limits set by Stahl (1978) are adequate, and more importantly, that the bitumens are indigenous, isotopically uncontaminated, and show no evidence of migration <u>into</u> the organic matter studied. In addition, the close correspondence of the bitumen isotope ratios to those of the TOC required for positive correlation using this method implies that crude oils are not derived from an isotopically light 'lipid' fraction in otherwise isotopically heavy organic matter (Silverman, 1971).

6.3. Conclusions

The range of isotope ratios for the oil, bitumen fractions and organic matter in this study is typical of Jurassic oils in general (Stahl, 1977) and North Sea oils and Kimmeridge Clay source rocks in particular (Cooper and Barnard, 1984). Using isotopic relationships developed by Sofer (1984), the oil is inferred to have a marine source, similar to the source rock bitumens analyzed, and in keeping with conclusions from the chapter 'SOURCE ROCK BITUMENS', drawn from pyrolysis and microscopy.

Correlations developed by Stahl (1978) indicate a positive oil-source correlation, although this may be affected by choice of liquid chromatographic separation method, and at any rate, only one potential source was considered. The same correlations applied to bitumen fractions also came up positive, indicating bitumens to be indigenous, with no isotopic evidence of migration into the source rock samples, and diesel contamination previously diagnosed being therefore isotopically similar to the bitumens.

Chapter 7
SUMMARY AND CONCLUSIONS

7.1. Reservoir oil

From regional comparison, the reservoir oil is a typical North Sea crude and correlates well with Kimmeridge Clay bitumens of near peak oil generation maturity. Correlation with the bitumens studied is not as good and it is concluded that the oil is more mature than the overlying sampled section of this formation. The oil has isotopic characteristics typical of a marine source and correlates well isotopically with the sampled section.

7.2. Source rock

Consideration of North Sea geology and geochemistry shows the Kimmeridge Clay Formation to be the only major source rock for North Sea oils. The section of this formation studied contained Type II organic matter, with possibly a slight contribution from Type III, and had marine isotopic characteristics. Maturity was evaluated by a combination of 10 indicators of varying reliability, but a concensus of early oil window maturity emerged, with some indicators including this in a wider maturity range. Despite this relatively low maturity, source rock samples rated from 'minor' to 'prolific' using several classification schemes, with the bulk ranging from 'good' to 'very good'. Also despite low maturity, isotopic correlation between oil and source rock was positive, as mentioned above.

7.3. Migration

7.3.1. Primary migration

The poor correlation between reservoir oil and source rock in this study indicates that in spite of the short migration path available, either primary migration has not taken place or it has been very minor and the resulting oil greatly diluted by crude from a deeper source rock section near peak maturity. The fact that, in the North Sea, oils of similar maturity to the bitumens of this study are very rare supports the conclusion that no migration has occurred. Additional confirmation can be had from isotopic data which indicate that the bitumens are indigenous, with no evidence of a downward progressive shift in the bitumen components to lower levels as migration progresses. In contrast to what was sought, therefore, evidence of primary migration from this study is of a negative nature.

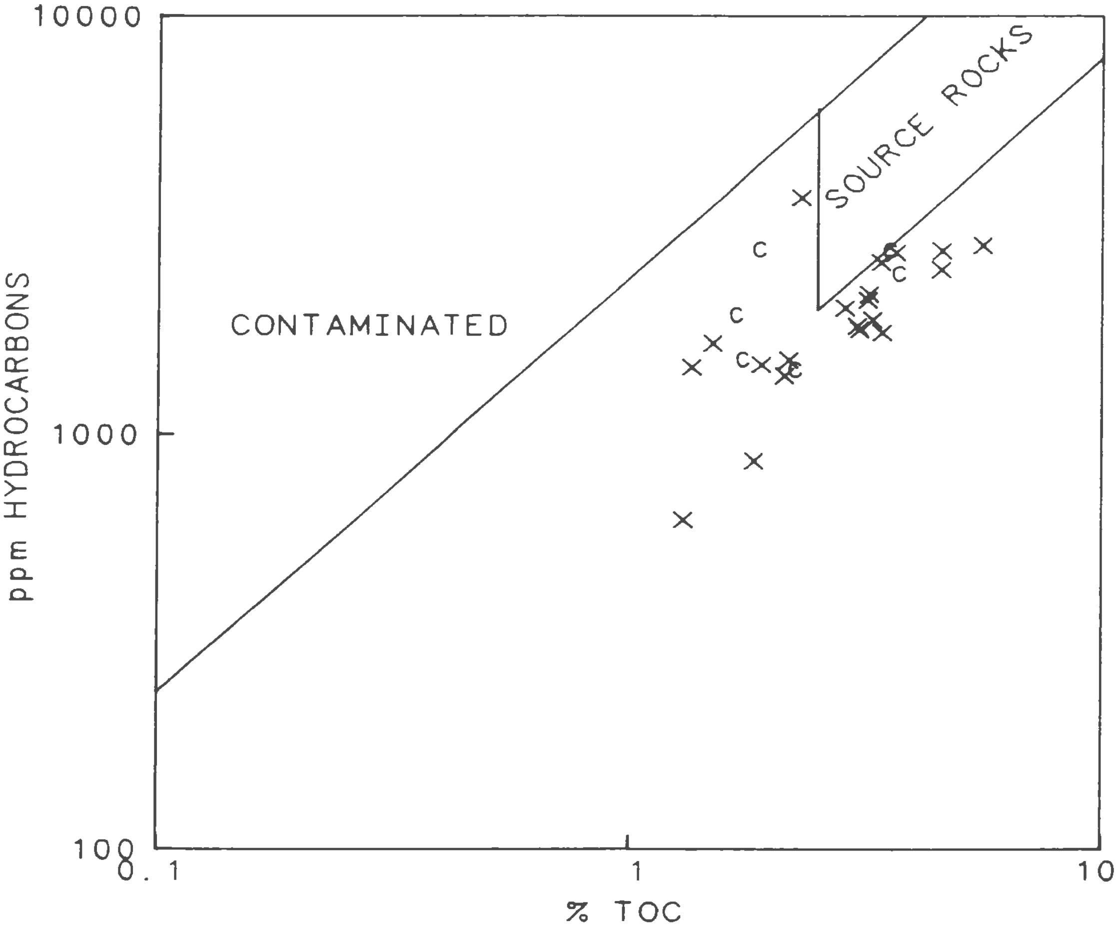
Conclusions can still be drawn, however, from negative evidence by considering circumstances under which migration has *not* taken place. Primary migration is a physico-chemical or physical process dependent on source rock maturity only to the extent that this affects bitumen supply. Thus the early oil window maturity of bitumens from this study should not prevent primary migration if liquid saturation of kerogen or source rock porosity is high enough. Various classifications based on TOC, bitumen, and hydrocarbon content have, as stated earlier, classified the rocks as good to very good, but they have proven to be inadequate for short range primary migration. This suggests that either the Kimmeridge Clay Formation has more difficulty expelling oils than most source rocks, or that classification schemes are too generous in their evaluation of source rocks. The abundance of oil derived from the Kimmeridge Clay where it is mature rules out the first alternative.

The 1% TOC value frequently quoted as a lower limit for effective oil source rocks is not based on oil-source correlation case histories (Jones, 1980). A higher value of about 2.5% TOC is recommended (Jones, 1980) as more realistic and arguments from this study suggest that other accepted effective source rock thresholds may also be too low. Using a TOC cutoff of 2.5% as suggested by Jones (1980), and a minimum hydrocarbon generation level of 80 mg/gTOC as used by Powell (1978) for prolific source rocks (tying in well with pre-expulsion samples from this study) results in an evaluation scheme as shown in Figure 7-1.

Implications of this are that many presumed source rocks (based on analysis or default only, without positive correlation) may be in fact incapable of expelling oil, and this should include the majority of Type III kerogens in oil-bearing Tertiary deltas as suggested in the chapter ‘INTRODUCTION’.

7.3.2. Diffusion

One example of molecular weight dependent depletion by diffusion was found at a shale/sandstone contact in this study, similar but more depleted than those reported in the literature. Such diffusion will by nature produce bitumen components (or their precursors as the case may be) more dispersed than in the source rock, and the fact that this is herein documented for a source rock too immature for primary migration implies that such diffusion will impair the source potential somewhat before expulsion is attained. Because diffusion may occur at most source rock-reservoir contacts, finely interbedded lithologies



(x=clean bitumen;c=contaminated bitumen)

Figure 7-1: ppm Hydrocarbons vs. TOC (with cutoff)

may be most seriously affected, and be outperformed by more massive shales contrary to what one would intuitively expect in terms of effective drainage.

REFERENCES

Aczel T. and Lumpkin H.,1972,'Detailed Characterization of Gas Oils by High and Low Resolution Mass Spectrometry' ACS, Div. Pet. Chem. Prepr. **17**(4):F66-F80.

Archie G.,1942,'The Electrical Resistivity Log as an Aid in Determining Some Reservoir Characteristics' Petr. Tech. **5**:54-61.

Arkell W.,1933,'The Jurassic System in Great Britain' Clarendon, Oxford:1-614.

Arkell W.,1956,'Jurassic Geology of the World' Oliver & Boyd, London:1-791.

Arthur M.,Dean W.,and Claypool G.,1985,'Anomalous ^{13}C Enrichment in Modern Marine Organic Carbon' Nature **315**:216-218.

ASTM D611-82,'Standard Test Method for Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents' 1984 Annual Book of ASTM Standards **05.01**:295-302.

ASTM D 2007-80,'Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils by the Clay-Gel Adsorption Chromatographic Method' 1984 Annual Book of ASTM Standards **05.02**:161-169.

ASTM D 2549-81,'Standard Method for Separation of Representative Aromatics and Nonaromatics Fractions of High-Boiling Oils by Elution Chromatography' 1984 Annual Book of ASTM Standards **05.02**:479-485.

ASTM D 2786-81,'Standard Method for Hydrocarbon Types Analysis of Gas Oil Saturates Fractions by High Ionizing Voltage Mass Spectrometry' 1984 Annual Book of ASTM Standards **05.02**:737-745.

ASTM D 3239-81,'Standard Method for Aromatic Types Analysis of Gas Oil Aromatic Fractions by High Ionizing Voltage Mass Spectrometry' 1984 Annual Book of ASTM Standards **05.03**:126-145.

ASTM D3279-73T,'Standard Test Method for Normal Heptane Insolubles' 1976 Annual Book of ASTM Standards **05.16**:793-796.

ASTM D 4055-81,'Standard Test Method for Pentane Insolubles by Membrane Filtration' 1984 Annual Book of ASTM Standards **05.03**:657-659.

Ayres M.,Bilal M.,Jones R.,Slentz L.,Tartir M.,and Wilson A.,1982,'Hydrocarbon Habitat in Main Producing Areas, Saudi Arabia' AAPG Bull. **66**:1-9.

Bailey N.,Jobson A.,and Rogers M.,1973,'Bacterial Degradation of Crude Oil: Comparison of Field and Experimental Data' Chem. Geol. **11**:203-221.

Bailey N.,Evans C.,and Milner C.,1974,'Applying Petroleum Geochemistry to Search for Oil: Examples from Western Canada Basin' AAPG Bull. **58**:2284-2294.

Baker D.,1962,'Organic Geochemistry of Cherokee group in Southeastern Kansas and Northeastern Oklahoma' AAPG Bull. **46**:1621-1642.

Baker D. and Claypool G.,1970,'Effect of Incipient Metamorphism on Organic Matter in Mudrock' AAPG Bull. **54**:456-468.

Barnard P.,Collins A.,and Cooper B.,1981,'Identification and Distribution of Kerogen Facies in a Source Rock Horizon: Examples from the North Sea Basin' *in* Brooks J.,(*ed.*),'Organic Maturation Studies and Fossil Fuel Exploration' Academic Press, London:271-283.

Barnard P. and Cooper B.,1981,'Oils and Source Rocks of the North Sea Area' *in* Illing L. and Hobson G.,(*eds.*), 'Petroleum Geology of the Continental Shelf of North-West Europe' Heydon & Son, London:169-175.

Behar F.,Pelet R.,and Roucache J.,1983,'Geochemistry of Asphaltenes' Adv. in Org. Geoch. **1983**:587-596.

Bissada K.,1983,'Petroleum Generation in Mesozoic Sediments of the Moray Firth Basin, British North Sea Area' Adv. in Org. Geoch. **1981**:7-15.

Björlykke K.,Dypvik H.,and Finstad K.,1975,'The Kimmeridgian Shale, Its Composition and Radioactivity' *in* Finstad K. and Selley R.,(*eds.*),'Jurassic Northern North Sea Symposium' Norsk Petroleumsforening, Oslo:1-20.

Blaser R. and White C.,1984,'Source-Rock and Carbonization Study, Maracaibo Basin, Venezuela' *in* Demaison G. and Murris R.(*eds.*), 'Petroleum Geochemistry and Basin Evaluation' AAPG Mem. **35**:229-252.

Bodenhausen J. and Ott W.,1981,'Habitat of the Rijswijk Oil Province, Onshore, The Netherlands' *in* Illing L. and Hobson G.,(*eds.*),'Petroleum Geology of the Continental Shelf of North-West Europe' Heyden & Son, London:301-309.

Boduszynski M.,1979,'Asphaltenes in Petroleum Asphalts - Composition and Formation' Am. Chem. Soc., Div. Pet. Chem. Prepr. **24**:935-948.

Bonham L.,1980,'Migration of Hydrocarbons in Compacting Basins' AAPG Bull. **64**:549-567.

Bray E. and Foster W.,1980,'A Process for Primary Migration of Petroleum' AAPG Bull. **64**:107-114.

Briant J. and Hotier G.,1983,'Étude de l'État des Asphaltènes dans les Mélanges d'Hydrocarbures: Taille des Amas Moléculaires' Rev. de l'IFP **38**:83-100.

Brooks J. and Chesher J.,1975,'Review of the Offshore Jurassic of the UK Northern North Sea' *in* Finstad K. and Selley R.,(*eds.*),'Jurassic Northern North Sea Symposium' Norsk Petroleumsforening, Oslo:1-24.

Brooks J. and Thusu B.,1977,'Oil-Source Rock Identification and Characterization of the Jurassic Sediments in the Northern North Sea' Chem. Geol. **20**:283-294.

Bruce C. and Parker E.,1975,'Structural Features and Hydrocarbon Deposits in the Mackenzie Delta' Proc. 9th World Petr. Congr. **2**:251-261.

Byrd W.,1975,'Geology of the Ekofisk Field, Offshore Norway' *in* Woodland A.,(*ed.*), 'Petroleum and the Continental Shelf of North-West Europe, Vol. **1**: Geology' Applied Science, Barking:439-446.

Cartmill J.,1976,'Obscure Nature of Petroleum Migration and Entrapment' AAPG Bull. **60**:1520-1530.

Chakhmakhchev V.,Punanova S.,and Zharkov N.,1983,'Percolation of Oil and Changes in its Composition in Porous Media (Based on Experimental Studies)' Int. Geol. Rev. **25**:1223-1228.

Chapman R.,1982,'Effects of Oil and Gas Accumulation on Water Movement' AAPG Bull. **66**:368-378.

Chappe B., Albrecht P., and Michaelis W.,1982,'Polar Lipids of Archaebacteria in Sediments and Petroleums' Sci. **217**:65-66.

Claret J.,Roucache J.,Gageonnet R.,Renard B.,and Du Rouchet J.,1973,'Caractérisation Géochimique des Huiles et Gisements et Comparaison avec les Hydrocarbures des Roches Non-Reservoir dans le Crétacé Supérieur et le Tertiare de la Region de Port Gentil (Gabon)' Adv. in Org. Geoch. **1973**:335-348.

Claypool G.,Love A.,and Maughan E.,1984,'Organic Geochemistry, Incipient Metamorphism, and Oil Generation in Black Shale Members of the Phosphoria Formation, Western Interior, United States' *in* Demaison G.and Murris R.,(*eds.*),'Petroleum Geochemistry and Basin Evaluation' AAPG Mem. **35**:139-158.

Combaz A. and De Matharel M.,1978,'Organic Sedimentation and Genesis of Petroleum in Makaham Delta, Borneo' AAPG Bull. **62**:1684-1695.

Connan J.,1972,'Laboratory Simulation and Natural Diagenesis 1: Thermal Evolution of Asphalts from the Aquitaine Basin (SW France)' Bull. Cen. Rech. Pau **6**:195-214.

Connan J.,1981,'Un Exemple de Biodégradation Préférentielle des Hydrocarbures Aromatiques dans des Asphaltes du Bassin Sud-Aquitain (France)' Bull. Cen. Rech. Ex-Prod. Elf-Aquitaine **5**:151-171.

Cooper B. and Barnard P.,1984,'Source Rocks and Oils of the Central and Northern North Sea' *in* Demaison G. and Murris R.,(*eds.*), 'Petroleum Geochemistry and Basin Evaluation' AAPG Mem. **35**:303-314.

Corbett L. and Petrossi U.,1978,'Differences in Distillation and Solvent Separated Asphalt Residues' Ind. Eng. Chem. Prod. Res. Dev. **17**:342-346.

Cordell R.,1973,'Colloidal Soap as Proposed Primary Migration Medium for Hydrocarbons' AAPG Bull. **57**:1618-1643.

Cornford C., Morrow J., Turrington A., Miles J., and Brooks J.,1983,'Some Geological Controls on Oil Composition in the UK North Sea' *in* Brooks J.,(*ed.*),'Petroleum Geochemistry and Exploration of Europe' Blackwell Scientific, Oxford:175-194.

Cornford C.,1984,'Source Rocks and Hydrocarbons of the North Sea' *in* 'Introduction to the Petroleum Geology of the North Sea', Glennie K. (ed.), Blackwell, Oxford:171-204.

Coustau H.,Rumeau J.,Sourisse C.,Chiarelli A.,and Tison J.,1975,'Classification Hydrodynamique des Bassins Sédimentaires: Utilisation Combinée avec d'Autres Méthodes pour Rationaliser l'Exploration dans des Bassins non-Productifs' *in* Proc. 9th World Petr. Congr. **2**:105-120.

Craig H.,1957,'Isotopic Standards for C and O and Correction Factors for Mass Spectrometric Analysis of CO_2' GECA **12**:133-149.

Dake L.,1983,'Fundamentals of Reservoir Engineering' Elsevier, Amsterdam, 443pp.

Darcy H.,1856,'Les Fontaines Publiques de la Ville de Dijon' Victor Dalmont, Paris.

Deegan C. and Scull B.,1977,'A Standard Lithostratigraphic Nomenclature for the Central and Northern North Sea' Report **77/25**, IGS, London:1-36.

Degens E.,1969,'Biogeochemistry of stable carbon isotopes' *in* Eglinton G.and Murphy M.,(*eds.*),'Organic Geochemistry'Springer Verlag,304-329.

Demaison G.,1977,'Tar Sands and Supergiant Oil Fields' AAPG Bull. **61**:1950-1961.

Demaison G. and Moore G.,1980,'Anoxic Environments and Oil Source Bed Genesis' AAPG Bull. **64**:1179-1209.

Dembicki H.,1984,'An Interlaboratory Comparison of Source Rock Data' GECA **48**:2641-2649.

Deroo G.,1976,'Corrélations Huiles Brutes-Roches Mères à l'Echelle des Bassins Sédimentaires' Bull. Cen. Rech. Pau **10**:317-335.

Deroo G.,Powell T.,Tissot B.,and McCrossan R.,1977,'The Origin and Migration of Petroleum in the Western Canadian Sedimentary Basin, Alberta' GSC Bull. **262**.

Dickey P.,1975,'Possible Primary Migration of Oil from Source Rock in Oil Phase' AAPG Bull. **59**:337-345.

Du Rouchet J.,1981,'Stress Fields: A Key to Oil Migration' AAPG Bull. **65**:74-85.

Du Rouchet J.,1984,'Migration in Fracture Networks; An Alternative Interpretation of the Supply of the 'Giant' Tar Accumulations in Alberta, Canada-I & II' Jour. Petr. Geol. **7**:381-402 and **8**:101-114.

Durand B.,1983,'Present Trends in Organic Geochemistry in Research on Migration of Hydrocarbons' Adv. in Organic Geochem. **1981**:117-128.

Durand B.,Espitalié J.,and Oudin J.,1970,'Analyse Géochimique de la Matière Organique Extraite des Roches Sédimentaires III: Accroissement de la Rapidité du Protocole Opératoire par l'Amélioration de l'Appareillage' Revue de l'Institut Français du Pétrole **XXV**:1268-1279.

Durand B. and Paratte M.,1983,'Oil Potential of Coals: A Geochemical Approach' *in* Brooks J. (*ed.*),'Petroleum Geochemistry and Exploration of Europe', Blackwell,Oxford, 255-265.

Eaton B.,1969,'Fracture Gradient Prediction and its Application in Oilfield Operations' Jour. Petr. Tech. **21**:1353-1360.

Ekweozor C. and Okoye N.,1980,'Petroleum Source Bed Evaluation of Tertiary Niger Delta' AAPG Bull. **64**:1251-1259.

El Rifai M.,1957,'Estrazione con Solvente di Idrocarburi Aromatici' Riv. di Combustibili **11**:811-840.

Espitalié J.,Madec M.,and Tissot B.,1980,'Role of Mineral Matrix in Kerogen Pyrolysis: Influence on Petroleum Generation and Migration' AAPG Bull. **64**:59-66.

Espitalié J., Marquis F., and Barsony I.,1984,'Geochemical Logging' *in* Voorhees K.,(*ed.*),'Analytical Pyrolysis - Techniques and Applications' Butterworths, London:276-304.

Evans C.,Rogers M.,and Bailey N.,1971,'Evolution and Alteration of Petroleum in Western Canada' Chem. Geol. **8**:147-170.

Evans T.and Coleman N.,1974,'North Sea Geothermal Gradients' Nature **247**:28-30.

Ferguson W.,1962,'Analytical Problems in Determining Hydrocarbons in Sediments' AAPG Bull. **46**:1613-1620.

Francis A.,1950,'Solvent Extraction of Hydrocarbons' *in* Farkas A.(*ed.*), 'Physical Chemistry of the Hydrocarbons' Vol. 1, Academic Press, New York, p 241-313.

Francis A.,1963,'Liquid-Liquid Equilibriums' Interscience, New York, 288 pp.

Fuller J.,1975,'Jurassic Source Rock Potential and Hydrocarbon Correlation, North Sea' *in* Finstad K. and Selley R.,(*eds.*),'Jurassic Northern North Sea Symposium' Norsk Petroleumsforening, Oslo:1-18.

Gallois R.,1976,'Coccolith Blooms in the Kimmeridge Clay and Origin of North Sea Oil' Nature **259**:473-475.

Goddard E.,Trask P.,De Ford R.,Rove O.,Singewald J.,and Overbeck R.,1980,'Rock-Color Chart' GSA, Boulder.

Goff J.,1983,'Hydrocarbon Generation and Migration from Jurassic Source Rocks in the East Shetland Basin and Viking Graben of the Northern North Sea' Jour. Geol. Soc. London **140**:445-474.

Gransch J.and Posthuma J.,1973,'On the Origin of Sulfur in Crudes' Adv. in Org. Geoch. **1973**:727-737.

Grob K. and Grob G.,1981,'Practical Capillary Gas Chromatography-A Systematic Approach' *in* Bertsch,Jennings,and Kaiser, (*eds.*), 'Recent Advances in Capillary Gas Chromatography' Verlag, Heidelberg, pp 97-117.

Han J. and Calvin M.,1969,'Occurrence of C_{22}-C_{25} Isoprenoids in Bell Creek Crude Oil' GECA **33**:733-742.

Hansen J. and Mikkelsen N.,1982,'Hydrocarbon Geological Aspects of Subsidence Curves: Interpretations Based on Released Wells in the Danish Central Graben' Bull. Geol. Soc. Denmark **31**:159-169.

Harms J.,Tackenberg P.,Pickles E.,and Pollock R.,1981,'The Brae Oilfield Area' *in* Illing L. and Hobson G.,(*eds.*),'Petroleum Geology of the Continental Shelf of North West Europe' Heyden & Son, London:352-357.

Hedberg H.,1974,'Relation of Methane Generation to Undercompacted Shales, Shale Diapirs,and Mud Volcanoes' AAPG Bull. **58**:661-673.

Hedberg H.,1980,'Methane Generation and Petroleum Migration' *in* Roberts W. and Cordell R.,(*eds.*), 'Problems of Petroleum Migration' AAPG Studies in Geology **10** :179-206.

Hedges J. and Stern J.,1984,'Carbon and Nitrogen Determinations of Carbonate-Containing Solids' Limnol.& Oceanogr **29**:657-663.

Herbeck E.,Heintz R.,and Hastings J.,1976,'Fundamentals of Tertiary Oil Recovery 6 - Micellar Solution Flooding' Petr. Eng. **48(7)**:44-56.

Hilpert L.,May W.,Wise S.,Chesler S.,and Hertz H.,1978,'Interlaboratory Comparison of Determinations of Trace Level Petroleum Hydrocarbons in Marine Sediments' Anal. Chem. **50**:458-463.

Hirsch D.,Hopkins R.,Coleman H.,Cotton F.,and Thompson C.,1972,'Separation of High Boiling Petroleum Distillates Using Gradient Elution Through Dual-Packed (Silica Gel-Alumina Gel) Adsorption Columns' ACS,Div. Pet. Chem. Prepr. **17**:A65-A74.

HirschbergA.,De Jong L.,Schipper B.,and Meijer J.,1984,'Influence of Temperature and Pressure on Asphaltene Flocculation' Soc. Pet. Eng. Jour. **24**:283-293.

Hodgson G.,1980,'Origin of Petroleum: In-Transit Conversion of Organic Compounds in

Water' *in* Roberts W. and Cordell R. (*eds.*), 'Problems of Petroleum Migration' AAPG Studies in Geology **10**:169-178.

Hoffmann C.and Strausz O.,1986,'Bitumen Accumulation in Grosmont Platform Complex, Upper Devonian, Alberta, Canada' AAPG Bull. **70**:1113-1128.

Hoffmann C.,MacKenzie A.,Lewis C.,Maxwell J.,Oudin J.,Durand B.,and Vandenbroucke M.,1984,'A Biological Marker Study of Coals, Shales, and Oils from the Makaham Delta, Kalimantan, Indonesia' Chem. Geol.**42**:1-23.

Honda H. and Magara K.,1982,'Estimation of Irreducible Water Saturation and Effective Pore Size of Mudstones' J. Pet. Geol. **4**:407-418.

Hood a.and O'Neal M.,1959,'Status of Application of Mass Spectrometry to Heavy Oil Analysis' Advances in Mass Spectrometry **1**:175-192.

Hoots H.,Blount A.,and Jones P.,1935,'Marine Oil Shale, Source of Oil in Playa Del Rey Field, California' AAPG Bull. **19**:172-205.

Hotier G. and Robin M.,1983,'Action de Divers Diluants sur les Produits Pétroliers Lourds: Mesure, Interprétation et Prévision de la Floculation des Aphaltènes' Rev. de l'IFP **38**:101-120.

Hunt J.,1979,'Petroleum Geochemistry and Geology' W.H. Freeman, San Francisco, 617pp.

Hunt T.,1861,'Notes on the History of Petroleum or Rock Oil' Can. Naturalist and Geologist **6**:241-255.

Illich H.,1983,'Pristane, Phytane, and Lower Molecular Weight Isoprenoid Distributions in Oils' AAPG Bull. **67**:385-393.

Illich H.,Haney F.,and Mendoza M.,1981,'Geochemistry of Oil from Santa Cruz Basin, Bolivia: Case Study of Migration-Fractionation' AAPG Bull. **65**:2388-2402.

Jewell D.,Albaugh E.,Davis B.,and Ruberto R.,1972,'Combination of Techniques for the Characterization of Residuals' ACS, Div. Pet. Chem. Prepr. **17**:F81-F91.

Johnson R.,1975,'The Base of the Cretaceous: A Discussion' *in* Woodland A.,(*ed.*),'Petroleum and the Continental Shelf of North-West Europe, Vol **1**:Geology' Applied Science, Barking:389-402.

Jonathan D.,Le Tran K.,Oudin J.,and Van Der Weide B.,1976,'Les Méthodes d'Étude Physico-Chimiques de la Matière Organique' Bull. Centre Rech. Pau-SNPA **10**:89-108.

Jones R.,1980,'Some Mass Balance and Geological Constraints on Migration Mechanisms' *in* Roberts W. and Cordell R.,(*eds.*), 'Problems of Petroleum Migration' AAPG Studies in Geology **10**:47-68.

Jones R.,1984,'Comparison of Carbonate and Shale Source Rocks' *in* Palacas J.,(*ed.*), 'Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks' AAPG Studies in Geology **18**:163-181.

Jones R.,1987,'Organic Facies' Adv. in Pet. Geoch. **2**:1-90.

Koots J. and Speight J.,1975,'Relation of Petroleum Resins to Asphaltenes' Fuel **54**:179-184.

Landes K.,1959,'Petroleum Geology', 2nd Ed.,Wiley & Sons,N.Y.,443pp.

Landais P. and Connan J.,1980,'Relation Uranium-Matière Organique dans Deux Bassins Permiens Français: Lodève (Hérault) et Cérilly - Bourbon - l'Archambault (Allier)' Bull. Cent. Rech. Expl.-Prod. Elf-Aquitaine **4**:709-757.

Laplante R.,1974,'Hydrocarbon Generation in Gulf Coast Tertiary Sediments' AAPG Bull. **58**:1281-1289.

Le Tran K.,Connan J.,Van Der Weide B.,1973,'Problèmes Relatifs à la Formation d'Hydrocarbures et d'Hydrogène Sulfuré dans le Bassin Sud-Ouest Aquitain' Adv. in Org. Geochem. **1973**:761-789.

Leenheer M.,1984,'Mississippian Bakken and Equivalent Formations as Source Rocks in the Western Canadian Basin' Org. Geoch. **6**:521-532.

Lewan M.,Winters J.,and McDonald J.,1979,'Generation of Oil-Like Pyrolyzates from Organic-Rich Shales' Sci. **203**:897-899.

Leythaeuser D.,Schaefer R.,and Yukler A.,1982,'Role of Diffusion in Primary Migration of Hydrocarbons' AAPG Bull. **66**:408-429.

Leythaeuser D.,Mackenzie A.,Schaefer R.,Altebäumer F.,and Bjoröy M.,1983,'Recognition of Migration and its Effects Within Two Coreholes in Shale/Sandstone Sequences from Svalbard, Norway' Adv. in Org. Geochem. **1981**:136-146.

Leythaeuser D.,Mackenzie A.,Schaefer R.,and Bjoröy M.,1984a,'A Novel Approach for Recognition and Quantification of Hydrocarbon Migration Effects in Shale-Sandstone Sequences' AAPG Bull. **68**:196-219.

Leythaeuser D.,Radke M.,and Schaefer R.,1984b,'Efficiency of Petroleum Expulsion from Shale Source Rocks' Nature **211**:745-748.

Leythaeuser D. and Schaefer R.,1984,'Effects of Hydrocarbon Expulsion from Shale Source Rocks of High Maturity in Upper Carboniferous Strata of the Ruhr Area, Federal Republic of Germany' Org. Geochem. **6**:671-681.

Lhioreau C.,Briant J.,and Tindy R.,1967,'Influence de la Pression sur la Floculation des Asphaltènes' Rev. de l'IFP **XXII**:797-806.

Lindgreen H.,1985,'Diagenesis and Primary Migration in Upper Jurassic Claystone Source Rocks in the North Sea' AAPG Bull. **69**:525-536.

Long R.,1979,'The Concept of Asphaltenes' Am. Chem. Soc.-Div. Pet. Chem. Prepr. **24**:891-900.

Louis M.,1964,'Études Géochimiques sur les 'Schistes Cartons' du Toarcien du Bassin de Paris' Adv. in Org. Geochem. **1964**:85-94.

Louis M. and Tissot B.,1967,'Influence de la Température et de la Pression sur la Formation des Hydrocarbures dans les Argiles à Kerogène' Proc. 7th World Petr. Congr. **2**:47-60.

MacKenzie A.,Leythaeuser D.,Schaefer R.,and Bjoröy M.,1983,'Expulsion of Petroleum Hydrocarbons from Shale Source Rocks' Nature **301**:506-509.

MacKenzie A. and Maxwell J.,1983,'Biological Marker and Isotope Studies of North Sea Crude Oils and Sediments' Proc. 11th World Petr. Congr. **2**:45-56.

Magara K.,1980,'Agents for Primary Hydrocarbon Migration: A Review' *in* Roberts W. & Cordell R.,(*eds*),'Problems of Petroleum Migration' AAPG Studies in Geology **10**:33-46.

Mattavelli L.,Ricchiuto T.,Grignani D.,and Schoell M.,1983,'Geochemistry and Habitat of Natural Gases in Po Basin, Northern Italy' AAPG Bull. **67**:2239-2254.

McAuliffe C.,1978,'Chemical and Physical Constraints on Petroleum Migration with Emphasis on Hydrocarbon Solubilities in Water' *in* Roberts W. and Cordell R.,(*eds.*),'Physical and Chemical Constraints on Petroleum Migration' AAPG Course Notes **8**:C1-C39.

McKirdy D.,Kantsler A.,Emmet J., and Aldridge A.,1984,'Hydrocarbon Genesis and Organic Facies in Cambrian Carbonates of the Eastern Officer Basin, South Australia' *in* Palacas J.,(*ed.*),'Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks' AAPG Studies in Geology **18**:13-31.

McRae J.,1985,'An Analysis of Grand Banks Oils Using Carbon and Nitrogen Isotopes' unpublished B.Sc.(Hons.) thesis, St. Francis Xavier University, Antigonish, N.S., 71pp.

Meissner F.,1984,'Petroleum Geology of the Bakken Formation, Williston Basin, North Dakota and Montana' *in* Demaison G. and Murris R.,(*eds.*), 'Petroleum Geochemistry and Basin Evaluation' AAPG Memoir **35**:159-179.

Meyer B. and Nederlof M.,1984,'Identification of Source Rocks on Wireline Logs by Density/Resistivity and Sonic Transit Time/Resistivity Crossplots' AAPG Bull.**68**:121-129.

Mileshina A.and Safonova G.,1963,'Variation in the Chemical Composition of Oils Under the Influence of the Absorbing Properties of Clayey Source Rocks' Pet. Geol. **8**:410-414.

Milner C.,Rogers M.,and Evans C.,1977,'Petroleum Transformations in Reservoirs' J. Geoch. Expl. **7**:101-153.

Mitchell D. and Speight J.,1973,'The Solubility of Asphaltenes in Hydrocarbon Solvents' Fuel **52**:149-152.

Moldowan M. and Seifert W.,1979,'Head to Head Linked Isoprenoid Hydrocarbons in Petroleum' Sci. **204**:169-171.

Momper J.,1978,'Oil Migration Limitations Suggested by Geological and Geochemical Considerations' *in* Roberts W. and Cordell R.,(*eds.*), 'Physical and Chemical Constraints on Petroleum Migration' AAPG Course Notes **8**:B1-B60.

Moschopedis S. and Speight J.,1976,'Investigation of Hydrogen Bonding by Oxygen Functions in Athabasca Bitumen' Fuel **55**:187-192.

Moschopedis S. and Speight J.,1977,'The Effect of Air Blowing on the Properties and Constitution of a Natural Bitumen' J. Mat. Sci. **12**:990-998.

Moschopedis S.,Fryer J.,and Speight J.,1976,'Investigation of Asphaltene Molecular Weights' Fuel **55**:227-232.

Moshier S.and Waples D.,1985,'Quantitative Evaluation of Lower Cretaceous Mannville Group as Source Rock for Alberta's Oil Sands' AAPG Bull. **69**:161-172.

Murris R.,1984,'Middle East: Stratigraphic Evolution and Oil Habitat' *in* Demaison G. and Murris R.,(*eds.*), 'Petroleum Geochemistry and Basin Evaluation' AAPG Memoir **35**:353-372.

Neruchev S. and Kovacheva I.,1965,'Influence of the Geologic Environment on the Oil Output of Source Rocks' Doklady Akademii Nauk SSSR **162**:203-205.

North F.,1985,'Petroleum Geology' Allen and Unwin, Boston, 607 pp.

Oudin J.,1970,'Analyse Géochimique de la Matière Organique Extraite des Roches Sédimentaires I: Composés Extractibles au Chloroforme' Revue de l'Institut Français du Pétrole **XXV**:3-15.

Oudin J.,1976,'Étude Géochimique du Bassin de la Mer du Nord' Bull. Cent. Rech. Pau **10**:339-358.

Palacas J.,Anders D.,and King J.,1984,'South Florida Basin - A Prime Example of Carbonate Source Rocks of Petroleum' *in* Palacas J.,(*ed.*),'Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks' AAPG Studies in Geology **18**:71-96.

Palmer S.,1984,'Effect of Water Washing on C_{15}+ Hydrocarbon Fraction of Crude Oils from N.W. Palawan, Philippines' AAPG Bull. **68**:137-149.

Pegrum R.,Rees G.,and Naylor D.,1975,'Geology of the North-West European Continental Shelf **2**:The North Sea' Graham Trotman Dudley, London:1-225.

Perrodon A.,1983,'Géodynamique des Bassins Sédimentaires et Systèmes Pétroliers' Bull. Cent. Rech. Expl.-Prod. Elf-Aquitaine **7**:645-676.

Peters K.,1986,'Guidelines for Evaluating Petroleum Source Rock Using Programmed Pyrolysis' AAPG Bull. **70**:318-329.

Philippi G.,1957,'Identification of Oil-Source Beds by Chemical Means' *in* Proc. 20th Int. Geol. Cong., Mexico City, 1956, **3**:25-38.

Philippi G.,1965,'On the Depth, Time, and Mechanism of Petroleum Generation' GECA **29**:1021-1048.

Powell T.,1978,'An Assessment of the Hydrocarbon Source Rock Potential of the Canadian Arctic Islands' GSC Paper **78-12**:82pp.

Powell T.,Macqueen R.,Barker J.,and Bree D.,1984,'Geochemical Character and Origin of Ontario Oils' Bull. Can. Pet. Geol. **32**:289-312.

Powell T.and McKirdy D.,1973,'The Effect of Source Material, Rock Type, and Diagenesis on the n-Alkane Content of Sediments' GECA **37**:623-633.

Powers M.,1967,'Fluid Release Mechanisms in Compacting Marine Mud Rocks and their Importance in Oil Exploration' AAPG Bull. **51**:1240-1254.

Price L.,1976,'Aqueous Solubility of Petroleum as Applied to its Origin and Primary Migration' AAPG Bull. **60**:213-244.

Price L. and Barker C.,1985,'Suppression of Vitrinite Reflectance in Amorphous Rich Kerogen - A Major Unrecognized Problem' Jour. of Petr. Geol. **8**:59-84.

Price L.,Wenger L.,Ging T.,and Blount C.,1983,'Solubility of Crude Oil in Methane as a Function of Pressure and Temperature' Org. Geoch. **4**:201-221.

Price L.,Ging T.,Love A.,and Anders D.,1986,'Organic Metamorphism in the Lower Mississippian - Upper Devonian Bakken Shales - II:Soxhlet Extraction' J. Pet. Geol. **9**:313-342.

Radke M.,Sittardt H.,and Welte D.,1978,'Removal of Soluble Organic Matter from Rock Samples with a Flow-Through Extraction Cell' Anal. Chem. **50**:663-665.

Radke M.,Willsch H.,and Welte D.,1980,'Preparative Hydrocarbon Group Type Determination by Automated Medium Pressure Liquid Chromatography' Anal. Chem. **52**:406-411.

Radke M., Welte D., and Willsch H.,1982,'Geochemical Study on a Well in the Western Canada Basin: Relation of the Aromatic Distribution Pattern to Maturity of Organic Matter' GECA **46**:1-10.

Radke M.and Welte D.,1983,'The Methylphenanthrene Index (MPI): A Maturity Parameter Based on Aromatic Hydrocarbons' Adv. in Org. Geoch. **1981**:504-512.

Radke M., Leythaeuser D., and Teichmüller M.,1984,'Relationship Between Rank and Composition of Aromatic Hydrocarbons for Coals of Different Origins' Org. Geoch. **6**:423-430.

Reitsema R.,1983,'Geochemistry of North and South Brae Areas, North Sea' *in* Brooks J.,(*ed.*),'Petroleum Geochemistry and Exploration of Europe' Blackwell Scientific, Oxford:203-212.

Rhys G.,1974,'A Proposed Standard Lithostratigraphic Nomenclature for the Southern North Sea and an Outline Structural Nomenclature for the Whole of the (UK) North Sea' Report **74/8**, IGS, London:1-14.

Roberts A.,Palacas J.,and Frost I.,1973,'Determination of Organic Carbon in Modern Carbonate Sediments' JSP **43**:1157-1159.

Roberts W.,1980,'Design and Function of Oil and Gas Traps' *in* Roberts W. and Cordell R.(*eds.*)'Problems of Petroleum Migration' AAPG Studies in Geology **10**:217-240.

Robinson C. and Cook G.,'Low Resolution Mass Spectrometric Determination of Aromatic Fractions from Petroleum' Anal. Chem. **41**:1548-1554.

Rohrback B.,Peters K.,and Kaplan I.,1984,'Geochemistry of Artificially Heated Humic and Sapropelic Sediments II - Oil and Gas Generation' AAPG Bull. **68**:961-970.

Rönnevik H.,Eggen S.,and Vollset J.,1983,'Exploration of the Norwegian Shelf' *in* Brooks J.,(*ed.*),'Petroleum Geochemistry and Exploration of Europe' Blackwell Scientific, Oxford:71-94.

Rubinstein I.,Spyckerelle C.,and Strausz O.,1979,'Pyrolysis of Asphaltenes: A Source of Geochemical Information' GECA **43**:1-6.

Rumeau J. and Sourisse C.,1973,'Une Example de Migration Primaire en Phase Gazeuse' Bull. Cen. Rech. de Pau **7**:53-67.

Sackett W.and Thompson R.,1963,'Isotopic Organic Carbon Composition of Recent Continental Derived Clastic Sediments of Eastern Gulf Coast, Gulf of Mexico' AAPG Bull. **47**:525-528.

Samman N.,Ignasiak T.,Chen C.,Strausz O.,and Montgomery D.,1981,'Squalene in Petroleum Asphaltenes' Science **213**:1381-1383.

Scalan R. and Smith J.,1970,'An Improved Measure of the Odd-Even Predominance in the Normal Alkanes of Sediment Extracts and Petroleum' GECA **34**:611-620.

Schmoker J. and Halley R.,1982,'Carbonate Porosity vs. Depth: A Predictable Relation for South Florida' AAPG Bull. **66**:2561-2570.

Schoell M.,1984,'Stable Isotopes in Petroleum Research' *in* Brooks J.and Welte D.,(*eds.*),'Advances in Petroleum Geochemistry I' Academic Press, London:215-245.

Schowalter T.,1979,'Mechanics of Secondary Hydrocarbon Migration and Entrapment' AAPG Bull. **63**:723-760.

Sclater J. and Christie P.,1980,'Continental Stretching: An Explanation of the Post-Mid-Cretaceous Subsidence of the Central North Sea Basin' J. Geoph. Res. **85**:3711-3739.

Seifert W. and Moldowan J.,1981,'Paleoreconstruction by Biological Markers' GECA **45**:783-794.

Selucky M.,Chu Y.,Ruo T.,and Strausz O.,1977,'Chemical Composition of Athabaska Bitumen' Fuel **56**:369-381.

Silverman S.,1965,'Migration and Segregation of Oil and Gas' *in* Young A. and Galley J,(*eds.*),'Fluids in Subsurface Environments' AAPG Memoir **4**:53-65.

Silverman S.,1971,'Influence of Petroleum Origin and Transformation on its Distribution and Redistribution in Sedimentary Rocks' Proc. 8th World Petroleum Congress,Moscow **2**:47-54.

Sluijk D. and Nederlof M.,1984,'Worldwide Geological Experience as a Systematic Basis for Prospect Appraisal' *in* Demaison G. and Murris R.,(*eds.*), 'Petroleum Geochemistry and Basin Evaluation' AAPG Memoir **35**:15-26.

Snyder L.,1961,'Applications of Linear elution Adsorption Chromatography to the Separation and Analysis of Petroleum' Anal. Chem. **33**:1527-1534.

Sofer Z.,1984,'Stable Carbon Isotope Compositions of Crude Oils: Application to Source Depositional Environments and Petroleum Alteration' AAPG Bull. **68**:31-49.

Speight J.,1978,'The Structure of Petroleum Asphaltenes - Current Concepts' Alberta Res. Council Info. Ser. **81**, 28pp.

Speight J.,1980,'The Chemistry and Technology of Petroleum' Marcel Dekker, New York, 498 pp.

Speight J.and Moschopedis S.,1981,'On the Molecular Nature of Petroleum Asphaltenes' Am. Chem. Soc., Adv. in Pet. Chem. Series **195**:1-15.

Stahl W.,1977,'Carbon and Nitrogen Isotopes in Hydrocarbon Research and Exploration' Chem. Geol. **20**:121-149.

Stahl W.,1978,'Source Rock-Crude Oil Correlation by Isotopic Type-Curves' GECA **42**:1573-1577.

Tannenbaum E.,Huizinga B.,and Kaplan I.,1986,'Role of Minerals in Thermal Alteration of Organic Matter - II: A Material Balance' AAPG Bull. **70**:1156-1165.

Tissot B.,1981,'Connaissances Actuelles sur les Produits Lourds du Pétrole' Rev. de l'IFP **36**:429-446.

Tissot B.,1984,'Géochimie des Résines et Asphaltènes' IFP Collection Colloques et Seminaires **40**:3-18.

Tissot B. and Pelet R.,1971,'Nouvelles Données sur les Méchanismes de Genèse et de Migration du Pétrole: Simulation Mathématique et Application à la Prospection' Proc. 8th World Petr. Congr. **2**:35-46.

Tissot B. and Welte D.,1978,'Petroleum Formation and Occurrence' Springer-Verlag, Berlin, 538pp.

Tissot B. and Welte D.,1984,'Petroleum Formation and Occurrence' Springer-Verlag, Berlin, 666pp.

Tissot B.,Califet-Debyser Y.,Deroo G.,and Oudin J.,1971,'Origin and Evolution of Hydrocarbons in Early Toarcian Shales, Paris Basin, France' AAPG Bull. **55**:2177-2193.

Tissot B.,Espitalié J.,Deroo G.,Tempére C.,and Jonathan D.,1973,'Origine et Migration des Hydrocarbures dans le Sahara Oriental (Algérie)' Adv. in Org. Geochem. **1973**:315-334.

Tissot B.,Pelet R.,Roucache J., and Combaz A.,1977,'Utilisation des Alkanes Comme Fossiles Géochimiques Indicateurs des Environments Géologiques' Adv. in Org. Geoch. **1975**:117-154.

Toth J.,1980,'Cross-Formational Gravity-Flow of Groundwater: A Mechanism of the Transport and Accumulation of Petroleum (The Generalized Hydraulic Theory of Petroleum Migration)' *in* Roberts W. and Cordell R.,(*eds.*), 'Problems of Petroleum Migration' AAPG Studies in Geology **10**:121-168.

Tyson R.,Wilson R.,and Downie C.,1979,'A Stratified Water Column Environmental Model for the Type Kimmeridge Clay' Nature **277**:377-380.

Ungerer P.,Behar E.,and Discamps D.,1983,'Tentative Calculation of the Overall Volume Expansion of Organic Matter During Hydrocarbon Genesis from Geochemistry Data. Implications for Primary Migration' Adv. in Org. Geochem. **1981**:129-135.

Ungerer P.,Bessis F.,Chenet P.,Durand B.,Nogaret E.,Chiarelli A.,Oudin J.,and Perrin J.,1984,'Geological and Geochemical Models in Oil Exploration; Principles and Practical Examples' *in* Demaison G. and Murris R.,(*eds.*), 'Petroleum Geochemistry and Basin Evaluation' AAPG Mem. **35**:53-77.

Van Cangh L. and Fripiat J.,1973,'Influence de l'Eau sur l'Adsorption d'Hydrocarbures par une Surface Hydrophile ou Hydrophobe' Adv. in Org. Geochem. **1973**: 925-938.

Van den Bark E.and Thomas O.,1981,'Ekofisk: First of the Giant Oil Fields in Western Europe' AAPG Bull. **65**:2341-2363.

Vandenbroucke M.,1972,'Étude de la Migration Primaire: Variation des Extraits de

Roche à un Passage Roche Mère/Reservoir' Adv. in Org. Geochem. **1971**:547-565.

Waples D.,1980,'Time and Temperature in Petroleum Formation: Application of Lopatin's Method to Petroleum Exploration' AAPG Bull. **64**:916-926.

Waples D.,1985,'Geochemistry in Petroleum Exploration' Inter. Human Resources Development Corp., Boston, 232 pp.

Williams J.,1974,'Characterisation of Oil Types in the Williston Basin' AAPG Bull. **58**:1243-1252.

Williams P. and Douglas A.,1983,'The Effects of Lithologic Variation on Organic Geochemistry in the Kimmeridge Clay of Britain' Adv. in Org. Geoch. **1981**:568-575.

Winters J.,Williams J.,and Lewan M.,1983,'A Laboratory Study of Petroleum Generation by Hydrous Pyrolysis' Adv. in Organic Geochem. **1981**:524-533.

Winters J. and Williams J.,1969,'Microbiological Alteration of Crude Oil in the Reservoir' ACS, Div. Pet. Chem. Prepr. **14**:E22-E31.

Zhuze T.,Ushakova G.,and Yushkevich G.,1962,'The Influence of High Pressures and Temperatures on the Content and Properties of Condensate in the Gas Phase of Gas-Oil Deposits' Geochemistry **6**:797-806.

Zhuze T.,Yushkevich G.,Ushakova G.,and Tumarev K.,1963,'Use of Phase-Composition Data in the System Oil-Gas at High Pressures for Ascertaining the Genesis of Some Pools' Petroleum Geology **7**:186-191.

Ziegler P.,1981,'Evolution of Sedimentary Basins in North West Europe' *in* Illing L. and Hobson G.,(*eds.*), 'Petroleum Geology of the Continental Shelf of North-West Europe' Heyden & Son, London:3-40.

Appendix A
DIESEL CONTAMINATION REMOVAL

Because the core under study was cut using a diesel-oil based drilling mud, the possibility existed of diesel invasion into the core and consequent contamination of contained organic matter. A sample of the actual diesel used in this mud was not available, thus it was not known if any specific chemical properties characteristic of the diesel could be used to identify contamination. The core had been slabbed prior to sampling (Fig. A-1), so a sample (7.7m) bounded by both core edge and slab cut was selected for study. Four small holes were drilled across this with an electric drill, and the drillings (approx. 1g each) crushed with mortar and pestle and solvent extracted (see: Solvent Extraction, page 47). Solvent and bitumen were rotary evaporated at 25°C and injected into a gas chromatograph with no further treatment. Chromatographic conditions were:

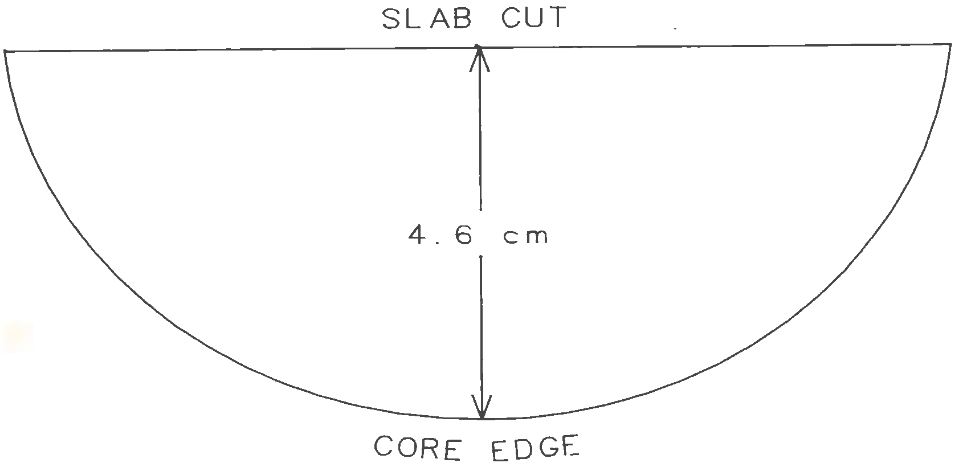


Figure A-1: Cross section of core

- Chromatograph: HP 5792
- Column: OV 101
- Temperature Program:
  - 3 min. at 70°C
  - 70°C - 270°C at 3°C/min.
  - 20 min. hold at 270°C

- Injector & detector Temperature: 280°C
- Split Injection

Variation between the chromatograms was noted in the diesel oil molecular weight range (approx. nC_{15} to nC_{19}) after evaporation. Differences in ratios of n-alkanes and isoprenoids were evident, but a distinctive naphthene hump as documented by Powell (1978) was absent, indicating contamination by straight-run rather than cracked diesel oil. The ratios: nC_{17}/Pristane, nC_{18}/Phytane, and $(nC_{15}+nC_{17})/2nC_{16}$ were calculated using peak heights only for each chromatogram (Table A-1).

Table A-1: Component ratios for contamination study

CM. FROM CORE EDGE	$\frac{nC_{17}}{Pr}$	$\frac{nC_{18}}{Ph}$	$\frac{nC_{15}+nC_{17}}{2nC_{16}}$
Drillings: 0.0-0.9	1.63	2.07	0.92
1.2-2.1	1.12	1.70	1.17
2.4-3.2	1.15	1.72	1.24
3.6-4.6	1.16	1.52	1.25
Saw Cuts: 0.3-0.4	1.84	1.84	0.98
0.6-0.9	1.19	1.72	0.96

Because n-alkanes are thought to migrate from source rocks more easily than isoprenoids (MacKenzie *et al.*(1983); Leythaeuser *et al.*(1984)) the first two ratios were expected to be higher in crude oils and refined products in general than in shale bitumens. In addition, crude oils and their products can be expected to have a low or non-existent odd-carbon predominance in contrast to shale bitumens which, depending on source and maturity, may show very high values (Philippi, 1965). An attempt was made to quantify this in the third ratio, but this will be vulnerable to any variation in nC_{15} content caused by varying intensity of solvent evaporation.

These ratios are shown plotted for the drilled samples in Fig. A-2 and for each ratio a departure to values more characteristic of straight-run diesel oil can be observed in the sample closest to the core edge. Although these are plotted as total vertical interval sampled (relative to the cross-section), due to the holes being round the ratios shown are weighted toward the values at the midpoints. No contamination was apparent from the slab cut.

To further define the depth of invasion, 2 smaller subsamples were cut near the core edge with a water-cooled electric saw, an easier, faster, and more precise technique.

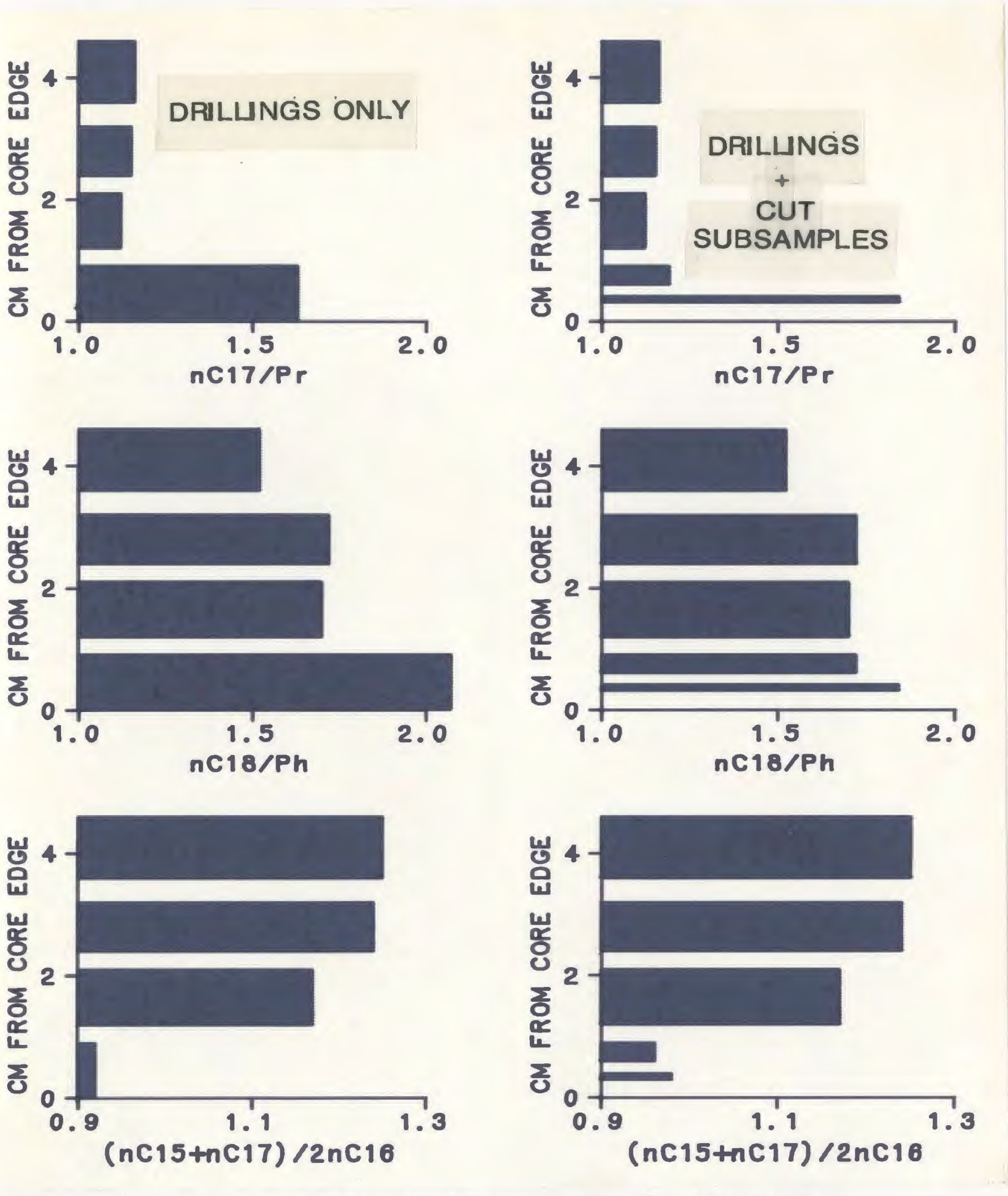


Figure A-2: Variation in component ratios across core

These are shown in Table A-1 and plotted in place of the lowest drilling (on the cross-section) in Fig. A-2.

From the nC_{17}/Pr ratio plots, invasion appears to extend about 0.75cm into the core. The ratio of nC_{18}/Ph indicates invasion to about 0.5cm, the high value for the core edge drilled sample probably due to material in the first 3mm not included in the saw-cut samples. The diesel range odd-carbon predominance shows a slight decrease 1.6cm from the edge and a more dramatic drop 0.5cm from the edge (Fig. A-2). Assuming the first slight drop to be natural variation in the shale, the subsamples indicate invasion of 0.9-1.2cm. This ratio is regarded as less reliable than the two previous.

Based on these results, 1.0cm of core, measured perpendicular to the edge, was removed with the water-cooled electric saw from visible core edges on all samples and all borders showing traces of mud solids, which indicate breakage before initial wiping down of the cores. These removed edges were stored in plastic bags and used for subsequent thin-section petrography, vitrinite reflectance, and visual kerogen typing. Small sample sizes prevented 1cm from being removed from all borders. Although many of these were created after wiping and drying or were relatively impermeable bedding planes, the possibility of remaining diesel oil contamination cannot be ruled out, particularly for samples showing no edge or slab cut whose initial orientation is thus unknown, or those in which the invasion depth may have exceeded 1cm.

Appendix B
TABULATED DATA

Table B-1: Data for lithological breakdown
* calculated from carbon loss data

M. Above Contact	Dry Wt. g.	% TOC (unextr.)	% TOC (extr.)	Bitumen g.	$CaCO_3$ %
92.0	55.9726	4.56	4.04	.3119	21.79
85.9	84.2162	3.43	3.04	.3227	15.91
79.3	24.3792	3.20	2.90	.1050	18.94
72.7	55.0601	3.66	3.29	.2918	14.76
66.4	50.5607	2.32	1.87	.3244	37.20
60.2	57.3912	3.59	3.02	.3131	18.44
54.4	61.8472	3.40	3.01	.3008	13.11
48.5	74.8739	1.85	1.71	.1541	34.75
43.1	39.1072	3.75	3.45	.2266	17.20
37.7	58.0955	4.56	4.07	.3279	17.99
32.8	48.6545	5.57	4.89	.2900	13.45
25.5	67.2659	1.50	1.27	.1945	51.48
23.5	29.8492	1.76	1.51	.0958	16.50
21.6	77.3172	1.91	1.48	.3561	47.79
19.6	57.1067	1.30	1.10	.0887	13.63
17.9	41.1711	2.13	1.89	.1226	16.65
15.8	78.9182	1.70	1.43	.2739	27.05
12.4	52.1647	3.05	2.71	.1799	10.31
10.5	59.7047	1.35	1.05	.1848	28.13
9.2	19.3010	3.25	2.81	.0907	21.00
7.7	91.0517	1.91	1.60	.3056	16.33
6.2	23.2249	2.85	2.53	.1106	11.32
4.9	54.1614	2.18	1.82	.1785	36.52
3.2	48.5323	3.02	2.72	.2013	9.79
1.4	56.9184	3.20	2.79	.3248	10.46
0.0	100.6915	2.27	1.99	.3250*	36.49

Table B-2: Bitumen fractionation results

* calculated from carbon loss data

SAMPL (m)	SAT. (g)	ARO. (g)	RES. (g)	ASP. (g)	BIT. (g)	S/A RATIO
92.0	.0708	.0687	.0741	.0983	.3119	1.0308
85.9	.0744	.0746	.0843	.0895	.3227	.9973
79.3	.0280	.0234	.0292	.0244	.1050	1.1962
72.7	.0749	.0757	.0691	.0721	.2918	.9893
66.4	.1134	.0739	.0949	.0422	.3244	1.5353
60.2	.0841	.0754	.0793	.0743	.3131	1.1149
54.4	.0809	.0796	.0755	.0648	.3008	1.0164
48.5	.0285	.0361	.0463	.0431	.1541	.7915
43.1	.0496	.0460	.0577	.0733	.2266	1.0768
37.7	.0740	.0861	.0866	.0811	.3279	.8596
32.8	.0592	.0788	.0776	.0745	.2900	.7516
25.5	.0634	.0480	.0484	.0348	.1945	1.3227
23.5	.0265	.0190	.0278	.0226	.0958	1.3941
21.6	.1334	.0827	.0739	.0661	.3561	1.6119
19.6	.0163	.0193	.0265	.0266	.0887	.8465
17.9	.0298	.0273	.0305	.0351	.1226	1.0928
15.8	.0975	.0561	.0620	.0584	.2739	1.7393
12.4	.0475	.0462	.0416	.0446	.1799	1.0278
10.5	.0508	.0358	.0472	.0510	.1848	1.4202
9.2	.0167	.0198	.0272	.0269	.0907	.8471
7.7	.0751	.0591	.1006	.0708	.3056	1.2718
6.2	.0220	.0250	.0294	.0342	.1106	.8799
4.9	.0396	.0425	.0484	.0480	.1785	.9321
3.2	.0432	.0457	.0538	.0587	.2013	.9453
1.4	.0601	.0641	.0651	.1355	.3248	.9378
0.0	.0864	.0587	.0839	.0959	.3250*	1.4720
-	-	-	-	-	-	-
OIL	.1568	.0554	.0152	.0047	.2320	2.8281
BLANK	0	.0003	.0005	.0001	.0009	0

Table B-3: Percentage composition of bitumens

SAMPL (m)	% SAT.	% ARO.	% RES.	% ASP.	% HC	% NSO
92.0	22.7	22.0	23.8	31.5	44.7	55.3
85.9	23.0	23.1	26.1	27.7	46.2	53.8
79.3	26.7	22.3	27.8	23.2	49.0	51.0
72.7	25.7	25.9	23.7	24.7	51.6	48.4
66.4	35.0	22.8	29.3	13.0	57.7	42.3
60.2	26.8	24.1	25.3	23.7	50.9	49.1
54.4	26.9	26.5	25.1	21.5	53.4	46.6
48.5	18.5	23.4	30.1	28.0	41.9	58.1
43.1	21.9	20.3	25.5	32.4	42.2	57.8
37.7	22.6	26.3	26.4	24.7	48.8	51.2
32.8	20.4	27.2	26.7	25.7	47.6	52.4
25.5	32.6	24.7	24.9	17.9	57.3	42.7
23.5	27.6	19.8	29.0	23.6	47.4	52.6
21.6	37.4	23.2	20.7	18.6	60.7	39.3
19.6	18.4	21.7	29.9	30.0	40.1	59.9
17.9	24.3	22.3	24.8	28.6	46.6	53.4
15.8	35.6	20.5	22.6	21.3	56.1	43.9
12.4	26.4	25.7	23.1	24.8	52.1	47.9
10.5	27.5	19.4	25.5	27.6	46.9	53.1
9.2	18.5	21.8	30.0	29.7	40.3	59.7
7.7	24.6	19.3	32.9	23.2	43.9	56.1
6.2	19.9	22.6	26.6	30.9	42.5	57.5
4.9	22.2	23.8	27.1	26.9	46.0	54.0
3.2	21.4	22.7	26.7	29.2	44.1	55.9
1.4	18.5	19.7	20.0	41.7	38.2	61.8
0.0	26.6	18.1	25.8	29.5	44.7	55.3
-	-	-	-	-	-	-
OIL	67.6	23.9	6.5	2.0	91.4	8.6
BLANK	0.0	33.0	54.9	12.1	33.0	67.0

Table B-4: Rock-normalized bitumen composition

SAMPL (m)	SAT. (ppm)	ARO. (ppm)	RES. (ppm)	ASP. (ppm)	BIT. (ppm)	HC (ppm)
92.0	1265	1227	1324	1757	5572	2492
85.9	883	886	1001	1063	3832	1769
79.3	1150	961	1196	999	4306	2111
72.7	1361	1375	1255	1310	5301	2736
66.4	2243	1461	1877	835	6415	3704
60.2	1465	1314	1382	1295	5456	2779
54.4	1308	1287	1220	1048	4863	2595
48.5	381	482	619	576	2058	863
43.1	1268	1177	1475	1874	5794	2445
37.7	1274	1482	1491	1397	5644	2756
32.8	1217	1619	1594	1530	5960	2835
25.5	943	713	719	517	2892	1656
23.5	886	636	932	756	3210	1522
21.6	1725	1070	956	855	4606	2795
19.6	286	338	464	466	1554	623
17.9	725	663	740	851	2979	1388
15.8	1236	710	785	740	3471	1946
12.4	910	885	798	855	3448	1795
10.5	851	599	790	855	3095	1450
9.2	868	1024	1412	1395	4698	1892
7.7	825	649	1105	778	3357	1474
6.2	947	1076	1266	1473	4763	2024
4.9	731	785	893	886	3295	1516
3.2	889	941	1108	1209	4148	1830
1.4	1056	1126	1143	2381	5706	2181
0.0	858	583	833	953	3227	1442

Table B-5: Carbon-normalized bitumen composition

SAMP. (m)	SAT. mg/gTOC	ARO. mg/gTOC	RES. mg/gTOC	ASP. mg/gTOC	BIT. mg/gTOC	HC mg/gTOC
92.0	27.7	26.9	29.0	38.5	122.2	54.6
85.9	25.8	25.8	29.2	31.0	111.7	51.6
79.3	35.9	30.0	37.4	31.2	134.6	66.0
72.7	37.2	37.6	34.3	35.8	144.8	74.8
66.4	96.7	63.0	80.9	36.0	276.5	159.6
60.2	40.8	36.6	38.5	36.1	152.0	77.4
54.4	38.5	37.9	35.9	30.8	143.0	76.3
48.5	20.6	26.0	33.4	31.1	111.2	46.6
43.1	33.8	31.4	39.3	50.0	154.5	65.2
37.7	27.9	32.5	32.7	30.6	123.8	60.4
32.8	21.8	29.1	28.6	27.5	107.0	50.9
25.5	62.9	47.5	47.9	34.5	192.8	110.4
23.5	50.4	36.1	52.9	43.0	182.4	86.5
21.6	90.3	56.0	50.0	44.8	241.1	146.3
19.6	22.0	26.0	35.7	35.9	119.5	47.9
17.9	34.0	31.1	34.7	40.0	139.9	65.1
15.8	72.7	41.8	46.2	43.5	204.2	114.5
12.4	29.8	29.0	26.2	28.0	113.1	58.9
10.5	63.0	44.4	58.5	63.3	229.3	107.4
9.2	26.7	31.5	43.4	42.9	144.6	58.2
7.7	43.2	34.0	57.9	40.7	175.7	77.2
6.2	33.2	37.8	44.4	51.7	167.1	71.0
4.9	33.5	36.0	41.0	40.6	151.1	69.5
3.2	29.4	31.2	36.7	40.0	137.3	60.6
1.4	33.0	35.2	35.7	74.4	178.3	68.2
0.0	37.8	25.7	36.7	42.0	142.2	63.5

Table B-6: Miscellaneous GC results

SAMPL (m)	**Pr/nC$_{17}$**	**Ph/nC$_{18}$**	**Pr/Ph**	**QC**	**MPI**	**% n-ALK in ARO.**
92.0	1.924	0.900	2.472	0.069	0.642	0.16
85.9	1.800	0.865	2.804	0.041	0.614	0.15
79.3	1.366	0.834	1.946	0.050	0.631	1.50
72.7	1.649	0.928	2.081	0.055	0.658	0.16
66.4	3.182	3.272	1.203	0.099	0.524	0.07
60.2	1.054	0.852	1.496	0.095	0.644	0.07
54.4	2.270	2.152	1.288	0.063	0.545	0.28
48.5	2.291	0.938	2.694	0.042	0.506	0.98
43.1	1.058	0.642	1.891	0.112	0.599	0.69
37.7	1.822	0.842	2.459	0.060	0.589	0.25
32.8	1.507	0.851	2.024	0.062	0.596	0.07
25.5	1.108	0.723	1.771	0.054	0.531	0.39
23.5	0.861	0.567	1.880	0.091	0.551	1.84
21.6	0.746	0.610	1.421	0.107	0.549	0.21
19.6	1.403	0.610	2.563	0.038	0.530	1.55
17.9	1.284	0.743	2.060	0.035	0.479	1.08
15.8	0.962	0.683	1.605	0.069	0.452	0.14
12.4	1.727	1.236	1.708	0.033	0.388	0.75
10.5	1.212	0.651	2.190	0.051	0.429	0.50
9.2	1.184	0.772	1.598	0.022	0.458	1.30
7.7	1.230	0.710	1.966	0.058	0.475	0.16
6.2	1.576	0.864	1.936	0.002	0.488	1.47
4.9	1.688	0.922	1.936	0.041	0.493	0.55
3.2	1.684	0.878	1.948	0.021	0.488	0.50
1.4	1.655	0.847	2.028	0.028	0.502	0.18
0.0	0.672	0.588	1.145	0.081	0.563	1.19
-	-	-	-	-	-	-
OIL	0.515	0.525	1.002	0.017	0.589	0.19

Table B-7: Carbon isotopic data (vs. PDB)

SAMP. (m)	**δ^{13}C Sat.**	**δ^{13}C Aro.**	**δ^{13}C Res.**	**δ^{13}C Asp.**	**δ^{13}C Ker.**	**δ^{13}C TOC**	**δ^{13}C TOC (extr.**	**CV**
92.0	-29.5	-28.9	-30.5	-29.5	-28.9	-29.6	-30.0	-1.30
85.9	-29.7	-29.0	-30.2	-29.1	-28.0	-28.7	-29.3	-0.74
79.3	-30.8	-29.9	-31.2	-29.6	-28.8	-29.2	-29.8	-0.10
72.7	-30.2	-28.8	-30.7	-28.2	-27.1	-27.9	-28.5	0.96
66.4	-23.5	-25.0	-28.1	-25.2	-25.7	-25.8	-27.5	-7.56
60.2	-27.2	-27.3	-29.6	-27.1	-26.2	-27.6	-28.3	-3.33
54.4	-27.1	-27.9	-29.8	-28.0	-27.5	-27.8	-29.4	-4.97
48.5	-29.6	-30.0	-31.0	-29.5	-28.5	-29.2	-30.2	-3.26
43.1	-29.2	-29.6	-30.1	-28.9	-28.6	-29.1	-29.3	-3.49
37.7	-29.4	-29.8	-31.6	-29.6	-29.2	-29.4	-30.7	-3.31
32.8	-28.5	-28.4	-31.3	-29.5	-28.7	-29.2	-30.8	-2.46
25.5	-29.0	-28.7	-31.0	-28.0	-27.2	-27.7	-29.0	-1.97
23.5	-29.1	-28.5	-30.8	-28.3	-27.7	-27.9	-29.1	-1.27
21.6	-27.9	-27.5	-29.4	-26.4	-25.6	-26.6	-27.1	-2.02
19.6	-29.5	-29.0	-30.2	-28.5	-27.8	-28.0	-28.9	-1.38
17.9	-29.4	-28.9	-29.9	-28.5	-27.8	-28.4	-28.8	-1.57
15.8	-29.3	-28.3	-29.6	-27.7	-26.8	-27.4	-27.9	-0.42
12.4	-29.3	-29.0	-30.8	-28.2	-27.4	-28.2	-29.0	-2.03
10.5	-29.2	-28.6	-30.7	-28.1	-27.3	-29.2	-28.9	-1.36
9.2	-28.4	-27.7	-29.2	-26.4	-25.4	-25.9	-26.9	-1.41
7.7	-30.3	-28.6	-30.4	-28.5	-27.6	-28.3	-28.6	1.47
6.2	-29.7	-28.7	-30.9	-28.9	-28.1	-28.6	-29.5	-0.21
4.9	-29.7	-28.9	-31.4	-29.1	-28.4	-28.8	-29.9	-0.69
3.2	-30.2	-28.9	-31.7	-29.8	-29.1	-29.7	-30.6	0.61
1.4	-30.1	-29.0	-31.5	-30.0	-29.3	-29.8	-30.7	0.24
0.0	-29.4	-28.7	-31.2	-29.1	-28.5	-29.0	-30.0	-0.83
-	-	-	-	-	-	-	-	-
OIL	-28.5	-27.8	-29.2	-28.3	-	-	-28.7	-1.22

Table B-8: MS results: saturate fractions (volume %)
(MA = monoaromatics)

COMP CLAS	66.4m	25.5m	17.9m	15.8m	12.4m	10.5m	0.0m	OIL
Chain	43.8	30.0	26.2	32.3	24.9	30.0	36.2	32.9
1 Ring	10.3	14.3	11.8	14.7	13.3	13.1	14.2	12.5
2 Ring	7.1	9.3	6.1	8.9	7.1	8.0	8.2	6.1
3 Ring	7.2	10.1	13.7	9.4	11.0	11.2	7.6	6.8
4 Ring	14.8	17.7	26.9	16.9	20.6	22.8	16.0	15.8
5 Ring	14.5	16.6	12.3	15.5	15.3	12.1	16.3	21.4
6 Ring	0.0	0.0	0.0	0.0	5.2	0.0	0.0	0.0
MA	2.4	1.9	3.0	2.3	2.6	2.7	1.4	4.6

Table B-9: MS results: aromatic fractions (volume %)

COMPOUND CLASS	66.4 m	25.5 m	17.9 m	15.8 m	12.4 m	10.5 m	0.0 m	OI
MONOAROMATICS:								
Alkylbenzenes	16.6	15.9	12.7	22.8	11.4	17.3	18.6	20.1
Naphthenebenzenes	15.7	15.0	12.9	13.1	12.2	12.6	12.2	14.2
Dinaphthenebenzenes	11.1	10.3	11.1	10.0	10.5	10.9	10.9	12.1
DIAROMATICS:								
Naphthalenes	10.7	10.7	11.6	10.1	7.7	12.8	13.1	9.5
Acenaphthenes,Biphenyls	8.6	8.8	10.3	8.2	9.8	9.6	9.1	9.1
Fluorenes	7.3	7.8	8.4	7.5	9.3	7.2	7.2	7.7
TRIAROMATICS:								
Phenanthrenes	7.0	8.2	9.0	8.6	7.2	8.2	8.8	7.3
Naphthenephenanthrenes	5.5	5.1	5.7	0.8	6.9	5.2	4.2	4.2
TETRAAROMATICS:								
Pyrenes	3.7	4.3	4.3	4.2	5.0	3.8	3.7	3.5
Chrysenes	1.2	1.6	1.4	1.6	2.5	1.3	0.9	1.1
PENTAAROMATICS:								
Perylenes	0.9	0.8	0.9	1.4	1.1	0.9	0.6	0.6
Dibenzanthracenes	0.3	0.4	0.6	0.4	0.4	0.6	0.1	0.6
THIOPHENO-AROMATICS:								
Benzothiophenes	2.5	1.9	1.9	0.0	2.2	1.5	1.8	1.5
Dibenzothiophenes	1.7	1.8	2.1	2.8	2.2	2.1	3.2	2.3
Naphthobenzothiophenes	0.1	0.0	0.0	0.2	0.5	0.2	0.3	0.3
UNIDENTIFIED AROMATICS:								
Class II	1.0	0.8	0.6	0.9	1.3	0.7	0.3	0.6
Class III	0.7	1.2	0.7	0.8	1.5	0.8	0.6	0.8
Class IV	3.4	3.3	3.8	5.0	5.5	3.4	2.6	2.8
Class V	0.8	1.1	0.7	0.9	0.5	0.2	0.5	0.4
Class VI	0.5	0.5	0.2	0.4	0.3	0.1	0.1	0.7
Class VII	0.5	0.3	0.2	0.2	1.3	0.2	0.3	0.6

Appendix C
GAS CHROMATOGRAMS

GC Conditions:

- Column : 30m DB-1 coated capillary
- Temperature Program :
  - 1 min hold at 80°C
  - 80°C to 320°C at 3°C/min
  - 10 min hold at 320°C
- Detector Temperature : 360°C
- On-Column Injection

C.1. Saturate fractions:

ip, vertical bars = isoprenoids
n = n-alkane, numbers = carbon atoms
key compounds identified at 66.4m

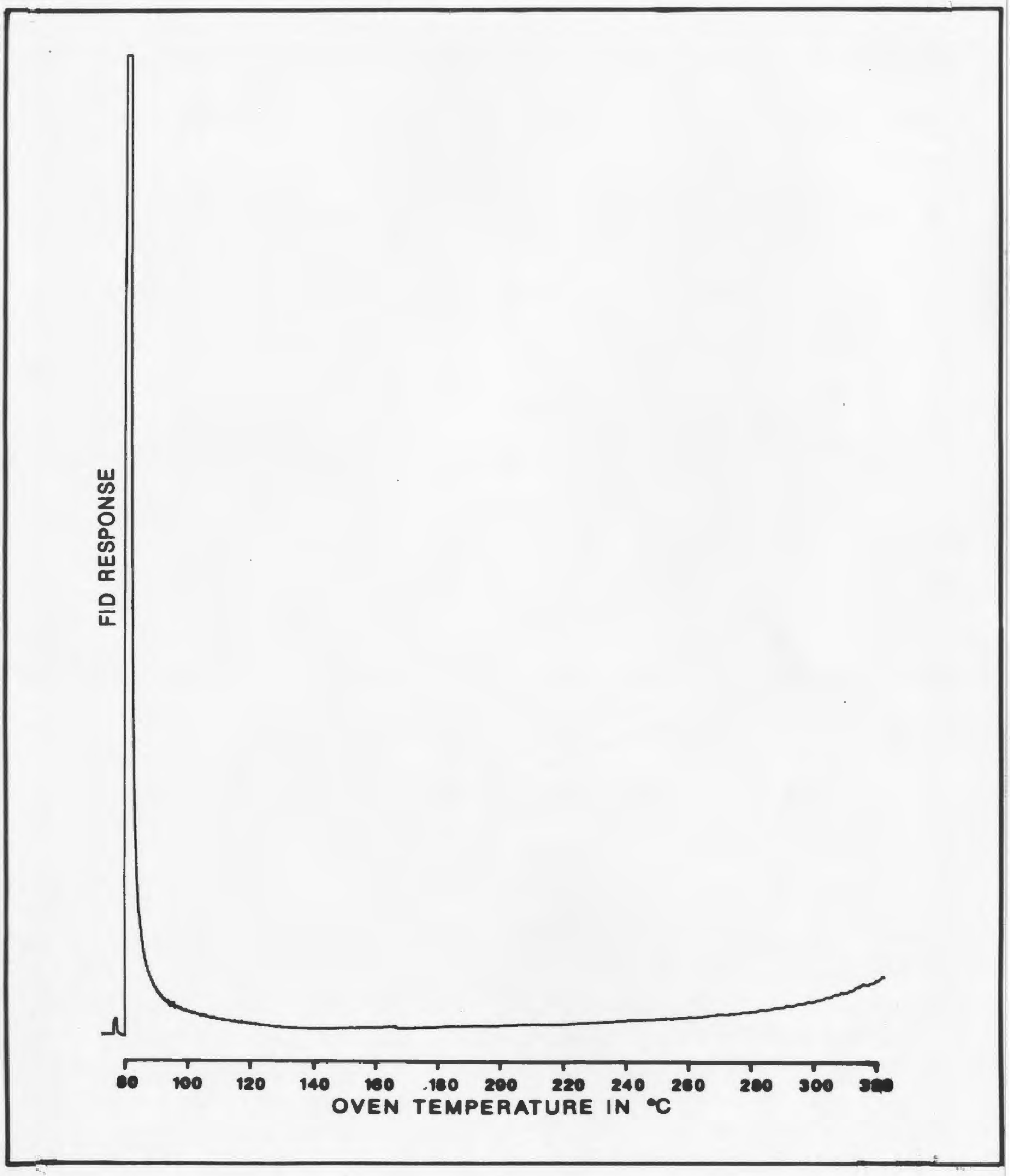


Figure C-1: Saturates, blank

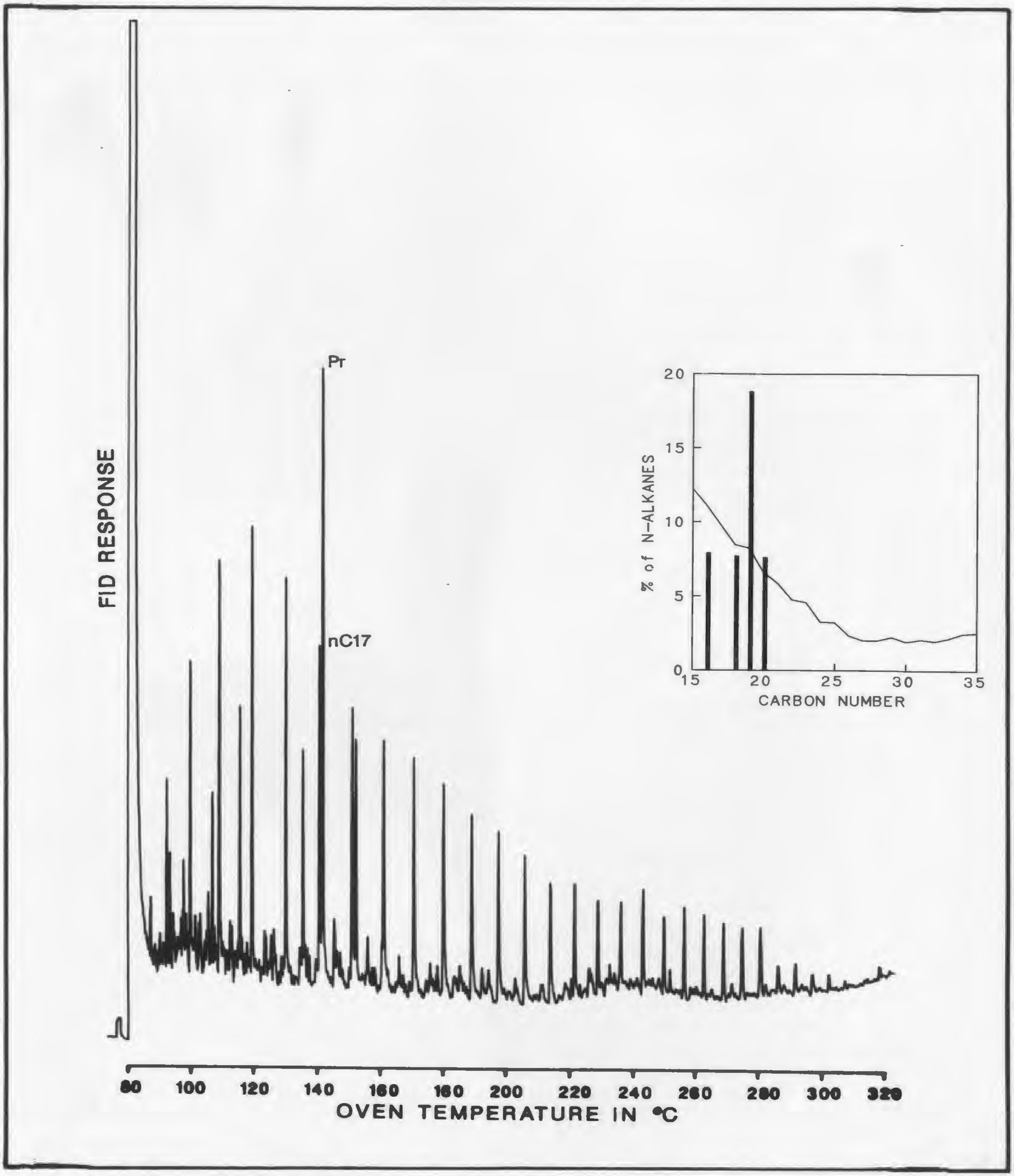


Figure C-2: Saturates, 92.0m

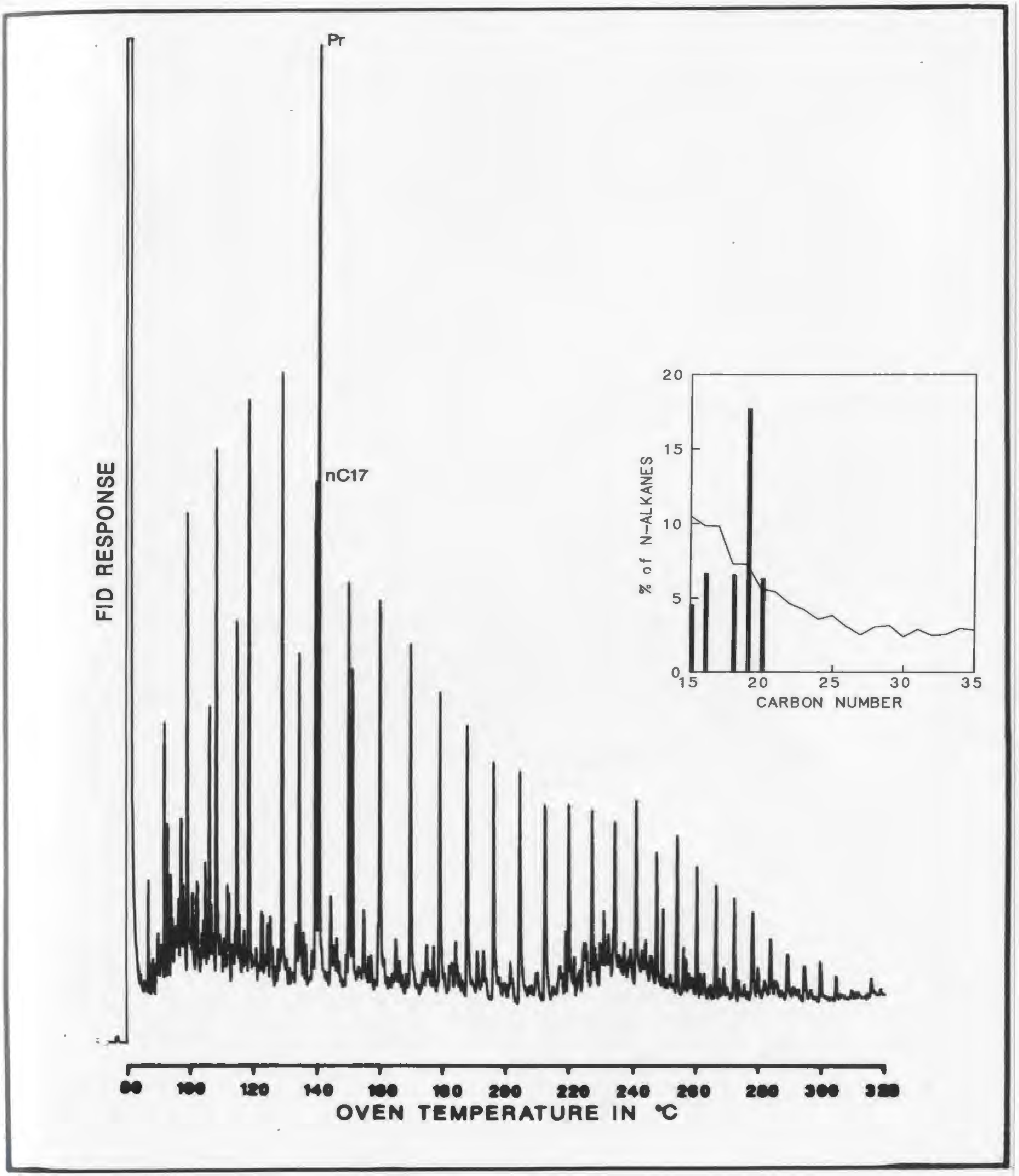


Figure C-3: Saturates, 85.9m

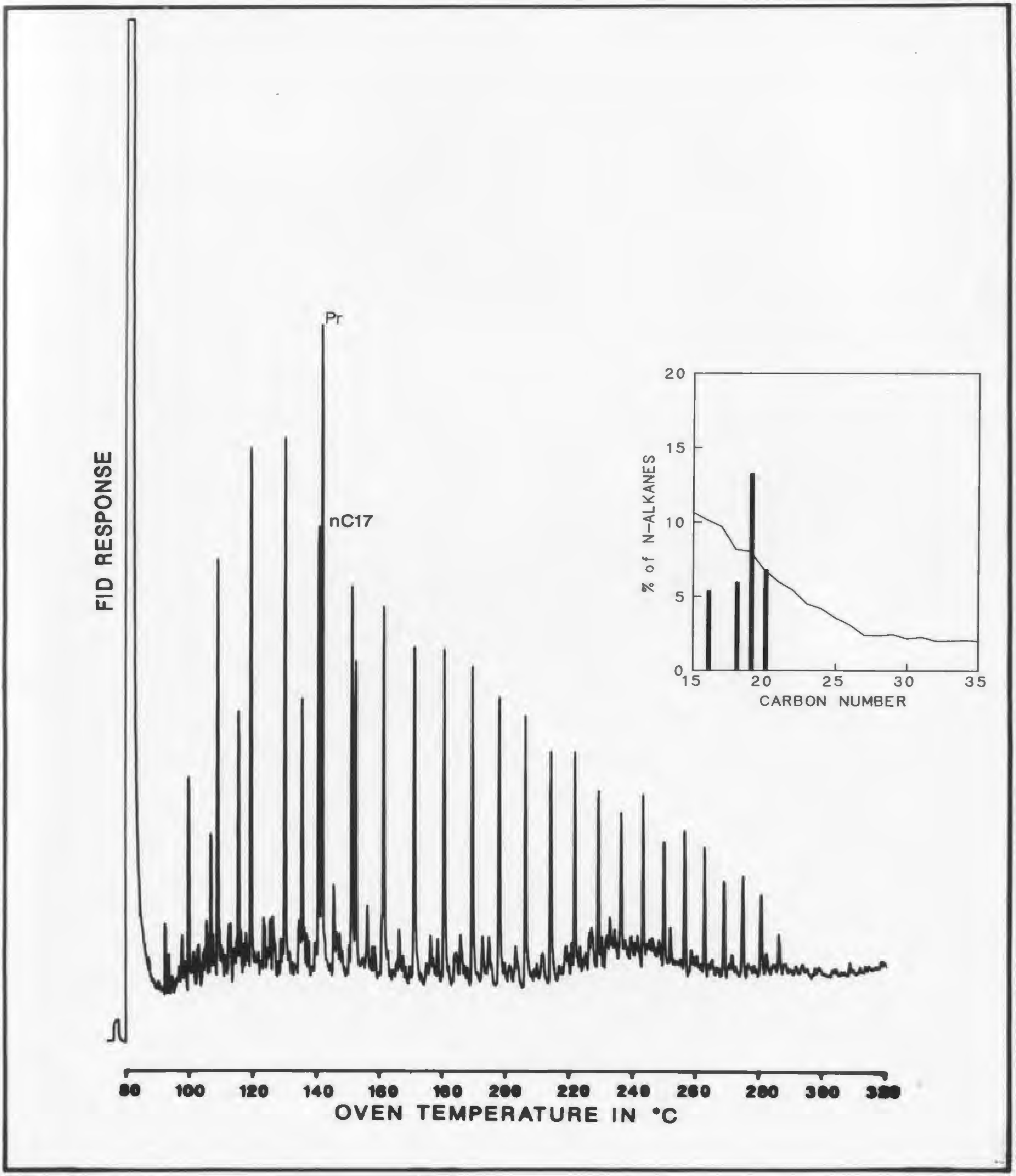


Figure C-4: Saturates, 79.3m

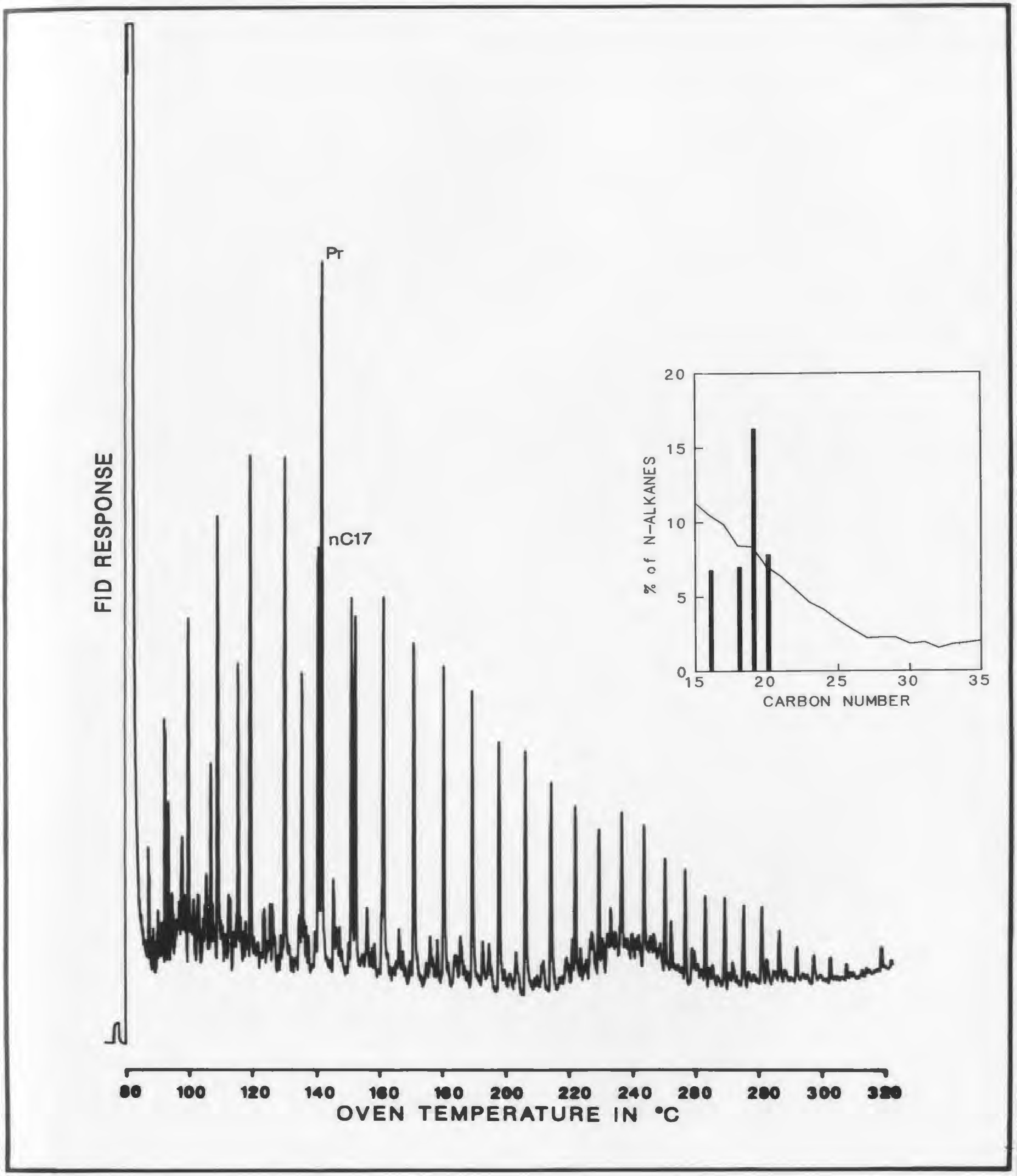


Figure C-5: Saturates, 72.7m

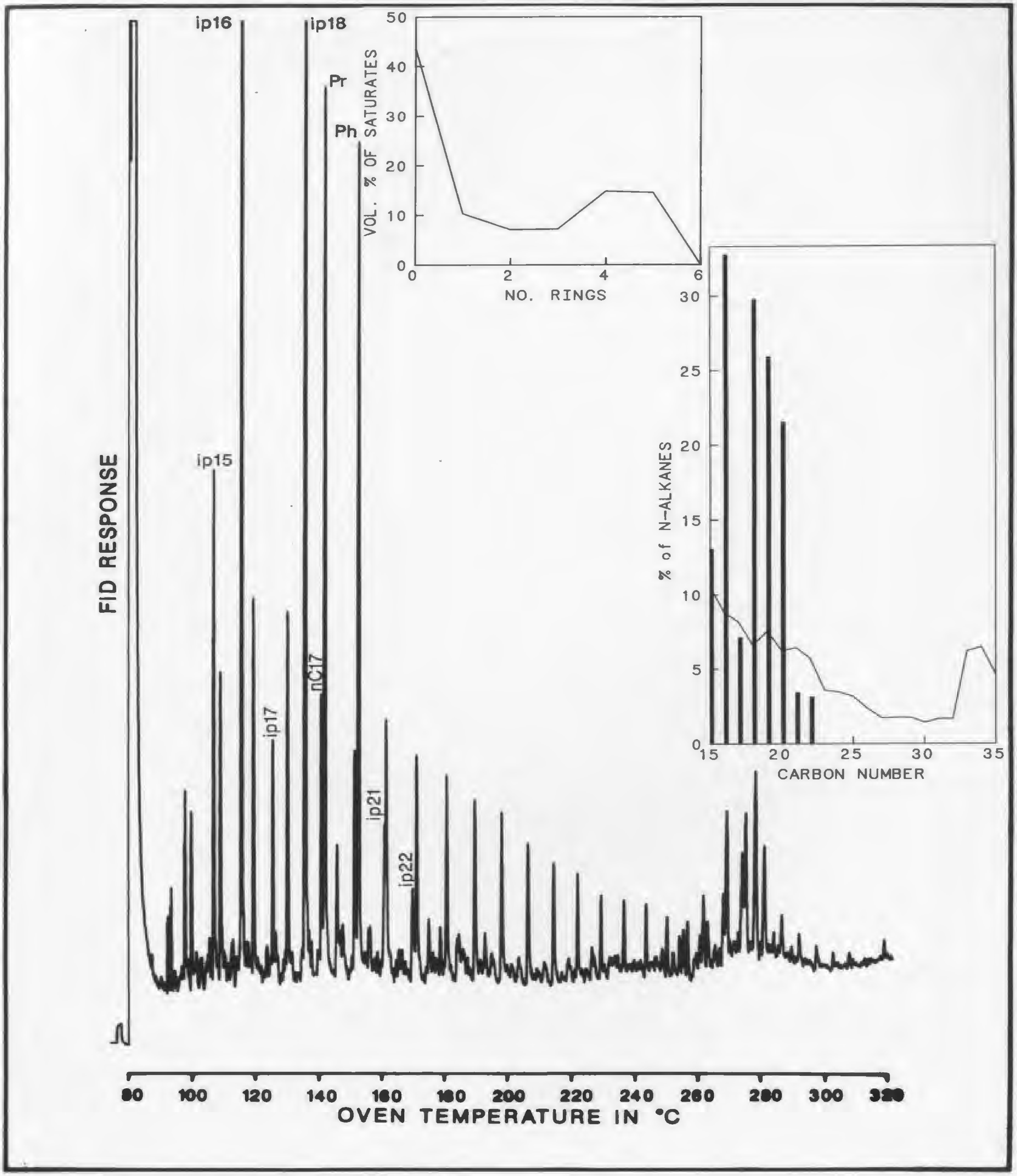


Figure C-6: Saturates, 66.4m

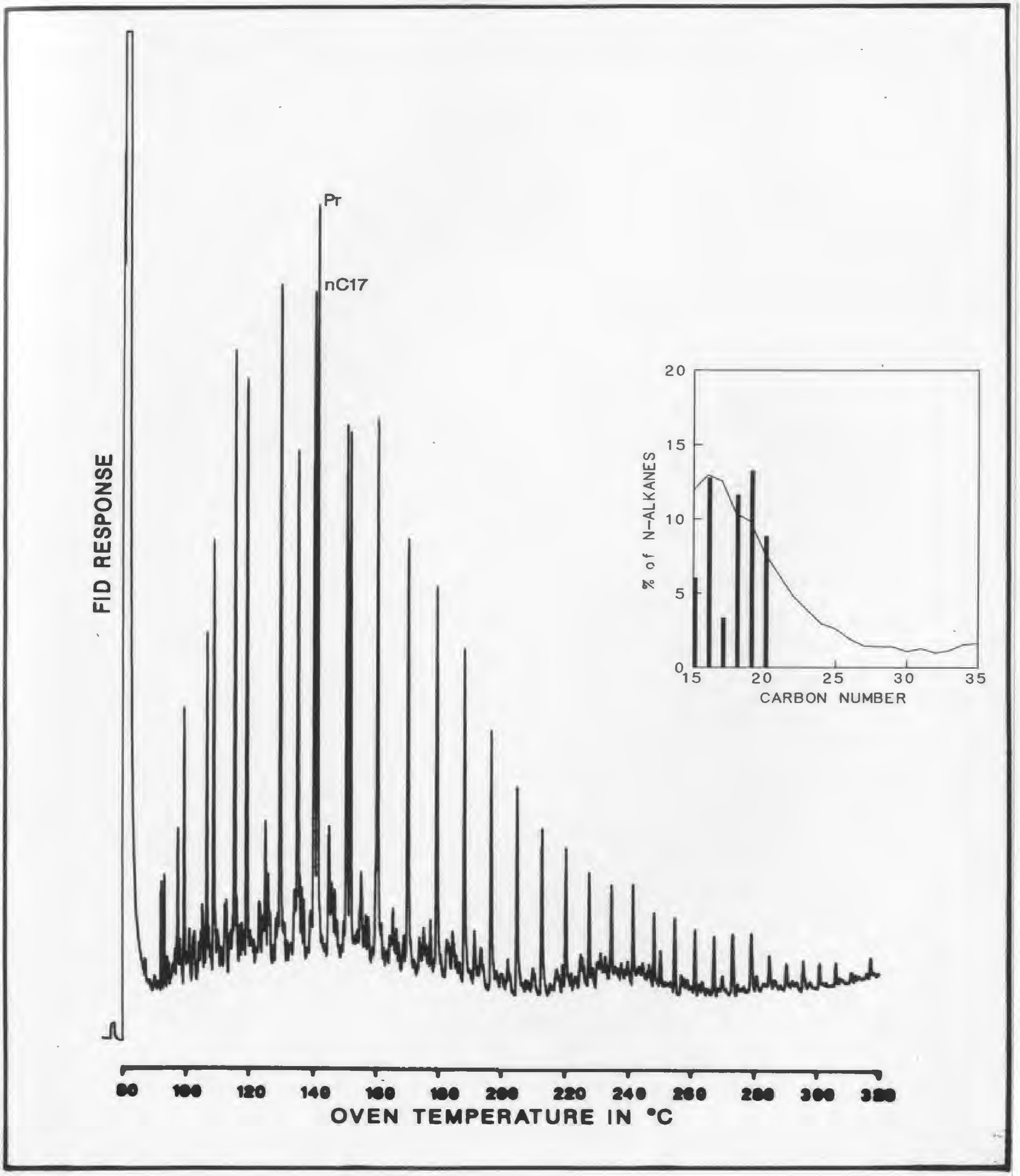


Figure C-7: Saturates, 60.2m

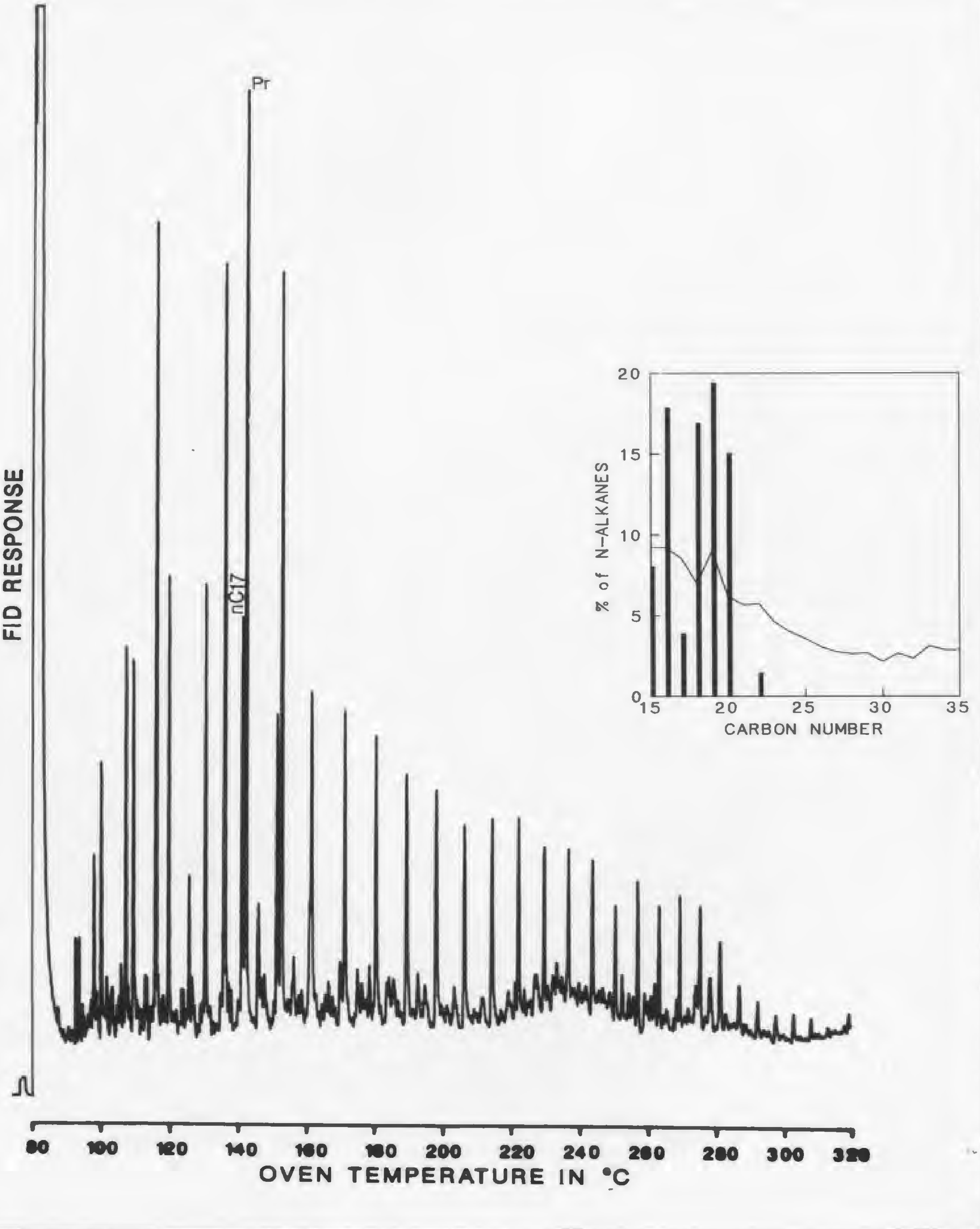


Figure C-8: Saturates, 54.4m

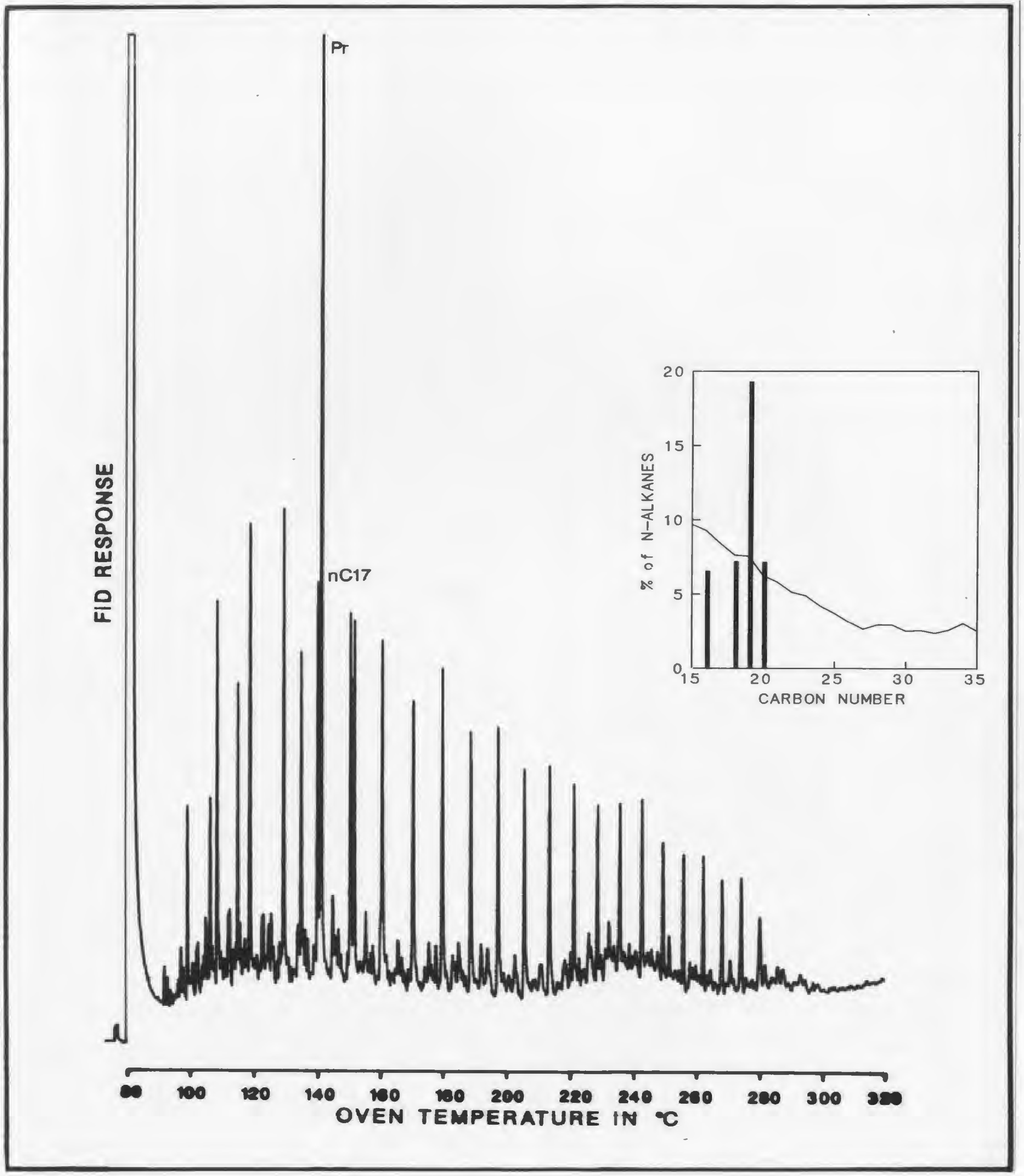


Figure C-9: Saturates, 48.5m

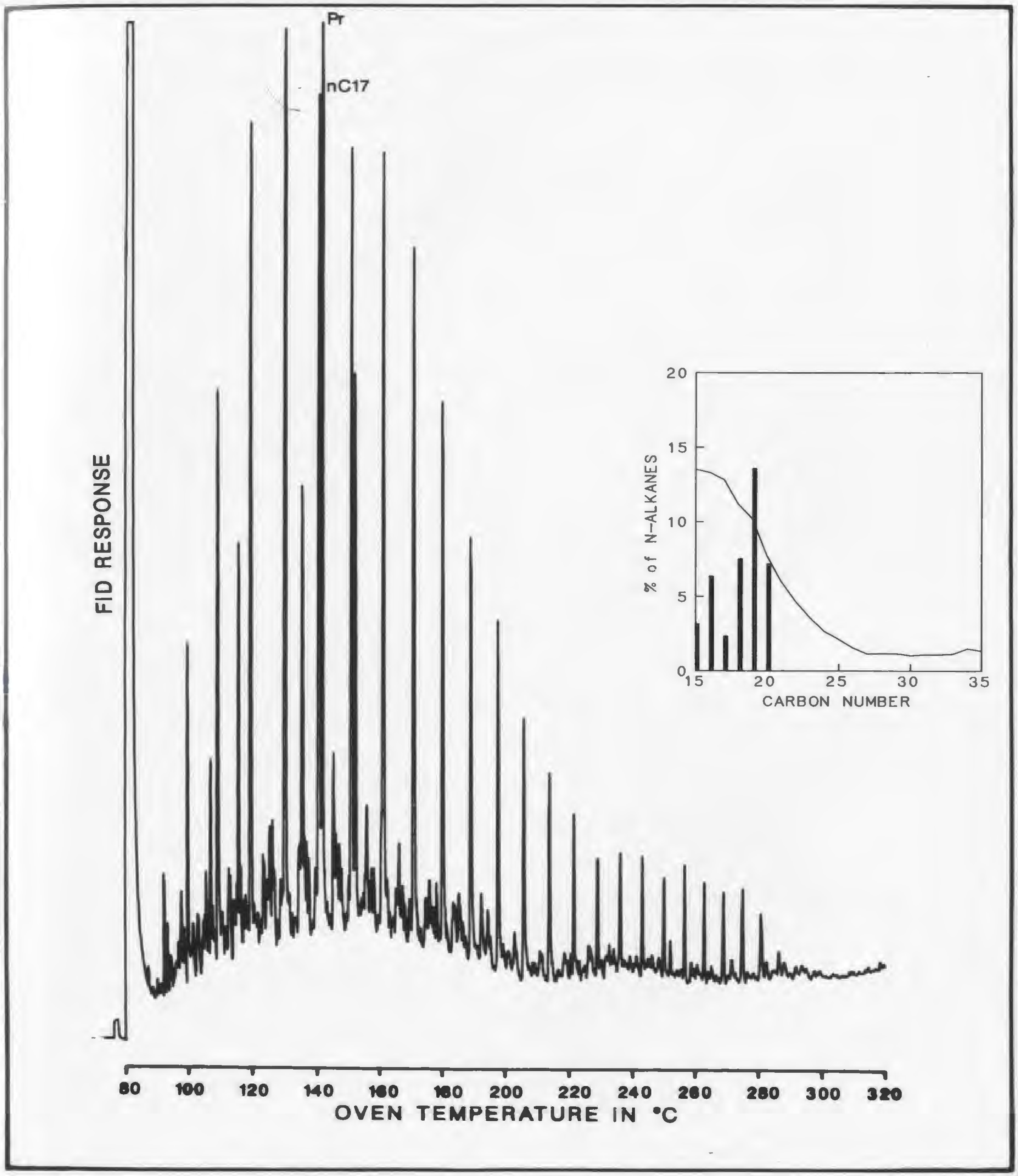


Figure C-10: Saturates, 43.1m

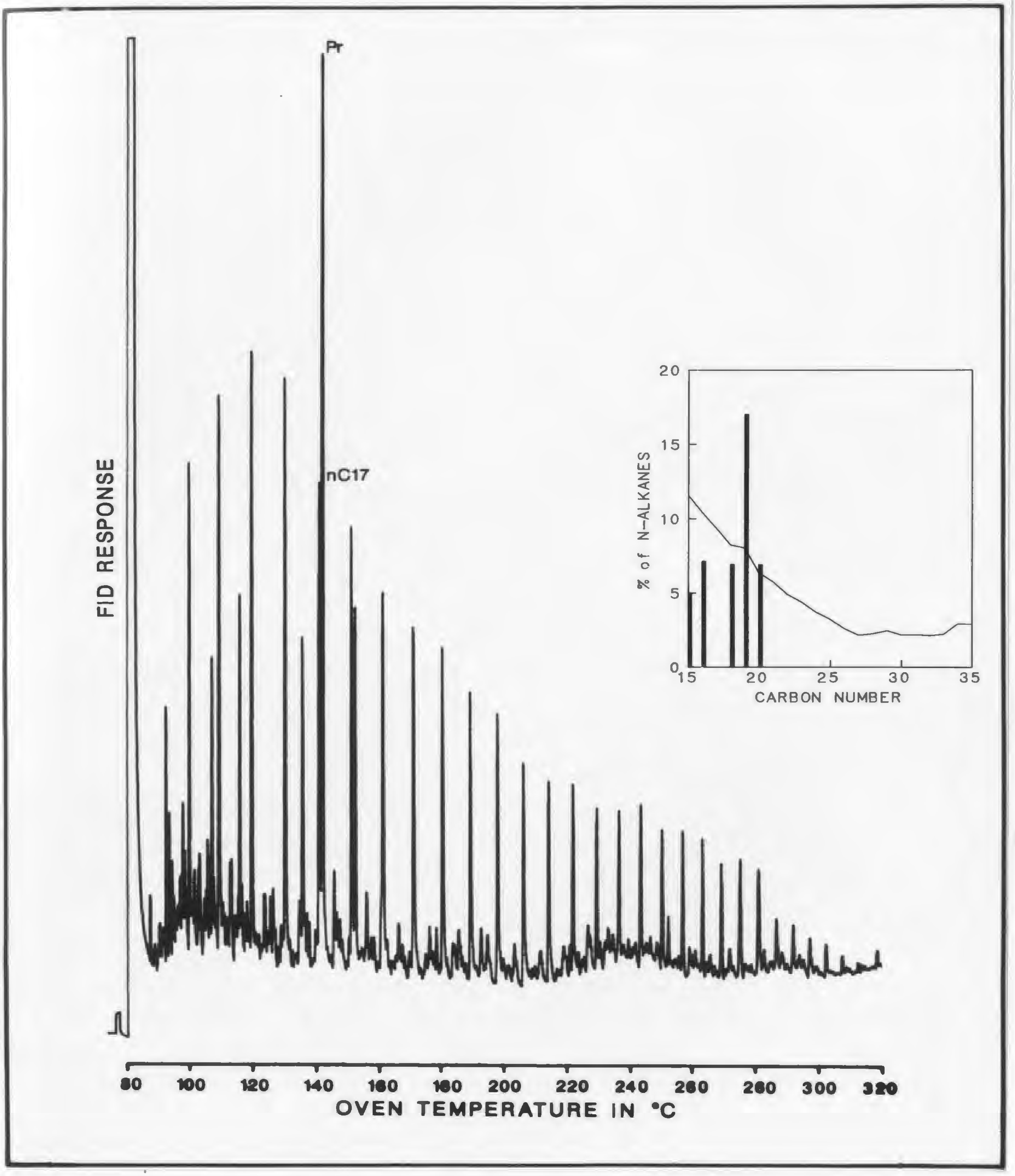


Figure C-11: Saturates, 37.7m

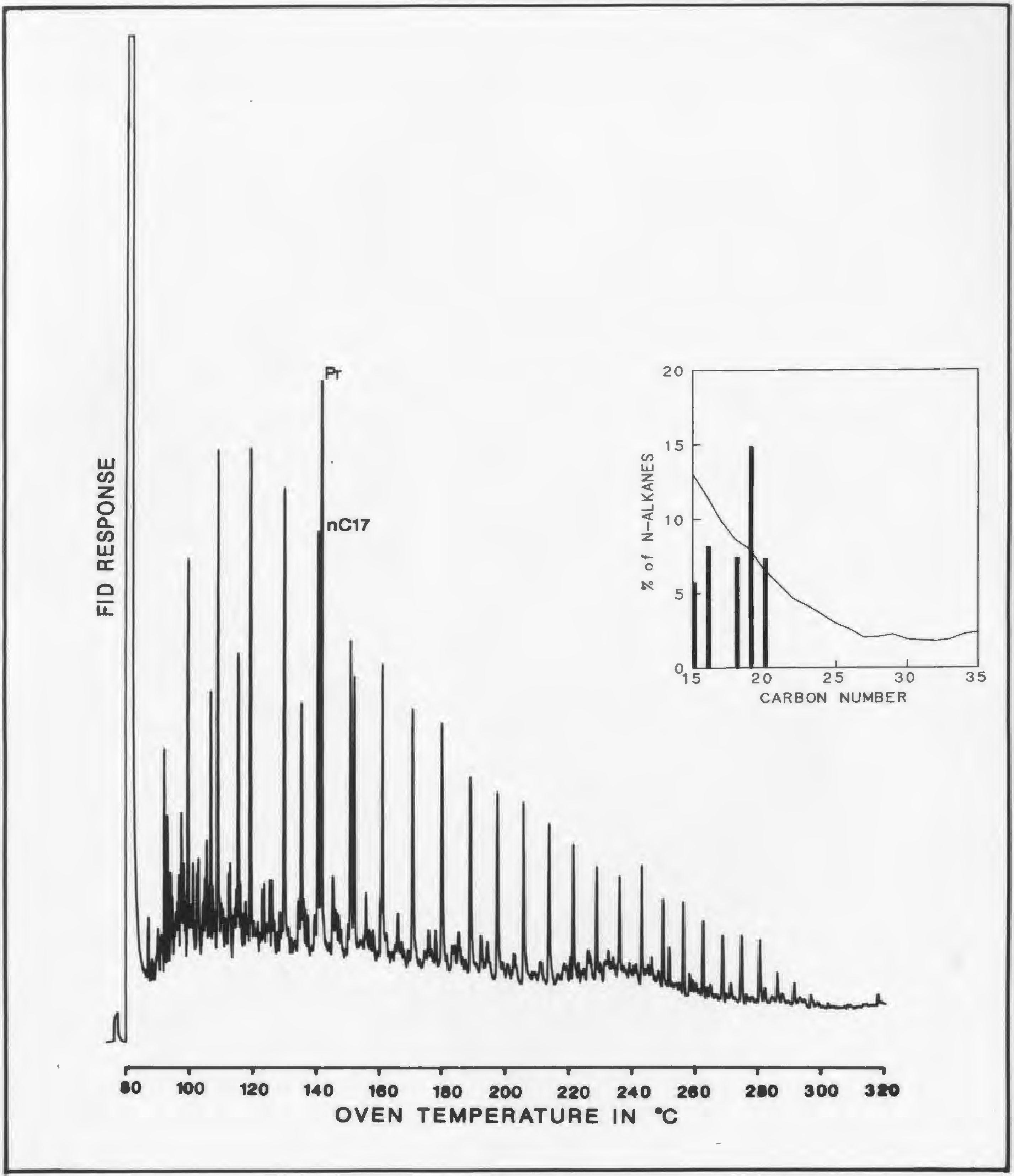


Figure C-12: Saturates, 32.8m

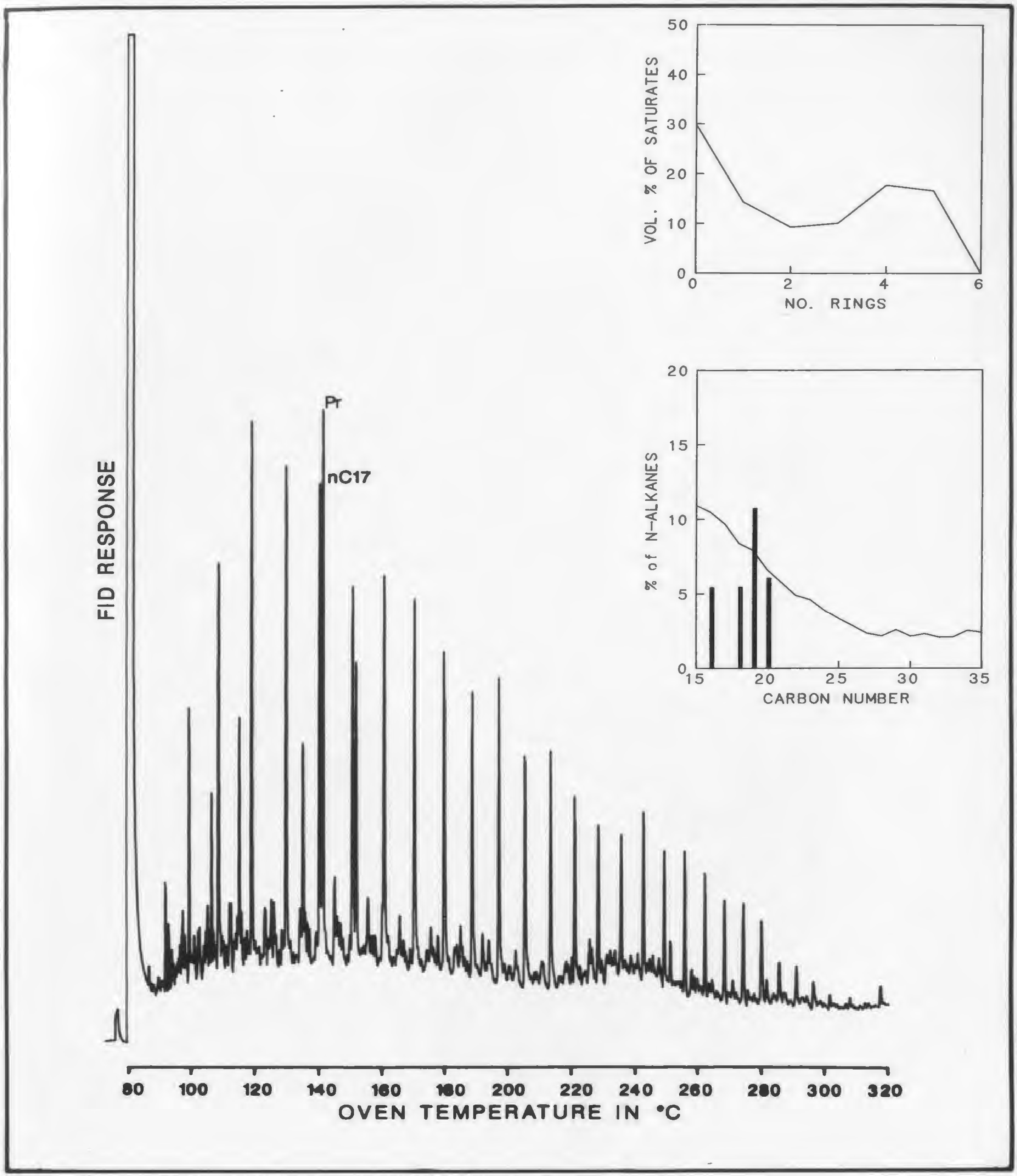


Figure C-13: Saturates, 25.5m

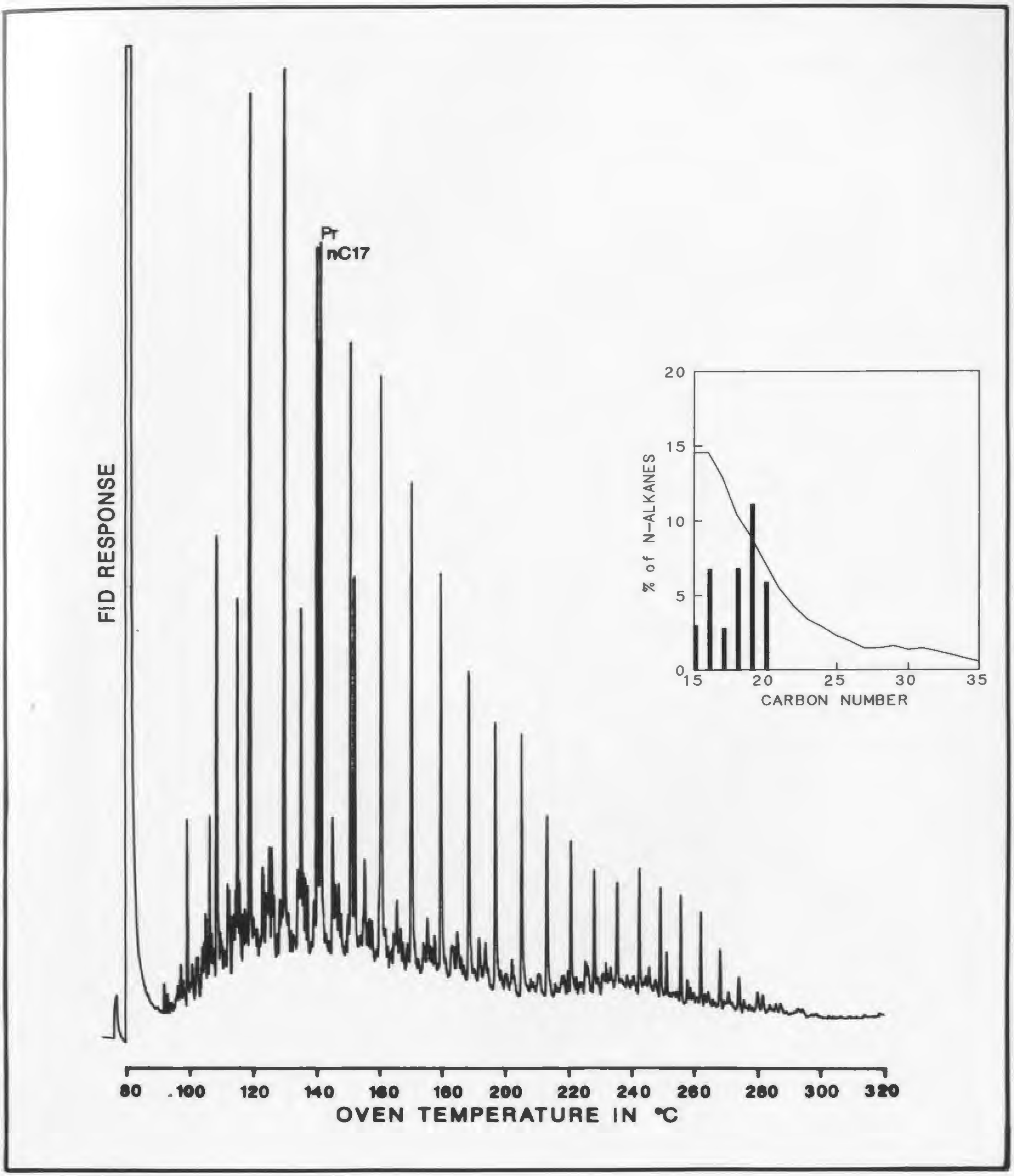


Figure C-14: Saturates, 23.5m

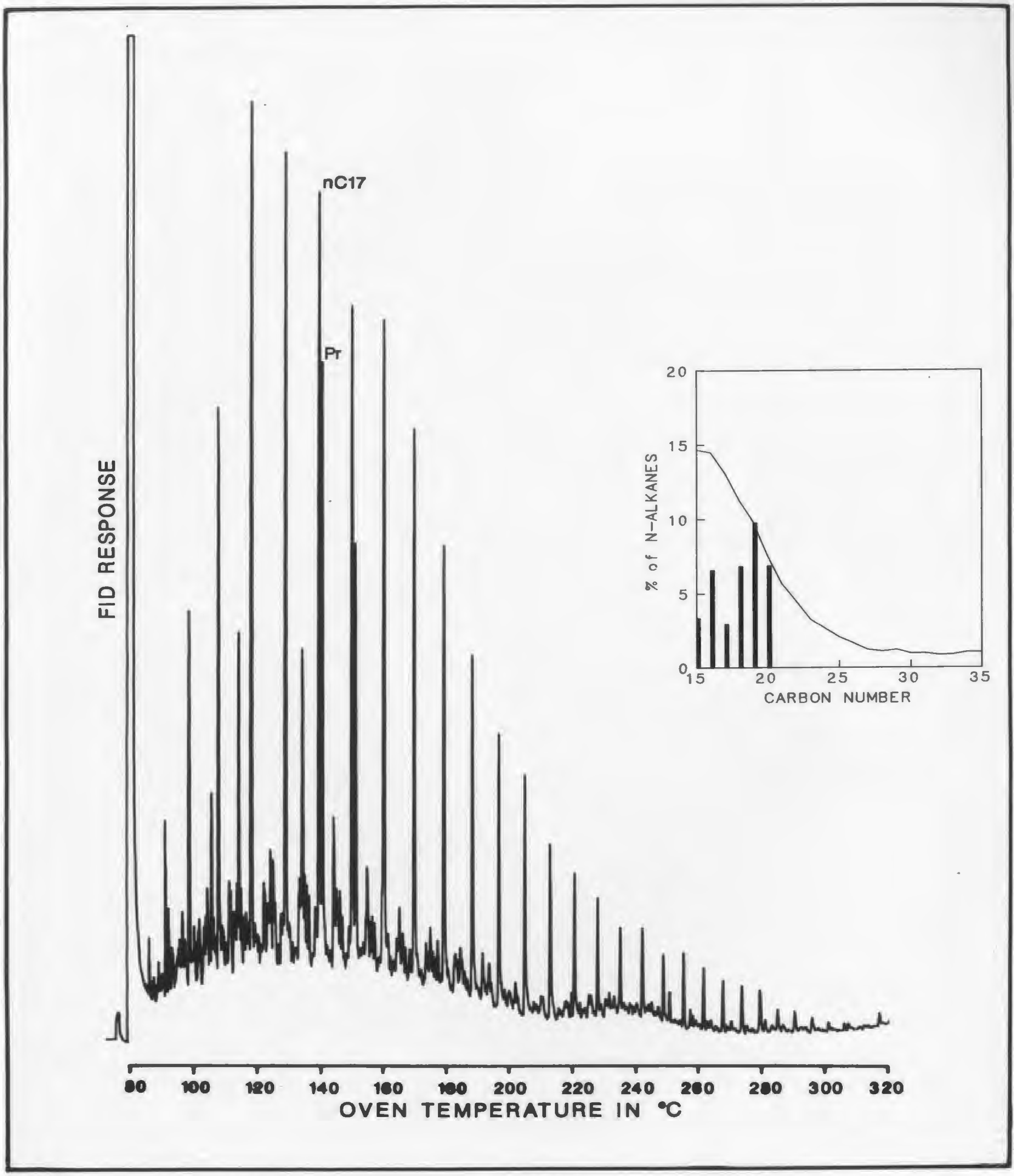


Figure C-15: Saturates, 21.6m

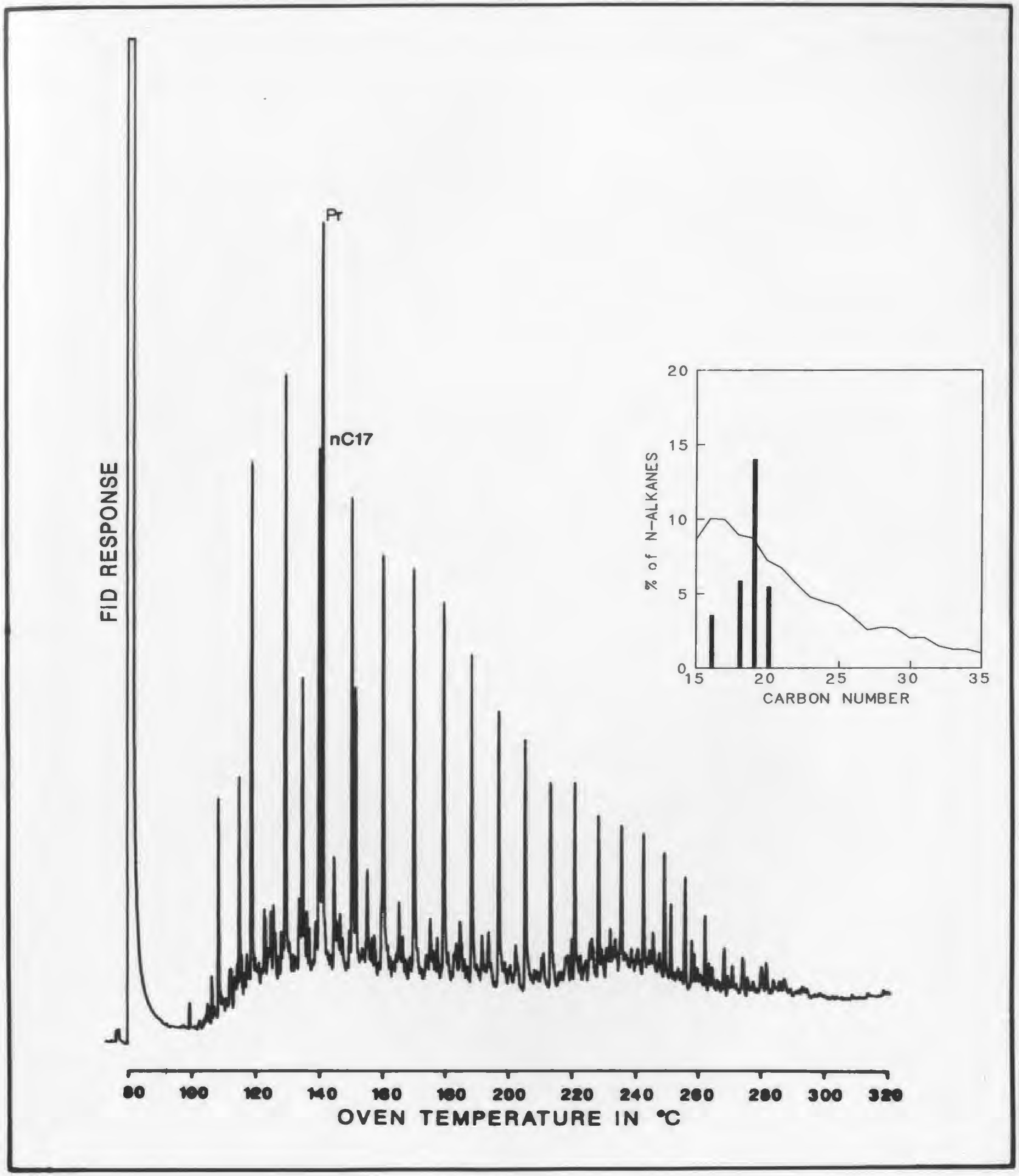


Figure C-16: Saturates, 19.6m

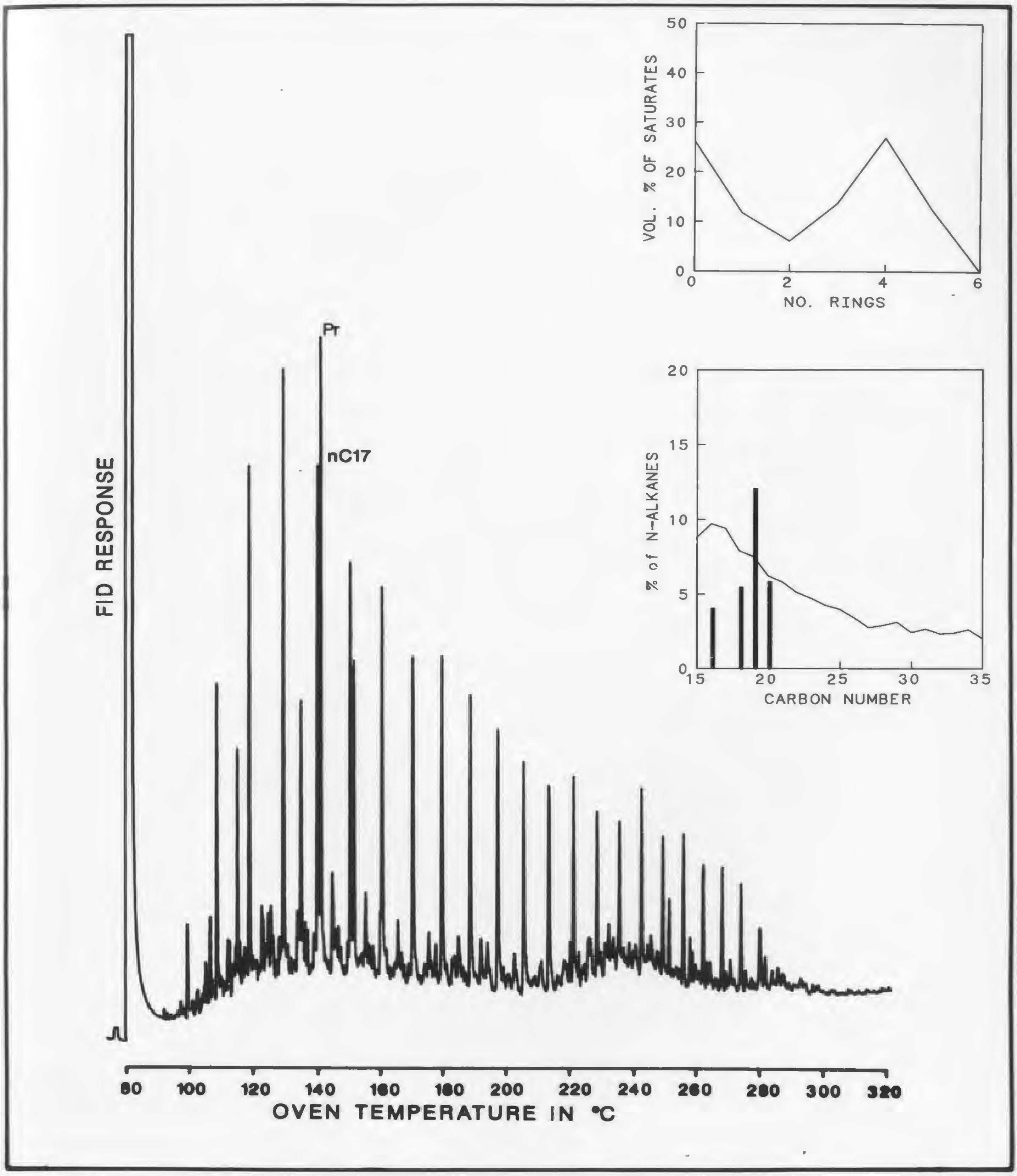


Figure C-17: Saturates, 17.9m

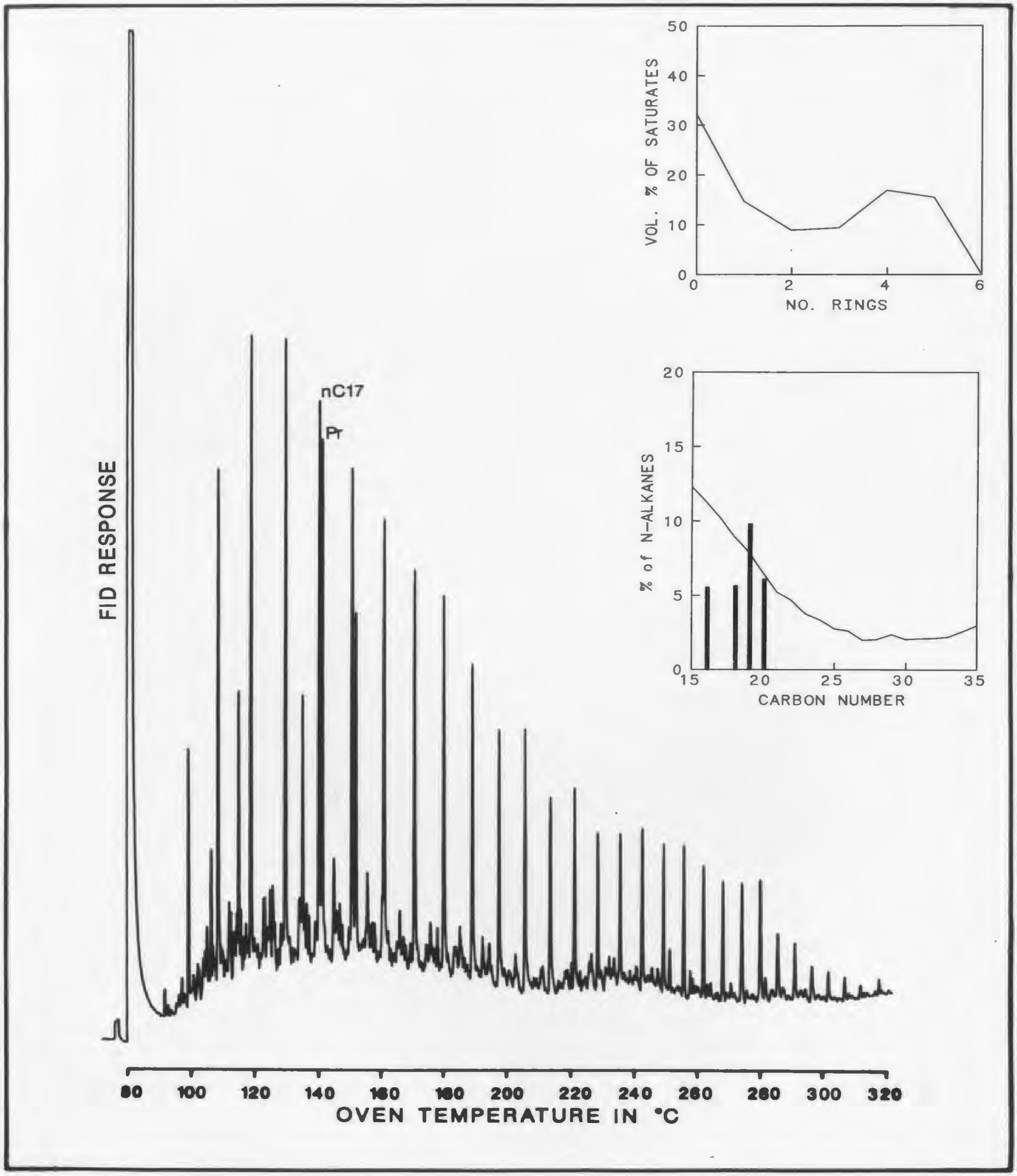


Figure C-18: Saturates, 15.8m

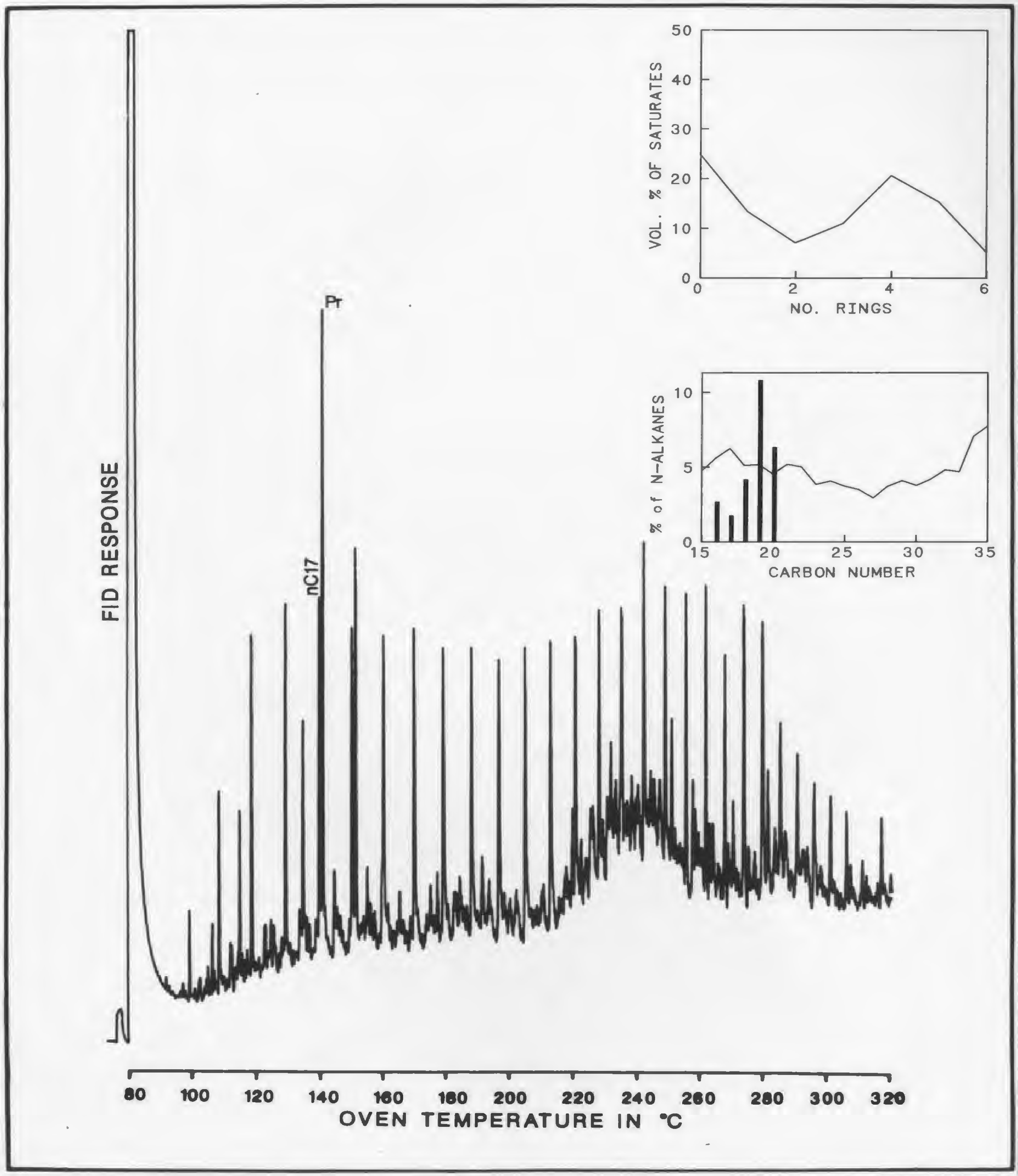


Figure C-19: Saturates, 12.4m

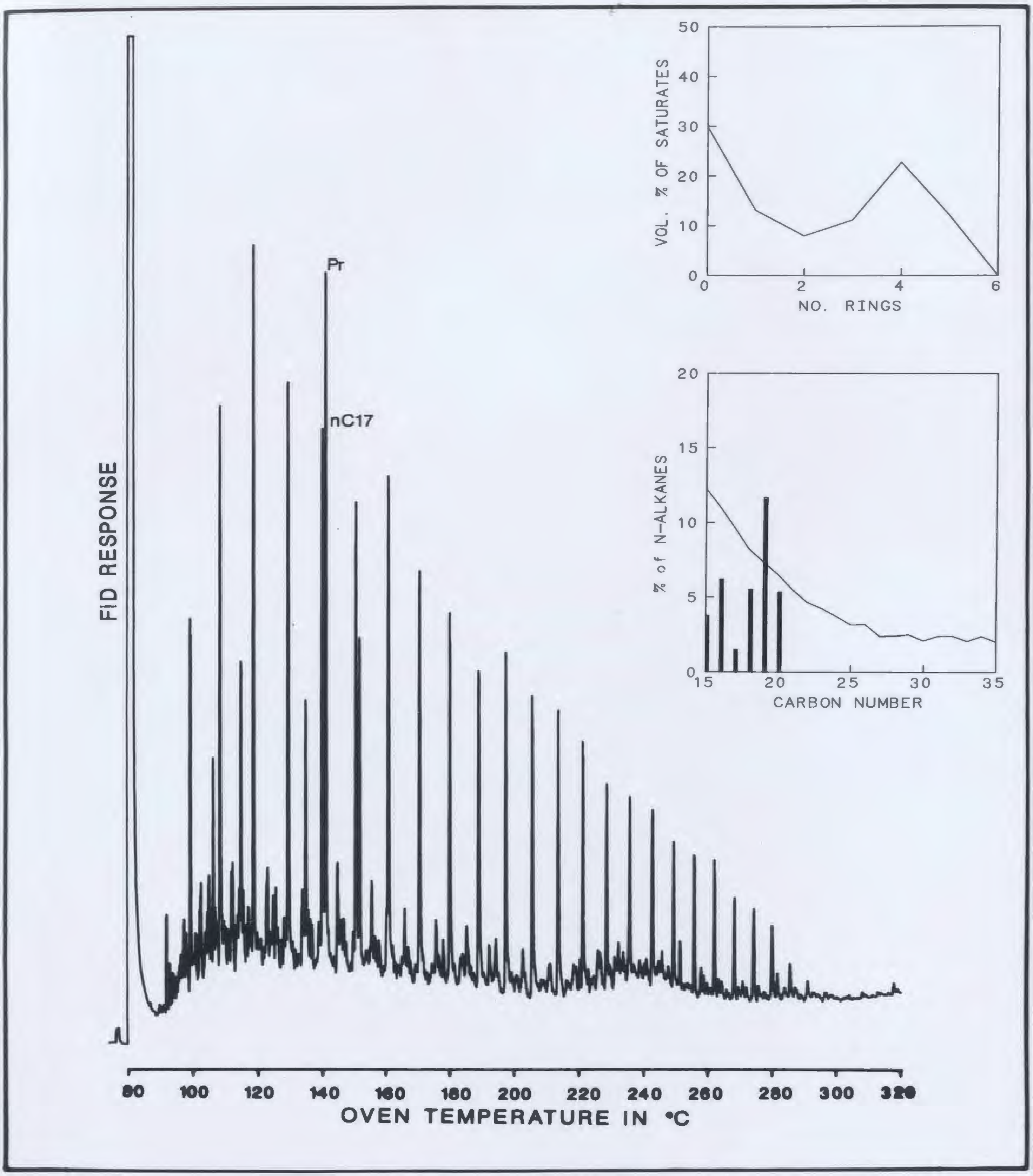


Figure C-20: Saturates, 10.5m

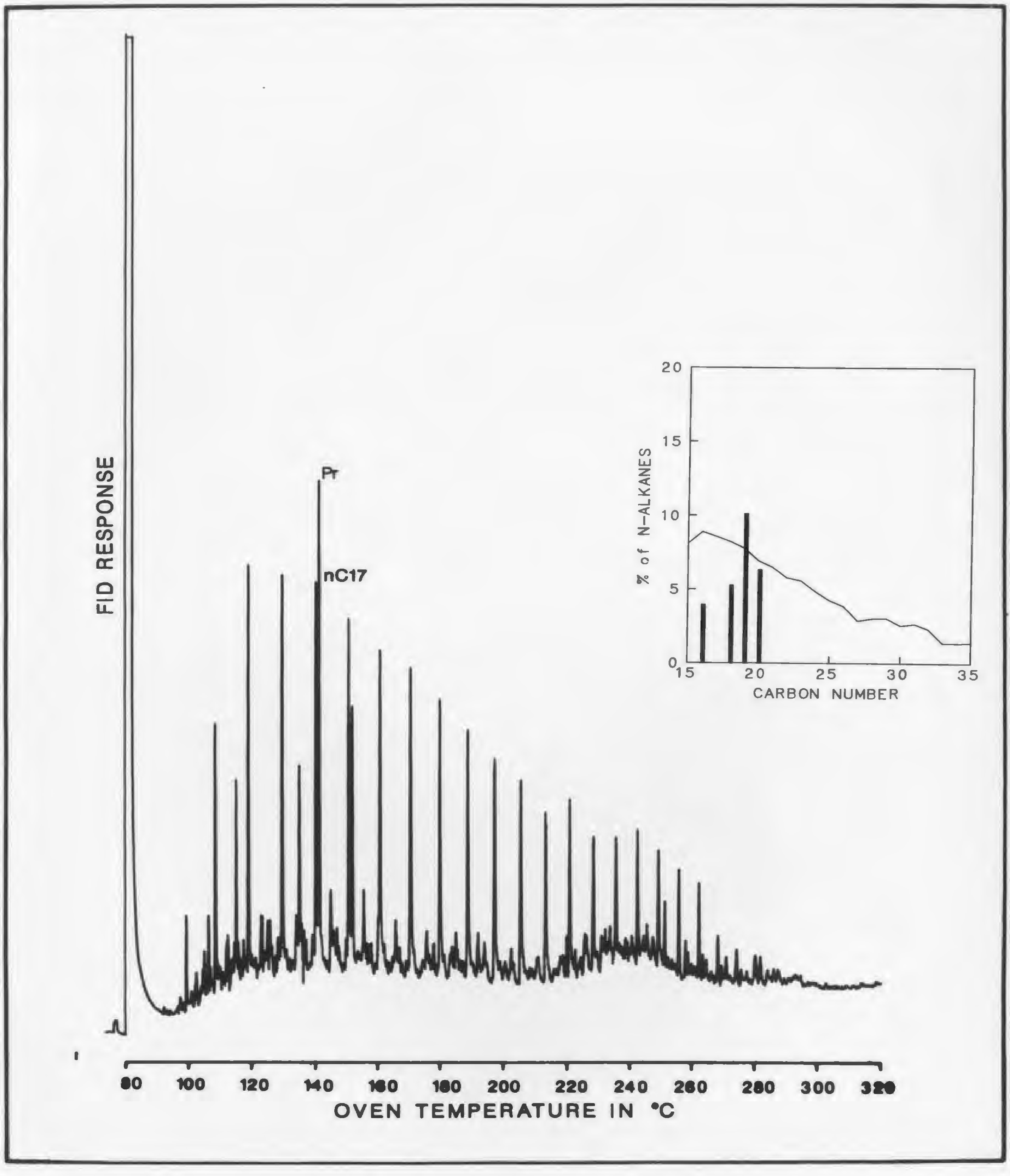


Figure C-21: Saturates, 9.2m

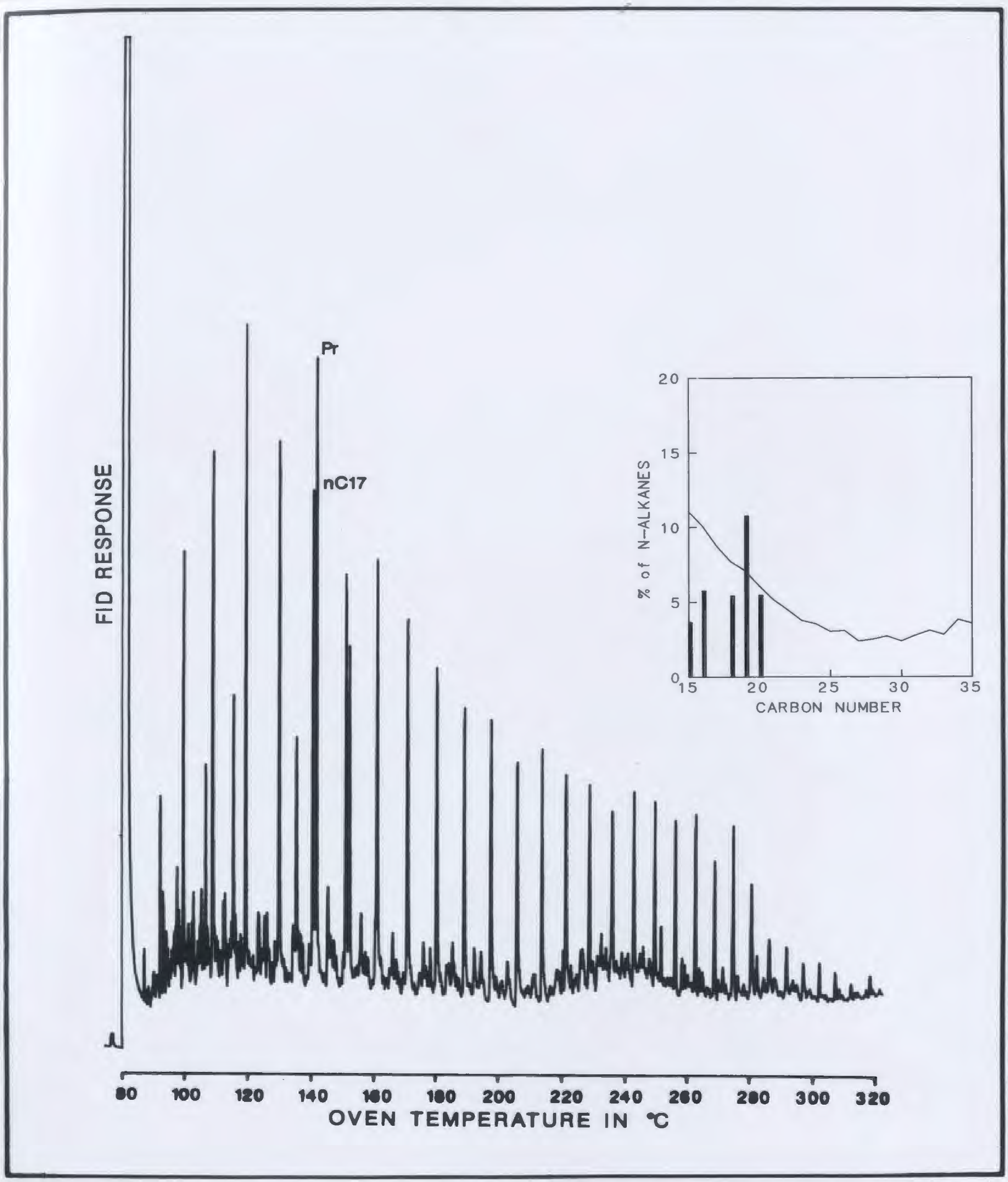


Figure C-22: Saturates, 7.7m

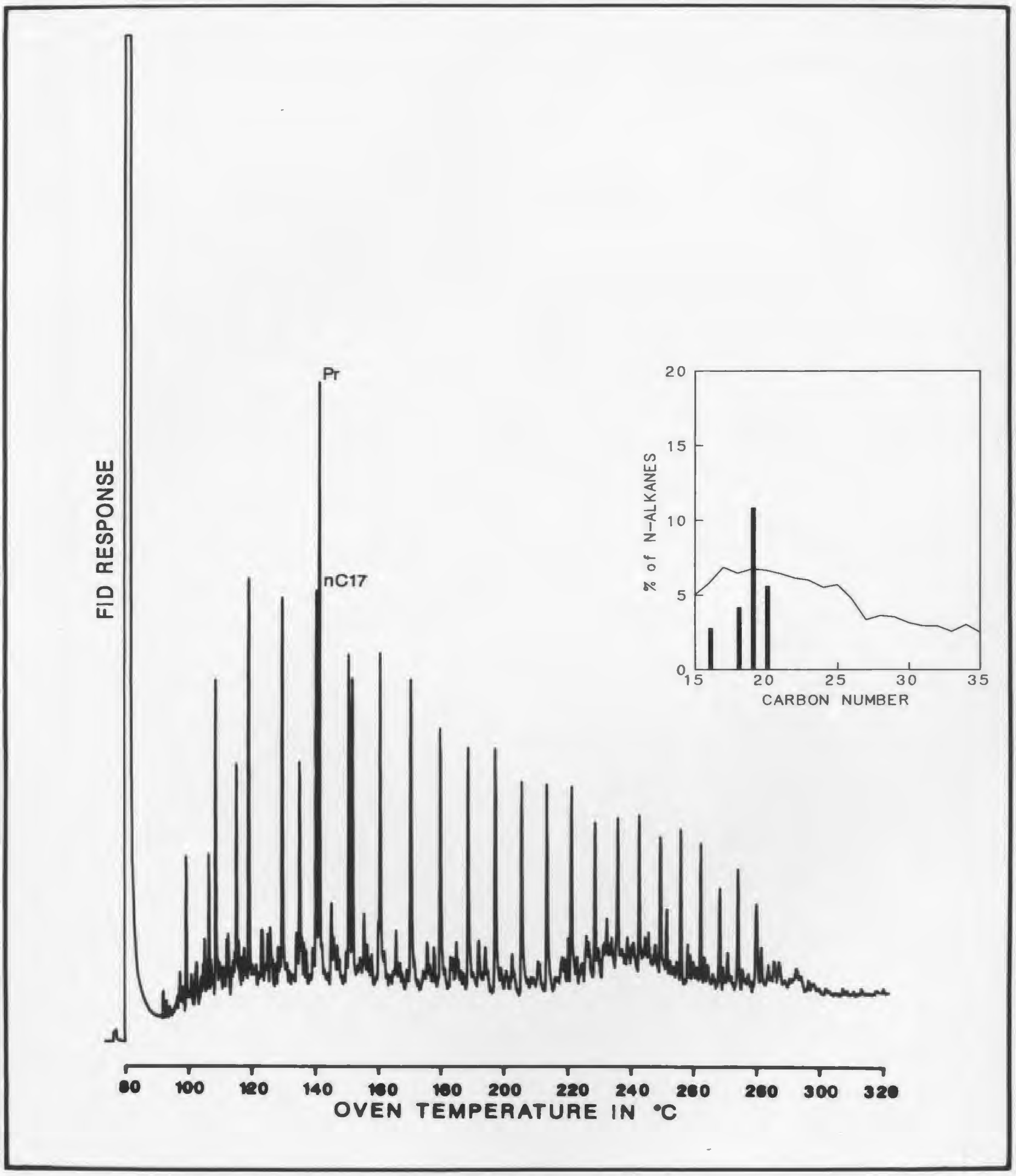


Figure C-23: Saturates, 6.2m

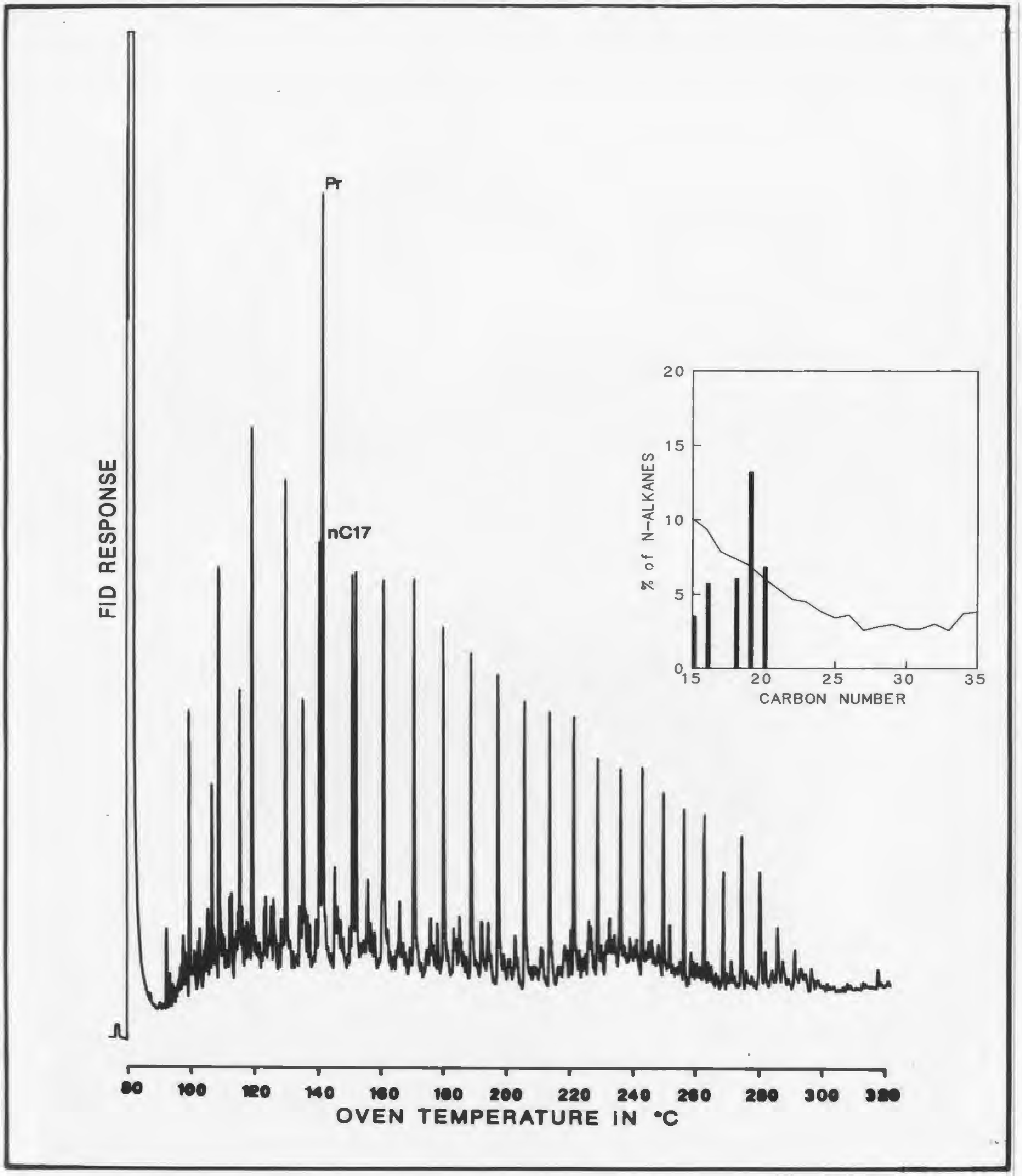


Figure C-24: Saturates, 4.9m

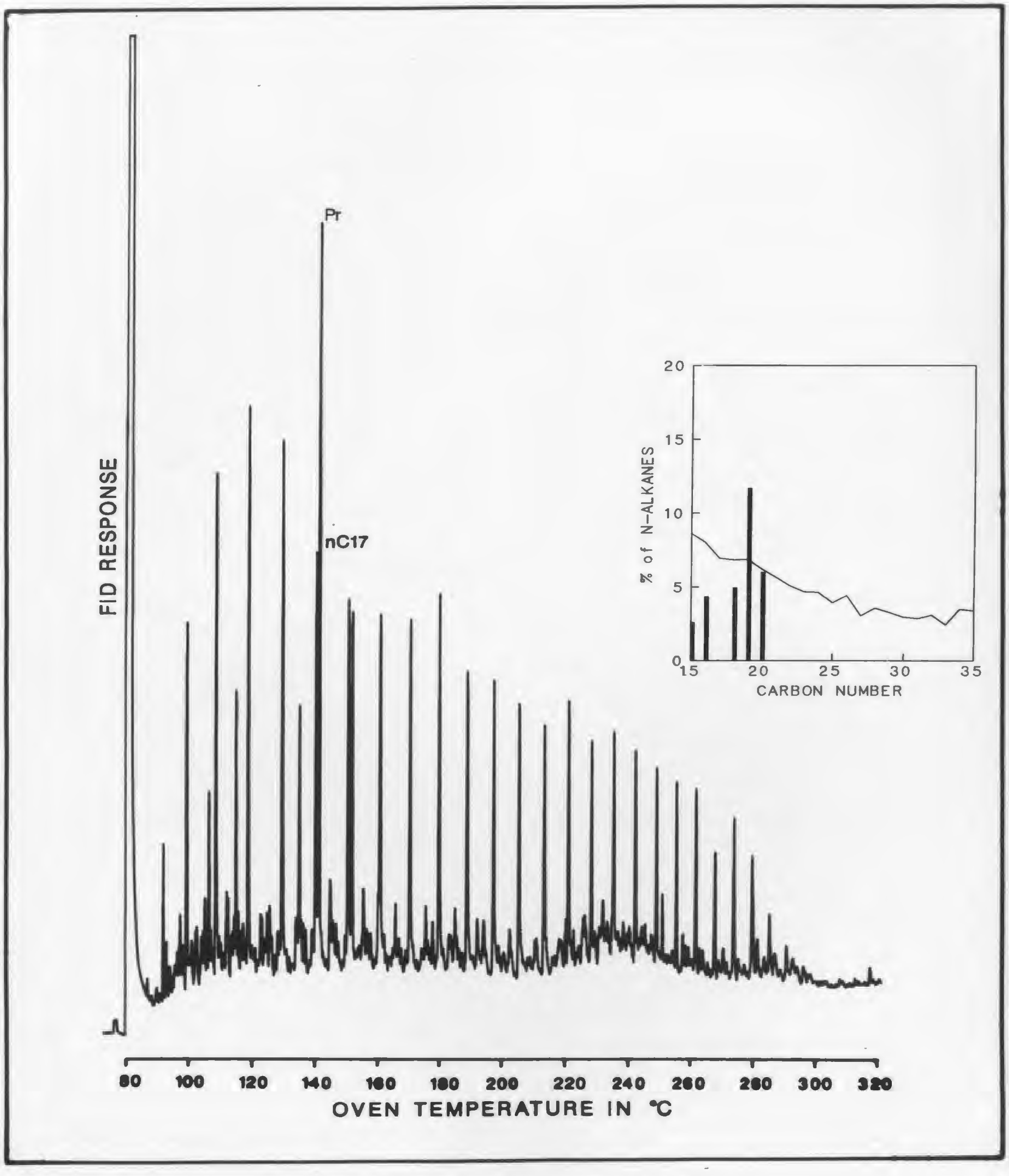


Figure C-25: Saturates, 3.2m

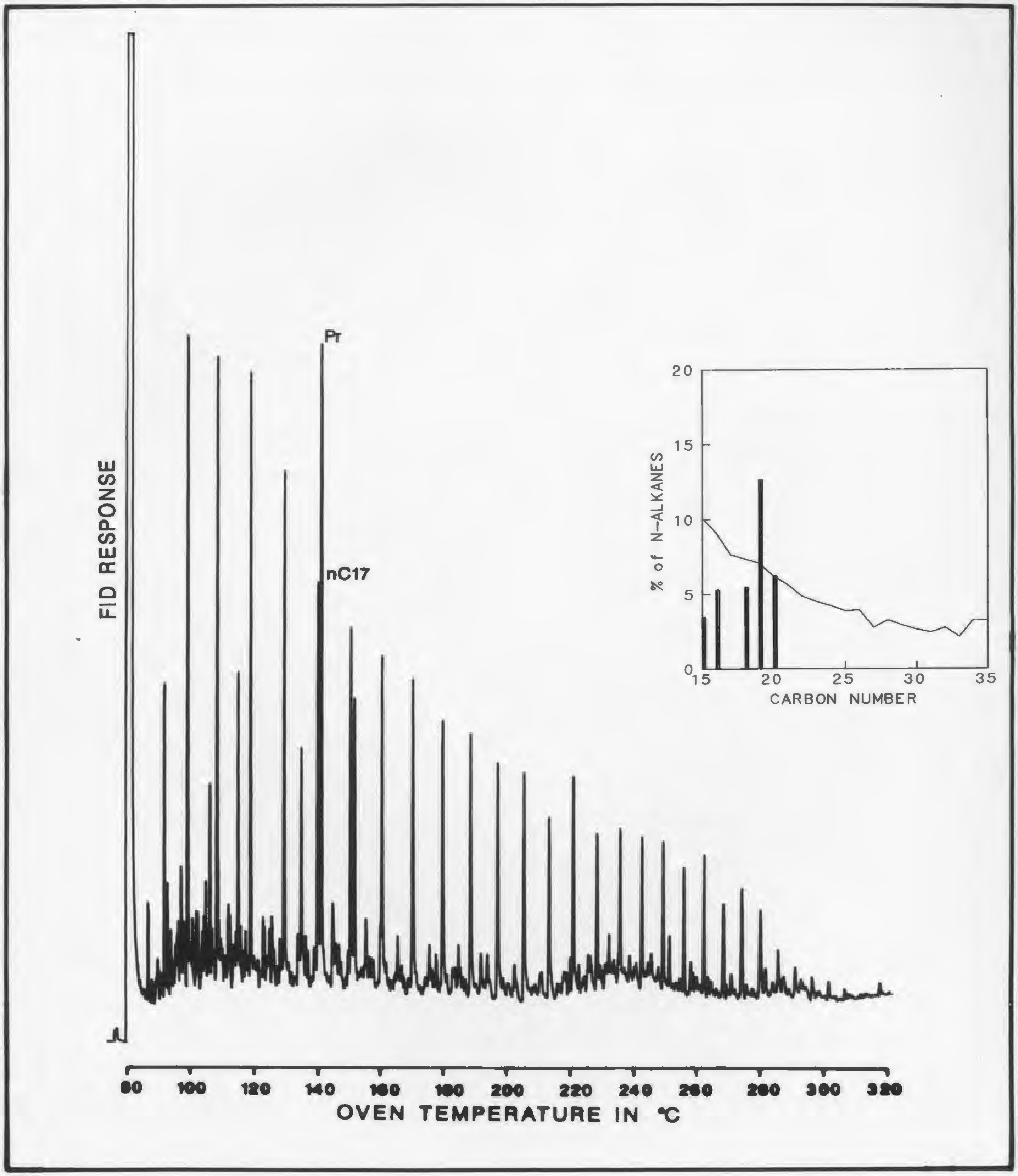


Figure C-26: Saturates, 1.4m

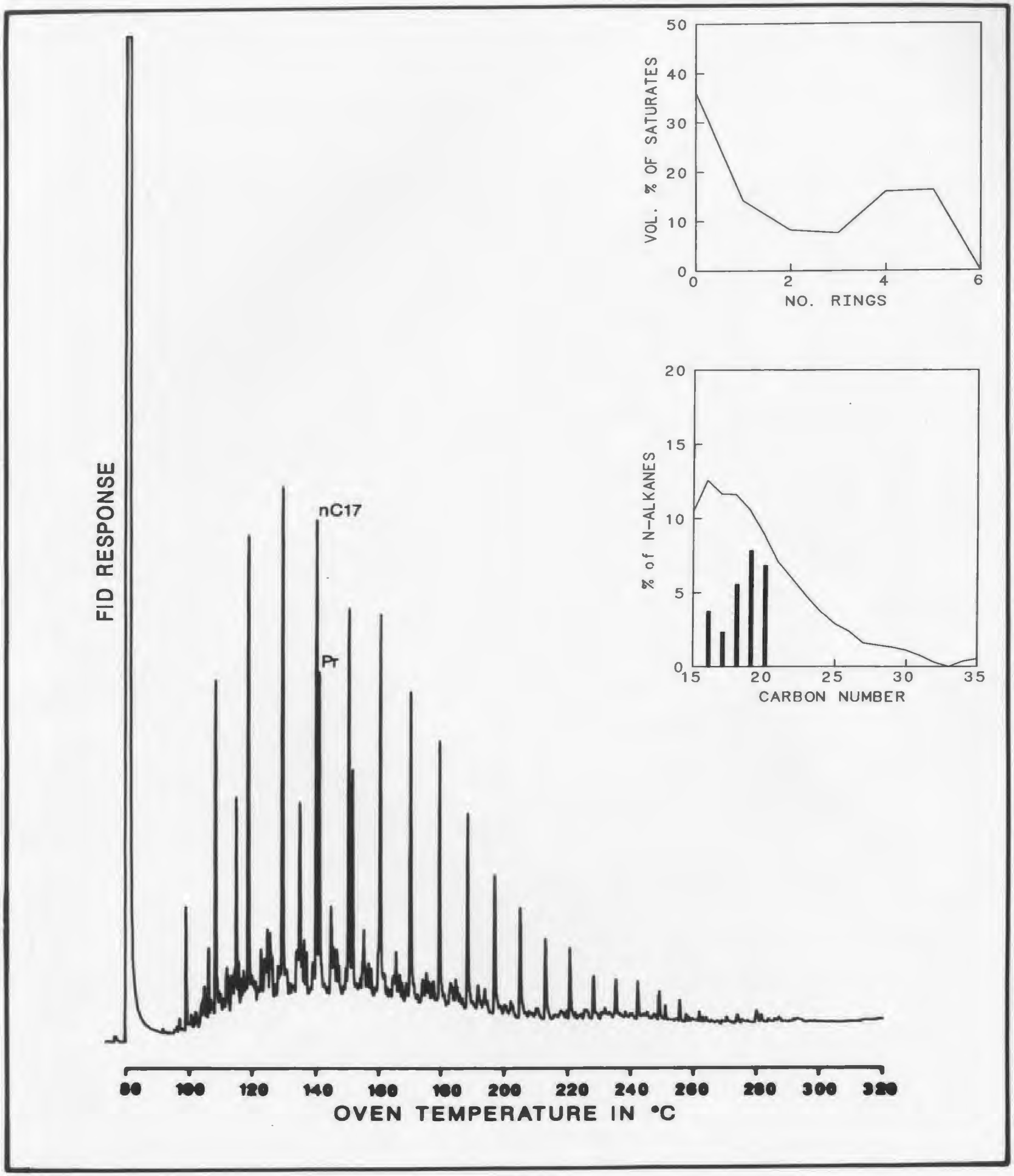


Figure C-27: Saturates, 0.0m

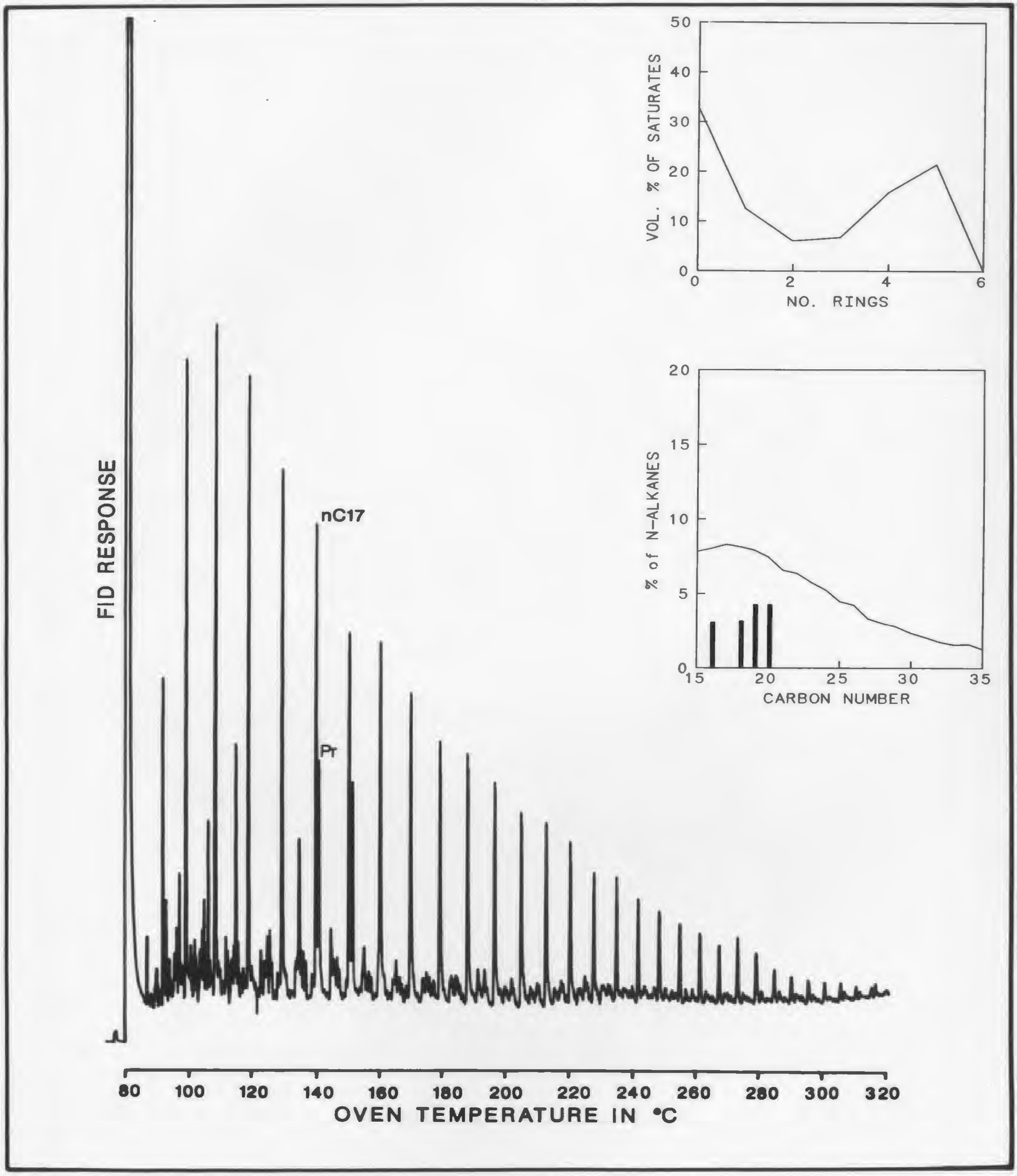


Figure C-28: Saturates, oil

C.2. Aromatic fractions:

P = phenanthrene, MP = methylphenanthrene
F = fluorene, BP = biphenyl, BT = benzothiophenes
DBT = dibenzothiophenes, NBT = naphthobenzothiophenes
key compounds identified at 66.4m

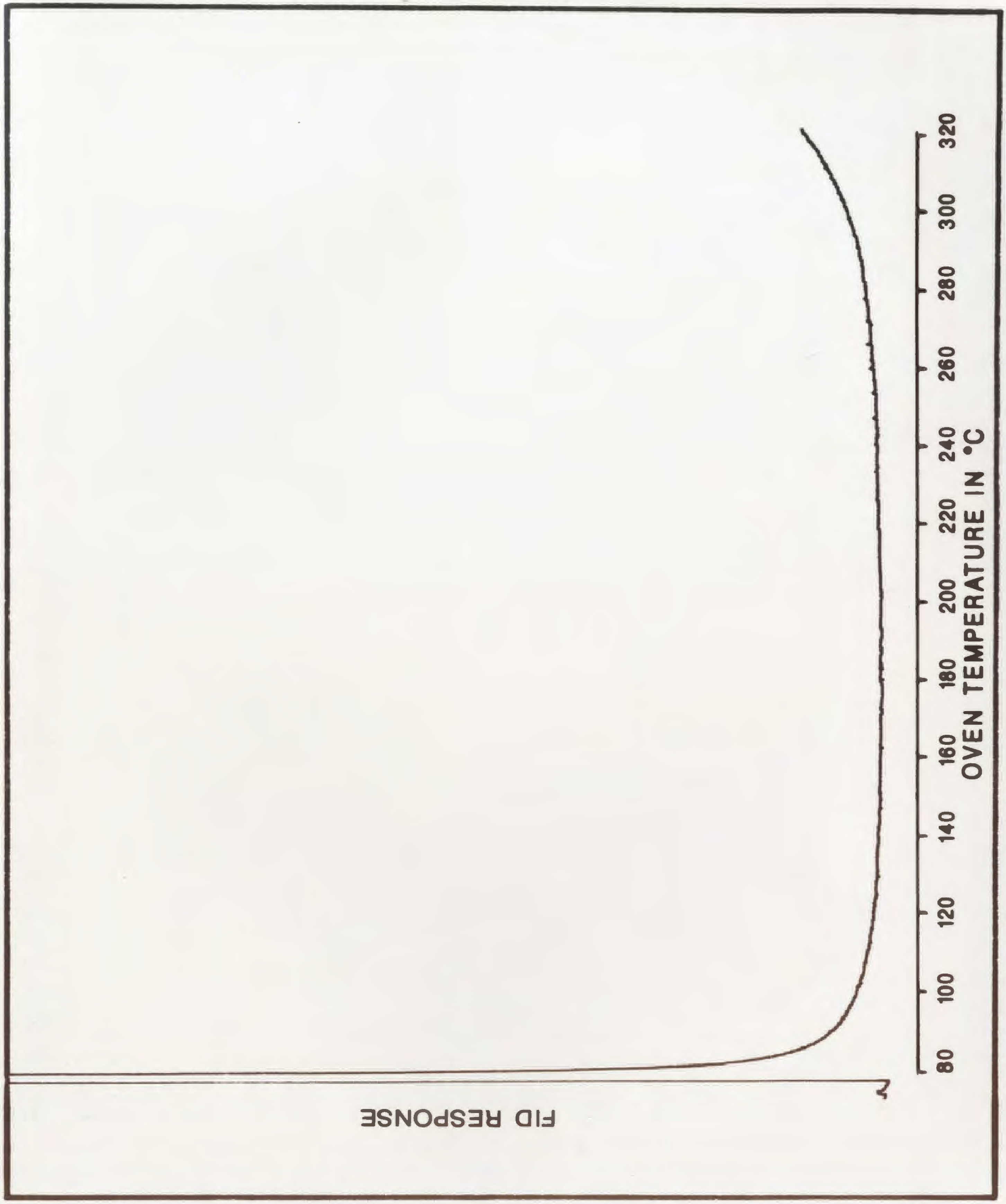


Figure C-29: Aromatics, blank

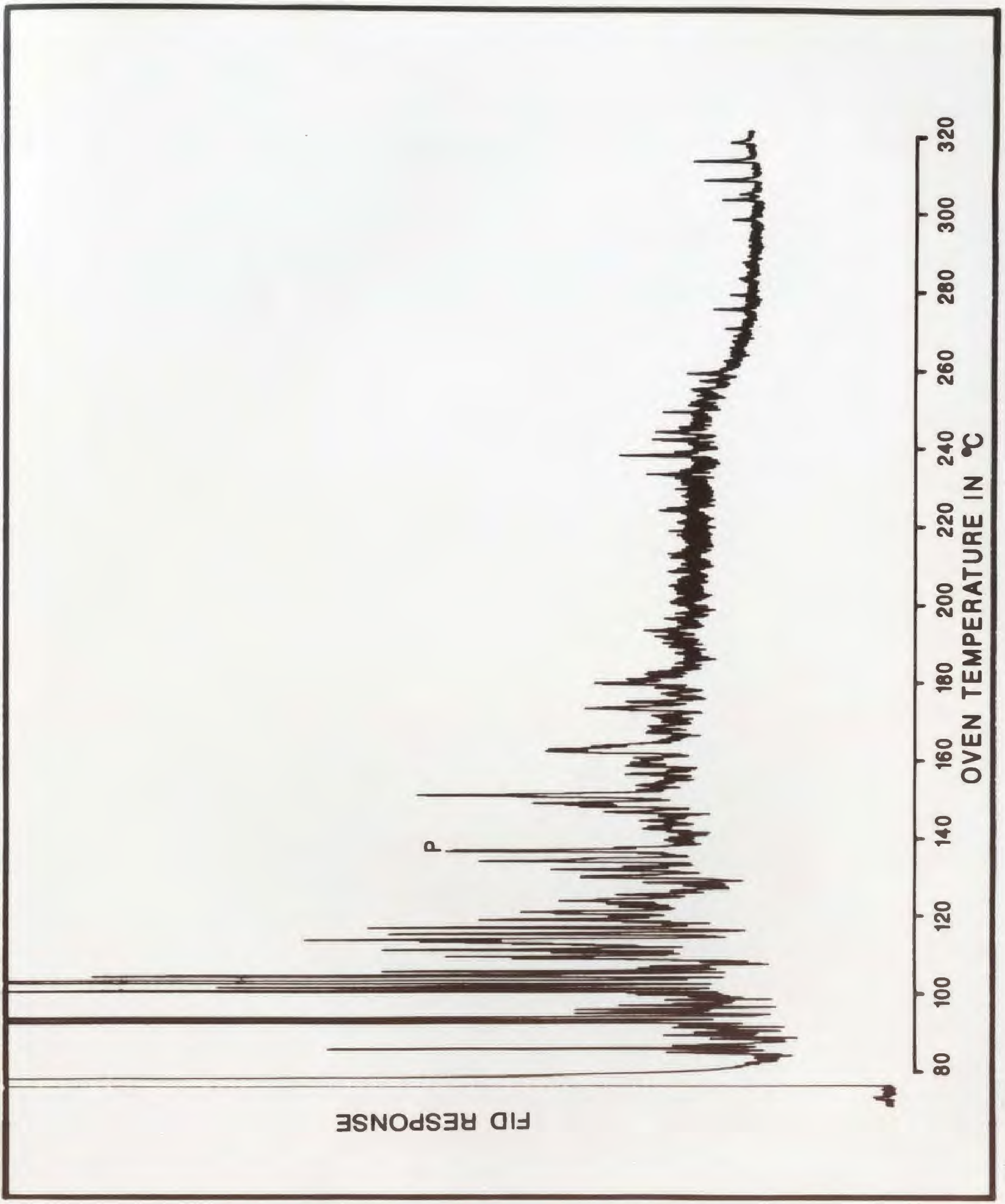


Figure C-30: Aromatics, 92.0m

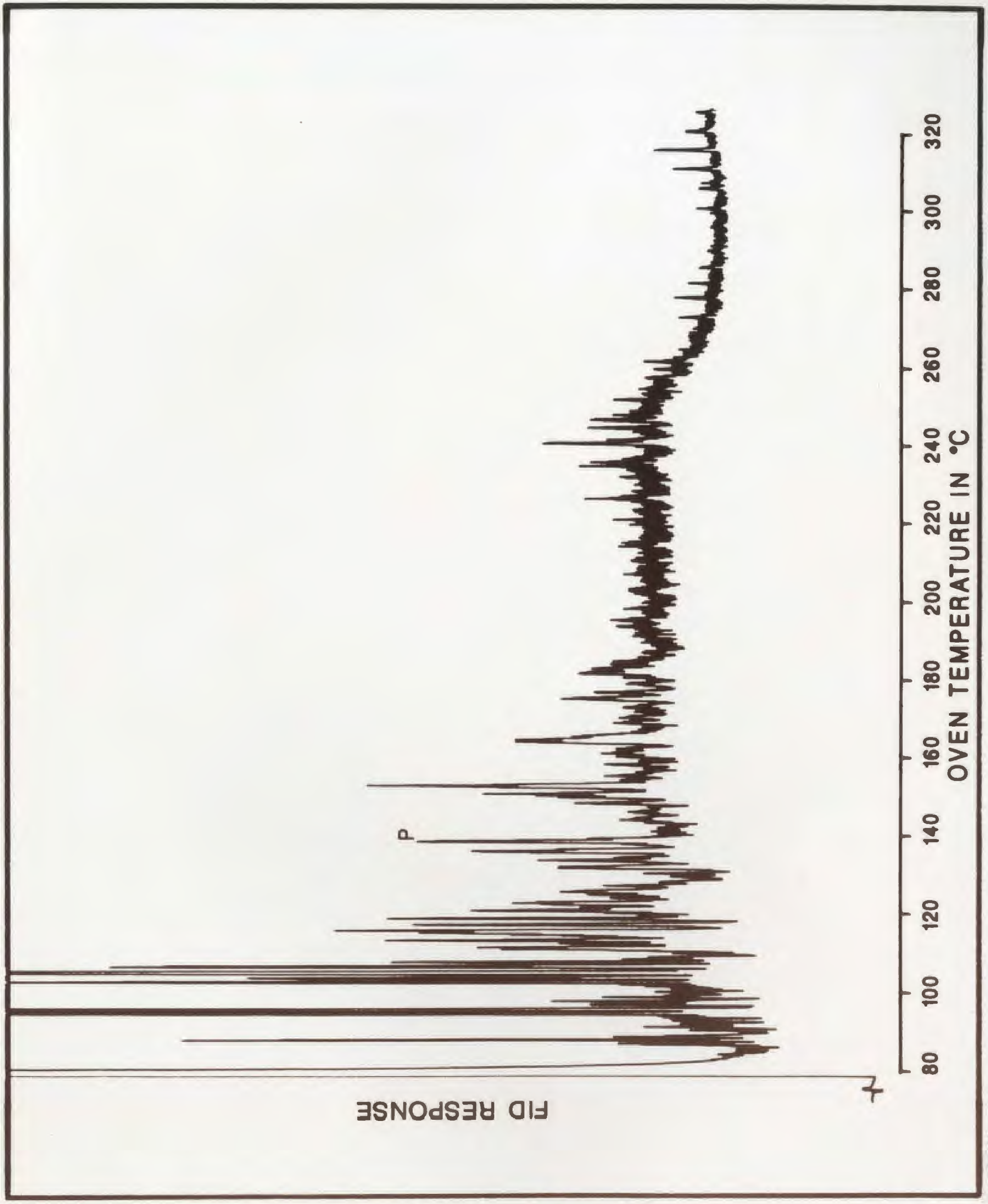


Figure C-31: Aromatics, 85.9m

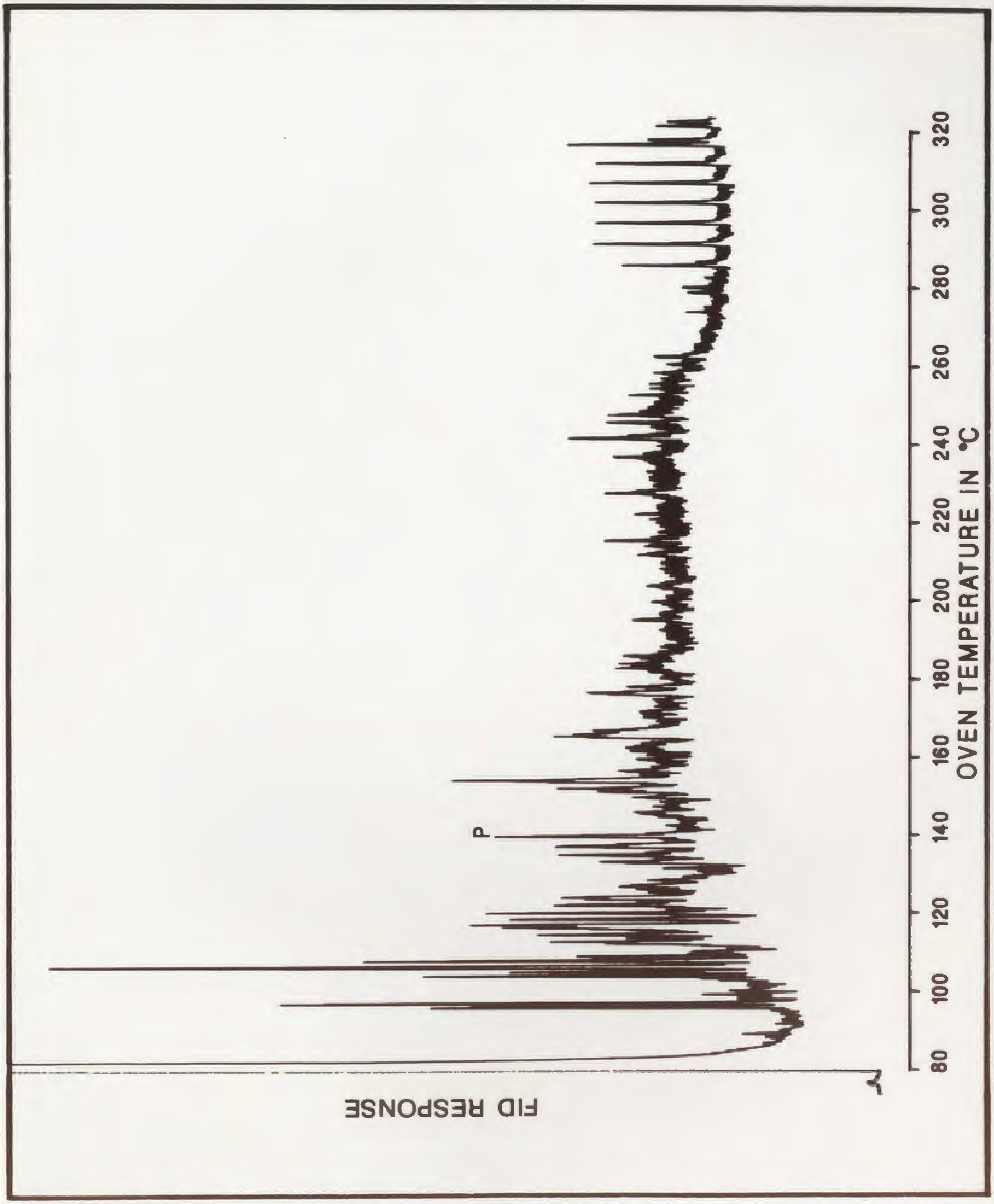


Figure C-32: Aromatics, 79.3m

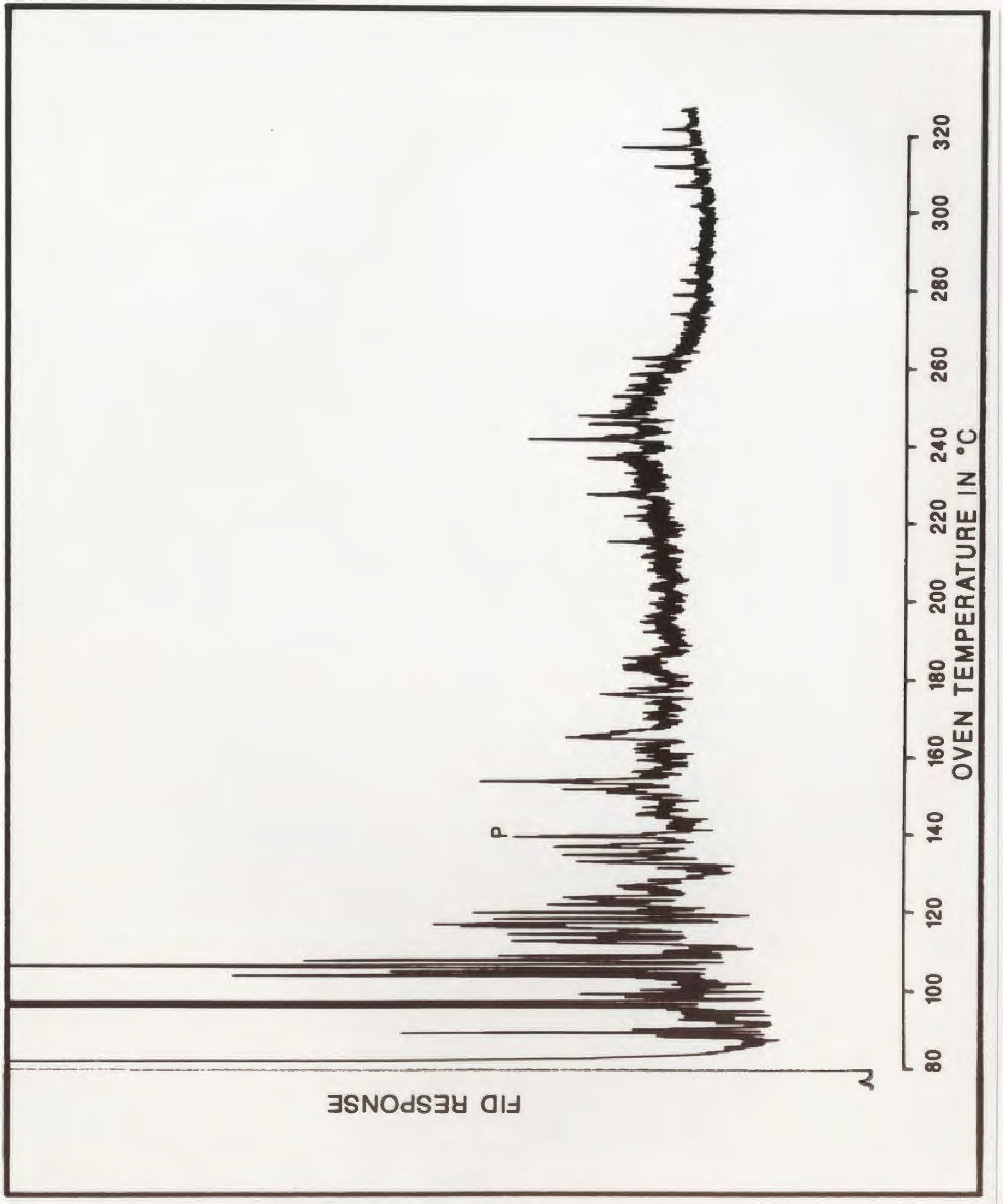


Figure C-33: Aromatics, 72.7m

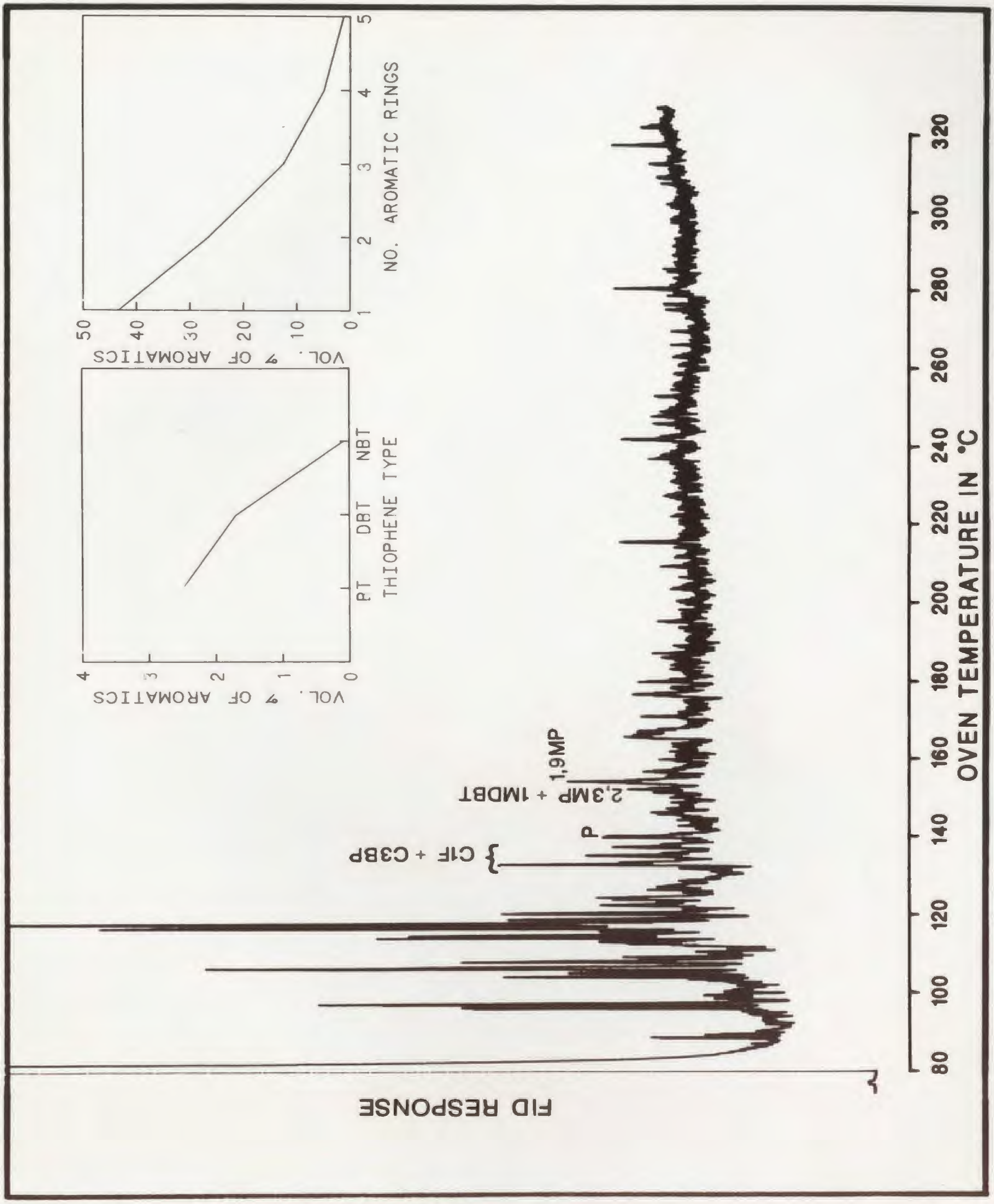


Figure C-34: Aromatics, 66.4m

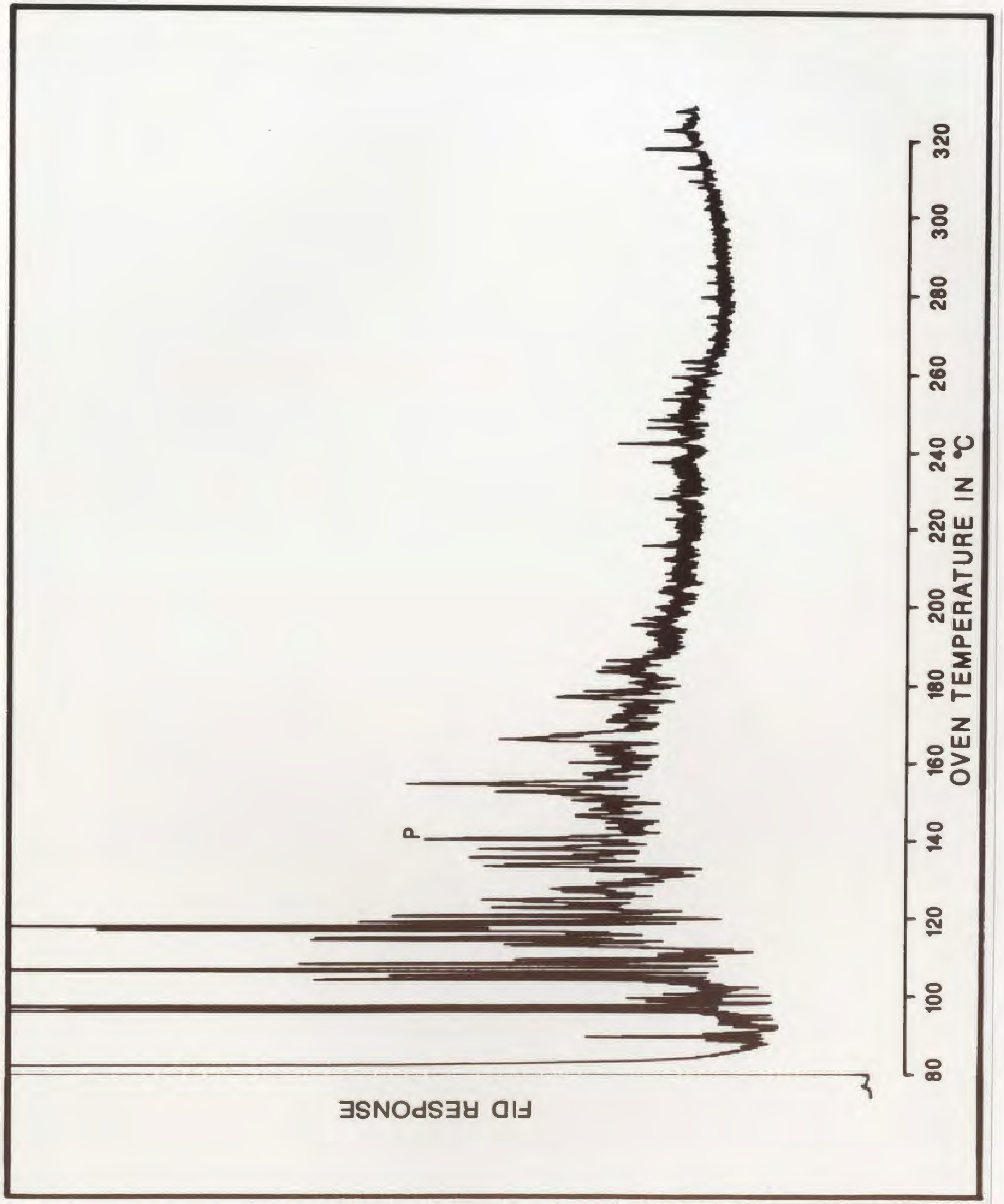


Figure C-35: Aromatics, 60.2m

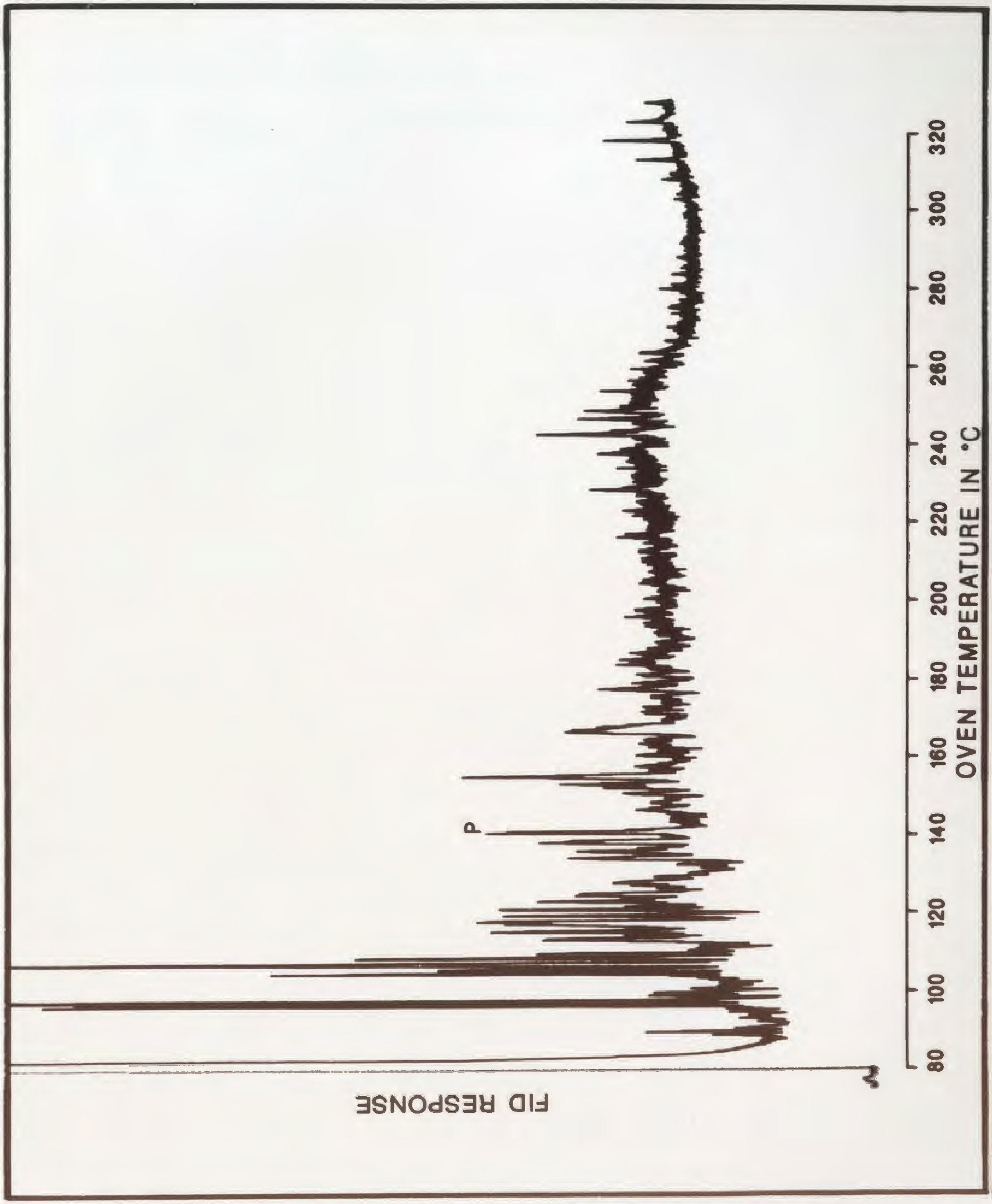


Figure C-36: Aromatics, 54.4m

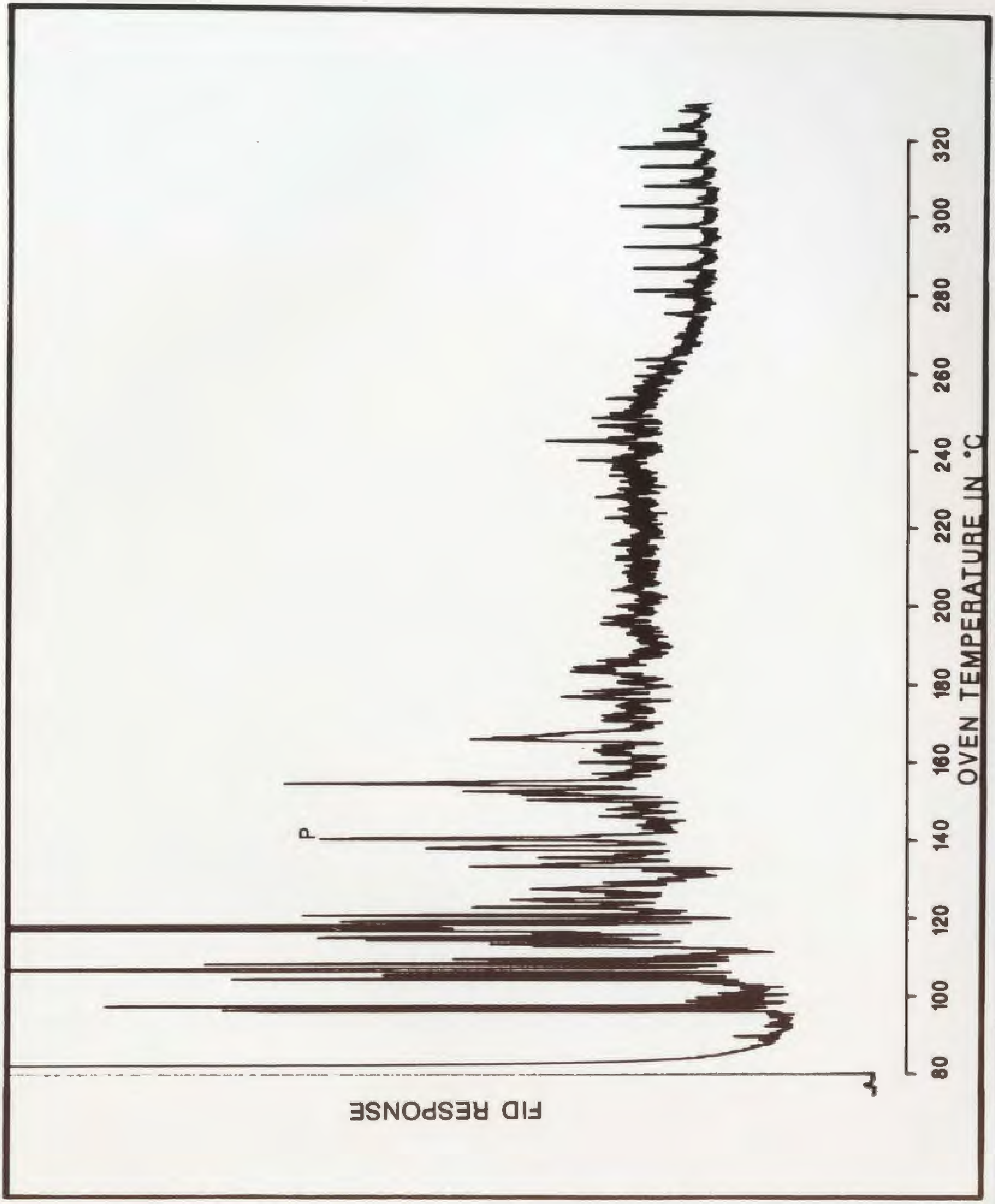


Figure C-37: Aromatics, 48.5m

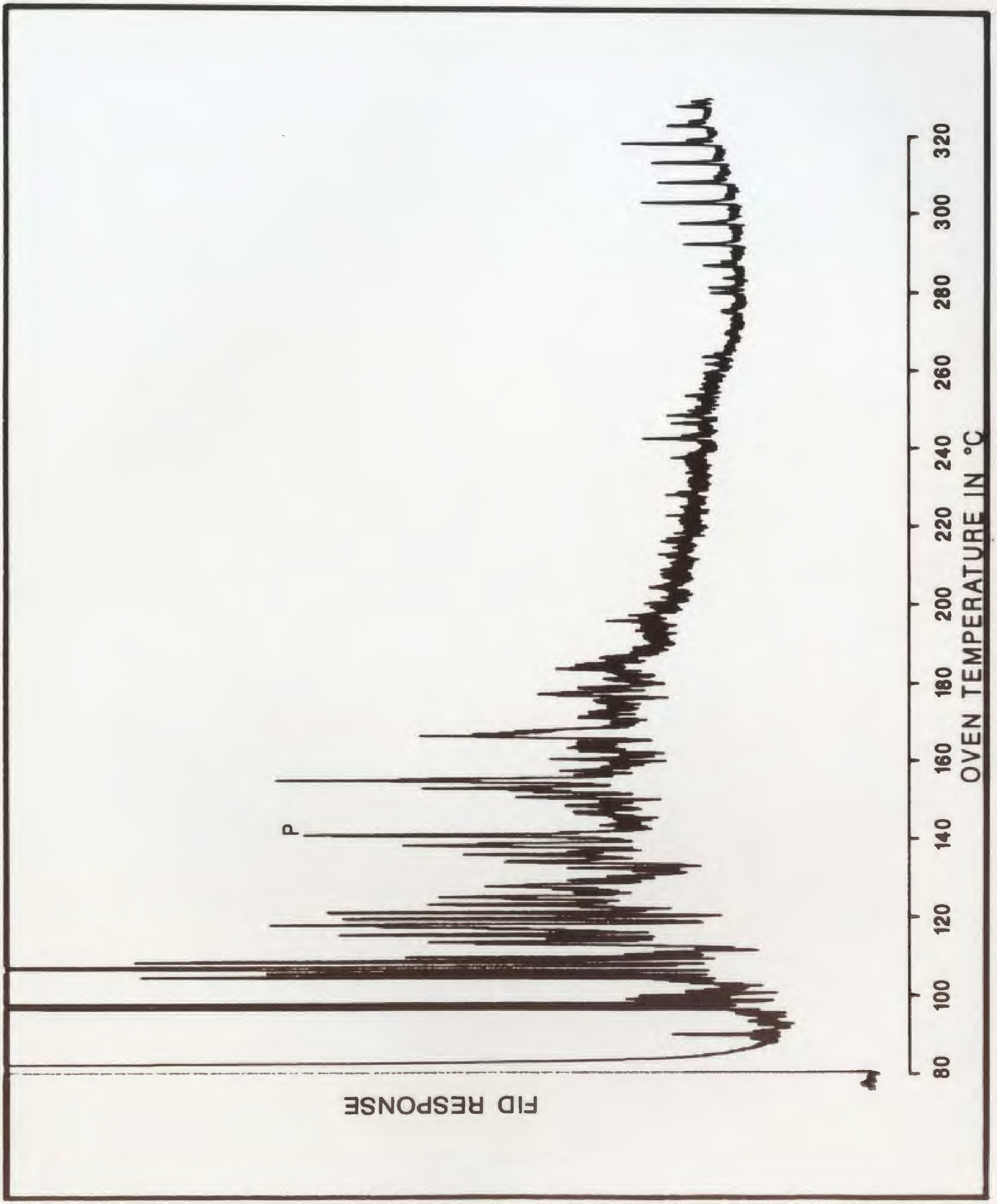


Figure C-38: Aromatics, 43.1m

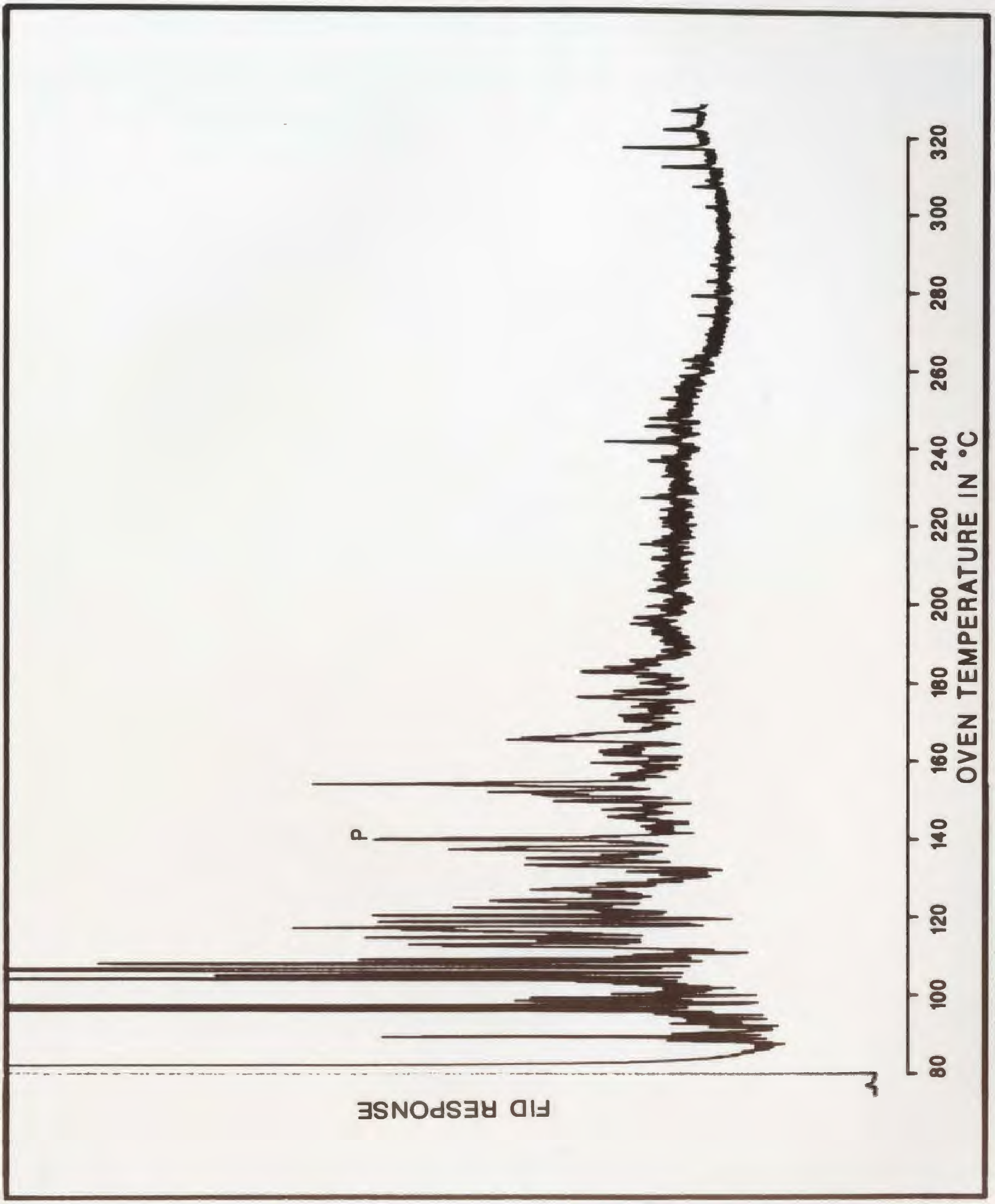


Figure C-39: Aromatics, 37.7m

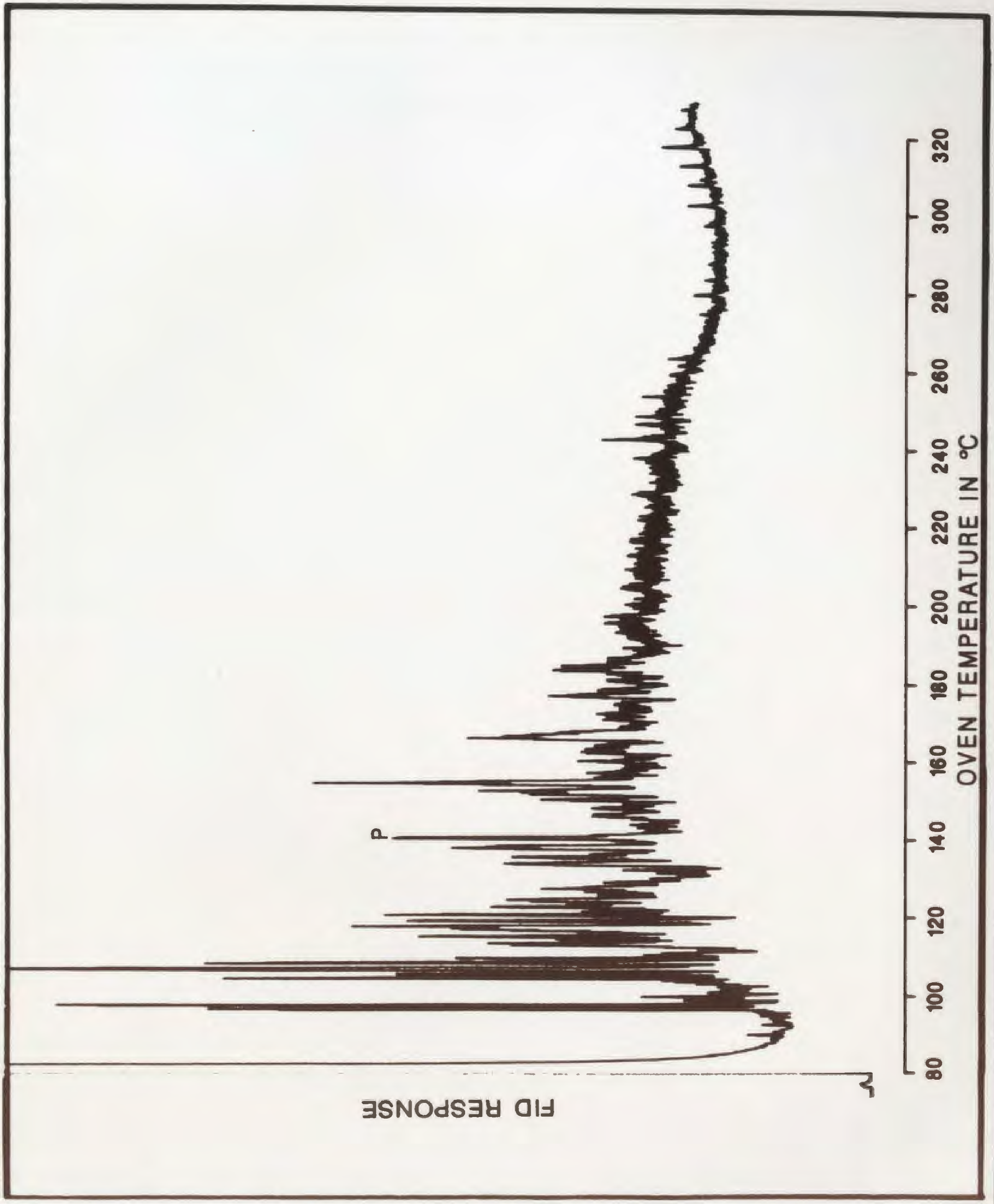


Figure C-40: Aromatics, 32.8m

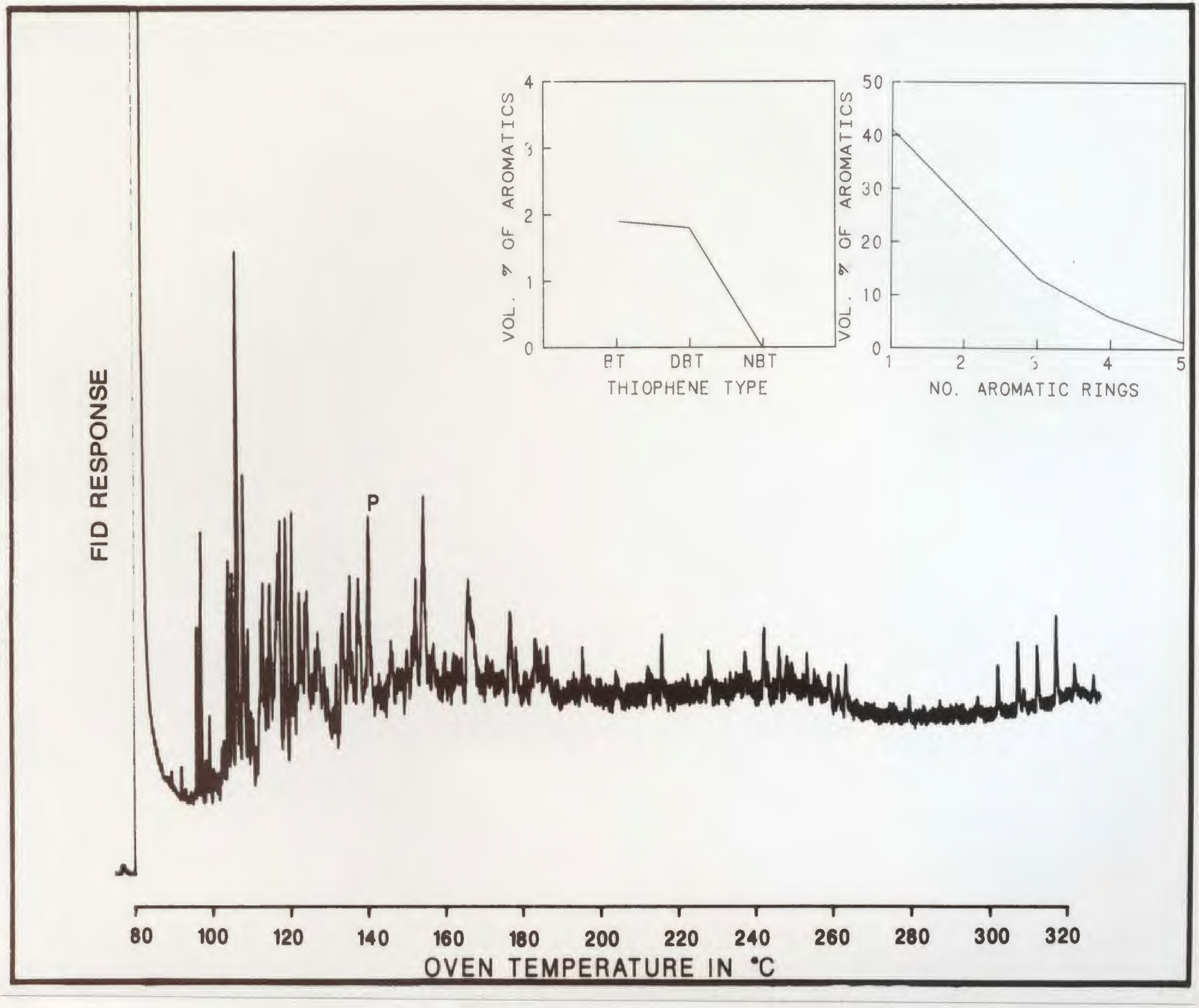


Figure C-41: Aromatics, 25.5m

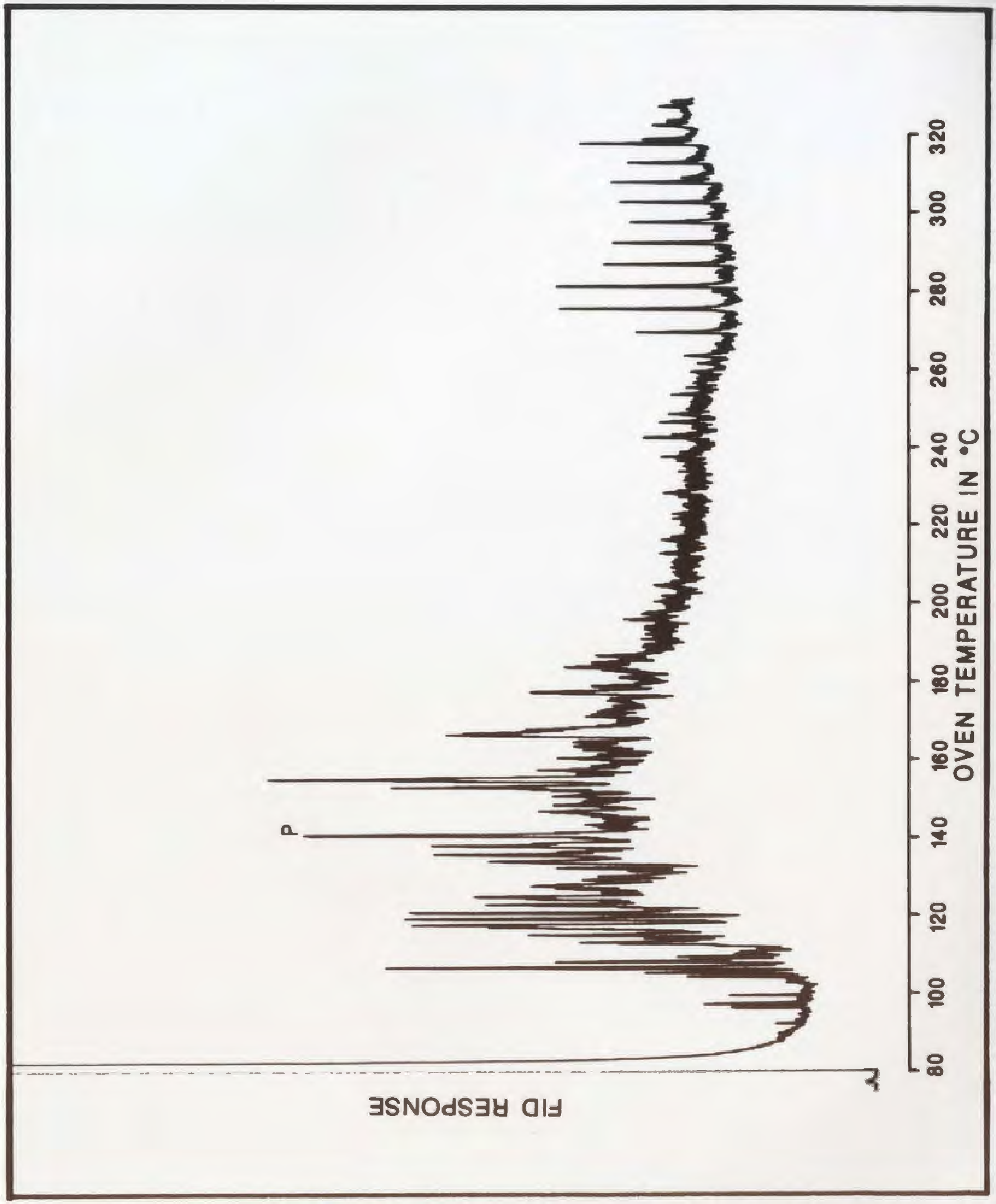


Figure C-42: Aromatics, 23.5m

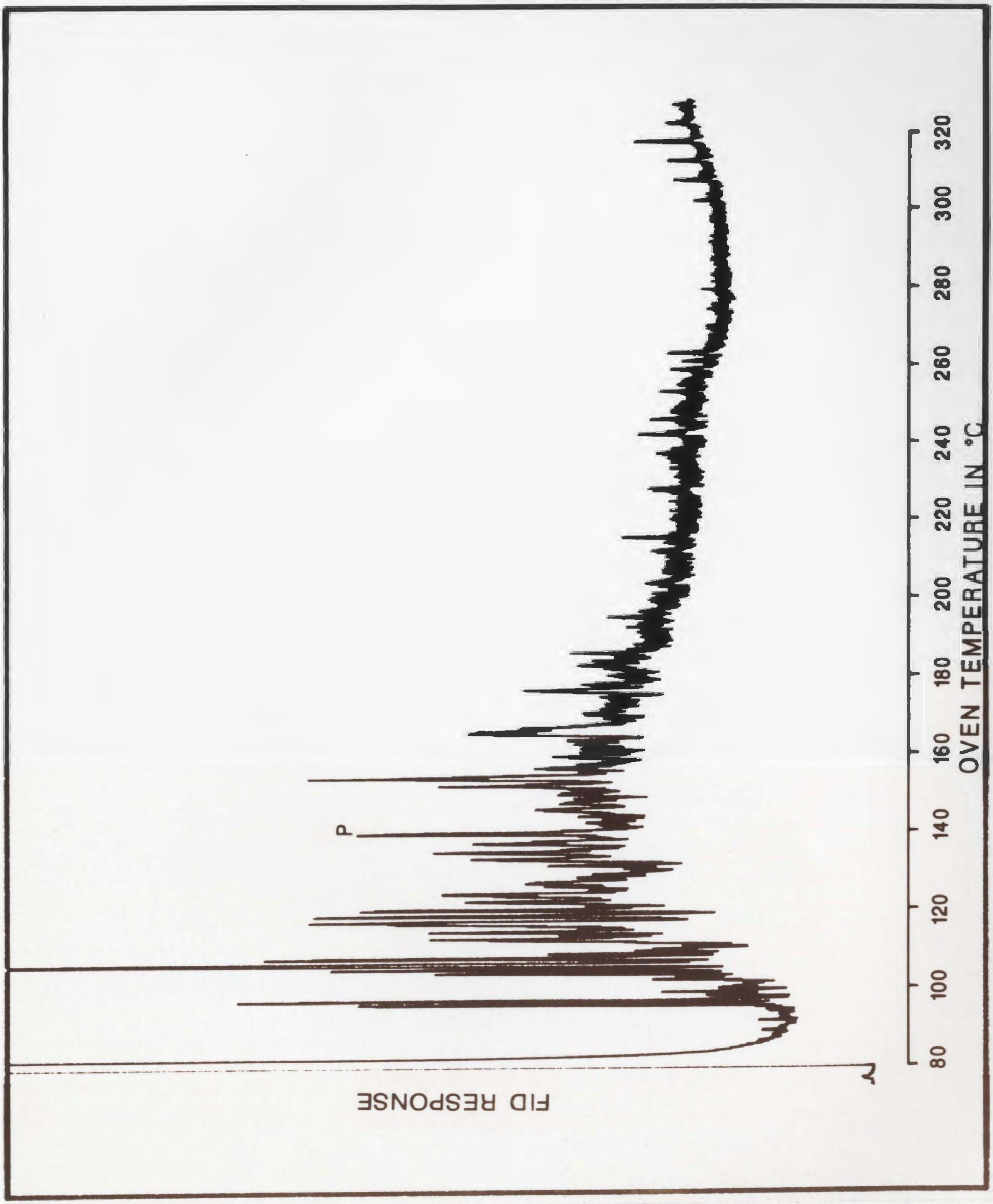


Figure C-43: Aromatics, 21.6m

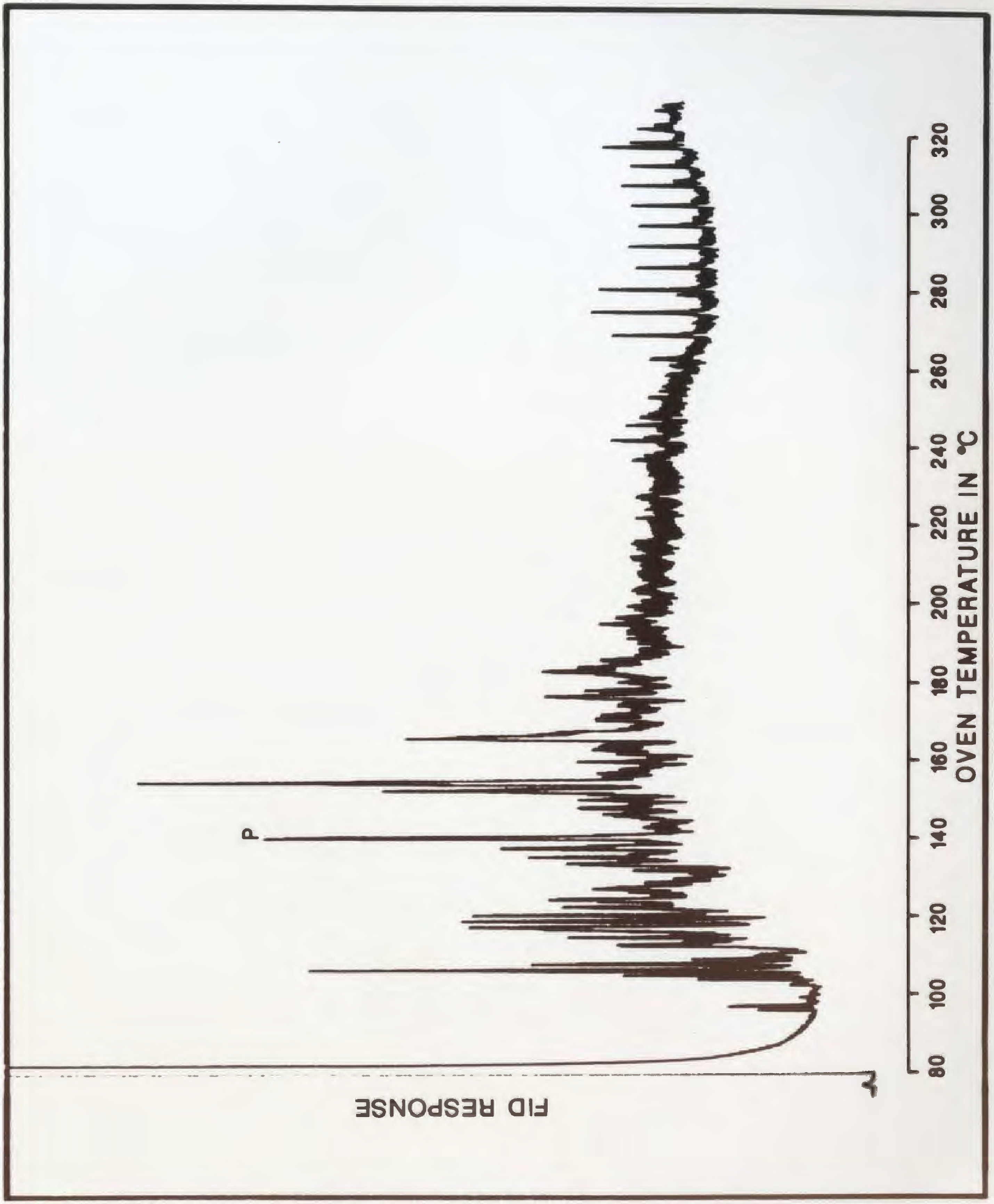


Figure C-44: Aromatics, 19.6m

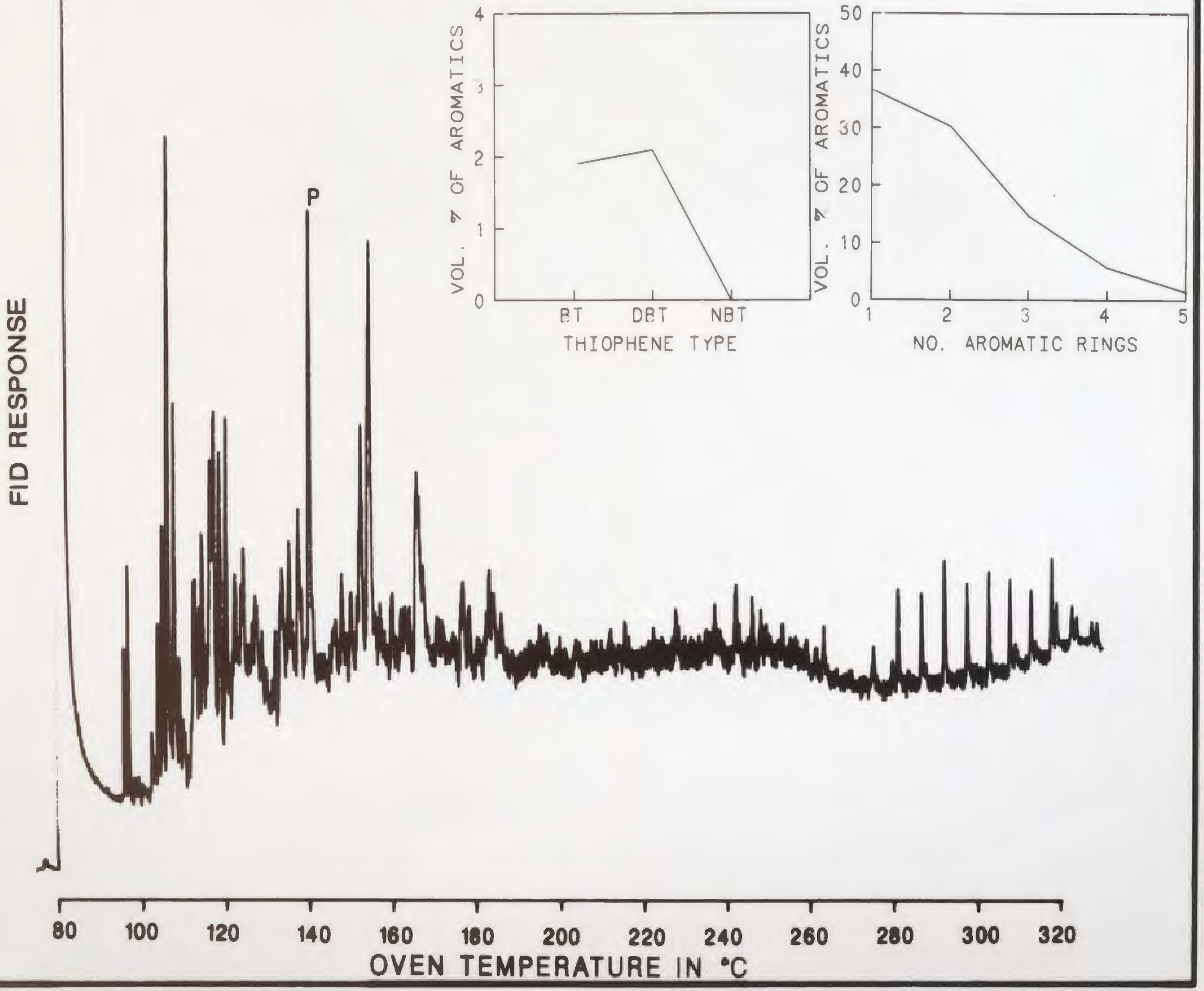


Figure C-45: Aromatics, 17.9m

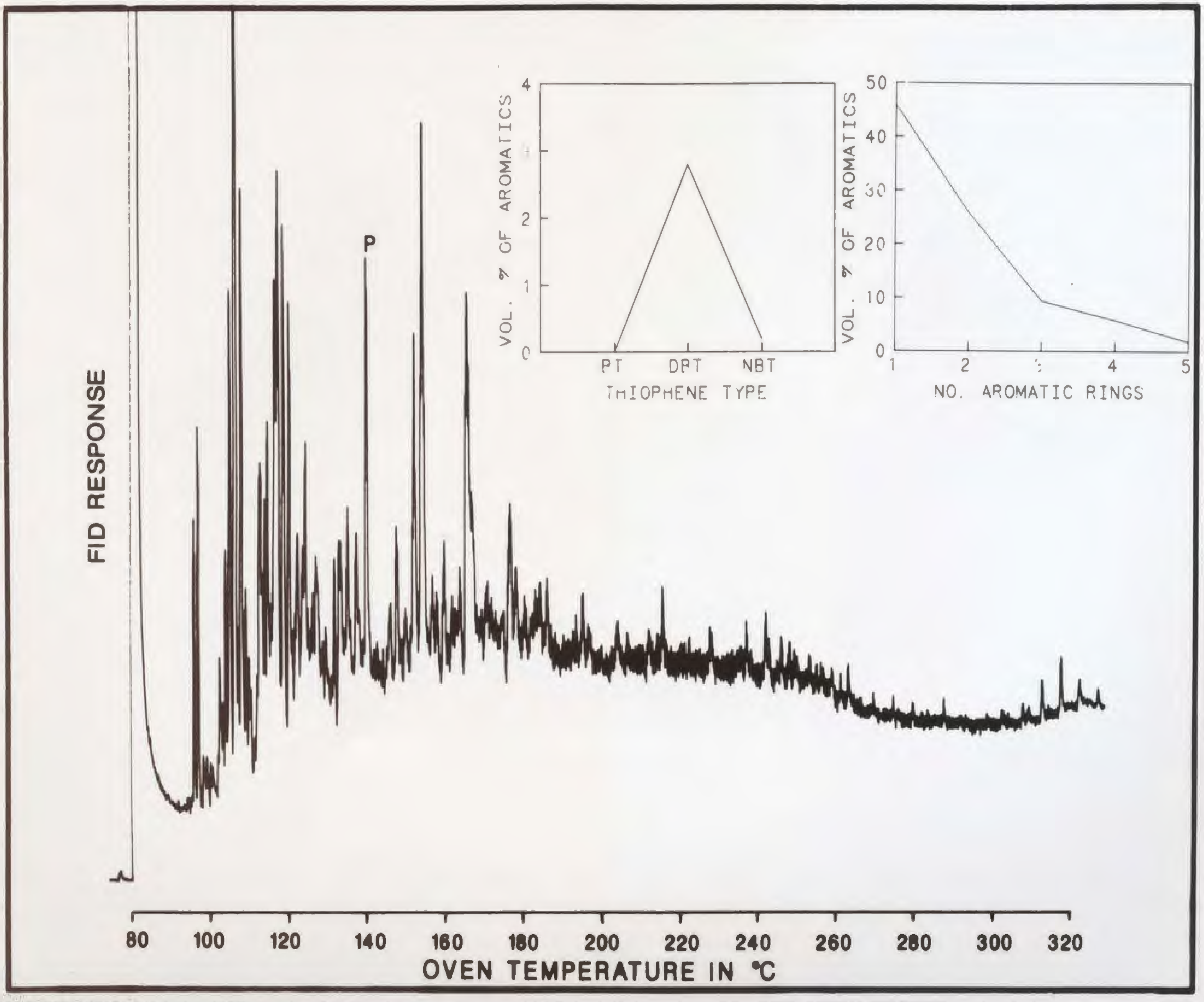


Figure C-46: Aromatics, 15.8m

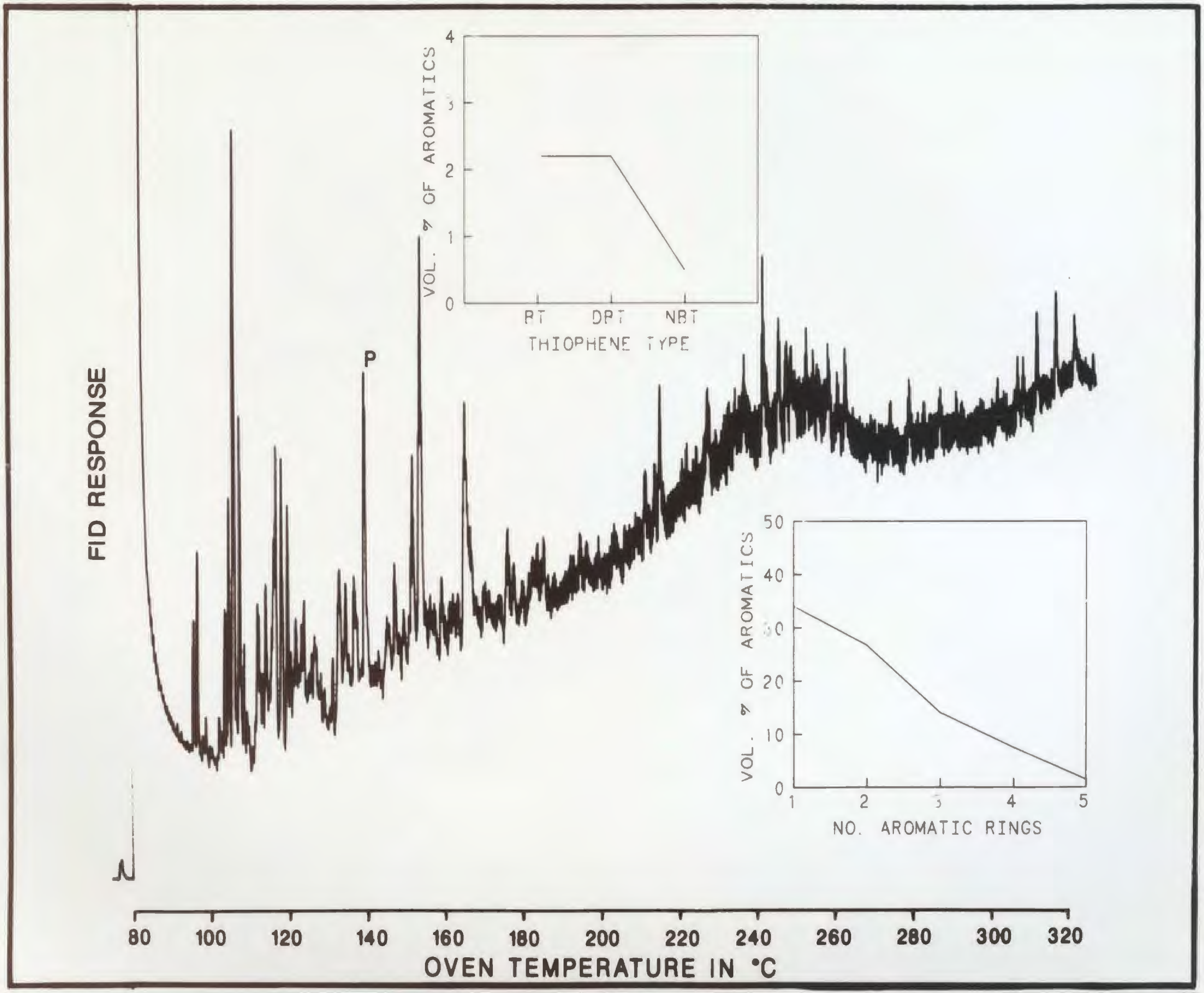


Figure C-47: Aromatics, 12.4m

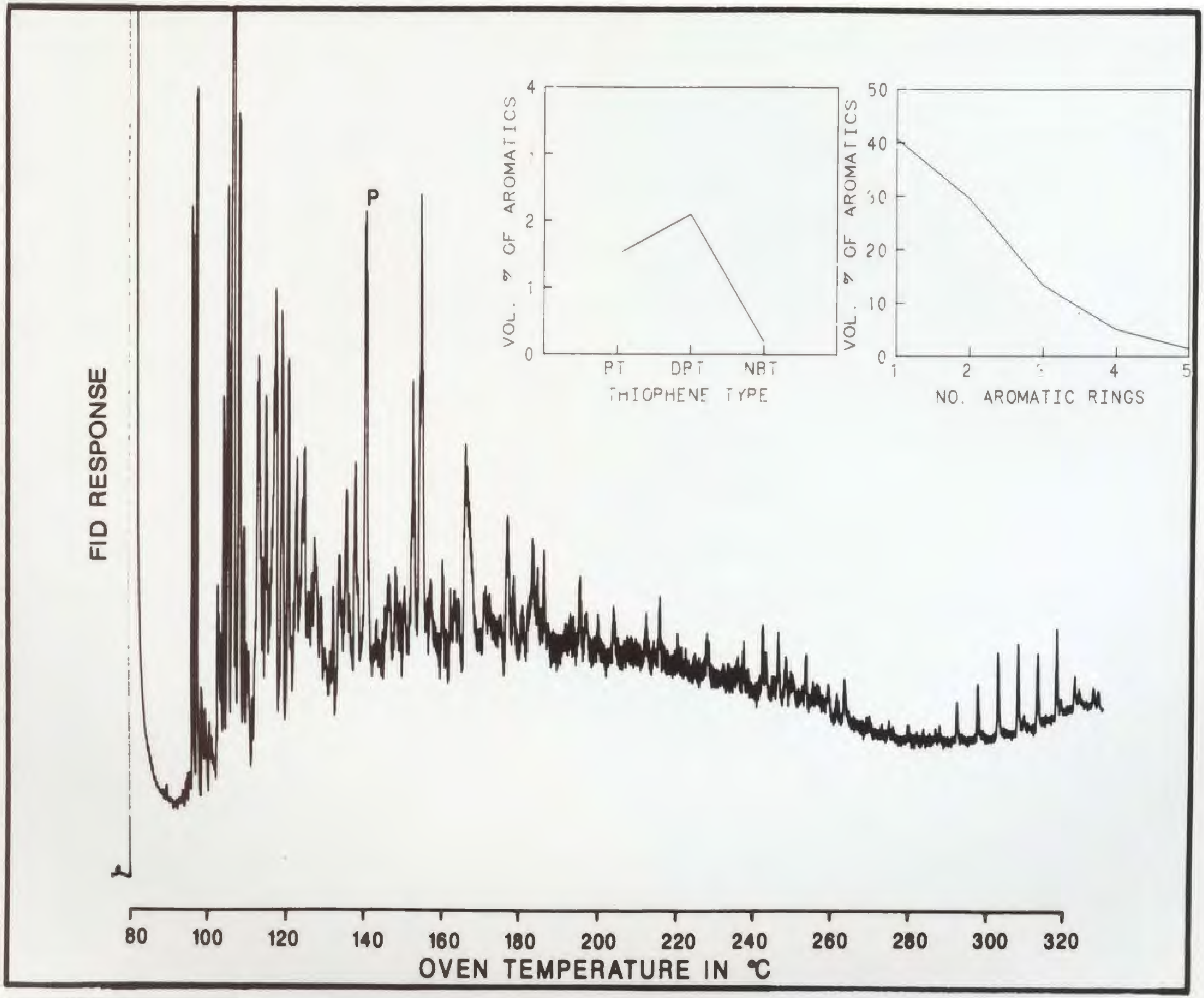


Figure C-48: Aromatics, 10.5m

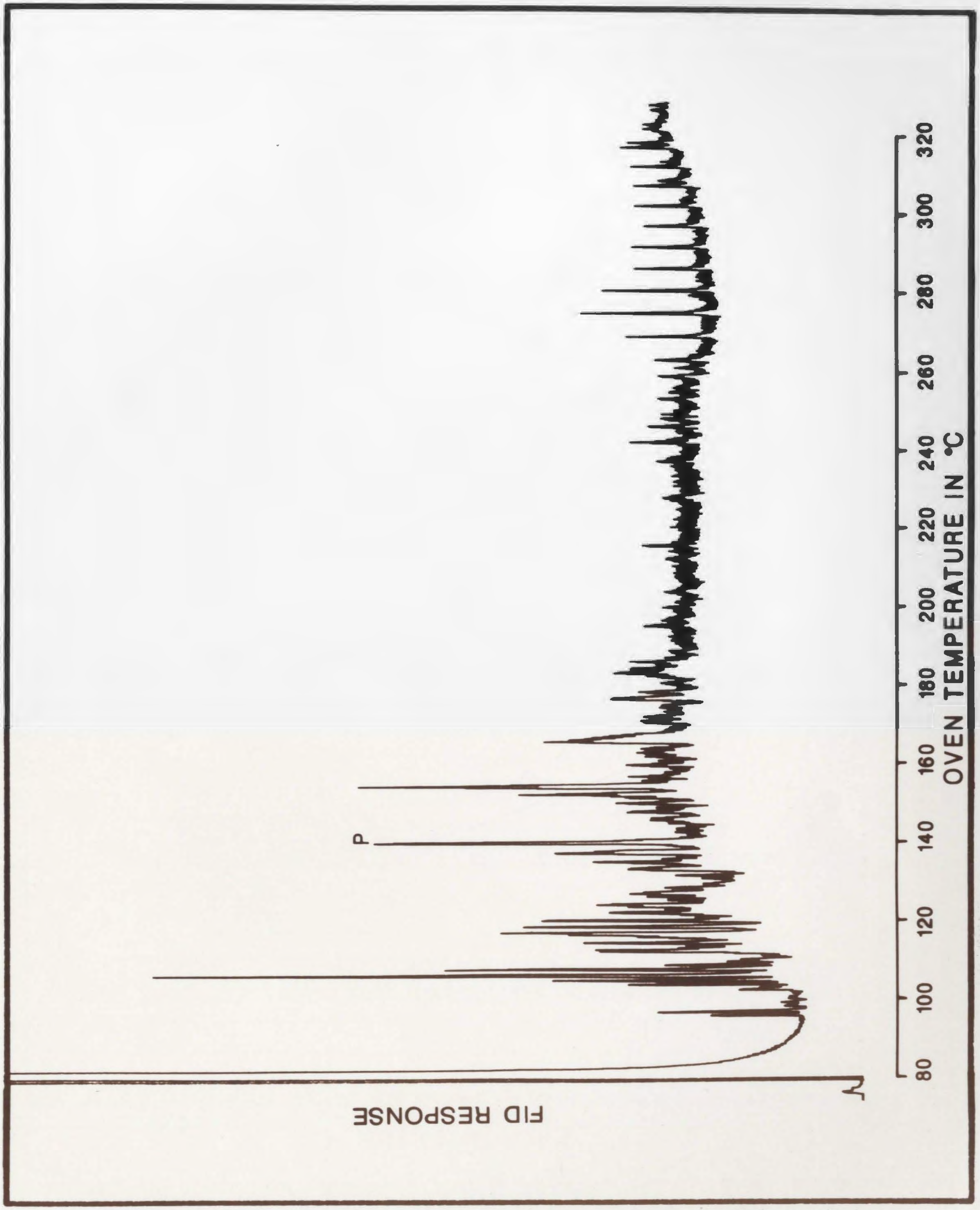


Figure C-49: Aromatics, 9.2m

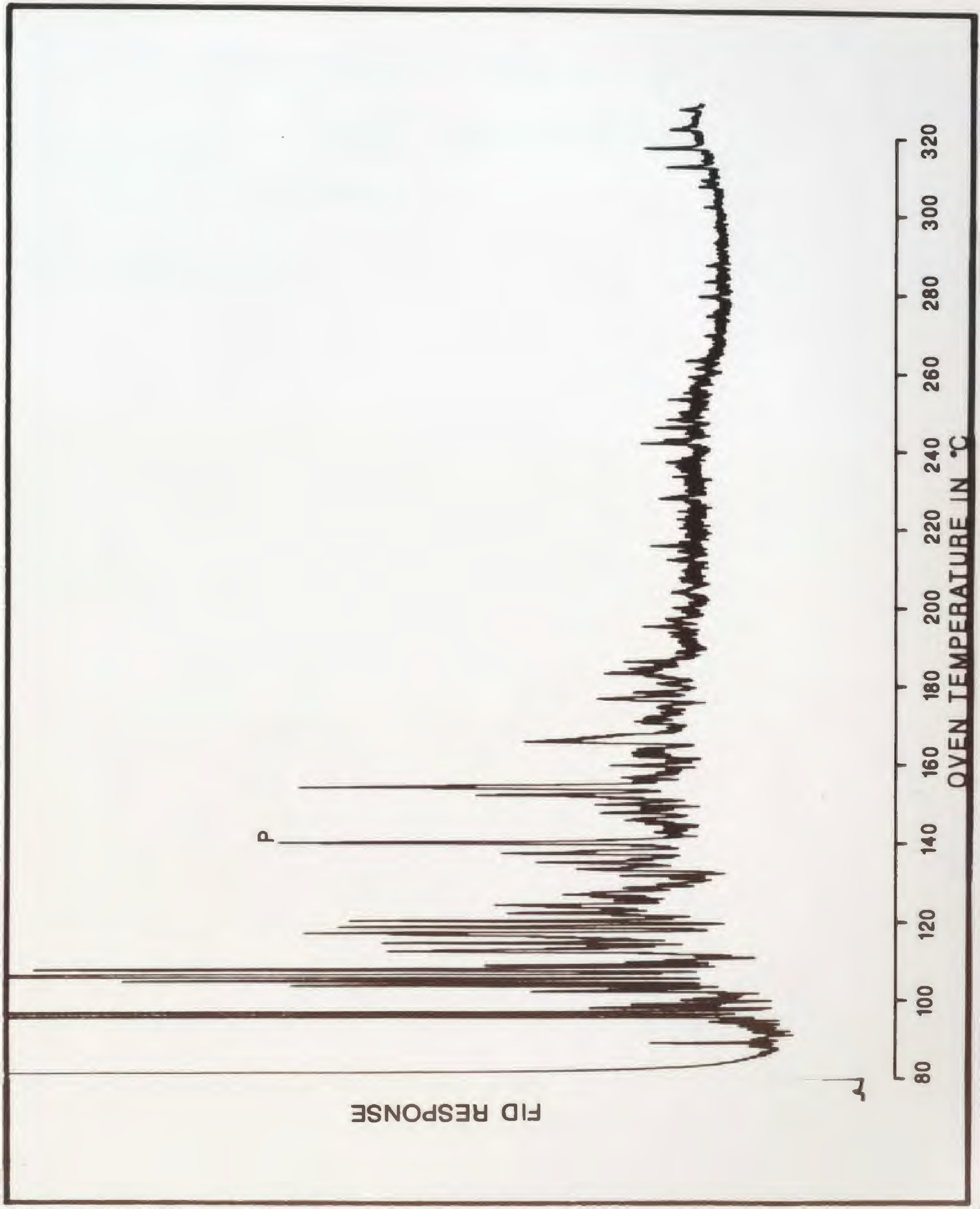


Figure C-50: Aromatics, 7.7m

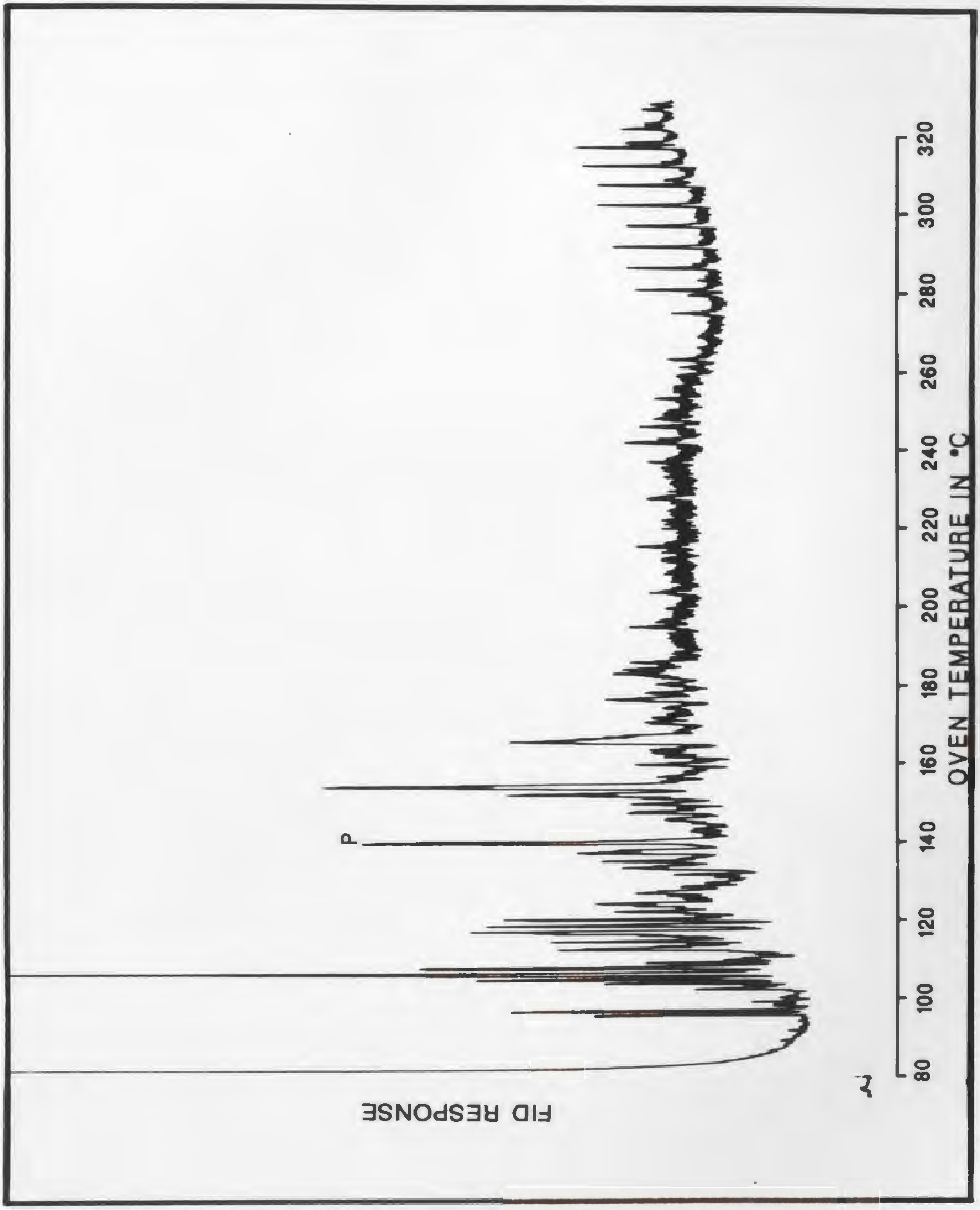


Figure C-51: Aromatics, 6.2m

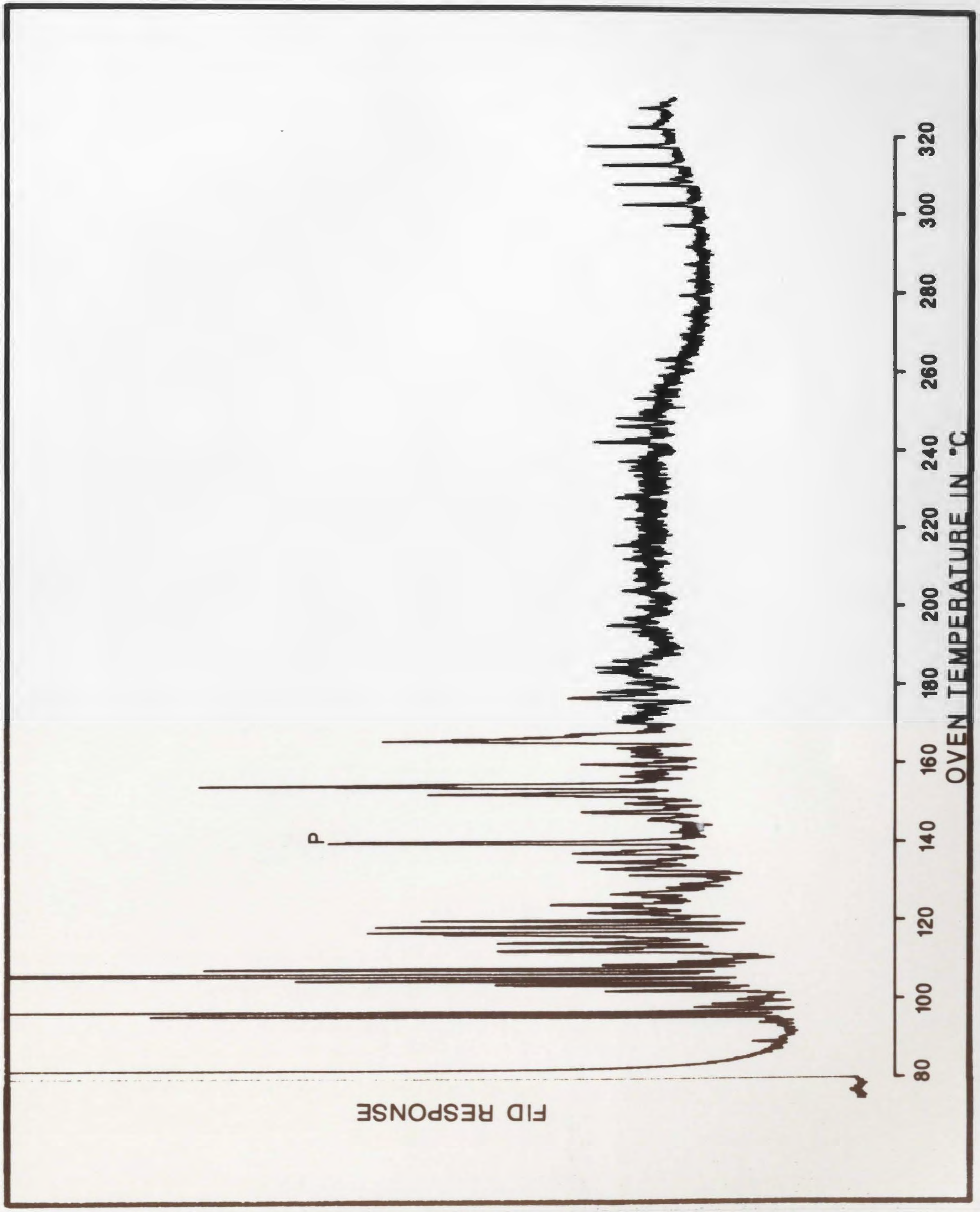


Figure C-52: Aromatics, 4.9m

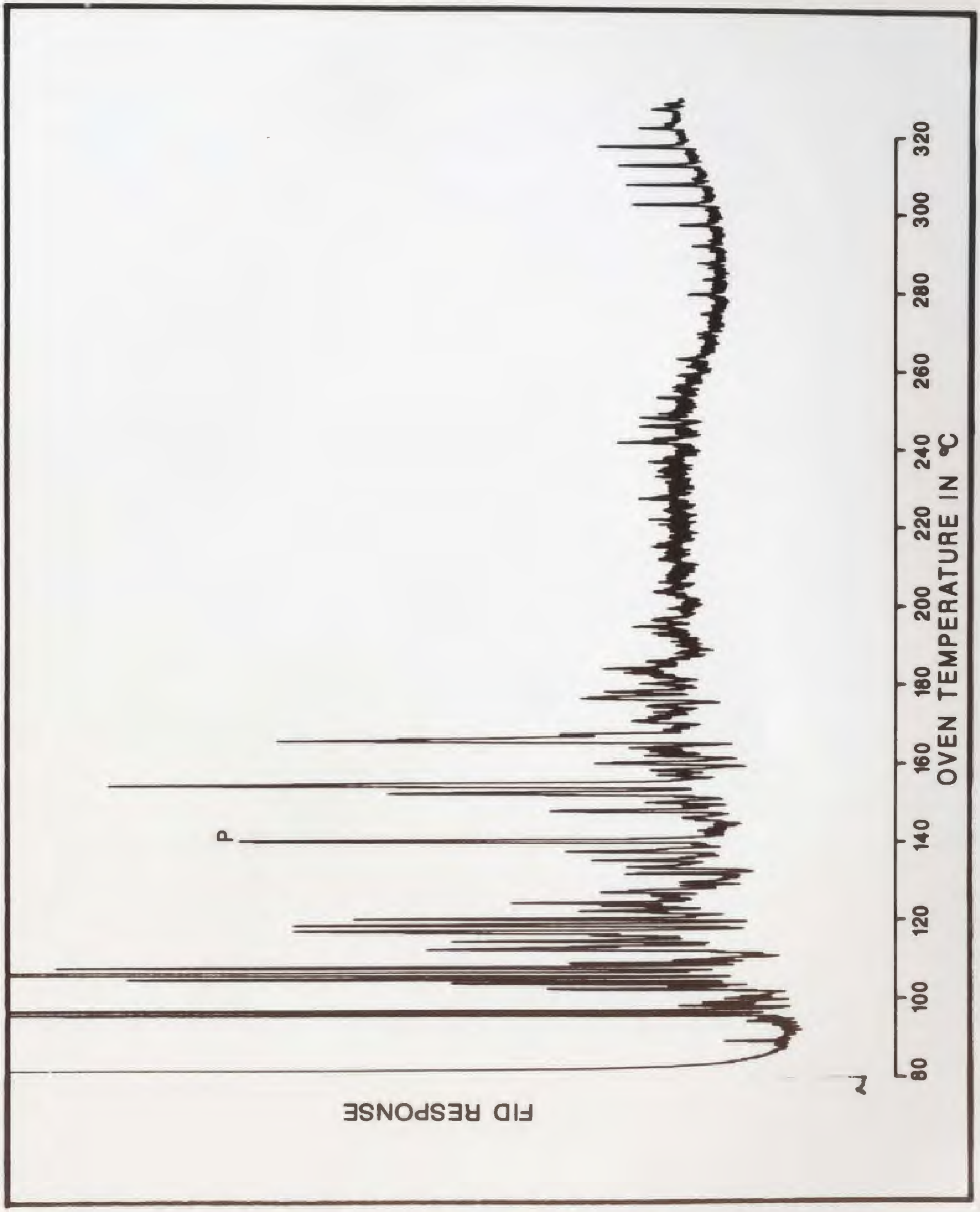


Figure C-53: Aromatics, 3.2m

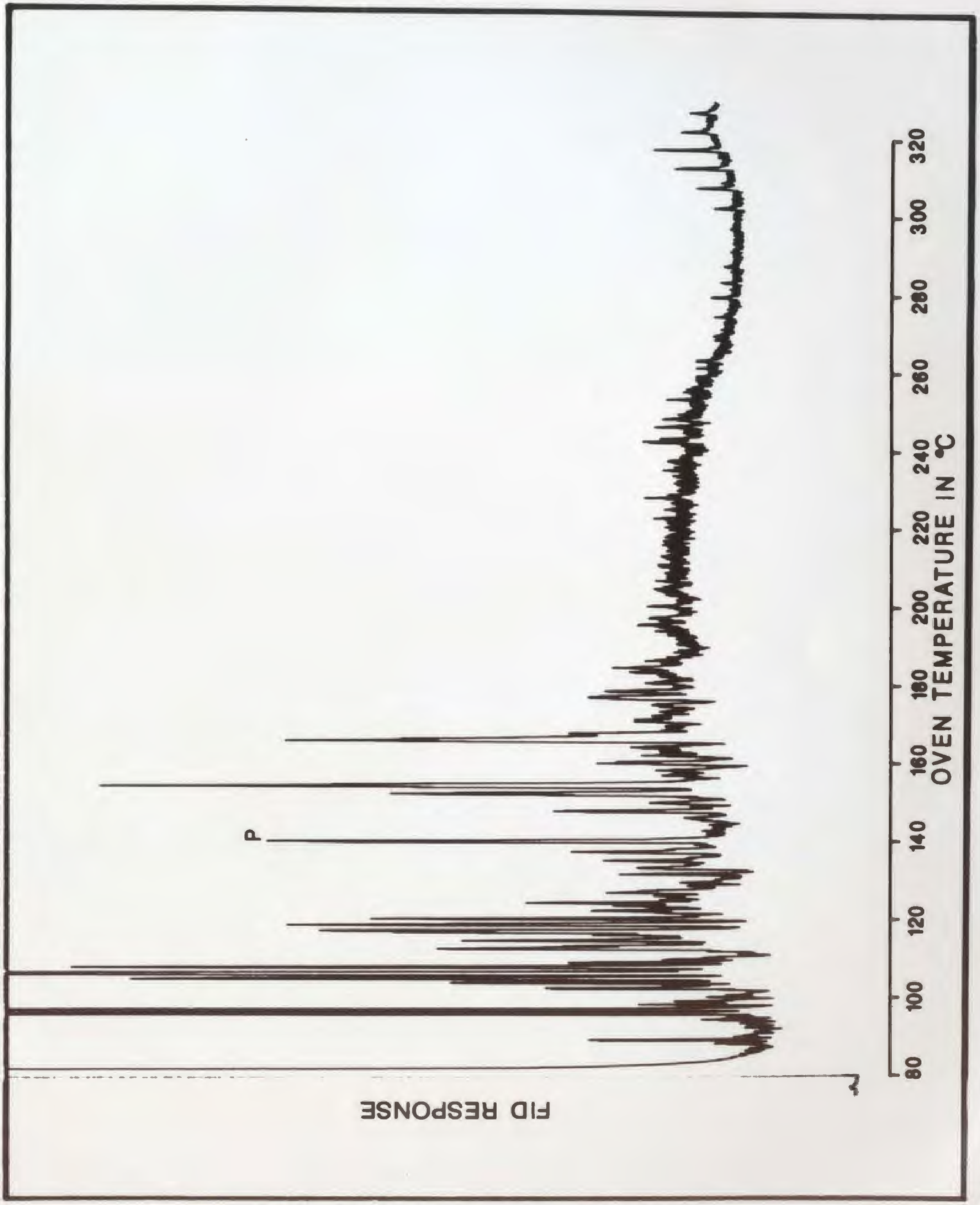


Figure C-54: Aromatics, 1.4m

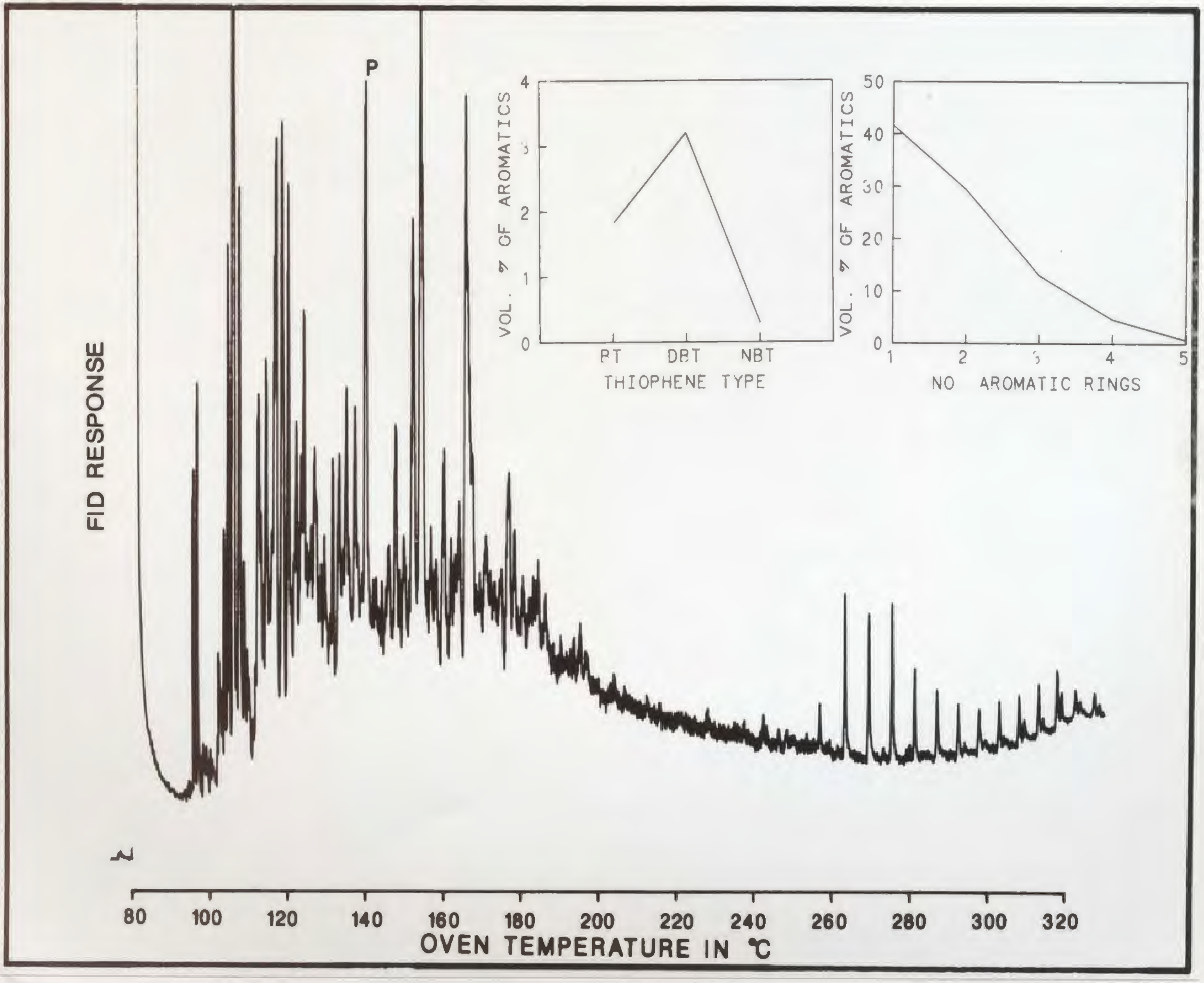


Figure C-55: Aromatics, 0.0m

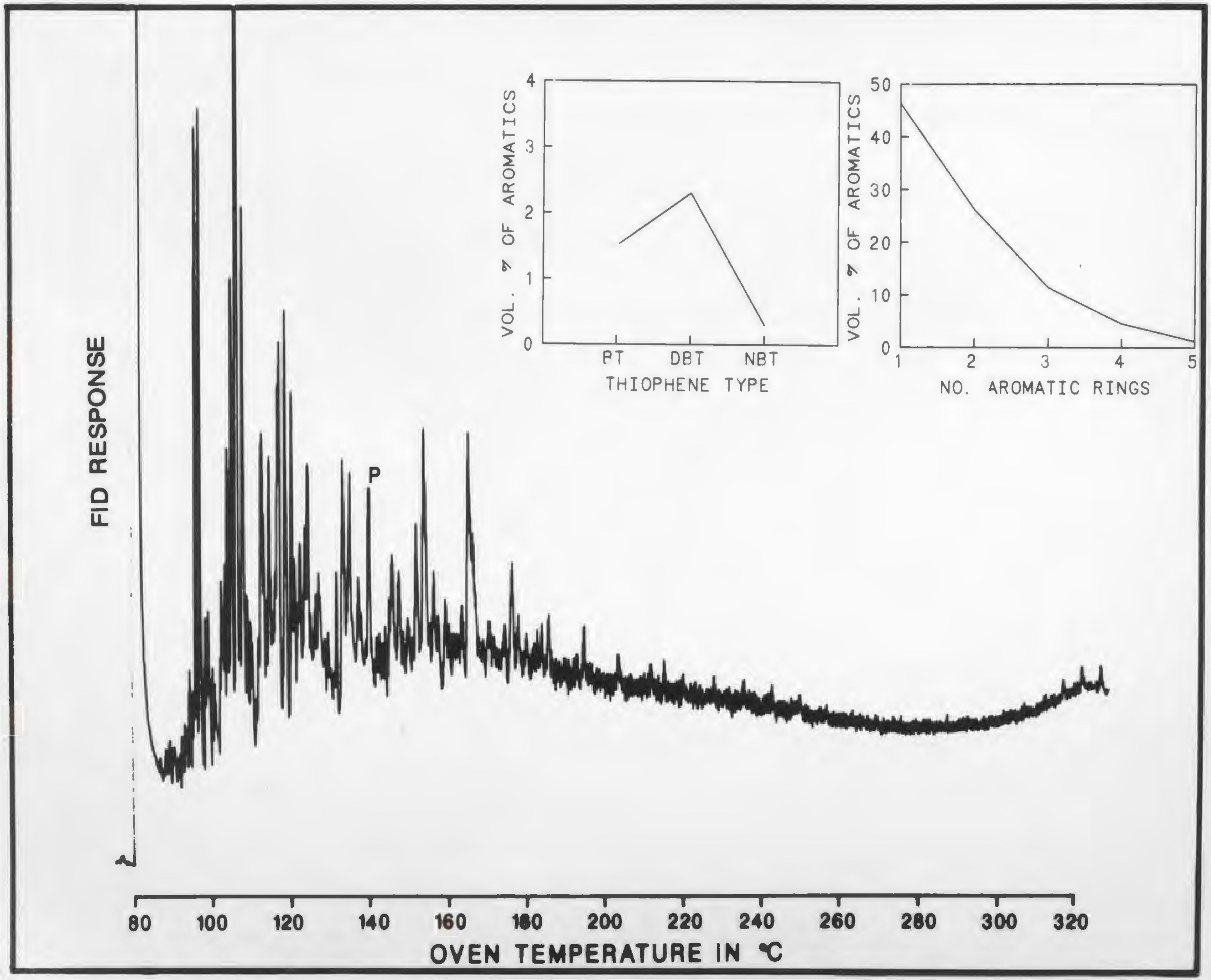


Figure C-56: Aromatics, oil