Chemical and Isotopic Investigations of Crude Oils in some Paleozoic Reservoirs: West-Central Kansas

by

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INTRODUCTION

Rich (1931, 1933) and Walters (1958) suggested that Paleozoic hydrocarbons of central and western Kansas migrated updip out of the Anadarko Basin during the mid- Permian. Crude oils in the region are trapped in reservoirs of Cambro- Ordovician, Mississippian, and Pennsylvanian age with minor production from the Permian. Walters (1958) concluded that the hydrocarbons, while migrating northward into Kansas, were differentially entrapped according to the principle outlined by Gussow (1954). In his publication, Gussow (1954) stated that oil and gas migrating through a series of traps will be selectively trapped (figure 1), with gas being trapped in the structurally lowest reservoirs, gas and oil in the intermediate depth reservoirs, and oil and or possibly water in the structurally highest reservoirs (depending on the amount of available hydrocarbons). Applying this principle to hydrocarbon occurrence in central Kansas along a line parallel to the southward paleo- dip of the Arbuckle Dolomite during mid- Permian time, Walters (1958) noted that gas is found in the structurally lowest reservoirs, gas and oil in the intermediate depth reservoirs, oil in the next reservoirs, and water in many of the structurally highest traps over the Central Kansas Uplift. While this mode of emplacement for hydrocarbons in central Kansas has been assumed, little published geochemical evidence exists supporting this hypothesis.

Recently some investigations have focused on the geochemistry of oil- field brines in Ness, Hodgeman, Ford, and Clark Counties in central Kansas (Chaudhuri, 1978; Broedel, 1983; Nicastro, 1983; Robinson, 1983). These investigations suggested that the oil- field waters in Ness, Hodgeman, and northern Ford Counties genetically are similar with a linear increase in the salinity of the waters southward or down dip. The oil- field waters from Clark County have salinities two to three times higher than those in Ness and Hodgeman counties to the north. This indicates a decreasing influence of meteoric water southward away from the Central Kansas Uplift. The chemical evolutionary history of the waters in the south was apparently different from that of northern counties. Current studies are underway at Kansas State University to determine the regional variation of the composition of oil- field brines in the Upper Pennsylvanian Lansing- Kansas City Formations.

This report focuses on vanadium- nickel ratios, API gravities, pristane/phytane ratios, gas- chromatographic data, sulphur contents, and carbon isotopic ratios of crude oils from Paleozoic reservoirs in a 10 county area of west- central Kansas (figure 2). The information obtained will add to the current base of knowledge of the geochemistry of hydrocarbon deposits in the area and provide further evidence for source and migration paths of hydrocarbons in west- central Kansas. The main objectives of this report are to correlate the Paleozoic crude oils produced from broad stratigraphic intervals on the western flank of the Central Kansas Uplift and provide a test for the concept of differential entrapment of hydrocarbons, as suggested by Walters (1958).

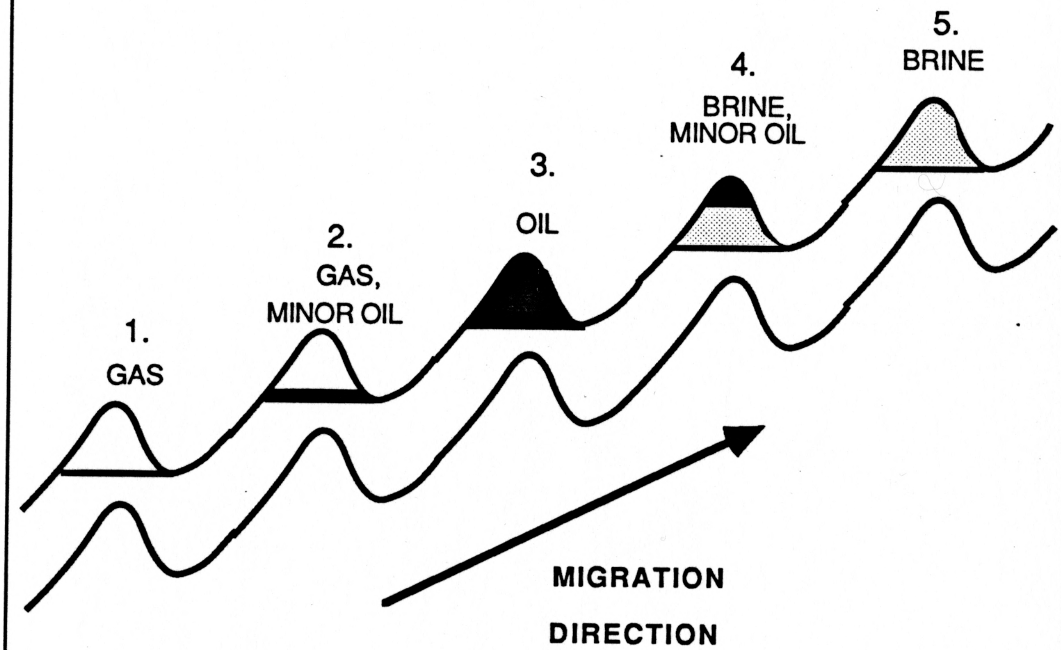


Figure 1. Schematic representation of the results of differential entrapment. Modified after Gussow (1954).

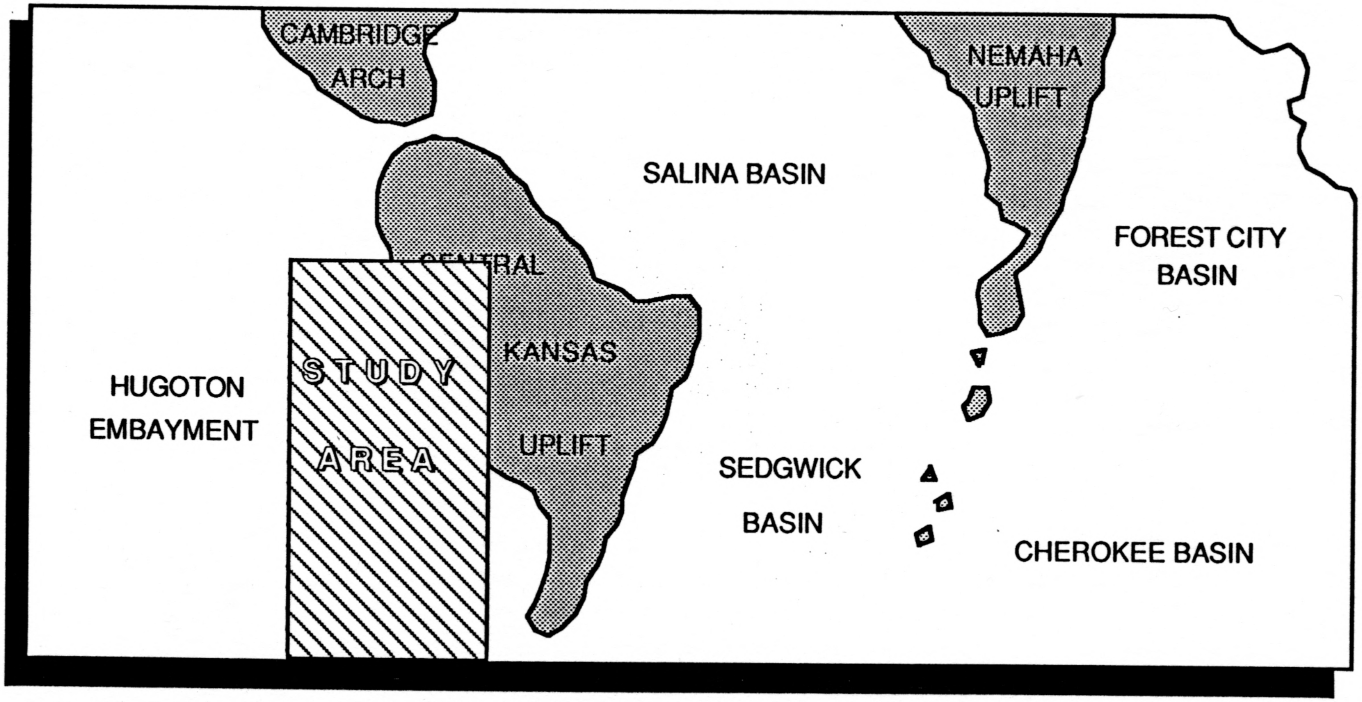


Figure 2. Major Structural Features Of Kansas.

Rationale

It is widely accepted that most petroleum hydrocarbons are generated by the thermal maturation of kerogen, which generally occurs finely disseminated in fine grained sedimentary rocks (Breger and Brown, 1962; Philippi, 1965; Louis and Tissot, 1967; Speers and Whitehead, 1969; Hunt, 1972). The potential of a kerogen to generate crude oil depends on its type, which in turn is dependent on the chemical nature of materials forming the kerogen (Horsfield and Douglas, 1980) and paleoenvironmental conditions during its deposition. Kerogens that are rich in hydrogen are considered to be potential crude oil sources, whereas kerogens low in hydrogen are classified as being potential gas sources (Forsman and Hunt, 1958; Breger and Brown, 1962; Tissot and others, 1974; Vandenbroucke and others, 1977; Tissot and Welte, 1978; Hunt, 1979). Thermal maturation of source kerogens is the primary factor in the conversion of kerogen to bitumen, and finally to crude oil.

Crude oil characteristics are mainly a function of kerogen- type (original source matter), thermal maturity, and the associated mineral matrix. Other secondary effects such as biodegradation, chromatographic effects, de- asphalting, water- washing, and inorganic oxidation also may occur and have varied effects on the chemical characteristics of a crude oil after generation. Horsfield and Douglas (1980) concluded that the mineralogy of source rocks is significant in controlling the composition of kerogen pyrolysis products. Their experiments showed that the relative content of low molecular weight pyrolysis products is higher for kerogens pyrolyzed in a mineral matrix than for isolated kerogens. Time plays a secondary role in crude oil generation; as length of burial increases, the temperatures required for the onset of generation are reduced, as in the "Oil- Window" concept (Barker, 1979). Since crude oil generation, and especially migration, is an inefficient process, most of the bitumens will remain in a given source rock (Barker, 1979). This suggests that any extractable organic matter from a source rock will show similarities in some chemical constituents not modified by maturation or degradation effects to a reservoired crude oil generated from it. Crude oils generated from the same source but reservoired in different traps will then show some compositional similarities. On the other hand, crude oils generated from different sources will have distinct compositional differences. Techniques such as vanadium to nickel ratios, pristane to phytane ratios (C_{19} and C_{20}. isoprenoid units), API gravity, carbon and hydrogen isotopic ratios, percent sulfur, and many others have been used in oil to oil and oil to source rock correlations. As effects of migration, maturation, bacterial degradation, and water washing can significantly change the character of any given parameter, a combination of techniques is desirable.

Crude oils commonly are analyzed for the American Petroleum Institute (API) gravity. Wide ranges in API gravities have been reported for crude oils ranging from less than 20 (heavy crudes) to more than 60 (very light oils), and wide ranges within a basin are not uncommon.

Vanadium and nickel concentrations have been determined in crude oils from various parts of the world (Shirey, 1931; Haberlandt, 1944; Hodgson, 1954; Scott and others, 1954; Ball and others, 1960; Hodgson and others, 1957; Guinn and Bellanca, 1969; Al- Sharistani and Al- Atyia, 1972; Yen, 1975). Concentrations of V and Ni range from a few parts per billion (ppb) to more than 1,200 parts per million (ppm). They are the only trace metals that occur in appreciable levels in crude oils and their chemistry has been studied extensively by many (Cannon, 1960; Boucher and others, 1968; Yen, 1975; Lewan, 1980; Lewan and Maynard, 1982; Lewan, 1984). It is thought that trace metals enter organic matter in marine sediments across the sediment- water interface through the process of diffusion (Lewan and Maynard, 1982). The proportion of vanadium to nickel in crude oils has been investigated (Witherspoon and Nagashima, 1957; Ball and others, 1960; Katchenkov, 1979; Lewan and Maynard,1984) and used in oil to oil correlations (Hodgson, 1954; Al- Sharistani and Al- Atyia, 1972; McKirdy and Horvath, 1976) and in oil to source rock correlations (Witherspoon and Nagashima, 1957; Baker, 1962; Taguchi, 1975). The behavior of vanadium and nickel has been suggested to be similar in geologic settings (Lewan, 1980; Lewan and Maynard, 1982) so that during oil generation, migration, bacterial degradation, water washing, and maturation, their ratio will remain relatively unchanged.

Among the most important hydrocarbons in crude oils for geochemical correlations are the isoprenoid compounds (called terpanes in alternative nomenclature). These molecules occur as straight chain hydrocarbons with a methyl group branch on every fifth carbon atom (figure 3a.). Isoprenoids are indicative of biological processes and are present in nearly all living systems, recent sediments, ancient sediments, and crude oils. The most common isoprenoids studied are pristane (C_{19}) and phytane (C_{20}) because they are relatively abundant and directly related to biological precursors.

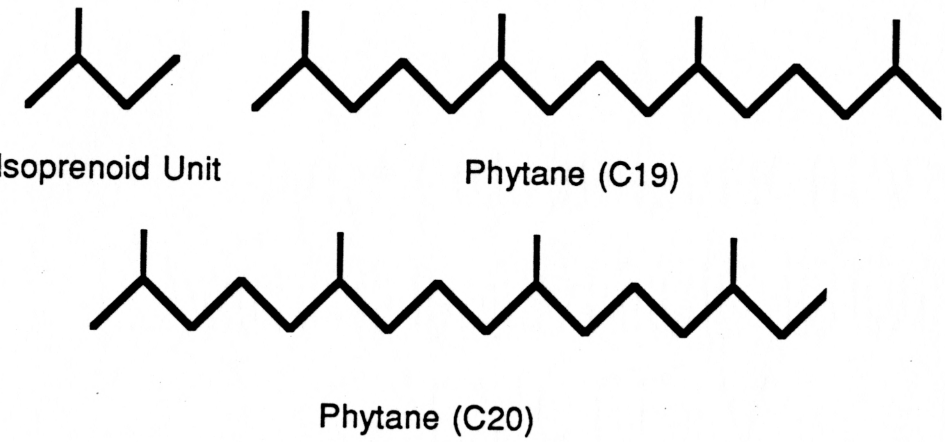


Figure 3a. Topographic representation of the isoprenoid hydrocarbons pristane and phytane showing the characteristic branching on every fifth carbon atom. After Barker (1979).

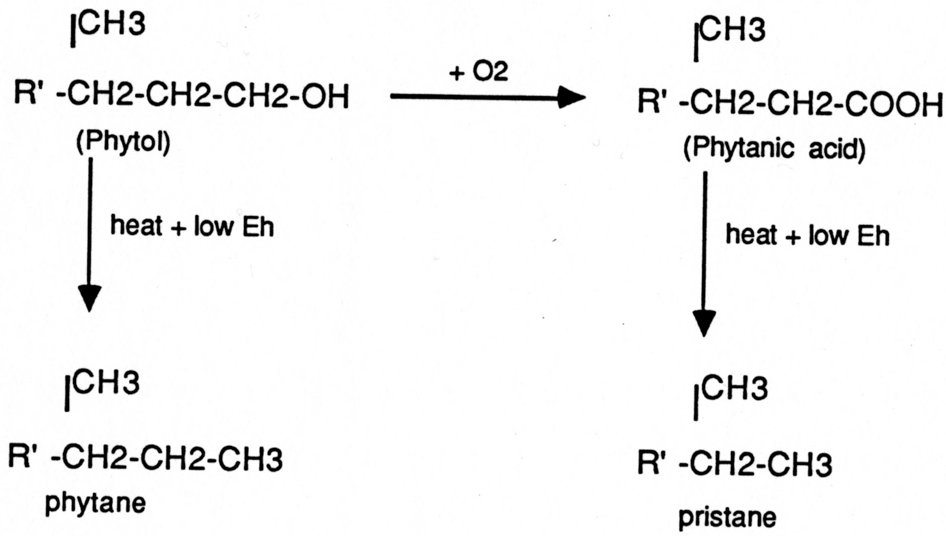


Figure 3b. Reaction paths of phytol producing pristane and phytane. Modified after Powell and McKirdy (1974).

Pristane and phytane have long been considered products of the decomposition of the phytol side chain of chlorophyll and related heme pigments (Brooks and others, 1968; Powell and McKirdy, 1975; Barker, 1979) although other minor sources are possible. During early decomposition of chlorophyll, two major products are produced: a metal bearing porphyrin compound and the branched alcohol phytol. Both pristane and phytane are considered to be generated by two principal reaction paths involving the breakdown of the phytol side chain (figure 3b.). Pristane is formed by the oxidation of phytol to phytanic acid and the subsequent decarboxylation, producing a branched isoprenoid hydrocarbon one carbon atom shorter than the parent. Phytane is produced by the dehydration and hydrogenation of phytol without the loss of the end carbon atom (Brooks and others, 1969). The formation of phytanic acid should then occur to a greater extent on land during the initial stages of aerobic plant decay than in marine conditions, where anaerobic decay is more likely (Powell and McKirdy, 1975).

Determination of the contents of the regular isoprenoids pristane and phytane in crude oils, coals, organic- rich sediments, and ancient rocks is a standard industry technique (Douglas, 1969). The ratio of pristane to phytane has been used extensively in oil to oil and oil to source rock correlations (Welte, 1965; Maksimov and Sofonova, 1973; Wehner, 1973; Erdman and Morris, 1974; Koons and others, 1974) and recently as an environmental indicator (Lijmbach, 1975; Powell and McKirdy, 1975; Welte and others, 1975; Barker, 1979). The ratios of pristane and phytane to the lighter isoprenoids may be useful as an indication of maturity (Williams, 1986).

Carbon isotopic data have been used to supplement geochemical investigations of crude oils, gases, asphalts, and organic constituents in recent and ancient sediments

(Ronov, 1958; Sackett and Thompson, 1963; Degens, 1969; Yemel, 1975; Sofer, 1984; Clayton and others, 1987). The conversion of organic matter, of marine and terrestrial origin, to oil and gas involves bacterial attacks in unconsolidated to produce humus substances. These humus compounds are then converted to kerogen as a consequence of increased diagenetic stress, and finally to hydrocarbons by thermal breakdown of kerogen. Characterization and correlation of petroleums can be made by carbon isotopic analysis. The carbon isotopic compositions are usually given in terms of $\delta\ ^{13}C$ values, which are expressed as:

$$\delta\ ^{13}C=\{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{std.}/(^{13}C/^{12}C)_{std.}\} *1{,}000 \text{ per mil}$$

The systematics of carbon isotopes in hydrocarbons have been discussed by Stahl (1977). Phototsynthesis and isotope exchange are two major processes by which carbon isotopes are fractionated in near- surface environments (Faure, 1977). The carbon isotopic composition of organic materials fixing carbon during photosynthesis depends on the source of CO_2 in the reservoir and the type of photosynthetic path followed. Biologically synthesized organic molecules are enriched in ^{12}C relative to the atmospheric CO_2 or dissolved CO_2 in the aqueous medium. The fractionation of the carbon isotopes is a consequence of the kinetic effects. The isotopic fractionation of carbon in plants occurs through preferential incorporation of ^{12}C from the ambient environment across the cell walls to the cytoplasm. This occurs through preferential incorporation of ^{12}C dissolved in the cytoplasm in the formation of phosphoglyceric acid by the action of enzymes and though synthesis of a variety of organic compounds from the phosphoglyceric acid (Faure, 1977).

The distributions of $\delta\,^{13}C$ values in different terrestrial and marine organisms have been amply summarized by Deines (1980). Terrestrial plants have a bimodal distribution of $\delta\,^{13}C$ values within the range of - 6.00 to - 36.00 per mil, with one mode of frequency peak around - 12.00 to - 15.00 per mil, and the other with a frequency peak around - 25.00 to - 28.00 per mil. The former is typical for many C_4 plants and the latter for many C_3 plants. Aquatic plant have the same range of $\delta\,^{13}C$ values as the terrestrial plants, but not with the bimodality of the latter. Marine plants are generally less depleted in ^{12}C than marine plankton, the former having a median $\delta\,^{13}C$ value around - 15.00 per mil and the latter having a broad frequency peak distribution between - 18.00 and - 28.00 per mil. Lacustrine plants appear to be more enriched in ^{12}C than marine plants exclusive of plankton. Marine algae have $\delta\,^{13}C$ values between - 6.00 and - 23.00 per mil. The differences in the carbon isotopic compositions among different aquatic plants can be attributed to the isotopic composition of the carbon pool from which the plants derive their carbon. Sackett and others (1965) found that the isotopic composition of plankton is also related to the growth temperature: planktons from high latitudes are more enriched in ^{12}C than planktons from low latitudes.

Organic carbons in recent marine sediments generally have $\delta\,^{13}C$ values between - 10.00 and - 30.00 per mil. Sackett and Thompson (1963) noted a landward change from about - 21.00 to - 26.00 per mil and a similar change with depth for Gulf Coast sediments. Although Sackett and Thompson attributed the changes to increased contributions of land-derived plants near shore, which are typically enriched in ^{12}C relative to aquatic marine plants, this simple explanation suffers from the lack a critical evaluations of different factors which can effect the isotopic composition of organic materials.

The carbon isotopic composition of kerogen in recent marine sediments is influenced by: (1) the relative amounts and the isotopic compositions of carbons derived from different sources, (2) isotopic effects in the transformation of living tissues to humic substances, and (3) isotope effects during diagenesis. The diagenetic changes may produce either ^{13}C or ^{12}C enrichment in the residual organic material, depending on the nature of the diagenetic processes. For example, bacterial degradation of organic matter will lead to ^{13}C enrichment in the residual matter, whereas decarboxylation reactions preferentially remove ^{13}C enriched groups with a consequent depletion in ^{13}C in the residual organic material.

The isotopic composition of a crude oil should be similar to or slightly lighter than the isotopic composition of the extract in the source rock, and the extracts are slightly depleted in ^{13}C relative to the kerogen. In general, crude oils are 1.50 to 2.00 per mil lighter than the kerogen from which the hydrocarbons were derived (Stahl, 1977). Most crude oils have $\delta\ ^{13}C$ values between - 21.00 and - 32.00 per mil with a prominent frequency distribution peak at - 28.00 to - 29.00 per mil. The differences in $\delta\ ^{13}C$ values of crude oils depend not only on the source of organic materials and their diagenetic evolution, but also on the relative amounts of isotopically different chemical components that make up the oils. Asphaltenes and tars are enriched in ^{13}C relative to the total oil. Waxes and cyclo- alkanes of lower molecular weights are slightly depleted in ^{13}C relative to the total oil, and lighter gases such as butane, ethane, and methane are even more depleted in ^{13}C relative to the total oil. Also, the saturate compounds are slightly depleted in ^{13}C relative to the lighter aromatic compounds. Thus, the isotopic composition of a crude oil may be shifted towards increased ^{12}C contents (lower $\delta\ ^{13}C$ values) with increased migration accompanying the relative enrichment of isotopically light saturates and the loss of isotopically heavy aromatics, asphaltenes, and heterocomponents (Stahl, 1977). In view of the isotopic shifts that can be associated with generation and migration of hydrocarbons, the carbon isotopic data are most useful for correlation and, possibly, characterization of crude oils to their source rocks.

Sample Description

This study is based on the geochemical analysis of 28 crude oils produced from a variety of Paleozoic sediments, representing different geologic ages and geographic areas within west- central Kansas. Crude oils collected for geochemical analysis are listed in table 1. The study area encompasses approximately 5,500 square miles of a petroleum-rich province of west- central Kansas, ranging from the Kansas- Oklahoma state line to approximately 126 miles north to the southwestern flank of the Central Kansas Uplift (figure 4). Samples were selected at random and represent broad stratigraphic intervals within the Upper Cambrian Arbuckle Limestone (2 samples), Ordovician Simpson Group (1 sample), Mississippian sediments of either Osagian or Meramecian age (9 samples), Lower Pennsylvanian sediments of Morrowan age (4 samples), Middle Pennsylvanian Cherokee Group (3 samples), Middle Pennsylvanian Marmaton Group (1 sample), Upper Pennsylvanian Lansing- Kansas City groups (7 samples), and the Upper Pennsylvanian Douglas Group (1 sample). Samples were collected over a large area in order to examine the regional variation in the oils. Because of the enormous lateral and vertical variation within the study area, any interpretations made in this study are at best preliminary.

Well- head samples were obtained during August 1985 with the assistance of personnel from Pickrell Drilling Co. of Great Bend, Kansas, KRM Petroleum Inc. of Wichita, Kansas, and Thunderbird Drilling of Protection, Kansas. Samples were collected in pre- rinsed one litre linear polyethylene bottles. Well heads were allowed to flow for a minimum of two minutes to flush lines of contaminates. In general, well- head samples were from 60 to 80 percent (by volume) oil, but several samples from the Kansas City

Group near the northern limits of the study area were up to 85 percent (by volume) brine water.

	Table 1. Crude oil samples from west-central Kansas.						
Sample Number	Well Name	County	Legal Description	Depth	Producing Zone	API	Dist. North
DB-1	Butler B. #1	Edwards	Sec. 07, T. 26S, R. 20W	4718	L-Kc	37.00	60
DB-2	Christian Church A #1	Ford	Sec. 36, T. 29S, R. 25W	5430	Morrow	40.00	36
DB-3	Moore U. #3	Ford	Sec. 32, T. 29S, R. 24W	5470	Morrow	47.00	36
DB-4	Hallings B. #5	Clark	Sec. 14, T. 30S, R. 22W	5475	Morrow	43.00	30
DB-5	Giles B. #1	Clark	Sec. 25, T. 30S, R. 22W	5384	Morrow	38.00	30
DB-6	Edmonston D. #1	Kiowa	Sec. 22, T. 29S, R. 19W	5199	Miss.	37.00	36
DB-7	Edrington A. #1	Kiowa	Sec. 36, T. 28S, R. 19W	4984	Kc	41.00	42
DB-8	Scheuerman A. #3	Rush	Sec. 34, T. 18S, R. 20W	4244	Cke	35.00	102
DB-9	Dehner A. #7	Rush	Sec. 29, T. 19S, R. 20W	4365	Miss.	36.00	96
DB-10	Beardslee D. #1	Ness	Sec. 02, T. 20S, R. 24W	4445	Miss.	38.00	90
DB-11	Cossman	Pawnee	Sec. 27, T. 21S, R. 15W	4300	Simp.		84
DB-12	Powers	Pawnee	Sec. 14, T. 21S, R. 16W	3600	Ab.		84
DB-13	Baer #6	Ness	Sec. 27, T. 16S, R. 24W	4500	Cke	36.50	114
DB-14	Cline B. #6	Ness	Sec. 15, T. 16S, R. 21W	4311	Cke	37.00	114
DB-15	Babcock G. #1	Ness	Sec. 25, T. 16S, R. 26W	4516	Miss.	37.00	114
DB-16	Dumler U. #1	Ness	Sec. 14, T. 17S, R. 26W	4503	Miss.	37.00	108
JB-1	Barnes	Ellis	Sec. 18, T. 14S, R. 19W		Kc	42.00	126
JB-2	Barnes B.	Ellis	Sec. 18, T. 14S, R. 19W		Kc+Ab	38.60	126
JB-3	Barnes B. #1	Ellis	Sec. 19, T. 14S, R. 19W		Marm	36.50	126
JE-1	Richards #1	Lane	Sec. 20, T. 16S, R. 29W		Kc	29.10	114
JE-2	Jennison B. #1	Lane	Sec. 20, T. 16S, R. 29W		Kc	38.40	114
JE-3	Magie #1	Lane	Sec. 17, T. 16S, R. 29W		Kc	29.00	114
LN-1	Morre 1-20	Ness	Sec. --, T. 17S, R. 24W		Miss.		108
LN-2	Null #2	Ness	Sec. --, T. 17S, R. 24W		Miss.		108
RC-1	Bird South #1	Comanche	Sec. 06, T. 33S, R. 19W	5192	Miss.	38.50	12
RC-2	Bird South #2	Comanche	Sec. 07, T. 33S, R. 19W	4749	L-Kc	42.00	12
RC-3	Collier Flats	Comanche	Sec. 36, T. 33S, R. 20W	4230	Dg.	37.00	12
VB-1	Bindley	Hodgeman	Sec. 33, T. 21S, R. 24W		Miss.		84

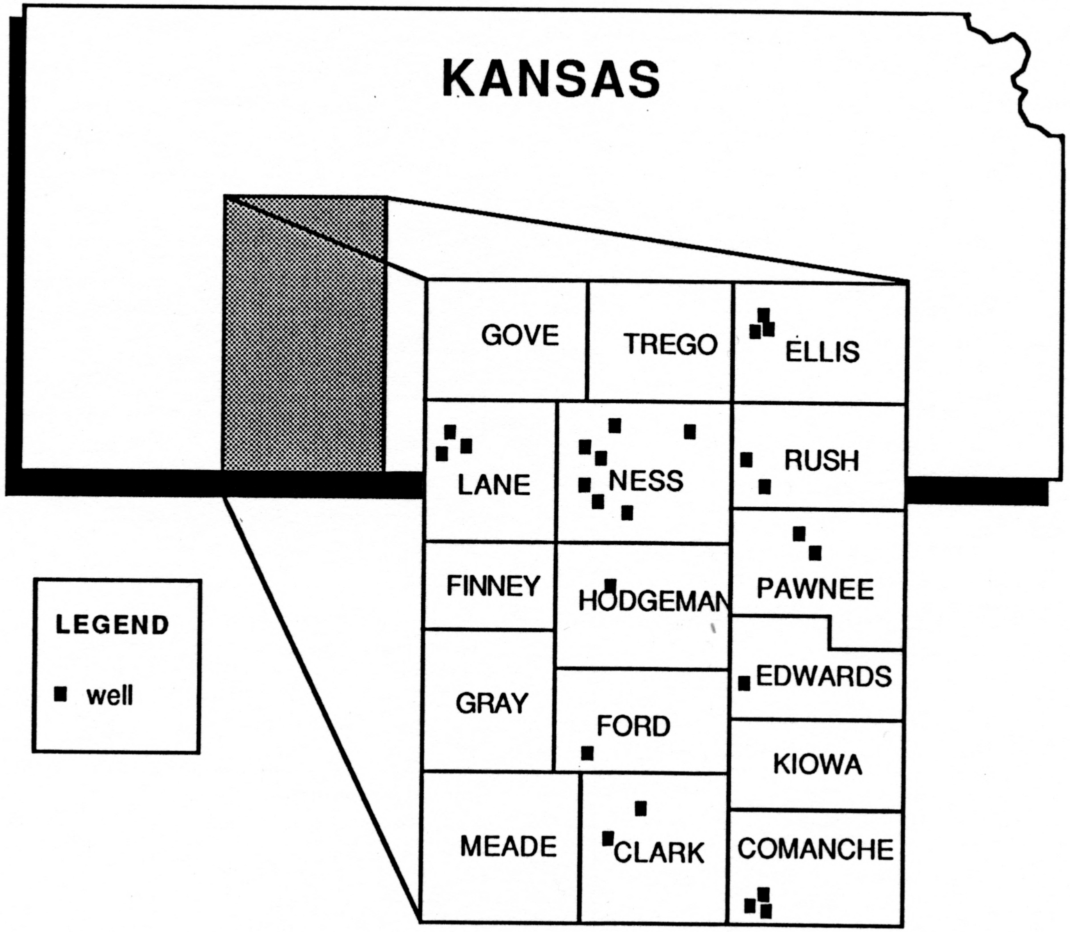


Figure 4. Approximate location of sampled wells.

Regional Geology

The study area is located on the western flank of the Central Kansas Uplift and the eastern portion of the Hugoton Embayment (figure 4). Structural development of the uplift commenced during the early Paleozoic (Lee, 1956; Merriam, 1963), with the most intense deformation occurring from mid- Mississippian to Early Pennsylvanian (pre-Desmoinesian) . This resulted in the removal of Mississippian and older rocks over the uplift. Contemporaneously, Mississippian deposition occurred in the down- warping Hugoton Embayment to the south and west of the Central Kansas Uplift. The embayment is a northern shelf- like extension of the much deeper Anadarko Basin to the south. Paleozoic rocks within the embayment consist predominantly of oolitic and fossil-fragmental limestones, indicating the predominance of warm, shallow epi- continental seas in the region.

Middle Cambrian through Mississippian sediments occur throughout western and central Kansas except for areas over the Central Kansas Uplift where they are upturned and over- stepped by younger rocks (figure 5). Several regional unconformities exist in the stratigraphic section in Kansas between the Precambrian and Upper Cambrian, pre-Mississippian and post- Devonian (Chattanooga Shale), pre- Pennsylvanian (Desmoinesian) and post- Mississippian, pre- Cretaceous and post- Jurassic, and the pre-Tertiary post- Cretaceous surface. All major divisions of the rock systems are represented in Kansas, but several series are missing. They are the Lower and Middle Cambrian, Upper Silurian (Cayugan), Lower Devonian, Upper Permian (Ochoan), Lower and Middle

Triassic, Lower and Middle Jurassic, and the Paleocene, Eocene, and Oligocene of the Tertiary.

The Precambrian basement complex in Kansas is composed of igneous and metamorphic rocks consisting mainly of granites, quartzites, and schists (Merriam, 1963). Pre- Mississippian rocks consists mainly of limestone and dolostone with minor sandstone and shale. The thickest sections of these rocks occur near basinal centers where they have been preserved from extensive erosion. These rocks are missing from uplifted areas such as the Central Kansas Uplift and Nemaha Uplift. As such, many unconformities exists in this part of the section (figure 6).

Mississippian rocks are present in the subsurface throughout Kansas, except for local areas over the Central Kansas Uplift, Cambridge Arch, and northern parts of the Nemaha Anticline (figure 7). The only outcropping Mississippian rocks (Osagian age) are found in the extreme southeastern corner of the state. In general, Lower Mississippian rocks are mainly marine, and younger Mississippian rocks are both marine and non- marine, reaching a maximum thickness of 1,700 feet in the Hugoton Embayment.

Pennsylvanian rocks reach an aggregate thickness of 3,100 feet with outcrops occurring in the eastern portion of the State (figure 8). Desmoinesian and younger Pennsylvanian rocks consists mainly of cycles of marine shales and limestones alternating with non- marine beds (Zeller, 1968). Pennsylvanian rocks are the youngest rocks in contact with the Precambrian in local areas over the Central Kansas Uplift.

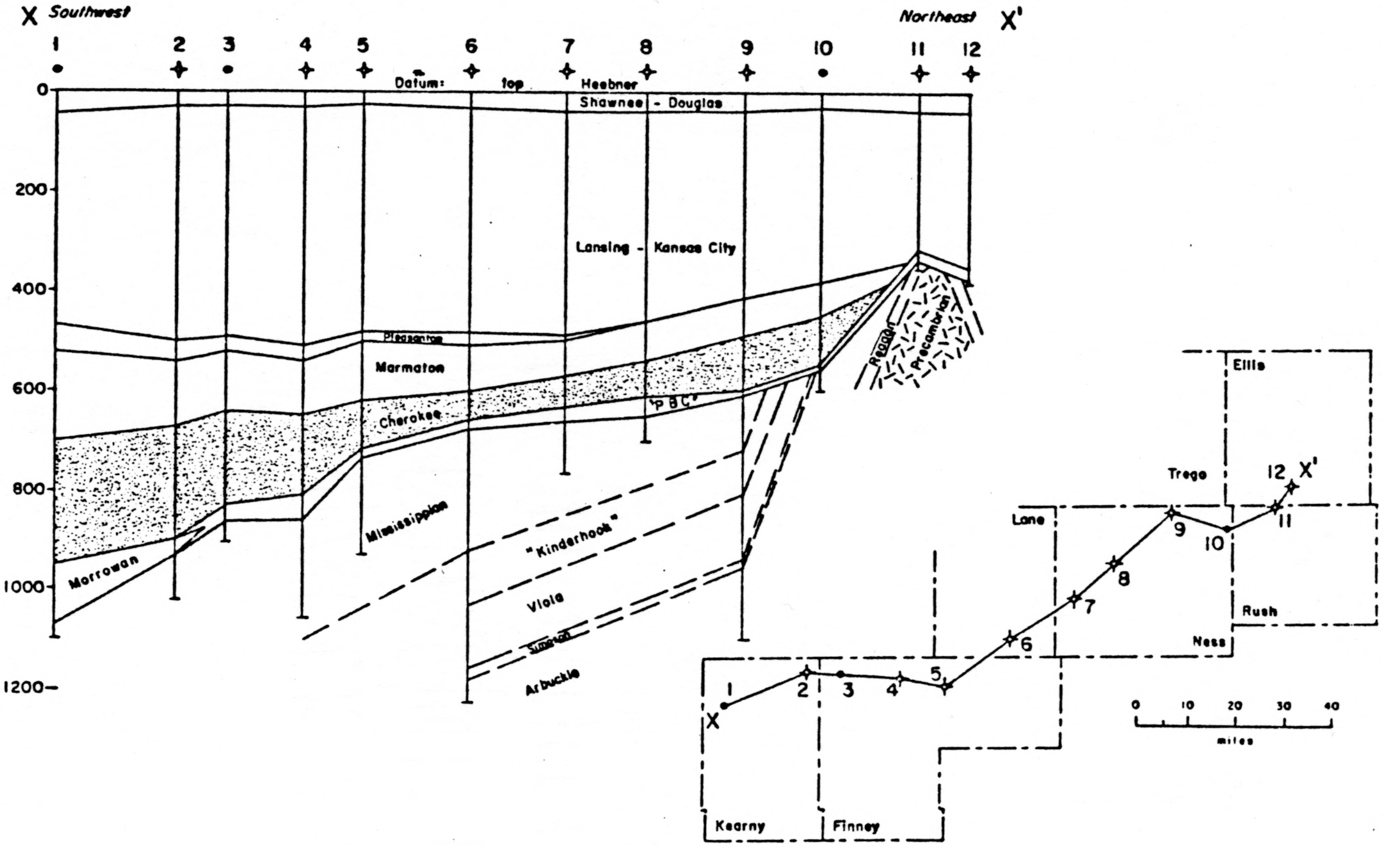


Figure 5. Southwest-northeast cross section from Kearny County to Ellis County showing stratigraphic relation of Cherokee rocks to younger and older units southwest of the Central Kansas Uplift. After Merriam (1963).

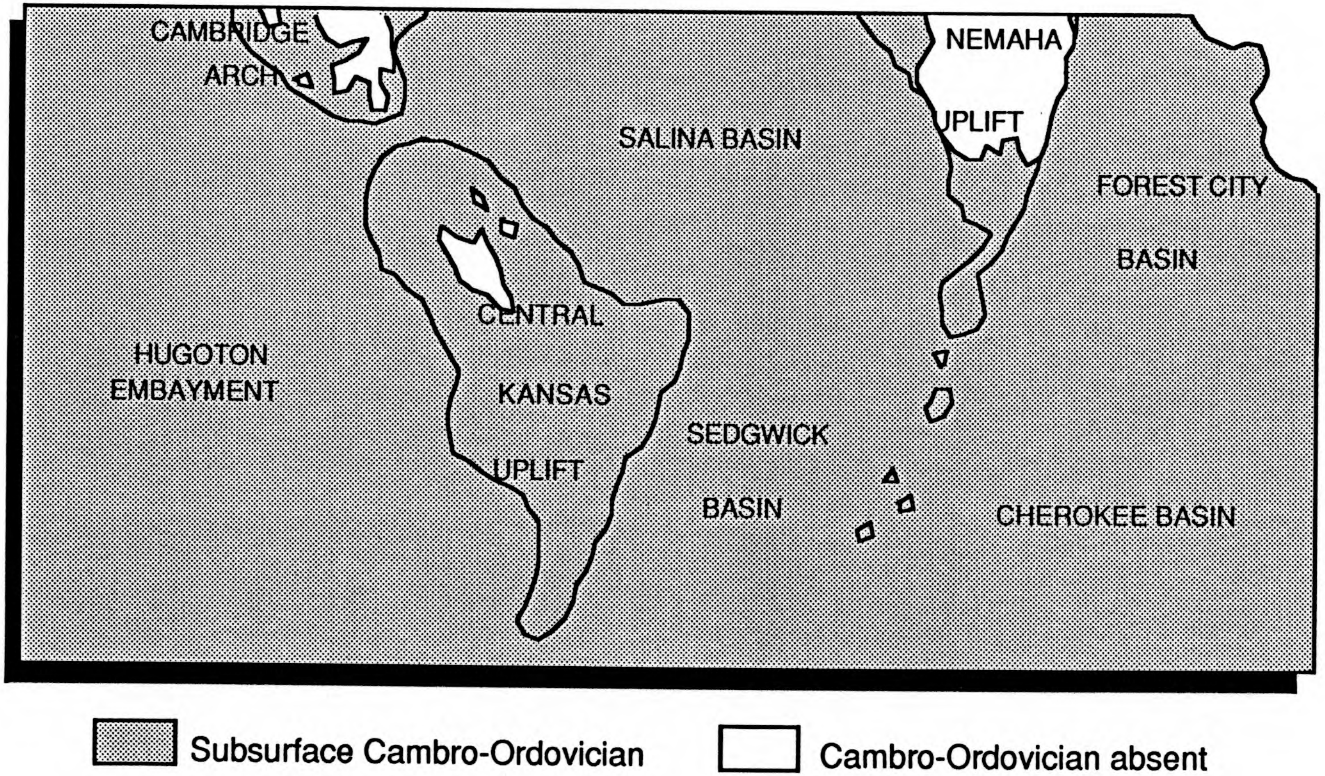


Figure 6. Distribution of Cambro-Ordovician rocks in Kansas. Modified after Merriam (1963).

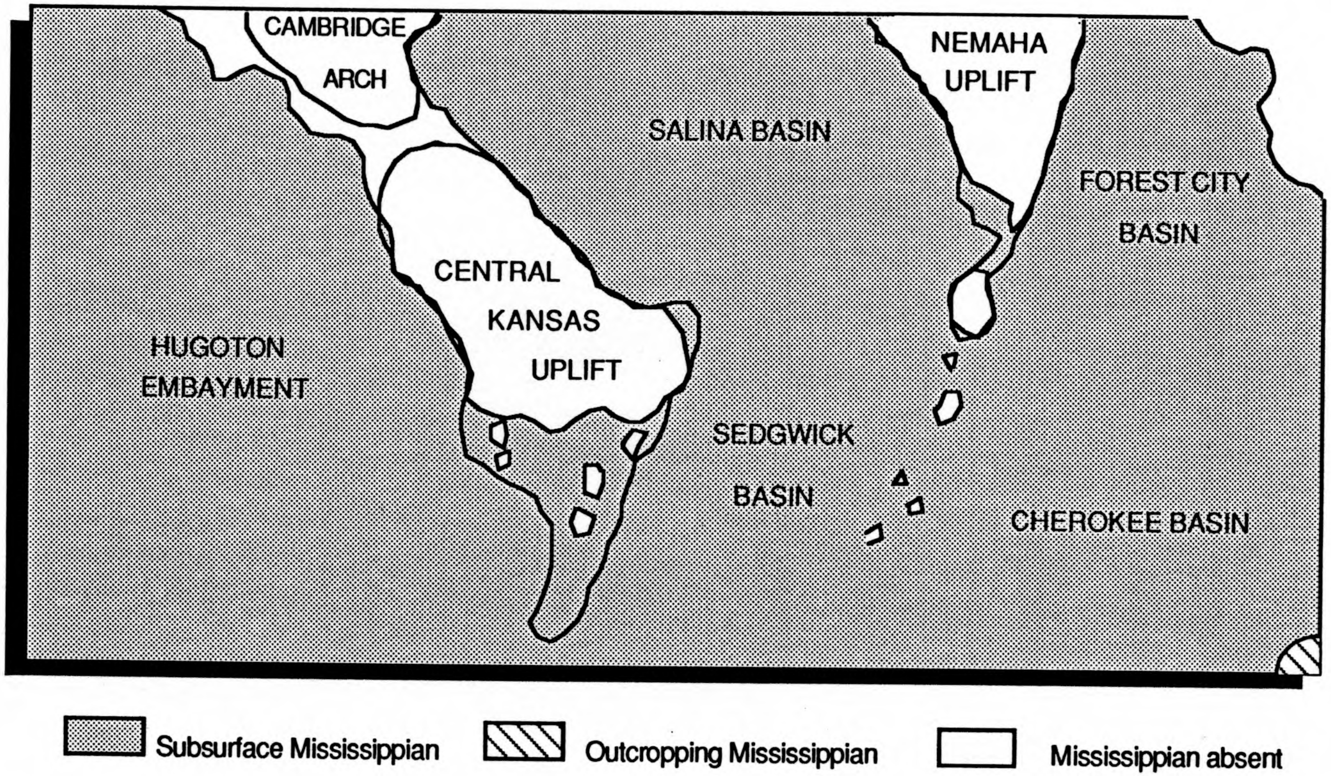


Figure 7. Distribution of Mississippian rocks in Kansas. Modified after Merriam (1963).

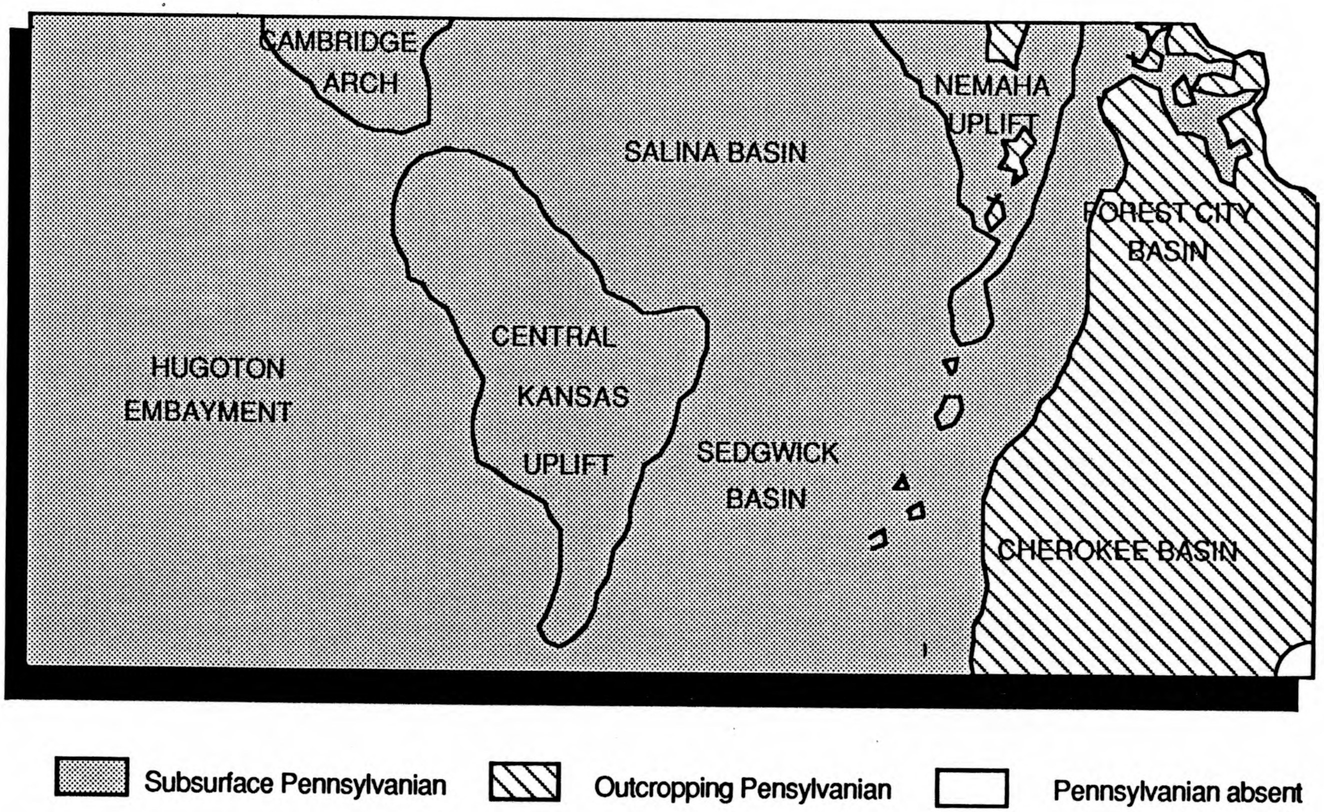


Figure 8. Distribution of Pennsylvanian rocks in Kansas. Modified after Merriam (1963).

Permian rocks are the youngest petroleum producing rocks in Kansas (Paul and Beene, 1983). They consist mainly of marine deposits in the lower part and non- marine deposits in the upper part. They are found in outcrop in the eastern portion of the state and attain a maximum thickness of 3,100 feet within the Hugoton Embayment (figure 9).

Most Mesozoic rocks in Kansas belong to the Cretaceous System; however, a small thickness of Jurassic rocks occurs in the subsurface in northwestern Kansas. Aggregate thickness of the Mesozoic rocks in Kansas is approximately 3,300 feet. Cretaceous rocks occur at the surface or immediately underlie much of the surface in central and western Kansas. They are mostly marine deposits, although non- marine units occur, such as the Cheyenne Sandstone and Dakota Formation. Deposits of Cenozoic age are widespread in the state as a discontinuous veneer upon the eastward sloping pre- Cenozoic erosional surface and comprise Tertiary deposits of western Kansas and Quaternary sediments that include glacial deposits in northeastern Kansas and non- glacial deposits of Pleistocene age in all parts of the State.

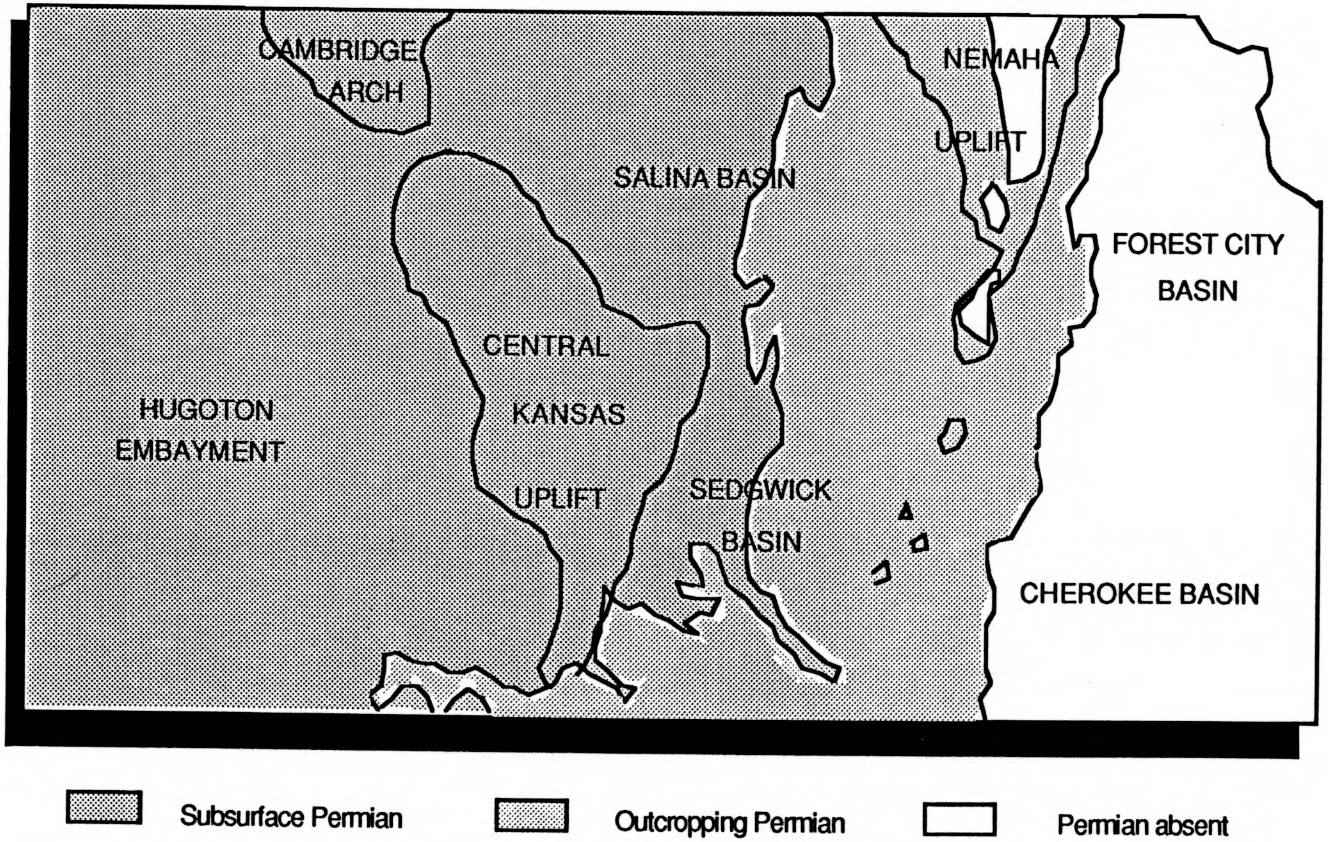


Figure 9. Distribution of Permian rocks in Kansas. Modified after Merriam (1963).

Methods Of Analysis

Vanadium and nickel concentrations were determined according to U.S. Air Force procedures using a Beckman Spectraspan model IV Direct Current Plasma (DCP) system located at the C.E.S.L. Laboratory, Department of Chemistry, Kansas State University. Crude oils were centrifuged at 1,500 rpm for ten minutes to remove water and particulate matter. Approximately eight grams ($\pm$ 0.002 gram) of each sample were diluted with two parts methyl- isobutyl- ketone (M.I.B.K.) to reduce viscosities for plasma analysis. Two standards were prepared for each element, a 50 parts per million (ppm) high standard and a 5 ppm low standard from certified 5,000 ppm Conostan organo- metallic reference solutions. High standards were prepared by diluting 1.003 grams of 5,000 ppm Conostan stock with 80.108 grams of M.I.B.K. and 18.888 grams of 75 base oil. Low standards were prepared by diluting 0.023 grams of Conostan stock with 49.996 grams of M.I.B.K. and 9.988 grams of 75 base oil. Base oil was added to the standards to match viscosities with the samples. All dilutions were made on a weight basis and results were converted to ppm solution values. A blank solution of 75 base oil in a M.I.B.K. matrix was used to correct for instrumental drift. During each analysis, three oil samples were run followed by a blank, high standard, and low standard. Detection limits were set at three times the pooled standard deviation of the blanks. Three separate runs were made for each element: November 1985, January 1986, and April 1986. Replicate analysis of the high (50 ppm) and low (5 ppm) standards indicate reproducibilities of plus or minus two standard deviations at the 5 percent level. Several oil samples were also analyzed by the Amoco Production Research Center in Tulsa, Oklahoma, to check analytical accuracies.

These were determined to vary no more than plus or minus 2 standard deviations at the 12 percent level.

Normal, branched, and cyclic hydrocarbons as well as lighter aromatic compounds, were separated and identified by gas chromatography at the Amoco Production Research Center. The chromatographic column used was a 50 m teflon coated capillary column. Chromatographic conditions were 'Hold' at 0 ^{0}C for two minutes, then an increase at a rate of 13.3 ^{0}C per minute. Chromatographic conditions were carried for 40 minutes. Individual molecules were identified as intensity peaks as a function of distillation temperature and reported as a percent of the total volume of extract.

Sulfur contents were determined at the Standard Oil Company Research Center in Naperville, Illinois. Analysis were made using X- ray fluorescence techniques and reported as weight percent of sulphur. Stable isotope determinations were made at the Conoco Research Laboratory in Ponca City, Oklahoma. Stable isotope values are reported as delta ^{13}C ($\delta\,^{13}$C) values in parts per thousand or per mil relative to PDB standard. The $\delta\,^{13}$C values were computed by the following equation;

$$\delta\,^{13}C=\{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{std.}/(^{13}C/^{12}C)_{std.}\} *1{,}000$$

Analytical reproducibilities were no more than ± 0.05 per mil at the 5 percent level

RESULTS

API Gravity

Results from geochemical analysis of western and central Kansas crude oils are given in table 2. Crude oils produced from the Upper Pennsylvanian Lansing- Kansas City (L-Kc) and Douglas (Dg) Groups exhibit the widest variability in API gravities, ranging from 29.0 (sample JE- 3) in a Kansas City oil from Ellis County to 42.0 (sample RC- 2) in a Lansing- Kansas City oil from southern Clark County. Average API gravity of crude oils from the Lansing- Kansas City and Douglas groups is 37.0 with a standard deviation (s) of 4.93. Two L- Kc oils from Ellis County (samples JE- 1, JE- 3) have unusually low gravities (29.1 and 29.0, respectively) especially when compared to a nearby Kansas City well (sample JE- 2) producing oil of API gravity 38.4. Such wide variability within a small geographic area is uncommon and may suggest microbial activity which will be examined in detail under 'Chromatographic Analysis'. One well of Marmaton production from Ellis County exhibited an API gravity of 36.5 near the average API gravity of Lansing- Kansas City oils (37.0). Oils from the Cherokee Group tend to be slightly heavier oils averaging 36.2 (s= 0.85) API gravity in three wells from the central portion of the study area in Ness County.

Four crude oils from Morrowan reservoirs in Clark and Ford Counties have API gravities averaging 42.0 (s= 3.39). Irrespective of drilling depth or geographic location, crude oils produced from Mississippian reservoirs (average API of 37.3, s= 0.81) are very similar in API gravity to Lansing- Kansas City oils (average API of 37.0). At present, API gravity data are unavailable for the Cambro- Ordovician and Simpson oils.

Generally, Kansas crude oils are relatively light, sweet (low sulfur) oils with API gravities in the 30 to 47 range. API gravities of Kansas crude oils analyzed in this investigation range from a low of 29.0 in a Kansas City (Kc) oil from Ellis County to 47.0 in a Morrowan (Mw) oil from Clark County. The average API gravity of all samples is 37.8, s= 1.75. Figure 10 illustrates the relationship between API gravity and the producing zone. The highest API gravities tend to be from Morrowan reservoirs within Clark County (average API of 42.0, s= 3.39), whereas the lowest gravity oils appear to be from the Cherokee reservoirs in Ness and Rush Counties (average API gravities of 36.2, s=1.04). However, analysis of variance indicate no significant difference between the API gravity of various producing zones at the 25 percent level.

Geographically there is a tendency for API gravities to decrease from the south to the north (figure 11). This relationship has a correlation coefficient (r) of - 0.46 and significance at the 2.5 percent level. This trend in conjunction with other parameters will be discussed in detail later.

Table 2. Geochemical analysis of crude oils from west-central Kansas.

Sample Number	ZONE	Northward Dist. (mi)	API	%S	CPI	Ni (ppm)	V (ppm)	V/(V+Ni)	V/(V+Ni) Group	Iso. Type	Normal Alkane Family	Pr/Phy	nC17/pris	nC18/phy	Delta 13 C
DB-1	L-Kc	60	37		1.09	0.32	0.46	0.60	?	F	I	1.36	0.79	0.97	-29.43
DB-2	Morrow	36	40		1.06	1.30	0.46	0.26	2	A	I	1.65	2.89	3.29	-29.11
DB-3	Morrow	36	47	0.12	1.12	1.20	0.46	0.28	2	A	I	1.70	3.88	4.08	
DB-4	Morrow	30	43	0.187	1.04	1.10	2.60	0.70	?	E	II	1.71	2.53	3.04	-28.80
DB-5	Morrow	30	38	0.221	1.05	2.20	7.20	0.76	?	E	II	1.67	2.27	2.82	
DB-6	Miss.	36	37		1.05	1.70	7.60	0.82	3	E	II	1.53	1.42	1.97	
DB-7	Kc	42	41	0.223	1.10	3.10	6.60	0.68	?	F	I	1.52	1.09	1.44	-29.07
DB-8	Cke	102	35		1.05	2.00	2.50	0.56	?	C	I	1.59	1.73	2.42	
DB-9	Miss.	96	36	0.318	1.02	0.24	0.72	0.75	?	C	I	1.56	1.55	2.15	
DB-10	Miss.	90	38	0.245	1.02	0.24	3.30	0.93	1	C	I	1.47	1.68	2.20	
DB-11	Simp	84			1.02	4.20	9.20	0.70	?	A	I	1.18	2.83	2.93	-30.31
DB-12	Ab	84			1.03	2.80	11.00	0.80	3	C	I	1.54	1.73	2.32	-30.31
DB-13	Cke	114	36.5		1.04	4.80	2.50	0.34	?	C	I	1.51	1.40	1.89	-30.24
DB-14	Cke	114	37	0.198	1.03	2.00	2.15	0.52	?	C	I	1.56	1.72	2.34	
DB-15	Miss.	114	37	0.204	1.02	0.35	3.00	0.90	1	C	I	1.47	1.58	2.13	
DB-16	Miss.	108	37		1.04	0.24	15.00	0.98	1	C	I	1.47	1.65	2.23	-30.30
JB-1	Kc	126	42		1.03	4.70	31.00	0.87	3	C	I	1.52	1.70	2.12	-30.47
JB-2	Kc+Ab	126	38.6		1.04	10.90	48.00	0.82	3	C	I	1.52	1.75	2.32	
JB-3	Marm.	126	36.5	0.49	1.04	11.00	57.00	0.84	3	C	I	1.46	1.85	2.32	-30.21
JE-1	Kc	114	29.1			8.40	26.00	0.76	3	C					-29.75
JE-2	Kc	114	38.4		1.03	2.40	19.00	0.89	3	C	I	1.59	1.68	2.24	-30.08
JE-3	Kc	114	29		1.07	4.40	19.00	0.81	3	C	I	1.25	1.46	0.99	-29.76
LN-1	Miss.	108		0.208	1.02	0.24	0.64	0.73	?	E	II	1.58	1.98	2.44	
LN-2	Miss.	108		0.292	1.02	1.12	4.30	0.80	3	C	I	1.41	1.52	1.98	
RC-1	Miss.	12	38.5		1.09	0.24	0.46	-	-	F	I	1.35	1.40	1.79	-28.77
RC-2	L-Kc	12	42		1.12	2.30	2.20	0.49	?	F	I	1.26	0.67	0.74	-29.35
RC-3	Doug.	12	37		1.09	2.00	0.46	0.19	2	F	I	1.34	0.87	1.03	-28.99
VB-1	Miss.	84		0.226	1.02	0.02	0.05	-	-	E	II	1.44	1.53	2.01	

Figure 10. Plot of API gravity vs. producing zone.

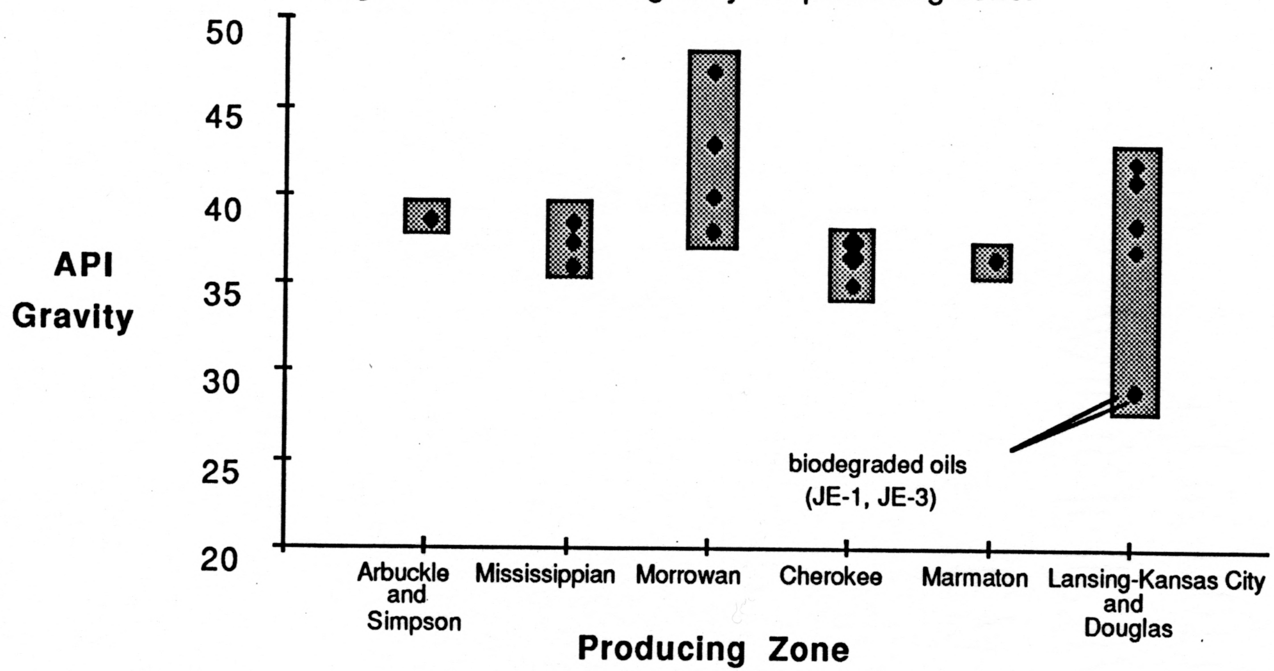
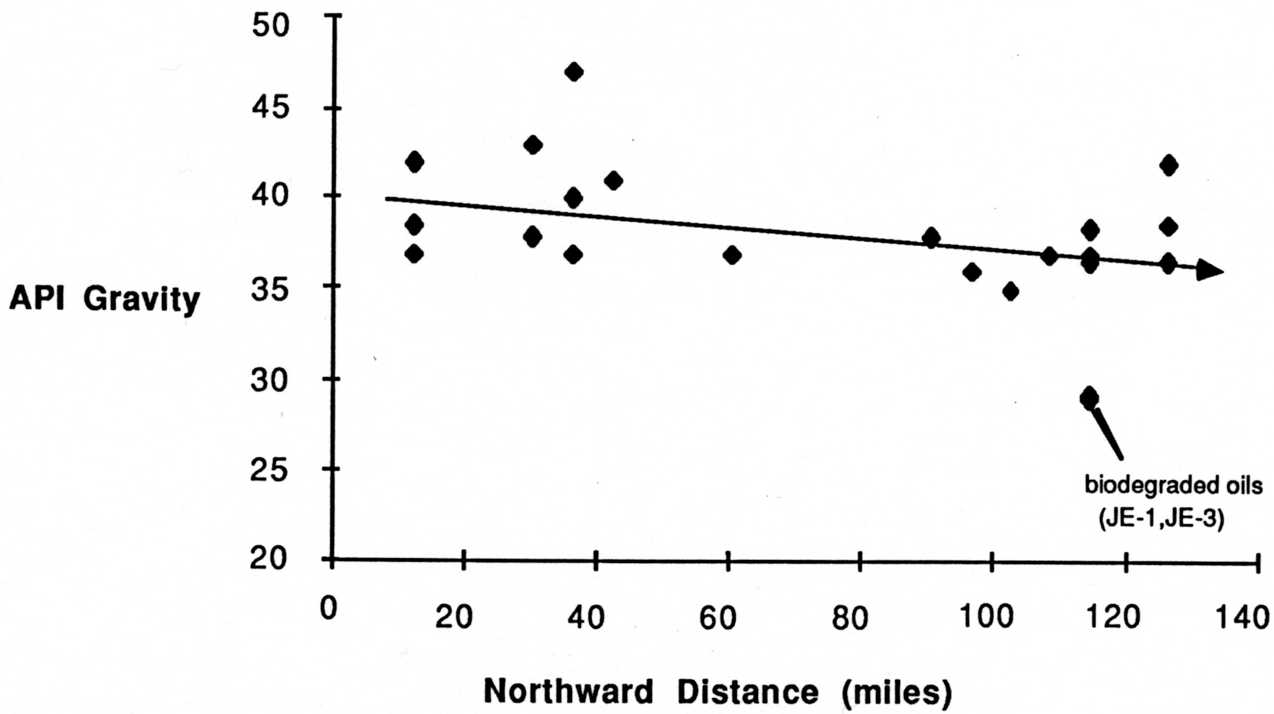


Figure 11. Plot of API gravity versus northward distance.



Chromatographic Analysis

Normal Alkane Distributions

Chromatographic analyses of west- central Kansas crude oils indicate the oils are normal waxy type crudes with relatively high concentrations of lighter (C_7- C_{15}) n- alkanes. Analyses also indicate two general families of crudes based on the whole oil n- alkane distributions, family I and family II crude oils (figure 12). Twenty- three of the twenty- eight oils analyzed have family I distributions which exhibit a gradual increase in n- alkane concentration to the nC_7 to nC_9 range, and then a gradual decrease in concentration with increasing carbon number. Family II oils exhibit a maximum in the nC_{14} to nC_{17} range.

Figure 13 is a chromatogram of a typical family I Central- Kansas crude oil from the Middle- Pennsylvanian Cherokee Formation, Rush County (sample DB- 8). The largest peaks are the n- alkanes which dominate the chromatogram. They exhibit the typical increase in concentration with decreasing carbon number. The oil contains moderate amounts of the heavier isoprenoids, pristane (PRIST) and phytane (PHYT), relative to the normal alkanes adjacent to them (nC_{17} /pristane and nC_{18} /phytane equal 1.73 and 2.42, respectively). The oil also contains near normal amounts of methyl- cyclohexane (MCHX). The numerous smaller peaks dispersed between the evenly distributed n- alkane peaks are various branched, cyclic, and aromatic compounds. Values for nC_{17}/pristane in family I oils average 1.70, s= 0.71, and nC_{18}/phytane average 2.09, s= 0.77. The ratios numerically illustrate the predominance of the n- alkanes over the branched alkanes in all but a few oils (DB- 1, L- Kc; RC- 2, L- Kc; and RC- 3, Dg).

Several family I oils exhibit slight degrees of biodegradation, DB- 9, Mississippian; DB- 13, Cherokee; JB- 1, Kansas City; JB- 3, Marmaton (see appendix A). As microbial activity intensifies, the range of n- alkanes attacked increases (Williams, 1986), and the relative concentration of MCHX generally increases as well as other 'non- preferred' compounds (microbial activity preferentially oxidizes the n- alkanes). The most heavily degraded oils analyzed are two family I oils both produced from the same Kansas City pool in Ellis County. The oils, sample JE- 3 (figure 14) and a similar oil, sample JE- 1, are produced from wells less than one mile apart. All the n- alkanes and some lighter isoprenoids (iP- 13 to iP- 18) in both have been greatly reduced. Also, the concentration of MCHX is greatly increased as are the various unresolvable compounds which are present as large background 'humps' below the nC_8- nC_{30} range. The API gravities of these oils are anomalously low (29.0 in sample JE- 3 and 29.1 in sample JE- 1) for the region. These oils are classified as slightly to moderately degraded using the classification devised by Connan (1984).

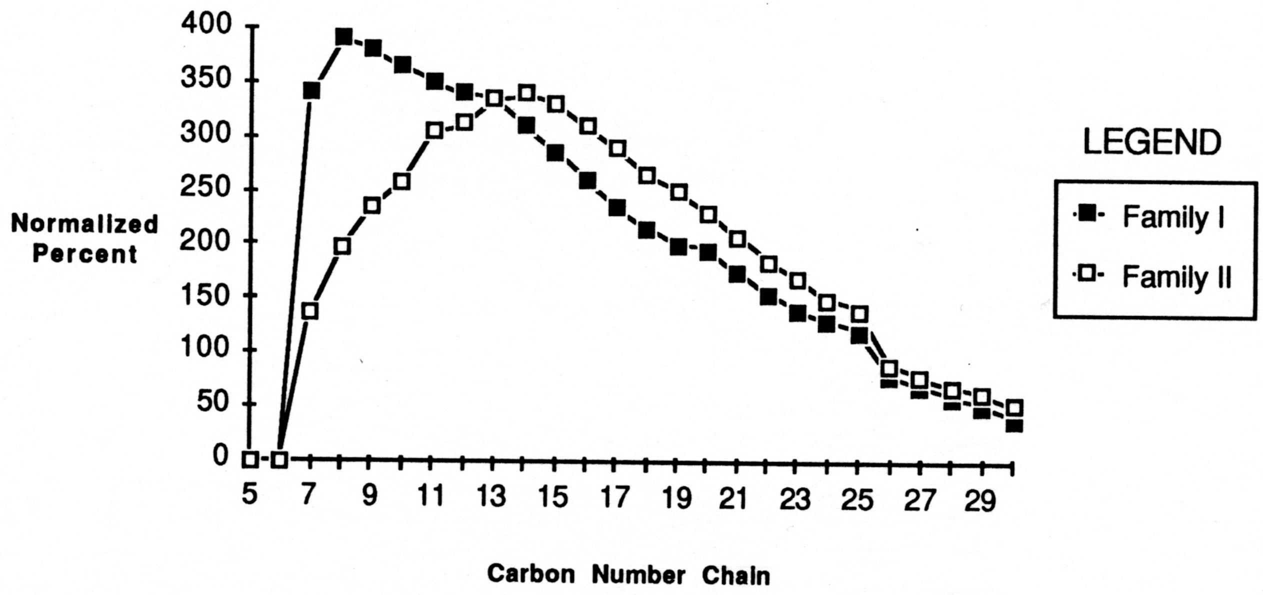


Figure 12. Family I and family II n-alkane distributions

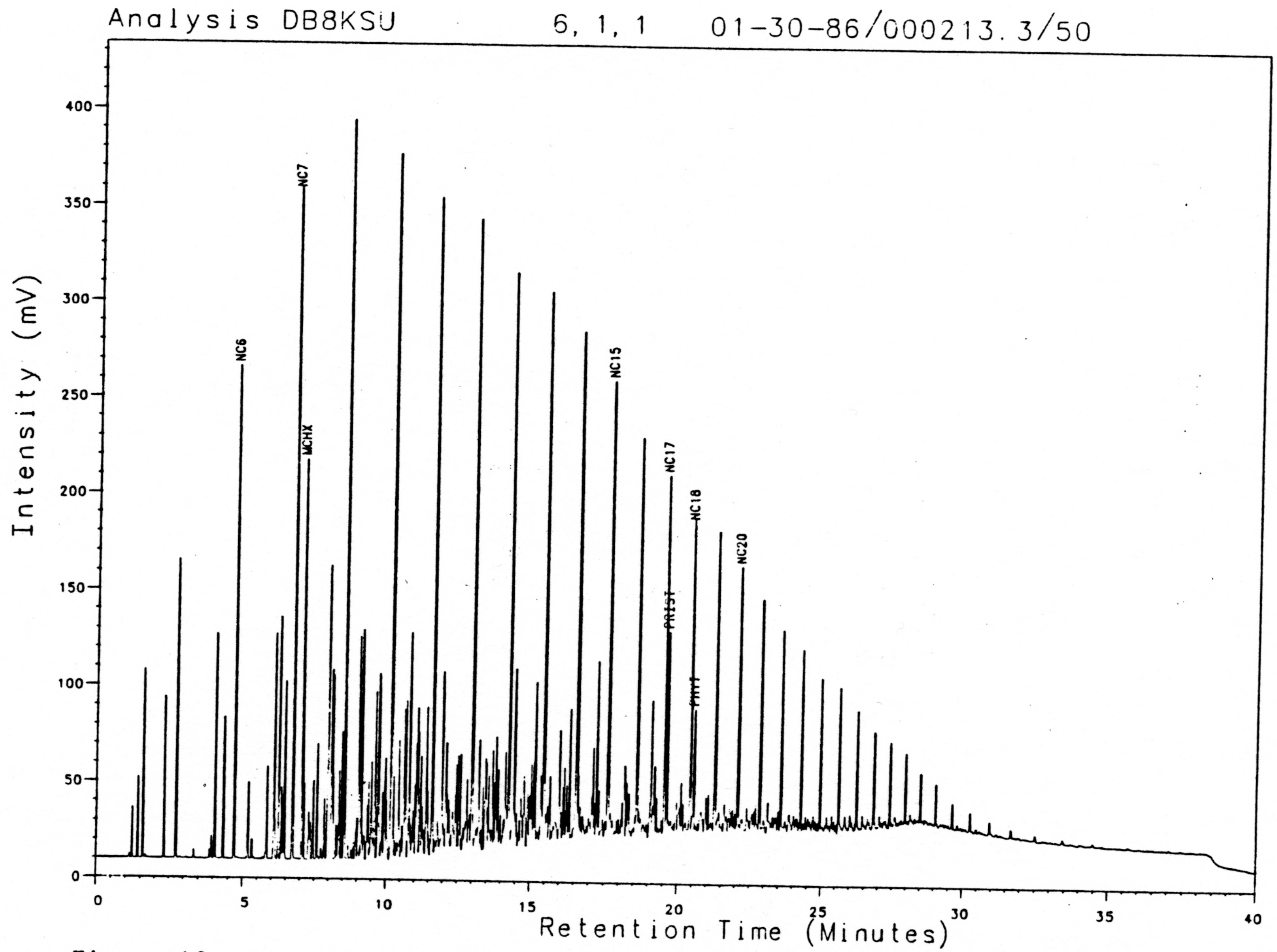


Figure 13.--Gas chromatogram of a typical family I oil, sample DB-8, Middle Pennsylvanian Cherokee Group.

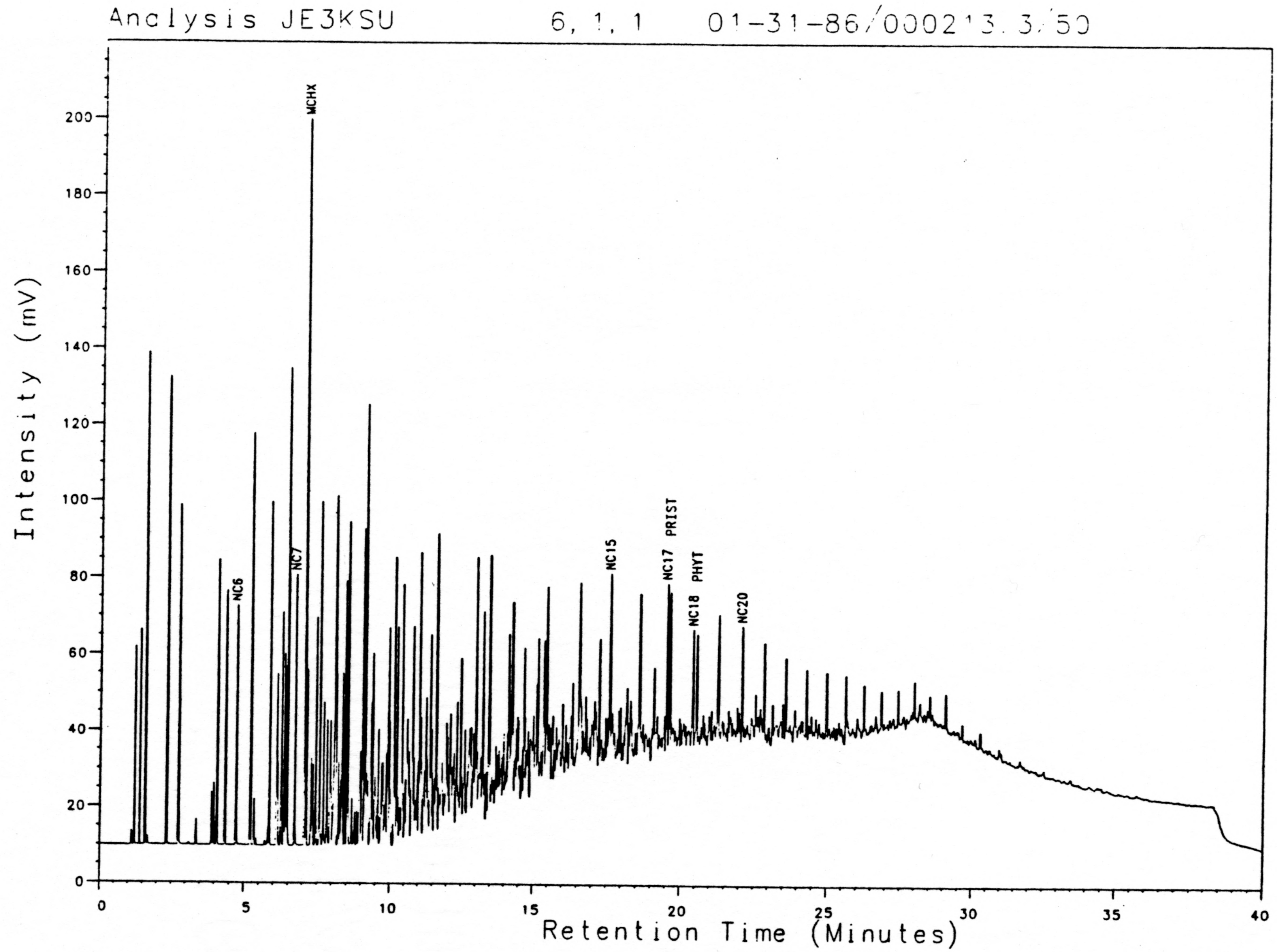


Figure 14.--Gas chromatogram of a biodegraded family I oil, sample JE-3, Upper Pennsylvanian Kansas City Group.

Five oils exhibit family II n- alkane distribution (DB- 4, DB- 5, DB- 6, LN- 1, VB- 1) and are produced from Mississippian and Morrowan reservoirs. Geographically, family II oils are produced from the southern portion of the study area between miles 30 and 84 (measured northward from the Kansas- Oklahoma border). The average API gravity (39.3) of family II oils is not statistically different from that of family I oils (38.1), as the null hypothesis (Ho: υI=υII) could not be rejected even at the 40 percent level. Values of nC_{17}/pristane and nC_{18}/phytane averaged 1.95 (s= 0.47) and 2.46 (s= 0.48) respectively, which are higher than those of family I oils. Figure 15 is a chromatogram of a Mississippian oil (sample DB- 6) produced from Clark County. The chromatogram represents a typical family II n- alkane distribution with the "bell- shaped" distribution of the n- alkanes being characteristic of these oils. The oil has an API gravity of 37, nC_{17} /pristane ratio of 1.42, and a nC_{18} /phytane value of 1.97. The oil appears to have undergone a slight amount of degradation, suggested by the high concentrations of MCHX, the low ratios of normal to branched alkanes, the appearance of a slight 'saddle' in the nC_{11} to nC_{14} range, and the slightly elevated background in the nC_8 to nC_{30} range.

A more degraded family II oil (sample DB- 5) is shown in figure 16. This is a Lower Pennsylvanian Morrowan oil produced approximately six miles south of the Mississippian oil (DB- 6) discussed in figure 15. Both the DB- 6 oil (figure 15) and the DB- 5 oil (figure 16) are classified as unaltered to slightly degraded in Connan's scheme (1984). Analyses of variance indicate no relationship between the n- alkane distribution and the producing zone.

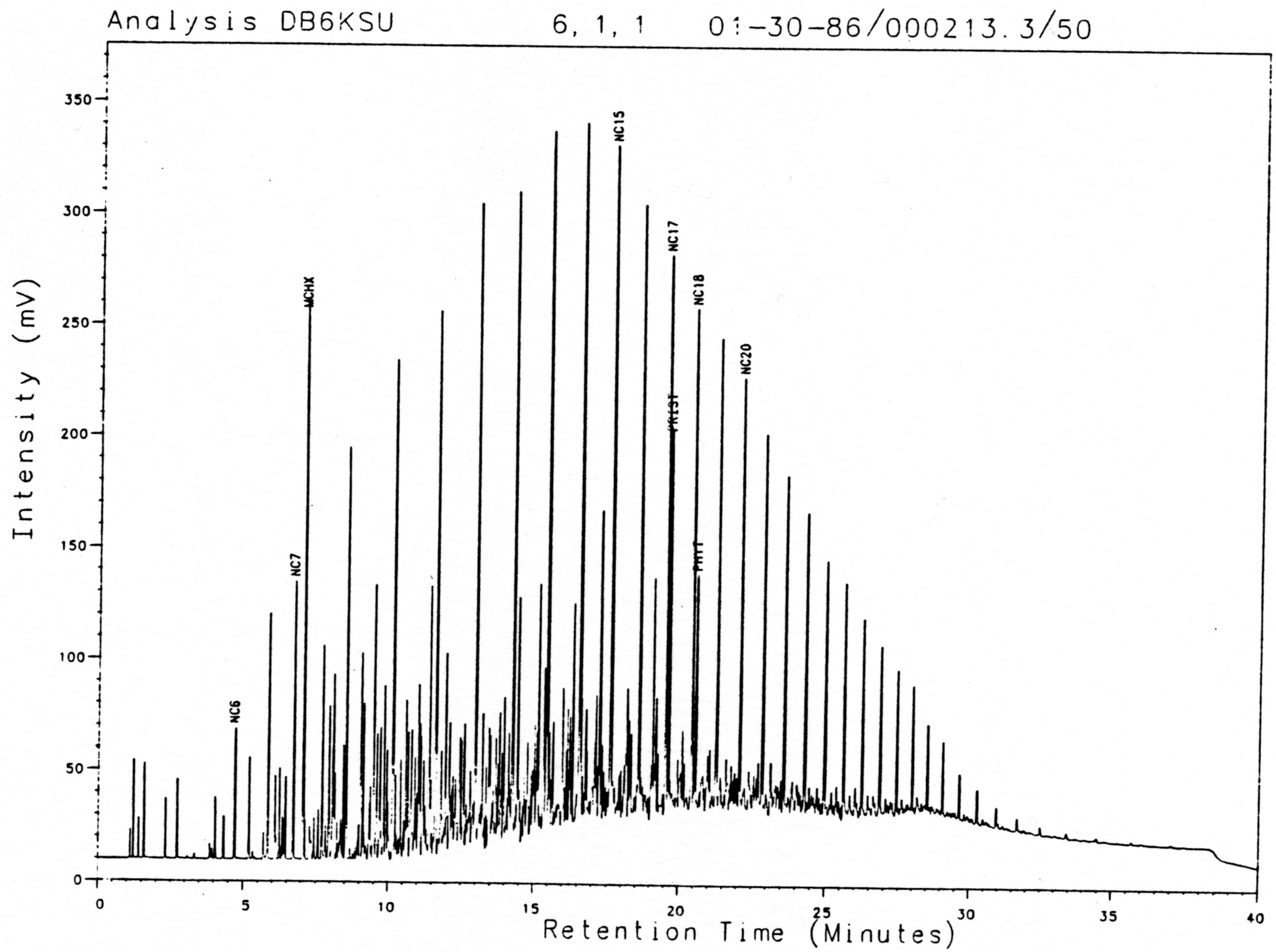


Figure 15.--Gas chromatogram of a typical family II oil, sample DB-6, Mississippian age.

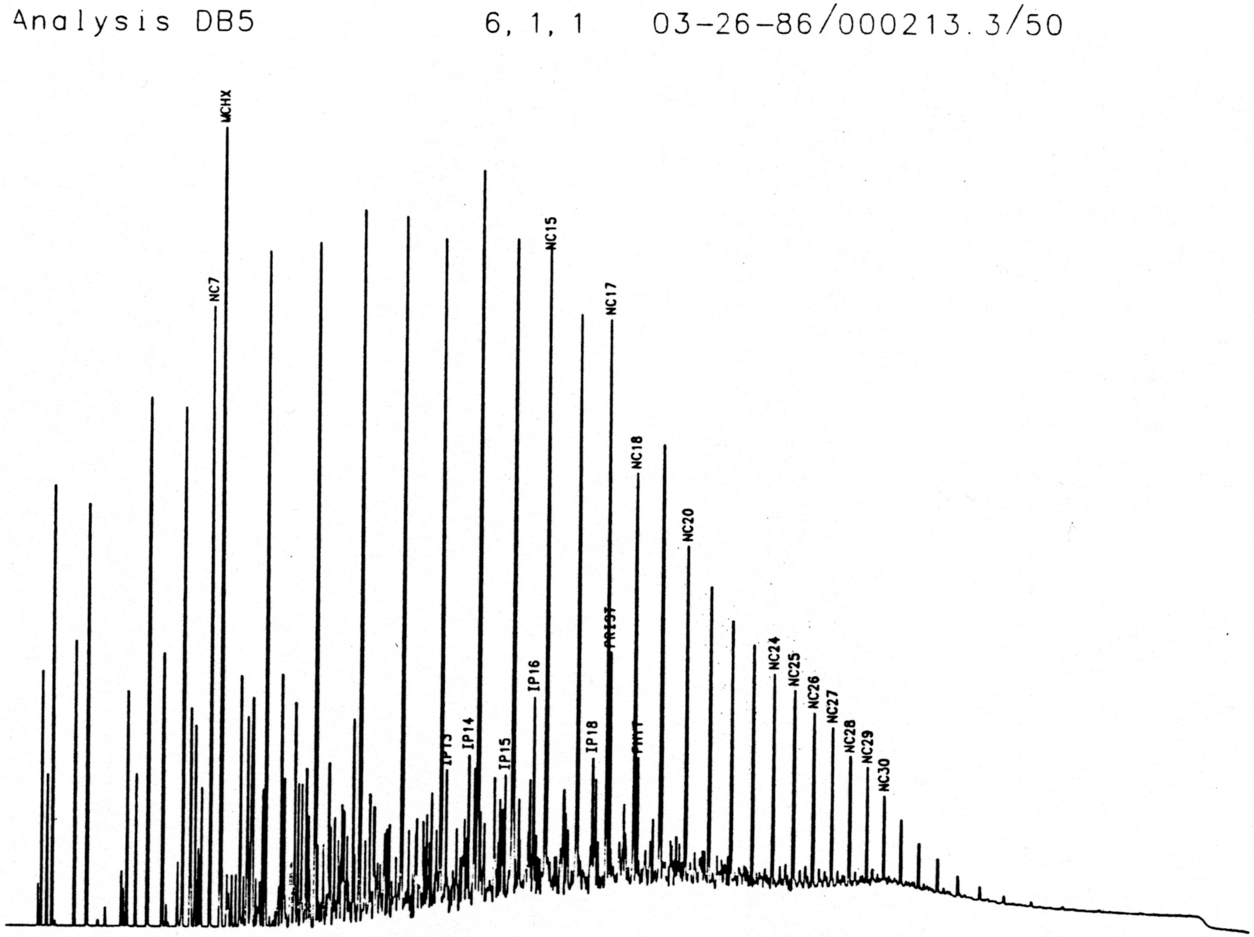


Figure 16.--Gas chromatogram of a slightly altered family II oil, sample DB-5, Lower Pennsylvanian Morrowan age.

Carbon Preference Index

The Carbon Preference Index (CPI) is a measurement of the odd- even n- alkane chain length preference in a crude oil. Several variations of the CPI ratio have been used (Bray and Evans, 1961; Cooper and Bray, 1969; Scalan and Smith, 1970), and this investigation will use a formula developed by the Amoco Production Research Center given as the following.

$$\left[\frac{(C_{25}+C_{27}+C_{29})}{(C_{24}+C_{26}+C_{28})} + \frac{(C_{25}+C_{27}+C_{29})}{(C_{26}+C_{28}+C_{30})}\right] x(1/2)$$

Crude oils from west-central Kansas exhibit CPI values near unity (table 2), ranging from 1.02 in several Mississippian oils to 1.12 in a Lower Pennsylvanian Morrowan oil from Clark County. CPI values near 5 have been reported in recent sediments, but values near 1 are typical for crude oils and ancient bitumens. Although Mississippian oils tend to have slightly lower CPI values than other oils in the area, the narrow ranges of the values in table 2 is easily within the normal variance of related crudes (Williams, 1986). No significant correlation exists between CPI and producing zone, geographic distribution, API gravity, or any other parameters investigated.

Isoprenoid Analysis

Analysis of the common isoprenoids iP- 13, iP- 14, iP- 15, iP- 16, iP- 18, iP- 19 (pristane), and iP- 20 (phytane) were given as intensity peaks by gas chromatography. Values for each isoprenoid were normalized by reporting the concentration of each as a percentage of the sum total isoprenoids in any given sample. The distributions (isoprenoid trends) of all samples can be described as four distinct types: A, C, E, and F (figure 17).

Oils with type A trends (DB- 2, DB- 3, DB- 11) have pristane greater than iP- 16, pristane greater than or nearly equal to iP- 13, iP- 15 greater than iP- 18, and slightly higher amounts of the higher molecular weight chains (figure 18). Morrowan and Simpson oils are represented by type A trends.

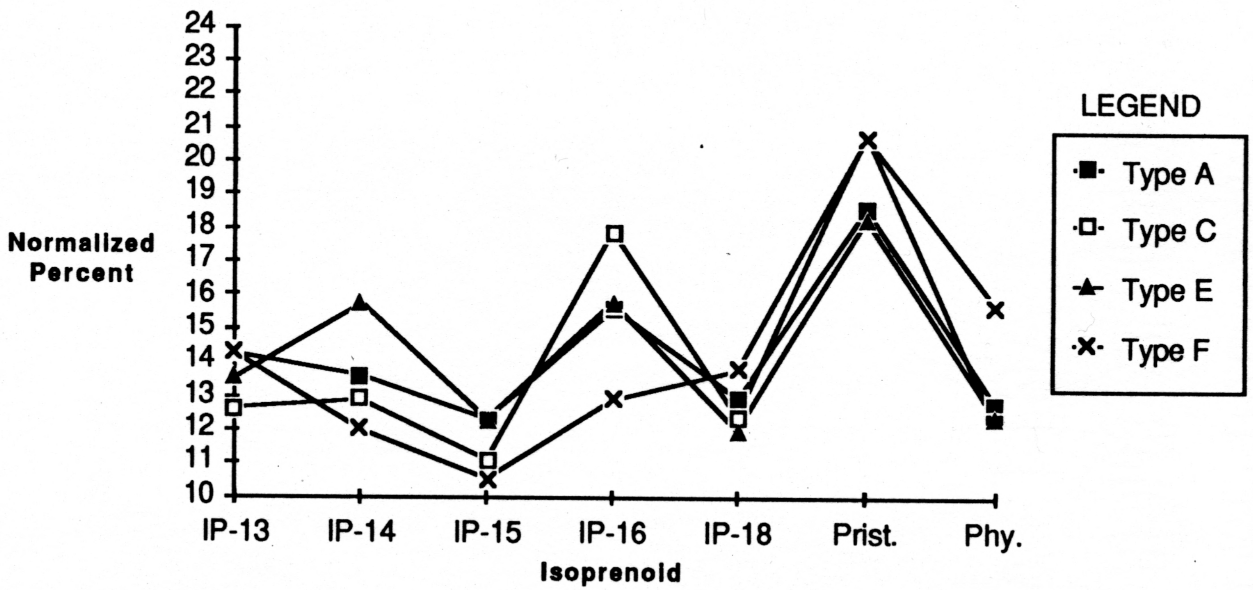
Oils exhibiting type C trends (DB- 8, DB- 9, DB- 12, DB- 13, DB- 14, DB- 15, DB- 16, JB- 1, JB- 2, JB- 3, JE- 1, JE- 2, JE- 3, LN- 2) are shown in figure 19. These oils have pristane greater than iP- 16, subequal amounts of iP- 15 and iP- 18, and a slight tendency for higher amounts of the heavier chains relative to type A oils. Oils of this type are produced predominantly from Lansing- Kansas City and Mississippian reservoirs. Oils from the Arbuckle, Marmaton, and Cherokee groups also exhibit type C isoprenoid trends.

Crude oils with type E trends (DB- 4, DB- 5, DB- 6, LN- 1, VB- 1) are illustrated in figure 20. These oils exhibit a strong predominance of pristane, with iP- 16 much greater than both iP- 13 and iP- 15 (contrasting with type A and C oils), and a strong preference for higher concentrations of the heavier chains through pristane. Type E oils, associated only with family II n- alkane distributions, are produced from Mississippian and Morrowan reservoirs.

Oils exhibiting type F distributions (DB- 1, DB- 7, RC- 1, RC- 2, RC- 3) are greatly depleted in the iP- 14 to iP- 18 range (relative to other types) and like types C and E oils have pristane dominant (figure 21). These oils are produced from a variety of reservoirs, Mississippian, Upper Pennsylvanian Lansing- Kansas City and Douglas groups, and they have also been identified down dip in Redfork reservoirs within Pototoc County, Oklahoma, several hundred miles to the south.

Analysis of variance and least significant difference tests (LSD) indicate a significant relationship between oil type and API gravity at the 10 percent level. Type C oils have slightly lower average API gravities (36.3, s= 3.6) than types A (43.5, s= 4.9), E (39.3, s= 3.2), and F (39.9, s= 2.3). Also, type C oils are distributed in the northern regions averaging 100 miles north of the Kansas- Oklahoma state line, whereas types A, E, and F average 52, 51, and 31 miles north respectively. This relationship between oil type and northward distance was significant at the 5 percent level.between the n- alkane distribution (family) and the isoprenoid distribution (type) as type E isoprenoid distributions are associated only with family II n- alkane distributions. No relationship exists between isoprenoid type and producing zone as the null was rejected even at the 25 percent level.

Figure 17. Isoprenoid profile types.



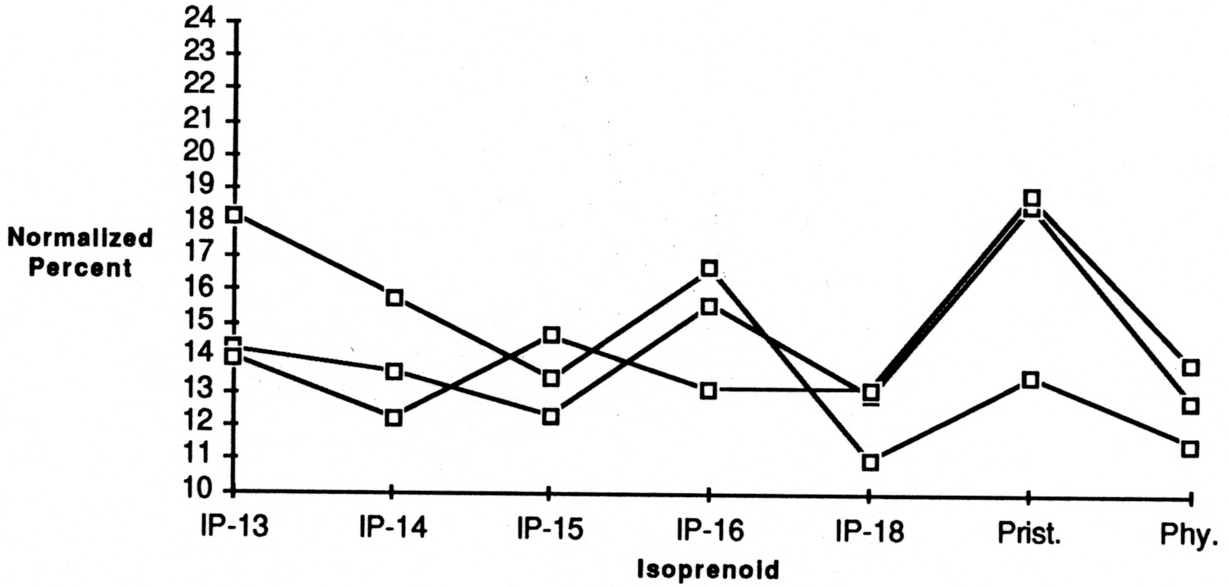


Figure 18. Type A isoprenoid profiles.

Figure 19. Type C isoprenoid profiles.

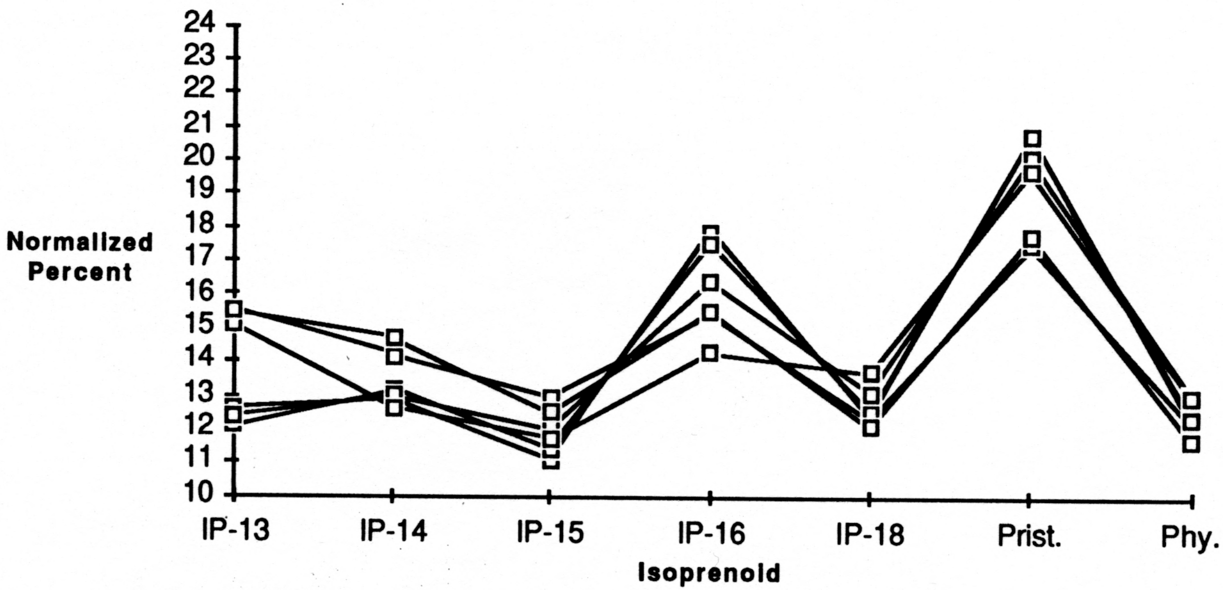


Figure 20. Type E isoprenoid profiles.

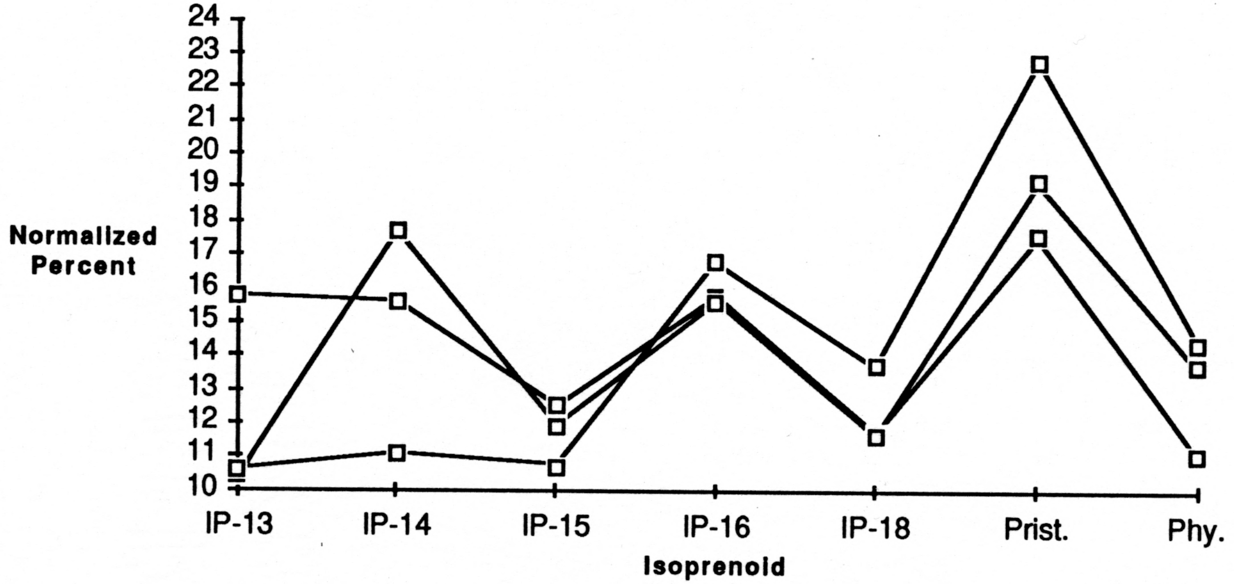
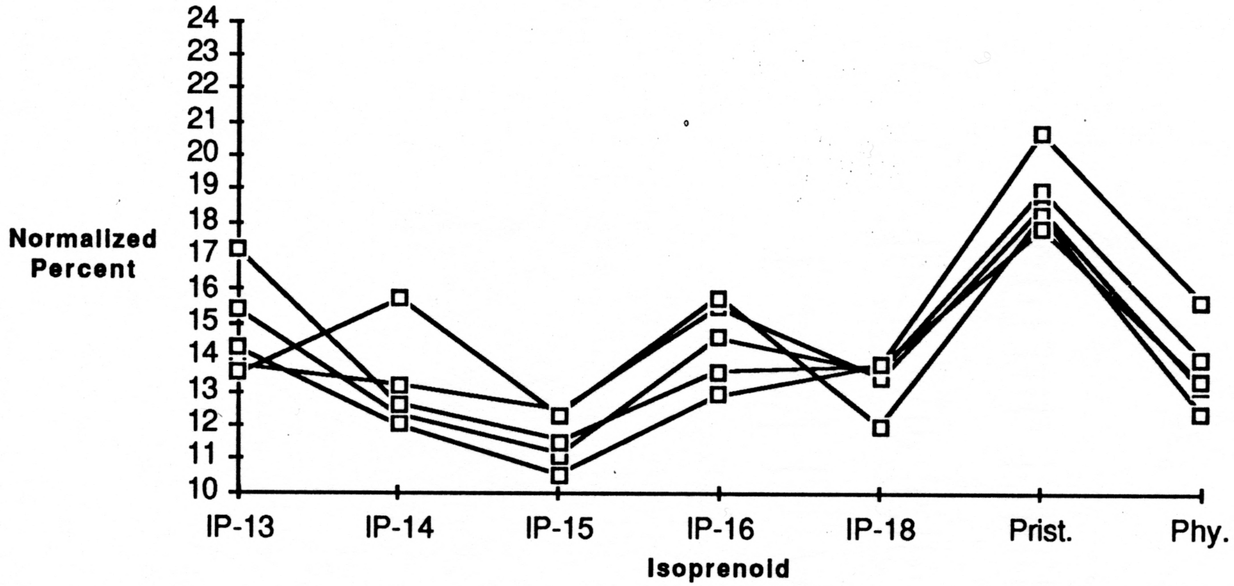


Figure 21. Type F isoprenoid profiles.



Pristane/Phytane Data

Values of pristane/phytane ranging from slightly less than one to more than 10 have been reported in crude oils (Powell and McKirdy, 1975; Barker, 1979). Crude oils from Central Kansas exhibit a high degree of uniformity in their pristane/phytane ratios ranging from a low of 1.18 in a Simpson oil from Pawnee County to 1.71 in a Morrowan oil from Clark County with a mean of 1.49, s=0.02 (table 2). There appears to be no relationship between pristane/phytane values and the producing zone, or any other parameters investigated. Also, the narrow range of pristane/phytane values, like the CPI values, are well within the natural variation expected in a single oil (Williams, 1986) and are not significant.

Sulphur Content

Sulphur contents of twelve randomly selected crude oil samples ranged from a low of 0.12 percent in a Morrowan oil (DB- 3, API of 47.0) from Clark County to a high of 0.49 percent in a Marmaton oil (JB- 3, API of 36.5) from Ellis County (table 2). Sulfur contents in the twelve oils averaged 0.24 percent (s= 0.09). There is no apparent relationship between sulphur content and producing zone; however, there is a strong preference for northern oils to be of higher sulphur content (figure 22). This relationship has a correlation coefficient of 0.54 and significance at the 10 percent level. As expected, a negative relationship exists between the sulphur content and API gravity (figure 23). This relationship has a regression coefficient of - 0.61 indicating significance at the 10 percent level. All twelve oils exhibited low sulphur contents by industry standards (less than 1 percent) and are classified as 'sweet' crudes.

Figure 22. Percent sulphur vs. northward distance.

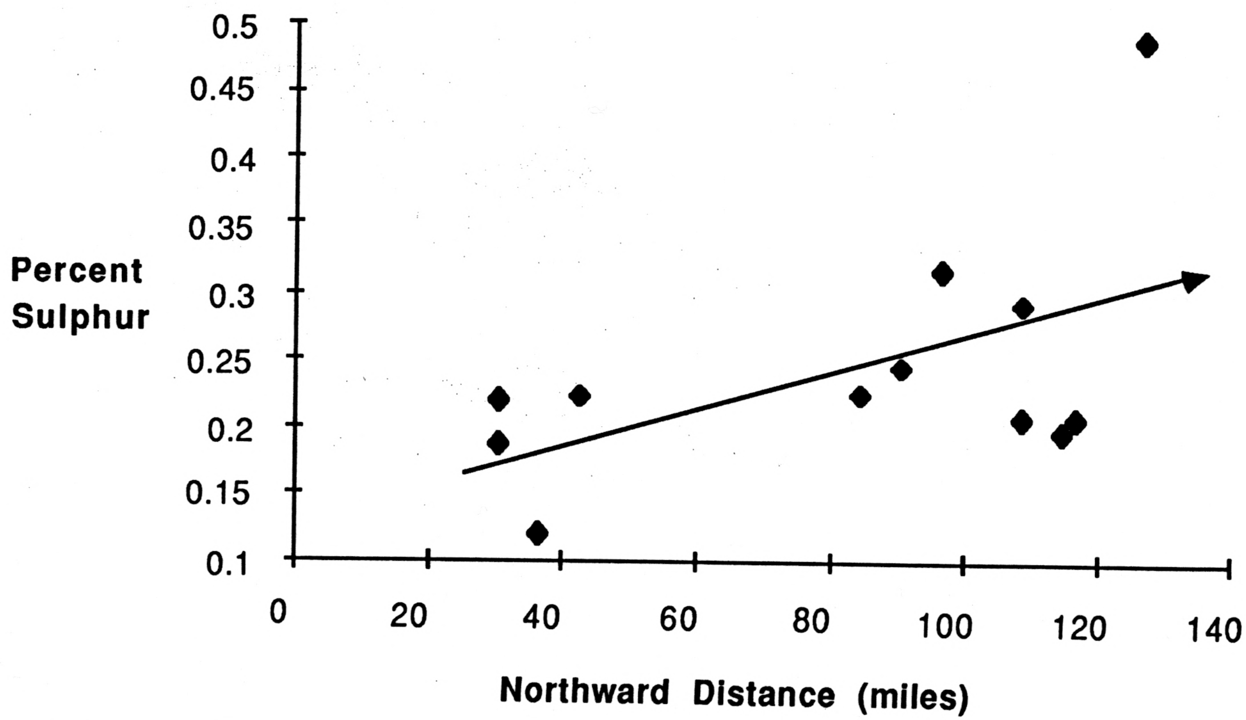
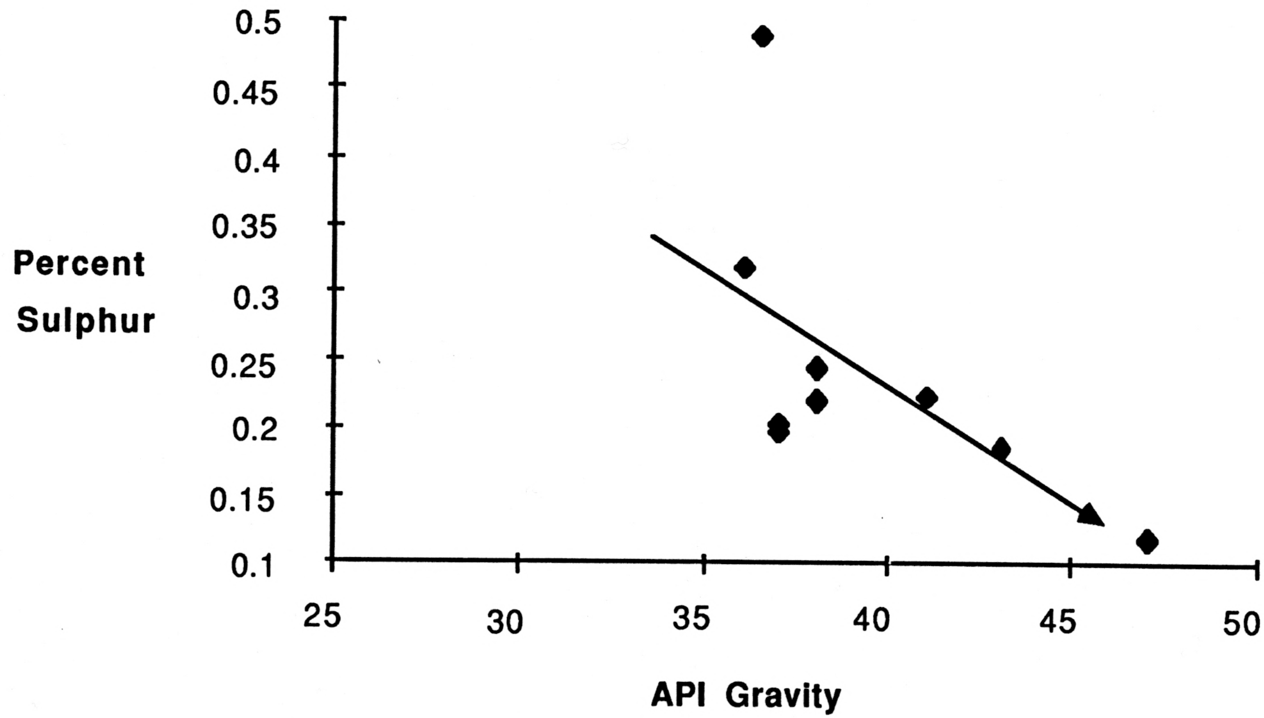


Figure 23. Percent sulphur vs. API gravity.



Carbon Isotopes

Results from whole- oil isotopic analysis of 16 randomly selected crude oils are listed in table 2. $\delta\ ^{13}C$ values ranged from a low of - 30.47 per mil in a Kansas City oil (JB- 1) from Ellis County to a high of - 28.77 per mil in a Mississippian oil (RC- 1) from southern Clark County. Carbon isotopic ratios averaged - 29.62 (s= 0.60) as compared with isotopic ratios in crude oils worldwide that range from - 16.2 to - 35.0 (Waples, 1985).

One of the strongest relationships seen is the negative relationship between the $\delta\ ^{13}C$ and the northward distance of the oils (figure 24). As south to north distance increases, the ^{13}C content decreases (figure 24), in contrast with the more common trend of increased ^{13}C content toward basinal margins (Waples, 1985). Regression analysis indicates a correlation coefficient of - 0.87, significant at the 0.1 percent level.

As normally expected, a trend of increasing ^{13}C content with increasing biodegradation (as observed from gas chromatographic data) is present within related oil types as the lighter ^{12}C isotope is metabolized more readily (Waples, 1985). Regression analysis indicates this trend has an r value of - 0.94, significant at the 1 percent level. Three separate groups of oils, each group representing production from an individual pool (connected by vertical dashed lines in figure 24) demonstrate the above relationship of increasing ^{13}C content with increasing bio- degradation, as an upward shift of plotting position (increase in $\delta\ ^{13}C$ ratio) with increasing biodegradation. The groups are listed in table 3 according to their northward distances.

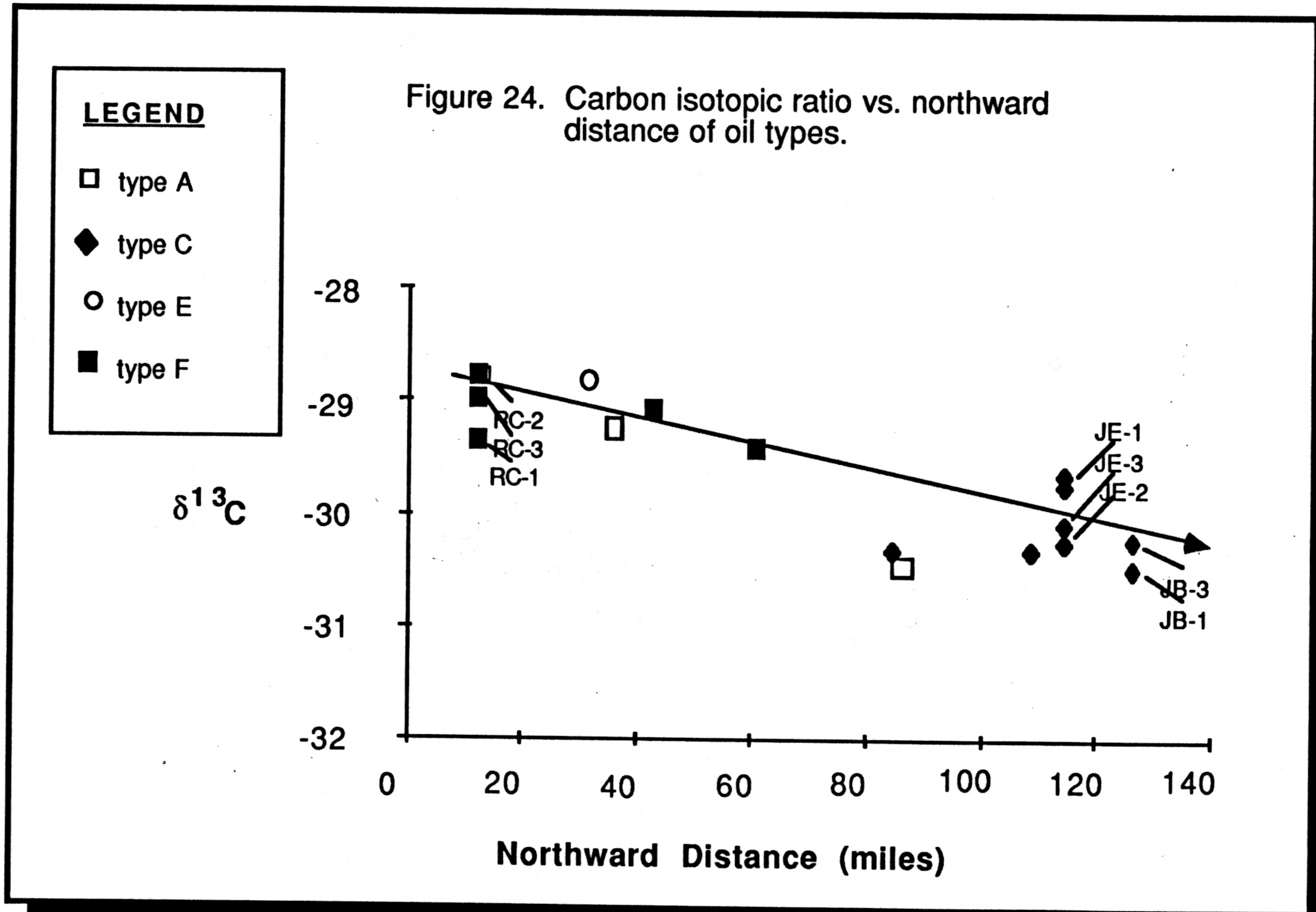


Figure 24. Carbon isotopic ratio vs. northward distance of oil types.

Table 3. Effect of increasing biodegradation (top to bottom) on delta 13C values of three oil groups plotted in figure 24.

Northward distance (mi)	Sample No.	API gravity	Producing zone	Delta 13C
12	RC-2	42	L-Kc	-29.35
12	RC-3	37	Doug	-28.99
12	RC-1	38.5	Miss.	-28.77
114	JB-1	42	Kc	-30.47
114	JB-3	36.5	Marm	-30.21
126	JE-2	38.4	Kc	-30.08
126	JE-3	29	Kc	-29.76
126	JE-1	29.1	Kc	-29.75

Trace Metals

Analyses of the trace metals vanadium and nickel are listed in table 2. The V concentrations range from below detection limit (0.5 ppm) in several samples to a maximum of 57.0 ppm in a Marmaton oil (JB- 3, API of 36.5) from Ellis County. Average V concentration in the 28 crude oils analyzed was 10.1 ppm (s= 14.3). Ni concentrations ranged from below detection limit (0.24 ppm) in several oils to a high of 11.0 ppm also in sample JB- 3. Average Ni concentration was 2.7 ppm (s= 2.9). A plot of V against Ni in the oils shows a positive relationship between the two (figure 25) as is typical (Hodgson and others, 1957; Witherspoon and Nagashima, 1957; Lewan and Maynard, 1982). The general trend between the two is linear with a correlation coefficient of 0.88, significant at the 0.5 percent level. Samples that had either V or Ni below detection limit were plotted at the detection limit for the missing data. Samples which had both V and Ni below detection limit (VB- 1 and RC- 1, both from Mississippian reservoirs), while plotted at the detection limits, were not used in any statistical analysis or correlation.

A plot of V concentration against API gravity showing a slightly negative relationship between the two (r value of - 0.21, significant at only the 40 percent level), is shown in figure 26. A similar plot of Ni concentration vs API gravity (figure 27) shows a negative trend (r value of - 0.28), indicating a slightly higher significance at the 20 percent level. In both cases the general trend is one of increasing metal concentration with decreasing API gravity.

Both metals exhibit positive spatial relationships with increasing south to north distance. A plot of the V concentration against northward distance of the oils (figure 28) shows a marked increase in V concentration as the northward displacement increases (r value of 0.52, significant at the 0.5 percent level). A similar trend exists between Ni concentration and northward displacement (figure 29, r value of 0.42, significant at the 5 percent level).

Figure 25. Plot of Vanadium vs. Nickel.

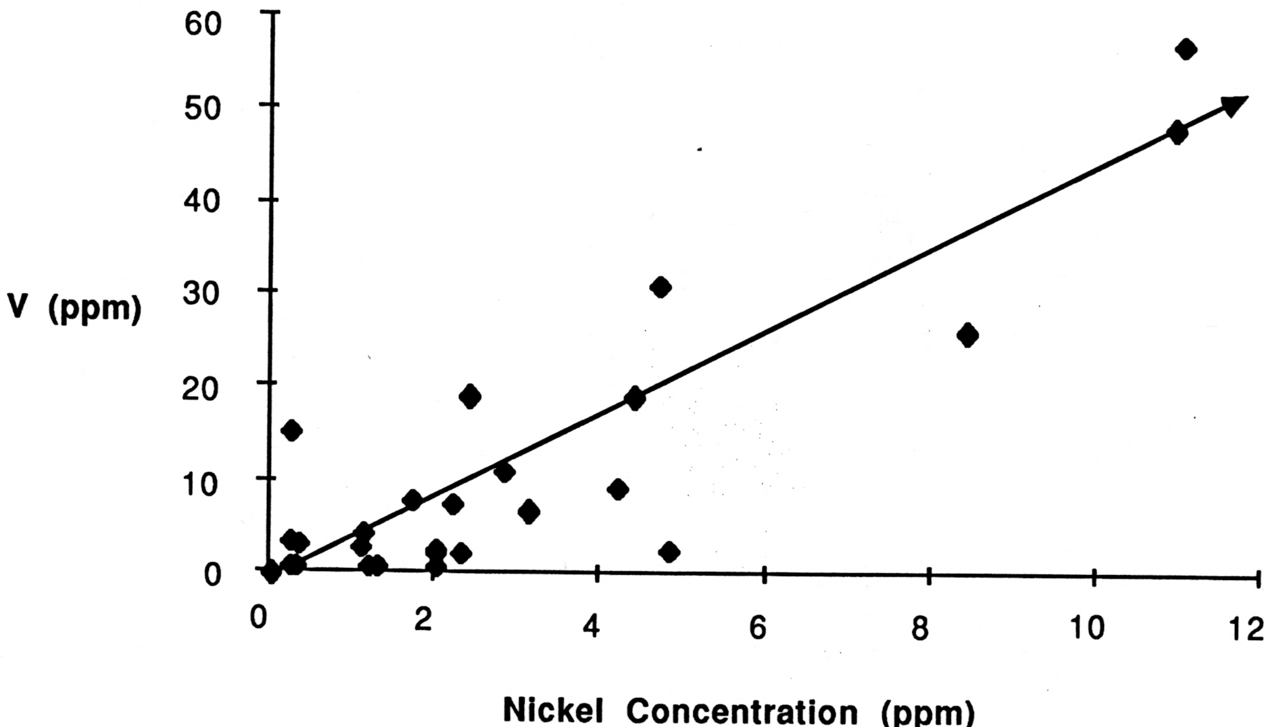


Figure 26. Plot of vanadium vs. API gravity.

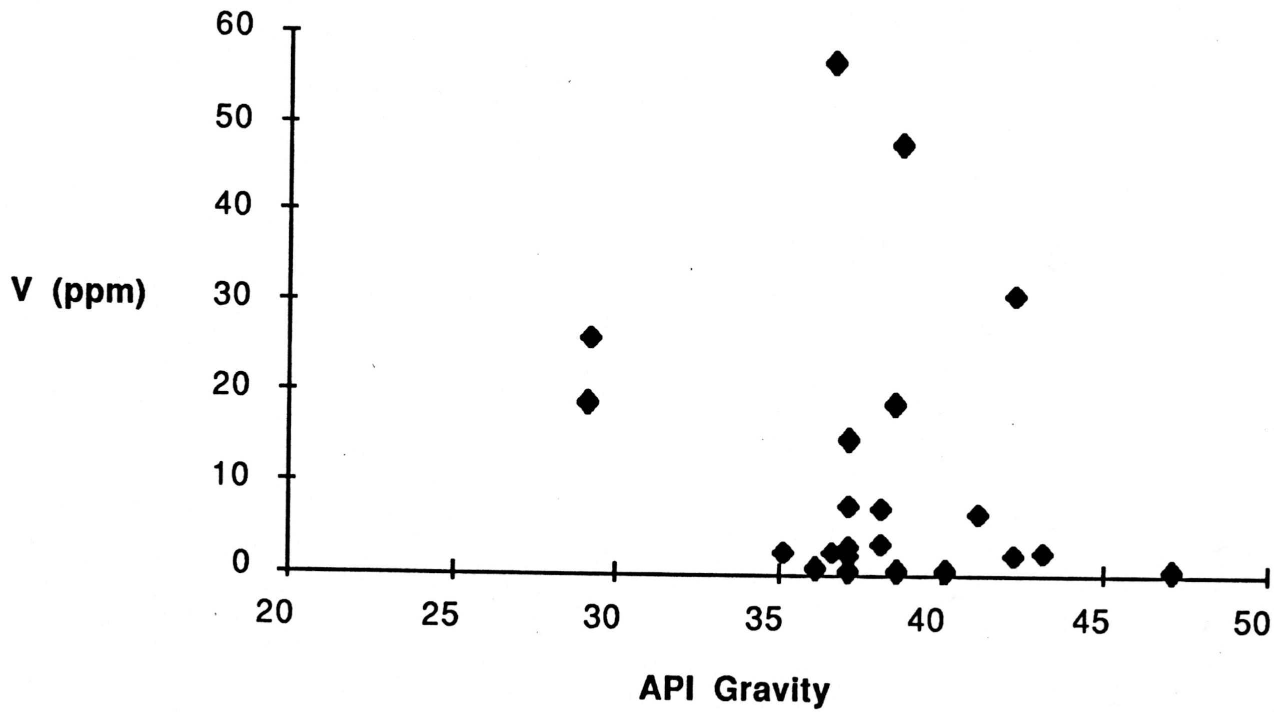
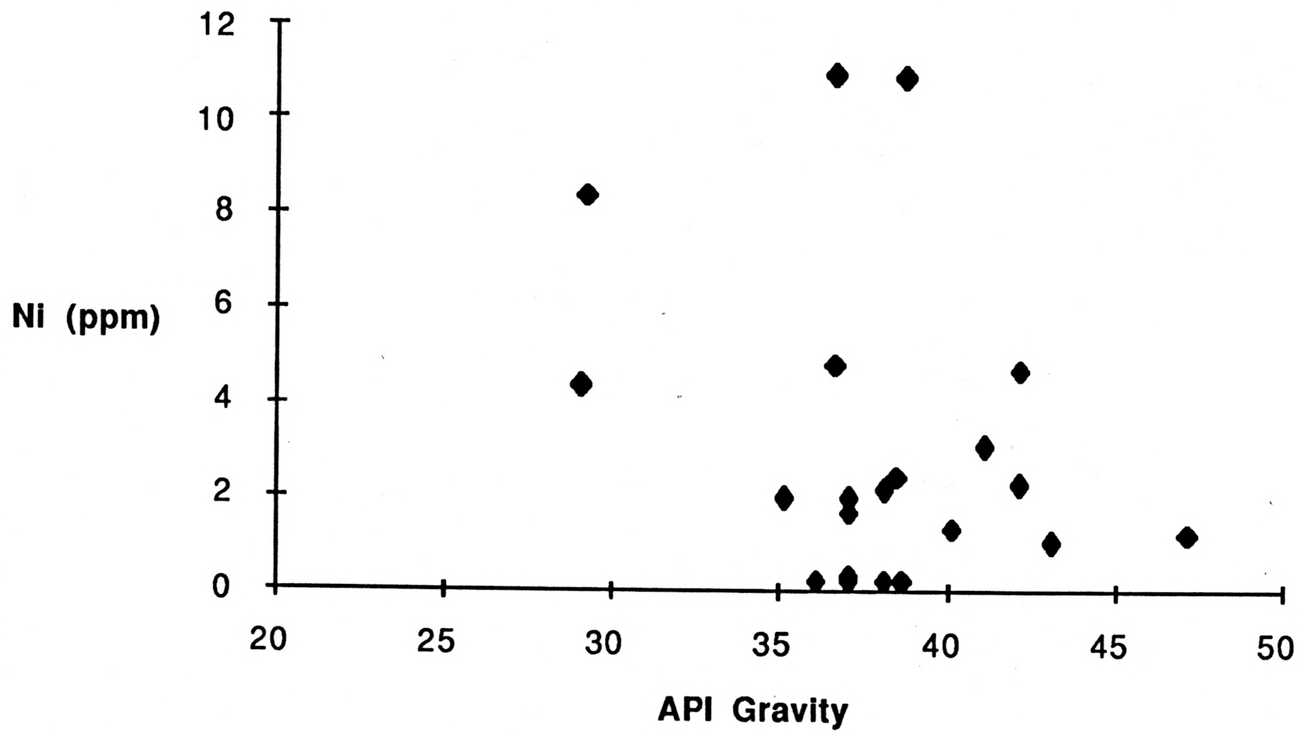


Figure 27. Plot of nickel vs. API gravity.



The fraction of V in the total quantity of V and Ni, expressed as V/(V+Ni), in each sample shows little to no correlation with the bulk parameters (API gravity, isotopic content, sulphur content) or the specific parameters (n- alkane distributions, isoprenoid trends, pristane/phytane ratios). However, a plot of the V/(V+Ni) ratio against northward displacement of the oils (figure 30) graphically illustrates the relationship between the two (r value of 0.54, significant at the 0.5 percent level).

Plots of V and Ni relative to the producing zones represented were made (figures 31 and 32). Stratigraphic zones represented include the Cambro- Ordovician Arbuckle Group and Ordovician Simpson Group (V and Ni average 22.7 ppm and 6.0 pm), Mississippian reservoirs (V and Ni average 3.9 ppm and 0.5 ppm), Lower Pennsylvanian Morrowan Sandstone (V and Ni average 2.7 ppm and 1.5 ppm), Middle Pennsylvanian Cherokee (V and Ni average 2.4 ppm and 2.9 ppm) and Marmaton Groups (57.0 ppm V and 11 ppm Ni), and the Upper Pennsylvanian Lansing- Kansas City and Douglas Groups (V and Ni average 13.1 ppm and 3.5 ppm). The highest concentrations of both V and Ni (57 ppm and 11 ppm) were from a Marmaton oil (sample JB- 3) from Ellis County (figures 31 and 32). Analysis of variance and least significance difference tests (LSD) indicate that significant differences exist between the Arbuckle- Simpson oils and Lansing- Kansas City oils at the 0.5 percent level. The remaining stratigraphic zones were not unique in their metal concentration.

Figure 28. Plot of V vs. northward distance.

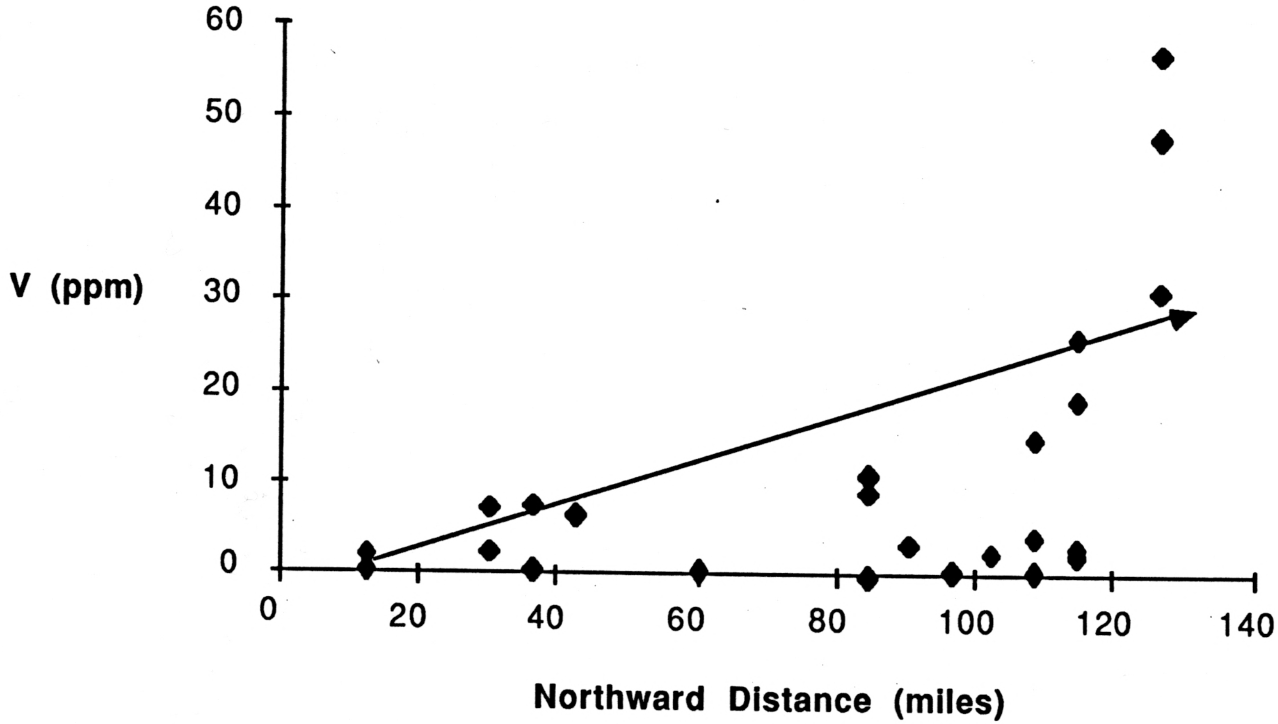


Figure 29. Plot of Ni vs. northward distance.

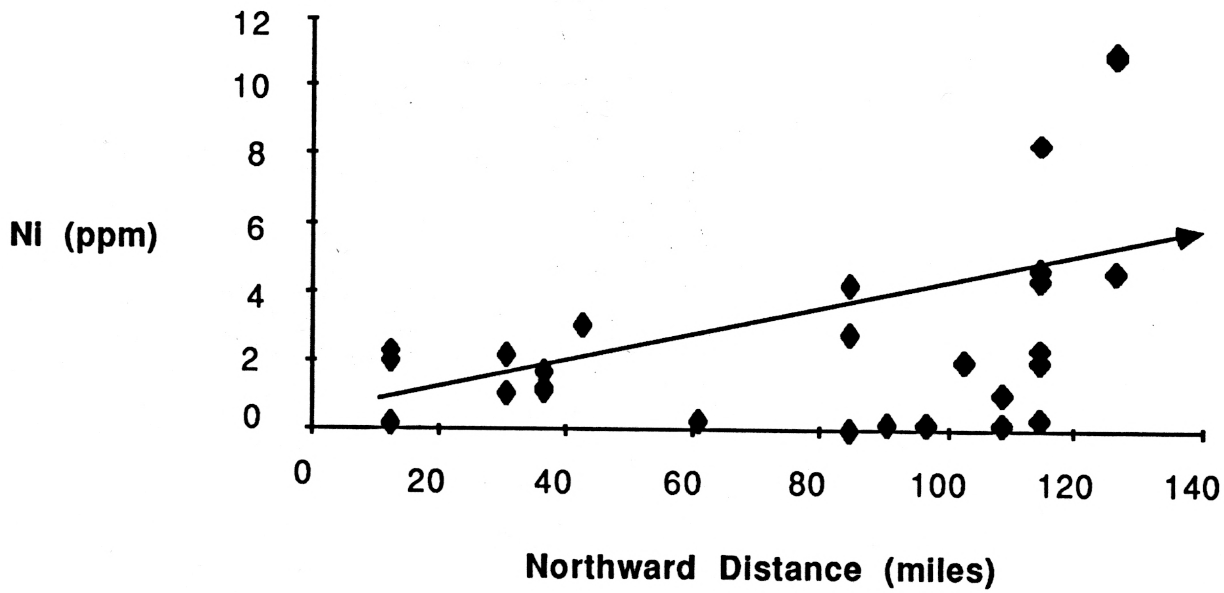


Figure 30. Plot of V/(V+Ni) vs. northward distance.

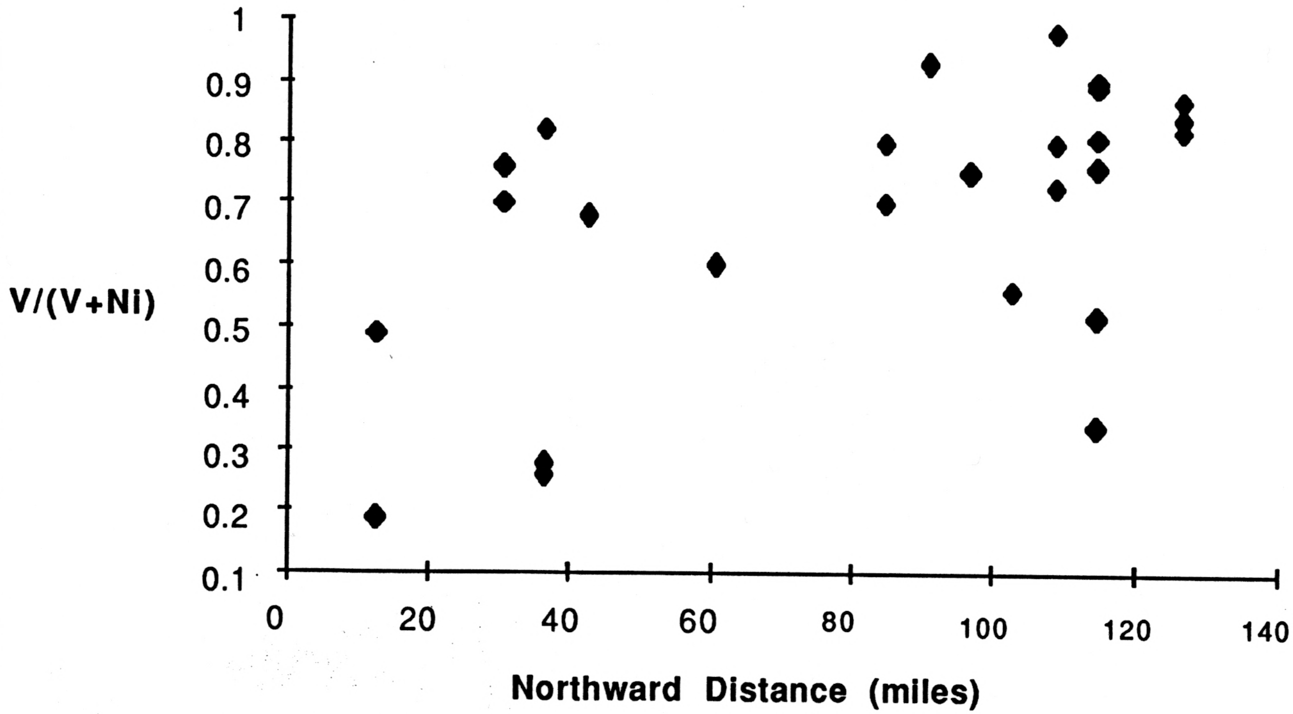


Figure 31. Plot of V vs. producing zone.

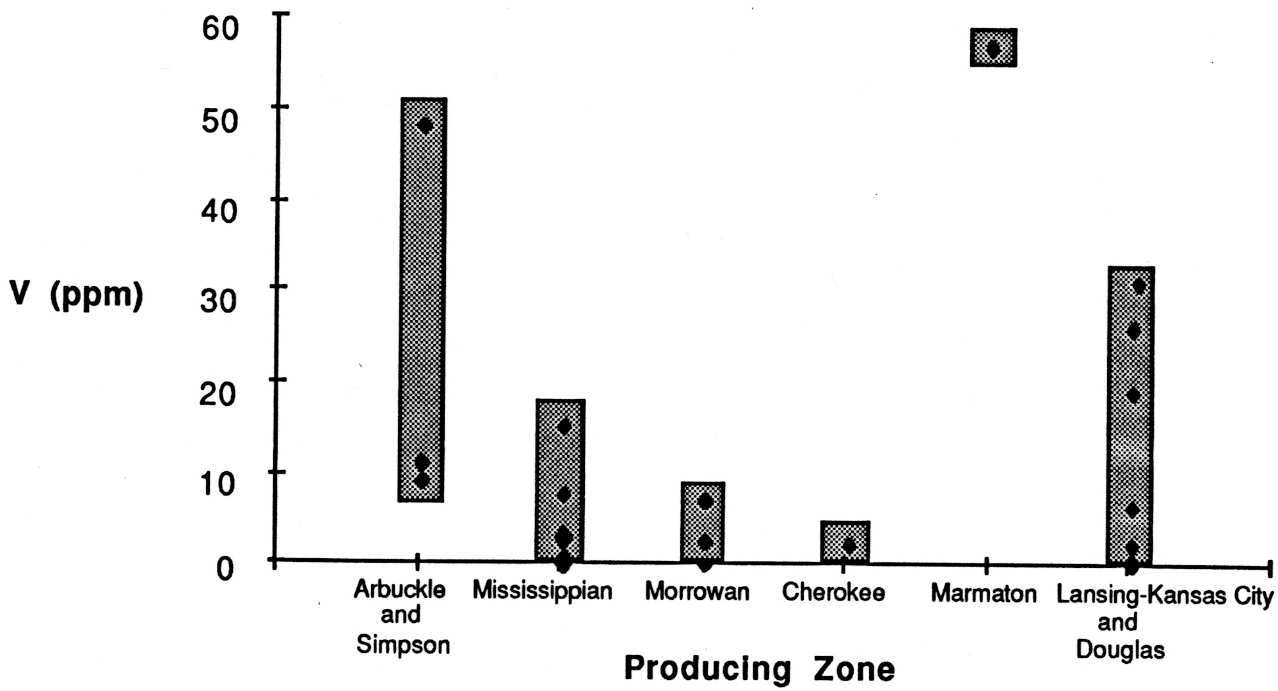
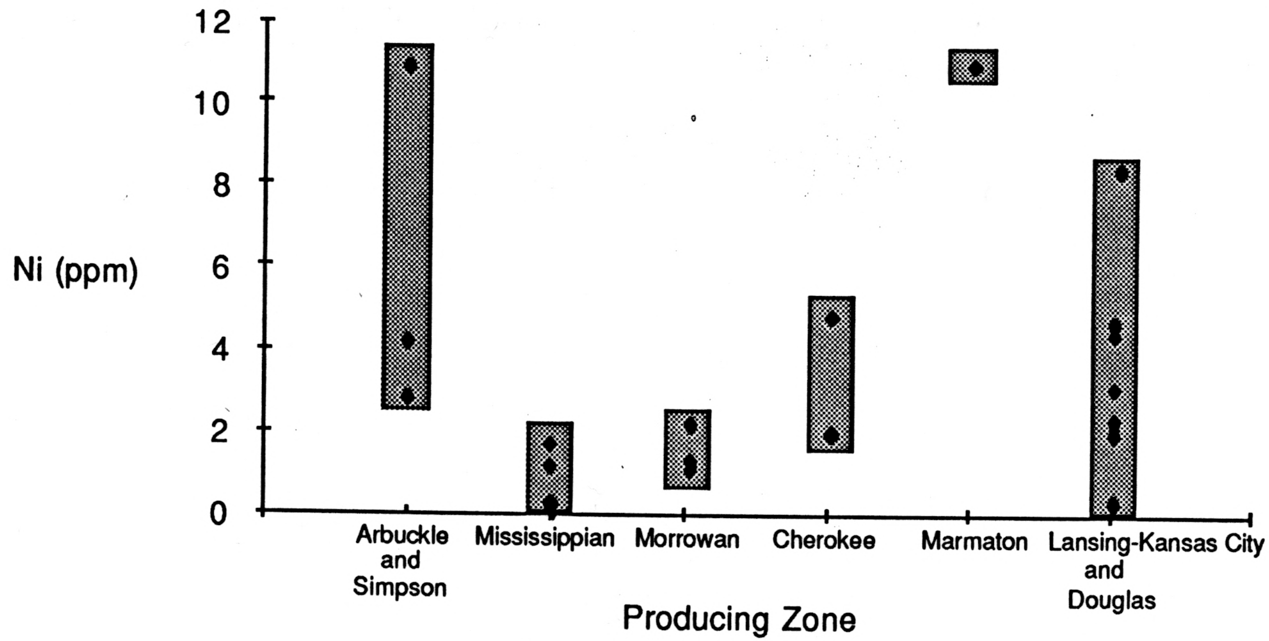
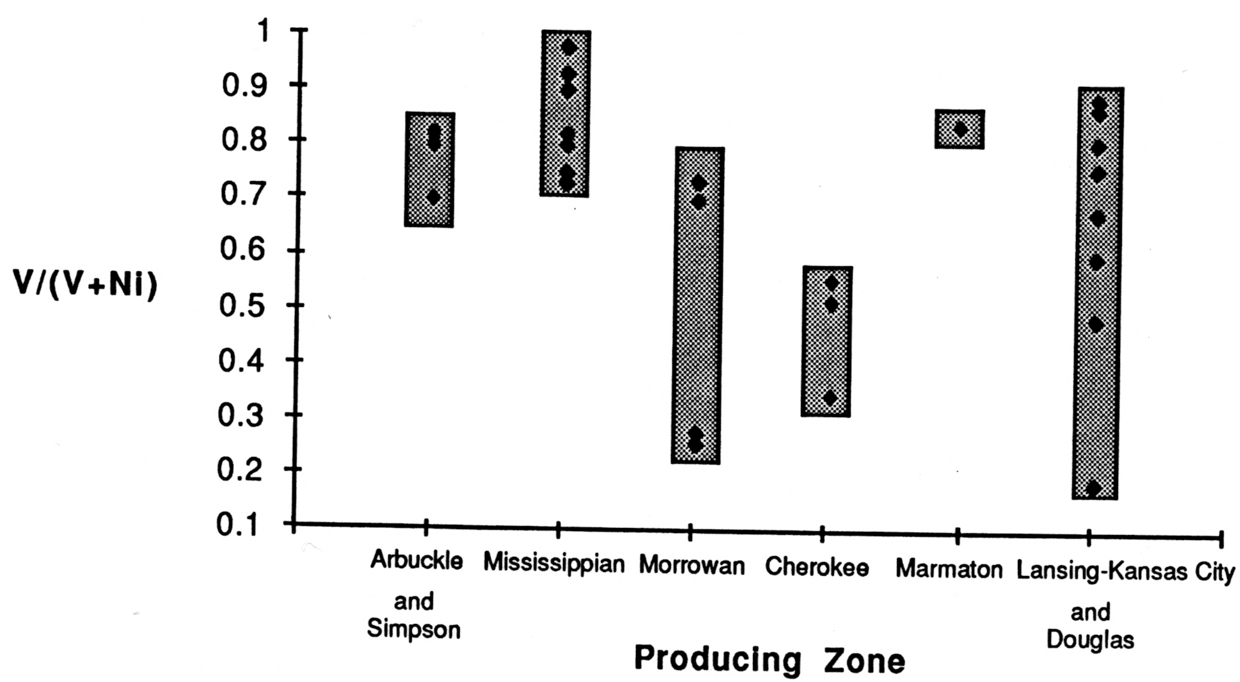


Figure 32. Plot of Ni content vs. producing zone.



The relationship between V/(V+Ni) and producing zone is shown in figure 33. From the plot it becomes apparent that little relationship exists between the V/(V+Ni) and producing zone because of the extensive overlap of the values between zones and wide variations within them. For example, V/(V+Ni) in Morrowan oils range from 0.26 to 0.89 (average of 0.5) that overlaps most other zones; however, Mississippian oils tend to have relatively high V/(V+Ni) values and a narrow range (0.73 to 0.98, average of 0.84). Lansing- Kansas City oils range from 0.49 to 0.89 (average of 0.66) that overlaps all zones except the Douglas oils. Analysis of variance tests rejected the null (each zone has a unique V/(V+Ni) ratio) below the 10 percent level.

Figure 33. V/(V+Ni) fraction of various producing zones.



DISCUSSION

Introduction

Correlation of crude oils from western and central Kansas based on the previous analytical results is the primary focus of this geochemical investigation. Secondary emphasis will be placed on possible migration paths and source area. Based on analytical results, the most distinguishable regularities for geochemical correlation are the following:

1. **The establishment of two general crude oil families based on the distribution of the normal paraffins.**
2. **The recognition of four oil types based on the distribution of the common isoprenoids.**
3. **The establishment of at least three groups of oils based on the V/(V+Ni)ratio.**
4. **The relation of crude oil composition to geographic location.**

The API gravity, carbon isotopic composition, and sulfur content provide additional support for the above regularities. Other geochemical parameters, such as pristane/phytane ratio and carbon preference index (CPI), produced inconclusive results. Any interpretation of the data based on the major parameters above also must include the following: do these features indicate the crude oils were derived from a single source bed (implying any stratigraphic bed of similar physical composition that contains essentially the same organic matter composition) or do the features indicate the oils were generated from multiple sources? The following discussion will focus on the significance of these relationships, their use in correlations, and how the geochemical data may fit into a differential entrapment model.

Pristane/phytane Data

Determination of the pristane/phytane ratio and its use as a biomarker is a standard technique in crude oil investigations. The pristane/phytane ratio of a crude oil is a reflection of the source of the original organic matter and paleoenvironmental conditions during decomposition and early burial. In general, higher pristane/phytane values indicate a source from mostly land- derived organic matter that has passed through a highly oxygenated phase in its decomposition (Powell and McKirdy, 1975; Waples, 1985). Lower values tend to indicate a more marine source for the original organic matter. Powell and McKirdy (1975) have shown that crude oils from Western Australia and Papua, New Guinea, with pristane/phytane ratios less than 3.0 (0.98 to 3.0) are associated with marine shales and carbonates. Oils that have intermediate values (3.0 to 4.5) are associated with marginal marine, clastic sedimentary rocks, or deltaic sequences exhibiting a marine influence. Pristane/phytane values greater than 4.5 (4.5 to 14) were detected in oils exclusively from lacustrine, fluvial, or deltaic sequences with little or no marine influence.

Based on work by Powell and McKirdy (1975) and Brooks and others, (1969), the low pristane/phytane ratios of Central Kansas crude oils (1.18 to 1.71; table 2) indicate they were generated from mostly marine organic source material. The relatively high concentration of phytane may indicate at least moderately reducing conditions were present at the time of deposition and early diagenesis. The narrow range of the values may indicate a common marine source or uniformity in composition and paleoenvironmental conditions of several sources. The narrow range in values is within normal variation of related crude oils (Williams, 1986), making it impossible to distinguish individual or groups of related oils.

Carbon Isotopes

The carbon isotopic composition of a crude oil reflects the isotopic composition of the source material (Barker, 1979). Oil generated from a more marine source will tend to be isotopically heavier (enriched in ^{13}C) than one generated from mostly terrestrial material. Values of $\delta\ ^{13}C$ in crude oils worldwide range from - 16.0 per mil to less than - 32.0 per ml (Waples, 1985), with the lower values generally associated with waxey type crudes (figure 34).

The distribution of carbon isotopes is by no means homogeneous within a crude oil. Lighter fractions of the oil, such as the normal, branched, and cyclo- alkanes are enriched in the lighter isotope, whereas high molecular weight compounds, such as asphaltenes and larger aromatics, tend to be enriched in the heavy isotope. These differences are principally due to the heavier isotope forming higher energy bonds that are not as readily broken during generation. The result is a fractionation during generation, so that crude oils as a whole are generally depleted in $\delta\ ^{13}C$ by as much as - 2.00 per mil relative to the source rock (Sofer, 1984). This fractionation also results in the heavy compounds being enriched in ^{13}C, as thermal cracking will break the lower energy ^{12}C bonds first (figure 35). This trend has been examined in detail by Sofer (1984). The heterogeneity in $\delta\,^{13}C$ values within a crude oil can be useful for correlation when combined with other techniques .

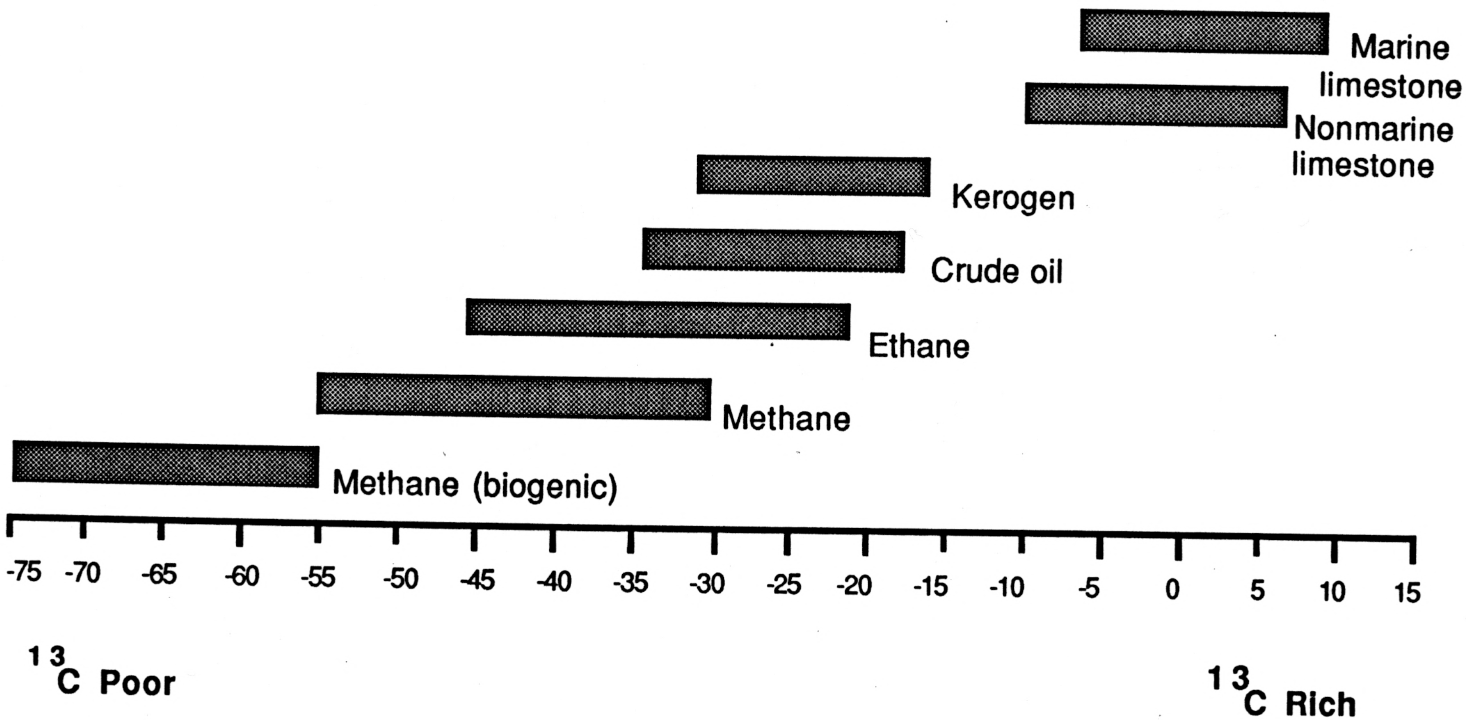


Figure 34. Ranges of carbon isotopic composition of various carbon containing materials. Modified after Waples (1985).

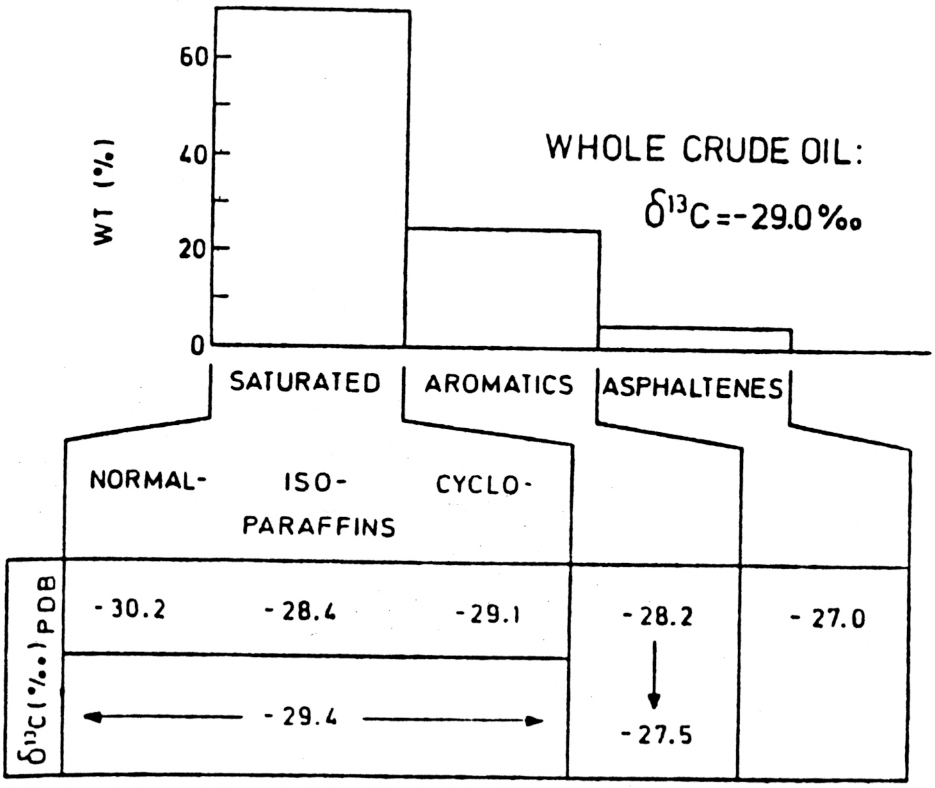
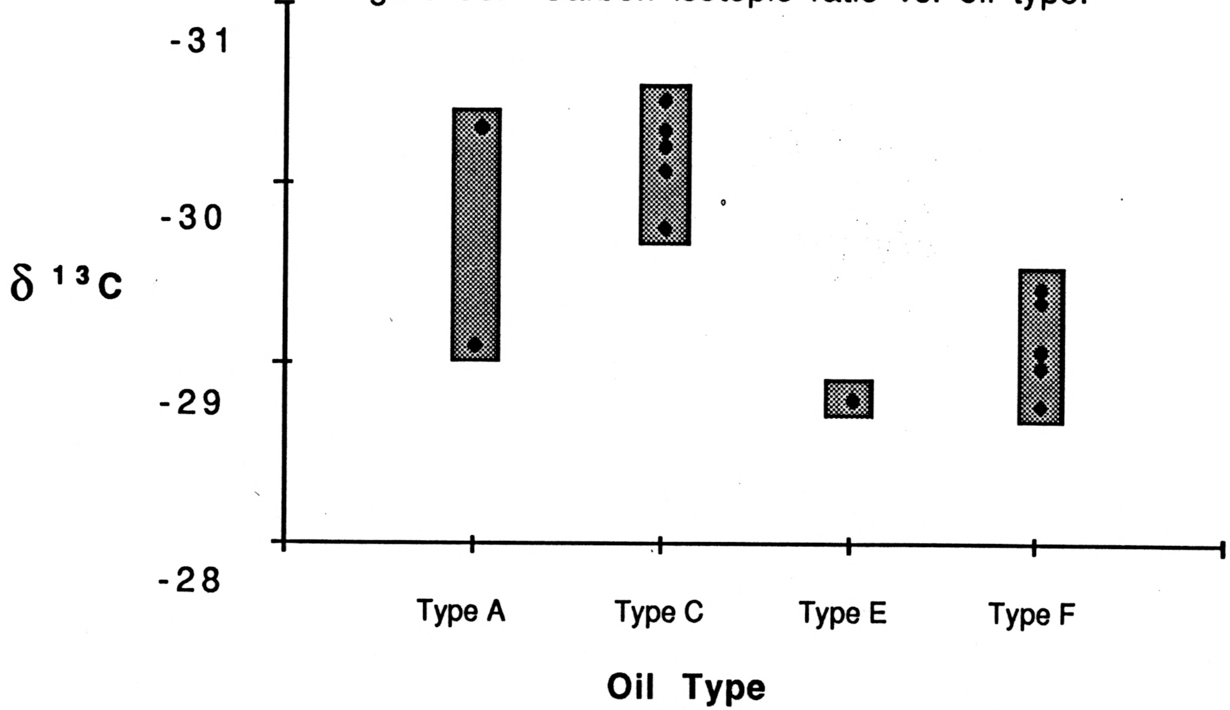


Figure 35. Generalized distribution of carbon isotopes within a crude oil. After Waples (1985).

Correlation of crude oils using isotopic values can be extremely complicated where some or all of the oils have undergone some sort of degradation processes (Waples, 1985; Williams, 1986). As previously mentioned, the two major degradation processes are water- washing and biodegradation. Both tend to attack and reduce the amount of lighter fractions in an oil. Biodegradation by the combined effects of aerobic and anaerobic bacteria tends to attack the middle length nC_9- nC_{18} n- alkanes first, then higher and lower chains, branched alkanes, cyclo- alkanes, and finally heavier aromatics. During microbial activity the whole oil $\delta^{13}C$ value may be increased by as much as 2.00 per mil as microbes remove the isotopically lighter n- alkanes and branched alkanes preferentially. Water- washing (the removal of lighter fractions by dissolution in undersaturated waters) tends to affect the lighter normal alkanes, aromatics such as benzene, toluene, and their low molecular weight derivatives. Water- washing also increases the $\delta^{13}C$ of the whole oil by removal of the light ^{12}C enriched fractions (Bailey and others, 1973; Barker, 1979; Connan, 1984; Waples, 1985). However, none of the oils analyzed exhibited selective removal of their lighter components characteristically seen in water- washed oils.

Whole oil $\delta^{13}C$ values from west- central Kansas crude oils range from- 28.77 to - 30.47 per mil (well within the range of normal crudes). Carbon isotope values appear to be related to the particular oil type based on isoprenoid distributions (table 2). The only type E oil analyzed (a Morrowan oil, DB- 4) is the most ^{13}C enriched with a $\delta^{13}C$ value of - 28.80 per mil. Types F, A and C are increasingly depleted in the heavier isotope with average $\delta^{13}C$ values of - 29.12 (s= 0.24), - 29.71 (s= 0.60), and - 30.14 (s=0.24) per mil respectively. Analysis of variance indicate a relationship between $\delta^{13}C$ oil type significant at the 0.5 percent level. LSD tests showed significant differences between the means of all oil types at the 90 percent level with the exception of a comparison between types E and F that was not significant at the 20 percent level. A plot of $\delta\ ^{13}C$ value versus oil type is shown in figure 36.

Figure 36. Carbon isotopic ratio vs. oil type.



Among the most interesting relationships is $\delta\ ^{13}C$ versus northward distance (figure 24). This plot illustrates the strong inverse relationship between the two (r= - 0.87, significant at the 0.1 percent level). If this trend of decreasing $\delta\ ^{13}C$ value with increasing northward distance was due to normally expected degradational processes on an oil migrating from south to north, the relationship between $\delta\ ^{13}C$ and northward distance would be positive. To generate the trend in $\delta\ ^{13}C$ values by normal degradational processes the oils would have to migrate from north to south. This is extremely unlikely because the oils would be migrating down dip from a structurally positive area. Thus, south to north migration of the oils cannot explain the negative trend between $\delta\ ^{13}C$ and distance. Chromatographic effects may produce a similar trend; however, other parameters, in particular API gravity, V, Ni, and S concentrations do not support this hypothesis. Chromatographic effects would produce lighter oils with lower V, Ni, and S concentrations to the north, in contrast to the data.

The trend in figure 24 also may be explained by a mixing of at least two end-members from two isotopically different sources, one enriched in ^{13}C ($\delta\ ^{13}C$ of about - 30.47 per mil) and one depleted in ^{13}C ($\delta\ ^{13}C$ of about - 28.77). In a simple two end-member model, such as the one described above, any ratio of mixing between the end members should fall on a straight line between the two. While the general trend between the postulated end members is linear (figure 24), there is significant deviation. As previously mentioned, biodegradation may explain some of the positive shifts in $\delta\ ^{13}C$ values and it is possible, although unlikely, that variation in other parameters, such as maturity and API gravity can explain the remaining variations. Unfortunately, API gravity data are not available on all samples and maturity level estimates are at best, uncertain.

The negative relationship between $\delta^{13}C$ and northward distance may be most easily explained by the relationship between oil type and the $\delta^{13}C$ ratio (significant at the 0.5 percent level). Those oils from the upper left region of figure 24 are without exception type F, and those oils in the lower right region are type C oils, whereas types A and E are intermediate. The data indicate the trend of $\delta^{13}C$ ratio versus northward distance is probably due to the heterogeneous geographic distribution of multiple oil types with differing isotopic compositions.

Normal Alkane Distributions

The composition of crude oil depends on the type of original organic matter, its environment of deposition, and degree of thermal maturation (Philippi,1965; Degens and Mooper, 1976). The ratio of marine to terrestrial organic matter is one of the most important variables influencing the composition of petroleum. Terrestrial plant remains are derived mainly from woody plant material and are composed of lignin and polysaccharides such as cellulose (Kent and others, 1962). In contrast, most marine matter is derived from plankton or other marine organisms and is depleted in lignin and cellulose and greatly enriched in lipids, such as fats, alcohols, steroids, carotenoids, and terpenoids (Philippi, 1974). Over 95 percent of marine organisms (by weight) are comprised of simple hydrocarbon skeletons and lipids. The normal alkanes (paraffins) in petroleum probably originate mostly from lipids (Cooper and Bray, 1963; Martian and others, 1963; Silverman, 1967; Philippi, 1974; Barker,1979). Most marine lipids are high in C_{16} and C_{18} carboxylic acids, although moderate amounts of C_{12} to C_{14} fatty acids are also present. Higher fatty acids in the C_{20} to C_{24} range are not abundant in marine lipids but do occur in some terrestrial plant oils (Philippi, 1974).

The strategies for the identification of marine versus nonmarine sources are varied (Martin and others, 1963; Philippi, 1965; Philippi, 1974;; Barker, 1979; Rashid, 1979). The abundance of low molecular weight n- alkanes (less than C_{24}) in ancient sediments from the Labrador shelf indicates that the organic matter was derived mainly from algal remains from marine sources (Eglinton and Hamilton, 1967; Rashid, 1979). For example, the abundant n- alkane content in the nC_{25} to nC_{31} range of Wilcox oils from the Texas Gulf Coast is caused by the presence of higher plant matter in the oils source material (Philippi, 1974). Martin and others (1963) suggested the high concentration of heavy n- alkanes in the nC_{15} to nC_{27} range from an unidentified Unita Basin oil is because the oils n- alkanes originated, in part, from plant waxes.

Based on work by Martin and others (1963) and Rashid (1979), the two families of crude oils from west- central Kansas may reflect two slightly different influences of original organic matter. However, the differences between the two families (figure 12) are not as great as those observed between terrestrial and marine sources by Rashid (1979) or Martin and others (1963). Both families of Kansas oils have high concentrations of low molecular weight n- alkanes (less than nC_{24}) and, based on similar studies by Rashid (1979), both are probably derived from mostly marine sources. It is unlikely that substantial amounts of terrestrial matter were present in their source rocks as concentrations of higher molecular weight n- alkanes (greater than nC_{24}) are relatively low. Family I oils have an enriched gasoline fraction relative to family II oils, yet both have nearly identical nC_{15} to nC_{25} distributions. The differences may be due to a slightly higher terrestrial influence in family II oils or slight differences in thermal maturity (both of which are impossible to distinguish from n- alkane data alone). If the differences are related to maturity, the higher maturity oils (family I) would be expected to be enriched in lower molecular weight compounds and possibly have higher API gravities.

As previously mentioned, the average API gravity of family I oils (37.6, s=3.9) is not statistically different from that of family II oils (39.3, s =2.6), even at the 40 percent level. Therefor there is no observable difference in the API gravity between the two types. Also, there are no significant differences between family I and family II oils in other geochemical parameters such as V and Ni concentration, isotopic data, sulfur content, CPI, pristane/phytane ratios, nC_{17} /pristane nC_{18} /phytane data, and V/(V+Ni) ratios.

The association of type E isoprenoid trend only with family II oils may indicate that the variation between the two families of n- alkane distributions(figure 12) is because of slight differences in the original source organic matter. If so, these differences are slight as both families of oils are enriched in marine derived (less than nC_{24}) n- alkanes.

Isoprenoid Distributions

Crude oils from western and central Kansas have been divided into four distinct types (A, C, E, F) based on the distribution of the common isoprenoids (figure 17). It is unlikely that mixing of any combination of two types would produce either of the remaining two.

Profiles of the regular isoprenoids have not been widely used as a correlation tool, as their mechanisms of formation are poorly understood. Pristane and phytane are probably produced by the degradation of the phytol side chain of chlorophyll, in particular chlorophyll a (Powell and McKirdy,1975; Brooks and others, 1968; Barker, 1979). Haug and Curry (1974) have indicated that regular iP- 16 and iP- 18 isoprenoids also are formed by mild thermal cracking of phytol (a side chain of chlorophyll and many heme pigments) and other low molecular weight isoprenoids probably are generated in a similar fashion. The relative abundance of the common isoprenoids (iP- 13, iP- 14, iP- 15, iP- 16, iP- 18, iP- 19, iP- 20) may be generated during early diagenesis (Haug and Curry, 1974; Rashid, 1979; Waples, 1985). Although changes in the abundance may occur during generation and maturation, (such as the slightly more rapid generation of pristane than phytane) these changes are slight and may be lost in the natural variation between samples (Waples, 1985).

It may be possible that isoprenoid profiles that are enriched in the low molecular weight compounds (type A) indicate a higher degree of thermal maturity than profiles that are depleted in these molecules (figure 18). Type A oils (family I n- alkane distribution) appear to be of higher maturity than types E, F, and C based on their higher average API gravities (43.0 for type A, 39.0, 39.1, 36.2, for types E, F, and C respectively) and higher ratios of nC_{17} /pristane- nC_{18} /phytane. Type E and F profiles (figures 20 and 21) are depleted in low molecular weight isoprenoids and have pristane greater than both iP- 16 and iP- 18. Type C oils appear to be of intermediate maturity even though their API gravities are significantly lower (36.2) than types E and F (API of 39 and 39.1 respectively). This may be due in part to the higher occurrence of biodegradation observed in type C oils that are generally from the more northern regions.

API Gravity

Correlation of crude oils based solely on API gravity is generally ineffective due to the many factors that may alter the API gravity, such as biodegradation, water- washing, inorganic oxidation, deasphalting, thermal cracking, chromatographic effects, and differential entrapment among others. Of the above, the first three lead to a decrease in the API gravity by oxidation, destruction, or removal of the lighter fractions. The latter effects tend to increase API gravities by selective removal or cracking of the heavier fractions during migration or within the reservoir.

API gravity data are best used in conjunction with other geochemical techniques. As applied to crude oils in west- central Kansas, API gravity data may be useful in explaining geographic trends in the S, V, and Ni concentrations of the oils. Moderate variations in API gravity in oils of a region are common. Slight differences in maturity level, heterogeneity of the source, migration histories, reservoir conditions, and microbial activity (among others) may result in API differences between closely related oils. Sharp decreases in API gravity are often the result of biodegradation, such as that observed in two Kansas City oils from Ellis County (JE- 1, JE- 3). This effect has been documented by many (Evans and others, 1971; Powell and McKirdy, 1975; Barker, 1979; Connan, 1984; Williams,1986).

Except for the more severely biodegraded Lansing- Kansas City oils (samples JE- 1 and JE- 3), the variances in the API gravities (table 2) are not unusual. Although slight differences in API gravity occur between different producing zones, the small differences are statistically insignificant as the null hypothesis (Ho: all stratigraphic zones produce similar API gravity oils) could not be rejected even at the 25 percent level.

The trend between API gravity and northward distance (figure 11) follows a trend of decreasing brine salinities northward within the area of the Central Kansas Uplift (Chaudhuri, 1978; Broedel, 1983; Nicastro, 1983). A similar trend was documented in the West Canada Basin by Bailey and others (1974). They noticed the association of tars and low API oils with low salinity formation waters in shallow reservoirs near basinal margins. Higher gravity oils were associated with higher salinity formation waters within deeper reservoirs away from basinal margins, and large gas accumulations were detected in the deepest reservoirs within the basins. Bailey and others (1974) attributed the decrease in API gravity of the oils near the basinal margins to interaction with meteoric formation waters. Surface- derived formation waters exert a detrimental effect upon pooled hydrocarbons because of microbial action (Winters and Williams, 1969) and water-washing (Evans and others,1971). These processes were observed in the Mississippian Canyon 5 of south- eastern Saskatchewan (Bailey and others, 1973). Although similar conditions of hydrocarbon accumulation exist in Kansas, only mildly degraded oils (samples JE- 1 and JE- 3, both Kansas City oils) are present, and a very few oils exhibit observable degrees of microbial activity.

As previously mentioned, regional dips in the study area are to the south and west, away from the axis of the Central Kansas Uplift. Chromatographic effects certainly are possible; however, they would tend to increase the API gravities to the north, toward the basinal margins, and not away from them, as indicated in this study. Walters (1958) postulated that the occurrence of heavier oils up dip and further north of lighter oils in west- central Kansas was due to gravity separation. The decrease in API gravities to the north also may be the result of deasphalting within southern reservoirs triggered by the movement of gas through the oils. Many fields in south- central Kansas coproduce gas and oil, such as the Collier Flats Field in Comanche County, Kansas, and huge gas accumulations exist down dip within the Hugoton Embayment to the southwest. Evidence for deasphalting may exist in reservoir rocks to the south; further studies are needed to address this issue. Geochemical data obtained in this study indicate the API gravities of crude oils in west- central Kansas are related to the specific oil type (A, C, E, F) and to isolated occurrences of biodegradation (as in samples JE- 1 and JE- 3).

Carbon Preference Index

Normal alkanes were among the first biomarkers to be extensively studied in crude oils. The high concentrations (10 to 20 percent by weight) of normal alkanes in most crude oils is related to the existence of these compounds in plant and algal lipids and by catagenic formation from longer chain compounds, such as fatty acids and alcohols (Waples, 1985). Eglinton and Hamilton (1963) reported that plant waxes contain n-alkanes with odd numbers of carbon atoms (especially 25, 27, 29, and 31 carbon- length chains) that are more abundant than even chains by a factor of ten or more. In contrast, marine algae and plankton have no odd- to- even preference in their n- alkanes or homologs, and maximum chain lengths are in the nC_{17} to nC_{22} range. The opposite trends are seen in the carboxylic acids and alcohols as terrestrial matter is enriched in even carbon-numbered chains and marine matter is enriched in odd carbon- numbered chains.

Bray and Evans (1961) proposed that n- alkanes could be generated in sediments during diagenesis, and these non- biologically generated n- alkanes would exhibit no odd-even preference. As more alkanes are generated, an original odd preference (as seen in many recent sediments) is 'swamped' and CPI values approach 1.0. Studies by Philippi (1965, 1973) confirmed the diagenetic generation of n- alkanes in sediments. Philippi also suggested that petroleum may be generated primarily from fatty acids and alcohols by hydrogenation and thermal cracking by reaction paths involving free radical generation. In general, these processes produce n- alkanes having one less carbon atom than their alcohol or acid parents (Dembicki, 1976). The suggestion is that acids and alcohols in marine organic matter,which have a high odd- even ratio, will generate n- alkanes with little odd-even preference when thermally cracked. For example, Bray and Evans (1961) found that 39 crude oils from widely differing geological settings contained near equal proportions of odd versus even n- alkanes and thus have CPI values near unity. The crude oil with the greatest preference contained only 1.13 times as much odd as even n- alkanes. Their analyses of 41 recent near- shore marine sediments indicated marked preferences for odd numbered n- alkanes with CPI values ranging from 2.4 to 5.5. However, analysis of 43 ancient marine sediments ranged from no preference to about 2.4. Strong tendencies towards even preferences (CPI less than 1.0) occur principally in evaporite and carbonate sediments where input of terrestrial matter is minimal and diagenetic conditions are mostly reducing (Dembicki and others,1976; Waples, 1985). Low CPI values thus indicate a more marine influence (Koons and others, 1965; Philippi, 1973).

Analysis of crude oils from west- central Kansas indicated little to no odd- even preference. CPI values ranged from 1.02 to 1.12 with an average of 1.05 (s=0.17, table

2). The relatively low CPI values of the oils may then reflect a more marine influence in their source material or maturity levels of the source rocks high enough at the time of generation to 'swamp' any original values. The high uniformity in the values (s=0.17) indicates the oils were either generated from similar types of source matter (mostly marine rocks) or generated from rocks of similar maturity or both. The variation in the CPI values from Kansas crude oils are within the natural variation of a single oil (Williams, 1986) and are probably insignificant.

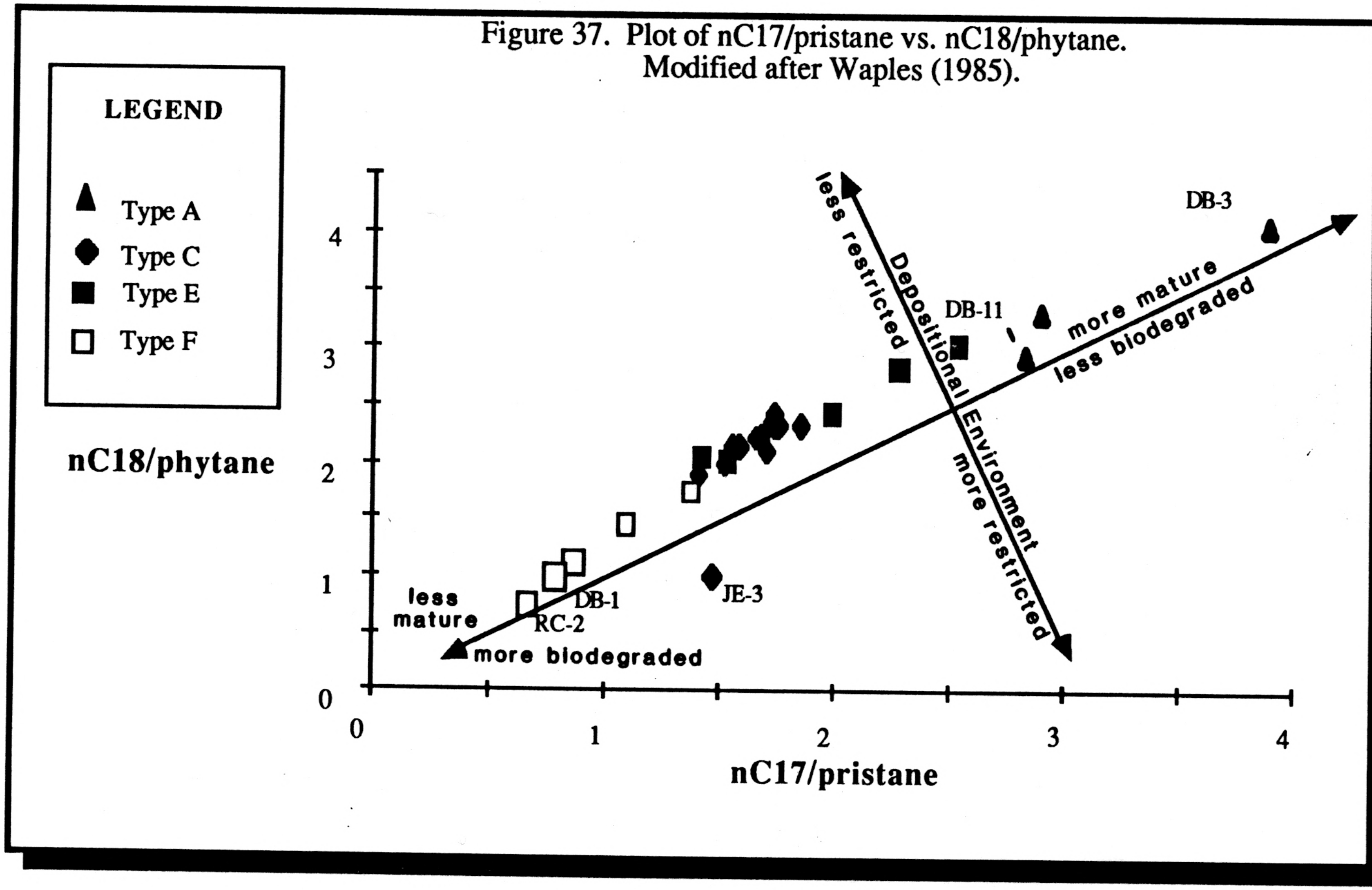
nC_{17}/pristane, nC_{18}/Phytane

The nC_{17}/pristane, nC_{18}/phytane, and n- alkane data can be used to infer degree of biodegradation, maturity, and diagenetic conditions (Mackenzie, 1984; Waples, 1985). In figure 37 the line labeled '**depositional environment**' reflects changes in the pristane/phytane ratio. The higher ratios ('**less reducing more oxidizing**') are thought to represent higher oxygen content of bottom waters (Powell and McKirdy, 1975). As previously mentioned, low pristane/phytane ratios ('**more restricted anoxic**') are thought to indicate reducing conditions as might be found in restricted environments (Waples,1985). The arrows labeled '**more mature less biodegraded**' and '**less mature more biodegraded**' reflect the decreased normal to branched alkane content of biodegraded oils (lower nC_{17}/pristane and nC_{18}/phytane values) and the increase in normal to branched alkanes (higher nC_{17}/pristane and nC_{18}/phytane values) with increasing maturity.

Several significant relationships are seen in western and central Kansas crude oils (figure 37). The narrow range in pristane/phytane values of all oils along the '**oxidizing-reducing**' line indicates their source matter was deposited in moderately oxidizing marine conditions and that little variation existed between the individual sources. Sample JE- 3 (Kansas City, type C, API=29.0) plots below the general trend probably as a result of microbial activity that has affected the branched as well as the normal alkanes (figure 14). As previously discussed, normal alkane distributions also indicate a mostly marine origin for the oils.

The ratios of nC_{17} /pristane and nC_{18} /phytane are, however, sensitive to changes in maturity and biodegradation (Barker, 1979; Durrand, 1983; Waples,1985; Williams, 1986). During generation more n- alkanes are produced relative to the iso- alkanes (Barker, 1979; Waples, 1985) and the n- alkane to isoprenoid ratios will increase with increasing maturity. Oils of higher maturity will plot in the upper right of figure 37 and those of lower maturity or more biodegraded will plot toward the lower left. Thus, type A oils are the most thermally mature oils and maturity decreases or biodegradation increases or both in order from types E, C, to type F. This also may explain the slight differences in average API gravities between the oils types (type A=43.0, type F=39.1, type E=39.0, and type C=36.2). Based on maturity levels inferred from figure 37, type A oils should exhibit the highest gravities followed by types E, C, and F respectively. Measured API gravities generally follow this except types E and F are in reverse order, possibly due to differences in source matter or other unknown causes.

Figure 37. Plot of nC17/pristane vs. nC18/phytane.
Modified after Waples (1985).



Several of the more biodegraded oils (JE- 3, Kansas City; RC- 2, Lansing- Kansas City; RC- 3, Douglas; DB- 1, Lansing- Kansas City) are previously identified from chromatographic and API data (figure 37). These oils are in the lower left, more biodegraded region of figure 37. The figure indicates as does the pristane/phytane and n-alkane data, that all oils analyzed appear to have been generated from mostly marine sources that had similar diagenetic histories. Slight discrepancies between the above parameters may be due to natural variation within source beds or other unknown factors.

Sulphur Data

Sulphur is generally associated with polar compounds contained within the heavier fractions of crude oil, particularly the asphaltenes (Barker, 1979; Connan, 1984; Waples, 1985). Sulfur content in crude oils world- wide ranges from less than 0.1 percent to more than 7.0 percent in Monterey oils from offshore Santa Maria, California (Waples, 1985). Oils having more than 0.5 percent sulphur are generally designated 'high sulfur' crudes and are derived from high sulphur kerogens. Most oils derived from lacustrine or ordinary clastic marine rocks will be of low sulphur content, whereas oils derived from euxinic or anoxic (restricted) marine sources will tend to be of high sulphur (Waples,1985).

As sulphur is closely associated with the heavier asphaltene fraction, high sulphur oils consequently have increased asphaltene contents and reduced API gravities. This relationship is widely accepted in the literature. Any process affecting the ratio of heavy to light fractions in a crude oil such as biodegradation, water- washing, chromatographic effects, differential entrapment, will also change the sulphur contents in a crude oil.

Biodegradation and water- washing will increase the sulphur content by removal of the lighter fractions, whereas chromatographic effects will decrease sulphur content in the direction of migration. Differential entrapment will tend to increase the sulphur content in the direction of migration as lighter low sulphur fractions are preferentially trapped first.

Analysis of 12 Kansas crude oils indicate the oils are of low sulfur ranging from 0.12 to 0.49 weight percent, although sulphur content was not determined in two of the heavier biodegraded oils (JE- 1, API of 29.1 and JE- 3, API of 29.0). The low sulphur contents and relatively high API gravities of the oils indicate they probably did not originate from euxinic or restricted marine sequences. This is in agreement with the pristane/phytane ratios (greater than 1.0) and V/(V+Ni) data (see following discussion).

The positive relationship between sulphur content and northward displacement (figure 22) is inverse of the trend between API gravity and northward distance (figure 11). This indicates the positive relationship between sulphur content and northward distance is controlled by the presence of lower API gravities to the north. Type C oils have lower API gravities and predominate in the northern areas. The most biodegraded oils and the lowest brine water salinities also are found in this area. It is unclear whether type C oils are genetically of lower API gravities and higher S or the occurrence of the oils in shallower, more northern reservoirs of lower salinities has allowed biodegradation effects to occur.

Trace Metals

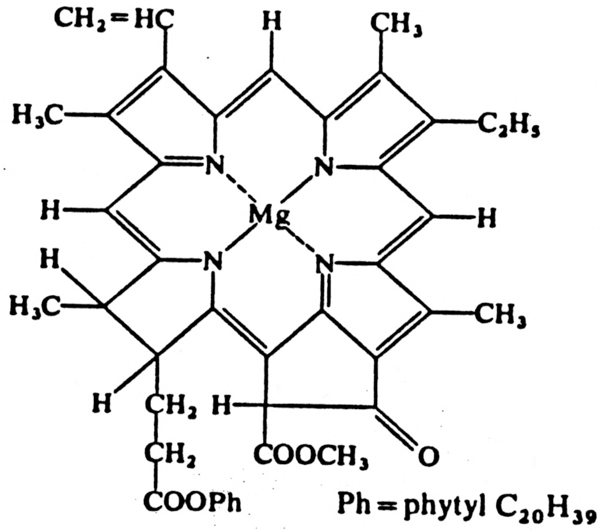
Introduction:

Vanadium and nickel are the most abundant trace metals naturally occurring in crude oils. They are present (figure 38) within the heavier fraction of crude oils as degraded chlorophyll type porphyrin complexes (Treibs, 1936; Hodgson, 1954; Corbett, 1967; Dwiggins and others, 1969; Filby, 1975; Lewan, 1980; Lewan and Maynard, 1982; Lewan, 1984). These organo- metallic complexes have been shown to be thermally stable to temperatures well above the stability for crude oils, in excess of 300^{0} C (Constantides and others, 1959; Corbett, 1967; Dwiggins and others, 1969; Filby, 1975; Lewan, 1980, 1984).

The proportion of V to Ni in crude oils has been suggested to remain constant regardless of water- washing, microbial degradation, inorganic oxidation, maturation, and does not vary significantly with geological setting (Hodgson, 1954; Brunnock and others, 1968; Davis and Gribbs, 1975; Lewan,1984). The proportion of the two in crude oils is related to the source rocks from which the oils were derived (Hodgson, 1954; Witherspoon and Nagashima,1957; Al- Sharistani and Al- Atyia, 1972). Lewan (1984) concluded that the ratio of V to Ni in crude oils is determined by the environmental conditions in which the source rocks were deposited. Lewan and Maynard (1982) have shown that it is feasible for the metals to be enriched in organic sediment by diffusion across the sediment- water interface. After the ratio is established during early diagenesis, the proportion of the two metals will remain constant in the organic sediment and any expelled crude oils. The use of V to Ni ratios as a correlation tool has been done by many

(Katchenkov, 1949; Hodgson, 1954; Scott and others,1954; Ball, 1956; Hodgson and others, 1957; Witherspoon and Nagashima, 1957; Al- Sharistani and Al- Atyia, 1972; McKirdy and Horvath, 1976).

(a) Chlorophyll *a*



(b) Vanadyl DPEP

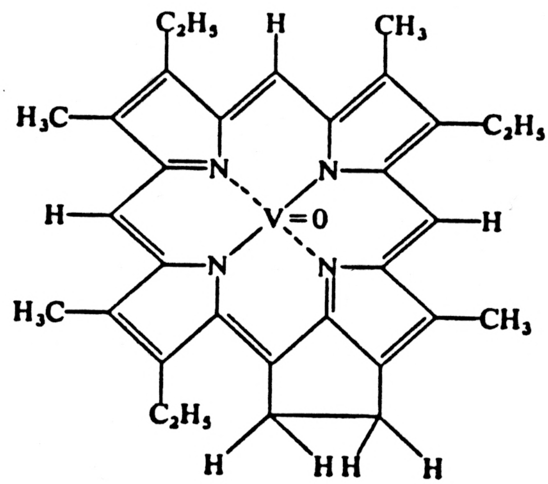


Figure 38. Structures of chlorophyll a and vanadyl DPEP. After Speers and Whitehead (1969).

V, Ni Contents:

Lower API gravities of northern oils reflect an increased proportion of higher molecular weight compounds. As most trace metals are associated with high molecular weight porphyrin complexes (Corbett, 1967; Dwiggins and others,1969; Filby, 1975), increased concentrations of these compounds may in part explain the positive relationship between V, Ni, and northward displacement of the oils (figures 28 and 29). A similar relationship between API gravity and V, Ni, concentrations was documented within the West Canada Basin (Hodgson, 1954). However, regression coefficients are relatively low (- 0.21 and - 0.28 for V and Ni versus API) indicating that although northern oils have slightly lower API gravities, the increase in metal contents is not simply because of higher contents of heavier molecular weight complexes in these oils. As previously discussed several northern oils are biodegraded and their metal concentrations are increased accordingly, but many non- biodegraded northern oils are probably of genetically higher initial metal concentrations.

Variation in API gravity also may explain variances within the metal concentrations of closely related oils. For example, within type E oils the relationship between API gravity and V, Ni concentration have r values of - 0.96 and- 0.81 . Two Morrowan type E oils (Samples DB- 4, Morrowan, and DB- 5, Morrowan) have V concentrations of 1.1 ppm and 2.2 ppm and Ni concentrations of 2.6 ppm and 7.2 ppm . Although not large, the increase in metal concentrations in sample DB- 5 is most readily explained by its lower API (38.0) versus (43.0) for sample DB- 4. A significant increase in sulfur also is noted from 0.187 percent in DB- 4 to 0.221 percent in DB- 5. However, this relationship does not always hold true for example, a type C oil (sample JB- 3, Marmaton) has the highest metal and S contents of all oils analyzed (57 ppm V, 11 ppm Ni, and 0.49 percent S), yet it has an intermediate API gravity of 36.5. Another type C oil (sample JE- 3, Kansas City) has lower metal concentrations (19 ppm V and 4.4 ppm Ni), yet it has a lower API than the Marmaton oil (JB- 3). Any correlation based on absolute concentrations, especially the metals, easily may be misinterpreted because of minor effects on the concentrations of the two, including slight changes in API gravity, differences in maturity, possible mineral reactions, or heterogeneity within the source matter (Lewan, 1985). Many of these effects, that occur in the generation and migration of crude oils are unknown or poorly understood (Durrand, 1983).

Higher maturity oils would be expected to have lower concentrations of V and Ni, with an increase in metal concentration as maturity decreased or biodegradation increased (as indicated from nC_{17} /pristane nC_{18} /phytane data). This relationship is not readily apparent in the trace metal data as types A and E have nearly equal average V, Ni concentrations (3.4 ppm V, 2.2 ppm Ni and 3.7 ppm V, 1.1 ppm Ni). Type C oils, however, do have increased metal concentrations (16.3 ppm V and 3.7 ppm Ni), although type F oils have reduced metal concentrations (2.0 pm V and 1.6 ppm Ni). The deviation from the predicted maturity trend in figure 37 (types A, E, C, F, in order of decreasing maturity or increasing biodegradation) again indicates possible variation of metal concentrations within the original source matter of each oil type. Within a single oil type, a trend of increasing metal concentration with increasing biodegradation or decreasing maturity can be seen. For example, within type A oils, the most mature oil (DB- 3, Morrowan) is located in the extreme upper right portion of figure 37. This oil has lower metal concentrations (0.46 ppm V and 1.2 ppm Ni) than the less mature or more biodegraded type A oils (such as sample DB- 11 9.2 ppm V, and 4.2 ppm Ni) that plot more toward the center of figure 37. This relationship also is detected in other oil types. For example, a biodegraded type C oil (sample JE- 3, API of 29.0, V of 3.3 ppm, and Ni of 0.24 ppm) from the Kansas City Group plots in the extreme lower left of figure 37. This oil has higher metal concentrations and a lower API gravity than other less biodegraded or more mature type C oils, that plot more towards the center of the figure (such as DB- 10, API=38, V=3.3 ppm, Ni=0.24 ppm).

V/(V+Ni)Values

Lewan (1984) suggested that redox potential, hydrogen ion activity, and sulfide activity are the most likely factors controlling the proportion of V to Ni in metallation in organic sediment. Vanadium is known to occur in crude oils in the quadrivalent state as the vanadyl cation (VO^{2+}; Roberts and others, 1961; Saraceno, and others, 1961; Marov and others, 1972) and nickel occurs as the bivalent nickelous (Ni^{2+}) cation . A summary of the Eh- pH relations governing the availability of vanadyl and nickelous cations has been compiled by Lewan (1984) and is shown in figure 39. The following discussion of Eh- pH controls is paraphrased from Lewan (1984).

regime I

Regime I represents conditions where vanadium occurs as quinquevalent ions($V_4O_{12}^{4-}$, $V_2O_7^{4-}$, VO_4^{3-}) and would not be readily available for metallation. Nickel occurs as the nickelous cation (Ni^{2+}) and would be readily available. Sulfur occurs principally as sulfate (SO_4^{2-}) in alkaline waters and would not be expected to be available for complexing with nickel or organic compounds. Crude oils generated from organic sediments deposited under regime I conditions would most likely have low V/(V+Ni) values, generally less than 0.10 (Lewan, 1984), and low sulfur contents.

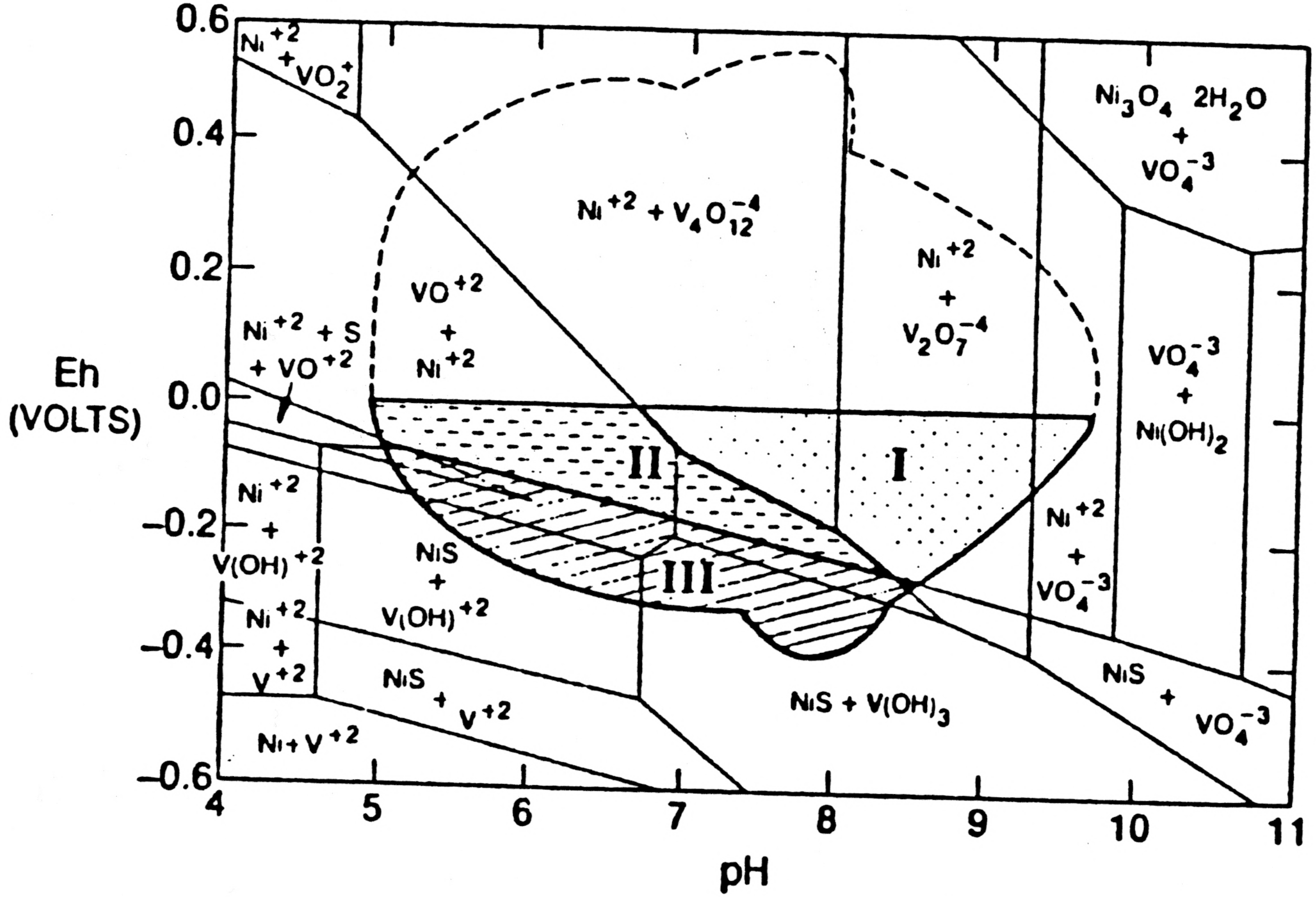


Figure 39. Eh-pH controls on stability of various vanadium and nickel species. After Lewan (1984).

regime II

Regime II occurs from pH 5 to pH values slightly greater than 8.0. In the alkaline portions of this regime, V is present in the quadrivalent state; however, it is complexed by the formation of aqueous hydroxides and would be unavailable for metallation. Nickel would be readily available under these conditions and oils generated from organic sediments deposited under this portion of regime II will have V/(V+Ni) values less than 0.50 (Lewan, 1984). In the more acidic portions of regime II vanadyl cations will not be hindered by aqueous hydroxide complexes and nickelous cations also will be readily available. The proportionality of V to Ni in these conditions will most likely be controlled by the ratio of the two in the interstitial waters and sea water. According to Goldberg (1961), the ratio of V to Ni in sea water should be near unity and organic sediments deposited under the acidic portions of regime II will have V/(V+Ni) values near 0.50. The ratio may be altered by many variables, including sorption- desorption onto particulate matter and by the presence of bacterially generated sulfide that will form insoluble nickel sulfide (NiS). According to Lewan (1984), the variety of controls on the V to Ni fraction in crude oils generated from sediments deposited under regime II conditions will produce considerable variations in the V/(V+Ni) ratios between 0.10 and 0.90. Sulfur contents also might be expected to be low because of the relatively low amount of bacterially generated sulfide present and the higher Eh's encountered.

regime III

Regime III exists only if a substantial number of sulfate- reducing bacteria are present within the sediment. Under these conditions nearly all sulfur exists in the reduced form, sulfide (S^{2-}). With large amounts of reduced sulfur present, nickel cations will be removed by the formation of insoluble nickel sulfides. This removal will be somewhat dependent on the amount of ferric iron (Fe^{3+})present as reaction kinetics dictate iron sulfides will form preferentially to nickel sulfides until all available oxidized iron is removed. Crude oils generated from organic sediments deposited under regime III conditions are expected to have high V/(V+Ni) values (greater than 0.50) and higher sulfur contents (greater than 1.0 percent).

V/(V+Ni) in Kansas Oils

No definitive rule exists for the interpretation of the V/(V+Ni) ratio in crude oils; however, Lewan (1985) has suggested a maximum deviation of 0.1 in the V/(V+Ni) ratio as the natural variation for related crude oils. This does not necessarily imply that oils with values within this limit are related, but more so that oils with wide differences in ratios are most likely not related. However, other geochemical factors must be considered in any correlation problem.

Crude oils from central Kansas have been grouped according to their V/(V+Ni) values and S contents (figure 40), and Eh- pH limits for the three regimes discussed above have been superimposed on the plot. As can be seen in the figure, all crude oils analyzed plot within regime II and will be discussed below according to their respective V/(V+Ni) ratios.

Group I oils

Crude oils from central Kansas have been arranged into three distinct groups based on Vand Ni concentrations and the V/(V+Ni) ratio (table 4). Group I oils are characterized by high V/(V+Ni) ratios (0.90 to 0.98), low vanadium concentrations (less than 0.35 ppm), similar isoprenoid and n- alkane distributions (type C and family I), their near equal values of nC_{17} /pristane (1.58 to 1.68) and nC_{18} /phytane (2.13 to 2.23), and their similar API gravities (37 to 38). Although two of the oils have V/(V+Ni) values in excess of 0.90 (samples DB- 10 and DB- 16, both Mississippian oils), they are still probably associated with Lewan's regime II as analytical inaccuracies of Ni concentrations in the 0.5 ppm and below range are elevated (15 to 20 percent). The three group I oils may be associated with source rocks that were deposited under environmental conditions in which both vanadyl and nickelous cations were available for metallation (figure 40). As sulfur content is low, the source matter of group I oils may have been deposited in moderately oxidizing conditions with little reduced sulfur present.

Group II oils

Group II oils are characterized by low V/(V+Ni) ratios (0.19 to 0.28), low vanadium concentrations (less than 0.46 ppm), type A and F isoprenoid distributions, and a tendency of high $\delta^{13}C$ values (- 28.99 to - 29.11 in two of the oils). As all three of these oils have vanadium concentrations below detection limit of 0.46 ppm, the detection limit value was substituted for the V concentration in the calculation of the V/(V+Ni) ratio. Thus the V/(V+Ni) values for group II oils are maximum limits and the actual ratios may be substantially lower. From their apparent low sulfur content (0.12 percent in one oil) and low V/(V+Ni) values, these oils could be generated from source rocks deposited in either regime I or regime II conditions. Regime I oils according to Lewan (1984) are associated with source organic matter deposited under higher Eh and pH conditions, not unlike the open lacustrine and playa facies of the Green River Formation although Green River oils have extremely low V/(V+Ni) ratios of less than 0.05. In such environments, a large contribution might be expected from terrestrial organic matter that would be reflected in the n- alkane distributions. Also under these conditions phytol would be more rapidly oxidized to phytanic acid and produce larger amounts of pristane relative to phytane. The low pristane/phytane ratios (1.34 to 1.70) and the Family I n- alkane distribution of group II oils does not support a regime I origin for the oils.

Figure 40. Plot of V/(V+Ni) vs. percent sulphur. Modified After Lewan (1984).

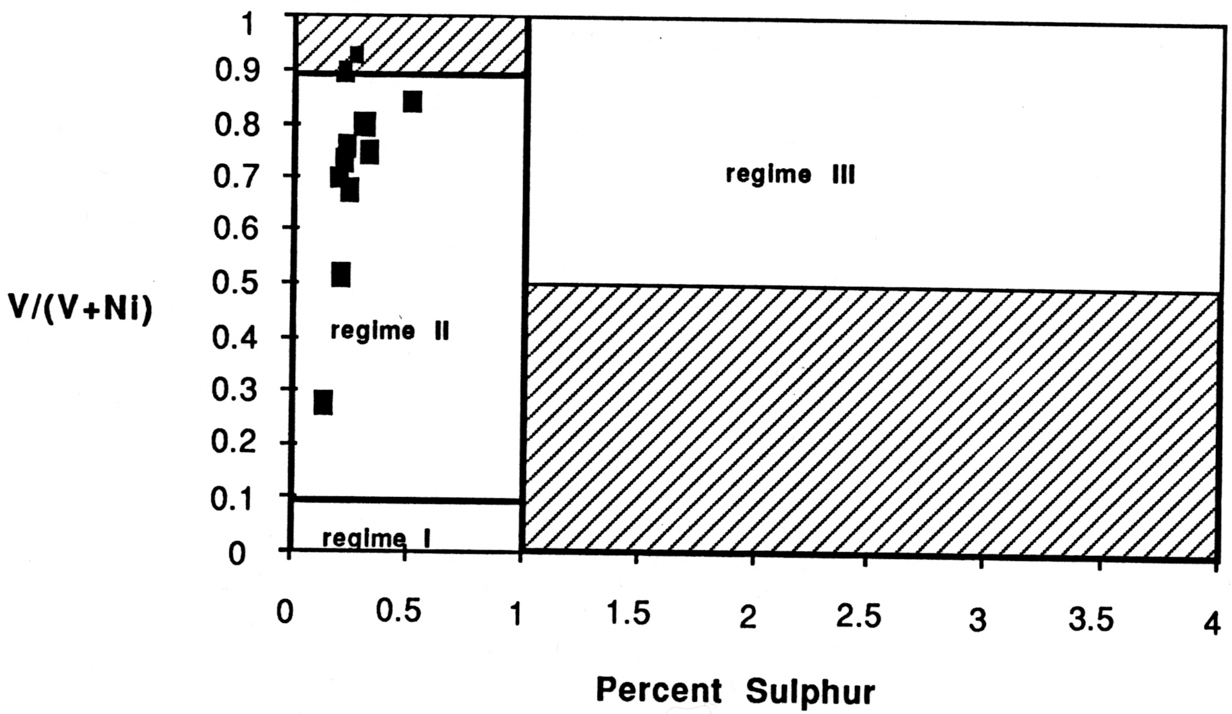


Table 3. Geochemical analysis west-central Kansas crude oils grouped by V/(V+Ni) ratio.

Sample Number	ZONE	Northward dist. (mi)	API Gravity	%S	CPI	Ni (ppm)	V (ppm)	V/(V+Ni)	V/(V+Ni) Group	Iso. Type	n-Alkane Family	Pr/Phy	nC17/pris	nC18/phy	Delta 13 C
GROUP I															
DB-10	Miss.	90	38	0.245	1.02	0.24	3.30	0.93	1	C	I	1.47	1.68	2.20	
DB-16	Miss.	108	37		1.04	0.24	15.00	0.98	1	C	I	1.47	1.65	2.23	-30.30
DB-15	Miss.	114	37	0.204	1.02	0.35	3.00	0.90	1	C	I	1.47	1.58	2.13	
GROUP II															
RC-3	Doug.	12	37		1.09	2.00	0.46	0.19	2	F	I	1.34	0.87	1.03	-28.99
DB-2	Morrow	36	40		1.06	1.30	0.46	0.26	2	A	I	1.65	2.89	3.29	-29.11
DB-3	Morrow	36	47	0.12	1.12	1.20	0.46	0.28	2	A	I	1.70	3.88	4.08	
GROUP III															
DB-6	Miss.	36	37		1.05	1.70	7.60	0.82	3	E	II	1.53	1.42	1.97	
DB-12	Ab	84			1.03	2.80	11.00	0.80	3	C	I	1.54	1.73	2.32	-30.31
LN-2	Miss.	108		0.292	1.02	1.12	4.30	0.80	3	C	I	1.41	1.52	1.98	
JE-1	Kc	114	29.1			8.40	26.00	0.76	3	C					-29.75
JE-2	Kc	114	38.4		1.03	2.40	19.00	0.89	3	C	I	1.59	1.68	2.24	-30.08
JE-3	Kc	114	29		1.07	4.40	19.00	0.81	3	C	I	1.25	1.46	0.99	-29.76
JB-1	Kc	126	42		1.03	4.70	31.00	0.87	3	C	I	1.52	1.70	2.12	-30.47
JB-2	Kc+Ab	126	38.6		1.04	10.90	48.00	0.82	3	C	I	1.52	1.75	2.32	
JB-3	Marm.	126	36.5	0.49	1.04	11.00	57.00	0.84	3	C	I	1.46	1.85	2.32	-30.21
UNDIFFERENTIATED															
RC-1	Miss.	12	38.5		1.09	0.24	0.46	-	-	F	I	1.35	1.40	1.79	-28.77
VB-1	Miss.	84		0.226	1.02	0.02	0.05	-	-	E	II	1.44	1.53	2.01	
RC-2	L-Kc	12	42		1.12	2.30	2.20	0.49	?	F	I	1.26	0.67	0.74	-29.35
DB-4	Morrow	30	43	0.187	1.04	1.10	2.60	0.70	?	E	II	1.71	2.53	3.04	-28.80
DB-5	Morrow	30	38	0.221	1.05	2.20	7.20	0.76	?	E	II	1.67	2.27	2.82	
DB-7	Kc	42	41	0.223	1.10	3.10	6.60	0.68	?	F	I	1.52	1.09	1.44	-29.07
DB-1	L-Kc	60	37		1.09	0.32	0.46	0.60	?	F	I	1.36	0.79	0.97	-29.43
DB-11	Simp	84			1.02	4.20	9.20	0.70	?	A	I	1.18	2.83	2.93	-30.31
DB-9	Miss.	96	36	0.318	1.02	0.24	0.72	0.75	?	C	I	1.56	1.55	2.15	
DB-8	Cke	102	35		1.05	2.00	2.50	0.56	?	C	I	1.59	1.73	2.42	
LN-1	Miss.	108		0.208	1.02	0.24	0.64	0.73	?	E	II	1.58	1.98	2.44	
DB-13	Cke	114	36.5		1.04	4.80	2.50	0.34	?	C	I	1.51	1.40	1.89	-30.24
DB-14	Cke	114	37	0.198	1.03	2.00	2.15	0.52	?	C	I	1.56	1.72	2.34	

Group III oils

Group III oils are characterized by moderately high V/(V+Ni) values (0.76 to 0.89), low $\delta^{13}C$ values (- 29.75 to - 30.47), high concentrations of both V and Ni (7.2 to 57.0 ppm V, and 1.7 to 11.0 ppm Ni), and the predominance of family I n- alkane distributions and type C isoprenoid trends. These oils have the highest sulphur contents (0.221 to 0.470 percent by weight) of any oils analyzed. The inclusion of two type E oils (DB- 5, Morrowan, V/(V+Ni) equal 0.76, and DB- 6, Mississippian, V/(V+Ni) equal 0.82) is questionable because of their low metal concentrations, unique isoprenoid and n- alkane distributions, and their lower northward distances. It is possible, although unlikely (Lewan, 1985), that a different source bed could generate the similar V/(V+Ni) values. These oils may belong to another distinct group of oils with V/(V+Ni) values nearer to 0.70 to 0.73, which is the range exhibited by other type E oils, whose V/(V+Ni) values overlap group III oils. At this point the groupings become most subjective and open to much interpretation. Another oil (JE- 1) exhibits low V/(V+Ni) and $\delta^{13}C$ values (0.76 and - 29.75) yet is like most group III oils in its n- alkane and isoprenoid distributions, metal concentrations, and northward displacement. This oil is the most severely biodegraded crude analyzed. The general relationship of increasing metal concentration with decreasing API gravity can be seen in this oil and two others from the same field (samples JE- 2 and JE- 3) with JE- 2 being the least biodegraded, JE- 3 moderately degraded, and JE- 1 the most severely degraded. Because JE- 1 is produced from the same field as other group III oils, and has matching n- alkane and isoprenoid distributions, it is included within group III oils.

Group III oils appear to fit into regime II based on the V/(V+Ni) ratios (greater than 0.50) and their relatively low sulfur contents (less than 0.50 percent in three of the oils). This implies these oils were generated from organic sediments which were deposited in the more acidic portions of regime II with little bacterially reduced sulfur present. This contrasts with group II oils which were probably generated from sediments deposited under the more basic portion regime II based on their lower V/(V+Ni) values.

The remaining ten oils, although not distinctive in their V/(V+Ni) values or other parameters investigated, fit within regime II. As previously mentioned, two group III oils exhibiting type E isoprenoid trends and family II n- alkane distributions (samples DB- 5 and DB- 6) may be associated with the remaining ungrouped type E oils (DB- 4, Morrowan, V/(V+Ni) equal 0.70, and LN- 1, Mississippian, V/(V+Ni) equal 0.73). The remaining eight oils are nondistinctive in their V/(V+Ni) ratios and may be complex mixtures of one or more other crudes.

Summary

Lewan (1984) in his discussion of regime II indicated that considerable variability in vanadium- nickel fractions may be expected not only from different rock units, but also from different facies of the same rock unit. This indicates that all of the V/(V+Ni) ratios seen in central Kansas crude oils could be generated from different zones or facies within the same marine rock unit, or from a variety of marine sources all deposited within regime II conditions. The nC_{17} /pristane and nC_{18} /phytane data (figure 37) also support a regime II source of moderately oxidizing unrestricted conditions during deposition of the source rocks. The similarities in the family I and family II n- alkane distributions, pristane/phytane ratios, isoprenoid distributions, and sulfur contents also support this hypothesis. However, it is impossible to determine if the variation seen in the V/(V+Ni) values and other geochemical parameters is due to multiple source beds all deposited under regime II conditions or due to hydrocarbons generated from several facies of a single source bed. The geographic distribution of the oils combined with the geochemical data may provide insight into the migration histories of the various oils and address the above question.

Migration And Source Area

Introduction

The section of sedimentary rocks in Kansas is relatively thin when compared to deeper basins, such as the Denver Basin to the west and the Anadarko Basin to the south. The maximum thickness of sedimentary rocks in Kansas within the Hugoton Embayment is only about 9,500 feet as compared to over 30,000 feet in the Anadarko Basin. The dip of Paleozoic strata in west- central Kansas are away from the Central Kansas Uplift and generally southward at no more than 10 degrees. The stratigraphy is relatively simple, consisting of thin beds of alternating sediments with limestone, shale, sandstone, and dolostone predominating. Geothermal gradients are relatively low and averag 1 to 2^0 f per 100 feet of depth. Although numerous organic rich shales are present in the subsurface, it is unlikely that these alone generated the large volumes of hydrocarbons found in western and central Kansas.

Crude oils are generated from organic- rich sediments by the processes of thermal maturation of bitumens. The temperature required for the onset of generation is modified by the effects of geological age and this effect has been included in the 'Oil Window' concept (figure 41) devised by Barker (1979). Source rocks in Kansas (based on an average geothermal gradient of 1- 2^0 f per 100 feet of depth) would have to be buried to a depth of 6,000 to 7,000 feet for a period of 150 million years to approach the initial stages of generation. After removal of the Permian and younger rocks, the depth of burial during the late Paleozoic is only on the order of 5,000 to 6,000 feet. At these depths it is extremely unlikely that the large volumes of hydrocarbons in western and central Kansas were derived exclusively from local sources. The presence of huge volumes of natural gas within the Hugoton Embayment (down dip from petroleum producing areas) may also support a theory of non- local sources. Such huge volumes of gas are generally associated with the thermal 'over- cooking' of organic- rich source rocks as the 'oil- window' is passed (figure 41). This thermal 'over- cooking' requires extreme depths of burial, well beyond the thickness of sedimentary rocks in Kansas.

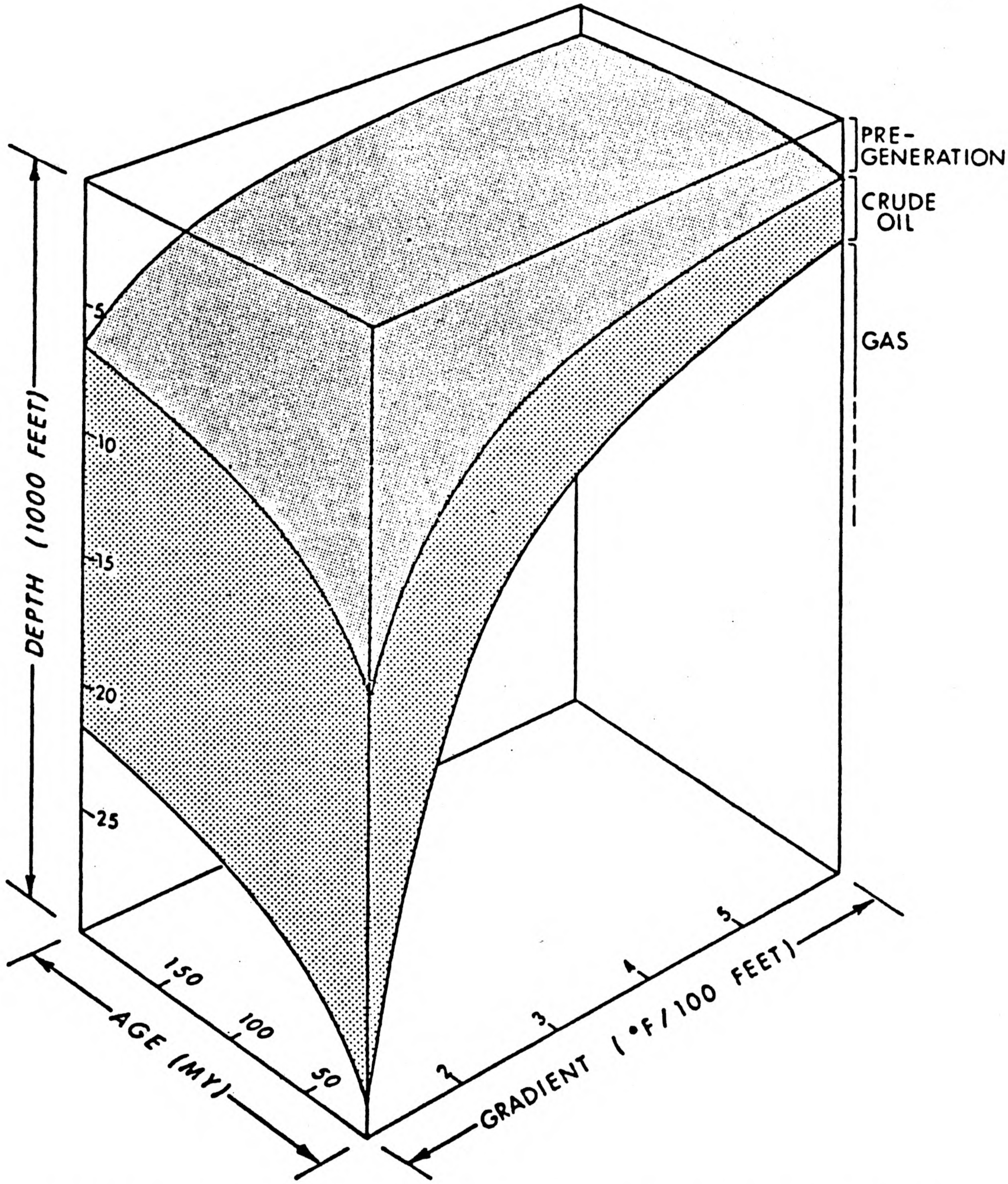


Figure 41. The generation and destruction of crude oil related to depth, age, and geothermal gradient. The top surface corresponds to oil generation and the bottom surface to destruction. Both boundaries represent gradational changes. After Barker (1979).

As local sources for the large hydrocarbon reserves in west and central Kansas seem unlikely, long distance lateral migration from outside areas is probable. Crude oils migrate mainly under the force of buoyancy updip to a reservoir (Waples, 1985). This updip migration tends to be normal to structural contours whenever possible. Regional hydraulic trends may modify the migration paths as will heterogeneity in the rock column; however, the general movement will be updip. Structural features such as faults, joints, and unconformities can provide excellent conduits for both lateral and vertical migration. Long distance migration of crude oils is relatively rare for several geological reasons; it occurs only in areas of stable tectonics where major but gentle downwarping has deposited a large thickness of source rocks,and has provided carrier beds as continuous blankets as conduits (Waples,1985). Historically, several occurrences of long distance migration are associated with the largest accumulations known, such as the Atha- Basca Tar Sands of Western Canada, heavy oils of the Orinoco Belt in Venezuela, and the Saudi Arabian accumulations.

Throughout the Paleozoic, regional dips were to the south in the general direction of the Anadarko Basin of Oklahoma, where large petroleum accumulations occur. These southward paleo- dips tend to eliminate Paleozoic migration from other basinal areas such as the Denver basin to the northwest as does the lack of substantial thicknesses of sediments to the north and east of Central Kansas. Probable source rocks such as the organic rich Woodford Shale have been well studied in the literature and the Woodford in particular is presumed to be the source for many Oklahoma crude oils (Williams, 1986).

Walters (1958) concluded that crude oils within the Arbuckle Group in Central Kansas migrated northward up dip from the Anadarko Basin and were differentially entrapped, because gas is found in structurally lower reservoirs (to the south) than oil, and water is found in some of the structurally highest reservoirs to the north (such as the Ellsworth Anticline, Ellsworth County). He also suggested that the Central Kansas Uplift acted as a barrier to oils migrating northward (in Permian time) in Arbuckle rocks as no Arbuckle production is found within the Salina Basin, to the north and east of the uplift. Geochemical data tend to support a southern source for the crude oils in Central Kansas as geographic trends (of south to north) exist in many of the parameters investigated (V and Ni contents , API gravities, sulfur contents, $\delta^{13}C$ values, and nC_{17} /pristane nC_{18} /phytane ratios.

The spatial distribution of oil types seems to suggest that either the oils were generated and accumulated at geologically different times, or they were generated at nearly the same time but followed different migration paths to the reservoir. These two models may be called 'time- pulse' and 'facies- pulse', respectively.

Time- Pulse Model

The "time- pulse" mechanism is most easily viewed as several source beds of various ages being buried within the Anadarko Basin. The oldest bed (bed 1) will reach the 'oil-window' first, and its associated oils will begin a first pulse of secondary migration. Successively younger source beds will reach the 'oil- window' at later times and their associated oils will migrate at progressively later times. This pattern of successive pulses of oil will continue until subsidence ceases or the availability of source beds is removed. According to the process of differential entrapment, oils generated in the first pulse will tend to accumulate in the lower most traps. Oils generated from beds reaching the 'oil window' at later times will bypass the lower most traps, already filled with pulse 1 oils, and move updip to the next available traps (figure 1). Under ideal conditions, crude oils trapped furthest from the basin will be the youngest oils, and those in the deepest traps (furthest from basinal margins) will be among the oldest oils.

Facies- Pulse Model

A similar effect may be produced by several generating facies of a single widely distributed source bed or by several beds scattered throughout the basin. In a "facies-pulse" mechanism, facies of a single source bed nearest the basinal axis will subside most quickly and reach the 'oil- window' first. Their associated oils will accumulate into the nearest available traps. Successive facies or beds nearer basinal margins will mature more slowly and reach the 'oil- window' at progressively later times. Oils generated from these facies or beds will be forced to migrate past the lower most traps (already filled) to the next available traps.

Summary

Either mechanism described above may result in the oils being differentially entrapped as applied to Arbuckle oils by Walters (1958). Witherspoon and Nagashima (1957) working in the Illinois Basin suggested that older crudes tend to have lower metal contents than younger oils. Similarly Hodgson (1957) noticed older oils in the West Canada Basin had lower metal contents than younger oils. Applying this principle to crude oils in west- central Kansas, type C oils which exhibit the highest metal contents and are located furthest from the basin (furthest north) may be the youngest oils in the region.

This is in agreement with the lower maturity of type C oils as indicated from the nC_{17} /pristane and nC_{18} /phytane data illustrated in figure 37. Type A oils which exhibit the lowest overall metal contents are located in deeper (more southern) traps and may be some of the oldest oils in the region. These older oils also appear to be the most mature oils based upon nC_{17} /pristane and nC_{18} /phytane data (figure 37). Type E oils, produced from intermediate depth traps, may then be of intermediate age. Type F oils, while interpreted to be of intermediate to low maturity from nC_{17} /pristane, nC_{18} /phytane data, are located in the deepest most southern traps in the region. This may indicate they accumulated before the more mature type A oils, or that type A oils simply bypassed these deeper traps which were later filled by type F oils.

Migration histories in Central Kansas are extremely complex due to the large number of possible source beds available, long times involved, myriads of possible migration paths (numerous available carrier beds, unconformities, faults, etc.), lack of sufficient barrier beds, horizontal rocks, low relief traps, thin oil columns, continuous reservoir porosity and permeability (Walters, 1958), probable long migration distances involved, and multiple directions of regional tilting throughout geologic time to mention a few. However, a southern source for the oils seems most probable and a mode of accumulation by differential entrapment seems likely.

CONCLUSION

Geochemical analysis of 28 Central Kansas crude oils indicate the oils are light (API gravities between 29.0 and 47.0) relatively unaltered crudes of low (less than 0.5 percent) sulfur content. Several oils exhibit evidence of slight degrees of microbial degradation and these oils are almost always associated with reduced brine water salinities. Specific geochemical analyses indicate the oils were generated from mostly marine dominated sources deposited under Lewan's (1984) regime II conditions.

Chromatographic analyses indicate the presence of two general families of oils. Family I oils are slightly enriched in light normal alkanes with n- alkane peaks in the nC_7 to nC_9 range, whereas family II oils exhibit n- alkane peaks in the nC_{14} to nC_{17} range. Analysis of normalized concentrations of regular isoprenoids (isoprenoid trends) iP- 13, iP- 14, iP- 15, iP- 16, iP- 18, iP- 19 (pristane), and iP- 20 (phytane) appears to be the most sensitive parameter as three and possibly up to four individual oil types are recognized (types A, C, E, F). Type E oils are unique to family II n- alkane distributions whereas type A, C, and F oils are associated with family I distributions.

Analysis of carbon isotopic data indicates a small but significant variation in the $\delta^{13}C$ values in crude oils from western and central Kansas from a low of - 30.47 per mil to a high of - 28.77 per mil. The $\delta^{13}C$ values exhibit a negative relationship with the northward distance (figure 23). This distribution may indicate a simple mixing model involving two end- members and suggests as few as two different oils in the region. However, this seems unlikely as variation in other geochemical parameters can not be explained by simple mixing of two isotopically different oils. The negative relationship between $\delta^{13}C$ value and northward distance (figure 23) is most likely due to the geographic distribution of low $\delta^{13}C$ value oils in the northern regions (type C oils) and high $\delta^{13}C$ value oils in the southern regions (predominantly type A and F oils).

V/(V+Ni) ratios suggest the presence of at least three related oil groups. Group I oils are enriched in V relative to Ni (up to 15 ppm V and 0.4 ppm Ni respectively) with V/(V+Ni) values between 0.90 and 0.98 and include only type C oils. They are produced from Mississippian reservoirs. Group II oils are greatly depleted in both metals (V less than 0.5 ppm and Ni less than 1.3 ppm) with maximum V/(V+Ni) values between 0.19 and 0.28 and include type A and Foils. Group II oils are produced from the Middle Pennsylvanian Morrowan Sandstone and Upper Pennsylvanian Douglas Group. Group III oils are enriched in both metals (up to 57 ppm V and 11 ppm Ni) with V/(V+Ni) values between 0.76 and 0.89 and include mainly type C oils with minor questionable amounts of type E oils. They are produced mainly from the Upper Pennsylvanian Lansing- Kansas City groups with the Middle Pennsylvanian Marmaton and Morrowan groups, Mississippian reservoirs, and Upper Cambrian Arbuckle Group also represented. Analysis of the above geochemical parameters indicates that a minimum of two (from $\delta^{13}C$ data) to as many as four different oils (from isoprenoid analysis) exist in Central Kansas.

Stratigraphic relations tend to suggest that the oils accumulated before the close of Permian time (Walters, 1958). Based on the 'oil- window' concept (Barker, 1979), local generation of the large volumes of hydrocarbons in western and central Kansas seems unlikely given the low geothermal gradients in the region (1 to 2^0 f per 100 feet of depth) and the relatively shallow thickness of Paleozoic sediments (less than 6,500 feet). Analysis of collected oils indicates little to no relationship between crude oil composition and producing zone. Distribution of related oils is spatial in a south to north orientation, suggesting evidence for a northward up- dip migration of oils generated within the Anadarko Basin of Central Oklahoma, and a mode of accumulation by differential entrapment, both suggested by Walters (1958).

This preliminary study suggests that southern oils (predominantly types A and F) may be the oldest and most mature oils in the region, whereas northern oils (exclusively type C) appear to be of younger origin and lesser maturity. The spatial relationships are most easily explained by differential entrapment of several oil types generated from different source beds at geologically different times ('time- pulse'), or generated from different facies of the same source bed and following different migration paths ('facies-pulse'), or a combination of both.

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APPENDIX A

Statistical Analysis

		Linear Regression Analysis					
							significance
Parameter	n	b	m	r	to	t	level
API vs distance	23	41.07	-0.004	-0.47	2.44	2.39	2.50%
S vs distance	12	0.13	0.001	0.54	2.03	1.78	10%
delta 13C vs distance	16	-28.99	-0.19	-0.87	6.6	4.02	0.10%
V vs distance	28	0.29	5.32	0.52	3.1	3.05	0.50%
Ni vs distance	28	1.09	0.88	0.42	2.36	2.05	5.00%
V/(V+Ni) vs distance	26	0.52	0.078	0.54	3.14	3.07	0.50%
V vs Ni	26	5.61	4.67	0.88	9.08	3.71	0.10%
S vs API gravity	9	0.78	-0.16	-0.61	2.04	1.83	10%
V vs API gravity	23	23.78	-19.5	-0.21	0.98	0.86	40%
Ni vs API gravity	23	6.35	-5.31	-0.28	1.34	1.32	20%
V/(V+Ni) vs API gravity	22	0.93	-0.36	-0.28	1.3	0.86	40%
nC17/pris vs distance	25	1.8	-0.003	-0.01	0.05		<50%
nC18/phy vs distance	25	2.2	-0.001	-0.04	0.05		<50%
delta 13C vs V/(V+Ni)	15	-6.2	-0.23	-0.56	2.44	2.145	5%
Group I Oils							
API vs distance	3	42	-0.04	-0.97	3.99	2.92	10%
V vs distance	3	-7.5	0.14	0.25	0.26	0.81	<50%
Group II Oils							
API vs distance	3	33.75	0.27	0.73	1.07	1.06	40%
Ni vs distance	3	2.4	-0.03	-0.99	7.02	6.21	2.50%
delta 13C vs distance	2	-28.93	-0.005	-0.99			
delta 13C va API	2	-33.43	0.12	1			
Group III Oils							
API vs distance	7	35.4	0.003	0.02	0.04	0.72	<50%
Ni vs distance	9	-2.6	0.07	0.56	1.79	1.39	20%
V vs distance	9	-15.9	0.39	0.52	1.61	1.39	20%
delta 13C vs distance	6	-30.15	0.0005	-0.02	0.04	0.73	<50%
delta 13C vs V/(V+Ni)	6	-27.2	-3.4	-0.56	1.35	0.92	40%
Type A Oils							
Ni vs distance	3	-0.96	0.06	0.99	7.02	6.21	2.50%
V vs distance	3	-6.1	0.18	0.99	7.02	6.21	2.50%
Type C Oils							
API vs distance	14	37.7	-0.008	-0.61	2.67	2.53	2.50%
Ni vs distance	16	-3.3	0.65	0.49	2.1	1.75	10%
V vs distance	16	-17.09	0.31	0.49	2.1	1.75	10%
delta 13C vs distance	9	-28.8	-0.01	-0.82	3.79	3.35	1.00%
delta 13C vs API	8	-29	-0.026	-0.22	0.55	0.71	<50%
delta 13C vs V/(V+Ni)	8	-30.1	-0.06	-0.04	0.1	0.71	<50%

		Linear Regression Analysis (cont'd)					
Parameter	**n**	**b**	**m**	**r**	**to**	**t**	**level**
Type E Oils							
API vs distance	3			-0.63	0.81	0.82	<50%
Ni vs distance	4	0.23	-0.02	-0.84	2.19	1.64	20%
V vs distance	4	7.8	-0.07	-0.72	1.47	0.98	40%
Type F Oils							
API vs distance	4	40.3	-0.03	-0.29	0.43	0.77	<50%
Ni vs distance	4	2.7	-0.02	-0.5	0.82	0.77	40%
V vs distance	4	1.85	0.018	0.14	0.2	0.77	<50%
delta 13C vs distance	5	-29.1	-0.003	-0.42	0.8	0.74	40%
delta 13C va API	4	-28.9	-0.007	-0.08	0.11	0.77	<50%
delta 13C vs V/(V+Ni)	4	-28.9	-0.46	-0.46	0.73	0.77	<50%

				ANALYSIS OF VARIANCE							
	Arb.					L-Kc					sig.
Parameter	+ Simp	Miss.	Morrow	Cke	Marm.	+ Dg	Fx	V1	V2	Fo	level
API vs Zone											
mean=	38.6	37.3	42	36.2	36.5	36.9					
std. dev.=	0	0.65	11.5	0.72	0	24.3					
n=	1	6	4	3	1	8	1.22	5	17	1.47	<25%
V vs zone											
mean=	22.7	3.94	2.68	2.38	57	13.09					
std. dev.=	319.7	20.3	7.57	0.03	0	129.6					
n=	3	9	4	3	1	8	6.95	5	22	4.61	0.50%
Ni vs zone											
mean=	5.97	0.51	1.45	2.93	11	3.45					
std. dev.=	12.5	0.25	0.19	1.74	0	5.18					
n=	3	9	4	3	1	8	7.82	5	22	4.61	0.50%
V/(V+Ni) vs zone											
mean=	0.77	0.84	0.5	0.47	0.84	0.66					
std. dev.=	0.003	0.007	0.05	0.01	0	0.05					
n=	3	7	4	3	1	8	2.92	5	20	2.16	10.00%
			Family I		Family II						
Family vs API											
mean=			37.63		39.33						
std. dev.=			15.33		6.89						
n=			20		3		0.49	1	21		<25%
Family vs distance											
mean=			83.2		57.6						
std. dev.=			1542.2		1045.4						
n=			22		5		1.7	1	25	1.39	75%
Family vs V/(V+Ni)											
mean=			0.68		0.75						
std. dev.=			0.04		0.002						
n=			22		4		0.4	1	24		<25%

				ANALYSIS OF VARIANCE (cont'd)							
		Type /	Type C	Type	Type F						sig.
delta 13C vs type							Fx	V1	V2	Fo	level
mean=		-29.71	-30.14	-28.8	-29.12						
std. dev.=		0.36	0.06	0	0.06						
n=		2	8	1	5		10.8	3	11	7.6	0.50%
V/(V+Ni) vs type											
mean=		0.41	0.77	0.75	0.49						
std. dev.=		0.04	0.03	0.002	0.03						
n=		3	15	4	4		5.4	3	22	3.78	2.50%
API vs type											
mean=		43.5	36.2	39.3	39.1						
std. dev.=		12.25	11.8	6.89	4.24						
n=		2	13	3	5		3.32	3	19	2.4	10.00%
Type vs distance											
mean=		52	110	57.6	27.6						
std. dev.=		512	147.2	1045	397.4						
n=		3	15	5	5		23.4	3	24	5.52	0.50%
	Group I		Group II		Group III						
delta 13C vs group											
mean=	-30.3		-29.05		-30.1						
std. dev.=	0		0.004		0.072						
n=	1		2		6		12.6	2	6	9.33	10%
distance vs group											
mean=	104		28		97.8						
std. dev.=	104		128		1188						
n=	3		3		10		6.44	2	13	3.39	75%
API vs group											
mean=	37.3		41.3		36.1						
std. dev.=	0.22		17.6		18.8						
n=	3		3		10		1.63	2	11		<25%
V vs group											
mean=	7.1		0.46		23.01						
std. dev.=	31.22		0		286.6						
n=	3		3		10		3.19	2	13		<25%
Ni vs group											
mean=	0.28		1.5		4.96						
std. dev.=	0.003		0.013		12.8						
n=	3		3		10		3.26	2	13		<25%

LSD TESTS (comparison of sample means)					
Parameter	X1-X2	LSD	significance level	Pooled ss	df
delta 13C vs type				0.124	12
type C vs type F	1.02	0.61	1%		
type C vs type E	1.34	1.14	1%		
type A vs type C	0.43	0.38	10%		
type A vs type E	0.91	0.76	10%		
type A vs type F	0.59	0.52	10%		
type E vs type F			<20%		
V/(V+NI) vs type				0.031	22
type A vs type C	0.36	0.32	1%		
type A vs type E	0.34	0.28	5%		
type C vs type F	0.28	0.21	5%		
type E vs type F	0.26	0.26	5%		
type A vs type F			<20%		
type C vs type E			<20%		
API gravity vs type				11.56	19
type A vs type C	7.3	5.41	5%		
type A vs type E	4.2	4.12	20%		
type A vs type F	4.4	3.77	20%		
type C vs type E	3.1	2.89	20%		
type C vs type F	2.9	2.37	20%		
type E vs type F			<20%		
Distance vs type				456.6	24
type A vs type C	58	37.7	1%		
type C vs type E	52.4	30.8	1%		
type C vs type F	82.4	30.8	1%		
type E vs type F	30	27.9	5%		
type A vs type F	24.4	20.5	20%		
type A vs type E			<20%		
delta 13C vs group				456.6	11
group I vs group II	1.25	1.23	1%		
group II vs group III	1.91	0.81	1%		
group I vs group III	0.24		<20%		

APPENDIX B

Gas Chromatographic Data

Analysis:6 DB1KSU.1.1
Reported on 01-Jul-86 at 21:01

M U L T I C H R O M V3.2

Analyst Name : Analysis ID:
Information :

METHOD FILE FOR GEOCHEM RESEARCH

Channel:6 Title: CHANNEL 6 Date 28-Jan-86 Time 8:21
Analysis:DB1KSU Sample Name:01-28-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
41	6.801	6.789	234084	330562	0.958	NC7
43	7.154	7.141	312092	534365	1.548	MCHX
186	14.503	14.477	147867	234238	0.679	IP13
200	15.202	15.175	129189	201871	0.585	IP14
225	16.371	16.341	115577	177023	0.513	IP15
243	17.277	17.245	138482	250580	0.726	IP16
250	17.641	17.609	179271	370410	1.073	NC15
277	19.118	19.083	139001	262848	0.761	IP18
285	19.562	19.527	159708	300622	0.871	NC17
287	19.663	19.628	199796	365153	1.058	PRIST
299	20.449	20.412	143258	283940	0.822	NC18
301	20.578	20.541	147302	273755	0.793	PHYT
314	21.296	21.257	151743	346874	1.005	NC19
327	22.100	22.060	135537	245405	0.711	NC20
372	24.976	24.930	76482	141181	0.409	NC24
382	25.622	25.576	69035	195329	0.566	NC25
392	26.242	26.195	57506	115062	0.333	NC26
401	26.840	26.791	52299	135162	0.392	NC27
410	27.416	27.366	45604	98868	0.286	NC28
417	27.973	27.923	51723	138225	0.400	NC29
426	28.507	28.455	37108	92643	0.268	NC30
Residual			15017450	29428290	85.244	
Total			17740160	34522390	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 DB2KSU.1.1
Reported on 22-Jul-86 at 10:20

MULTICHROM V3.2

Analyst Name :   Analysis ID:
Information :

METHOD FILE FOR GEOCHEM RESEARCH

Channel:6 Title: CHANNEL 6   Date 28-Jan-86 Time 9:20
Analysis:DB2KSU   Sample Name:01-28-86/000213.3/50 Sample ID: 0   Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
28	6.823	6.820	508149	1019694	2.996	NC7
29	7.164	7.161	436672	757160	2.225	MCHX
167	14.522	14.518	66761	97386	0.286	IP13
181	15.218	15.214	68486	109186	0.321	IP14
204	16.378	16.374	51601	79645	0.234	IP15
222	17.279	17.275	76009	132491	0.389	IP16
230	17.661	17.657	257828	516728	1.518	NC15
258	19.116	19.111	49483	86379	0.254	IP18
266	19.580	19.576	226149	420150	1.235	NC17
268	19.657	19.652	78191	126228	0.371	PRIST
283	20.458	20.453	155436	265129	0.779	NC18
285	20.571	20.567	47248	82937	0.244	PHYT
311	22.104	22.100	118095	195589	0.575	NC20
358	24.980	24.980	71034	125285	0.368	NC24
368	25.627	25.628	67265	133583	0.393	NC25
375	26.249	26.251	55316	112321	0.330	NC26
382	26.847	26.850	47004	95812	0.282	NC27
391	27.422	27.426	41491	91189	0.268	NC28
399	27.976	27.980	39454	82576	0.243	NC29
406	28.513	28.519	30859	70772	0.208	NC30
Residual			17359240	29431460	86.482	
Total			19851790	34031700	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 DB3 .1 .1
Reported on 12-May-86 at 13:06 Page 1

MULTICHROM V3.2

Analysis ID:

Analyst Name :
Information :

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Channel:6 Title: CHANNEL 6 Date 26-Mar-86 Time 11:22
Sample Name:03-26-86/000213.3/50 Sample ID: 0 Bottle:1
Analysis:DB3
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
32	6.640	6.646	528399	1004425	3.673	NC7
35	6.962	6.968	443570	725954	2.654	MCHX
171	14.294	14.307	53417	79423	0.290	IP13
186	15.001	15.014	49029	82203	0.301	IP14
208	16.173	16.187	39042	57839	0.211	IP15
226	17.079	17.094	61890	105884	0.387	IP16
233	17.464	17.480	253739	478492	1.750	NC15
262	18.919	18.935	36841	61994	0.227	IP18
270	19.382	19.399	212705	394792	1.443	NC17
271	19.458	19.475	56888	90191	0.330	PRIST
287	20.258	20.275	133156	214522	0.784	NC18
289	20.370	20.388	33598	56149	0.205	PHYT
320	21.901	21.920	93863	139026	0.508	NC20
377	24.774	24.796	41983	64621	0.236	NC24
388	25.422	25.444	38035	52068	0.190	NC25
398	26.044	26.067	26567	41457	0.152	NC26
409	26.644	26.667	20913	27405	0.100	NC27
419	27.221	27.245	16877	24933	0.091	NC28
428	27.779	27.803	13742	20275	0.074	NC29
437	28.317	28.341	9962	14252	0.052	NC30
Residual			15239460	23614000	86.340	
Total			17401760	27349900	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 DB4 .1 .1
Reported on 12-May-86 at 13:07

Page 1

MULTICHROM V3.2

Analyst Name :
Analysis ID:
Information :

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Channel:6 Title: CHANNEL 6 Date 26-Mar-86 Time 12:43
Analysis:DB4 Sample Name:03-26-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
28	6.653	6.654	389977	632637	1.747	NC7
29	6.987	6.987	469267	803821	2.220	MCHX
166	14.304	14.305	72682	109772	0.303	IP13
181	15.011	15.012	74376	128808	0.356	IP14
203	16.184	16.185	64060	100755	0.278	IP15
221	17.093	17.094	103568	1[illegible]393	0.509	IP16
229	17.483	17.484	340475	743214	2.052	NC15
261	18.934	18.935	71583	126943	0.351	IP18
269	19.404	19.405	303852	689782	1.905	NC17
270	19.478	19.479	120430	201344	0.556	PRIST
286	20.278	20.279	213178	419936	1.160	NC18
298	20.384	20.385	70973	124255	0.343	PHYT
317	21.919	21.920	166468	300782	0.831	NC20
377	24.788	24.789	100775	189049	0.522	NC24
387	25.433	25.435	93512	180276	0.498	NC25
398	26.057	26.058	80861	170849	0.472	NC26
409	26.657	26.658	69737	111654	0.308	NC27
418	27.232	27.234	59494	126244	0.349	NC28
429	27.789	27.790	52589	113582	0.314	NC29
438	28.326	28.327	41392	86731	0.240	NC30
Residual			16860460	30666850	84.688	
Total			19819720	36211680	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 DBS ,1 ,1
Reported on 12-May-86 at 13:09

M U L T I C H R O M V3.2

Analyst Name : Analysis ID:
Information :

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Channel:6 Title: CHANNEL 6 Date 26-Mar-86 Time 13:35
Analysis:DBS Sample Name:03-26-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
28	6.652	6.650	329610	490614	1.282	NC7
29	6.986	6.983	424525	690647	1.804	MCHX
163	14.309	14.304	81197	126099	0.329	IP13
175	15.017	15.011	88567	157320	0.411	IP14
197	16.190	16.184	76756	121552	0.318	IP15
216	17.098	17.092	117790	218130	0.570	IP16
224	17.487	17.480	357077	790354	2.065	NC15
255	18.938	18.931	84051	176022	0.460	IP18
263	19.408	19.401	316365	739924	1.933	NC17
264	19.482	19.475	139993	245576	0.642	PRIST
280	20.284	20.277	234221	454276	1.187	NC18
282	20.390	20.383	83440	146001	0.381	PHYT
312	21.928	21.920	194531	366221	0.957	NC20
370	24.800	24.791	124565	241398	0.631	NC24
382	25.448	25.439	115653	237292	0.620	NC25
392	26.070	26.061	103324	224635	0.587	NC26
403	26.670	26.661	95007	154896	0.405	NC27
413	27.246	27.236	79427	171722	0.449	NC28
421	27.802	27.792	73170	152221	0.398	NC29
432	28.338	28.328	57457	118057	0.308	NC30
Residual			16955320	32255110	84.265	
Total			20132050	38278070	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 DB6KSU.1.1
Reported on 01-Jul-86 at 21:00

MULTICHROM V3.2

Analyst Name :
Analysis ID:
Information :

METHOD FILE FOR GEOCHEM RESEARCH

Channel:6 Title: CHANNEL 6 Date 30-Jan-86 Time 14:02
Analysis:DB6KSU Sample Name:01-30-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
28	6.727	6.716	124870	153636	0.433	NC7
29	7.069	7.057	248764	347518	0.979	MCHX
167	14.442	14.418	115486	178750	0.504	IP13
182	15.153	15.128	121452	208691	0.588	IP14
203	16.333	16.306	111945	178494	0.503	IP15
222	17.248	17.219	152933	305690	0.861	IP16
228	17.631	17.602	316242	718871	2.025	NC15
256	19.098	19.066	121971	250985	0.707	IP18
265	19.560	19.528	266191	613457	1.728	NC17
266	19.644	19.612	187588	340874	0.960	PRIST
282	20.448	20.414	241683	516884	1.456	NC18
284	20.559	20.525	122505	224180	0.632	PHYT
297	21.293	21.258	228057	519918	1.465	NC19
314	22.097	22.060	209989	410135	1.156	NC20
365	24.972	24.931	126457	247210	0.697	NC24
375	25.619	25.576	116416	217841	0.614	NC25
386	26.242	26.199	99799	195645	0.551	NC26
398	26.840	26.795	87225	192427	0.542	NC27
408	27.417	27.371	76421	176527	0.497	NC28
418	27.972	27.926	69233	142542	0.402	NC29
426	28.508	28.460	51368	112460	0.317	NC30
Residual			14268670	29238500	82.382	
Total			17465320	35491220	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 DB7 ,1 ,1
Reported on 12-May-86 at 13:10

MULTICHROM V3.2

Analyst Name :
Information :

Analysis ID:

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Channel:6 Title: CHANNEL 6 Date 26-Mar-86 Time 14:27
Analysis:DB7 Sample Name:03-26-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
33	6.679	6.679	458463	783062	1.731	NC7
36	7.013	7.013	526216	1086644	2.402	MCHX
178	14.319	14.318	126183	220481	0.487	IP13
192	15.022	15.021	105048	183513	0.406	IP14
213	16.194	16.194	97296	148353	0.328	IP15
234	17.101	17.100	119102	222271	0.491	IP16
242	17.472	17.471	213468	446692	0.987	NC15
270	18.940	18.939	114234	216623	0.479	IP18
278	19.390	19.389	179241	338379	0.748	NC17
280	19.482	19.481	164836	284872	0.630	PRIST
295	20.274	20.273	155283	324960	0.718	NC18
297	20.393	20.392	108298	191557	0.423	PHYT
329	21.921	21.920	141625	244534	0.541	NC20
384	24.794	24.793	78145	142613	0.315	NC24
395	25.442	25.441	72026	124089	0.274	NC25
408	26.067	26.065	59913	111184	0.246	NC26
421	26.667	26.665	55782	87262	0.193	NC27
431	27.244	27.243	46573	108006	0.239	NC28
439	27.802	27.801	49529	107712	0.238	NC29
449	28.340	28.339	37363	80600	0.178	NC30
Residual			22231640	39782220	87.944	
Total			25140270	45235630	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 DB8KSU.1.1
Reported on 18-Jul-86 at 16:56

M U L T I C H R O M V3.2

Analyst Name : Analysis ID:
Information :

METHOD FILE FOR GEOCHEM RESEARCH

Channel:6 Title: CHANNEL 6 Date 30-Jan-86 Time 14:56
Analysis:DB8KSU Sample Name:01-30-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
38	6.747	6.750	349631	553973	2.213	NC7
41	7.072	7.075	207898	286065	1.143	MCHX
178	14.448	14.447	95831	141799	0.567	IP13
192	15.154	15.153	88476	138721	0.554	IP14
214	16.332	16.330	73598	108587	0.434	IP15
233	17.243	17.241	97677	169766	0.678	IP16
239	17.623	17.620	242416	483198	1.931	NC15
265	19.091	19.087	75505	140280	0.560	IP18
273	19.549	19.545	191754	345799	1.382	NC17
275	19.632	19.628	110572	175289	0.700	PRIST
292	20.436	20.431	168406	295594	1.181	NC18
294	20.549	20.544	69691	115343	0.461	PHYT
323	22.086	22.080	142419	231745	0.926	NC20
377	24.964	24.960	82052	130848	0.523	NC24
388	25.613	25.609	77092	112244	0.448	NC25
398	26.237	26.233	64121	110354	0.441	NC26
410	26.837	26.833	52703	76660	0.306	NC27
420	27.413	27.410	46844	79406	0.317	NC28
430	27.970	27.967	40732	69874	0.279	NC29
438	28.508	28.505	29703	56118	0.224	NC30
Residual			12040010	21207320	84.731	
Total			14347130	25028980	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 DB9 ,1 ,1
Reported on 12-May-86 at 13:51

MULTICHROM V3.2

Analysis ID:

Analyst Name :
Information :

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Channel:6 Title: CHANNEL 6 Date 26-Mar-86 Time 15:23
Analysis:DB9 Sample Name:03-26-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
26	6.698	6.693	404016	640240	1.583	NC7
27	7.016	7.011	271806	382735	0.946	MCHX
165	14.326	14.315	132714	212548	0.525	IP13
179	15.029	15.018	121559	216848	0.536	IP14
200	16.200	16.189	109992	168868	0.417	IP15
220	17.109	17.097	138863	284816	0.704	IP16
227	17.490	17.478	314716	717167	1.773	NC15
254	18.947	18.933	111533	225984	0.559	IP18
263	19.406	19.392	251541	556666	1.376	NC17
264	19.489	19.475	161997	282903	0.699	PRIST
281	20.289	20.275	230941	456278	1.128	NC18
283	20.400	20.386	107596	192880	0.477	PHYT
315	21.936	21.920	195691	369624	0.914	NC20
369	24.807	24.789	122719	228331	0.565	NC24
380	25.454	25.436	109611	258783	0.640	NC25
391	26.077	26.058	97815	223104	0.552	NC26
404	26.676	26.657	82189	135807	0.336	NC27
415	27.253	27.234	72224	164261	0.406	NC28
424	27.809	27.789	65006	136864	0.338	NC29
435	28.346	28.325	52455	116417	0.288	NC30
Residual			17848950	34477260	85.238	
Total			21003930	40448390	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 DB10 ,1 ,1
Reported on 12-May-86 at 14:28

MULTICHROM V3.2

Analyst Name :
Analysis ID:
Information :

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Channel:6 Title: CHANNEL 6 Date 26-Mar-86 Time 16:47
Analysis:DB10 Sample Name:03-26-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
41	6.678	6.674	353476	533760	1.463	NC7
42	7.003	6.999	333333	497910	1.365	MCHX
177	14.316	14.307	99585	155200	0.425	IP13
190	15.022	15.013	94275	161831	0.444	IP14
211	16.196	16.186	89821	128761	0.353	IP15
231	17.103	17.093	108191	216925	0.595	IP16
238	17.481	17.470	259904	530314	1.454	NC15
267	18.943	18.932	89788	183234	0.502	IP18
276	19.401	19.389	217222	421334	1.155	NC17
278	19.483	19.471	129204	223450	0.613	PRIST
294	20.286	20.273	194455	410603	1.126	NC18
296	20.398	20.385	88934	161326	0.442	PHYT
328	21.933	21.920	179563	318732	0.874	NC20
383	24.806	24.790	110740	210366	0.577	NC24
394	25.454	25.439	103461	188333	0.516	NC25
405	26.077	26.061	90109	215253	0.590	NC26
416	26.676	26.659	78862	130892	0.359	NC27
426	27.252	27.236	71034	177058	0.485	NC28
437	27.810	27.793	64320	155337	0.426	NC29
446	28.346	28.328	53550	121080	0.332	NC30
Residual			16483810	31338280	85.905	
Total			19284650	36479960	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 DB11KSU,1,1
Reported on 01-Jul-86 at 21:15

M U L T I C H R O M V3.2

Analyst Name :   Analysis ID:
Information :

METHOD FILE FOR GEOCHEM RESEARCH

Channel:6 Title: CHANNEL 6   Date 30-Jan-86 Time 15:55
Analysis:DB11KSU   Sample Name:01-30-86/000213.3/50 Sample ID: 0   Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
28	6.770	6.762	69188	87353	0.342	NC7
29	7.137	7.128	521516	1000931	3.919	MCHX
171	14.460	14.443	75688	111556	0.437	IP13
188	15.164	15.146	65830	104976	0.411	IP14
208	16.340	16.320	55801	82468	0.323	IP15
227	17.248	17.227	69661	119742	0.469	IP16
233	17.623	17.602	174297	333725	1.307	NC15
260	19.093	19.070	45733	79522	0.311	IP18
269	19.549	19.525	158655	263694	1.032	NC17
271	19.631	19.607	56102	93500	0.366	PRIST
288	20.437	20.412	139565	232652	0.911	NC18
290	20.551	20.526	47660	80969	0.317	PHYT
303	21.283	21.258	135552	236123	0.925	NC19
321	22.087	22.060	125481	196200	0.768	NC20
375	24.968	24.938	71812	112658	0.441	NC24
386	25.614	25.584	66777	95483	0.374	NC25
398	26.238	26.206	57934	86488	0.339	NC26
410	26.838	26.805	45306	64309	0.252	NC27
421	27.416	27.382	40240	63556	0.249	NC28
430	27.972	27.938	34727	58656	0.230	NC29
438	28.511	28.477	26685	46275	0.181	NC30
Residual			13760590	21988700	86.097	
Total			15844800	25539540	100.000	

Sample Type: SA   Scale Factor: 1.000   Amount: 1.000
Method: METH2   Calibration: CAL3   Type: UC   Using:Area

Analysis:6 DB12KSU.1.1
Reported on 18-Jul-86 at 17:24

Page 1

MULTICHROM V3.2

Analyst Name : Analysis ID:
Information :

METHOD FILE FOR GEOCHEM RESEARCH

Channel:6 Title: CHANNEL 6 Date 30-Jan-86 Time 16:51
Analysis:DB12KSU Sample Name:01-30-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
28	6.806	6.790	347616	541036	2.181	NC7
30	7.144	7.129	390344	641261	2.585	MCHX
167	14.470	14.459	90582	135109	0.545	IP13
182	15.173	15.163	85378	132110	0.532	IP14
204	16.346	16.336	67875	98796	0.398	IP15
223	17.252	17.243	83379	145142	0.585	IP16
230	17.630	17.621	199460	387549	1.562	NC15
256	19.097	19.088	62408	116050	0.468	IP18
264	19.550	19.542	161616	272656	1.099	NC17
266	19.637	19.629	93344	145406	0.586	PRIST
283	20.438	20.430	140344	232404	0.937	NC18
285	20.552	20.545	60543	98393	0.397	PHYT
315	22.087	22.080	118873	188460	0.760	NC20
371	24.964	24.960	70240	107606	0.434	NC24
383	25.613	25.609	65067	112270	0.453	NC25
393	26.237	26.233	54752	84938	0.342	NC26
404	26.836	26.833	43979	72752	0.293	NC27
414	27.413	27.411	39462	65504	0.264	NC28
425	27.970	27.968	34811	58552	0.236	NC29
434	28.507	28.505	26319	48637	0.196	NC30
Residual			12692790	21125170	85.148	
Total			14929190	24809800	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 DB13KSU.1.1
Reported on 18-Jul-86 at 15:43

Page 1

MULTICHROM V3.2

Analyst Name :
Analysis ID:
Information :

METHOD FILE FOR GEOCHEM RESEARCH

Channel:6 Title: CHANNEL 6 Date 31-Jan-86 Time 8:09
Analysis:DB13KSU Sample Name:01-31-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
38	6.753	6.760	373680	604415	1.842	NC7
39	7.087	7.093	369468	589527	1.796	MCHX
178	14.440	14.441	100684	158625	0.483	IP13
194	15.148	15.148	99982	167249	0.510	IP14
214	16.328	16.328	85973	132316	0.403	IP15
234	17.239	17.238	109046	198652	0.605	IP16
240	17.614	17.613	214460	446343	1.360	NC15
266	19.089	19.087	88445	175695	0.535	IP18
275	19.543	19.541	178249	330633	1.008	NC17
277	19.631	19.628	127358	214916	0.655	PRIST
292	20.431	20.428	159022	316956	0.966	NC18
294	20.548	20.544	84356	152355	0.464	PHYT
325	22.084	22.080	143731	251516	0.766	NC20
379	24.964	24.960	88400	163721	0.499	NC24
391	25.612	25.608	83425	142839	0.435	NC25
403	26.238	26.233	72865	163110	0.497	NC26
413	26.837	26.832	62778	132948	0.405	NC27
423	27.414	27.410	57472	123561	0.377	NC28
433	27.971	27.967	55076	113545	0.346	NC29
441	28.510	28.506	42430	91104	0.278	NC30
Residual			15395450	28145390	85.769	
Total			17992430	32815430	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

nalysis:6 DB14.1.1
eported on 12-May-86 at 15:00

M U L T I C H R O M V3.2

Analysis ID:

Analyst Name :
Information :

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Date 27-Mar-86 Time 9:12

Channel:6 Title: CHANNEL 6 Bottle:1
Analysis:DB14 Sample Name:03-27-86/000213.3/50 Sample ID: 0
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
42	6.596	6.600	436062	755702	2.699	NC7
45	6.917	6.921	288470	415488	1.484	MCHX
184	14.290	14.299	113960	198139	0.708	IP13
198	14.996	15.005	99615	161641	0.577	IP14
221	16.170	16.181	89727	126582	0.452	IP15
241	17.080	17.091	112266	207273	0.740	IP16
248	17.460	17.472	270402	553754	1.977	NC15
277	18.921	18.934	85760	155287	0.555	IP18
285	19.378	19.391	211530	377739	1.349	NC17
287	19.461	19.474	123146	198270	0.708	PRIST
304	20.262	20.276	185055	327252	1.169	NC18
306	20.373	20.387	79076	128602	0.459	PHYT
336	21.906	21.920	152963	254131	0.907	NC20
394	24.778	24.794	83852	127645	0.456	NC24
406	25.426	25.442	75978	111202	0.397	NC25
417	26.048	26.065	62809	100803	0.360	NC26
429	26.647	26.664	50906	69980	0.250	NC27
440	27.226	27.244	45680	70738	0.253	NC28
449	27.781	27.799	39813	64920	0.232	NC29
459	28.318	28.336	30775	55060	0.197	NC30
Residual			13625240	23543300	84.073	
Total			1626[illegible]30	28003510	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 DB15.1.1
Reported on 12-May-86 at 15:35

MULTICHROM V3.2

Analyst Name : Analysis ID:
Information :

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Channel:6 Title: CHANNEL 6 Date 27-Mar-86 Time 10:06
Analysis:DB15 Sample Name:03-27-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
42	6.642	6.642	430934	722475	1.669	NC7
43	6.971	6.971	419398	689523	1.593	MCHX
182	14.306	14.305	122658	194646	0.450	IP13
196	15.010	15.009	111106	199363	0.460	IP14
218	16.186	16.185	104743	159559	0.369	IP15
238	17.092	17.091	129738	266345	0.615	IP16
245	17.474	17.474	297687	650786	1.503	NC15
274	18.932	18.931	107581	228105	0.527	IP18
282	19.391	19.390	244964	540742	1.249	NC17
283	19.473	19.472	154764	271591	0.627	PRIST
300	20.276	20.275	224226	422731	0.976	NC18
302	20.386	20.385	105780	194131	0.448	PHYT
334	21.921	21.920	198590	378504	0.874	NC20
388	24.793	24.792	123619	244842	0.566	NC24
400	25.440	25.439	113685	283496	0.655	NC25
409	26.063	26.062	100516	255350	0.590	NC26
422	26.661	26.660	85836	147835	0.341	NC27
432	27.240	27.239	75963	186476	0.431	NC28
440	27.796	27.794	69890	181012	0.418	NC29
450	28.331	28.330	57148	122206	0.282	NC30
Residual			19128150	36953470	85.356	
Total			22406980	43293170	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 DB16KSU.1.1
Reported on 21-Jul-86 at 08:55

M U L T I C H R O M V3.2

Analyst Name : Analysis ID:
Information :

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Channel:6 Title: CHANNEL 6 Date 15-Jul-86 Time 13:26
Analysis:DB16KSU Sample Name:7-15-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
38	6.782	6.810	259232	360007	1.350	NC7
39	7.114	7.142	258378	373938	1.402	MCHX
170	14.377	14.409	88415	135855	0.509	IP13
184	15.074	15.108	89407	147550	0.553	IP14
206	16.236	16.270	73231	117547	0.441	IP15
222	17.131	17.166	95450	173565	0.651	IP16
229	17.502	17.537	242218	457725	1.716	NC15
258	18.952	18.988	77153	146430	0.549	IP18
267	19.402	19.438	197949	345720	1.296	NC17
269	19.486	19.522	111091	247230	0.927	PRIST
284	20.280	20.317	174541	308137	1.155	NC18
286	20.393	20.430	73231	130706	0.490	PHYT
316	21.912	21.950	148660	270903	1.016	NC20
366	24.760	24.760	92581	177644	0.666	NC24
375	25.401	25.393	87545	187701	0.704	NC25
386	26.017	26.000	74406	152818	0.573	NC26
396	26.610	26.585	62012	127459	0.478	NC27
406	27.180	27.148	55839	113147	0.424	NC28
415	27.732	27.693	48858	96717	0.363	NC29
423	28.263	28.217	37047	75344	0.282	NC30
Residual			11807820	22530640	84.458	
Total			14155070	26676790	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 JB1KSU.1.1
Reported on 18-Jul-86 at 21:05

MULTICHROM V3.2

Analyst Name :
Analysis ID:
Information :

METHOD FILE FOR GEOCHEM RESEARCH

Channel:6 Title: CHANNEL 6 Date 31-Jan-86 Time 10:06
Analysis:JB1KSU Sample Name:01-31-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
29	6.747	6.780	327962	502459	1.601	NC7
32	7.082	7.115	342306	544516	1.735	MCHX
171	14.447	14.459	103385	162537	0.518	IP13
187	15.156	15.166	98135	161155	0.513	IP14
207	16.334	16.341	83425	127296	0.406	IP15
226	17.247	17.251	103201	193748	0.617	IP16
232	17.626	17.629	245895	511469	1.629	NC15
259	19.094	19.094	80510	162518	0.518	IP18
267	19.551	19.549	201978	373839	1.191	NC17
269	19.636	19.633	118538	196240	0.625	PRIST
283	20.439	20.435	164912	331117	1.055	NC18
285	20.552	20.548	77962	137275	0.437	PHYT
316	22.089	22.080	140344	240898	0.767	NC20
369	24.967	24.960	80236	141087	0.449	NC24
380	25.614	25.608	72850	121484	0.387	NC25
390	26.238	26.232	61462	131359	0.418	NC26
400	26.838	26.833	50002	107224	0.342	NC27
411	27.416	27.411	45127	95481	0.304	NC28
422	27.972	27.968	41045	88205	0.281	NC29
429	28.510	28.506	31820	72521	0.231	NC30
Residual			14792660	26987260	85.975	
Total			17263830	31389690	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 JB2 ,1 ,1
Reported on 12-May-86 at 20:36

MULTICHROM V3.2

Analyst Name : Analysis ID:
Information :

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Channel:6 Title: CHANNEL 6 Date 27-Mar-86 Time 13:13
Analysis:JB2 Sample Name:03-27-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
30	6.749	6.749	344965	511239	1.953	NC7
33	7.071	7.071	354209	538032	2.056	MCHX
175	14.312	14.312	108421	163693	0.625	IP13
189	15.016	15.016	93924	151266	0.578	IP14
211	16.189	16.189	86004	115270	0.440	IP15
234	17.096	17.096	106376	180621	0.690	IP16
242	17.474	17.474	248840	495785	1.894	NC15
272	18.937	18.937	78725	132003	0.504	IP18
279	19.392	19.392	199612	359300	1.373	NC17
281	19.476	19.476	114188	180456	0.690	PRIST
296	20.276	20.276	174770	298564	1.141	NC18
298	20.388	20.388	75108	114694	0.438	PHYT
331	21.920	21.920	143182	222288	0.849	NC20
387	24.791	24.791	79946	120371	0.460	NC24
398	25.438	25.438	74254	105428	0.403	NC25
408	26.063	26.063	60837	134113	0.512	NC26
421	26.660	26.660	49770	70944	0.271	NC27
432	27.238	27.238	44917	75026	0.287	NC28
443	27.794	27.794	39027	67501	0.258	NC29
454	28.332	28.332	31584	56196	0.215	NC30
Residual			13867890	22078250	84.361	
Total			16374220	26171040	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 JB3KSU.1.1
Reported on 01-Jul-86 at 21:42

MULTICHROM V3.2

Analyst Name : Analysis ID:
Information :

METHOD FILE FOR GEOCHEM RESEARCH

Channel:6 Title: CHANNEL 6 Date 31-Jan-86 Time 11:01
Analysis:JB3KSU Sample Name:01-31-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
26	6.753	6.744	189938	241795	0.846	NC7
27	7.090	7.080	246231	352914	1.235	MCHX
166	14.447	14.427	92001	142510	0.499	IP13
182	15.156	15.135	89285	147100	0.515	IP14
203	16.336	16.313	79061	121041	0.424	IP15
222	17.247	17.223	100821	188402	0.659	IP16
229	17.624	17.601	225722	483388	1.692	NC15
257	19.094	19.069	79610	163173	0.571	IP18
265	19.551	19.525	193371	359007	1.256	NC17
267	19.636	19.609	113731	193558	0.677	PRIST
282	20.439	20.411	162470	323284	1.131	NC18
284	20.553	20.525	77764	139153	0.487	PHYT
296	21.286	21.257	158014	308951	1.081	NC19
313	22.090	22.060	138589	242175	0.848	NC20
366	24.971	24.937	80022	154087	0.539	NC24
377	25.621	25.586	75734	189563	0.663	NC25
387	26.246	26.210	63694	154375	0.540	NC26
397	26.846	26.809	53970	128066	0.448	NC27
409	27.423	27.386	48869	130509	0.457	NC28
418	27.979	27.941	45192	109903	0.385	NC29
426	28.518	28.479	35666	91076	0.319	NC30
Residual			12403350	24208010	84.726	
Total			14753100	28572040	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 JE2KSU.1.1
Reported on 20-Jul-86 at 08:53

MULTICHROM V3.2

Analyst Name :   Analysis ID:
Information :

METHOD FILE FOR GEOCHEM RESEARCH

Channel:6 Title: CHANNEL 6   Date 31-Jan-86 Time 13:50
Analysis:JE2KSU   Sample Name:01-31-86/000213.3/50 Sample ID: 0   Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
32	6.780	6.780	431057	729015	2.271	NC7
35	7.107	7.107	349814	549996	1.713	MCHX
175	14.443	14.440	90994	143876	0.448	IP13
191	15.151	15.147	90048	149736	0.466	IP14
211	16.330	16.326	72346	111040	0.346	IP15
231	17.240	17.235	91146	167937	0.523	IP16
237	17.618	17.613	213919	433475	1.350	NC15
263	19.090	19.085	67280	135057	0.421	IP18
272	19.546	19.540	171016	309122	0.963	NC17
274	19.631	19.626	101676	167343	0.521	PRIST
291	20.433	20.427	142800	252625	0.787	NC18
293	20.550	20.544	63862	111896	0.349	PHYT
324	22.087	22.080	118721	197129	0.614	NC20
375	24.969	24.960	68562	120847	0.376	NC24
385	25.616	25.606	63160	104687	0.326	NC25
397	26.240	26.230	53871	112044	0.349	NC26
407	26.839	26.829	44600	96839	0.302	NC27
417	27.416	27.405	39629	94209	0.293	NC28
427	27.972	27.961	35860	83672	0.261	NC29
435	28.510	28.498	28311	71817	0.224	NC30
Residual			15701680	27961260	87.097	
Total			18039440	32103630	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2   Calibration: CAL3   Type: UC   Using:Area

Analysis:7 JE3KSUR2.1.1
Reported on 21-Jul-86 at 16:18

M U L T I C H R O M V3.2

Analyst Name : Analysis ID:
Information :

Channel:7 Title: CHANNEL 7 Date 21-Jul-86 Time 15:32
Analysis:JE3KSUR2 Sample Name:7-21-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA	Identity
27	6.441	6.460	28604	36352	0.697	NC7
28	6.780	6.800	82906	116421	2.231	MCHX
165	14.170	14.199	9590	15439	0.296	IP13
177	14.839	14.868	16423	36522	0.700	IP14
197	16.018	16.049	11054	15369	0.295	IP15
215	16.921	16.953	14410	23761	0.455	IP16
222	17.278	17.310	22020	40534	0.777	NC15
250	18.759	18.787	10698	29393	0.563	IP18
257	19.197	19.224	19868	28728	0.551	NC17
259	19.292	19.319	17800	30352	0.582	PRISTANE
276	20.082	20.107	13683	20691	0.397	NC18
278	20.209	20.234	12746	20169	0.387	PHYTANE
309	21.729	21.750	12930	23594	0.452	NC20
361	24.600	24.630	7504	11073	0.212	NC24
370	25.248	25.280	7937	12417	0.238	NC25
376	25.868	25.902	6219	10446	0.200	NC26
386	26.467	26.503	4902	7257	0.139	NC27
395	27.042	27.080	4581	9032	0.173	NC28
403	27.600	27.640	4276	7326	0.140	NC29
411	28.138	28.180	3256	5697	0.109	NC30
Residual			2763370	4717167	90.406	
Total			3074776	5217741	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH Calibration: CAL3 Type: UC Using:Area

Analysis:6 LN1 ,1 ,1
Reported on 12-May-86 at 17:31

M U L T I C H R O M V3.2

Analyst Name :   Analysis ID:
Information :

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Channel:6 Title: CHANNEL 6   Date 27-Mar-86 Time 14:12
Analysis:LN1   Sample Name:03-27-86/000213.3/50 Sample ID: 0   Bottle:1
Sample 1   Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
28	6.660	6.655	81594	99970	0.225	NC7
29	7.007	7.001	383935	605012	1.359	MCHX
168	14.309	14.297	93359	142021	0.319	IP13
183	15.017	15.004	97952	173808	0.390	IP14
206	16.189	16.176	93695	145319	0.326	IP15
227	17.099	17.085	147363	299888	0.674	IP16
235	17.491	17.477	402551	996955	2.239	NC15
265	18.940	18.925	120002	247071	0.555	IP18
273	19.416	19.400	394922	1023268	2.298	NC17
274	19.488	19.472	199673	362405	0.814	PRIST
290	20.292	20.276	308429	694624	1.560	NC18
292	20.396	20.379	126518	223720	0.503	PHYT
324	21.938	21.920	273454	588754	1.322	NC20
382	24.809	24.789	184612	393003	0.883	NC24
393	25.457	25.436	175014	387267	0.870	NC25
404	26.079	26.058	163172	376592	0.846	NC26
416	26.678	26.656	141885	267088	0.600	NC27
428	27.253	27.231	123451	274014	0.615	NC28
439	27.809	27.786	113975	276462	0.621	NC29
448	28.344	28.321	96914	191547	0.430	NC30
Residual			17758020	36750380	82.550	
Total			21480490	44519160	100.000	

Sample Type: SA   Scale Factor: 1.000   Amount: 1.000
Method: METH2   Calibration: CAL3   Type: UC   Using:Area

Analysis:6 LN2 .1 .1
Reported on 12-May-86 at 18:02

M U L T I C H R O M V3.2

Analyst Name : Analysis ID:
Information :

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Channel:6 Title: CHANNEL 6 Date 27-Mar-86 Time 15:19
Analysis:LN2 Sample Name:03-27-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
26	6.693	6.689	265641	363786	0.835	NC7
27	7.020	7.015	305744	445196	1.021	MCHX
168	14.322	14.312	128121	205410	0.471	IP13
182	15.027	15.016	122322	218749	0.502	IP14
204	16.199	16.187	115196	176965	0.406	IP15
225	17.107	17.095	143090	298558	0.685	IP16
232	17.487	17.474	305500	727804	1.670	NC15
260	18.947	18.933	123726	249558	0.572	IP18
269	19.406	19.392	260941	604615	1.387	NC17
270	19.488	19.474	171428	315612	0.724	PRIST
286	20.290	20.276	239288	561513	1.288	NC18
288	20.399	20.384	121879	226108	0.519	PHYT
320	21.936	21.920	214414	430493	0.988	NC20
374	24.807	24.789	136422	280264	0.643	NC24
385	25.454	25.436	128334	338751	0.777	NC25
395	26.078	26.059	114707	236751	0.543	NC26
407	26.676	26.657	95938	170963	0.392	NC27
417	27.253	27.234	85439	215392	0.494	NC28
425	27.809	27.789	80907	184676	0.424	NC29
436	28.346	28.325	68638	141011	0.323	NC30
Residual			18459830	37199070	85.336	
Total			21687510	43591220	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 RC1KSU.1.1
Reported on 20-Jul-86 at 09:17

M U L T I C H R O M V3.2

Analyst Name : Analysis ID:
Information :

METHOD FILE FOR GEOCHEM RESEARCH

Channel:6 Title: CHANNEL 6 Date 31-Jan-86 Time 15:50
Analysis:RC1KSU Sample Name:01-31-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
27	6.778	6.780	235457	316184	0.965	NC7
28	7.119	7.121	398401	630550	1.925	MCHX
167	14.450	14.439	129494	205722	0.628	IP13
182	15.157	15.144	103079	166006	0.507	IP14
204	16.337	16.322	92825	142355	0.435	IP15
225	17.250	17.234	122597	220901	0.674	IP16
230	17.626	17.609	230330	475853	1.453	NC15
259	19.101	19.082	114601	235588	0.719	IP18
268	19.558	19.538	223295	441371	1.347	NC17
270	19.647	19.626	159281	284481	0.868	PRIST
285	20.449	20.427	210752	436256	1.332	NC18
287	20.564	20.543	117698	208492	0.636	PHYT
318	22.104	22.080	187618	358663	1.095	NC20
371	24.983	24.960	110786	201809	0.616	NC24
383	25.632	25.609	99890	171105	0.522	NC25
394	26.254	26.232	81289	142946	0.436	NC26
407	26.853	26.831	70027	113504	0.346	NC27
417	27.429	27.406	57205	116282	0.355	NC28
425	27.984	27.962	55103	110937	0.339	NC29
435	28.521	28.499	37959	74088	0.226	NC30
Residual			14787600	27707840	84.576	
Total			17625350	32760930	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 RC2KSUR,1,1
Reported on 20-Jul-86 at 20:27

MULTICHROM V3.2

Analyst Name :   Analysis ID:
Information :

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Channel:6 Title: CHANNEL 6   Date 20-Jul-86 Time 11:51
Analysis:RC2KSUR   Sample Name:7-20-86/000213.3/50 Sample ID: 0   Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
28	6.762	6.730	163850	219418	0.969	NC7
30	7.103	7.072	249466	419222	1.851	MCHX
170	14.374	14.360	110770	197864	0.874	IP13
185	15.069	15.056	92650	140680	0.621	IP14
207	16.229	16.218	81243	131576	0.581	IP15
225	17.124	17.116	99844	172240	0.761	IP16
231	17.480	17.472	115226	197698	0.873	NC15
257	18.948	18.943	107047	189168	0.835	IP18
266	19.384	19.381	100668	157070	0.694	NC17
267	19.484	19.481	160074	290162	1.281	PRIST
282	20.263	20.262	91848	157961	0.698	NC18
284	20.393	20.392	121162	236598	1.045	PHYT
309	21.898	21.900	90139	148390	0.655	NC20
360	24.747	24.750	45848	78717	0.348	NC24
370	25.389	25.392	41098	66594	0.294	NC25
381	26.004	26.008	32473	58017	0.256	NC26
392	26.598	26.602	29661	56594	0.250	NC27
401	27.169	27.173	26167	49532	0.219	NC28
410	27.722	27.727	29848	70692	0.312	NC29
419	28.253	28.258	20677	45871	0.203	NC30
Residual			11028240	19561830	86.381	
Total			12838000	22645900	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 RC3KSU.1.1
Reported on 20-Jul-86 at 09:37

MULTICHROM V3.2

Analyst Name : Analysis ID:
Information :

METHOD FILE FOR GEOCHEM RESEARCH

Channel:6 Title: CHANNEL 6 Date 4-Feb-86 Time 10:03
Analysis:RC3KSU Sample Name:02-04-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
38	6.758	6.780	236678	326640	1.431	NC7
42	7.094	7.116	289629	470445	2.061	MCHX
195	14.448	14.455	127129	221416	0.970	IP13
209	15.154	15.160	92840	144855	0.635	IP14
233	16.333	16.337	84783	124537	0.546	IP15
251	17.246	17.247	100027	169737	0.744	IP16
256	17.611	17.612	132973	265393	1.163	NC15
281	19.094	19.093	102118	181244	0.794	IP18
289	19.540	19.537	115516	189764	0.831	NC17
291	19.638	19.635	132302	218931	0.959	PRIST
307	20.431	20.427	98593	169394	0.742	NC18
309	20.558	20.553	98379	164086	0.719	PHYT
339	22.068	22.080	91925	140609	0.616	NC20
389	24.974	24.960	43582	68702	0.301	NC24
402	25.623	25.607	38889	57137	0.250	NC25
414	26.244	26.227	31832	50085	0.219	NC26
427	26.843	26.825	27998	41609	0.182	NC27
437	27.419	27.399	24206	43222	0.189	NC28
447	27.974	27.953	26724	58770	0.257	NC29
457	28.510	28.487	18888	40963	0.179	NC30
Residual			11682370	19676090	86.209	
Total			13597380	22823630	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

Analysis:6 VB1 .1 .1
Reported on 12-May-86 at 16:26

M U L T I C H R O M V3.2

Analyst Name : Analysis ID:
Information :

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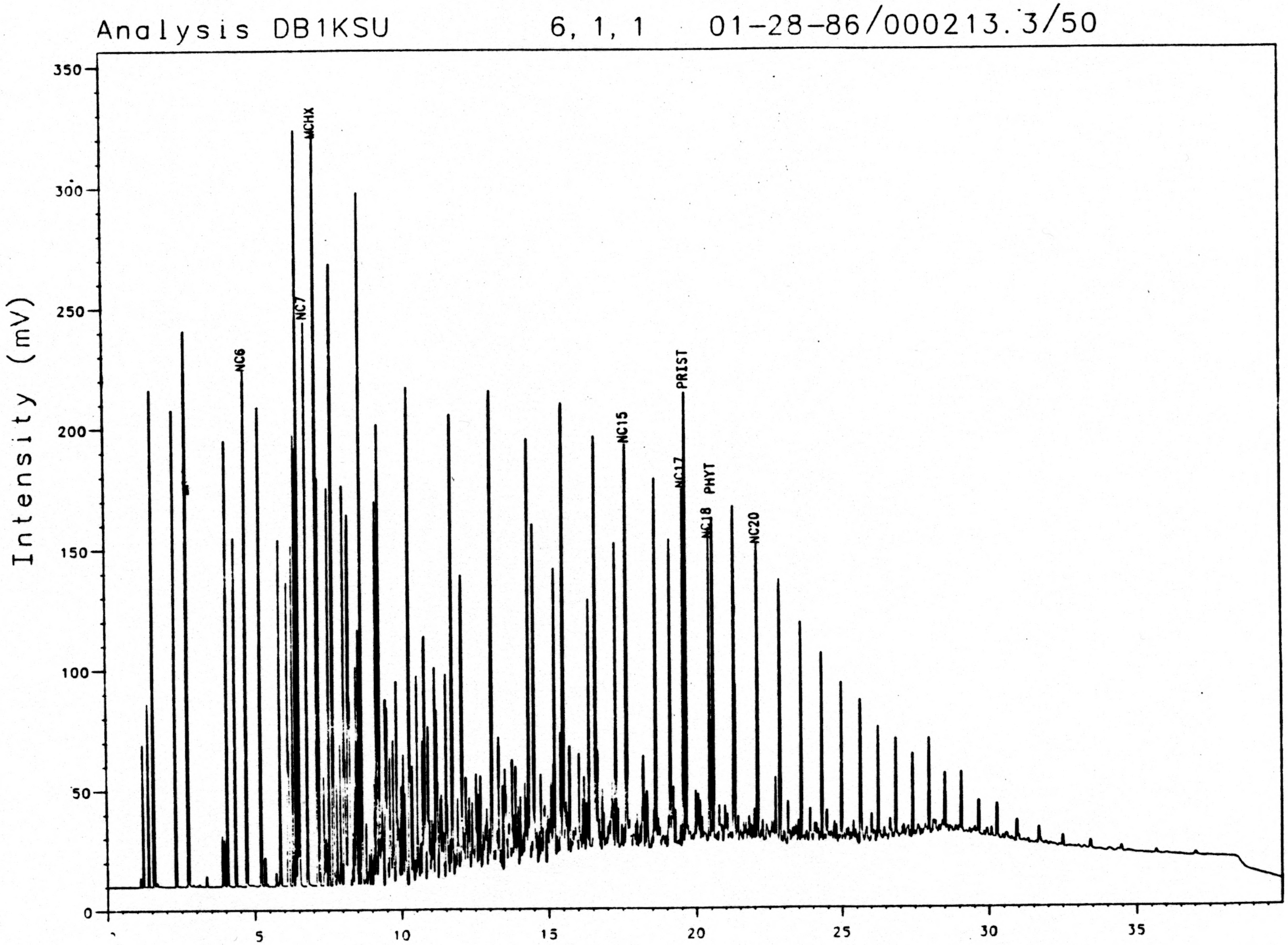
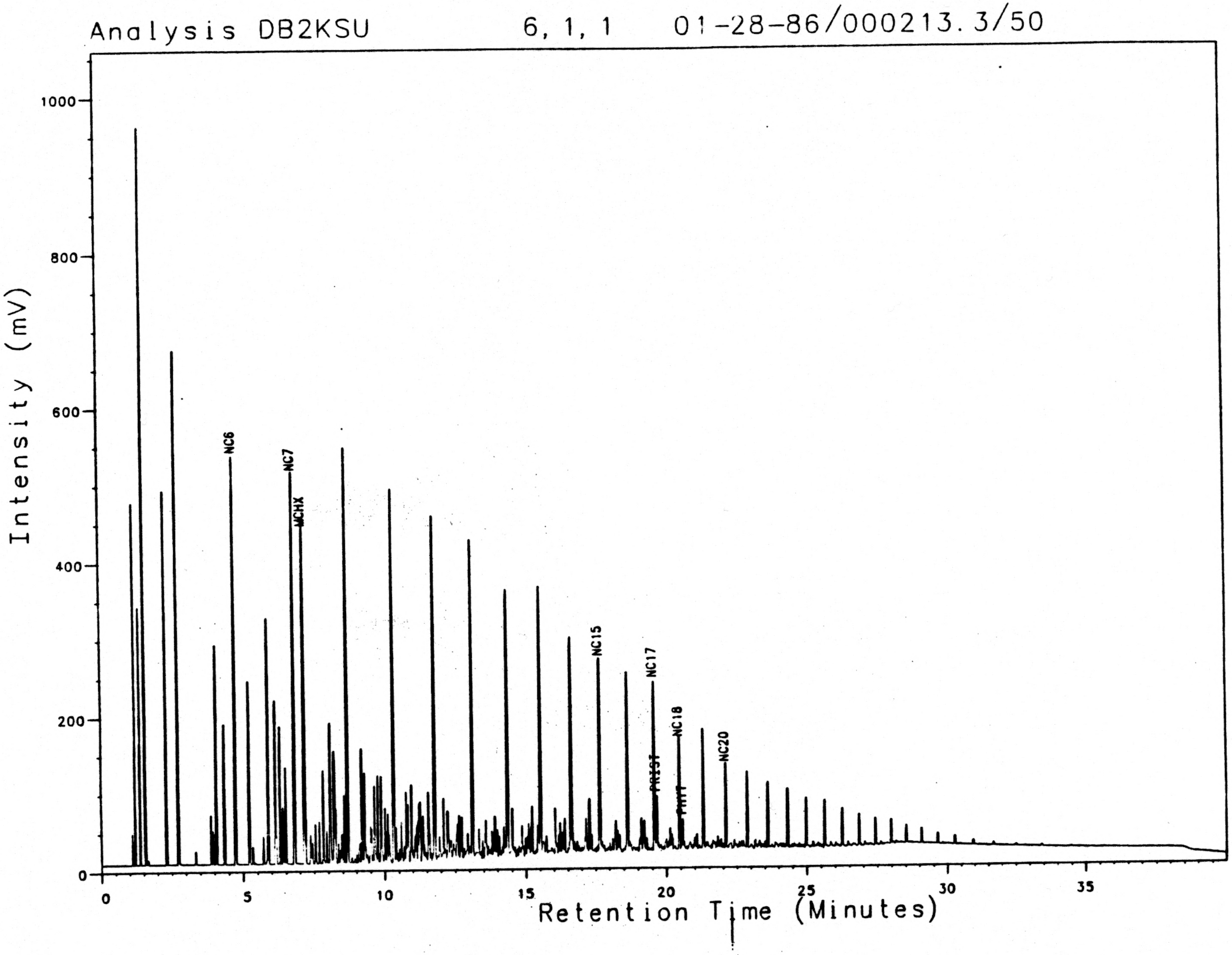
Channel:6 Title: CHANNEL 6 Date 27-Mar-86 Time 10:55
Analysis:VB1 Sample Name:03-27-86/000213.3/50 Sample ID: 0 Bottle:1
Sample 1 Injection 1

Peak	R/T m.	RT Corr	Hght uV	Area uVs	AREA%	Identity
26	6.664	6.660	153338	188271	0.407	NC7
27	6.999	6.995	276750	395489	0.854	MCHX
165	14.313	14.305	131478	211417	0.457	IP13
178	15.019	15.010	130059	235625	0.509	IP14
200	16.193	16.183	128838	197928	0.427	IP15
221	17.102	17.092	162272	344246	0.743	IP16
228	17.486	17.475	356711	887403	1.916	NC15
255	18.342	18.331	140878	314645	0.679	IP18
264	19.403	19.392	308918	743863	1.606	NC17
265	19.486	19.474	202146	379023	0.818	PRIST
281	20.288	20.275	280779	593751	1.282	NC18
283	20.396	20.383	140099	264053	0.570	PHYT
314	21.933	21.920	253372	594409	1.283	NC20
367	24.803	24.788	162501	352926	0.762	NC24
378	25.450	25.435	151422	317342	0.685	NC25
389	26.073	26.057	139794	294368	0.636	NC26
403	26.671	26.655	119072	215124	0.465	NC27
414	27.248	27.231	105902	261641	0.565	NC28
423	27.803	27.786	97616	237476	0.513	NC29
434	28.340	28.323	80419	176702	0.382	NC30
Residual			18605670	39106280	84.441	
Total			22127040	46312040	100.000	

Sample Type: SA Scale Factor: 1.000 Amount: 1.000
Method: METH2 Calibration: CAL3 Type: UC Using:Area

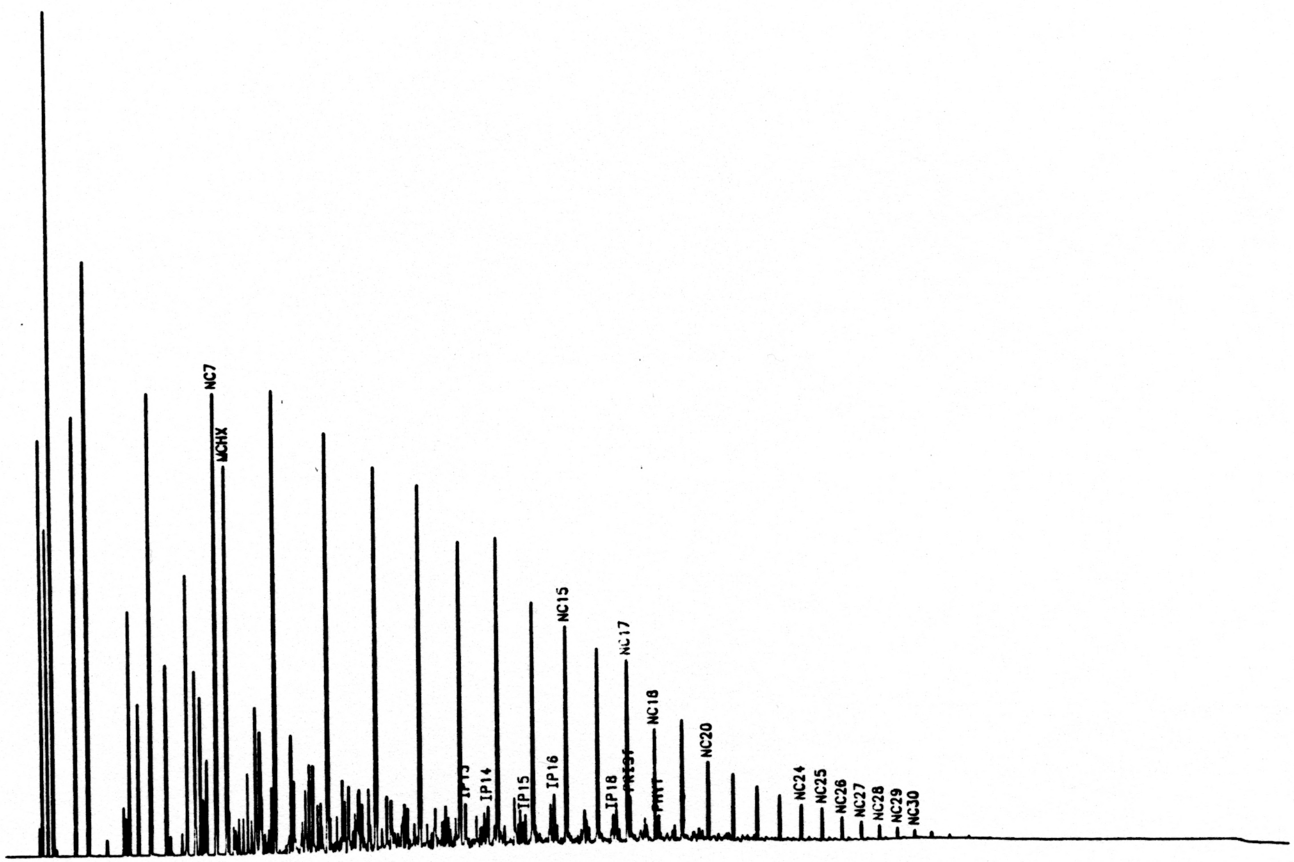


Analysis DB1KSU
6, 1, 1
01-28-86/000213.3/50
Intensity (mV)
350
300
250
200
150
100
50
0
5
10
15
20
25
30
35
NC6
NC7
MCHX
NC15
PRIST
NC17
PHYT
NC18
NC20



Analysis DB2KSU
6, 1, 1
01-28-86/000213.3/50
Intensity (mV)
1000
800
600
400
200
0
NC6
NC7
MCHX
NC15
NC17
PRIST
NC18
PHYT
NC20
0
5
10
15
20
25
30
35
Retention Time (Minutes)

Analysis DB3 6, 1, 1 03-26-86/000213.3/50



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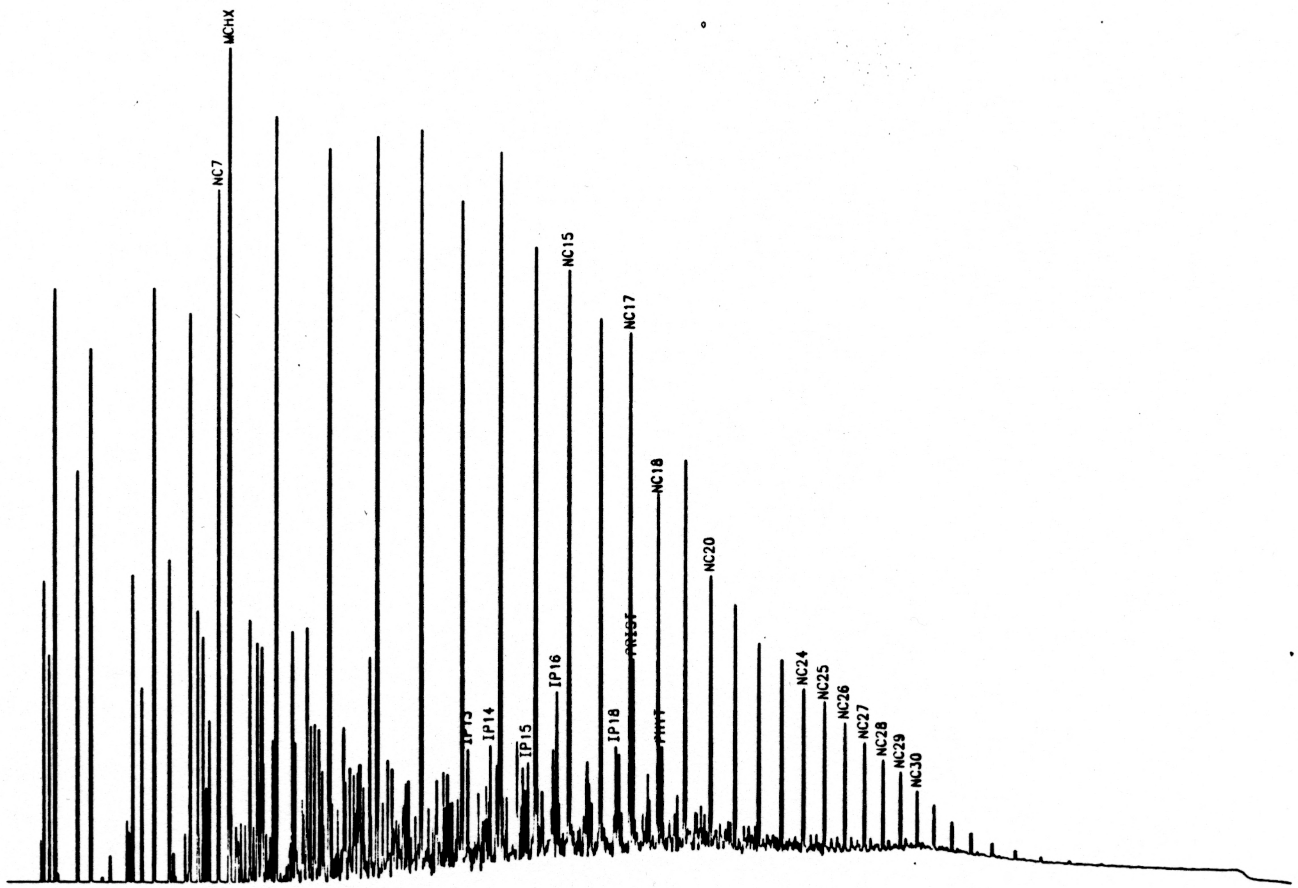

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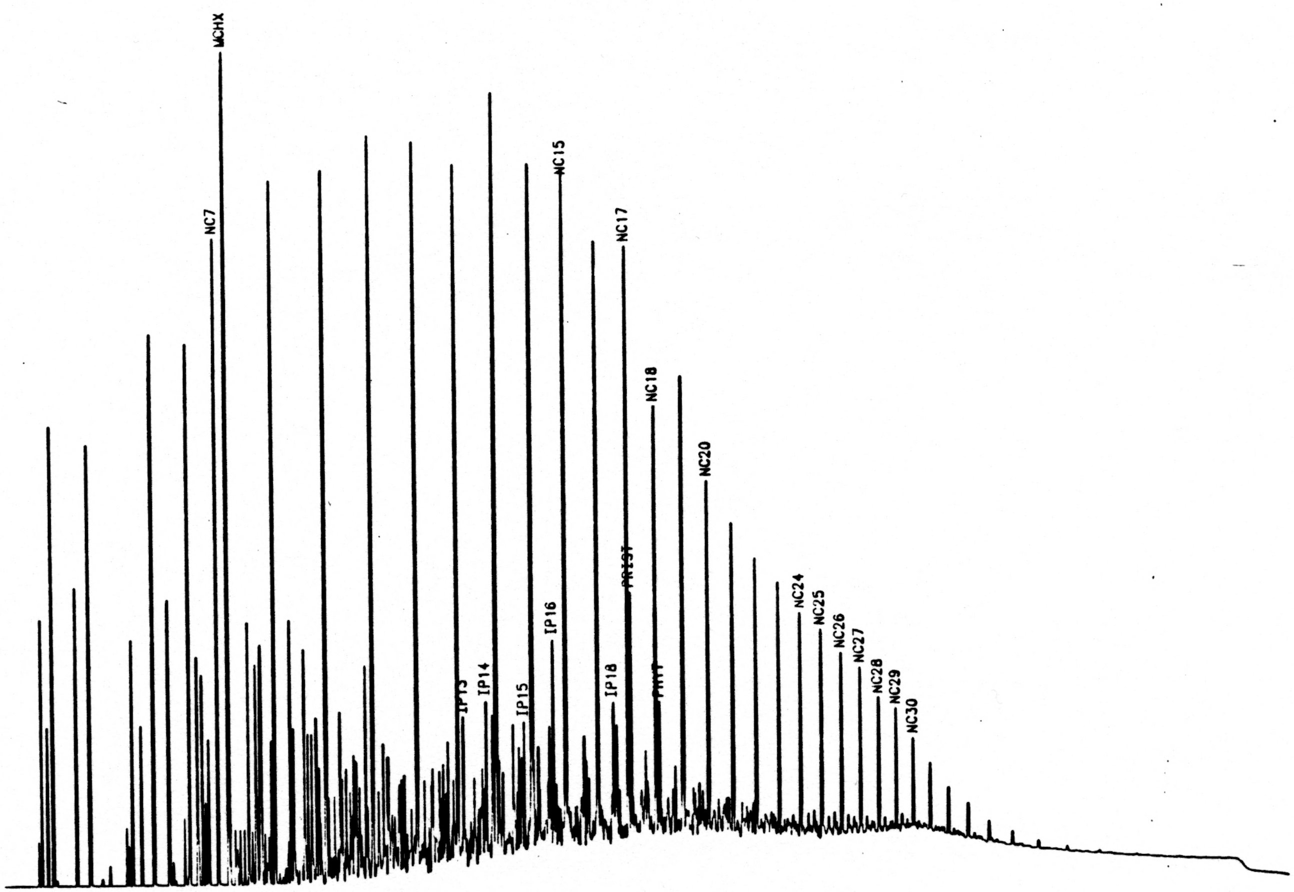

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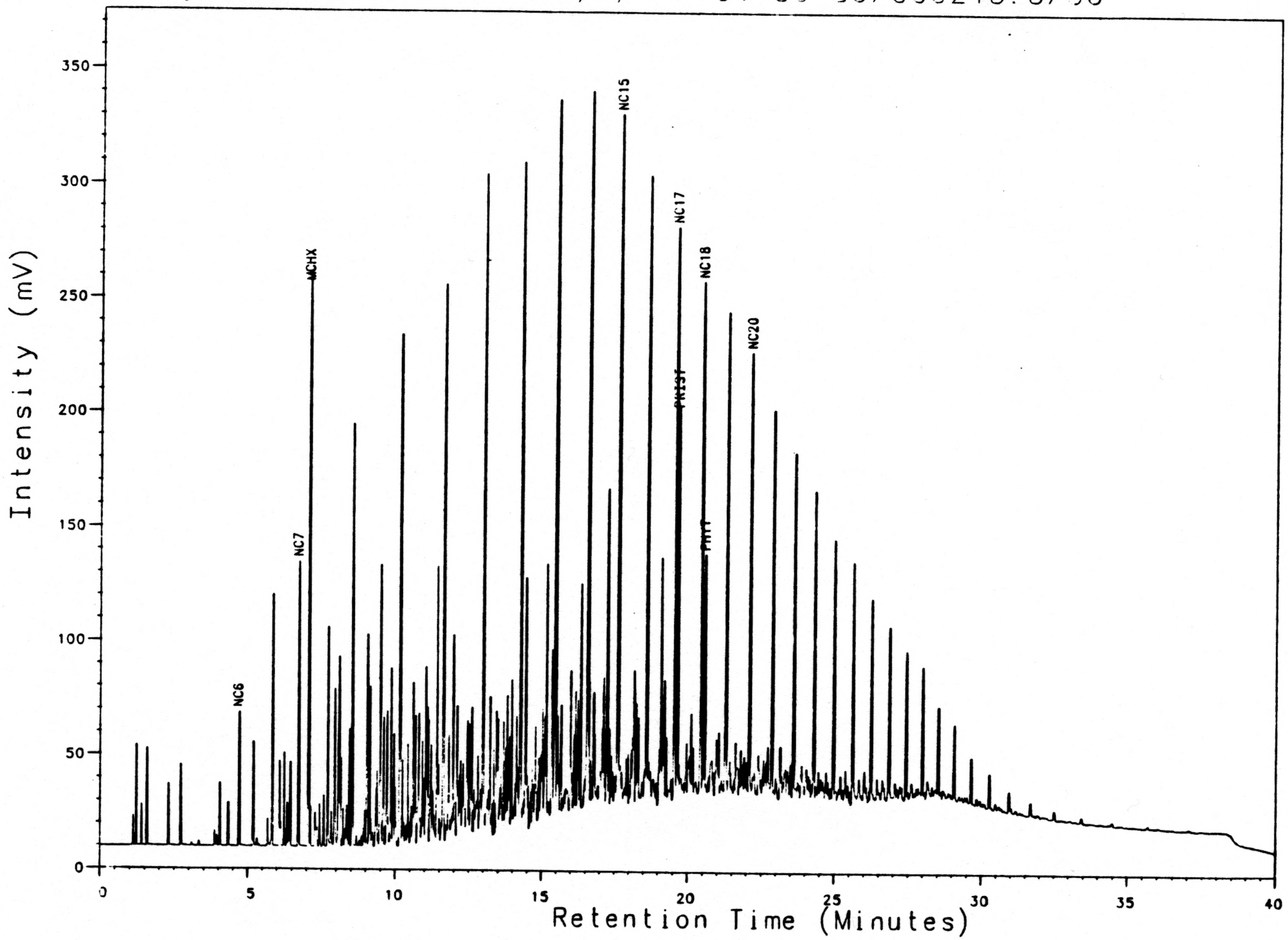
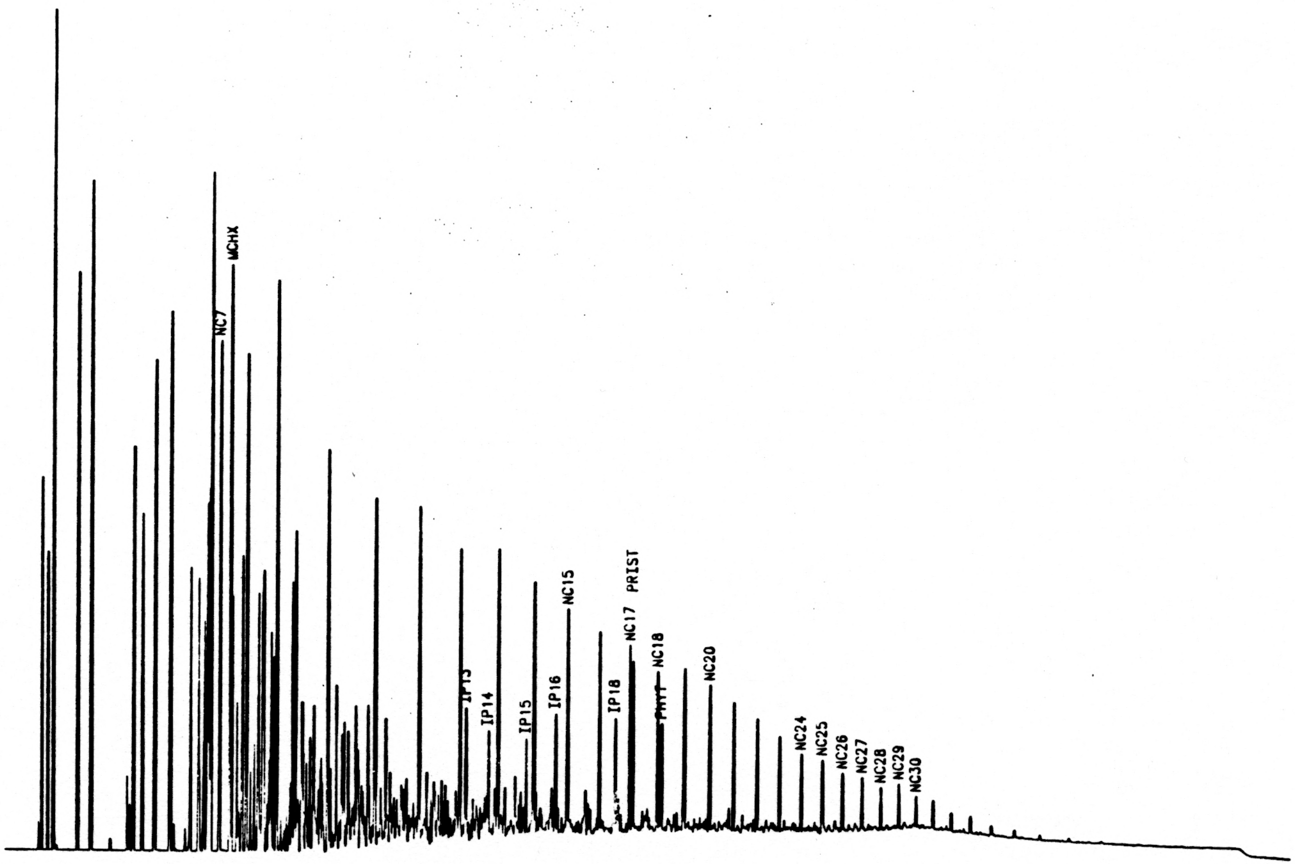
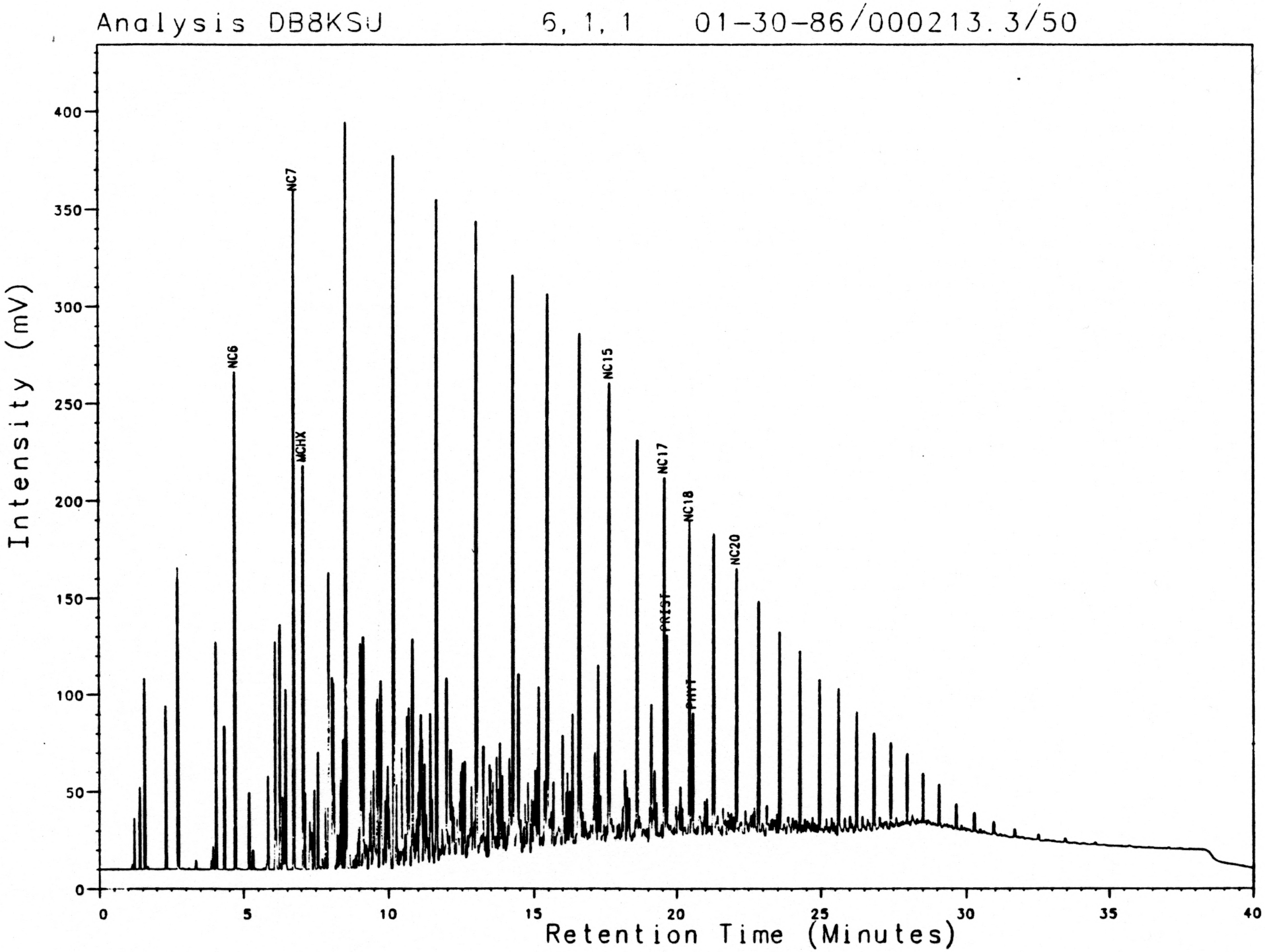


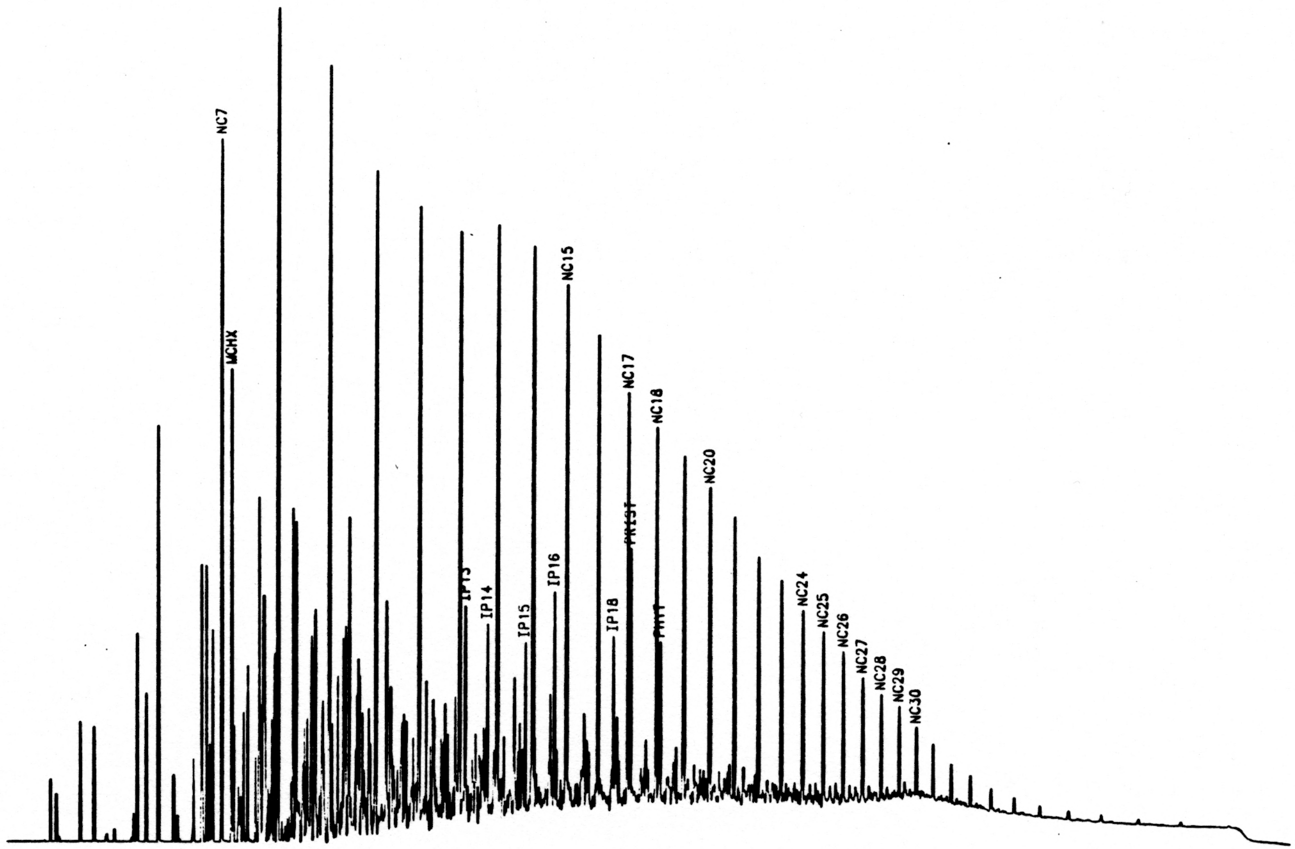
Analysis DB7 6, 1, 1 03-26-86/000213.3/50



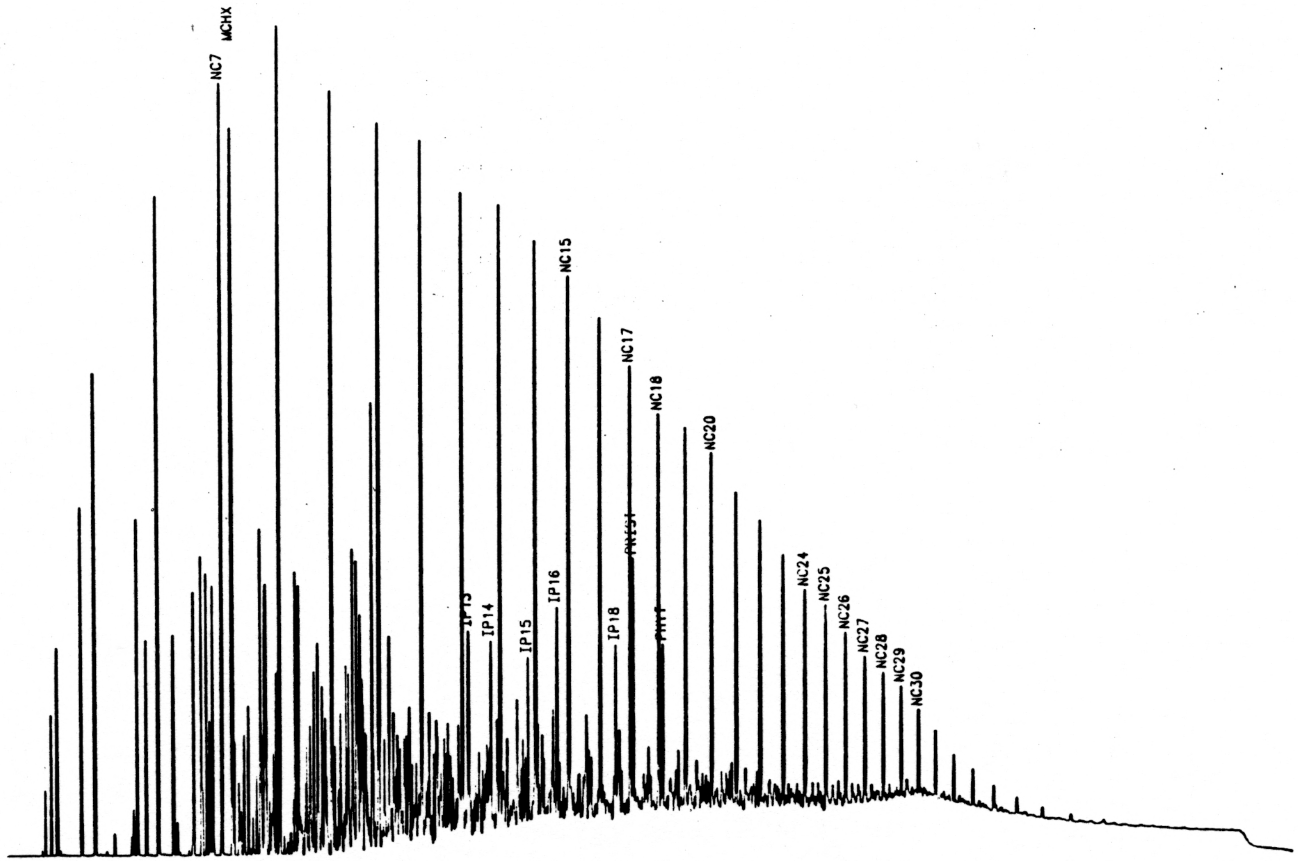


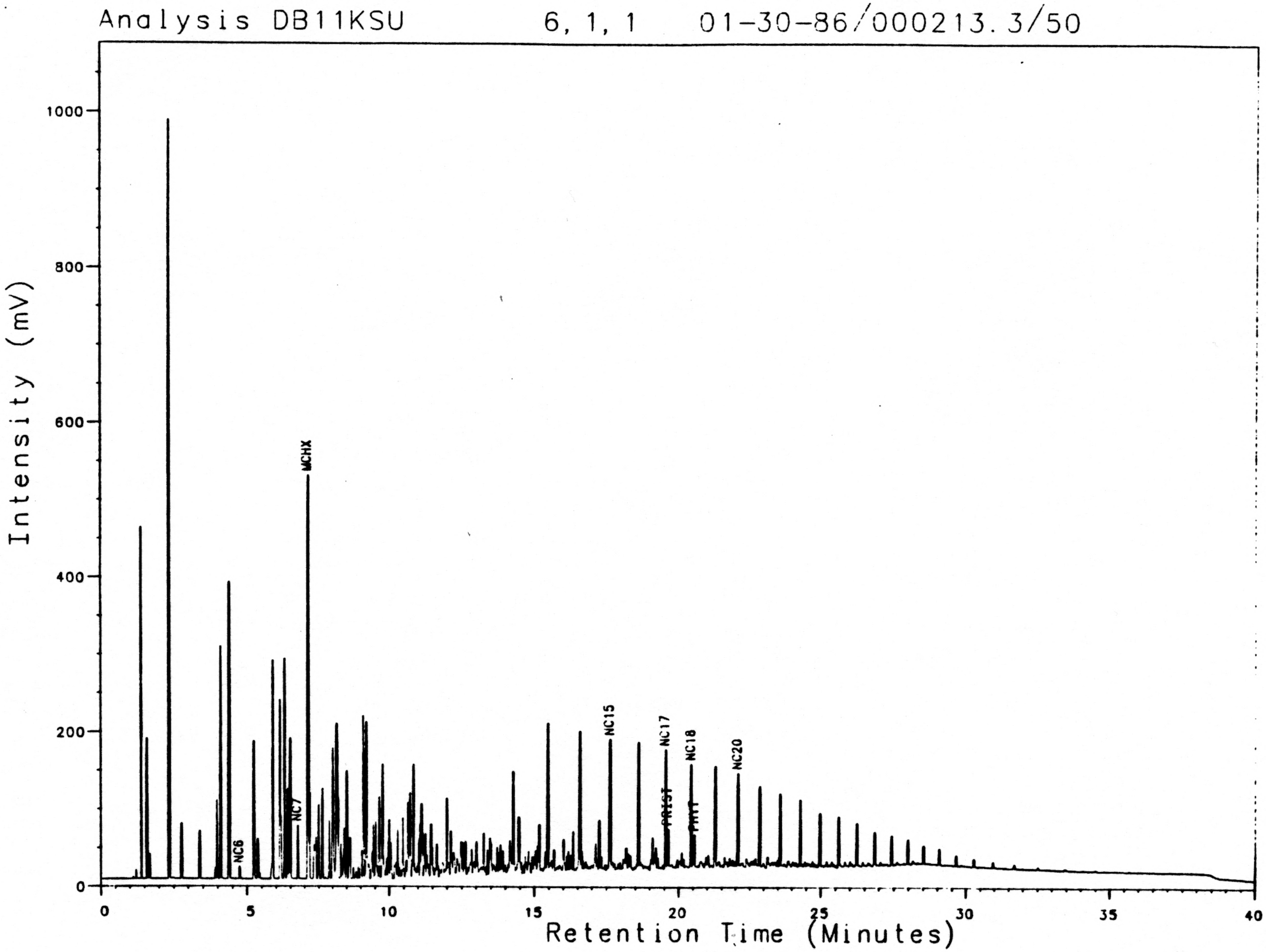
Analysis DB8KSU 6, 1, 1 01-30-86/000213.3/50
Intensity (mV)
Retention Time (Minutes)
NC6
NC7
MCHX
NC15
NC17
PRIST
NC18
PHYT
NC20
0
50
100
150
200
250
300
350
400
0
5
10
15
20
25
30
35
40

Analysis DB9 6, 1, 1 03-26-86/000213.3/50

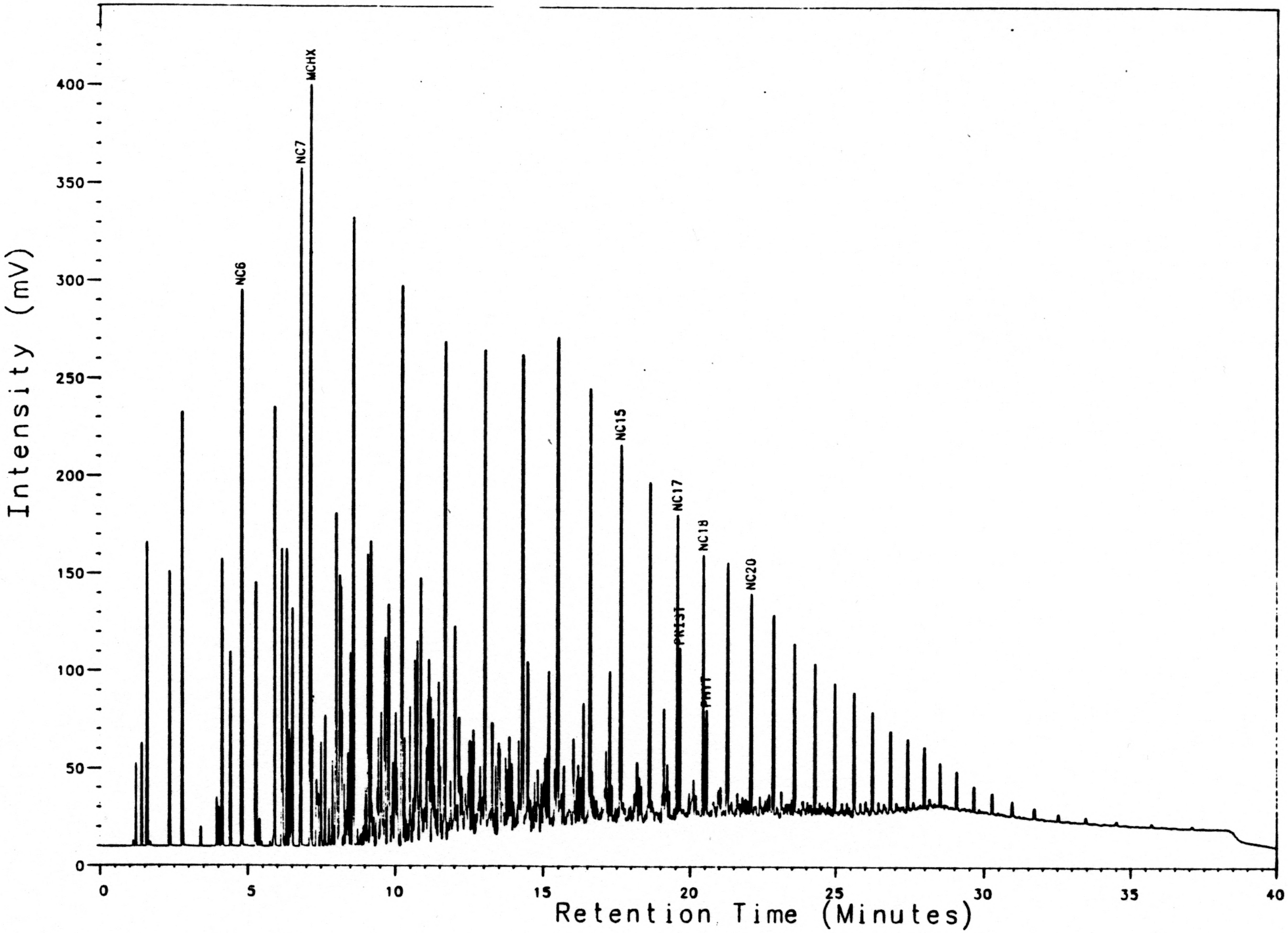


Analysis DB10 6, 1, 1 03-26-86/000213.3/50

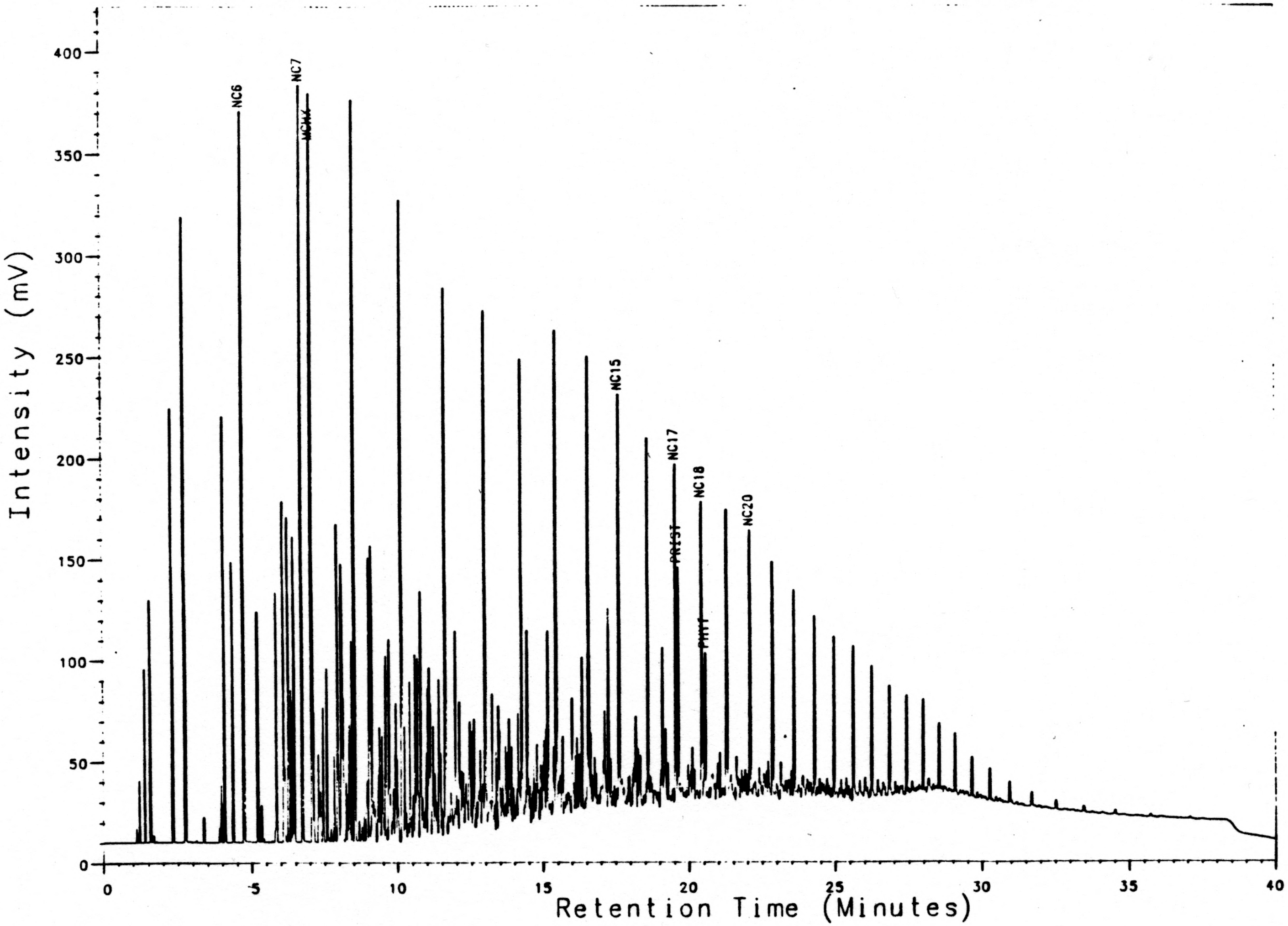



Analysis DB11KSU
6, 1, 1
01-30-86/000213.3/50
Intensity (mV)
1000
800
600
400
200
0
MCHX
NC6
NC7
NC15
NC17
PRIST
NC18
NC20
0
5
10
15
20
25
30
35
40
Retention Time (Minutes)

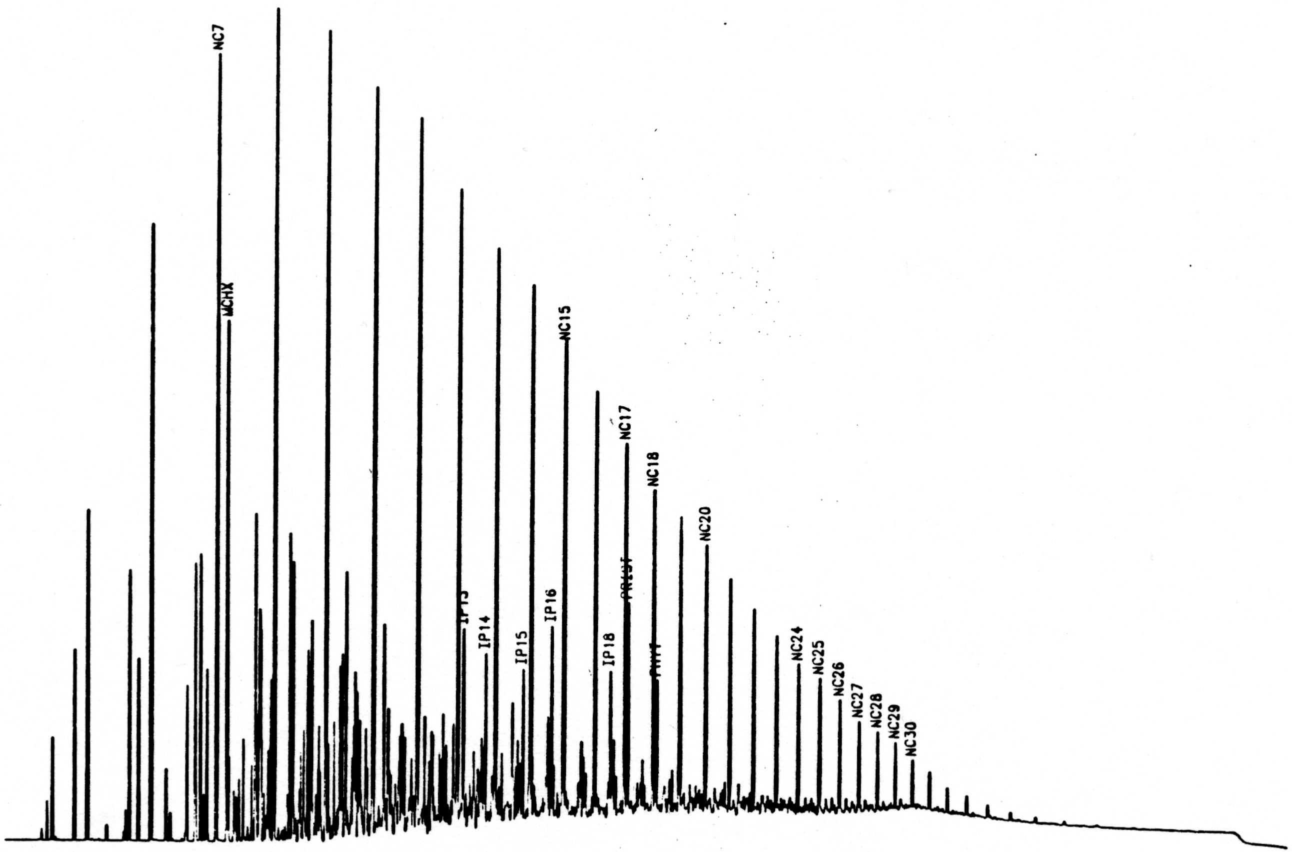
Analysis DB12KSU 6, 1, 1 01-30-86/000213.3/50



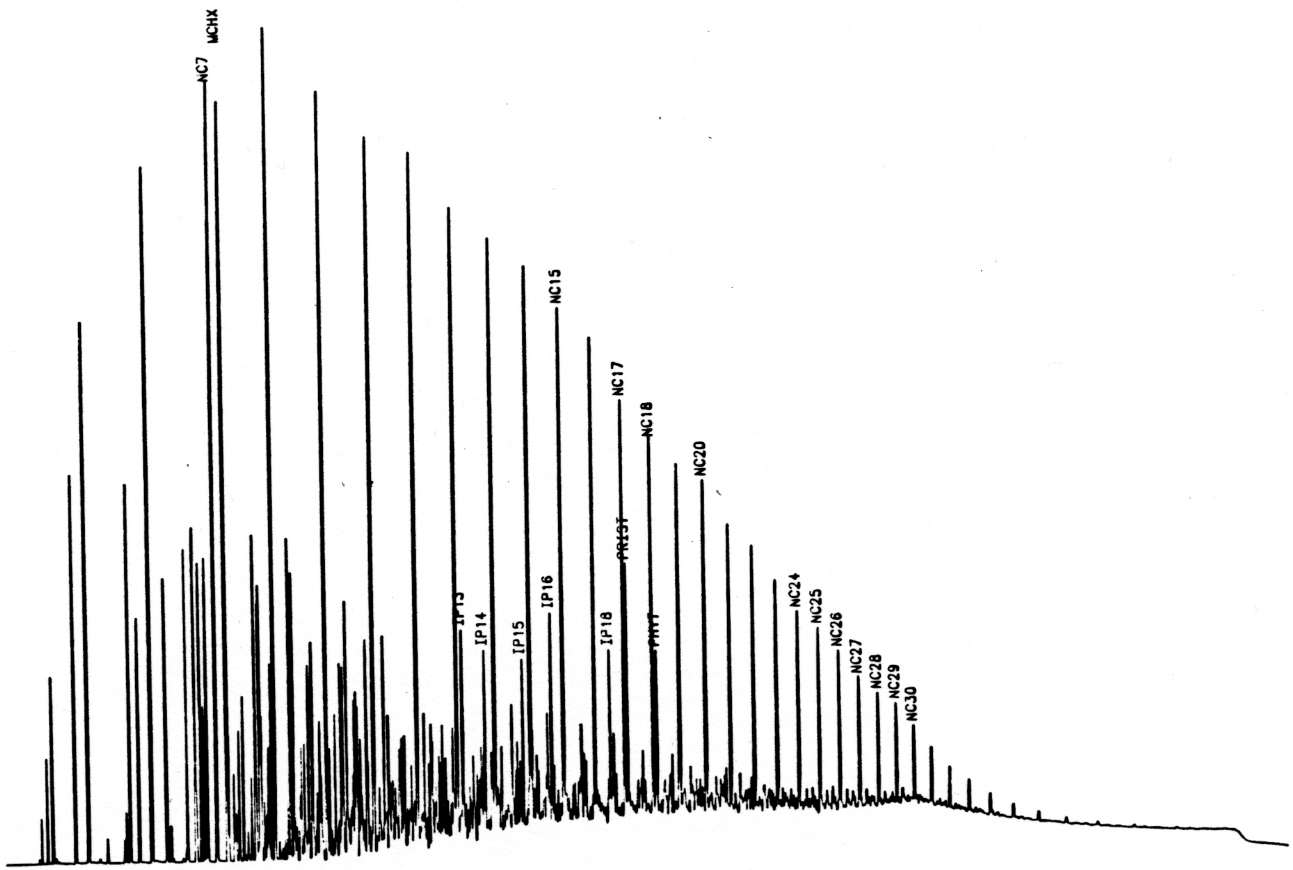
Analysis D313KSU 6, 1, 1 01-31-86/000213.3/50

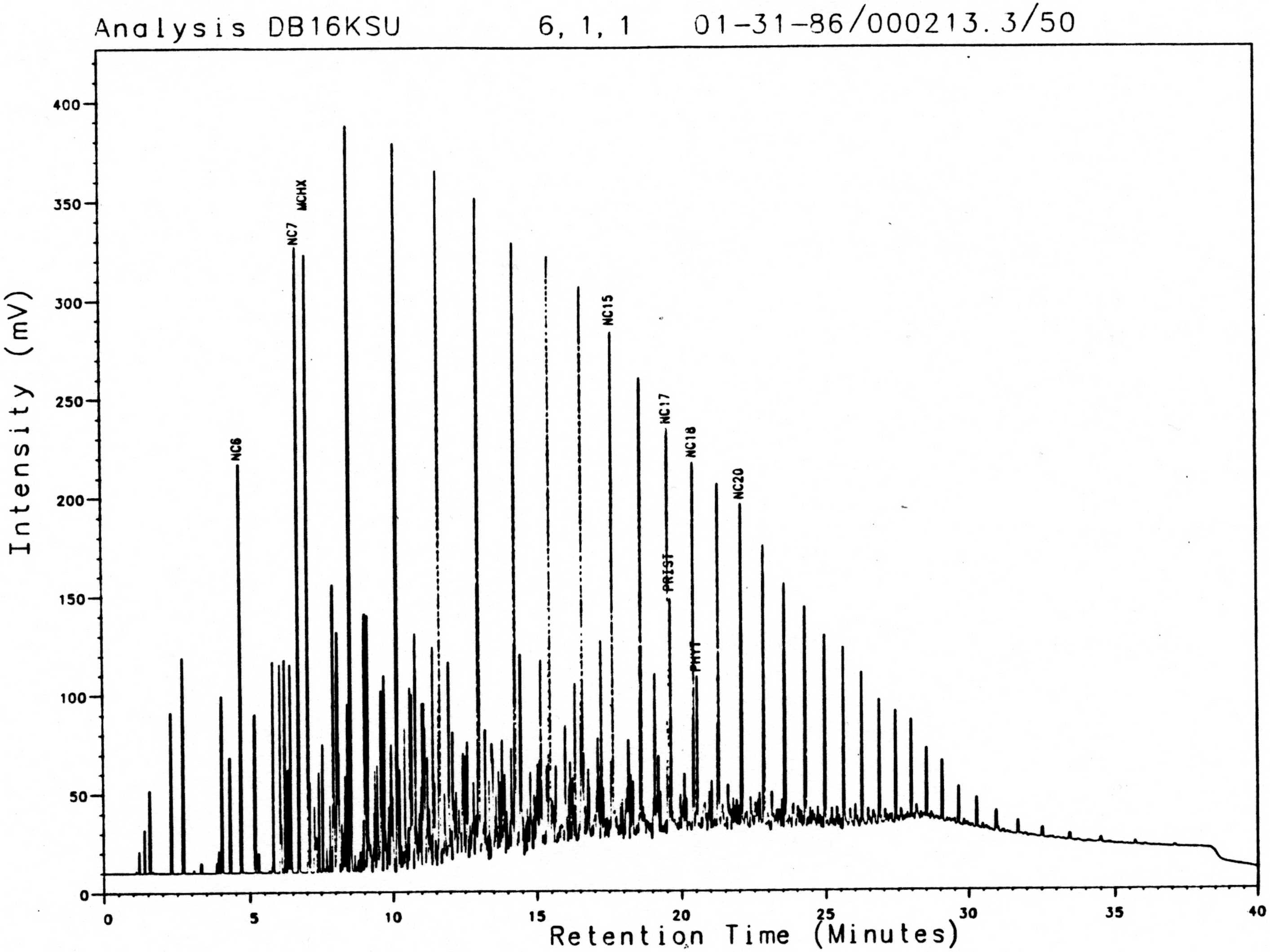


Analysis DB14 6, 1, 1 03-27-86/000213.3/50

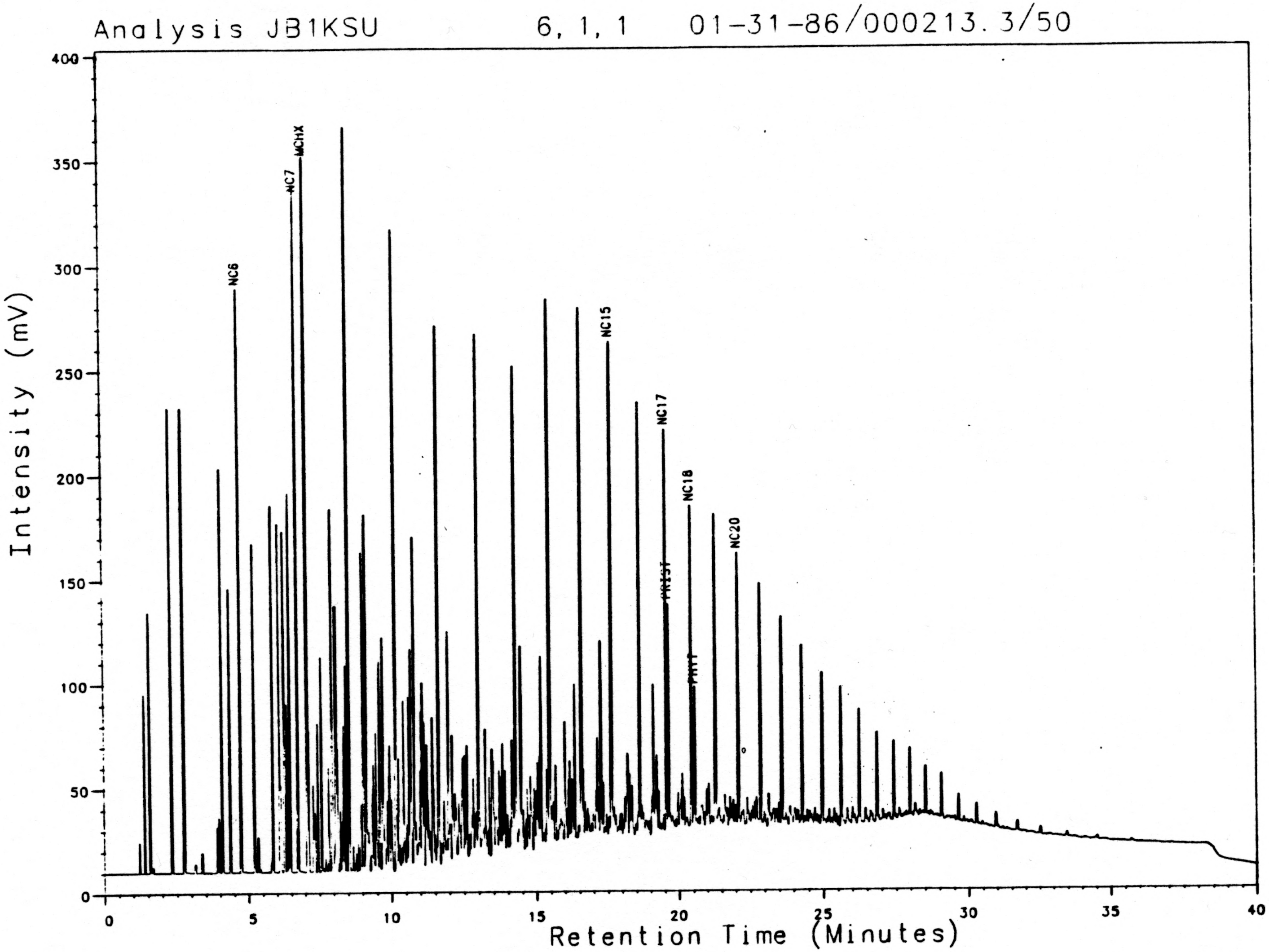


Analysis DB15 6, 1, 1 03-27-86/000213.3/50

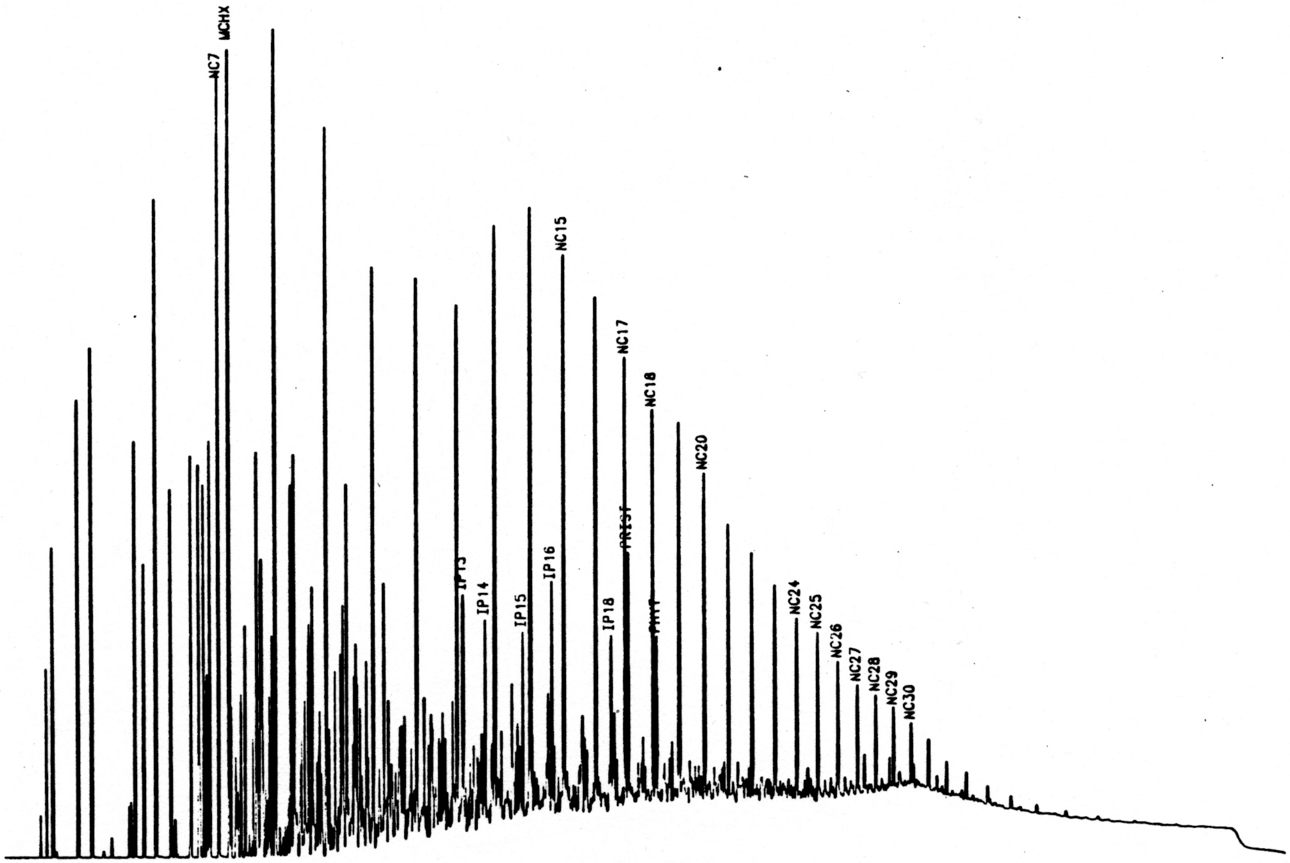




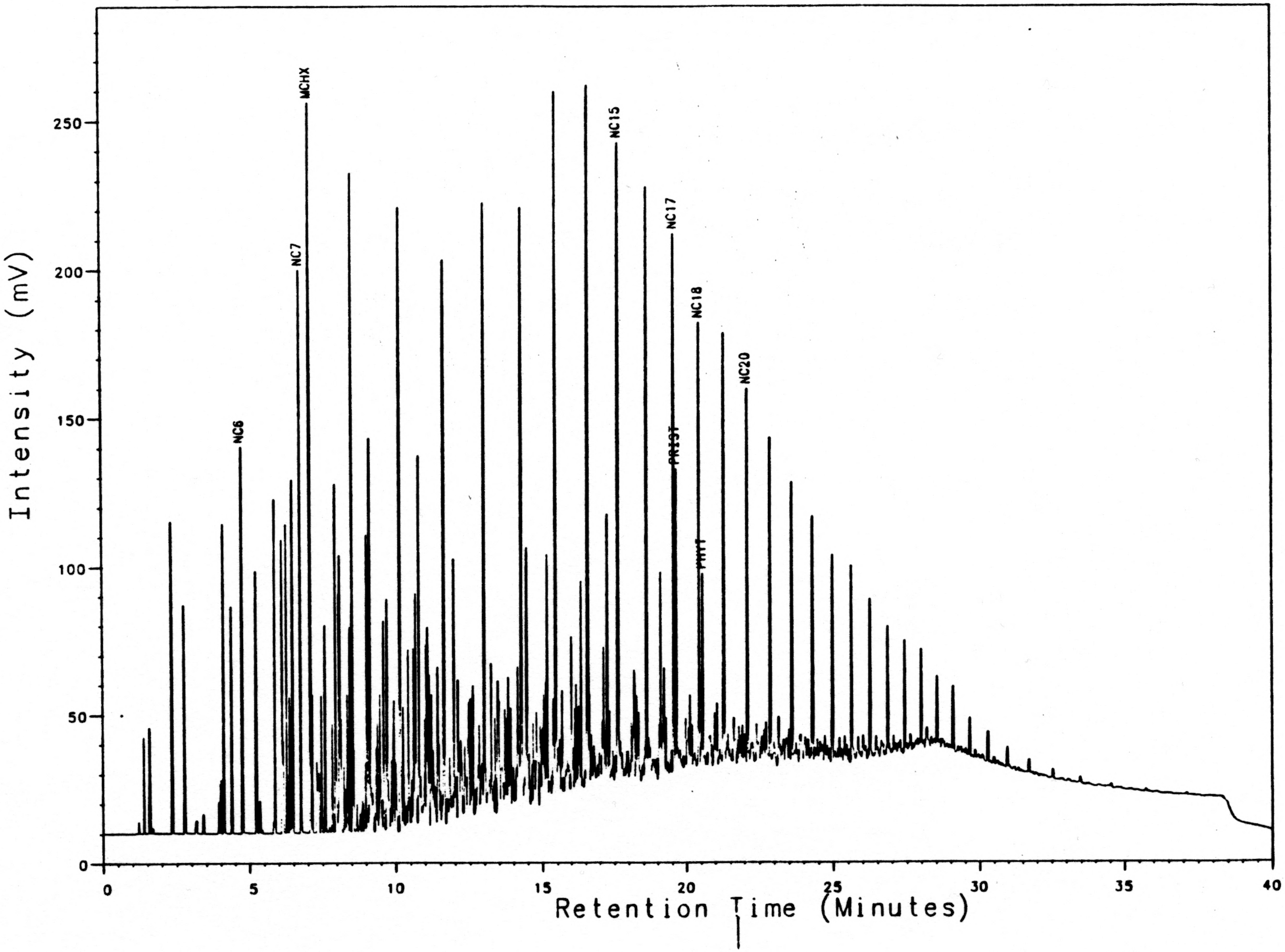
Analysis DB16KSU 6, 1, 1 01-31-86/000213.3/50
Intensity (mV)
Retention Time (Minutes)
0
50
100
150
200
250
300
350
400
0
5
10
15
20
25
30
35
40
NC6
NC7
MCHX
NC15
NC17
NC18
NC20
PRIST
PHYT


Analysis JB1KSU 6, 1, 1 01-31-86/000213.3/50
Intensity (mV)
Retention Time (Minutes)
NC6
NC7
MCHX
NC15
NC17
PRIST
NC18
PHYT
NC20
0
50
100
150
200
250
300
350
400
0
5
10
15
20
25
30
35
40

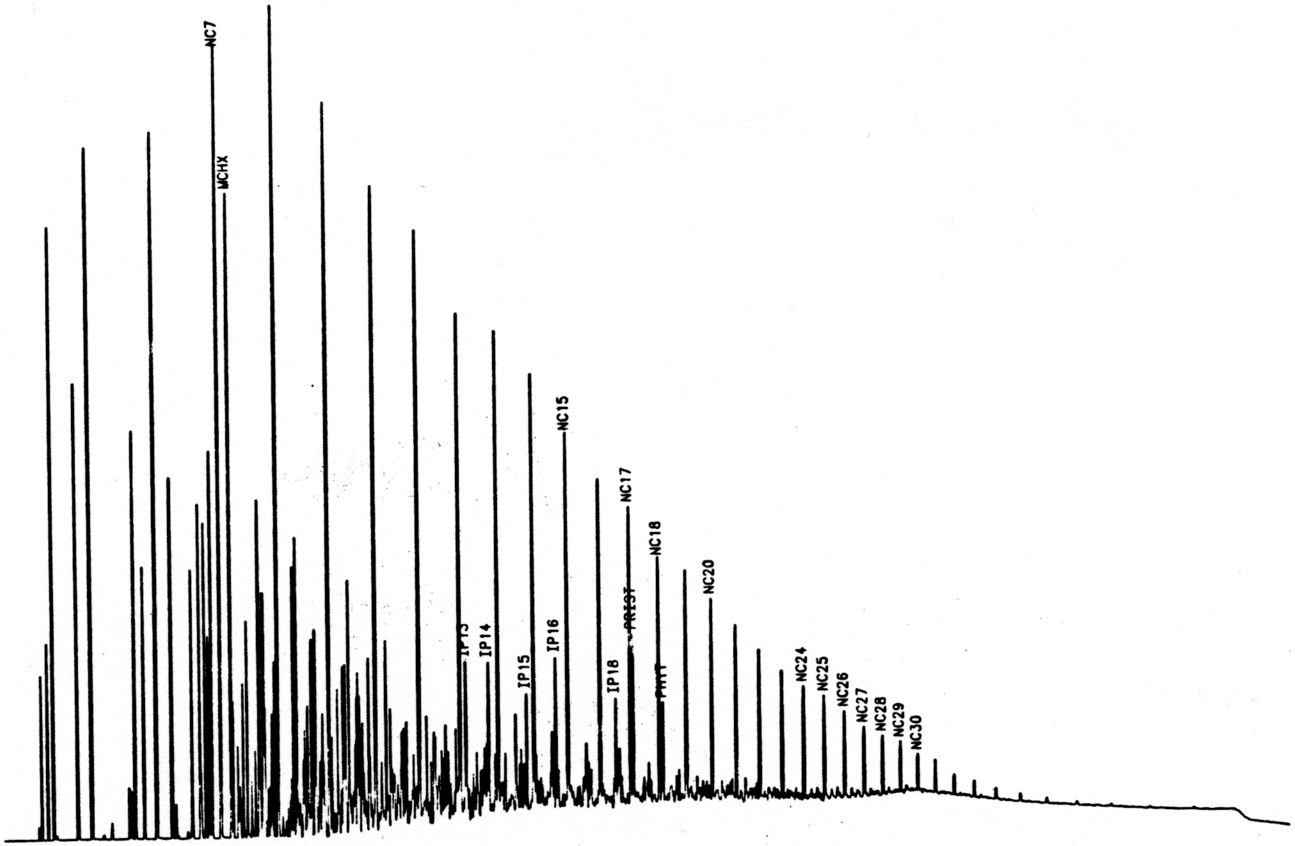
Analysis JB2 6, 1, 1 03-27-86/000213.3/50

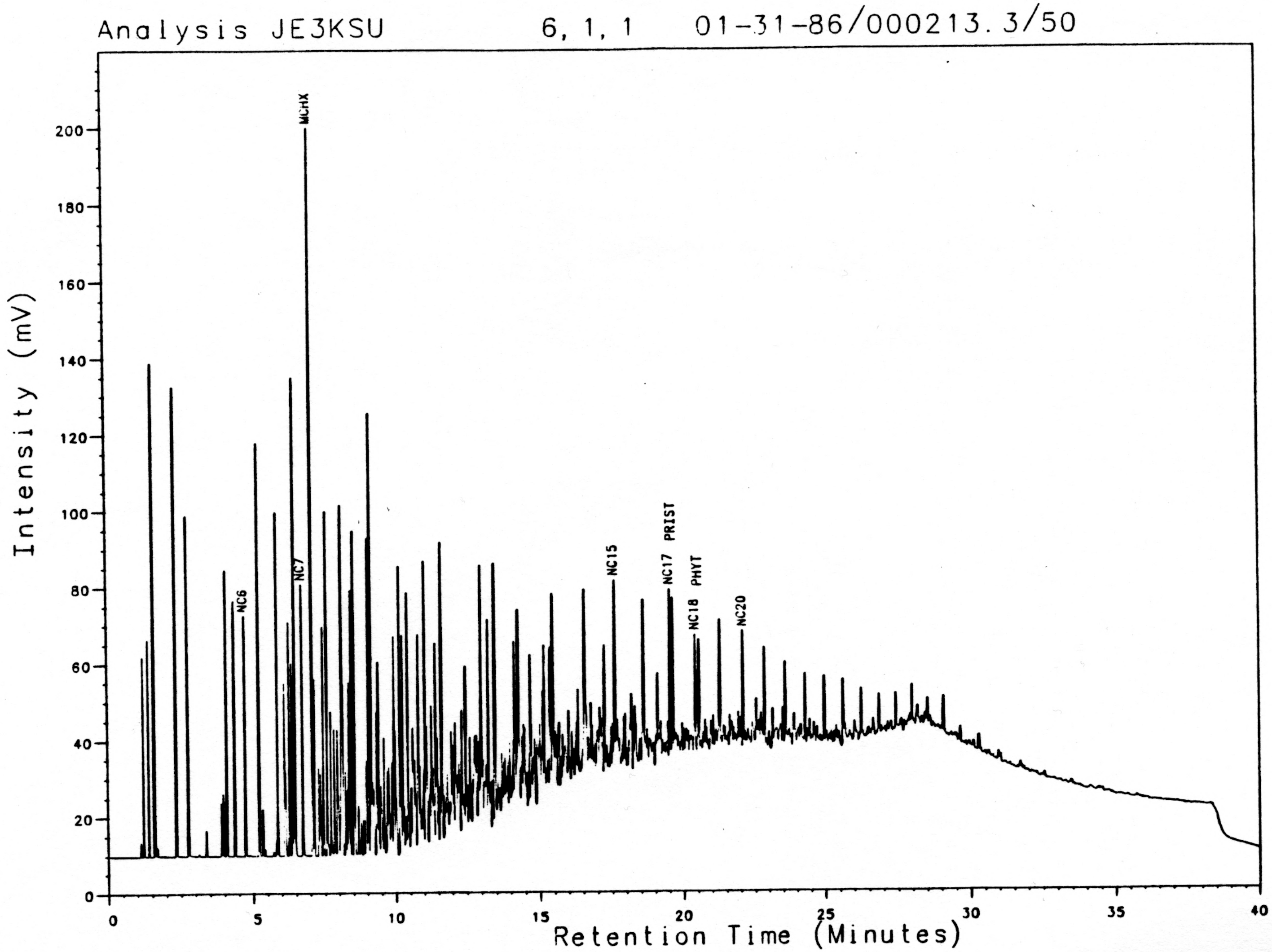


Analysis JB3KSU 6, 1, 1 01-31-86/000213.3/50

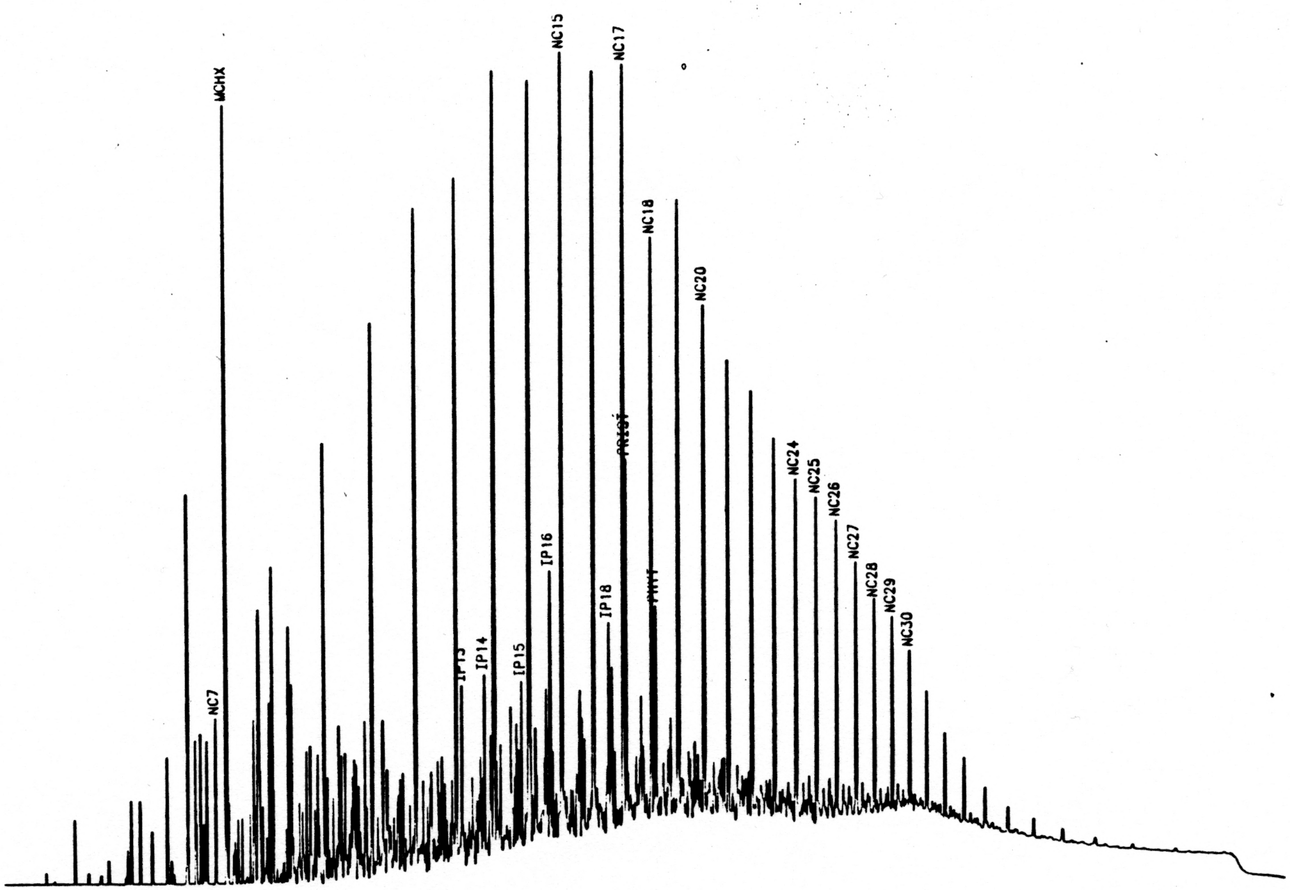


Analysis JE2KSU 6, 1, 1 01-31-86/000213.3/50

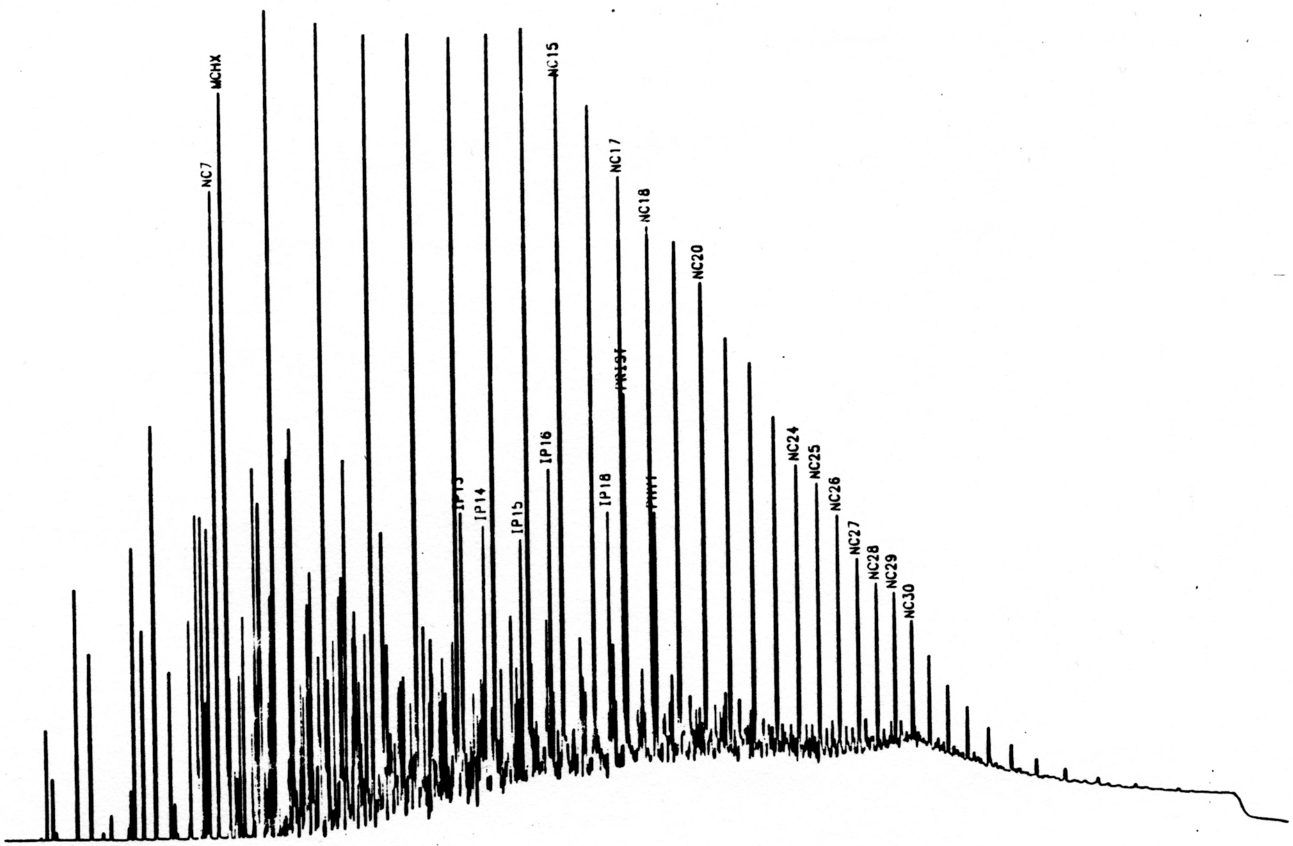



Analysis JE3KSU
6, 1, 1
01-31-86/000213.3/50
Intensity (mV)
Retention Time (Minutes)
MCHX
NC6
NC7
NC15
NC17
PRIST
NC18
PHYT
NC20
0
20
40
60
80
100
120
140
160
180
200
0
5
10
15
20
25
30
35
40

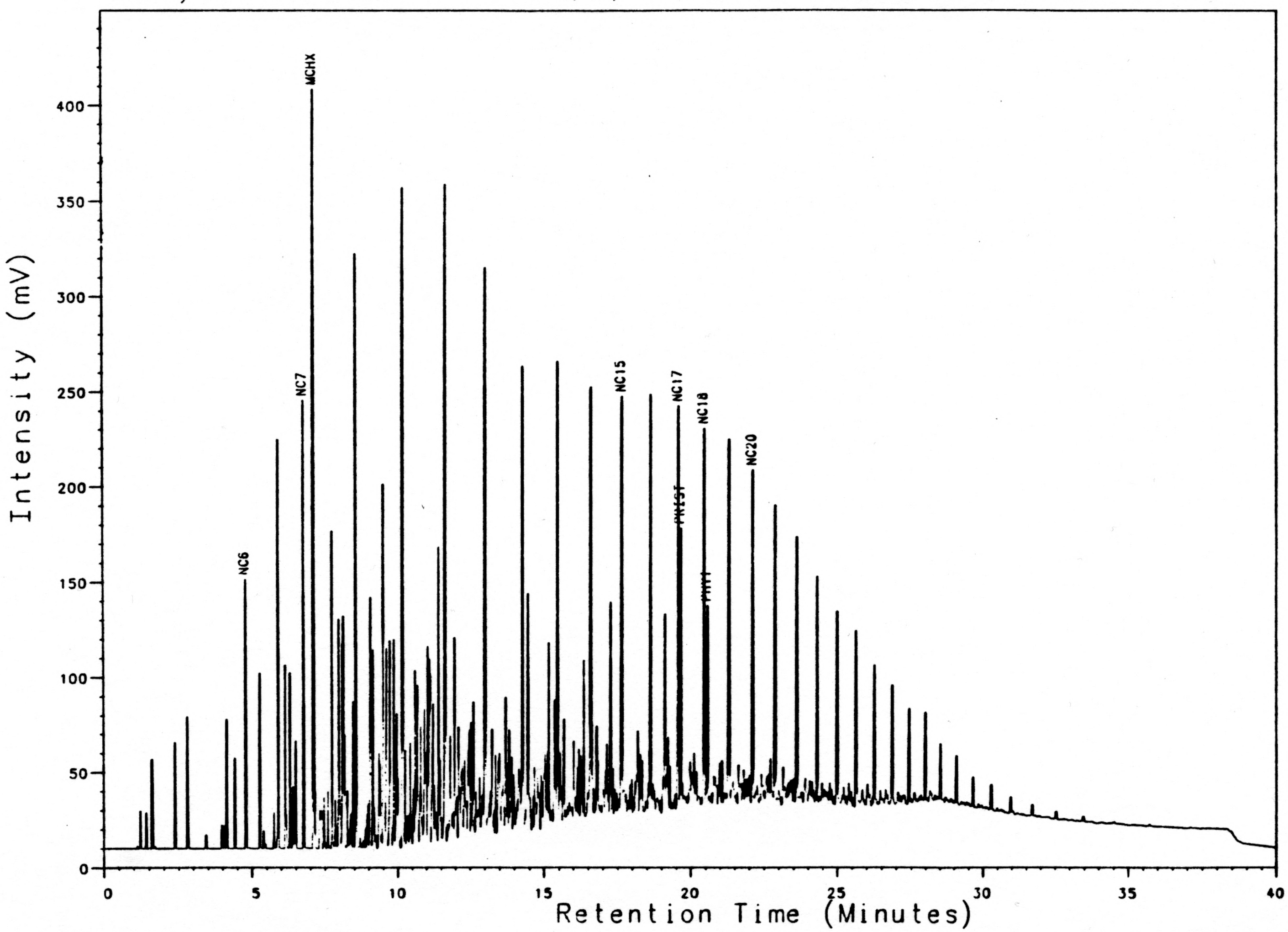
Analysis LN1 6, 1, 1 03-27-86/000213.3/50



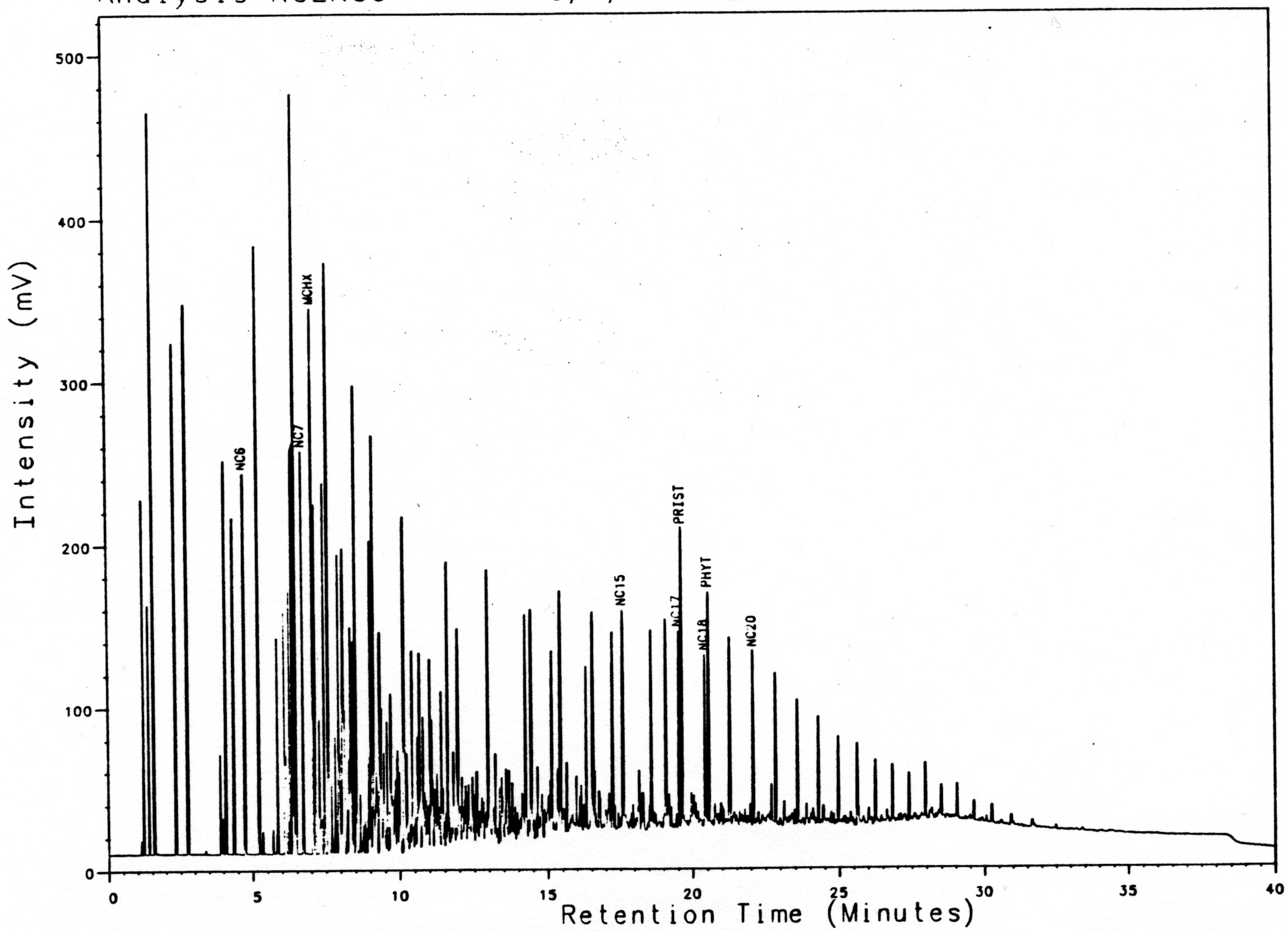
Analysis LN2 6, 1, 1 03-27-86/000213.3/50

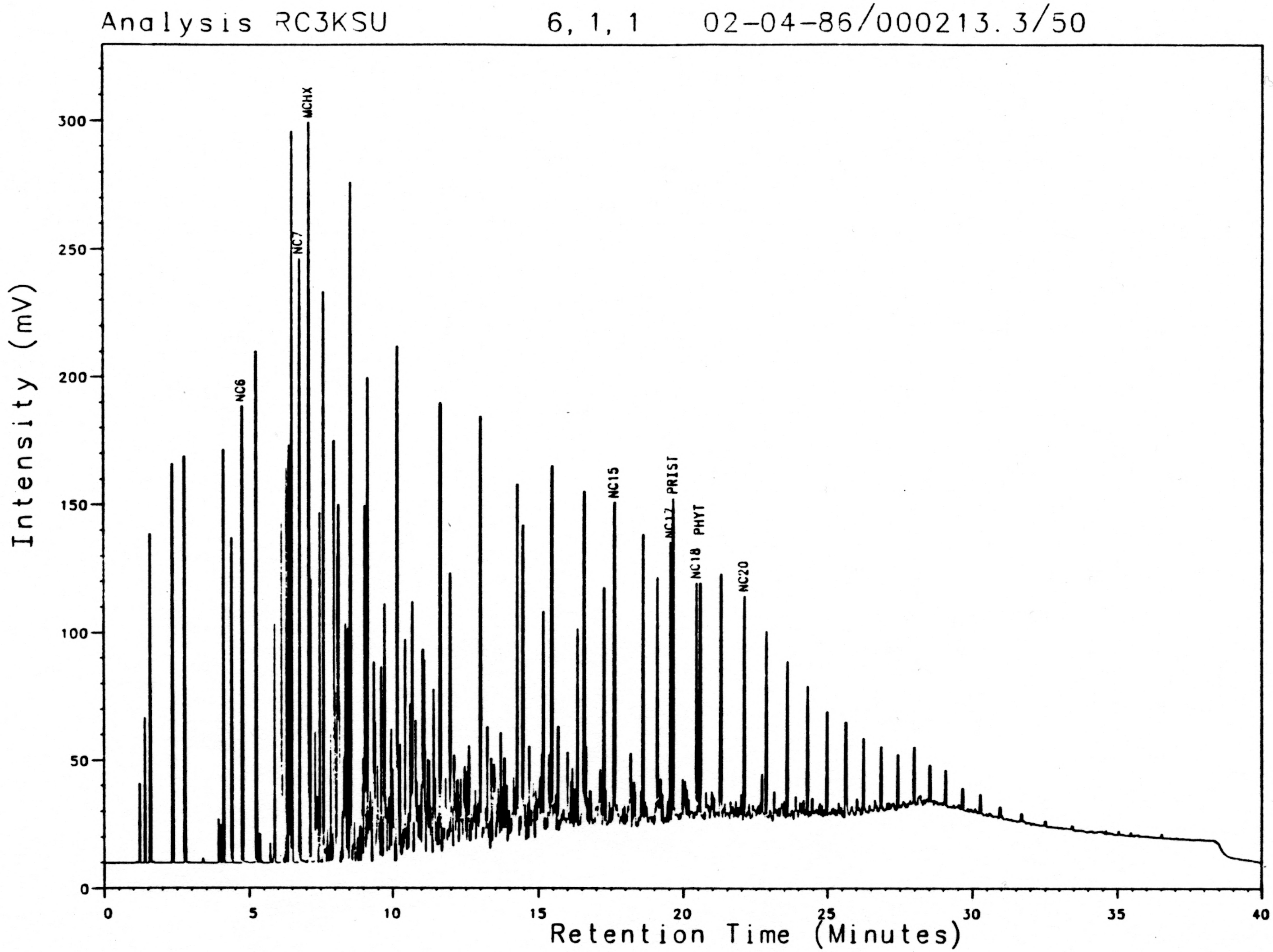


Analysis RC1KSU 6, 1, 1 01-31-86/000213.3/50

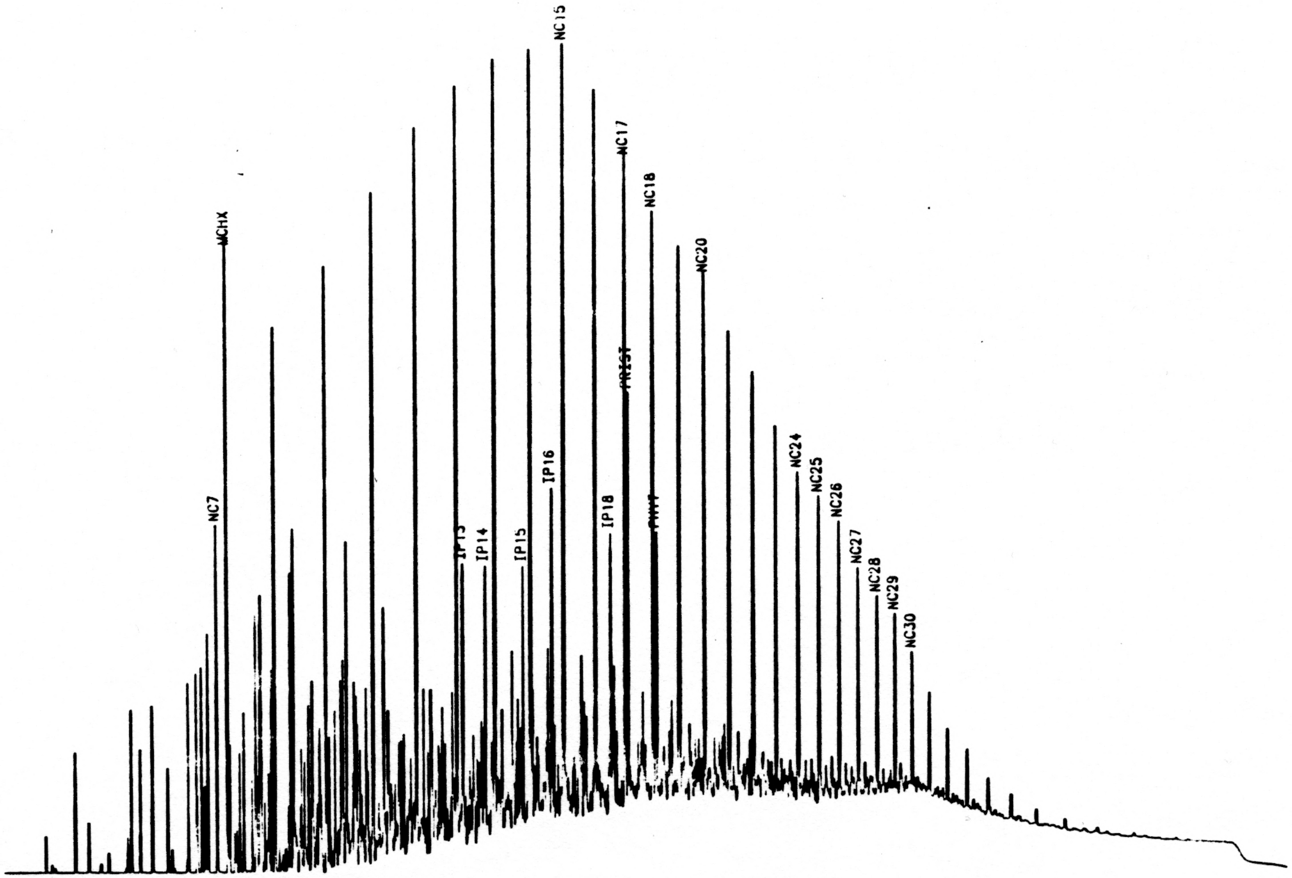


Analysis RC2KSU 6, 1, 1 02-04-86/000213.3/50




Analysis RC3KSU 6, 1, 1 02-04-86/000213.3/50
Intensity (mV)
Retention Time (Minutes)
NC6
NC7
MCHX
NC15
NC17
PRIST
NC18
PHYT
NC20
0
50
100
150
200
250
300
5
10
15
20
25
30
35
40

Analysis VB1 6, 1, 1 03-27-86/000213.3/50



Chemical and Isotopic Investigations of Crude Oils in some Paleozoic Reservoirs: West-Central Kansas

by

John G. Schumacher

B. S. Kansas State University, 1984
M. S. Kansas State University, 1988

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the requirements for the degree

MASTER OF SCIENCE

Department of Geology

Kansas State University
Manhattan, Kansas

1988

ABSTRACT

Twenty-eight Paleozoic crude oils from a 5,000 square mile area on the western flank of the Central Kansas Uplift in western Kansas were analyzed for their API gravities, V, Ni, and S contents, organic chemical compositions, and carbon isotopic compositions. The major purpose of this investigation was to determine the genetic relations among these oils.

The crude oils had moderate API gravities between 29 and 47 and low sulphur contents of less than 0.49 weight percent. Normal alkane distributions broadly suggest two families of oil, one enriched in nC_7-nC_9 (Family I) and the other enriched in nC_{13}-nC_{17} (Family II). Based on the trend of normalized concentrations of the common isoprenoids between iP-13 and iP-20 and the oils may be further subdivided into four types: type A oils are those greatly enriched in iP-13 and iP-16 but considerably impoverished in iP-18 and iP-20 and types C, E, and F were greatly enriched in iP-19 with type C being relatively depleted in iP-15, iP-18, and iP-20, type E being much depleted in all others except iP-16, and type F being depleted in all others except iP-13. Types A, C, and F have the Family I n-alkane distribution characterized by nC_7-nC_9 enrichment, whereas type E oils have the Family II n-alkane distribution with nC_{13}-nC_{17} enrichment. The type A oils also had the highest nC_{17} /pristane and nC_{18} /phytane values of 3.9 and 4.1, respectively; whereas, the type F oils had the lowest values of 0.7 and 1.0, respectively.

The type A and type F oils, the most and the least mature oils in the region, are restricted to southern areas, whereas the type C oils predominate in northern areas and the type E oils are intermediately dispersed. No particular stratigraphic significance can be attached to the geochemical characteristics of the oils. Combination of the n-alkane, pristane/phytane, and nC_{17} /pristane-nC_{18} /phytane data indicates that all the oils were generated from sources deposited under moderately oxidizing marine conditions.

Concentrations of V ranged from less than the detection limit of 0.5 ppm to 57.0 ppm, whereas that of Ni ranged from less than the detection limit of 0.2 ppm to 11 ppm. Both V and Ni concentrations increased northward (r values of 0.52 and 0.42, respectively) while the API gravity decreased in the same direction (r equal -0.47). Three groups of oils were distinguished by V/(V+Ni) ratios: Group I has the ratio between 0.90 and 0.98, Group II less than 0.28, and Group III from 0.76 to 0.89. Following Lewan's interpretation of the V/(V+Ni) and S values, all oils analyzed originated from a moderately oxidizing, mostly marine dominated source.

The $\delta^{13}C$ values of the crude oils ranged from -28.8 to -30.5. Unlike the trace-element (V, Ni , and S) and organic-geochemical (nC_{17} /pristane-nC_{18} /phytane) data that tend to exhibit positive relations with increasing northward distance, the $\delta^{13}C$ values, like the API gravity data, exhibit a negative trend (r equal -0.87) with increased northward distance.

The geographic trends seen in the geochemical parameters of the oils are most easily explained by a mechanism of differential entrapment of generally more mature (and possibly older) oils of higher $\delta^{13}C$ values and lower V, Ni, and S contents in the south and less mature (possibly younger) oils enriched in V, Ni, S, and ^{12}C in more northern traps.