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B.K. Wines*, T. Vermeulen, and R.H. Fish
(*M.S. Thesis)

August 1983

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MOLECULAR CHARACTERIZATION AND FINGERPRINTING OF VANADYL PORPHYRIN AND NON-PORPHYRIN COMPOUNDS IN THE ASPHALTENES OF HEAVY CRUDE PETROLEUMS USING HPLC-GFAA ANALYSIS

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August 1983

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CHAPTER 1

Introduction

The study of trace metals in crude petroleums has been of interest to geochemists for many years. Since the two most abundant metals, vanadium and nickel, are present in forms which differ greatly from those which are believed to have been present in the original petroleum biomass, it is believed that a better understanding of the distribution of vanadium and nickel in petroleums will provide useful information on the diagenesis and maturation of petroleums.[1-3] The study of vanadyl porphyrins in particular has led to much speculation on the means of vanadyl incorporation into the porphyrin ring. Vanadyl porphyrins, the only vanadyl compounds which have been identified in crude petroleums at the present, were first reported by Treibs in 1934,[4-7] but the mechanism by which the vanadyl ion was incorporated into the porphyrin system has yet to be deduced. It is believed by some researchers that vanadyl non-porphyrins acted as intermediates in the transport of the vanadyl ions to the porphyrin rings,[8] but since there have been no positive identifications of vanadyl non-porphyrins in petroleums, these theories cannot be tested. Characterization of the vanadyl non-porphyrins will therefore aid in the understanding of the reactions which affected trace metal distribution during the maturation of the petroleums.

The study of vanadyl compounds in crude petroleums is also important to the petroleum industry. As the world supply of conventional light crude petroleums has diminished it has become necessary to turn to the heavy crude petroleums as refinery feedstocks.[9-11] The use of heavy crude petroleums presents a number of problems to refinery operation: they are more viscous than the light crude petroleums; they have large highly aromatic constituents; they have high trace metal concentrations; and they are richer in heteroatoms; especially sulfur. These properties can be overcome using modifications of conventional refinery techniques, but the catalysts involved in cracking and desulfurization are poisoned by vanadium and nickel compounds.[11,12] Heavy crude petroleums have vanadium concentrations which range from 10 ppm to over 1000 ppm and nickel concentrations which range from 1 ppm to about 200 ppm.[13] Even though these metals are only present in trace quantities, continuous flow of heavy crudes over a catalyst bed soon leaves large amounts of the metal deposited in the catalyst pores, thus rapidly deactivating the catalyst.[14]

To efficiently overcome the effect of metals on the catalysts it is necessary to understand how they are coordinated within the petroleum.[15] This information will aid in the development of improved techniques for removing metals and in the design of catalyst pellets which are less susceptible to interactions with the metal containing compounds. Experiments are already being performed using the identified vanadyl and nickel porphyrin compounds to model catalyst poisoning, but without vanadyl and nickel non-porphyrin compounds these experiments can not accurately model the poisoning behavior of heavy crude petroleums.[14,16-19]

Within heavy crude petroleums there is a high molecular weight fraction known as the asphaltenes. This fraction is especially difficult to process because it is high in condensed aromatic compounds and heteroatoms and usually contains at least half of the trace metals present in the petroleum.[19-22] Asphaltenes are of particular interest in the study of vanadyl compounds, since it is believed by some researchers that the vanadyl porphyrins and asphaltenes were formed in the same period of the petroleum diagenesis.[23] A previous study by Komlenic et. al. examined the distribution of vanadium and nickel compounds in whole crude petroleums by analysis with high performance liquid chromatography coupled with a graphite furnace atomic absorption spectrophotometer (HPLC-GFAA).[24] A similar examination of vanadium compounds contained in the asphaltene fraction of the petroleum would be helpful in establishing the influence of the asphaltene environment on the distribution of vanadium compounds, as well as nickel compounds, in heavy crude petroleums.

1 A. Heavy Crude Petroleums

Heavy crude petroleums differ from conventional light crude petroleums in three major aspects: they are richer in trace metals, especially vanadium and nickel; they have greater concentrations of the heteroatoms, nitrogen, oxygen, and sulfur; and they contain a greater amount of high molecular weight, highly aromatic, asphaltic compounds.[10] In the study of heavy crude petroleums, the petroleum is usually considered to consist of three fractions; the oils, the resins and the asphaltenes.[25] Asphaltenes are defined as a solubility class by their precipitation from forty volumes of a light, straight chain hydrocarbon.[26] The amount of asphaltenes present in a crude petroleum varies from less than one weight percent to over twenty weight percent of the whole petroleum, but even though the asphaltenes represent less than twenty five percent of the whole petroleum, they are richer in heteroatoms and trace metals than both the resins and oils together.[20,27] The predominant structural unit within the asphaltenes are large aromatic sheets with alkyl side chains. These units interact via $\pi - \pi$ interactions between the aromatic sheets and via functional groups in the alkyl chains.[28]

The fraction of the crude petroleum which is not precipitated with the asphaltenes is known as the maltenes and is composed of the paraffinic oils and the resins. The maltenes are fractionated into oils and resins by column chromatography or solvent selective extraction.[29] As their name implies, the paraffinic oils are predominantly composed of saturated hydrocarbons and are of no interest in the study of trace metals. The resins are intermediate between the paraffins and asphaltenes in terms of average molecular weight, aromaticity, heteroatom content, and trace metal content.[30] There is evidence of some stacking between resins, as well as strong interactions with the aromatic portions of the asphaltenes.[28] In the heavy crude petroleum the resins solublize the asphaltenes, which are by themselves insoluble in petroleum.[25] Studies performed with the separated resins and asphaltenes of several petroleums have demonstrated that there is a unique relationship between the resin and asphaltene of a given crude petroleum; an asphaltene can only be solublized by its native resin. This relationship between asphaltenes and their resins has led some researchers to propose that the resins are asphaltene precursors.[29]

1 B. Asphaltenes

1 B. 1. Definition

Although there is a history of controversy in the literature, the generally accepted definition of an asphaltene is the fraction of a petroleum which is insoluble in 40 volumes of a low molecular weight, straight chain hydrocarbon.[25,26] Pentane, hexane, and heptane are the three most commonly used solvents, with pentane being the most common solvent used in the recent research conducted in this country. In the literature, precipitations using volume of solvent to petroleum ratios of 6:1, 10:1, and 25:1 have all been reported and are still appearing in some current publications, but 40:1 is the most acceptable solvent to petroleum ratio.[11,21,22,27,31-33]

In the choice of precipitating solvents there has been a question as to which solvent precipitated "true asphaltenes". The amount of asphaltenic material precipitated is related to the carbon number of the precipitating solvent; pentane producing the largest amount of material and heptane the least.[34] It was discovered that asphaltenes precipitated from pentane, which were subsequently re-precipitated from heptane, gave higher yields of asphaltenes than were obtained by heptane precipitation of crude petroleums.[11,29] This behavior suggests that some compounds in the maltenes are trapped in the asphaltenes as they are precipitated from pentane. Some of these trapped maltenes could be soluble in heptane, but steric restrictions would prevent them from being extracted from the asphaltene. Since the use of heptane results in less entrapment of maltenes than does pentane, it was thought to produce a "truer" asphaltene. Current practice recognizes the validity of asphaltene precipitation from any of the three common solvents, but acknowledges a distinction between pentane-asphaltenes, hexane-asphaltenes, and heptane-asphaltenes.[26,34]

Further variations in the nature of the precipitated asphaltenes result from the conditions under which the precipitation is performed. There are several papers in the literature in which the asphaltenes are heated and/or centrifuged during precipitation. The complex nature of the asphaltenes makes the composition of the precipitated material susceptible to either of these conditions.[35,36] This is especially true of centrifugation, which has been shown to lower the vanadium concentration of the asphaltenes by as much as 30 percent.[33]

1 B. 2. Structure

The difficulty in establishing the proper method of asphaltene precipitation is a result of the complex nature of the asphaltenes. The first concepts which provided the basis for the current understanding of the asphaltene structure were developed by Nellenstein in 1923 and Pfeiffer and Saal in 1939.[37] Nellenstein was the first to suggest that the asphaltenes be looked at as colloid systems. Pfeiffer and Saal expanded on this model by proposing that the asphaltenes were large micelles which were peptized by compounds in the maltenes.[37] The Pfeiffer and Saal model of native asphaltenes was based on a nucleus of associated asphaltene molecules coated with a layer of resin molecules. A steady gradient of molecular weights was thought to exist within the micelle, varying from several thousand dalton macromolecules at the heart of the micelle, to small paraffin like molecules at the outer surface of the resin layer.[37,38]

The first major advance on the work of Pfeiffer and Saal came in 1967 when Dickie and Yen presented their model for the structure of asphaltenes.[28] This model, shown in Figure 1, was based on extensive work with vapor pressure osmometry, X-ray diffraction, ultracentrifugation, gel permeation chromatography, mass spectrometry, and electron microscopy. As the figure illustrates, the asphaltene is a complex macropolymer. The fundamental building blocks of the asphaltene are condensed aromatic sheets with alkyl side chains. The sheets stack via $\pi - \pi$ interactions to form the particles, or unit cells, and the particles interact to form micelles. Depending on the functional groups contained in the alkyl side chains, there are many possible intra- and inter-micelle interactions which can effect the apparent size or structure of the asphaltenes.[21,22] The large aromatic regions make it possible for aromatics in the resins to

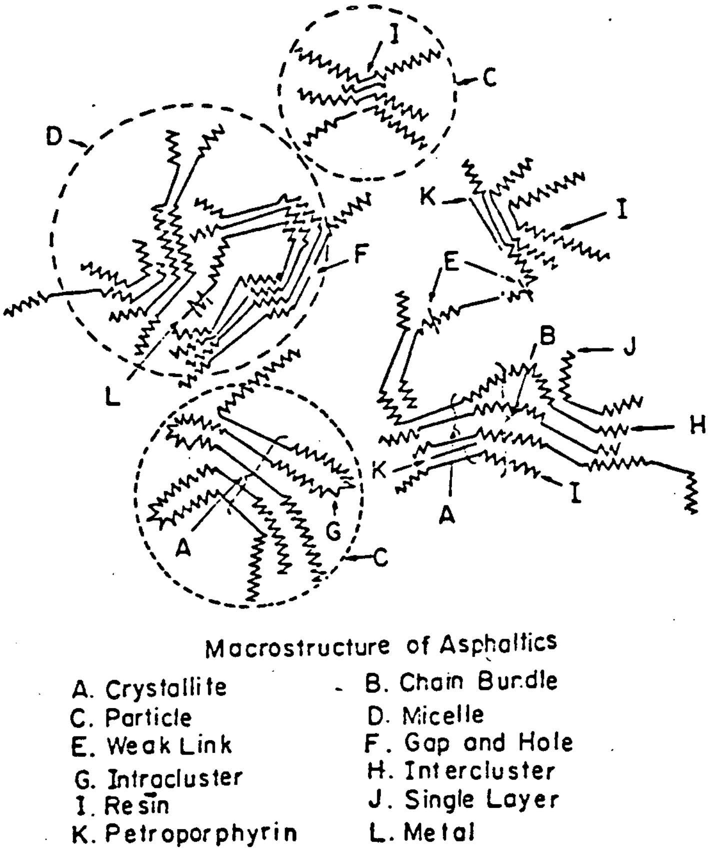


Figure 1. Schematic of asphaltene macrostructure from J. P. Dickie and T. F. Yen, "Anal. Chem.", 39(14), 1847, (1967)[28]

interact with the asphaltenes, as well as providing good sites for porphyrins and other aromatic compounds to bond within the asphaltene structure. Within this structure trace metals can be coordinated by ligands which are bound to the asphaltenes or by heteroatoms at defect sites in the aromatic sheets. Resins associate with the asphaltenes via $\pi - \pi$ interactions or hydrogen bonding.[25]

The central section of the particle, the crystallite, lends itself to examination by x-ray diffraction studies. The central aromatic regions are found to have diameters on the order of 12 Å and consist of between 3 and 6 sheets at a spacing of about 3.5 Å.[25] ^{13}C and ^{1}H nuclear magnetic resonance spectroscopy (NMR) have been combined with infrared spectroscopy (IR) in several algorithms for calculating the extent of aromaticity and alkyl substitution of the asphaltene sheets.[39] Because of the complex nature of the asphaltenes, such studies can only give rough approximations of the distribution of carbon atoms. In general at least 45 percent of the carbon atoms appear to be involved in aromatic systems, and the remaining carbons are involved in alkyl side chains of about four to eight carbon atoms. The aromatic sheets appear to contain between 6 and 20 rings.[25]

1 B. 3. Molecular Weight of Asphaltenes

The large variety of interactions possible in the Dickie and Yen model of asphaltenes help to explain why different techniques for measuring asphaltene molecular weights have given results ranging from 1000 to 300,000 daltons;[38] the ability of a technique to overcome the various interactions among the micelles and side chains determines the size of the particle which is being studied. One of the most common means of determining asphaltene molecular weights is vapor pressure osmometry (VPO). Repeated studies have shown that the molecular weights determined by this technique are weak functions of temperature and strong functions of the solvent used in the determination and the concentration of the asphaltene in the solvent.[42] When data for various concentrations are plotted, it is found that the molecular weights of the asphaltenes tend toward a minimum at infinite dilution and when data for different solvents are compared the solvents with the highest dielectric constants give the lowest molecular weights. At large dilutions in a solvent with a high dielectric constant, such as nitrobenzene, individual micelle weights can be measured.[38] When these results are combined with the X-ray diffraction results, unit sheet weights of 800 to 3500 daltons are calculated.[28]

Finally it should be noted that when molecular weights of asphaltenes are measured, it is an average molecular weight that is calculated. Size exclusion chromatography shows that the asphaltenes actually contain a continuum of molecular weights ranging from less than 100 daltons to over 10,000 daltons.[34] Studies of petroleum asphalts conducted by Boduszynski have cast doubt on the actual existence of asphaltene constituents with molecular weights as high as 10,000 daltons.[40,41] According to Boduszynski, asphaltenes are composed of highly polar or polarizable compounds with molecular weights between 380 and 1800 daltons and an average molecular weight of about 1000 daltons. Molecular weights in excess of 1800 daltons are attributed to strong interactions between functional groups, which are not overcome by the solvents used in molecular weight determinations by VPO and gel permeation chromatography. During precipitation, agglomerates are formed through interactions between functional groups. Pyrroles, phenols, amides, carboxylic acids, and polynuclear aromatics are among the functional groups which have been identified in the asphaltenes by Boduszynski.[40,41]

1 B. 4. Asphaltene-Resin Equilibria

VPO analysis of asphaltene molecular weights demonstrated that the degree of association between asphaltene particles is not only a function of the asphaltene structure, but also of the environment. Electron spin resonance spectroscopy (ESR) studies of the free radicals in asphaltenes provide a means of studying the degree of asphaltene association. At least half, if not all, of the free radicals present are associated with charge transfer equilibria between the stacked aromatic sheets. Since the ESR signal intensity decreases with increasing dilution, it is concluded that an equilibrium exists between the forces which cause the solvent to complex with the asphaltenes and the forces which cause the aromatic sheets to stack.[43] Similar interactions are assumed to exist for asphaltenes in whole petroleums, but since all of the work with asphaltenes is performed using material that has been precipitated from the native petroleums, it is difficult to study these interactions.

It has been generally accepted that Pfeiffer and Saal were correct in stating that asphaltene micelles formed large units which were peptized in mass by the resins,[37] but work by Koots and Speight indicates that this may not be the actual state in the whole petroleum.[29] Based on work with isolated resins and their interaction with various precipitated asphaltenes, Koots and Speight have shown that it is likely that it is the individual micelles which are peptized in the whole petroleums and not large agglomerations of micelles. The size of the micelles is governed by the equilibria between resin - asphaltene interactions and asphaltene - asphaltene interactions.[29,38]

1 B. 5. Heteroatoms

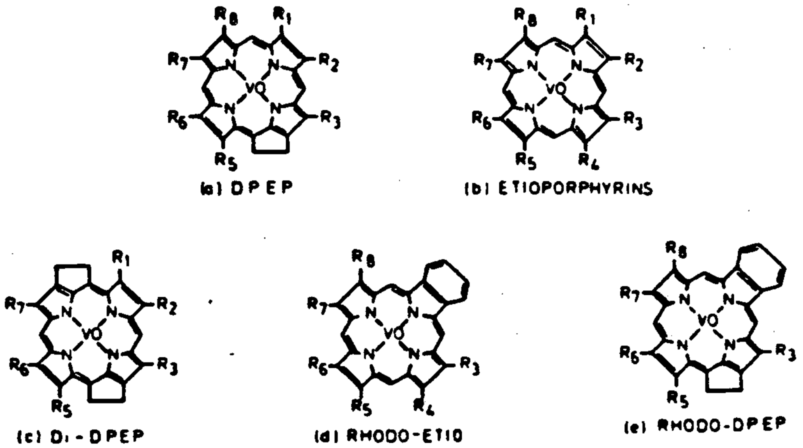
Nitrogen, oxygen, and sulfur are the most abundant heteroatoms in asphaltenes. Although the concentrations of these elements vary between petroleums, nitrogen and oxygen are typically present at concentrations on the order of 1 to 2 weight percent.[25] Sulfur concentrations vary widely from petroleum to petroleum and may be present at concentrations lower than 1 percent or greater than 5 percent.[25] Several researchers have noted that there is a roughly linear correlation between sulfur concentration and asphaltene and vanadium concentration.[25] Nitrogen is believed to be located principally in heterocycles. Oxygen and sulfur are believed to be involved in functional groups within the alkyl side chains and in heterocycles.[25,44]

Sulfur has received more attention than the other heteroatoms because of its role in catalyst poisoning. Various catalytic cracking experiments indicate that sulfur is located at important links in the structure of asphaltenes, since vanadium removal is always paralleled by sulfur removal.[21,45-47] Based on the catalytic experiments and further experiments directed at breaking carbon-sulfur bonds, some researchers have concluded that asphaltenes are sulfur polymers.[48] It is the breakdown of the polymer structure through sulfur removal in catalytic hydrodesulfurization which disrupts the asphaltene structure sufficiently to allow the vanadium compounds to leave the asphaltene structure and interact with the catalyst.

The three heteroatoms are important in the study of vanadyl and nickel compounds in heavy crude petroleums, since they are present in the ligands which chelate the metal species. The chelating atoms may be present either as defect centers in the aromatic sheets of asphaltenes or as members of distinct ligand molecules.[49-51] The system which has received the most study to date is the porphyrin ring, which has a chelating site with four nitrogen atoms (see Fig. 2). Mass spectrometry (MS) and electron spin resonance spectroscopy (ESR) data indicate that the trace metals in the crude petroleums may also be coordinated by the following heteroatom combinations: NO_3, N_2O_2, N_3O, O_3S, S_4, S_3N, or S_2N_2 ligand systems.[1]

1 B. 6. Trace Metals

The most abundant trace metals in asphaltenes are vanadium and nickel. Vanadium is present at concentrations varying from 100 ppm to over 5000 ppm in asphaltenes.[3,13] Nickel is present at



(a) DPEP

(b) ETIOPORPHYRINS

(c) Di-DPEP

(d) RHODO-ETIO

(e) RHODO-DPEP

Figure 2. Classes of porphyrins found in petroleums.[61]

Figure 3. Axial coordination of basic solvent to a vanadyl compound in a square planar ligand.[50]

concentrations varying from 10 ppm to about 500 ppm.[21] Vanadium is usually in the form of the vanadyl ion (VO^{2+}).[52] In a tetradentate vanadyl compound one of the coordination sites perpendicular to the ligand plane is occupied by the oxygen atom, leaving only one site vacant to interact with other species.[53,54] It is the presence of this open site which makes it possible to extract vanadyl compounds from asphaltenes with coordinating solvents such as pyridine (see Fig. 3). When coordinated in tetradentate ligands, nickel (Ni^{2+}) ions satisfy all bonds in the ligand plane and therefore are less polar and surface active than vanadyl complexes, although strong ligands can axially coordinate to them.[20,55] The differing electronic structures of the vanadyl and nickel ions results in differing behavior during catalyst poisoning and is also believed to have had a strong effect on the relative distributions of the metals in the petroleums during the process of diagenesis.[46,56]

Because of its electronic structure, vanadium can be studied by ESR. At room temperature the ESR spectrum of asphaltenic vanadium is characterized by a sixteen line anisotropic hyperfine structure, but at temperatures in excess of 200°C the predominant species is characterized by an 8 line isotropic structure.[21] The change in the spectrum indicates that at elevated temperatures the vanadyl compounds are free to tumble at rates sufficiently rapid to time-direction average out the anisotropies. A similar but less dramatic effect is observed when asphaltenes are dissolved in solvents with high dielectric constants. Since dilution is believed to affect the extent of extent of stacking of aromatic sheets, Tynan and Yen suggest that the vanadyl compounds are either coordinated to the surface of the micelles or trapped within the layers of the crystallites.[21,57] Based on ESR data, an activation energy of 14 kcal/mole has been calculated for the transformation from bound to free vanadyl complexes. This activation energy is too low to account for a primary chemical bond but is of the right order of magnitude for a two step process involving the dissociation of aromatic sheets, followed by either the dissociation of an aromatic ligand system from an aromatic site within an asphaltene molecule or the breaking of a coordination bond between a heteroatom and the vacant coordination site of a tetradentate vanadyl compound. Further work by Shibata et. al. at temperatures up to 400°C has shown that there is a second type of dissociation of vanadyl compounds from asphaltenes at temperatures above 340°C.[58]

1 B. 7. Metallic Complexes of Porphyrins

Metal compounds in crude petroleums are characterized as either porphyrin or non-porphyrin.[8] Porphyrins are 16 member aromatic rings composed of four pyrrole rings joined by methylene bridges. The four nitrogen atoms are capable of chelating vanadyl ions (VO^{2+}) and nickel ion (Ni^{2+}) to form very stable metallo-organic complexes. Vanadyl porphyrin concentrations vary from petroleum to petroleum and in some petroleums they account for over 50 percent of the total vanadium present.[20,50,59] Detection of porphyrins is facilitated by their UV-VIS spectra, which is distinguished by an intense absorption at approximately 408 nm, the Soret band, and secondary absorbances between 500 and 600 nm.[13] Using the secondary absorbances it is possible to identify the three major classes of porphyrins which occur in crude petroleums. The two most abundant classes are the etio porphyrins (ETIO) and the deoxophylloerythroetioporphyrins (DPEP).[8,60] The third class consists of porphyrins with a benzo-ring fused to one of the pyrrole groups and is known as the rhodoporphyrins; these rhodoporphyrins exist with both the etio and DPEP structures (see Fig. 2).[61] Within each class of porphyrins, there is a great variety in the length of the alkyl side chains.[62] Work with etio porphyrins has confirmed the existence of porphyrins with carbon numbers ranging from C_{28} to over C_{60}.[61] Most researchers believe that the porphyrins present in the heavy crude petroleums are all derived from chlorophyll pigment, although there is some disagreement on this point.[13,63,64]

1 B. 8. Metallic Complexes of Non-Porphyrins

Metallic complexes of non-porphyrin ligands lack an intense and characteristic absorption band like the Soret band at 408 nm and are, therefore, much more difficult to analyze than metallo-porphyrins. Even the definition of what constitutes a non-porphyrin complex is not consistent in the literature. It is agreed that compounds lacking a Soret band (408 nm) are non-porphyrins, but some researchers also classify porphyrins with extended aromatic systems as non-porphyrins.[3] This later condition would make rhodoporphyrin the only non-porphyrin which has been positively identified in crude petroleums. In this study, any ligand with the aromatic, four pyrrole ring structure (see Fig. 2) is considered a porphyrin; regardless of the nature of the side chains or any extended aromaticity.

In the literature, two general classes of vanadyl complexes of non-porphyrins have been reported.[31] The first class consists of non-extractable vanadyl complexes. After metallic porphyrin complexes have been extracted from an asphaltene, the remaining material is still rich in vanadium. These vanadyl non-porphyrin compounds have weak absorptions at about 410 nm over strong background absorptions. Molecular weight distribution studies show that this material contains large molecular weight compounds, which are probably either large molecules containing vanadyl ions coordinated to heteroatoms in the asphaltene structure or smaller vanadyl compounds which have become entrapped in the asphaltene structure. It is likely that vanadyl porphyrins are trapped within the structure, with background absorbances masking the weaker secondary absorbances. According to Rogers, most of the compounds in this class of vanadyl non-porphyrins are associated with systems involving nitrogen heterocycles.[65]

The other class of vanadyl non-porphyrins consists of compounds with molecular weights of the same order of magnitude as the porphyrins (approximately 300 to 800 daltons). Experimental work indicates that these compounds may have NO_3, N_2O_2, N_3O, O_3S, S_4, S_3N, or S_2N_2 ligand environments.[1] Several compounds have been suggested as possible non-porphyrin ligands for trace metals. The systems that have been proposed include β- diketones, β- ketoimines, β- dithiones, glyoxal bis(o-mercaptoanils), and reduced porphyrin rings.[50] In general, the proposed non-porphyrin ligands have ring systems that vary from 12 to 16 membered rings and are less stable in dilute acid than the corresponding porphyrins. At present there have been no successful studies on the speciation of vanadyl non-porphyrin compounds in heavy crude petroleums.

1 C. Previous Analysis of Vanadyl Compounds in Petroleums

1 C. 1. Vanadyl Porphyrins

Vanadyl porphyrins were first identified in crude petroleums by Treibs in 1934.[4-7] Treibs removed porphyrins from petroleums by acid demetallation with a mixture of acetic acid and HBr and identified the separated porphyrin ligands on the basis of their distinctive UV-VIS spectra. By varying the extraction conditions, Treibs was able to selectively remove several porphyrin classes and made the first identification of ETIO and DPEP porphyrins in crude petroleums. Up until the late 1960's acid demetallation continued to be the preferred technique for porphyrin extraction, with improvements to Treibs method made by Groennings in 1953 and Dunning in 1960.[66,67] Methanesulfonic acid, p-toluenesulfonic acid, phosphoric acid, and sulfuric acid have also been used for demetallation.[1]

When the acid solution is separated from the petroleum it is found that there are not enough porphyrins present to have chelated all of the vanadium present in solution.[27] Also, there is some vanadium which resists acid extraction from the petroleum. The vanadium in solution in excess of that required for association with the observed porphyrin concentration is believed to have been liberated from non-porphyrin compounds, which may have decomposed in the acid. It is also possible that some non-porphyrin ligands remain trapped in the asphaltenes. The inextractable vanadium is likely to be present in vanadyl porphyrin and non-porphyrin compounds which are inaccessible to the acid by virtue of the asphaltene structure. A further possibility is that there are some vanadyl compounds present which are stable with respect to acid demetallation, since studies with aryl substituted porphyrins, such as vanadyl TPP (see Fig. 4), have shown them to be stable in acid solutions.[50,68]

Many researchers have used the spectra of demetalled porphyrins as a means of measuring porphyrin concentration in the petroleum.[2,27] Based on an assumed extinction coefficient for either the Soret band or one of the characteristic bands between 500 nm and 600 nm, Beer's law is used to calculate the concentration of porphyrins present in solution. This technique introduces several inaccuracies. The various porphyrin types, principally ETIO and DPEP, have differing maximum absorbance wavelengths and extinction coefficients. To obtain an accurate value of the porphyrin concentration it is necessary to know the relative abundance of the various petroporphyrins; information which is usually not available without extensive analysis of the porphyrin solution. Acid demetallation also makes it impossible to distinguish between nickel and vanadyl porphyrins and may effect the side chains of porphyrins. Sugihara tried to overcome the effects of demetallation by taking UV-VIS spectra of whole petroleums in dilute solutions, but this technique is still affected by the necessity of arbitrarily averaging extinction coefficients.[69] An additional complication in using metallated petroleums is the need to average in the effect of nickel porphyrin absorbances. The predominance of ETIO and DPEP porphyrins in crude petroleums probably keeps the error involved in the various methods of spectroscopically determining metallo-porphyrin concentrations to within ten percent.

Some researchers have used solvent extraction to remove vanadyl porphyrins from petroleums prior to demetallation. Typically pyridine is used as the coordinating solvent for extracting vanadyl compounds, but some extractions have been performed using methanol and toluene.[70,71] The extracted vanadyl porphyrins are often purified by TLC or LC prior to demetallation with sulfuric or methanesulfonic acid.[61,72] Relatively little chromatography has been done with the metallated porphyrins, since the demetallated porphyrins are easier to separate using conventional chromatographic column packings.[24,71,88]

Mass spectrometry studies of extracted, demetalled porphyrins gave the first corroboration of the UV-VIS spectra which had indicated the presence of ETIO and DPEP porphyrins in petroleums.[60,73,74] In addition, mass spectrometry studies provided the first evidence that the porphyrins existed as homologues series varying in carbon number from C_{28} to over C_{60}.[61,75] Some researchers have found the molecular weight distributions within homologous series to be Gaushad occurred in diagenesis,[50] but Barwise and Whitehead report that the distribution is skewed toward higher molecular weights.[61]

Recently Eglinton et. al. have used demetallated porphyrins to establish the structure of several naturally occurring porphyrins.[72] Using HPLC and TLC, single porphyrin peaks were isolated. These porphyrins were oxidized to maleimides using chromium trioxide. GC-MS analysis of the maleimides was used to determine the alkyl substitution pattern on the pyrrole rings. The presence of pthaleimides in the oxidation products of some porphyrins confirmed the presence of rhodoporphyrins in the petroleums. All of the petroporphyrins identified by Eglinton et. al. appear to be derived from chlorophyll a.

1 C. 2. Vanadyl Non-porphyrins

As mentioned above, acid demetallation experiments proved that not all of the vanadium present in crude petroleums was bound in porphyrin rings.[59] The non-porphyrin vanadium compounds are divided into two general classes: non-porphyrinic compounds which can be extracted in an acid solution, where some of the compounds may decompose, and compounds which resist acid extraction and remain in the petroleums.[31] These two classes of non-porphyrins have both been studied to varying degrees.

Spencer and Rogers have examined the large macromolecular metallo-non-porphyrins.[76] The vanadyl porphyrins are initially extracted from asphaltenes via liquid chromatography. The material remaining behind after the porphyrins are removed has a molecular weight distribution similar to that of the original asphaltene and a UV-VIS spectrum featuring a week absorbance maximum at about 410 nm and no absorbance peaks in the 500 nm to 600 nm range. Rogers used a chromatographic technique described by Latter to separate the vanadyl non-porphyrins into several functional classes. Most of the vanadium was found to elute in a fraction which was rich in nitrogen heterocycles.[65]

Mass spectrometry provided the first evidence of a ligand system other than four nitrogens. Some of the peaks observed by Yen can only be explained by N_3O or NO_3 ligand systems.[50] Dickie has also used mass spectrometry to locate N_2O_2, O_3S, S_4, S_3N, S_2N_2 ligand systems in resins.[1]

The most powerful tool for locating ligand systems other than N_4 is ESR spectroscopy. The two ESR parameters which are useful for determining the chelating environment are the isotropic g_o value and A_o, the hyperfine splitting constant. Of these two parameters g_o is especially valuable since it is almost entirely dependent on the coordinating atoms alone, while A_o shows some variation with solvent effects and substituent variations.[77] Many pure vanadyl compounds have been analyzed by ESR spectroscopy and rough correlations between A_o, g_o, and the ligand environment have been developed.[78-82] Based on this data, Yen has reported that Boscan asphaltenes have A_o and g_o values intermediate between an N_4 and an N_2O_2 environment. Dickson has measured the A_o and g_o values for chromatographically separated fractions of maltenes and asphaltenes and found that some of the less fractions of maltenes and asphaltenes and found that some of the less polar fractions may have an S_4 environment, while the polar fractions and whole maltenes appear to have an N_2O_2 environment.[77]

In general the ESR spectra of asphaltenes are most similar to those of vanadyl porphyrins, which were probably present to some extent in all of the fractions studied above. Because of the presence of N_4 ligands in all of the fractions, the assignment of ligand types is usually not made by exact agreement with the experimental g_o values derived from pure compounds, but on the basis of the direction and magnitude of deviations from the g_o values for N_4 ligands.[77]

The simplest distinction between metallo-porphyrins and metallo-non-porphyrins is the absence of the Soret band (408 nm). A fraction of Sdom crude petroleum has been reported that does not have a Soret absorption and is easily demetallated.[50] Unfortunately, no further work with this vanadyl non-porphyrin fraction has been reported.

1 C. 3. Column Chromatography and HPLC Analysis of Petroleums

Column chromatography has been used to analyze petroleums in different ways. Several column chromatography techniques have been developed to separate petroleums into saturates, neutral aromatics, and heterocycles and similar HPLC techniques are being developed.[83,84] Rogers has used one of these techniques in determining the general environment of large molecular weight vanadyl non-porphyrins.[65] Gel permeation chromatography has been used to study the molecular weight distribution within petroleums and asphaltenes using both conventional column chromatography and HPLC systems. Typically spherogel or lichrospher packings are used as the stationary phase with THF serving as the mobile phase.[32,85] These molecular weight separations are improved by using several columns with varying pore sizes in series.[28,86] The eluting compounds are monitored by UV-VIS absorbance at a fixed wavelength (usually 254 nm) to produce a profile of the molecular weight distribution, but since the various constituents of petroleums do not have equal absorbances at a given wavelength this technique gives only an approximate indication of the abundance of material at various molecular weights. Asphaltenes analyzed by gel permeation chromatography are found to have molecular weight distributions which are skewed toward molecular weights in the range of 10,000 daltons, but still have considerable amounts of material with molecular weights ranging well below 1000. It has been suggested by some researchers that molecular weights in excess of 2000 daltons do not actually represent individual molecules, but are composed of agglomerations of smaller molecules, which are formed by strong interactions between functional groups.[40,41] Even if this theory is correct, gel permeation chromatography profiles can still be used as fingerprints, since the extent of agglomeration appears to be unique to each petroleum.[85,86]

Column chromatography using silica gel or alumina is an alternate technique for removing metallo-porphyrins from petroleums.[60] Unlike acid extraction, chromatographic extraction does not present any danger of altering the structure of the petroleum components and the retention of the metal in the porphyrin makes it possible to distinguish between vanadyl and nickel porphyrins. If the solvent system is selected properly it is even possible to separate nickel porphyrins from the more polar vanadyl porphyrins.[87] Hajibrahim has worked at optimizing this separation on the basis of the retention times of model vanadyl and nickel porphyrins.[88] Purification of the isolated porphyrins can be achieved through TLC, further liquid chromatography or HPLC coupled with visible detectors operating at 410 nm.[8,89,90] Hajibrahim has done extensive HPLC work with both both metalloporphyrins and acid demetallated porphyrins. This work established the presence of structural isomers in petroporphyrins as some of the peaks which were easily separated by HPLC gave identical mass spectrometry data.[89] Hajibrahim also noted that the visible absorption data from HPLC runs with porphyrins of different crude petroleums were unique and suggested that HPLC analysis of porphyrins would be an effective method of fingerprinting petroleums.[71]

Barwise and Whitehead have used HPLC in conjunction with mass spectrometry to identify five series of porphyrins in Boscan crude petroleum: DPEP, ETIO, Di-DPEP (having two cycloalkano rings attached to the porphyrin ring), rhodo-ETIO, and rhodo-DPEP.[61] Eglinton et. al. have used reverse phase HPLC as part of a separation scheme to identify the petroporphyrins present in a U.S. bitumen.[72] Using techniques similar to those of Barwise and Whitehead, the structures of two ETIO and two DPEP porphyrins were determined. Experiments were also made in developing HPLC fingerprints of petroleums and source rocks. Two useful fingerprints were described: those of total porphyrins (as extracted over silica by column chromatography) and those of porphyrin fractions formed by demetallation of the metallo-porphyrins of a single metal. Both fingerprints are of use in tracing the migration of crude petroleum pools, but, when samples are taken from varying depths in the pool, the second type is especially useful in studying the maturation processes that produced the petroporphyrins.[72]

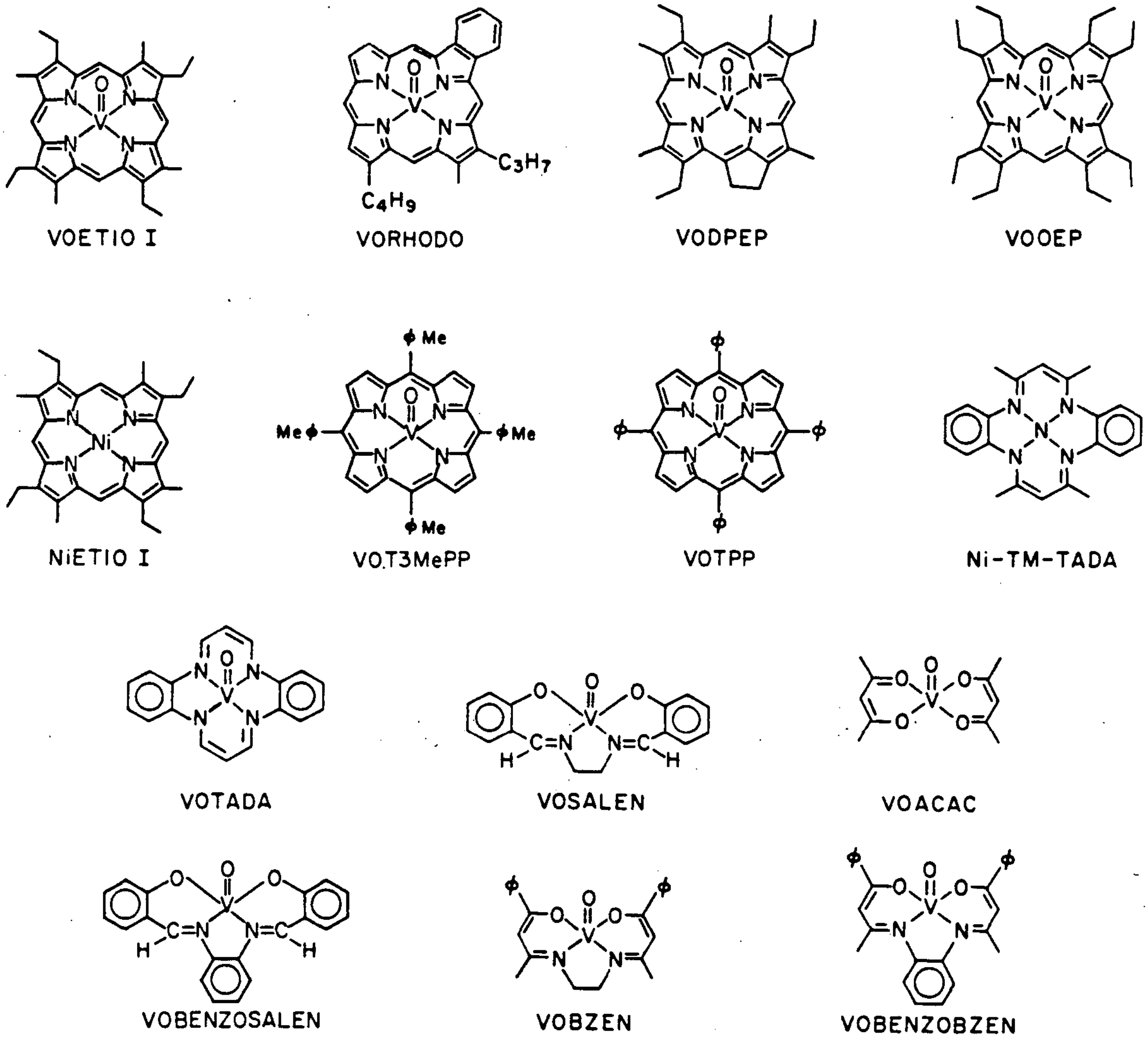
1 D. High Performance Liquid Chromatography - Graphite Furnace Atomic Absorption Spectrophotometry (HPLC-GFAA) Analysis

In speciation work with purified metallo-porphyrin fractions, HPLC with visible absorbance detection has proven to be a powerful tool, but the present state of metallo-non-porphyrin analysis does not present the possibility of working with highly purified fractions. Therefore, it cannot be assumed that all peaks detected during HPLC analysis of suspected metallo-non-porphyrins actually represent metallo-organic compounds and, therefore, on-line metal detection becomes essential for effective element specific analysis. Spencer has attempted to use off-line vanadium detection, but the technique is cumbersome and much information is lost between sampling times.[76] The use of an on-line graphite furnace atomic absorption spectrophotometer (GFAA) provides element specific detection of metals at parts per million levels and sacrifices none of the speed and efficiency of HPLC analysis. Since samples are taken every 40 seconds, a continuous histogram of metal concentration is generated, which can be directly correlated with the UV-VIS absorbance spectra of samples eluting from the HPLC column.

The use of the HPLC-GFAA combination has already proven effective in trace metal analysis of geochemical systems. Brinckman et. al. have used such a system to study the association of arsenic with iron in high molecular weight (2000 to 4000 dalton) fractions of shale oils.[91-93] Fish et. al. have made the first successful speciation of organoarsenic and inorganic arsenic compounds occurring in retort waters and process waters generated in shale oil production.[94-96] Most recently, Fish and Komlenic have used HPLC-GFAA to characterize the vanadyl compounds of heavy crude petroleums.[97]

1 D. 1. Model Compounds

Analysis using HPLC-GFAA requires model compounds in order to compare the retention times and UV-VIS spectra of known compounds with those of naturally occurring compounds. Figure 4 shows several vanadyl model compounds used in our studies (Rhodo and DPEP porphyrins were not actually available to us). Previous workers have established the existence of naturally occurring ETIO, Rhodo, and DPEP porphyrins and raised serious doubts as to the existence of VOT3MePP and VOTPP in crude petroleums.[61,72] Although these last two porphyrins are not likely to occur naturally , it is probable that other porphyrins with extended conjugation patterns do exist in the petroleums. Like the synthetic conjugated porphyrins, the naturally occurring conjugated porphyrins should have Soret bands shifted to



XBL 8211-3357A

Figure 4. Model Porphyrin and Non-Porphyrin Compounds

slightly higher wavelengths and be stable in strong acids.

The lower two rows of Figure 4 show four of the model vanadyl non-porphyrin compounds used in this study. These compounds have not yet been identified in the petroleums, but they possess ligand environments which have been tentatively identified.[1] The vanadyl non-porphyrins shown here represent only four of the many possible non-porphyrin ligand systems and much work is needed in the preparation of model compounds for the speciation of vanadyl non-porphyrins. In general, vanadyl non-porphyrin compounds absorb mainly in the UV region, although sufficient conjugation may result in some absorbance in the visible region. Vanadyl dibenzotetraazacyclotetradecane (TADA) complexes have broad absorbance maxima in the same wavelength region as the vanadyl porphyrin Soret band but, as is true for all vanadyl non-porphyrin compounds, their absorbance intensities are weaker than those of vanadyl porphyrin compounds by a factor of a thousand.[50] The vanadyl non-porphyrin compounds also tend to be more susceptible to acid hydrolysis than their porphyrin analogues.

In addition to their use in speciation studies, model compounds are also useful in the development and optimization of HPLC solvent gradients.

1 D. 2. Fingerprinting

A fingerprint of a petroleum sample is an analytical spectrum which uniquely identifies it. Geochemically, fingerprinting is used as a means of tracing the migration of petroleums. The developmental work with this technique has focussed on metallo-porphyrins and demetallated porphyrins extracted from petroleums and proposed source rocks.[100] The porphyrin extracts are analyzed using HPLC coupled with visible absorbance detection at 410 nm and the resulting chromatograms are compared for common peaks. Metallo-porphyrin fingerprints of samples taken at varying depths in a deposit are also a means of studying the effects of maturation on the structure of porphyrins.[72]

Fingerprinting by HPLC-GFAA analysis of petroleums also promises to be useful in the exploration for suitable heavy crude petroleum feedstocks. The fingerprints of petroleums and polar extracts of petroleums reflect the metal content of the petroleum, the chemical nature of metallo-organic compounds in the petroleum, and the asphaltene content of the heavy crude petroleum.[24] When more information is available on the identity of vanadyl non-porphyrins and their individual effects on catalyst poisoning, fingerprinting should be an effective means of estimating the effect of a given heavy crude petroleum on catalyst deactivation.

From an environmental standpoint, fingerprints are important as a means of identifying the sources of petroleum spills. Infrared spectroscopy and gas chromatography have both been used for spill identification, but their usefulness is restricted by the effects of weathering.[98] Both techniques are greatly influenced by the lighter components of the petroleums and it is these lighter components which are most susceptible to weathering in the marine environment. After nine days at sea it is extremely doubtful that a positive identification of a spill source could be made.[99] Trace metals are concentrated in the heavy components of crude petroleums, making their distribution much less susceptible to weathering effects. Fingerprinting techniques based on trace metal analysis should therefore provide a much better method for identifying petroleums involved in spills.

CHAPTER 2

Statement of Purpose

Vanadium is present in heavy crude petroleums in two major forms: vanadyl porphyrins and vanadyl non-porphyrins. Of these two forms, only the vanadyl porphyrins have been successfully identified at present.[61,72] The distribution of vanadium between these two forms and the individual structures of the molecules which constitute the two classes of vanadyl compounds are of interest to the petroleum industry and to geochemists.

The petroleum industry is interested in the ways in which vanadium is complexed in heavy crude petroleums because of its powerful catalyst poisoning activity in the hydrodesulfurization and cracking steps of refining.[101] To deal effectively with this problem it is necessary to understand the forms in which vanadium is complexed in the crude petroleums. At present modeling studies of catalyst poisoning are performed using only vanadyl porphyrins, which account for less than half of the vanadium present in heavy crude petroleums.[14,16,50,67,102] These modeling experiments may not be viable until vanadyl non-porphyrin structures are successfully identified and then used in catalyst poisoning experiments.

Geochemists are concerned with vanadium because the forms in which it is complexed in the petroleum may be a function of the age and burial depth of the petroleum deposit.[1-3] Understanding the structure of the vanadyl non-porphyrins may also give new insight into the mechanisms by which vanadium was incorporated into the porphyrin structures.

Attempts have been made to analyze vanadyl non-porphyrins in crude petroleums using column chromatography, mass spectrometry, electron spin resonance, and electronic absorbance spectra.[50,76-82] These techniques are sensitive to differences in vanadyl porphyrin and non-porphyrin systems, but the lack of an effective technique for separating the vanadyl non-porphyrins from the vanadyl porphyrins in the petroleums has prevented the identification of metallo-non-porphyrin compounds. The crucial step in identifying the vanadyl non-porphyrins is therefore the development of a technique to separate vanadyl non-porphyrins from vanadyl porphyrins. High performance liquid chromatography coupled with a graphite furnace atomic absorption spectrophotometer (HPLC-GFAA) has already been successfully used in the identification of arsenic compounds in oil shale, shale oil, and shale oil retort waters and is a promising technique for separating petroleum derived samples.[91-97] The variety of HPLC columns available for use in analysis makes it possible to investigate several different modes of separation and the use of element specific GFAA analysis makes it possible to locate the HPLC effluent peaks which contain vanadium. In addition, the use of a rapid scanning ultraviolet-visible absorbance spectrometer to monitor the HPLC column effluent allows peaks to be characterized as vanadyl porphyrin or non-porphyrin without the use of off-line analysis.

In a previous study by Komlenic et. al.,[24] heavy crude petroleums and their polar extracts were analyzed using HPLC-GFAA analysis. In the present study this analytical technique has been used to study the precipitated asphaltene fraction of four heavy crude petroleums. Asphaltenes were studied for two reasons: (1) Asphaltenes contain approximately 50 percent of the vanadium present in crude petroleums, even though they can represent less than 10 percent of the mass of the petroleum sample. In addition, several previous researchers have noted that a large percentage of the vanadyl compounds present in the asphaltenes appear to be non-porphyrins.[27] (2) The proposed structures of resins and asphaltenes,[28,40,41] as well as the precipitation behavior of asphaltenes, indicate that there are differences in the chemical environments of these two petroleum fractions. These differences should be reflected in the distribution of vanadyl compounds between the asphaltenes and the maltenes.

The complexity of the asphaltene system makes it extremely difficult to identify individual vanadyl compounds in the asphaltenes. Because of this, the emphasis of this study is the molecular characterization of classes of vanadyl compounds; with special emphasis placed on differentiating the locations of non-porphyrin and porphyrin compounds in the HPLC-GFAA analyses of the asphaltenes and their polar solvent extracts. Steric exclusion chromatography (SEC) columns are used to determine the molecular weight distribution of vanadium in the asphaltenes and extracts. Amino and reverse phase (C_{18}) HPLC columns were also used in the HPLC-GFAA analysis of the

Table 1. Biogeochemical Parameters of Four Heavy Crude Petroleums and their Asphaltenes

Petroleum	Metal Concentration in Whole Petroleum (ppm)[a]		Metal Concentration in Precipitated Asphaltene (ppm)[a]		Wt. % of Asphaltene in Crude[b]	Sulfur Content (wt. %)[c]	Geological Age[d]	Date of Origin (million years)[d]	Depth (m)[d]
	V	Ni	V	Ni					
Boscan	1100	103	3700	350	23	5.50	Ogliocene/ Eocene	26 - 54	840
Cerro Negro	560	118	1600	360	21	3.85	Miocene/ Pliocene	2.5 - 26	1800
Wilmington	49	60	360	430	6.9	1.55	Miocene/ Pliocene	2.5 - 26	900
Prudhoe Bay	10	9	250	96	3.7	1.06	Paleogene/ Cretaceous	65 - 136	900

(a) Determined by x-ray fluorescence spectroscopy.

(b) Mass of precipitated asphaltene divided by orginal mass of heavy crude petroleum.

(c) From reference 113.

(d) From reference 23.

polar solvent extracts of the asphaltenes. Since they are more amenable to analysis by the various techniques available for identifying the structure of molecules (e.g. ESR, MS, UV-VIS spectra), attention will be focused on the low molecular weight compounds removed in the solvent selective extraction. The vanadium fingerprints generated in the HPLC-GFAA analysis will also be examined in terms of being unique with respect to the individual heavy crude petroleums.

Four heavy crude petroleums were selected for study on the basis of their wide range of vanadium and asphaltene concentrations. Prudhoe Bay and Wilmington, from Alaska and California respectively, have low vanadium and asphaltene concentrations. Boscan and Cerro Negro are Venezuelan crudes with high levels of vanadium and asphaltenes. Important biogeochemical information for these petroleums is given in Table 1. The analysis of four crude petroleums is a departure from recent practice in the literature, in which it has become common to focus attention on a single high vanadium crude petroleum such as Boscan. By studying four heavy crude petroleums, we hope to detect correlations between the vanadium concentration and other physical properties of the petroleum.

CHAPTER 3

Results

3 A. Precipitation of Asphaltenes from Heavy Crude Petroleums

Although it is now standard practice to precipitate asphaltenes from petroleums using forty volumes of the precipitating solvent to one volume (40:1) of the heavy crude petroleum,[26] several other solvent to petroleum ratios have been commonly used in past research.[11,21,22,27,31-33] To check the effect of solvent volume on precipitation both 40:1 and 10:1 volume ratios of solvents were used and the properties of the resulting asphaltenes were compared. Pentane was used as the precipitating solvent. Tables 2 and 3 contain the results of the 10:1 and 40:1 solvent ratio precipitations, respectively. The data presented in these tables are based on between three and five precipitations of each petroleum at each solvent ratio. The weight percent of precipitated asphaltenes was determined from the weight of the initial petroleum sample and the weight of the dried asphaltene. The pentane soluble fraction of the petroleum, the maltenes, was also dried and weighed. The material recovery, combined weight of the collected asphaltenes and maltenes, varied between 90 and 100 percent of the initial petroleum weight. This amount of material recovery is consistent with that reported by other researchers.[33] Metal contents were determined by x-ray fluorescence spectroscopy. Within experimental error, the percentage

Table 2. Vanadium and Nickel Concentrations in Asphaltenes Precipitated Using a Ten to One Solvent Ratio

	ppm in Crude Petroleum[a]		ppm in Asphaltene[a]		Wt. % of Asphaltene in Crude Petroleum[b]	% of Total Metal in Asphaltene[c]		$\frac{\text{ppm in 40:1 Asphaltene}}{\text{ppm in 10:1 Asphaltene}}$[d]	
	V	Ni	V	Ni		V	Ni	V	Ni
Boscan	1100	103	4310	374	25	98	91	0.86	0.94
Cerro Negro	560	118	1680	379	20	60	64	0.95	0.95
Wilmington	49	60	422	473	6.2	53	49	0.85	0.91
Prudhoe Bay	19	9	280	120	2.9	43	39	0.87	0.80

(a) Determined by x-ray fluorescence spectroscopy.

(b) Mass of precipitated asphaltene divided by original mass of heavy crude petroleum

(c) $$\frac{\text{(ppm metal in asphaltene)} \times \text{(wt. \% of asphaltene in crude petroleum)}}{\text{(ppm metal in crude petroleum)}}$$

(d) From Table 3.

of nickel precipitated in the asphaltene of a given petroleum is the same as the percentage of vanadium precipitated in the asphaltene. This is true for both volume ratios of the precipitating solvent. The asphaltenes apparently have equal affinities for compounds of the two metals. This result differs from that obtained by Abu-Elgheit for four Middle Eastern crude petroleums, in which nickel was more concentrated in the asphaltenes.[103]

As can be seen from comparing the weight percent of asphaltenes precipitated using the two solvent ratios, varying the amount of the precipitating solvent has very little effect on the mass of asphaltenes produced. An increase in the solvent ratio does however affect the vanadium concentration in the precipitated asphaltene by as much as 15 percent. In comparison with the experimental error involved in the precipitation of the asphaltenes, a change of this magnitude would not seem significant, except that the deviation for all four petroleums is consistently to lower vanadium concentrations in the asphaltenes of the higher solvent ratio. Since the mass of asphaltenes precipitated from the petroleums is fairly independent of the solvent to petroleum ratio, the vanadium not incorporated in the 40:1 precipitated asphaltenes must be complexed in low molecular weight metallo-organic compounds. Further support for this hypothesis is provided by the SEC-HPLC-GFAA analysis of the 10:1 and 40:1 precipitated asphaltenes. SEC analysis separates the components of the asphaltenes on the basis of molecular size. When the SEC vanadium profiles of the 10:1 and 40:1 precipitated asphaltenes are compared,

Table 3. Vanadium and Nickel Concentrations in Asphaltenes Precipitated Using a Forty to One Solvent Ratio

	ppm in[a] Crude Petroleum		ppm in[a] Asphaltene		ppm in[a] Maltene		Wt. % of[b] Asphaltene in Crude Petroleum	% of Total[c] Metal in Asphaltene	
	V	Ni	V	Ni	V	Ni		V	Ni
Boscan	1100	103	3700	350	280	30	23	77	78
Cerro Negro	560	118	1600	360	110	26	21	60	64
Wilmington	49	60	360	430	17	32	6.9	51	49
Prudhoe Bay	19	9	250	96	10	4	3.7	49	39

(a) Determined by x-ray fluorescence spectroscopy.

(b) Mass of precipitated asphaltene divided by original mass of crude petroleum.

(c) $$\frac{\text{(ppm metal in asphaltene)x(Wt. \% asphaltene in crude petroleum)}}{\text{(ppm metal in crude petroleum)}}$$

there are no differences between the two which cannot be accounted for by experimental error. The increase in solvent ratio should have the greatest effect on lower molecular weight compounds. Since the 40:1 asphaltene is not deficient in low molecular weight vanadium compounds relative to the 10:1 asphaltene, low molecular weight vanadium compounds must be incorporated in higher molecular weight structures during the precipitation of the asphaltenes. The increase in solvent volume therefore has the effect of uniformly decreasing the vanadium concentration at all molecular weights within the asphaltene structure. Since precipitation from forty volumes of solvent is now standard practice in asphaltene research, this procedure was used in all further experiments.[25,26]

3 B. Separation of Asphaltene Components by Solvent Selective Extraction

The emphasis of this research has been the characterization of low molecular weight, less than 1000 dalton, vanadyl compounds in the asphaltenes. To extract these compounds from the asphaltene matrix, a solvent selective extraction procedure described by Baker was used.[70] This technique is the same as that used by Fish and Komlenic in the characterization of vanadyl compounds in heavy crude petroleums.[97] Between 0.5 and 1.5 grams of asphaltene were dissolved in 40 ml of xylenes and then extracted with 50 ml of a four to one mixture of pyridine and water. After removal of the polar, pyridine-water, phase some of the asphaltenes precipitated out of the xylenes. A sufficient volume of xylene was added to redissolve the asphaltenes and the extraction was repeated using another 50 ml of the pyridine-water solution. The asphaltene was extracted in this manner a total of ten times. By the tenth extraction, a total volume of about 150 ml xylene was required to dissolve all of the asphaltene. The large volume of xylene required to dissolve less than 1.5 grams of extracted asphaltene suggests that the low molecular weight asphaltene compounds help to solublize the asphaltenes in xylene in a manner similar to the way in which the resins solublize the asphaltenes in the crude petroleum. After the polar phase was removed from the xylenes, it was filtered and then dried under vacuum. The dried extract was then redissolved in methylene chloride prior to HPLC analysis. When the extracts were allowed to stand before removal of the pyridine- water solvent, two phases formed; a lower, brightly colored phase and a smaller brown to black phase. On close examination the upper phase was found to be of the same color as the lower phase, but much more concentrated. In this study the lower phase was collected and analyzed as the extract. HPLC-GFAA analysis of the upper phase demonstrated that the composition of this phase was similar to that of the lower phase, but lacked the most polar constituents of the lower phase.

The extraction procedure removes vanadyl compounds through interaction between the lone pair electrons of the the pyridine and the vanadium atom in the vanadyl ion. The vanadyl porphyrins, as well as the vanadyl non-porphyrins which are thought to exist in petroleums, are coordinated in square planar environments.[81,104,105]

Interaction with pyridine provides axial coordination to the vanadyl ion; generating a square pyramidal configuration (see Fig. 3). Although the technique was developed for the isolation of vanadyl porphyrins, the extraction mechanism should be equally effective for the removal of vanadyl non-porphyrins, as well as metallo-organic nickel compounds.

In solution, both Boscan and Cerro Negro extracts have the wine red color associated with vanadyl porphyrins and show strong Soret bands (408 nm) in their electronic (UV-VIS) spectra.[66,77,107] The Wilmington extract is orange and shows a weaker Soret band against a strong background absorption which rises at wavelengths below 450 nm. The Prudhoe Bay extract is yellow and has a weak Soret band over a very strong background absorption. Successive extractions of a sample produced more faintly colored extracts, which took on the color of the earlier extracts upon concentration by solvent removal. After ten extractions of a sample, the extracts of all four asphaltenes were pale yellow and had low vanadium concentrations. The color and UV-VIS spectra of the extracts indicates that Wilmington and Prudhoe Bay asphaltenes have much lower porphyrin concentrations than the two Venezuelan heavy crude petroleums. Fish and Komlenic reported similar results for the polar extracts of the heavy crude petroleums.[97]

Table 4 shows the effects of extraction on the vanadium concentration of the asphaltenes. The extracted asphaltenes have vanadium concentrations which vary by as little as five percent from the unextracted asphaltenes. This behavior is very different from that

Table 4. Solvent Selective Extractions of Asphaltenes.

	ppm V in Asphaltene[a]	ppm V in Extracted Asphaltene[b]	Estimated ppm V in Extract[c]	Mass of Asphaltene Extracted (gram)	% of Asphaltene Mass Extracted[d]	ppm V in Extracted Asphaltene / ppm V in Asphaltene
Boscan	3700	3500	8100	1.50	4	0.95
Cerro Negro	1600	1500	4200	1.02	4	0.93
Wilmington	360	340	470	0.50	13	0.96
Prudhoe Bay	250	210	440	0.66	19	0.82

(a) Determined by x-ray fluorescence spectroscopy.

(b) Determined by comparing GFAA cup analysis of asphaltene and extracted asphaltene.

(c) Calculated from mass removed by extraction and difference in vanadium concentration in the asphaltenes and extracted asphaltenes as dtermined in footnotes (a) and (b).

(d) $$\frac{(\text{grams of asphaltene}) - (\text{grams of extracted asphaltene})}{(\text{grams of asphaltene})} \times 100$$

observed by Fish and Komlenic;[97] in their experiments five extractions were sufficient to produce an extracted petroleum with a vanadium concentration less than half that of the crude petroleum. The parts per million (ppm) of vanadium in the extracts of the asphaltenes were estimated from the differences in vanadium concentration and total mass of the asphaltenes and extracted asphaltenes. As is shown in Table 4, the extracts were much richer in vanadium than the asphaltenes. The differences in the amount of starting material for the extractions were due to the amount of asphaltenes available from each crude petroleum and the varying initial concentrations may have effected the equilibrium distribution of micelles within the xylene phase. Such concentration effects should have been minimized by the addition of sufficient xylene to redissolve all remaining asphaltenes between successive extractions.

3 C. Separation of Asphaltene Components by Column Chromatography

In addition to the solvent selective extraction of the asphaltenes, a column chromatography technique described by Spencer et. al. was used to separate the asphaltene components of Boscan and Prudhoe Bay petroleums.[108] This procedure involves absorbing the dissolved asphaltene on an alumina dry column and eluting the metalloporphyrins with dimethylformamide. Most of the the extracted asphaltene compounds are then recovered by elution with chloroform, but a small amount of this material remains irreversibly bound to the alumina. To compare the two separation procedures a chromatographically extracted Boscan asphaltene was re-extracted with pyridine/water (4:1). The second extraction failed to remove any colored material from the dissolved asphaltene. Since the solvent selective extraction is not capable of removing all colored, extractable compounds in ten extractions, the chromatographic extraction is shown to be more effective in removing compounds with absorbances in the visible region. SEC analysis of the chromatographically extracted material established the presence of vanadyl compounds with molecular weights in excess of 1000 daltons. These experiments show that the chromatographic separation extracts more compounds, over a broader range of molecular weights, than does the solvent selective extraction.

The chromatographically separated extracts of Boscan and Prudhoe Bay asphaltenes have the same colors as their solvent extracted counterparts, wine red and yellowish-brown, respectively. Figure 5 compares the spectra of the extract and the extracted asphaltene of Boscan asphaltene as prepared by the chromatographic separation and the solvent selective extraction. The major difference between the spectra of the chromatographic extract and the spectra of the solvent selective extract is the presence of a peak at 270 nm in addition to the Soret band at 408 nm. The spectra of the solvent selective extracted asphaltene and the chromatographically separated asphaltene have very weak peaks where a Soret band would be expected. The chromatographically separated asphaltene has a slight shoulder below 300 nm, where the extract has a strong peak. Because of the weakness of the Soret band in the separated asphaltene, Spencer considers this

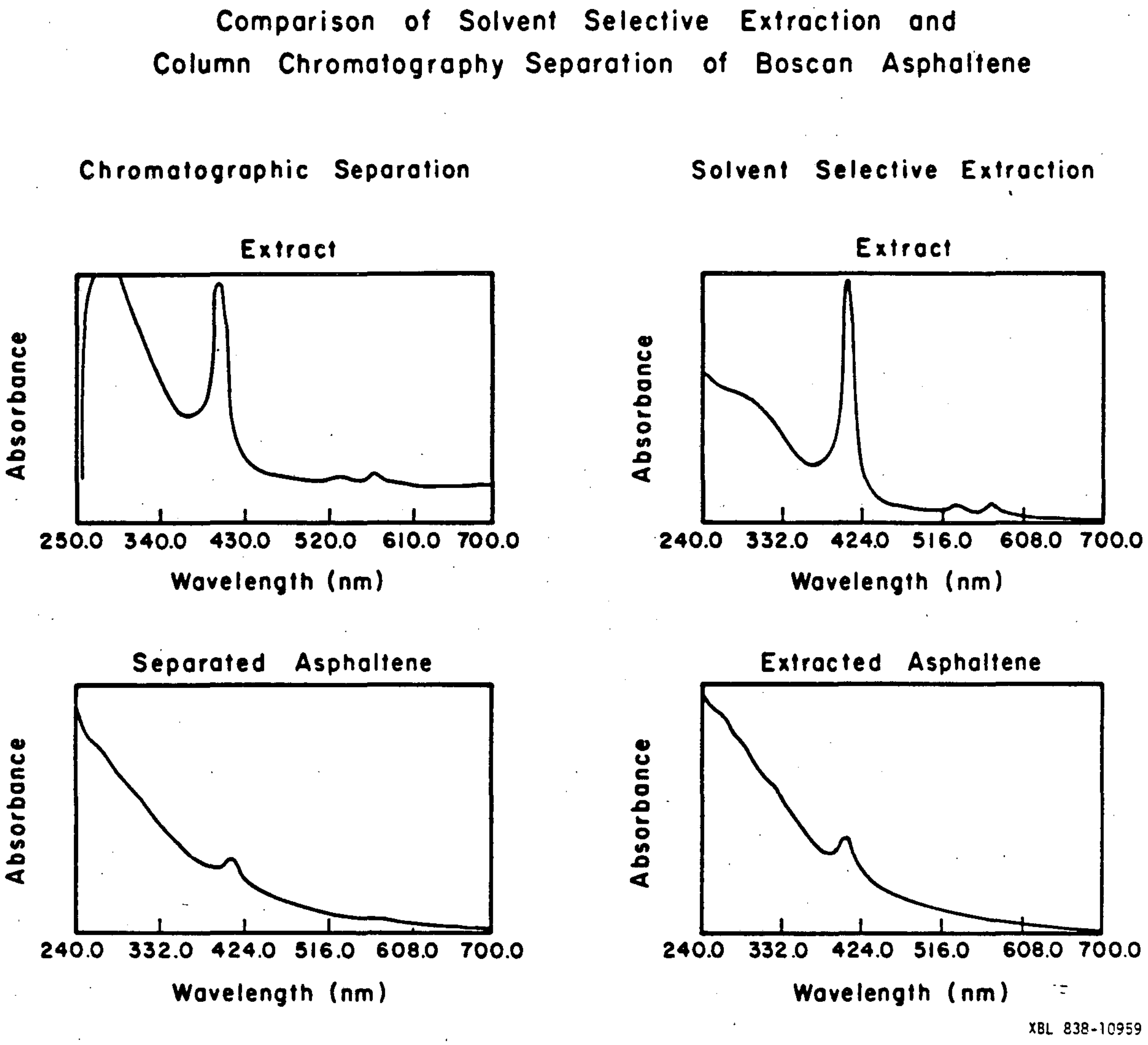


Figure 5. Comparison of Solvent Selective Extraction and Column Chromatography Separation of Asphaltenes.

fraction to be composed of vanadyl non-porphyrins.[108]

3 D. Rapid Scan UV-VIS Analysis

One of the electronic absorbance (UV-VIS) spectrometers used in monitoring the HPLC effluent was a Beckman 165 variable wavelength detector. This detector is capable of scanning an eluting peak at a rate of 20 nm per second and is referred to in this study as the rapid scan UV-VIS detector. The rapid scanning rate smooths out some fine detail in the electronic spectra, but strong features like the vanadyl porphyrin Soret band (408 nm) are not greatly affected. The rapid scan detector is thus an excellent means of differentiating between vanadyl porphyrins and non-porphyrin compounds in an eluting peak. Among the details which are somewhat smoothed out by the rapid scanning rate are the secondary peaks between 500 and 600 nm in the spectra of porphyrins. This region is important in the analysis of vanadyl porphyrins since it is the location and relative intensity of the secondary bands which provide an easy means of differentiating between non-metallated porphyrins and the various subclasses within the vanadyl porphyrins. When the absorbances in this region were distinct in the rapid scan UV-VIS spectra, the peaks were usually typical of vanadyl etioporphyrin, with a small peak at approximately 530 nm and a slightly larger peak at approximately 570 nm.[8,54,70] In some cases a slight shoulder at 590 nm can be observed. Such an absorbance indicates the presence of vanadyl rhodoporphyrins.[50] A non-metallated porphyrin would have more than 2 bands in the 500 nm to 600 nm region, with the lower wavelength bands having the more intense absorbances.

Non-metallated porphyrin absorbances were not detected in this research. The one possible instance of non-metallated porphyrins observed in this research is the first peak of the amino column HPLC-GFAA analysis of Boscan and Cerro Negro asphaltene extracts (see Fig. 12 and 13). The electronic absorbance spectrum of this peak has a weak Soret band, but the corresponding vanadium histogram shows this peak to be free of vanadium. Unfortunately the signal is too weak for secondary bands in the 500 nm to 600 nm region to be detected and the possibility that the weak Soret is caused by nickel porphyrins entrained in the solvent peak cannot be ruled out. Because many researchers have reported that there is more vanadium than porphyrins present in the heavy crude petroleums, it seems highly unlikely that there actually are any non-metallated porphyrins present in the heavy crude petroleums analyzed in this study, however non-metallated porphyrins have been reported in deep-sea sediments.[109] In this study it is assumed that rapid scan UV-VIS spectra with definite Soret bands are caused by vanadyl porphyrins. Since the rapid scan UV-VIS detector was used to analyze the effluents from several different HPLC columns, the spectra are reported with the results of the individual columns.

3 E. SEC-HPLC-GFAA Analysis

Steric exclusion chromatography (SEC) separates samples on the basis of molecular size; large molecules are excluded from the pores in the packing and elute earliest, while smaller molecules spend more time in the pore structure and elute at greater retention times. By calibrating the columns with metallo-organic standards, it is possible to correlate retention time with molecular weight. Since molecular size is not always directly proportional to molecular weight, it is important to calibrate the columns with standards which are chemically similar to the compounds being studied.

Asphaltene samples were at first analyzed with the HPLC-GFAA system equipped with a 50 Å and a 100 Å SEC column in series. This combination gave good separations for molecular weights below 1000 daltons, but was ineffective for molecular weights above 3000 daltons. Since the asphaltenes contain the highest molecular weights present in the petroleums, this was not an acceptable upper limit for analysis. The addition of a 1000 Å SEC column improved the separation of lower molecular weight compounds slightly and extended the effective upper range of the system to 10,000 daltons. Figure 6 shows the calibration curve for the three column system. The model compounds used to calibrate this system lie on a fairly straight line, with the exception of VOTPP, which has a longer retention time than similar molecular weight compounds. This may be due to the extended aromaticity of VOTPP, since the possibility of interactions between aromatic systems and some SEC column packings has been considered in the literature.[110-112] Polystyrene standards were used for molecular weights in excess of 1000 daltons, since there are no model metallo-organic standards available at these molecular weights. The polystyrene standards are accurate within ten percent.

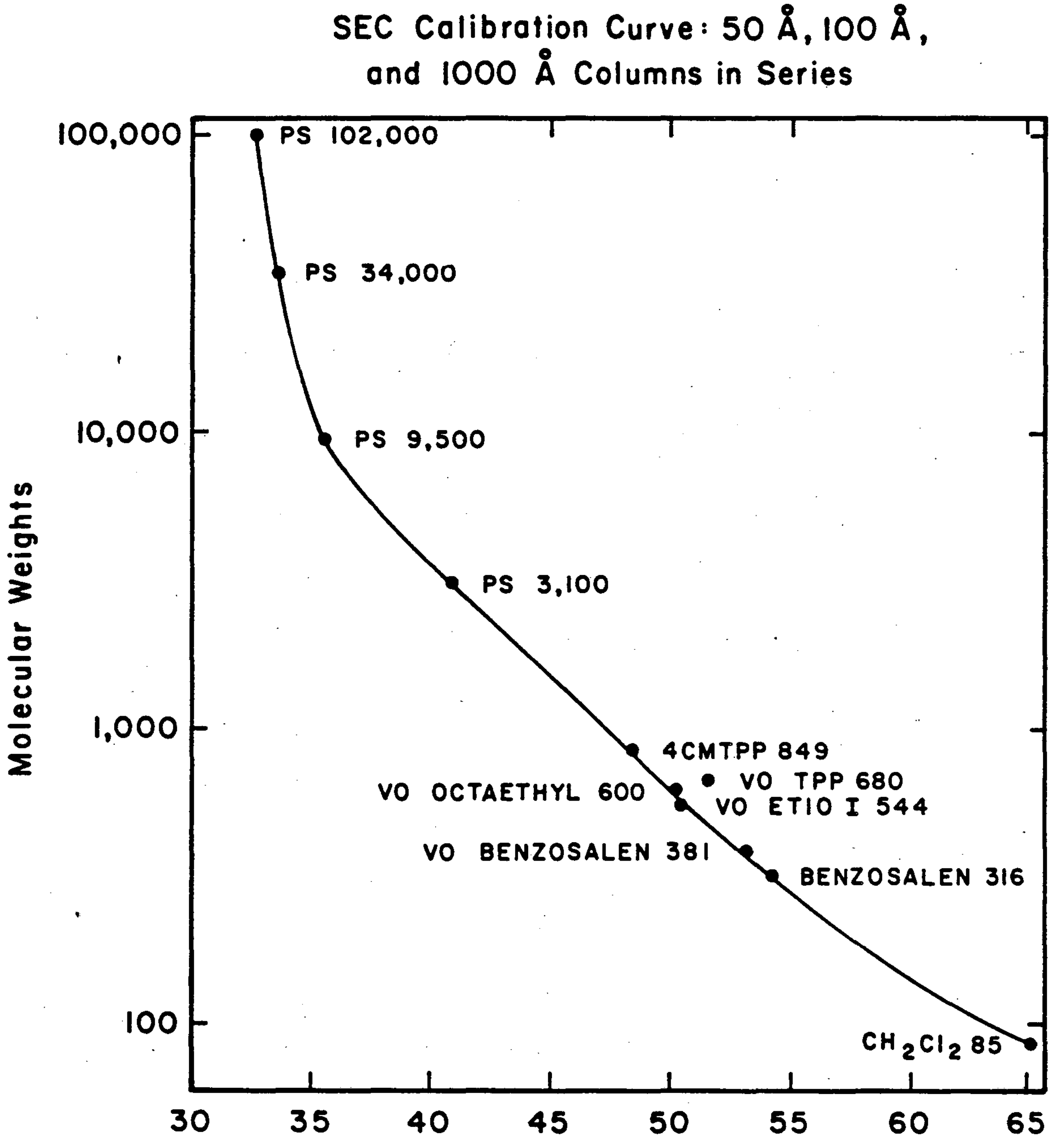


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Figure 6. Plot of Log Molecular Weight Versus Retention Time for the SEC Column Combination.

Figures 7 - 11 show the results of the SEC-HPLC-GFAA analysis of the maltenes, asphaltenes, polar extracts and extracted asphaltenes. To facilitate comparison with the results obtained by Komlenic et. al. for the heavy crude petroleums and their extracts,[24] the molecular weight distribution of vanadyl compounds has been broken down into four regions: molecular weights less than 400 daltons; molecular weights between 400 and 900 daltons; molecular weights between 900 and 2000 daltons; and molecular weights greater than 2000 daltons. The region below 400 daltons was believed to be entirely composed of vanadyl non-porphyrins, since none of the known vanadyl porphyrins in heavy crude petroleums have molecular weights below 400 daltons (a vanadyl porphyrin without alkyl substitution on the pyrrole rings would have a molecular weight of 380 daltons). The molecular weight region between 400 and 900 daltons corresponds to the molecular weights of known vanadyl porphyrins as well as several of the proposed vanadyl non-porphyrins. The two higher molecular weight regions, which are too large to be attributed to individual vanadyl porphyrins, represent either small vanadyl metallo-organic compounds entrapped in high molecular weight asphaltene complexes or very large non-porphyrin compounds within the asphaltene micelles. Above 2000 daltons complete particles may be eluting.[51]

Figure 7 shows the molecular weight distribution of vanadyl compounds in Boscan asphaltene, maltene, and polar extract. The data for the extracted asphaltene is in Figure 11. The continuous spectra are the visible absorbances at 408 nm, the wavelength corresponding

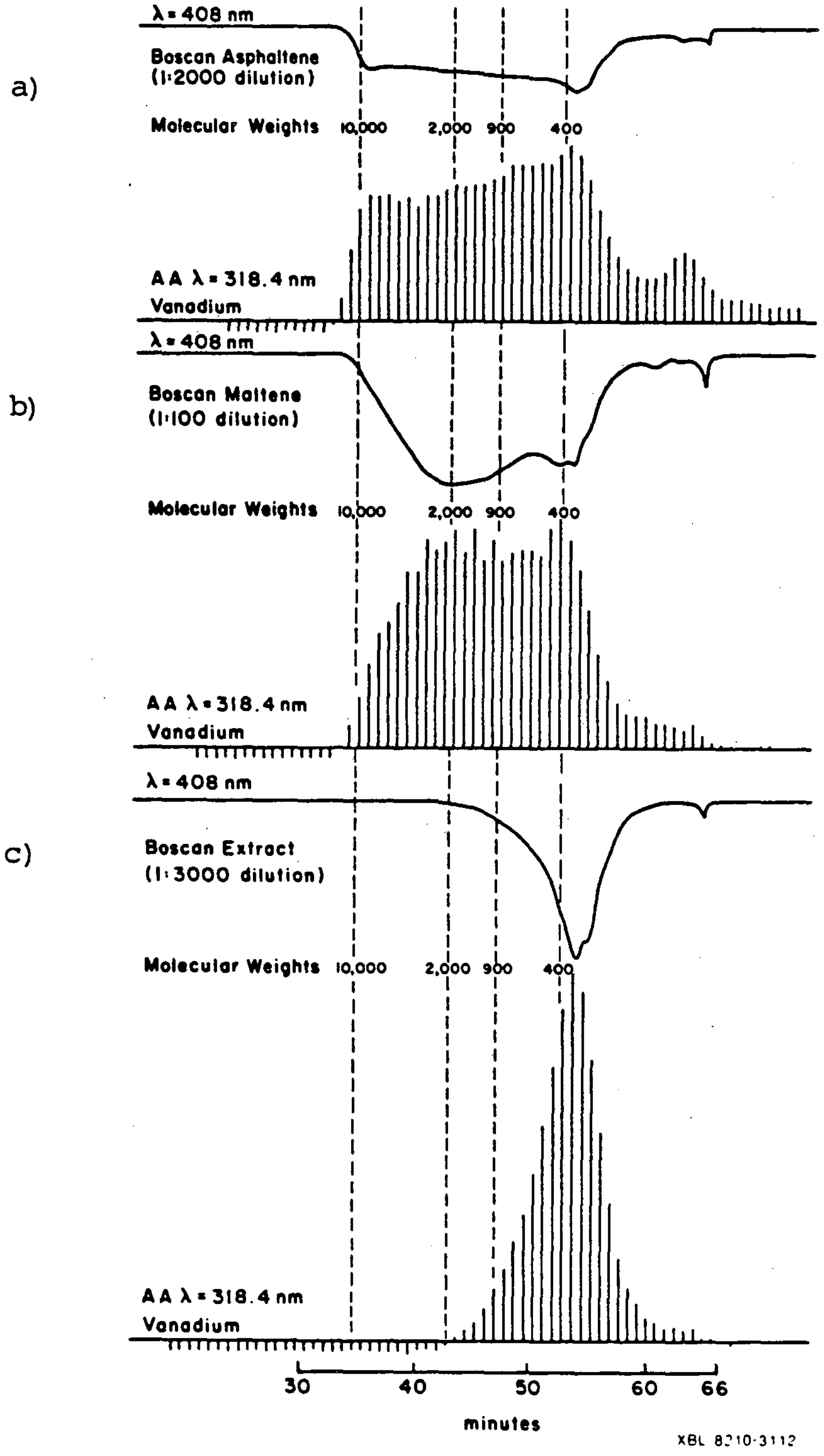


Figure 7. SEC-HPLC-GFAA Data for a) Boscan Asphaltene, b) Boscan Maltene, and c) Extract of Asphaltene.

to the Soret band of the most abundant vanadyl porphyrins in heavy crude petroleums.[8,60] Absorbance at 408 nm cannot be taken as proof of the presence of vanadyl porphyrins since other organic ligands and vanadyl non-porphyrin compounds in the petroleums have very broad absorbance shoulders that extend well past 408 nm. The presence of vanadyl porphyrins can only be assumed when the absorbance at 408 nm is significantly more intense than the absorbance at other wavelengths.[108] Even fractions of petroleums which other researchers have labelled as vanadyl non-porphyrin have weak absorbance peaks at about 408 nm, over a strong background absorbance.[76,108] The histograms represent the broad category of vanadium compounds present in the sample as detected by GFAA analysis. Each vertical line in the histogram represents a single vanadium analysis on the GFAA. The distance between the lines, or peaks, represents the 40 second interval at which the HPLC effluent was automatically sampled. The most intensely absorbing point in the 408 nm absorbance spectrum is referred to as the maximum of the visible absorbance profile. Other points in the spectrum which represent local maximums are referred to as secondary maxima. Similarly, the highest peak in the histogram is the maximum of the vanadium profile and local maximum peak heights are referred to as secondary maxima. For all of the samples studied with the SEC columns the visible absorbance (408 nm) and histogrammic vanadium profile have parallel shapes.

The Boscan asphaltene has fairly uniform visible absorbance and vanadium profiles over the range from 8000 daltons to 380 daltons,

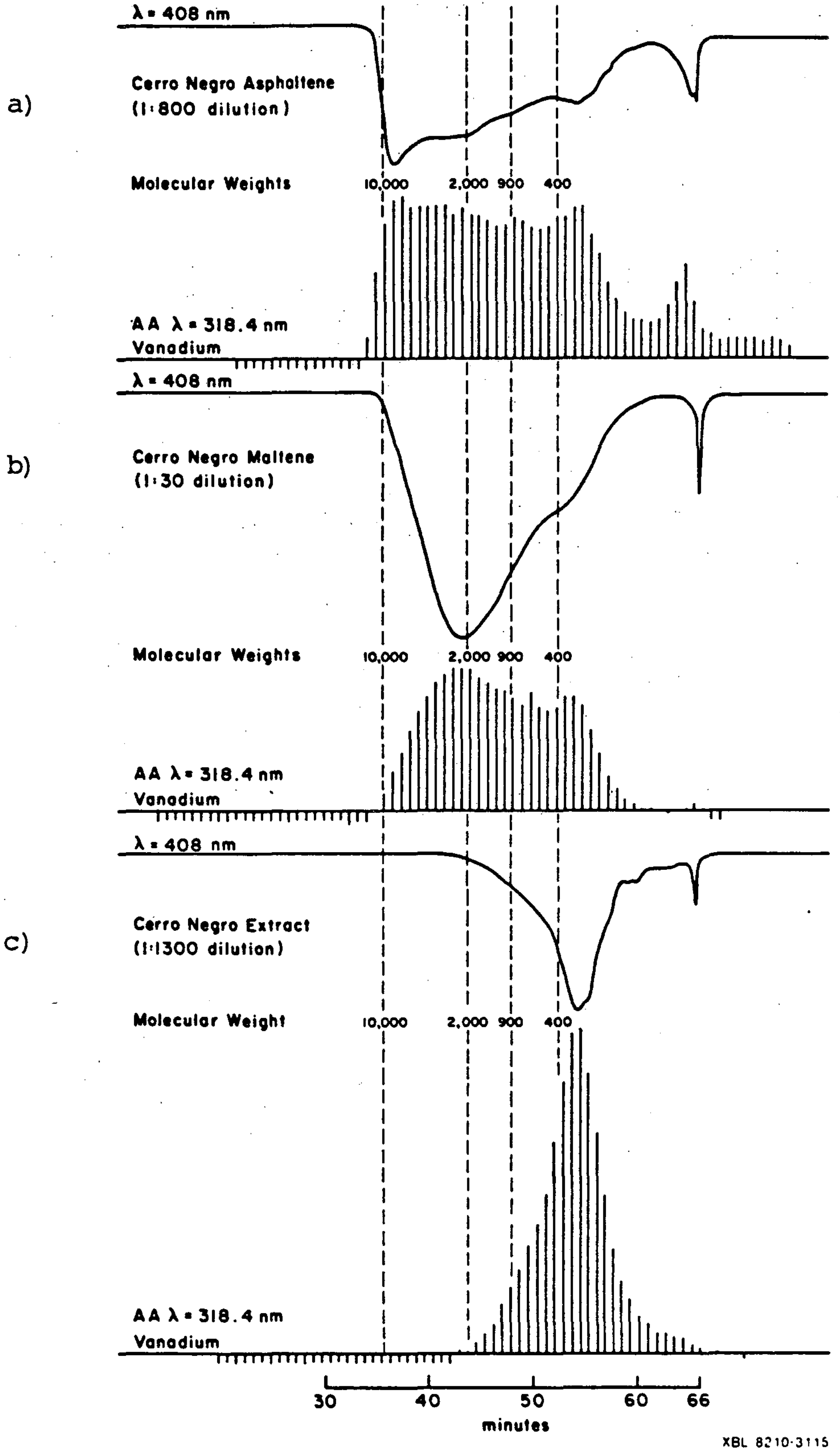


Figure 8. SEC-HPLC-GFAA Data for a) Cerro Negro Asphaltene, b) Cerro Negro Maltene, and c) Extract of Asphaltene.

with the maximum absorbance for both spectra occurring at 380 daltons and a secondary maximum at 8000 daltons. As can be seen from Figures 8, 9, and 10 this behavior is unique to Boscan asphaltenes. It should also be noted that in all four asphaltenes very little vanadium is present at molecular weights greater than 10,000 daltons. The vanadyl compounds which elute with molecular weights greater than 2000 daltons probably do not represent single molecules, but associations of various vanadyl compounds with asphaltene micelles. Such a view of the high molecular weight constituents of asphaltenes is consistent with both the Dickie and Yen and the Boduszynski theories of asphaltene structure.[28,40,41] We expected from the structural differences, which are believed to exist between the maltene and asphaltene fractions, that the maltene absorbances would be skewed toward lower molecular weights than the asphaltenes. The Boscan maltene meets this expectation with maximum absorbances at 2000 daltons and a secondary peak maximum at about 380 daltons. These lower molecular weights in the maltenes can either be explained in terms of smaller molecules in the resins, as is predicted from the Dickie and Yen model of asphaltenes and resins,[28] or weaker associations between resin molecules than between asphaltene molecules, as is expected from the Boduszynski description of asphaltenes.[40,41] The extract of the asphaltene has a single peak maximum at about 380 daltons. Since 380 is too low a molecular weight to represent vanadyl porphyrins with alkyl substituents, the extracts were selected for study as a possible source of vanadyl non-porphyrins.

The results of the SEC-HPLC-GFAA analysis of Cerro Negro asphaltene, maltene, and extract are given in Figure 8. For the asphaltene the maximum absorbances for both the visible and the vanadyl profiles are at 8000 daltons. Both absorbances then decrease in intensity at the lower molecular weight regions. Faint peaks can be observed at 2000 and 900 daltons and a stronger peak is present at 370 daltons. Features of the visible spectrum are more distinct than those of the Boscan asphaltene, since the Cerro Negro sample requires less dilution to keep the vanadium signal on scale. The maltene sample shows a strong maximum at 2000 daltons and a significantly weaker peak at about 370 daltons. The spectra of the extract are similar to those of the Boscan extract, with maximum vanadium peak heights and visible absorbances at 380 daltons.

Figure 9 shows the experimental results for the visible absorbance and vanadium profiles in the Wilmington samples. Since the vanadium levels in Wilmington are significantly lower than for the Boscan and Cerro Negro petroleums, it was not possible to find a dilution which gave both an on scale visible absorbance and an on scale vanadium histogram. Samples were run at two dilutions and the resulting chromatograms were combined to facilitate study of the vanadium distribution. Like the Cerro Negro asphaltene, the Wilmington asphaltene has a maximum absorbance at 8000 daltons, but the visible absorbance and vanadium concentration both drop off more rapidly with decreasing molecular weights than they do in the Cerro Negro asphaltene. The maltene visible absorbance has a maximum at

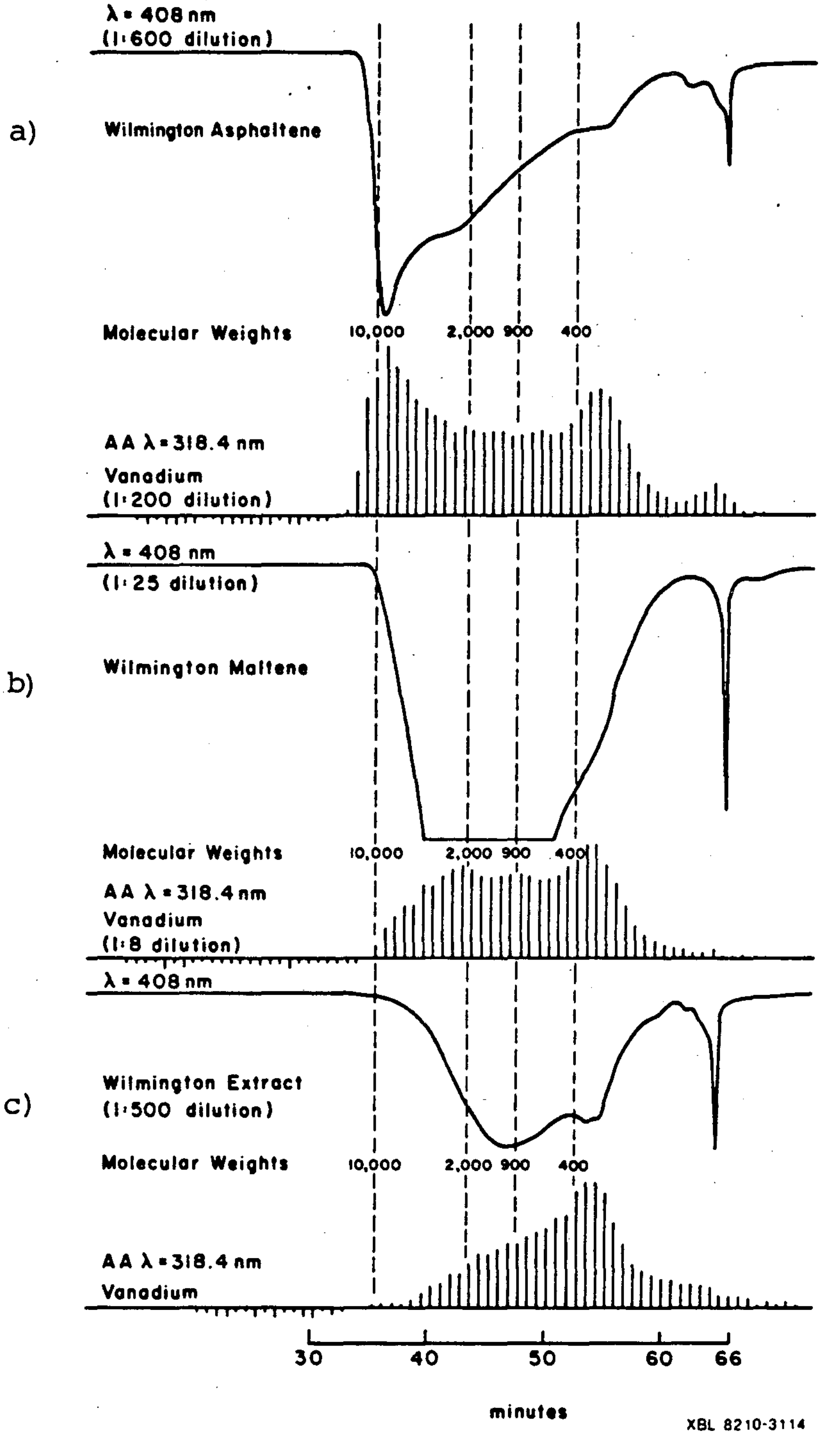


Figure 9. SEC-HPLC-GFAA Data for a) Wilmington Asphaltene, b) Wilmington Maltene, and c) Extract of Asphaltene.

about 2000 daltons (truncated in the figure) and drops rapidly with lower molecular weights. The vanadium histogram for the maltene is almost identical to the histogram of the asphaltene at molecular weights below 3000. The visible absorbance spectra of the extract has peak maxima at 1000 and 380 daltons. Maxima in the vanadium histograms of the extract and maltene have relative magnitudes which are the opposite of the relative magnitudes of the corresponding visible absorbance maxima. This is especially noticeable with the extract; the most intense visible absorption is at a molecular weight of 1000, while the vanadium histogram at this point has only a broad shoulder. The maximum peak height in the histogram is at 380 daltons and coincides with the secondary maximum in the visible spectrum. The presence of vanadium in the extract at molecular weights greater than 2000 daltons is unique to the extract of Wilmington asphaltene.

The molecular weight distribution of vanadium in Prudhoe Bay crude petroleum fractions is give in Figure 10. In the asphaltene the maximum visible absorbance and maximum vanadium peak height are at 7000 daltons. Visible absorbance decreases at lower molecular weights without exhibitting any secondary maxima. The vanadium profile has a dramatic drop in intensity at molecular weights below 7000 daltons and a small peak at 380 daltons. With its maximum absorbance at 2000 daltons, the visible spectrum of the Prudhoe Bay maltene is very similar to that of the Cerro Negro maltene. The maximum height of the vanadium profile lies at 6000 daltons and does not correspond to a visible absorption maxima. With a single maximum at 380 daltons

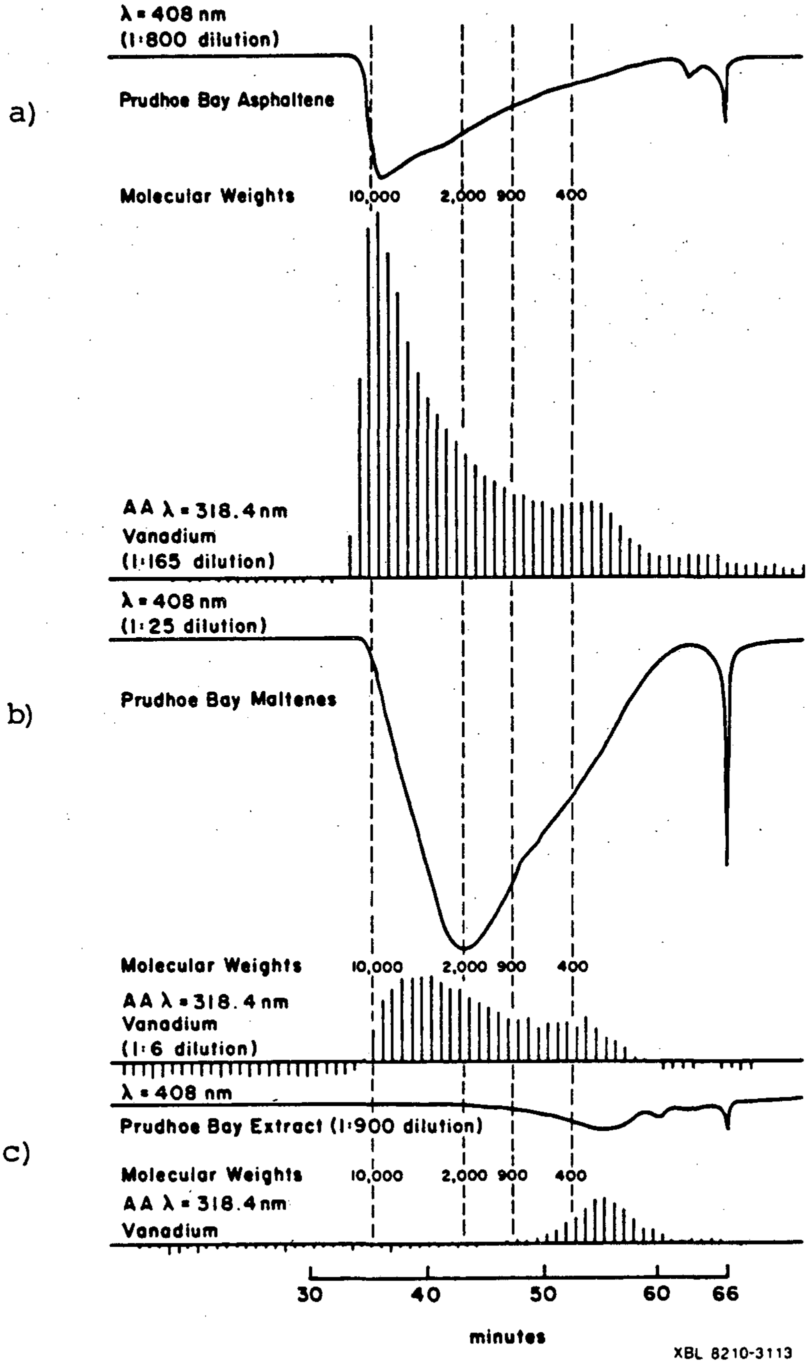
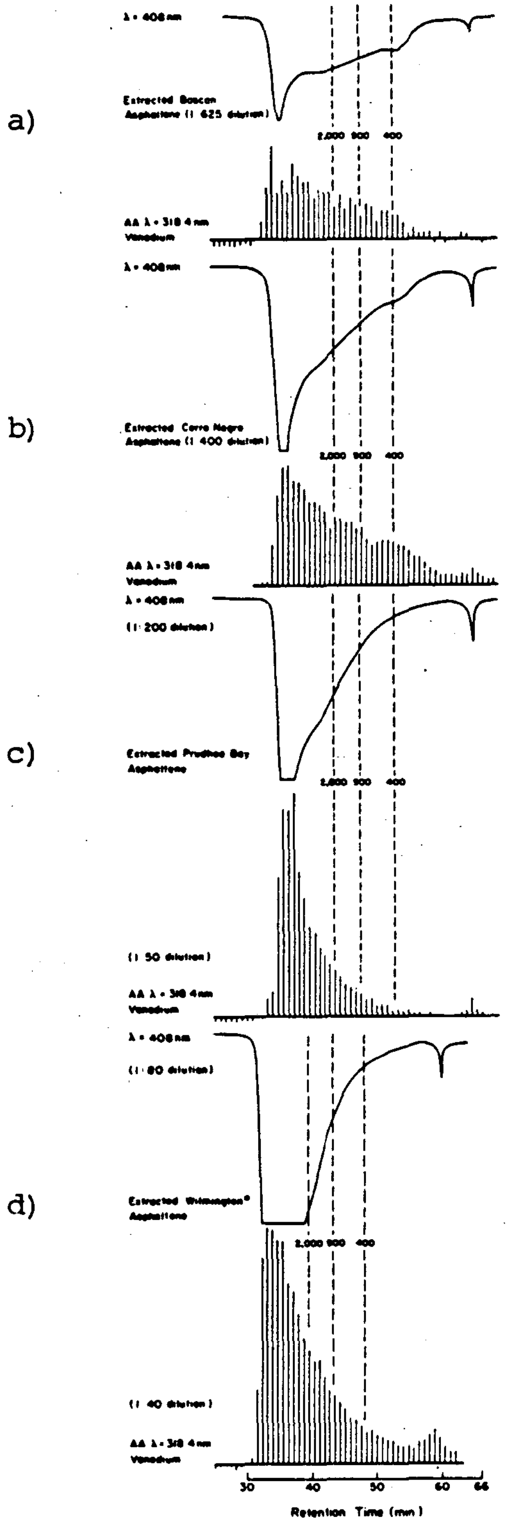


Figure 10. SEC-HPLC-GFAA Data for a) Prudhoe Bay Asphaltene, b) Prudhoe Bay Maltene, and c) Extract of Asphaltene.

for both the visible absorbance and vanadium profiles, the Prudhoe Bay extract is similar to the extracts of the Venezuelan petroleums.

Figure 11 shows the visible absorbance and vanadium profiles of the extracted asphaltenes. The most intense absorbances are still at molecular weights of about 8000 daltons, but the visible absorbance and vanadium profiles have more pronounced decreases in intensity at lower molecular weights than do the whole asphaltenes. Polar extraction clearly has the greatest effect on the lower molecular weight vanadyl compounds.

Table 5 is a numerical summary of the preceding 5 figures. The vanadium distribution is given as the percentage of the total vanadium present in a fraction that is found in a given molecular weight range. These percentages are calculated from the output of the digital integrator which processes the signal from the GFAA. The peak heights in a given molecular weight region were summed and then divided by the total peak height of the histogram, as calculated by the digital integrator. The values in Table 5 are based on between three and five SEC-HPLC-GFAA analyses per fraction. Several trends, which appear to be correlated with the asphaltene content of the heavy crude petroleum, can be observed in the various fractions of the petroleums. Boscan asphaltene has the most uniform distribution of vanadyl compounds over the four molecular weight regions and is also the most asphaltenic petroleum. As the petroleums become less asphaltenic their respective asphaltenes have vanadium distributions which increasingly favor the higher molecular weight region. In



*Calibration of columns changed during storage

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Figure 11. SEC-HPLC-GFAA Data for Extracted Asphaltenes of a) Boscan, b) Cerro Negro, c) Prudhoe Bay, and d) Wilmington Petroleums.

Prudhoe Bay asphaltene, which only accounts for 3.7 percent of the mass of the whole crude petroleum, 56 percent of the vanadium is present at molecular weights greater than 2000 daltons. This compares with only 33 percent in the same region for Boscan asphaltene. For the maltenes the trend is toward greater vanadium concentration in the two middle molecular weight regions for the less asphaltenic petroleums. A likely explanation for this is that there are certain compounds in the petroleums which will always be precipitated by forty volumes of pentane. These large compounds may be considered the backbone of the asphaltene. In addition to these compounds there are compounds which interact either chemically or stericly with the precipitating compounds. These latter compounds will come out of solution with the backbone compounds. Since this action is basically an entrapment of molecules in the precipitating asphaltenes it should have the greatest effect on small, low molecular weight compounds. In Prudhoe Bay crude petroleum the distribution of vanadium retained in the maltenes reflects this behavior; vanadium has principally been removed from the very high and very low molecular weight regions. In the highly asphaltenic petroleums, such as Boscan, there is a greater supply of the backbone asphaltene compounds, making it possible to entrain vanadyl compounds from the entire range of molecular weights. This is shown by the uniform intensity of the vanadium profile of the asphaltene (see Fig. 7) over the range from 8000 to 400 daltons.

Table 5. The Percent Vanadium in Each Molecular Weight Category of Vanadyl Compounds In the Four Heavy Crude Petroleums and their Asphaltenes, Maltenes, Polar Extracts, and Extracted Asphaltenes by 50/100/1000 Å SEC-HPLC-GFAA Analysis[a]

	BOSCAN				CERRO NEGRO				WILMINGTON				PRUDHOE BAY			
Molecular Weight[b]	>2000	<2000 >900	<900 >400	<400	>2000	<2000 >900	<900 >400	<400	>2000	<2000 >900	<900 >400	<400	>2000	<2000 >900	<900 >400	<400
Whole Crude Oil	28	20	23	29	31	22	20	26	31	29	23	17	28	23	19	30
Asphaltene	33	19	19	29	34	16	16	34	37	16	17	30	56	15	12	17
Maltenes	29	24	27	21	33	26	25	16	18	32	32	17	23	34	30	13
Polar Extract	0	4	31	65	0	5	26	69	9	14	25	52	0	0	13	87
Extracted Asphaltene	58	16	15	11	59	15	12	14	80	10	8	2	85	8	4	4

(a) Percentage of total vanadium determined by method of summing peak heights digitized with an integrator for the molecular weight region designated. The molecular weight regions were determined by the calibration curve in Figure 3.

(b) Daltons

Further support for the inclusion of lower molecular weight maltene compounds in the asphaltene matrix is provided by the visible absorbance and vanadium histogram maxima of the asphaltenes and maltenes in Figures 7 - 10. The peak maxima below 400 daltons is present in both the maltenes and the asphaltenes of all four petroleums. In addition, several of the petroleums show corresponding maxima in the chromatographs of the asphaltenes and maltenes at molecular weights of up to 2000 daltons. These corresponding maxima are attributed to the presence of the same group of vanadyl compounds in both the asphaltenes and maltenes.

In all four of the asphaltene extracts the majority of the vanadium eluted at less than 400 daltons and very little material eluted at greater than 900 daltons. The one exception to this is Wilmington extract, in which there was a small percentage of vanadium at molecular weights of over 2000 daltons. But even in Wilmington over half of the vanadium in the extract eluted in the lowest molecular weight region. Fish and Komlenic[97] showed that low molecular weight vanadium compounds could be extracted from all molecular weights in a heavy crude petroleum. As can be seen from Table 5 this is also true of the asphaltenes.

The last line of Table 5 shows the vanadium distribution in the extracted asphaltenes. Extraction removes vanadyl compounds principally from the three lower molecular weight regions. Comparing the percentage of vanadium at molecular weights of over 2000 daltons in the asphaltenes with that in the extracted asphaltenes shows that the

Table 6. Vanadium Present in Each Molecular Weight Category of Vanadyl Compounds In Asphaltenes and Extracted Asphaltenes by 50/100/1000 Å SEC-HPLC-GFAA Analysis

	BOSCAN				CERRO NEGRO				WILMINGTON				PRUDHOE BAY			
	grams V x 10^3				grams V x 10^4				grams V x 10^5				grams V x 10^5			
Molecular Weight [a]	>2000	<2000 >900	<900 >400	<400	>2000	<2000 >900	<900 >400	<400	>2000	<2000 >900	<900 >400	<400	>2000	<2000 >900	<900 >400	<400
Asphaltene [b]	1.83	1.05	1.05	1.61	5.54	2.61	2.61	5.54	6.70	2.90	3.10	5.40	8.40	2.25	1.80	2.55
(weight %) [c]	(33)	(19)	(19)	(29)	(34)	(16)	(16)	(34)	(37)	(16)	(17)	(30)	(56)	(15)	(12)	(17)
Extracted [d] Asphaltene	2.92	0.86	0.76	0.55	8.67	2.21	1.76	2.06	11.8	1.48	1.18	0.30	8.60	0.82	0.41	0.41
(weight %) [c]	(58)	(16)	(15)	(11)	(59)	(15)	(12)	(14)	(80)	(10)	(8)	(2)	(85)	(8)	(4)	(4)

(a) Daltons

(b) Grams of vanadium calculated from the mass of the asphaltene sample, the ppm vanadium in the sample as determined by x-ray fluorescence spectroscopy, and the weight percent of the total vanadium present in the sample as determined in footnote (c).

(c) Percentage of total vanadium determined by method of summing peak heights digitized with an integrator for the molecular weight region designated. The molecular weight regions were determined using the calibration curve in Figure 2.

(d) Grams of vanadium calculated from the mass of the extracted asphaltene sample, the ppm vanadium in the sample as determined by comparative GFAA cup analysis of the asphaltenes and extracted asphaltenes, and the weight percent of the total vanadium present in the molecular weight category as determined in footnote (c).

percentage of vanadium in this region increases by 20 to 30 percent for all four extracted asphaltenes. Considering the small percentage of the asphaltenic vanadium which is removed in the extraction, this is a very large increase. Table 6 shows a mass balance of the vanadium present in the asphaltenes and the extracted asphaltenes. The numbers in parentheses are taken from Table 5. The grams of vanadium present in the asphaltene are calculated from the ppm vanadium in the asphaltene as measured by x-ray fluorescence spectroscopy, the percentages given in Table 5, and the mass of the asphaltene sample. The grams of vanadium in the extracted asphaltene were calculated in the same way as for the whole asphaltene, except that the ppm vanadium was determined by comparing the GFAA cup analysis peak heights of the asphaltene and extracted asphaltene. In the molecular weight region over 2000 daltons there is actually more vanadium present in the extracted asphaltene than in the whole asphaltene, while in the three lower molecular weight region there is substantially less vanadium in the extracted asphaltene. Evidently the extraction process concentrates vanadyl compounds in the higher molecular weight region as well as removing them from the asphaltene matrix. Some of this transfer of vanadium from low to high molecular weights can be attributed to effects associated with dissolving the precipitated asphaltenes in xylenes. To examine the extent of this effect a Boscan asphaltene sample was dissolved in xylenes, agitated, and then recovered by distilling off the xylenes. When this sample was analyzed on the SEC-HPLC-GFAA system, the vanadium concentration in the greater than 2000 dalton region was found to have increased from

33 percent of the total vanadium present in the sample to 43 percent of the total vanadium, while the concentration in the less than 400 dalton region dropped by the same amount. However, even when no vanadium is extracted, this shift to higher molecular weights is only sufficient to account for a little over half of the increase in vanadium concentration at molecular weights of over 2000 daltons in the extracted asphaltenes.

It appears that during the pyridine-water extraction there is a competition for low molecular weight vanadyl compounds between pyridine and the large asphaltene molecules. Some of the vanadyl compounds which are initially coordinated by pyridine are subsequently entrapped by high molecular weight asphaltene molecules. Based on the results of Fish and Komlenic,[97] which proved that low molecular weight vanadyl compounds were extracted from even the highest molecular weight region, it seems likely that some low molecular weight vanadyl compounds are actually extracted from high molecular weight complexes. The extraction of these compounds is concealed by the large amount of re-entrapment of low molecular weight compounds extracted from the three lower molecular weight regions. In the heavy crude petroleums, a noticeable amount of re-entrapment of the extracted low molecular weight vanadyl compounds is prevented by the dispersion of the high molecular weight asphaltene micelles in the maltenes.

3 F. Amino Column (Normal Phase) Analysis of Polar Extracts by HPLC-GFAA

As mentioned in the presentation of the SEC analysis results, the polar extracts of the asphaltenes were studied because the SEC analysis indicated that they contained a large percentage of low molecular weight vanadyl non-porphyrins. These extracts were analyzed using a bonded phase, amino column with the HPLC-GFAA system. This column separates samples on the basis of polarity; low polarity compounds pass quickly through the column, while the more polar compounds interact with the amino groups on the packing and elute later. One disadvantage of using a polar column is the possibility that highly polar compounds may interact with the amino groups strongly enough to become irreversibly bound to the packing. In this analysis a solvent gradient from hexane to methylene chloride was used to enhance separation.

Figures 12 through 15 show the results of HPLC-GFAA analysis of the polar extracts using the amino column. The format of the figures is the same as that for the SEC results; the upper, continuous line is the visible absorbance spectra and the lower, histogrammic output is the metal concentration as detected by the GFAA. At the top of each Figure is a calibration spectra, which is a composite of several calibration runs using metallo-organic standards. Visible absorbance was set to maximize the absorption of the model compounds; vanadyl porphyrins were detected at 408 nm and the vanadyl non-porphyrin standards were run at 300 nm. As can be seen on the calibration

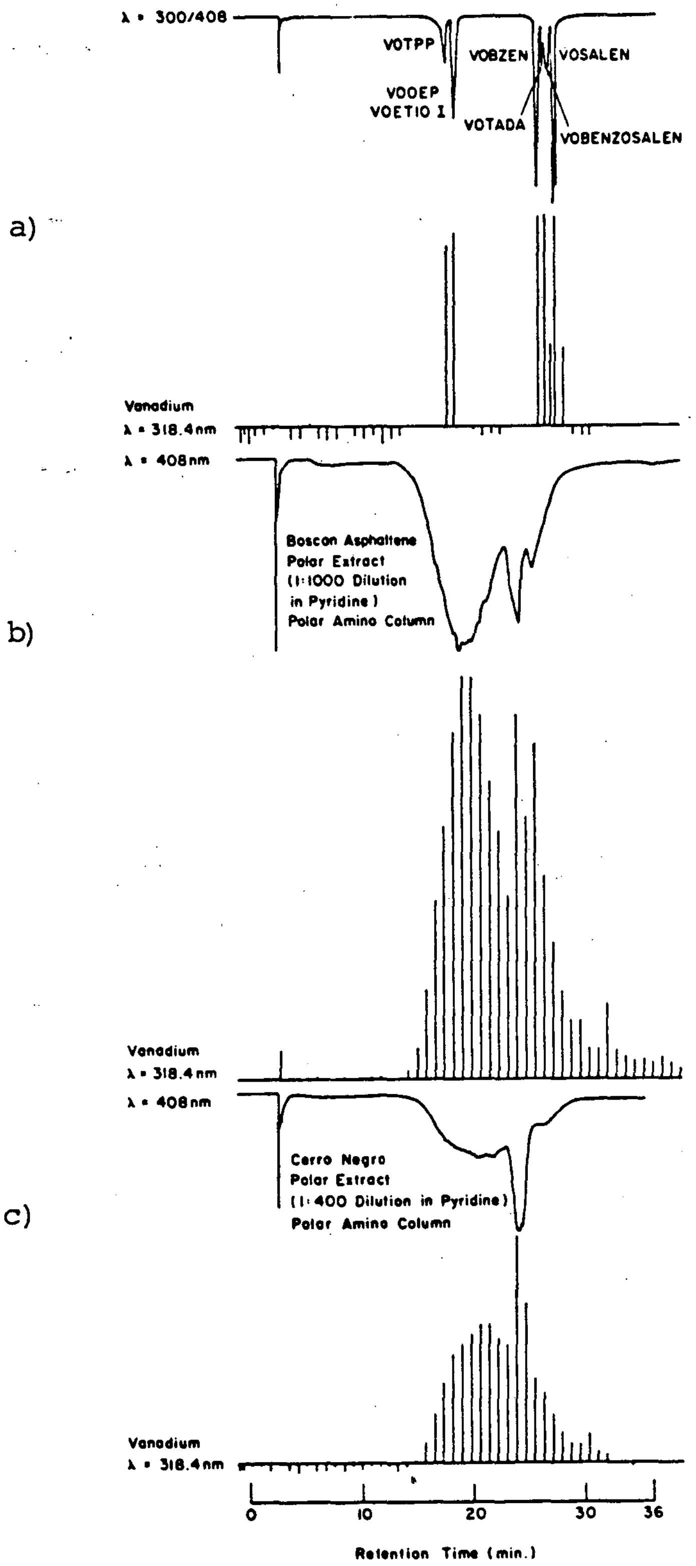

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Figure 12. Polar Amino Column HPLC-GFAA Data for a) Standards, b) Boscan Asphaltene Extract, and c) Cerro Negro Asphaltene Extract.

spectrum, vanadyl octaethylporphyrin and vanadyl etioporphyrin have identical retention times on the amino column. At 408 nm two large peaks are observed in the visible spectrum of the polar extracts. When UV-VIS detection is set at 320 nm another peak is visible just beyond the solvent front. These three peaks have retention times of 2 to 14 minutes, 14 to 22 minutes, and 22 to 28 minutes. For convenience they are referred to as peaks one, two, and three respectively. Only peaks two and three are associated with vanadium.

Polar extracts were dissolved in pyridine before injection into the HPLC system. Pyridine was selected because it was one of the solvents used in the extraction and it easily dissolved the dried extracts. Tests with the model vanadyl compounds demonstrated that, despite its strong affinity for metallo-organic vanadyl compounds, dissolution in pyridine produced no change in retention time when compared with standards dissolved in methylene chloride or methanol. When nickel standards were dissolved in pyridine it was found that some of the injected standard eluted with the solvent peak. Because of this the amino column was not run with the GFAA equipped for nickel detection.

Figure 12 shows the results of amino column analysis of Boscan and Cerro Negro extracts. In Boscan extract the second peak has the most intense visible absorption and vanadium histogram. The third peak is split into doublets with maxima at approximately 24 and 25 minutes. Rapid scan UV-VIS spectra were taken of all three peaks and are shown in the left column of Figure 13. Peak one (t = 7 min.) has

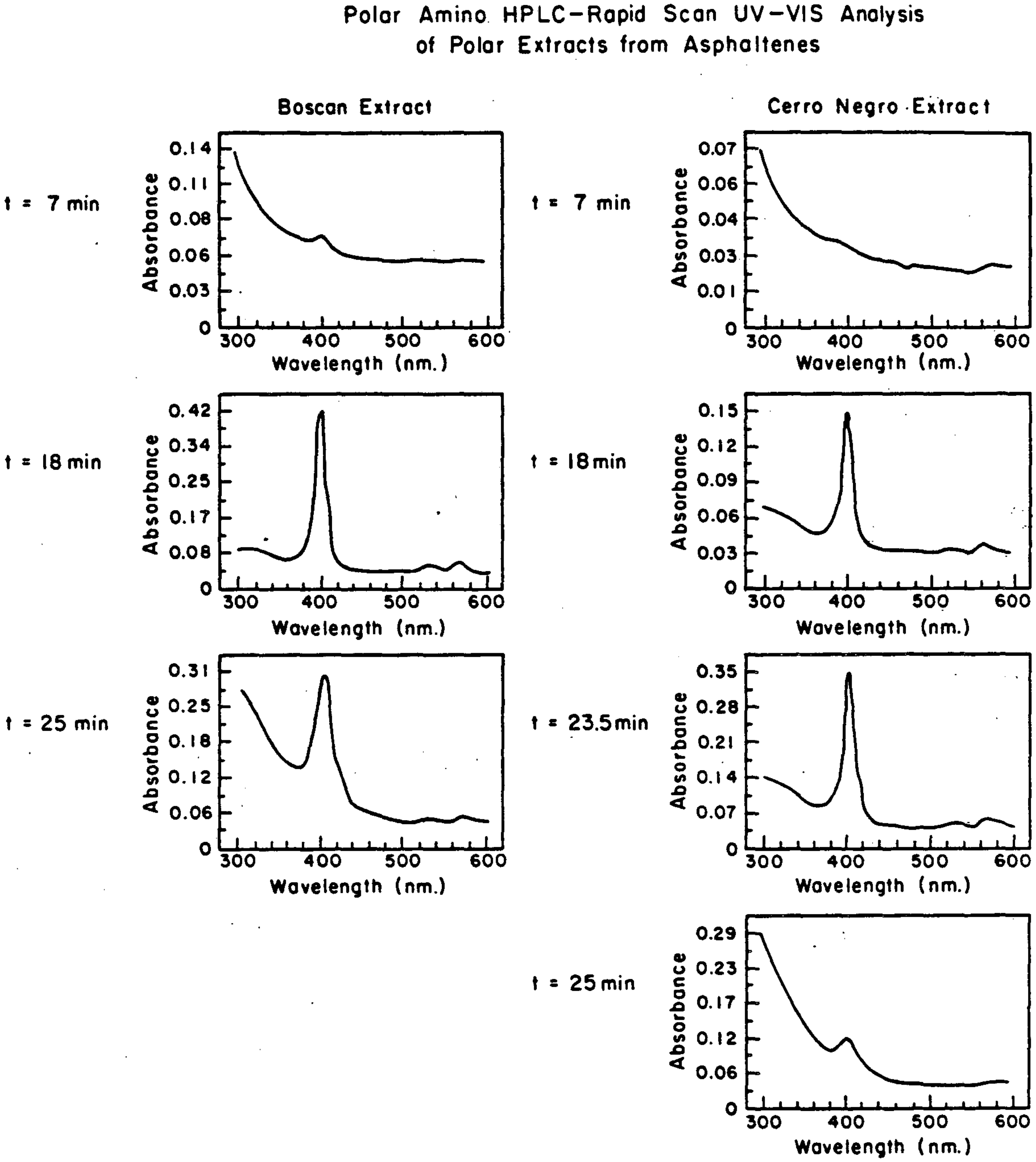

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Figure 13. Rapid Scan UV-VIS Data for Polar Amino Column HPLC Analysis of Boscan and Cerro Negro Asphaltene Extracts.

only a very slight peak at 408 nm, which is too weak to be assigned to a vanadyl porphyrin, and features a strong background absorbance at lower wavelengths. Peak two (t = 18 min.) has a typical vanadyl porphyrin spectra with an intense Soret band at 408 nm and secondary absorptions at 530 and 570 nm. The retention time of this peak corresponds well with the model vanadyl porphyrin compounds. Peak three has a UV-VIS spectrum featuring both porphyrinic and non-porphyrinic absorptions. The retention time of this peak is close to the retention time of the vanadyl non-porphyrin standards.

The lower half of Figure 12 shows the results from the Cerro Negro extract. Peak two is shorter than peak three, which is almost entirely composed of the first peak of the doublet. The right column of Figure 13 shows the rapid scan UV-VIS spectra of the three peaks of the Cerro Negro extract. Peaks one and two are similar to the corresponding peaks in Boscan. In peak three, UV-VIS spectra were taken of both parts of the doublet. The first half of the doublet (t = 23.5 min.) has a porphyrin absorption profile which is almost identical to peak two, but twice as intense, while the second half of the doublet appears to be predominantly non-porphyrin. None of the model vanadyl porphyrins available in this study have retention times matching the vanadyl porphyrins detected in peak three. Close examination of the spectra of this vanadyl porphyrin at 570 nm reveals that the absorption is broadened to include wavelengths over 590 nm. This indicates that vanadyl rhodoporphyrins may be present among the unidentified vanadyl porphyrins.[50]

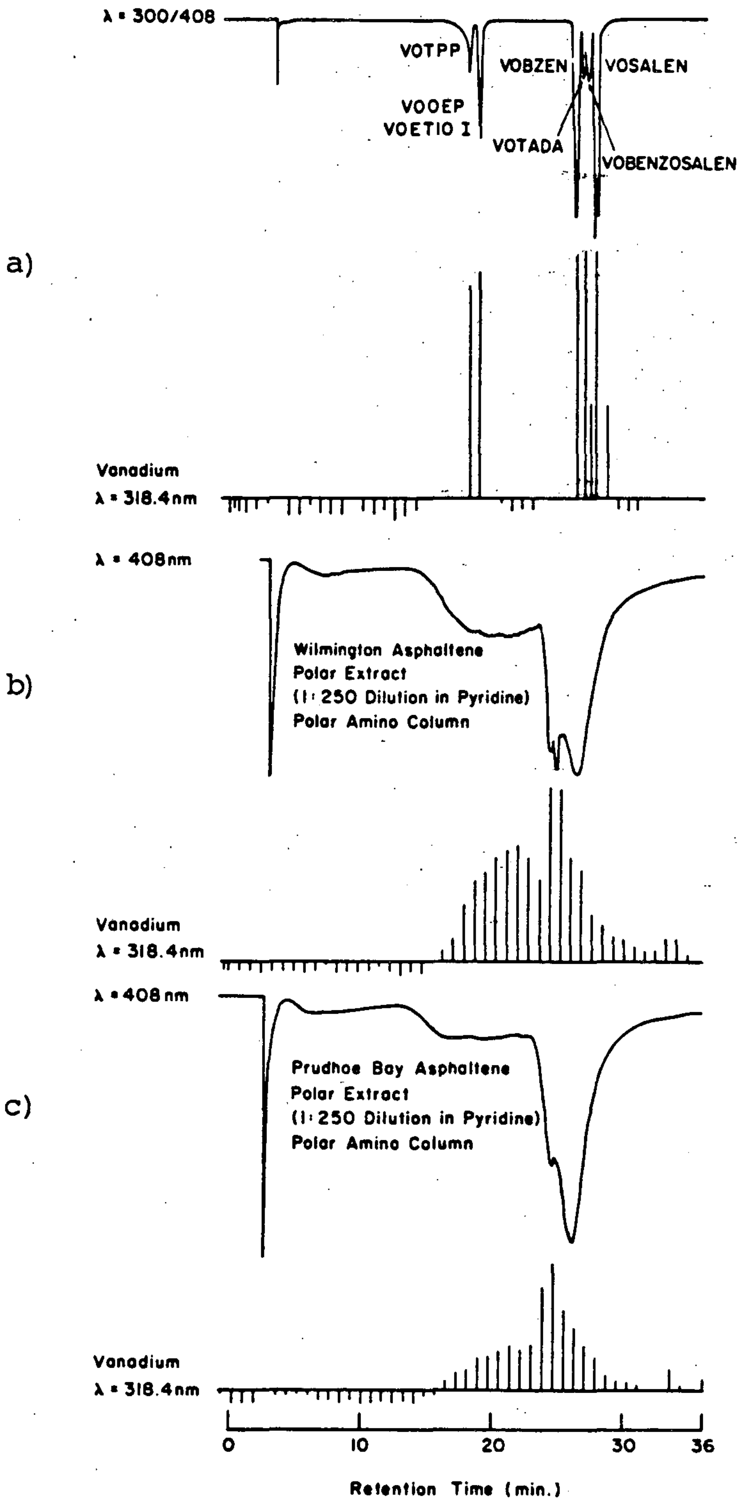

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Figure 14. Polar Amino Column HPLC-GFAA Data for a) Standards, b) Wilmington Asphaltene Extract, and c) Prudhoe Bay Asphaltene Extract.

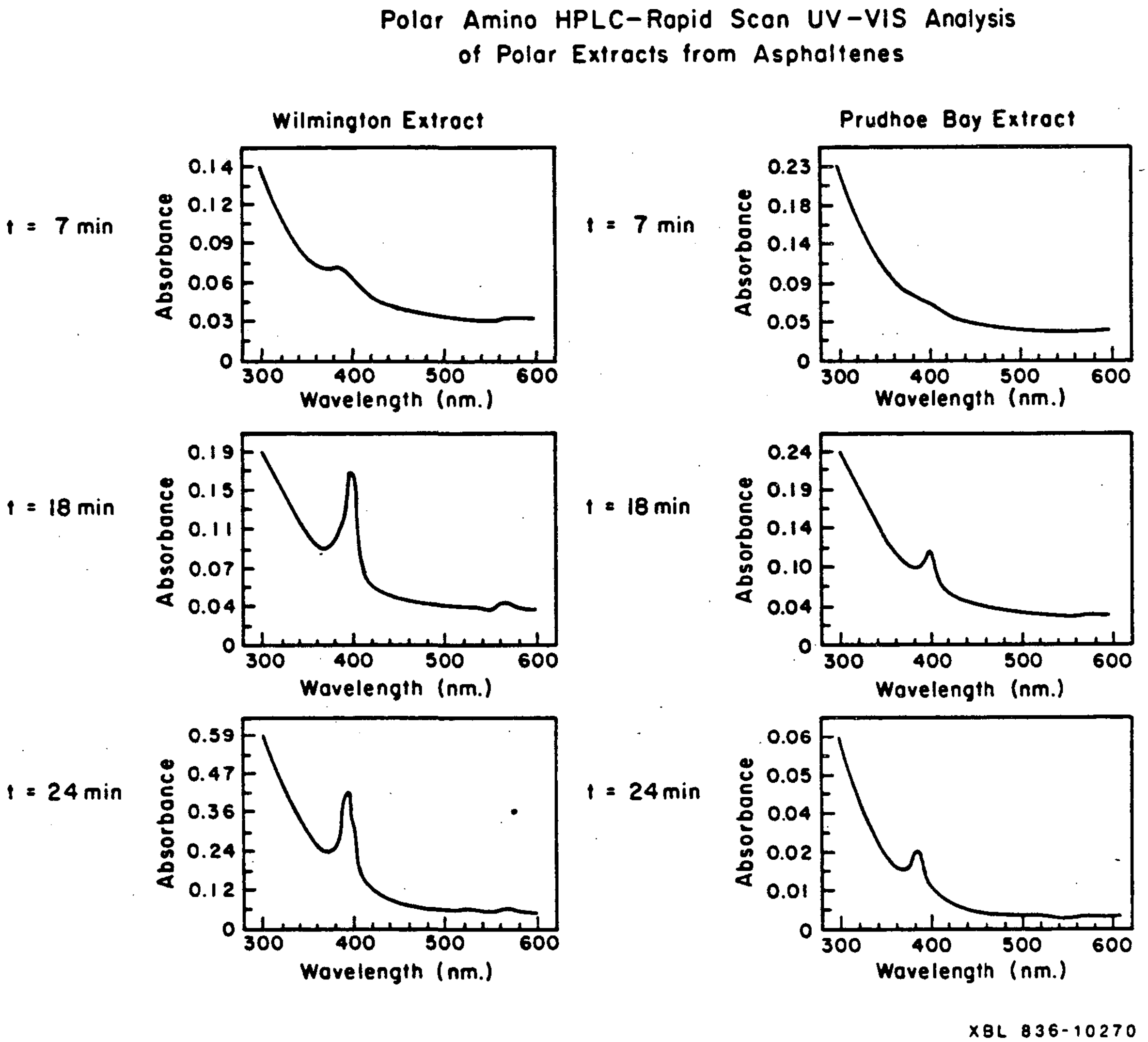

Figure 15. Rapid Scan UV-VIS Data for Polar Amino Column HPLC Analysis of Wilmington and Prudhoe Bay Asphaltene Extracts.

Results for the extracts of Wilmington and Prudhoe Bay asphaltenes are shown in Figure 14. Even at 408 nm, both of these extracts show some absorption at peak one (retention time of 6 to 10 minutes). In both of these extracts the second peak is less intense relative to the third peak than it was for the two Venezuelan petroleums. This tendency for peak three to dominate the visible spectra is especially pronounced with Prudhoe Bay. Peak three is also a doublet in these two extracts; in Wilmington the two halfs have almost equal intensity, but in Prudhoe Bay the second half dominates. All of the rapid scan spectra for these two extracts (see Fig. 15) feature strong background absorbances at lower wavelengths. Several of the spectra have peaks near 408 nm, but there is no evidence of secondary absorptions at 530 nm or 570 nm. Prudhoe Bay extract shows almost no evidence for the presence of vanadyl porphyrins.

In summary, there are a few general tendencies which can be observed in the spectra as the asphaltene content of the parent petroleum decreases. Going from Boscan to Prudhoe Bay, the porphyrinic, second peak decreases in size, while peaks one and three increase. Within peak three, lower asphaltene content is associated with an increase in the relative intensity of the second half of the doublet. Also, the purity of the vanadyl porphyrins in peak two declines and the vanadyl non-porphyrin character of the third peak increases with decreasing asphaltene content. Vanadyl compounds are divided into three classes by the amino column: peak two contains vanadyl porphyrins with elution times corresponding to the vanadyl

Table 7. The Percent Vanadium in Each Vanadium Containing Peak Eluting from the Amino Column[a]

	Peak Two (t = 14 to 22 min.)	Peak Three (t = 22 to 28 min.)
Boscan	59	41
Cerro Negro	58	42
Wilmington	49	51
Prudhoe Bay	33	67

(a) Percentage of total vanadium determined by method of summing of peak heights digitized with an integrator for the elution peak designated.

porphyrin standards; peak three contains vanadyl non-porphyrins and vanadyl compounds with porphyrinic spectra which do not coincide with the retention times of any of the model vanadyl porphyrins available in this study. The distribution of vanadium between peaks two and three is given in Table 7. The percentages given in Table 7 reflect the correlation between low asphaltene content and high vanadyl non-porphyrin concentration.

3 G. Reverse Phase Analysis of Polar Extracts by HPLC-GFAA

Reverse phase analysis of the polar extracts was performed on an octadecylsilane column (C_{18}), using a solvent gradient from a mixture of methyl alcohol and water (3:1 v/v) to 100 percent THF. On this column the nonpolar compounds interact most with the packing and the most polar compounds elute first near the solvent peak. Because of the weak interactions between the reverse phase column and the sample there is little danger of sample loss on the column and compounds that may have been trapped on the amino column are easily eluted. Figures 16 through 21 show the results of the reverse phase HPLC-GFAA analysis. At the top of each figure is a composite chromatogram of the metallo-organic standards. Since the most polar compounds elute first on this column, the polar, vanadyl non-porphyrin standards elute near the solvent peak and the vanadyl porphyrin standards are the last to be eluted. Preliminary tests with vanadyl and nickel model compounds demonstrated that the retention times of both groups of standards were unaffected by the use of pyridine as the injection solvent. Metal analysis was therefore made using the GFAA for both

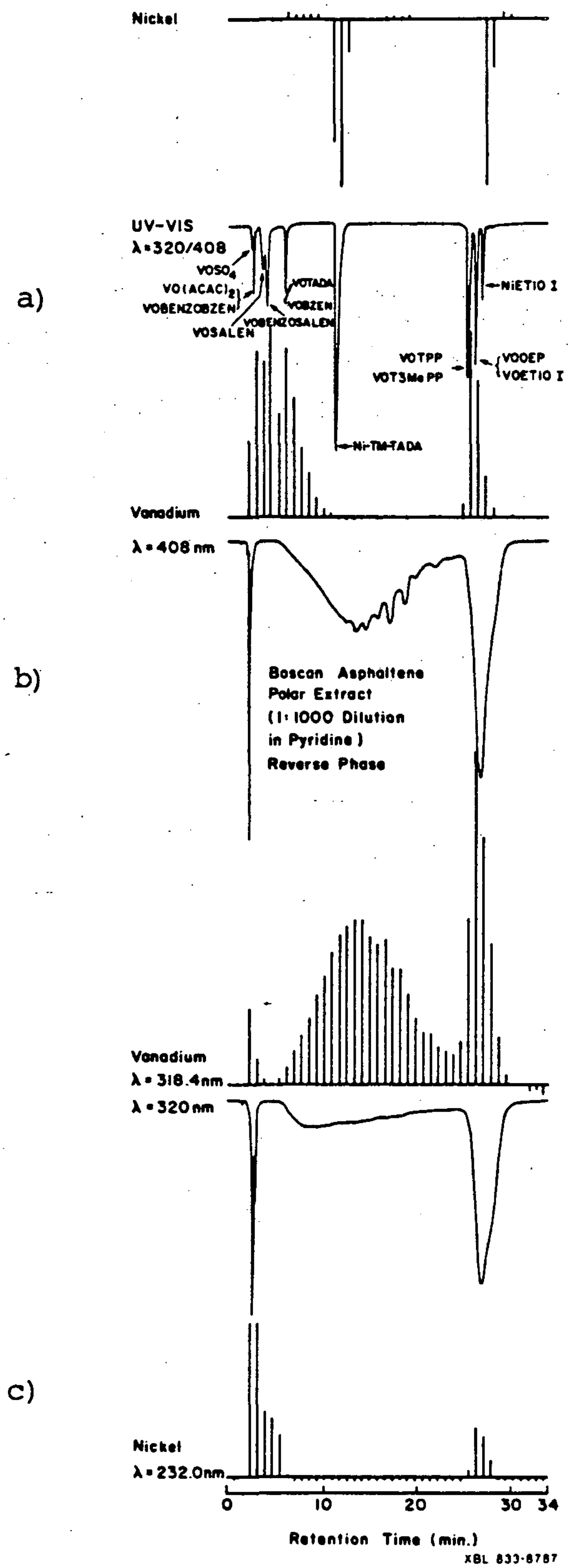

Figure 16. Reverse Phase HPLC-GFAA Data for a) Standards and Boscan Asphaltene Extract Monitored for b) Vanadium Content and c) Nickel Content.

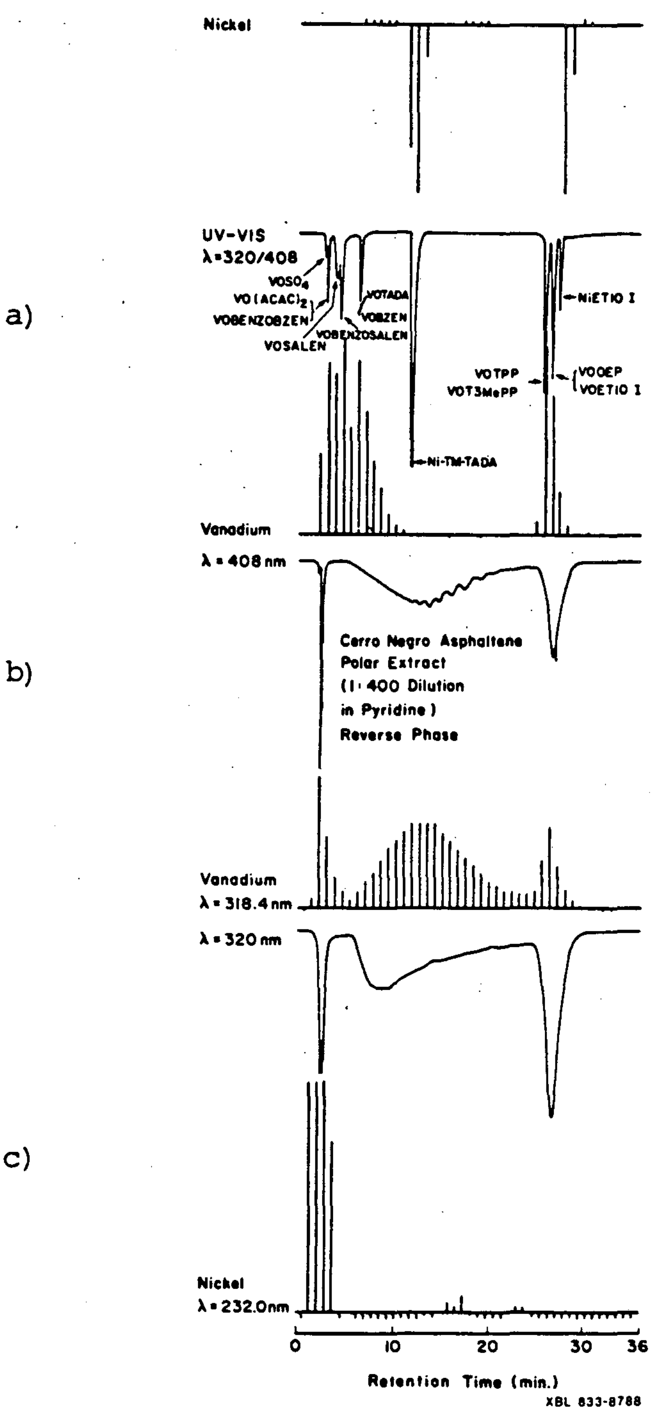

Figure 17. Reverse Phase HPLC-GFAA Data for a) Standards and Cerro Negro Asphaltene Extract Monitored for b) Vanadium Content and c) Nickel Content.

vanadium (318.4 nm and nickel (232.0 nm) detection.

Figure 16 shows the UV-VIS absorption and vanadium and nickel histogram profiles of the Boscan extract. In the top third of the figure is the composite chromatogram of the metallo-organic standards. The middle third of Figure 16 shows the visible absorption at 408 nm and the vanadium histogram. The lower third shows the UV absorption at 320 nm and the nickel histogram. As was true of the SEC results, the 408 nm absorbance closely parallels the vanadium concentration. The profiles are easiest to understand in terms of three peak areas: the first, or solvent peak, extends from about two to four minutes retention time; the second peak extends from about four to 22 minutes; and the third peak extends from about 22 to 30 minutes. The solvent peak is associated with the vanadyl non-porphyrin standards and in Boscan extract only four percent of the vanadium is associated with it. Unfortunately this peak was too narrow to analyzed with the rapid scanning UV-VIS detector. The second peak represents 60 percent of the vanadium and has several small peaks within it, which possibly represent the members of a homologous series. Figure 18 shows a rapid scan UV-VIS spectrum taken at the center of this peak; it is clearly vanadyl porphyrinic, but does not coincide with the retention times of any of the model vanadyl porphyrins. The 320 nm spectrum has a maximum near the leading edge of peak two. This peak is found in the spectra of all four of the extracts and is not associated with vanadium or nickel. Peak three contains 30 percent of the vanadium and corresponds with the reten-

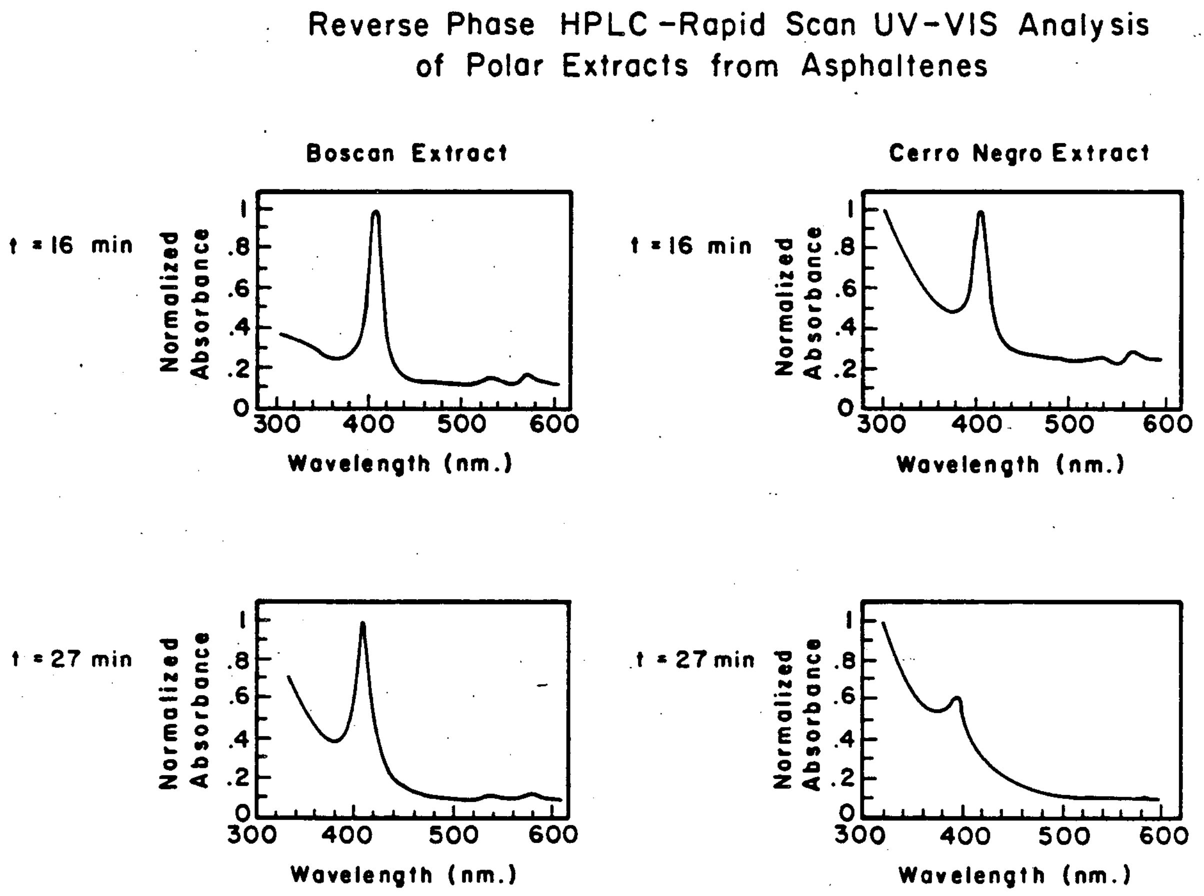

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Figure 18. Rapid Scan UV-VIS Data for Reverse Phase HPLC Analysis of Boscan and Cerro Negro Asphaltene Extracts.

tion times of the model vanadyl and nickel porphyrins; it has strong absorbances at both 408 nm and 320 nm. The rapid scan of peak three (see Figure 18) shows both vanadyl porphyrinic and vanadyl non-porphyrinic behavior. Nickel is concentrated almost entirely near the solvent peak, but 8 percent of the nickel elutes with peak three at a retention time comparable with that of nickel etioporphyrin. The nickel histogram near the solvent peak has been truncated in the figure because the histogram was far offscale at this peak. This was also done with the nickel histograms of the three other asphaltene extracts.

Figure 17 shows the chromatograms of the Cerro Negro extract. The electronic absorbance and vanadium and nickel profiles are similar to the Boscan results, but differ in the relative magnitude of the peaks. Absorbance at 320 nm in the leading edge of peak two is larger relative to the third peak and at 408 nm the smaller peaks within the second major peak are less distinct. The percentages of vanadium in peaks one, two, and three are 17, 68, and 15 percent, respectively. Nickel is concentrated almost entirely in peak one, with one percent of the nickel eluting in each of the remaining peaks. Rapid scan data for the Cerro Negro extract shows that it is similar to the Boscan extract, but less porphyrinic (see Figure 18).

The results for Wilmington extract are given in Figure 19. At 408 nm the second peak is much weaker than the third peak and in peak three the UV absorbance at 320 nm is more intense than the absorbance at 408 nm. Rapid scan analysis (see figure 21) shows only a slightly

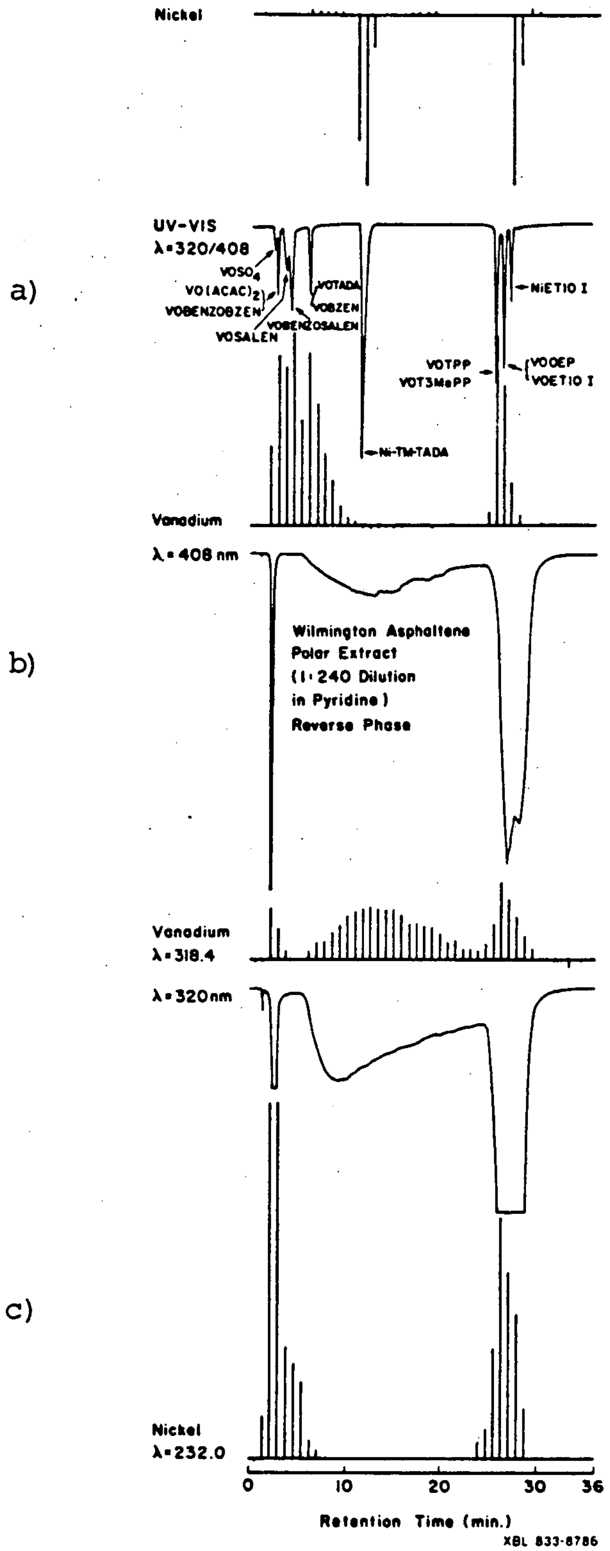


Figure 19. Reverse Phase HPLC-GFAA Data for a) Standards and Wilmington Asphaltene Extract Monitored for b) Vanadium Content and c) Nickel Content.

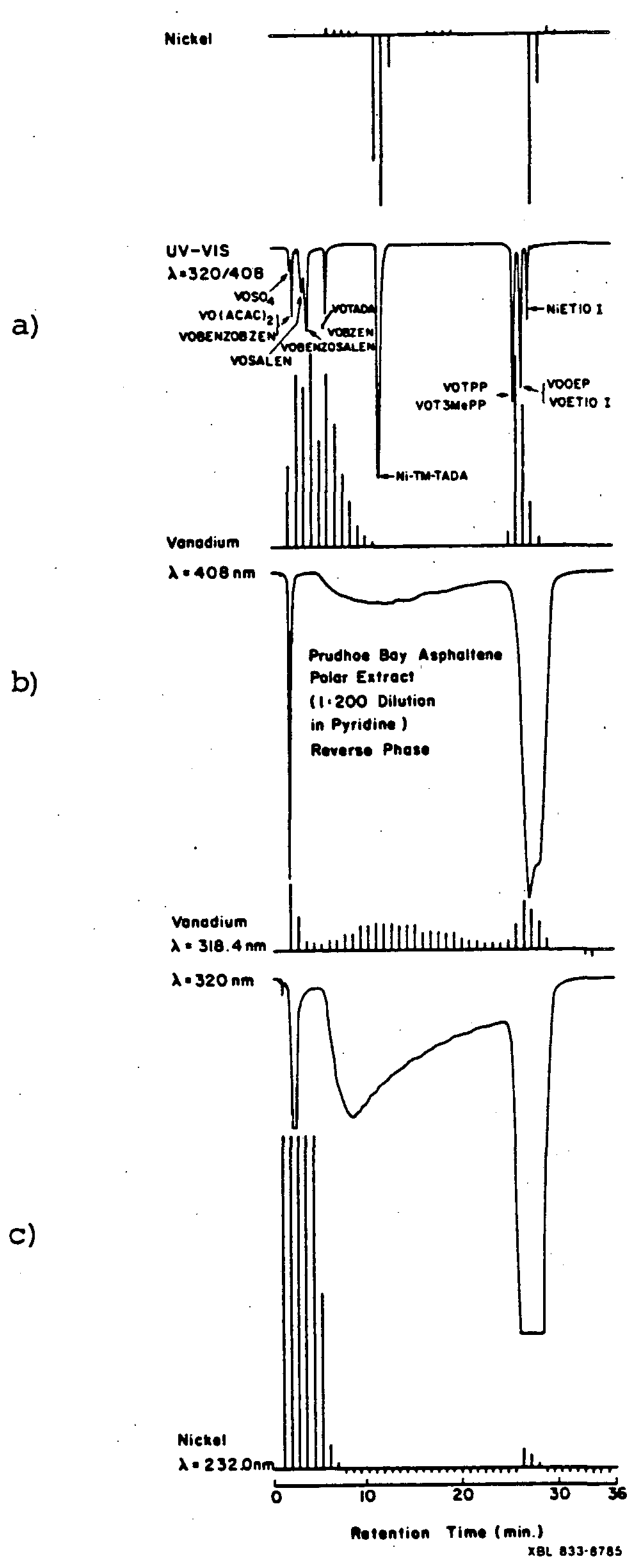


Figure 20. Reverse Phase HPLC-GFAA Data for a) Standards and Prudhoe Bay Asphaltene Extract Monitored for b) Vanadium Content and c) Nickel Content.

vanadyl porphyrinic character. Wilmington has both the highest nickel concentration and the most unique nickel profile of the four asphaltenes; although 67 percent of the nickel is still eluted near the solvent peak, 33 percent elutes with peak three at a retention time that is consistent with the model nickel porphyrin.

The results for the Prudhoe Bay extract are given in Figure 20. The 408 nm and 320 nm absorbance spectra and vanadium histogram are similar to the Wilmington results, but the diminishing of the second peak at 408 nm and the increased intensity of the 320 nm spectrum relative to the 408 nm spectrum are more pronounced. The rapid scan results in Figure 21 show that there is very little vanadyl porphyrin character in peak two and no porphyrinic character in peak three.

In general, the reverse phase column appears to separate vanadium into four classes. Peak one contains a small amount of vanadyl non-porphyrins. Peak two contains vanadyl porphyrins which are not among the standards available in this study. Peak three contains two classes of compounds, vanadyl porphyrins with retention times similar to the model vanadyl porphyrins and vanadyl non-porphyrins with absorbances in the ultraviolet region. Nickel compounds are predominantly non-porphyrin, with the exception of about a third of the nickel in the Wilmington extract. As was true of the amino column results, there are general features of the profiles which change with the asphaltene concentration of the parent petroleum. High asphaltene petroleums have strong visible absorbance and high vanadium content in peak two. Rapid scan UV-VIS spectra of these petroleums show

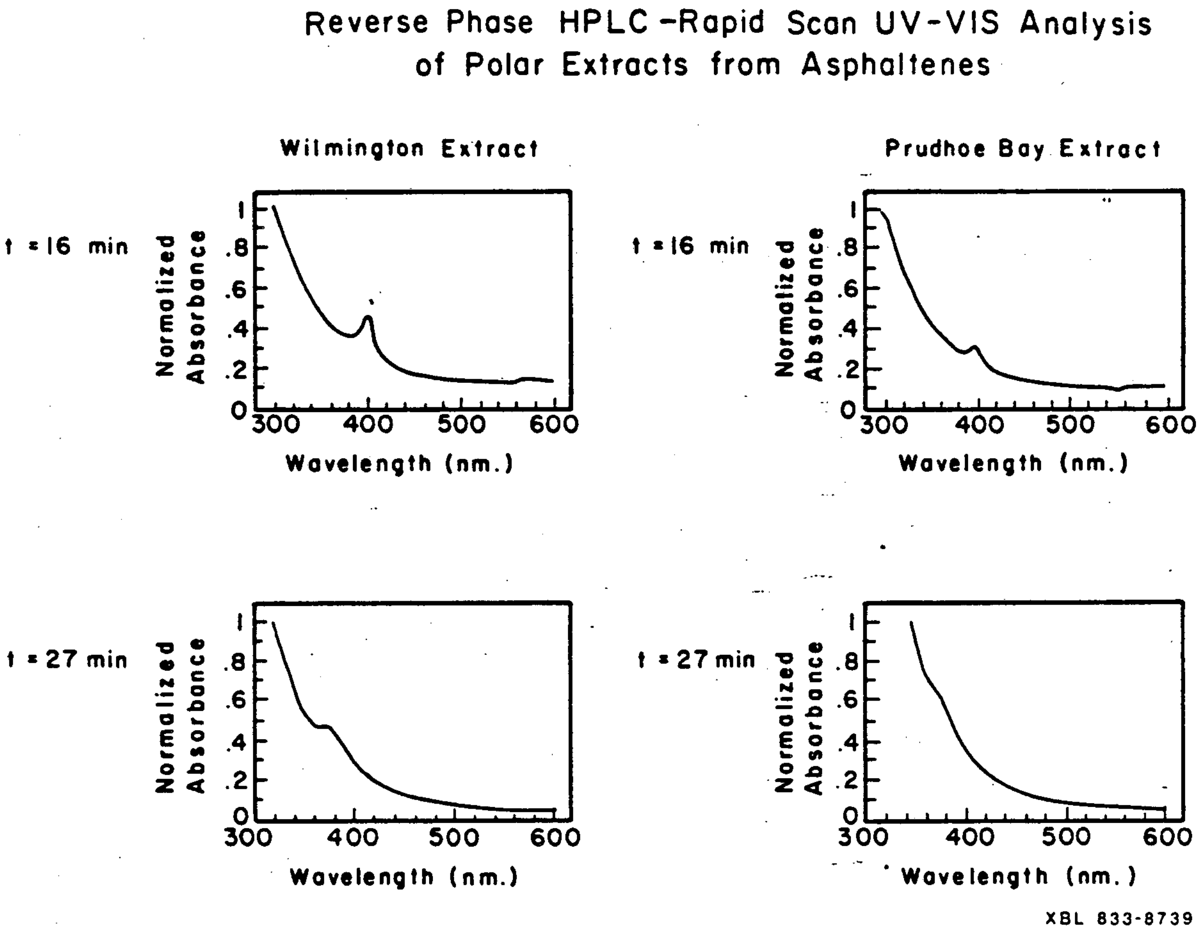


Figure 21. Rapid Scan UV-VIS Data for Reverse Phase HPLC Analysis of Wilmington and Prudhoe Bay Asphaltene Extracts.

strong Soret bands. The extracts of petroleums with lower asphaltene contents have strong absorbances at both 320 nm and 408 nm in the third peak. The rapid scans of these extracts have little vanadyl porphyrinic character. Metal distribution among the three peaks of the chromatograms is given in Table 8. The percentage of vanadium eluting in peak two with the unknown vanadyl porphyrin compounds is not as strongly influenced by the asphaltene content of the parent petroleum as the known vanadyl porphyrins in the second peak of the amino column analysis were. Peak three, which coincides with the retention time of the vanadyl and nickle porphyrin standards as well as showing vanadyl non-porphyrin behavior, does not have as consistent a relationship between the percentage of vanadium present and the asphaltene content of the source petroleum. This behavior is probably the result of the dual nature of the compounds eluting in this peak; the concentration of vanadyl porphyrins decreases with decreasing asphaltene content while the concentration of vanadyl non-porphyrins increases.

3 H. Extraction of Prudhoe Bay Maltene by Column Chromatography

Since asphaltenes were found to be richer in vanadyl porphyrins than the whole crude petroleums, a Prudhoe Bay maltene was extracted by column chromatography in an attempt to isolate a vanadyl non-porphyrin fraction. Figure 22 shows the UV-VIS spectrum of this maltene extract. The maximum absorbance is at 270 nm and there are no weak Soret bands present. Analysis with the GFAA confirmed the presence of vanadium in this vanadyl non-porphyrin extract. When the

Table 8. The Percent Vanadium and Nickel in Each Peak Eluting from the Reverse Phase Column[a,b]

	Peak One (t = 2 to 4 min.)		Peak Two (t = 4 to 22 min.)		Peak Three (t = 22 to 30 min.)	
	V	Ni	V	Ni	V	Ni
Boscan	4	92	66	0	30	8
Cerro Negro	17	98	68	1	15	1
Wilmington	9	67	66	0	25	33
Prudhoe Bay	18	99	58	0	24	1

(a) Percentage of total vanadium determined by method of summing peak heights digitized with an integrator for the elution peak designated.

(b) Percentage of total nickel determined by method of summing peak heights digitized with an integrator for the elution peak designated.

extract was run on the reverse phase column, it eluted with the third peak at a retention time corresponding to the unknown vanadyl non-porphyrins observed during reverse phase analysis of the solvent selective extracts. ESR analysis shows that the vanadium in this fraction is coordinated by four sulfur atoms.[106] The absorbance peak at 270 nm resembles the absorbance of the Boscan chromatographic extract at that wavelength. Since there are vanadyl porphyrin compounds which are common to all four crude petroleums, it is reasonable to expect that there are classes of vanadyl non-porphyrins which are also present in all four crude petroleums. The UV-VIS spectra of the Boscan and Prudhoe Bay asphaltene chromatographic extracts are consistent with this hypothesis.

3 I. Rapid Scan UV-VIS - SEC-HPLC-GFAA Analysis

Figure 23 shows a series of rapid scan UV-VIS spectra of a Boscan asphaltene during SEC-HPLC-GFAA analysis. This represents the first time that such an analysis of an asphaltene has been made. The molecular weights given for the various retention times are taken from Figure 6, The 50 Å - 100 Å - 1000 Å SEC column calibration curve. At high molecular weights there is only a slight peak at 408 nm. As the molecular weight of the compounds surrounding the vanadyl ion decrease, the background absorbances decrease and the peak at 408 nm becomes much more clearly defined. This change occurs gradually with increasing retention time until finally, at 55 minutes, the spectrum is definitely metallo-porphyrinic. The peak at 408 nm is clearly a Soret band and weak side bands appear between 500 and 600

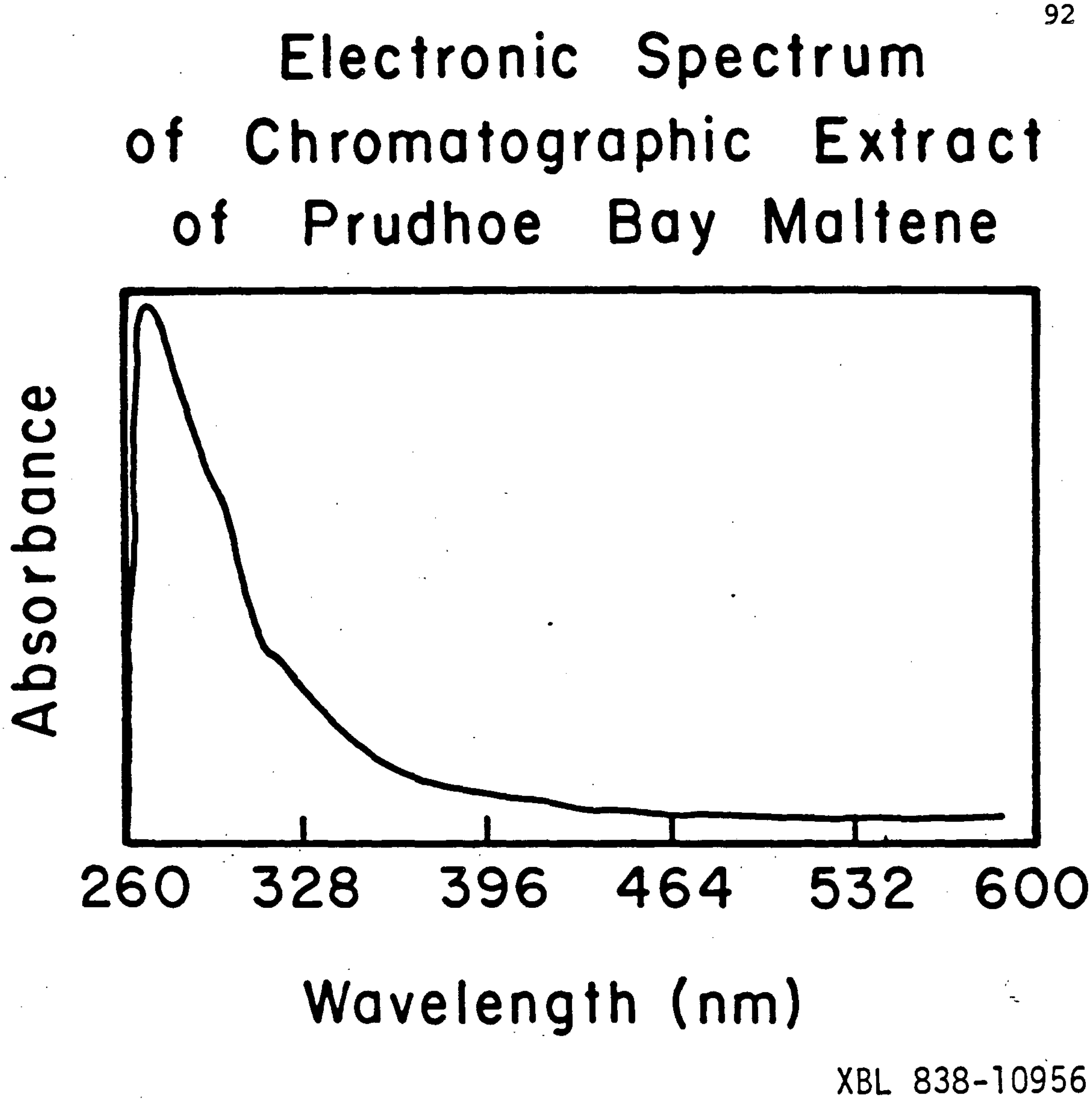
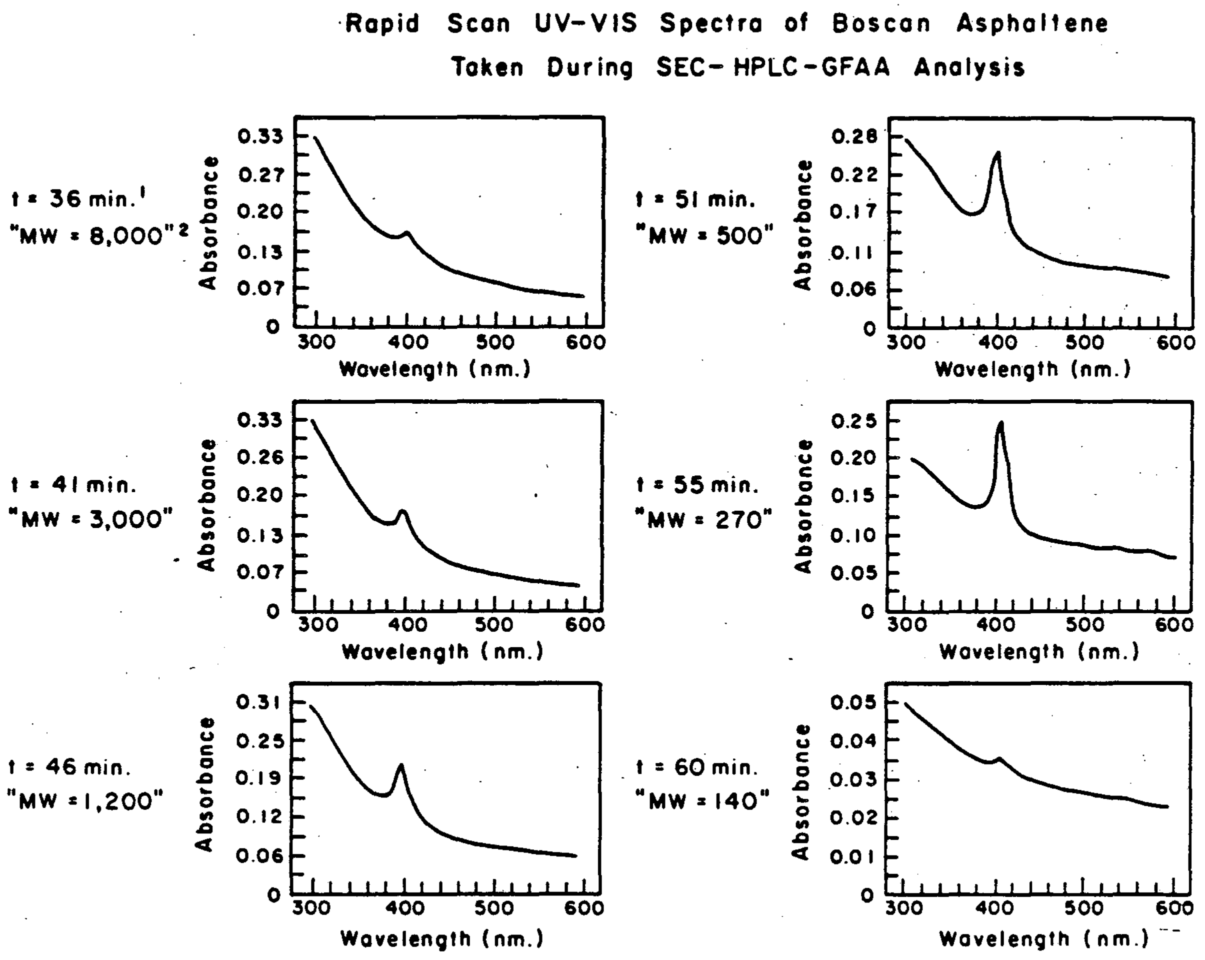


Figure 22. Electronic Spectrum of Vanadyl Non-Porphyrin Extract of Prudhoe Bay Maltene.

nm. This gradual increase in the clarity of the Soret band shows that it is indeed a Soret band which is barely observable over the strong background absorbances of the 2000 dalton asphaltene molecules. When the asphaltene molecules surrounding the vanadyl porphyrin are smaller, they have less intense visible absorbances and the Soret band appears to be relatively more intense. This result shows that vanadyl porphyrins account for a greater percentage of the vanadyl compounds present in petroleum than has been previously reported. The entrapment of some vanadyl porphyrins in large asphaltene molecules has prevented them from being detected by standard acid de-metallation or solvent selective extraction techniques.

The most intensely porphyrinic spectra in Figure 23 occurs at a retention time which should correspond to a molecular weight of only 270 daltons. This is physically impossible. It is evident that, even though the calibration curve was derived from model vanadyl porphyrins, it does not accurately represent the retention times of vanadyl porphyrins injected with the complete asphaltene matrix. This means that the extracts are not as highly non-porphyrinic as was originally assumed from the SEC results, although the normal and reverse phase analyses do establish the presence of vanadyl and nickel non-porphyrins in the extracts. Further evidence of the extraction of vanadyl non-porphyrins is provided by the percentages of vanadium extracted from each asphaltene; the least porphyrinic asphaltenes show the greatest percentages of vanadium removal during extraction.



1. Retention time
2. Molecular weight based on the calibration curve for the 50 Å - 100 Å - 1000 Å SEC column, derived from model vanadyl compounds and polystyrene standards

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Figure 23. Data for Rapid Scan UV-VIS Analysis of Boscan Asphaltene During SEC-HPLC-GFAA Analysis.

This analysis also casts doubt on the accuracy of many molecular weight studies in the literature, in which it has been common to use polystyrene standards or model compounds to calibrate analytical columns.[28,32,85,86]

Despite the inaccuracy of the calibration curve, the relative distribution of vanadyl compounds between the four molecular weight regions is still valid, since, even though the true value of the molecular weights selected as the boundaries between the regions was uncertain, the size of the regions was constant and the order of magnitude of the molecular weights was correct. The SEC-HPLC-GFAA analysis is still an accurate means of making comparisons between asphaltenes and their components.

CHAPTER 4

Discussion

4 A. Asphaltene Structure

One of the major difficulties in asphaltene research is the variation among definitions of what is being studied. Although it is generally accepted that asphaltenes are the material which is precipitated from a petroleum by forty volumes of pentane, hexane, or heptane, there is a great variety in the methods of performing the precipitation.[26] Variations in the reported precipitations involve: degree or absence of heating of the solution; time allowed for precipitation, amount or absence of centrifugation, and the use of further re-precipitations of the asphaltene. All of these variations in the precipitating procedure can effect the nature of the asphaltenes that are removed from the petroleum. Some of the differences in the asphaltenes are easily noticed. The choice of the precipitating solvent has a noticeable effect on the mass and aromaticity of the asphaltenes precipitated.[34] If centrifugation is used to separate the precipitated material, the speed and duration of the centrifugation affects the ppm of vanadium in the collected asphaltene.[33] The temperature at which the precipitation is performed has subtler effects on the asphaltenes produced; the total weight may remain relatively unaffected, but slight variations in the carbon to hydrogen ratio suggest that the composition of the precipitated asphaltene may have varied.[36] In addition, some researchers reprecipitate their asphaltenes to remove any maltenes which may have become entrapped in the asphaltenes.[27,57] Since asphaltenes are defined as a solubility class, such a secondary precipitation may remove more material and produce an asphaltene with a higher average molecular weight, but whether the remaining material is therefore inherently more asphaltenic depends more on how the researcher defines an asphaltene, than on any inherent physical basis.

In this study the precipitating conditions were kept gentle to minimize secondary effects. The petroleums were added to forty volumes of pentane at room temperature and gently agitated for twenty-four hours. After agitation, the asphaltenes were separated by filtration and washed until the rinse solvent was clear. The one variation in precipitating conditions which we investigated was the ratio of the volume of precipitating solvent to the volume of petroleum. As mentioned in the results of the precipitations, both ten to one and forty to one volumes of pentane to petroleum were used. Within experimental error, the amount of material precipitated remained constant with the variation in solvent volume, but the vanadium concentration of the precipitated material was noticeably lower in the asphaltenes from the forty to one volume precipitation. The distribution of vanadium in the SEC-HPLC-GFAA analysis was relatively unaffected by the volume of pentane used in the precipitation. These results lead to two conclusions about the nature of the vanadyl compounds which are not incorporated in the forty to one precipitated asphaltenes. Since a four-fold increase in solvent volume increased their solubility in pentane and because their absence did not greatly affect the mass of collected asphaltenes, these compounds are relatively low (less than 1000 daltons) molecular weight metallo-organic vanadyl compounds. Also, since the SEC vanadium profile was virtually unaffected by the reduction in vanadium concentration, the low molecular weight vanadium compounds must be associated with asphaltene constituents which cover the entire range of molecular weights present in the asphaltenes. This distribution of low molecular weight vanadyl compounds within high molecular weight asphaltene structures is consistent with the Yen model of asphaltenes (see Fig. 1)[28] and the work of Fish and Komlenic,[97] which demonstrated that lower molecular weight vanadyl compounds could be extracted from the entire range of molecular weights present in the whole heavy crude petroleums.

The results of the extraction experiments give further insight into the complicated nature of the asphaltenes. Vapor pressure osmometry (VPO) studies of asphaltene molecular weights have demonstrated that the degree of association between asphaltene molecules is strongly influenced by the polarity and functionality of the solvent used in the measurements.[38] An equilibrium apparently exists between the interactions of asphaltene molecules with each other and with the solvent. In the whole petroleum the resins form a very complex solvent in which the asphaltenes are dispersed. When asphaltenes are precipitated the asphaltene-resin interactions become weakened and the asphaltene-asphaltene interactions dominate, forming larger micelles. This view of the mechanisms occurring during precipitation is supported by the results of the extraction experiments of the whole petroleums and the asphaltenes. Fish and Komlenic reported the removal of 50 to 87 percent of the vanadium present in the whole petroleum and SEC-HPLC-GFAA analysis showed that vanadyl compounds had even been extracted from compounds with molecular weights greater than 2000 daltons.[97] SEC-HPLC-GFAA analysis of precipitated asphaltenes and maltenes has established that compounds in that high molecular weight region are primarily asphaltenic. Extraction of the precipitated asphaltenes removed only 5 to 18 percent of the vanadium present. Furthermore, SEC-HPLC-GFAA analysis of the extracted asphaltenes failed to show a reduction of in the amount of vanadium present at molecular weights over 2000 daltons. The existence of larger micelles in the precipitated asphaltenes accounts for the differences in behavior. Xylene is not sufficiently polar to disrupt the larger asphaltene micelles formed during precipitation, so in effect there is less "surface area" from which to extract asphaltenes.

Although less vanadium is removed from the precipitated asphaltenes, the solvent selective extraction of vanadyl compounds does reveal that not all of the vanadyl compounds are equally attracted by the asphaltene molecules. Both the normal phase and the reverse phase HPLC-GFAA analysis of the asphaltene extracts showed that the concentration of vanadyl porphyrins was much higher in the asphaltene extracts than in the extracts of whole crude petroleums. This affinity of vanadyl porphyrins for the asphaltene micelles probably results from the aromaticity of the porphyrin ring. Normal and reverse phase HPLC-GFAA analysis of the four asphaltene extracts also demonstrated that asphaltene concentration is related to vanadyl porphyrin concentration; the asphaltene extracts from the most asphaltenic petroleums have strongly porphyrinic UV-VIS spectra, while the low asphaltene content petroleums show very weak porphyrin character in their spectra.

Prudhoe Bay crude petroleum is the oldest petroleum analyzed in this study. It also has the lowest vanadium concentration, the lowest asphaltene content, and the lowest metallo-porphyrin concentration of the four petroleums studied. The mechanisms of vanadyl porphyrin and asphaltene formation proposed by Radchenko offer one explanation for the correlation of these factors,[23] but the results of this study suggest another explanation for the metallo-porphyrin level in Prudhoe Bay. Speight has alluded to the possibility of self-precipitation of asphaltenes from crude petroleums.[29] During the maturation of the heavy crude petroleums, the formation of asphaltenes creates an ever increasing difference between the highest molecular weight compounds in the petroleum and the lowest. Eventually a point may be reached at which the balance of oils, resins, and asphaltenes is not suitable for maintaining large amounts of asphaltenes in solution. At this point, some of the asphaltenes will precipitate to the bottom of the reservoir.[22,43] Since the metallo-porphyrins interact strongly with the asphaltenes, many of them would be removed from the petroleum during such a self-precipitation. Migration may also be a cause of low asphaltene and vanadyl porphyrin concentrations, since micelles are believed to be left behind during petroleum migration.[63]

4 B. Biogeochemical Information

The mechanisms responsible for the formation of nickel porphyrins, vanadyl porphyrins, and asphaltenes are still poorly understood. In an extensive review article, Radchenko attributed nickel porphyrins to nitrogen rings derived from the original petroleum biomass and vanadyl porphyrins to pigments derived from the sulfur bacteria responsible for secondary sulfurization of the petroleum.[23] The formation of asphaltenes was ascribed to the activity of sulfur bacteria and other unspecified processes occurring during oxidative phases in the diagenesis of the petroleums. Other researchers have attributed the porphyrin rings of both vanadyl and nickel porphyrins to pigments present in the original biomass of the petroleum. According to this theory nickel porphyrins were predominant during the early stages of maturation and were later converted to vanadyl porphyrins.[1] At present, the only complete structures determined for both vanadyl and nickel porphyrins are consistent with an origin as chlorophyll a and therefore support a common origin for both metallo-porphyrin groups.[72]

The results of the present study are in agreement with a single source for the porphyrin rings of vanadyl and nickel porphyrins.

This is demonstrated by the Wilmington and Prudhoe Bay crude petroleums, which are relatively similar in sulfur and asphaltene content, but differ greatly in age. Of these two petroleums Wilmington, which is the younger, has the higher concentration of nickel porphyrins. Apparently, the conversion of nickel porphyrins to vanadyl porphyrins is more complete in Prudhoe Bay petroleum.

Figure 24 shows the logarithm of the vanadium concentrations of the whole petroleums, maltenes, and asphaltenes as a function of asphaltene concentration. A similar figure prepared by Fish and Komlenic for the whole petroleums showed that there was a linear relation between the logarithm of the vanadium concentration and the asphaltene content of the petroleum.[97] Since the correlation was only based on four petroleums, it cannot be assumed that all petroleums will conform to this relationship. It definitely can not be extended to light petroleums, since Radchenko's review of petroleum data established that there was a dramatic difference in metalloporphyrin distribution between petroleums with less than 0.3 % sulfur and petroleums with higher sulfur contents.[23] All four of the petroleums studied by us have sulfur concentrations of over one percent. Since the ppm vanadium in the four petroleums correlated well with the asphaltene concentration it was thought that the ppm vanadium in the asphaltenes would show the same correlation. As can be seen in Figure 24, there is a definite pattern of increasing vanadium concentration in the asphaltenes with increasing asphaltene content of the the petroleum, although it is not as linear as the relation-

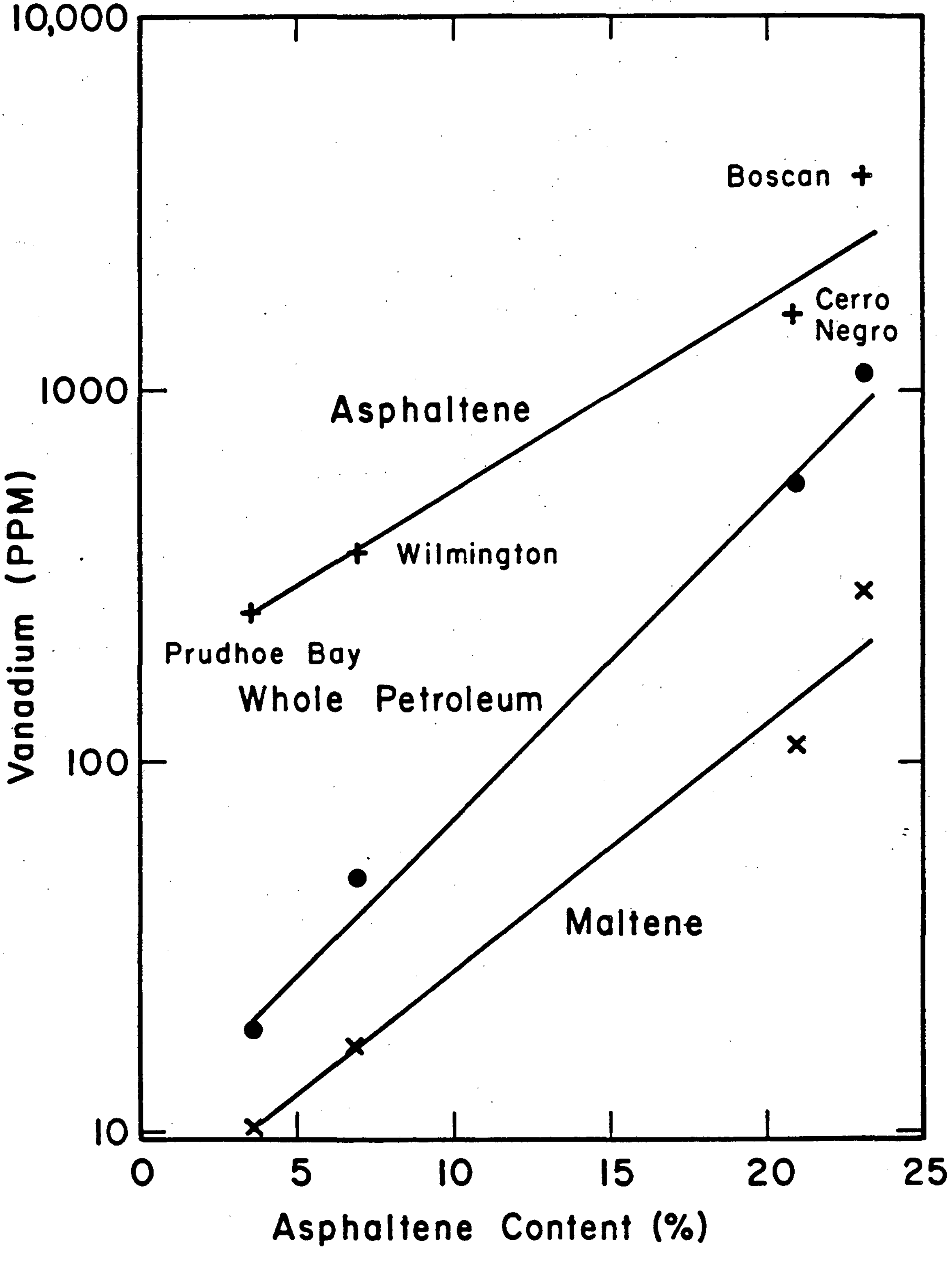

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Figure 24. Plot of Log Vanadium Concentration (ppm) Versus Asphaltene Content for Boscan, Cerro Negro, Wilmington, and Prudhoe Bay Asphaltenes, Petroleums, and Maltenes.

ship for the whole petroleums. Vanadium concentration in the maltenes also shows a linear correlation with asphaltene content. The fact that the vanadium concentration in both the maltenes and the asphaltenes shows a relationship with the asphaltene content of the whole petroleums, suggests that it may be incorrect to look at the metal concentration as a function of asphaltene content; rather it may be more correct to say that metal content and asphaltene content are both functions of the composition and the aging of the petroleum. This view is in agreement with research that indicates that the primary difference between the asphaltenes and the resins may be the extent of condensation in the asphaltenes and that there are significant functional similarities between the resins and asphaltenes of individual petroleums.[29,30]

Fish and Komlenic also noted that the nickel concentration reached a maximum at about 100 ppm.[97] Work by Erdman and Harju has also indicated that asphaltenes are saturated with respect to nickel concentration at a lower concentration than the vanadium concentration.[27] If Fish and Komlenic had observed a true maximum nickel concentration as a function of asphaltene concentration, then this saturation should also be evident in the precipitated asphaltenes.[97] As can be seen from Figure 25, such a saturation behavior does appear to exist in the four petroleums studied. The only deviations from the results of Fish and Komlenic are the nickel concentration of Wilmington asphaltene and maltene, which are higher than the nickel concentrations of the Venezuelan asphaltenes and maltenes. This

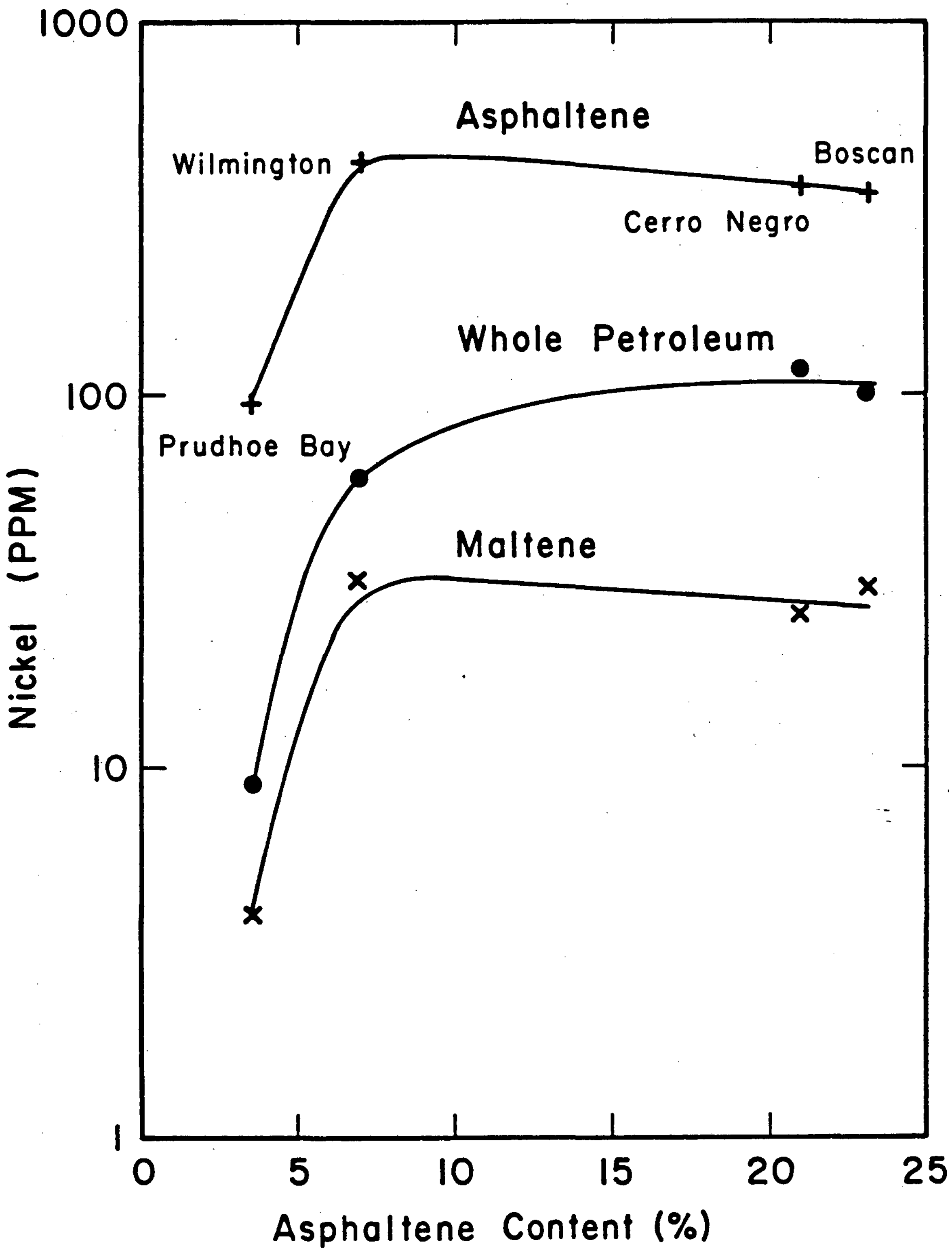

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Figure 25. Plot of Log Nickel Concentration (ppm) Versus Asphaltene Content for Boscan, Cerro Negro, Wilmington, and Prudhoe Bay Asphaltenes, Petroleums, and Maltenes.

higher nickel concentration in Wilmington asphaltene is probably a function of the high concentration of nickel porphyrins in Wilmington petroleum. Apparently the nature of the ligands coordinating to the nickel ion affects the saturation limit of nickel in petroleum; i.e., petroleums appear to be able to solvate higher levels of porphyrinic nickel. This observation may have bearing on the correlation between vanadium concentration and asphaltene concentration. In Boscan asphaltene, which has the highest vanadyl porphyrin concentrations, the total vanadium concentration and the percentage of vanadium involved in porphyrins is higher than would be expected from the linear relationship between asphaltene content and vanadium content observed for the other three petroleums. This is also true of the vanadium concentration of Boscan maltene. Vanadyl porphyrins, therefore, appear to be more soluble in heavy crude petroleums than vanadyl non-porphyrins.

In the study of vanadyl compounds in petroleums, three classifications have often been used: extractable vanadyl non-porphyrins, extractable vanadyl porphyrins, and high molecular weight non-extractable vanadyl compounds. Rogers considered these latter compounds non-porphyrins because of their high molecular weights and their UV-VIS spectra, which show only a slight peak at 408 nm.[108] However, ESR analysis of these compounds did show that most of the vanadium in these compounds had a four nitrogen ligand environment.[108] The rapid scan UV-VIS analysis of a Boscan asphaltene during SEC-HPLC-GFAA analysis demonstrated that the small peak at 408 nm gradually becomes a distinct Soret band as the molecular weight of the surrounding asphaltene molecules decreases. This can be explained by two probable systems within the asphaltenes; either a large aromatic molecule containing a porphyrin like coordination site or a vanadyl porphyrin trapped within a large asphaltene molecule. At present, it is not within the capability of our experimental equipment to distinguish between these two possibilities.

Normal and reverse phase analysis demonstrated that there are two broad classes of vanadyl compounds in the polar extract which have yet to be identified. Reverse phase analyses showed that most of the extracted vanadyl non-porphyrins were not comparable to the model vanadyl non-porphyrins available in this study. Both normal and reverse phase analysis demonstrated that a significant fraction of the eluting compounds with vanadyl porphyrin spectra spectra did not correspond with the elution times of the model vanadyl porphyrins used to calibrate the columns. It is likely that these porphyrins were vanadyl Rhodo and DPEP porphyrins, which were not available for our study. In future work, it will be necessary to have a greater array of model compounds. Among the compounds that should be considered are the hydrogenated vanadyl porphyrins. In the reducing environment of the crude petroleum reservoir,[114,115] it is possible that the porphyrin rings may become hydrogenated and there has been a report of non-metallated, hydrogenated porphyrins in shale.[116] If the ring is sufficiently hydrogenated, the stability of the metalloporphyrin may be weakened to the point where demetallation and decomposition of the porphyrin ring is possible. This may represent a mechanism by which porphyrins have been demetalled in older petroleum deposits. The elucidation of the vanadyl porphyrin and non-porphyrin structures will be necessary before mechanisms of metallo-porphyrin formation and

4 C. Isolation of Vanadyl Non-Porphyrins

One of the greatest difficulties in identifying vanadyl non-porphyrins is the presence of vanadyl porphyrins and their strong visible absorbance (408 nm), which overshadows the spectra of the vanadyl non-porphyrins. Even with normal and reverse phase HPLC-GFAA, it is difficult to separate the vanadyl porphyrins from the vanadyl non-porphyrins. This is especially true of the asphaltenes. Despite several studies which indicated that the asphaltenes were richer in vanadyl non-porphyrins than the maltenes,[27] the relative abundance of vanadyl porphyrins versus vanadyl non-porphyrins is greatest in the asphaltenes. The precipitation of asphaltenes, therefore, accomplishes some of the desired separation by precipitating vanadyl porphyrins with the asphaltenes. Maltenes are left deficient in vanadyl porphyrins and should be excellent sources of vanadyl non-porphyrins. This was confirmed for the maltene of Prudhoe Bay, the least porphyrinic petroleum studied, by extracting it with the chromatographic extraction procedure.[108] The extract was found to contain vanadium and its UV-VIS spectra had a single peak at 270 nm. The absence of even a weak Soret band established that this fraction contains only vanadyl non-porphyrins. When analyzed with reverse phase HPLC–GFAA, the vanadyl compounds eluted in the final peak, at the same retention time as the unknown vanadyl non-porphyrins present in the solvent selective extracts of the asphaltenes of all four petroleums. The isolation of a vanadyl non-porphyrin fraction represents a significant step toward the identification of the first vanadyl non-porphyrin. Off line analytical techniques like electron spin resonance spectroscopy and mass spectrometry are now needed to provide more structural information about these compounds.

The isolation of a vanadyl non-porphyrin fraction from a crude petroleum illustrates the inadequacy of catalyst poisoning models which are based solely on vanadyl porphyrins. Rankel has noted that the differences between vanadium deposition studies of model petroleums composed of vanadyl porphyrins and the actual petroleums is not only a matter of the rates of vanadium deposition on the catalyst, but also of the differing stability of vanadyl non-porphyrins and vanadyl porphyrins in the presence of hydrogen and hydrogen sulfide.[14] Silbernagel has also found that the chemical form of a metal compound has an important effect on catalyst poisoning.[15]

4 D. Nickel Compounds in Asphaltenes

Because nickel is generally present in crude petroleums at lower concentrations than vanadium, relatively little research has been directed at identifying nickel compounds. In experiments in which column chromatography has been used to remove vanadyl porphyrins from the petroleum matrix, a light pink band eluting near the bright red vanadyl porphyrin band has generally been assumed to contain nickel porphyrins, but little work has actually been done to identify the constituents of this band.[108] Several factors have contributed to the assumption that the non-vanadyl peak extracted from petroleums is predominantly made up of nickel porphyrins. Vanadyl and nickel porphyrins are both known to exist in petroleums and shale oil deposits and the lack of paramagnetism in the electronic structure of nickel makes it impossible to use ESR to establish the true chelating environment of nickel compounds in petroleums.[64,117]

The results of the reverse phase HPLC-GFAA analysis show that very little of the nickel in the asphaltene extracts is actually present as nickel porphyrins. For the Boscan, Cerro Negro, and Prudhoe Bay extracts, over 90 percent of the nickel present is clearly non-porphyrin. Wilmington is the exception, with a third of the nickel eluting at a retention time consistent with nickel porphyrins. This difference is probably the result of conditions during the aging of the Wilmington petroleum. As chlorophylls are transformed into porphyrins during the diagenesis of the petroleum, pheophytinization (magnesium removal) is among the first transformations to occur.[116] Studies have found that demetallation of chlorophylls has begun even in recently buried feedstocks.[1] The vacant coordination site is subsequently occupied by nickel and vanadyl ions.[20] Nickel, because of its smaller size and greater symmetry, is believed to coordinate more readily with the porphyrin ring than does vanadyl ion.[59,63] During maturation of the petroleum, the nickel is slowly replaced by the vanadyl ion, which forms more stable metalloporphyrin complexes.[114] Wilmington is not the youngest or the most shallowly buried petroleum of the four studied, but it does have the least severe combination of these two factors. The high concentration of nickel porphyrins is, therefore, a consequence of less severe aging compared to the other three petroleums.

In addition to the relatively small amount of research with nickel compounds in crude petroleums, there is another factor which has prevented previous discovery of the high level of nickel non-porphyrins. The nickel compounds found in the reverse phase HPLC-GFAA analysis are highly polar. Most current research with porphyrins in crude petroleums uses column chromatography on silica or alumina packing to isolate the porphyrins. The highly polar nickel compounds are probably irreversibly bound to the column packing. The use of a solvent selective extraction procedure is not common in recent research, but it prevents the loss of nickel non-porphyrins through interaction with a fractionating column. The use of reverse phase HPLC also prevented the loss of polar compounds which might be irreversibly retained on a normal phase column.

The discovery of large amounts of nickel non-porphyrins has a direct bearing on current research studying refinery catalyst poisoning by trace metals. Since it has generally been accepted that a substantial fraction of the nickel present in heavy crude petroleums is coordinated in porphyrin rings, studies of the poisoning mechanisms have used nickel porphyrins to model the naturally occurring nickel compounds.[18,19,118] Since most of the suspected non-porphyrin chelating systems are less stable with respect to demetallation than porphyrins, these studies will fail to adequately model the quantity or deposition pattern of nickel on catalysts.[63] Before modeling studies of nickel poisoning can be improved, it will be necessary to isolate and identify the nickel non-porphyrins.

The identification of nickel non-porphyrins should also provide important bio-geochemical information. Knowing the structures of these compounds should give insight into their sources in the petroleum feedstock.

4 E. Comparison of Solvent Selective Extraction and Chromatographic Separation Techniques

Two extraction techniques were used in this study. The solvent selective extraction described by Baker was used for almost all of the experimental work,[70] but a chromatographic separation developed by Rogers was also used in some of the final experiments.[108] The individual characteristics of these extraction techniques have already been discussed in the presentation of results, but it is useful to compare these two methods of removing polar compounds from asphaltenes.

The principal disadvantage of the solvent selective extraction is the need to dissolve the asphaltenes in a non-polar solvent which is immiscible in the the pyridine-water extraction solvent. Non-polar solvents are ineffective in breaking up the large micelles in precipitated asphaltenes and many vanadyl compounds which are entrapped during the precipitation are inaccessible to extraction. On the positive side for an investigation directed at characterizing low molecular weight vanadyl compounds, solvent selective extraction produces an extract with a narrow range of molecular weights, centered about 400 daltons.

In the column chromatography technique, the asphaltenes are dissolved in methylene chloride prior to absorbing them on alumina. Methylene chloride is a much more effective solvent for breaking up asphaltene micelles than xylene. This can be seen by comparing the 50 Å - 100 Å - 1000 Å SEC-HPLC-GFAA analysis of the whole petroleums by Komlenic with the similar analysis of the asphaltenes and maltenes reported in this study.[24] Methylene chloride was used as the injection solvent for all of these analyses and a mass balance of the vanadium present in each molecular weight region shows that the vanadium in the maltenes and asphaltenes of a given region sum to the vanadium present in the same region of the whole crude petroleum. Clearly, methylene chloride is sufficiently polar to overcome intermicellular forces in the crude petroleum as well as in the precipitated asphaltenes. The use of methylene chloride in the chromatographic extraction, therefore results in a more complete extraction of vanadyl compounds from the asphaltene micelles than is possible with solvent selective extraction. Another result of the more complete breakdown of the micelles is an extract with a fairly uniform molecular weight distribution extending from less than 400 daltons to over 2000 daltons. The solvent selective extract has almost no vanadyl compounds at molecular weights over 900 daltons. Besides the broader molecular weight distribution in the extract, the major drawback of the column chromatography extraction is the loss of some of the asphaltenic material which is irreversibly bound to the column packing. This effect does, however, provide some additional information about the asphaltenes. The electronic spectrum of a solvent selective extract rises continually below 450 nm. In the chromatographic extract, the loss of some of the large, background absorbing compounds reduces the absorbance below 300 nm sufficiently to reveal a shoulder or weak peak at about 270 nm. Analysis of the extracted Prudhoe Bay maltene has associated this peak with vanadyl nonporphyrins.

4 F. Applications of HPLC-GFAA Fingerprints of Asphaltenes

1. Identification of Oil Spills

Petroleums have typically been characterized and identified by infrared spectroscopy and gas chromatography; analytical techniques which are greatly affected by the light components in the petroleum.[98] In the case of an oil spill, several days at sea are sufficient for evaporative losses and the dissolution of light compounds in water to have altered the infrared spectra and gas chromatograph beyond positive identification.[99] Trace metal analysis provides a more durable basis for analysis, since a majority of the trace metals in petroleums are associated with the heavy components in the petroleums. Since asphaltenes are virtually unaffected by the light components in petroleums, trace metal analysis of precipitated asphaltenes should provide the most durable means of identifying the weathered petroleums in oil spills. SEC-HPLC-GFAA analysis of the four asphaltenes used in this study demonstrated that each asphaltene was a unique trace-metal fingerprint.

2. Characterization of Heavy Crude Petroleums

In addition to providing unique fingerprints of the asphaltenes and their polar extracts, HPLC-GFAA analysis can provide some basic structural information about petroleums. SEC-HPLC-GFAA profiles of the asphaltenes are strongly influenced by the asphaltene content of the petroleum; uniform vanadium distribution between 8000 and 400 daltons indicates that the petroleum is highly asphaltenic. Normal and reverse phase HPLC-GFAA analysis of the polar extracts of asphaltenes indicates the relative abundance of vanadyl porphyrins and non-porphyrins in the petroleum. Reverse phase chromatography with GFAA nickel analysis is a means of determining the abundance of nickel porphyrins in the petroleum.

Although general traits have been observed which relate the HPLC-GFAA chromatograms to vanadyl porphyrin, vanadyl non-porphyrin, and asphaltene contents in the crude petroleum, good empirical correlations between the spectra and composition of asphaltenes cannot really be based on the results of only four petroleums. Analysis of a larger variety of petroleums will be necessary to improve the general correlations observed in this study.

CHAPTER 5

Conclusions

The major findings of this study are:

(1) Micelles in the precipitated asphaltenes are larger than the asphaltene micelles which exist in the heavy crude petroleum and it is more difficult to extract vanadyl compounds from precipitated asphaltenes than from heavy crude petroleums.

(2) Vanadium is present in asphaltenes in molecules or complexes with molecular weights between 8000 and 100 daltons. Very little vanadium is complexed in compounds with molecular weights of over 10,000 daltons.

(3) The molecular weight distribution of vanadyl compounds in the asphaltenes is affected by the asphaltene content of the heavy crude petroleum. Higher asphaltene content petroleums have more uniform vanadium distributions in their asphaltenes.

(4) SEC column retention times of vanadyl porphyrins in the petroleum or asphaltene matrix are greater than the retention times of model vanadyl porphyrins.

(5) Heavy crude petroleums with high asphaltene contents have higher concentrations of vanadyl porphyrins.

(6) Low molecular weight vanadyl compounds can be extracted from all

molecular weight regions in the asphaltenes.

(7) Solvent selective extraction produces an extract with a smaller molecular weight distribution than that resulting from chromatographic extraction techniques and is not as effective in removing molecules from the interior of micelles.

(8) Vanadyl compounds present in the maltenes can be entrapped in the asphaltenes during precipitation.

(9) Precipitated asphaltenes have higher vanadyl porphyrin contents than the whole heavy crude petroleums.

(10) Nickel compounds are primarily present in heavy crude petroleums as nickel non-porphyrins.

(11) Although asphaltenes appear to become saturated with nickel at concentrations in excess of 400 ppm, no such upper limit of vanadium concentration was observed in the asphaltenes.

(12) The higher vanadyl porphyrin concentration of the asphaltenes makes it difficult to extract pure vanadyl non-porphyrins from that fraction. Therefore, despite the large amount of vanadyl non-porphyrins which are undoubtedly present in the asphaltenes, experimental limitations make the maltenes a better sources of vanadyl non-porphyrins.

(13) Fingerprints obtained from SEC-HPLC-GFAA analysis of asphaltenes or normal and reverse phase HPLC-GFAA analysis of polar extracts can

provide information on the composition of the asphaltenes.

CHAPTER 6

Recommendations for Future Work

1) Since vanadyl porphyrins are concentrated in the asphaltenes during precipitation, the successful identification of vanadyl non-porphyrins in the polar extracts of asphaltenes is hindered by the intense electronic absorbance and ESR spectra of the vanadyl porphyrins. The maltene fraction of the petroleums should be a better source of vanadyl non-porphyrins. With a large percentage of the vanadyl porphyrins leaving the petroleum during the precipitation, maltenes of low porphyrin petroleums like Wilmington and Prudhoe Bay should only contain non-porphyrin vanadium. Future attempts to identify vanadyl non-porphyrins should be directed at the maltenes of these two petroleums.

2) More model compounds must be synthesized to aid in the characterization of effluent peaks in the HPLC-GFAA analysis. Two classes that deserve special attention are oxygen and sulfur ligand systems and hydrogenated metallo-porphyrin compounds.

3) It may be possible to improve the chromatographic separation of asphaltene extracts on the HPLC-GFAA system by re-chromatographing peaks collected from normal phase columns on reverse phase columns and vice versa. In the presentation of the results of the amino column HPLC-GFAA analysis it was noted that vanadium was separated into two peaks; one containing vanadyl porphyrins which corresponded

to the model vanadyl porphyrin compounds and the other containing a combination of unidentified vanadyl porphyrin and non-porphyrin compounds. The reverse phase column eluted the unidentified vanadyl porphyrins in one peak and eluted the identified vanadyl porphyrins and unidentified vanadyl non-porphyrins in a combined peak. By collecting the effluent peaks of one column it should be possible to take advantage of the differing separation behavior on the other column to produce higher purity vanadyl non-porphyrin samples.

4) In order to identify the vanadyl non-porphyrins it will be necessary to use off-line techniques such as electron spin resonance spectroscopy and mass spectrometry.

CHAPTER 7

Experimental

7 A. Reagents

HPLC grade chloroform, dimethylformamide, (DMF), hexane, methanol, methylene chloride (CH_2Cl_2), and pentane were purchased from Burdick and Jackson (Muskegon, MI). Solvents were filtered and degassed before use in the HPLC system. Extractions of polar compounds from the petroleums were performed with reagent grade pyridine and xylenes (Mallinckrodt; Paris, KY) and quartz-distilled water. The activated alumina, 40 - 60 mesh, was obtained from Matheson, Coleman, and Bell (Los Angeles, CA).

The Cerro Negro, Wilmington, and Prudhoe Bay heavy crude petroleums were obtained from Dr. Dexter Sutterfield at the Bartlesville Energy Technology Center, while Boscan heavy crude petroleum was provided by Dr. J. Lubkowitz of INTEVEP Caracas, Venezuela.

Polystyrene standards for steric exclusion (SEC) column calibrations were obtained from Altex (Berkeley, CA). Vanadyl tetra (3-methyl phenyl) porphyrin (VOT3MePP), tetra (4-carbomethoxy) phenylporphyrin (T4CMPP), vanadyl etioporphyrin I (VOEtio), and nickel etioporphyrin I (NiEtio) were purchased from Midcentury (Posen, IL). Vanadyl tetraphenylporphyrin (VOTPP), was purchased from Strem Chemicals (Newburyport, MA). Other vanadyl and nickel compounds were prepared from the free ligands: vanadyl salen (VOSalen) and vanadyl benzosalen (VOBenzosalen) according to the procedure of Beilig et. al.;[119] VOBZEN according to the procedure of Dilli and Patsalides;[120] vanadyl dibenzotetraazacyclotetradecane (VOTADA) according to the procedure of Burchill and Honeybourne;[121] and nickel dibenzotetraazacyclotetradecane (NiTADA) according to the procedures of Dilli and Patsalides and Sakata.[120,122]

Standards for calibrating the various HPLC columns were prepared by dissolving the compounds in HPLC grade solvents compatible with the solvent gradients used in the analysis. Fresh standards were prepared for each column, since the solutions tended to decompose slightly even when stored away from light.

7 B. Apparatus

A schematic of the HPLC-GFAA system is shown in Figure 26. For the steric exclusion chromatography work, an Altex 420 gradient programmer was used with two Altex 100 A solvent delivery pumps. The samples were injected into a 250 μL sample loop and then separated on a series combination of 50 and 100 Å pore size μspherogel columns (Altex, 8.0 mm I.D. x 300 mm length) or of 50, 100, and 1000 Å pore size μspherogel columns. After passing through the columns the sample was monitored at 408 nm for petroleum samples, or 254 nm for polystyrene standards, using an Altex 155-90 variable wavelength detector. The sample then flowed through a length of teflon tubing to a Perkin-Elmer AS-1 autosampler, which had been equipped with a flow through teflon receiving cup to allow continuous sampling of the HPLC effluent stream. At 40 second intervals the autosampler

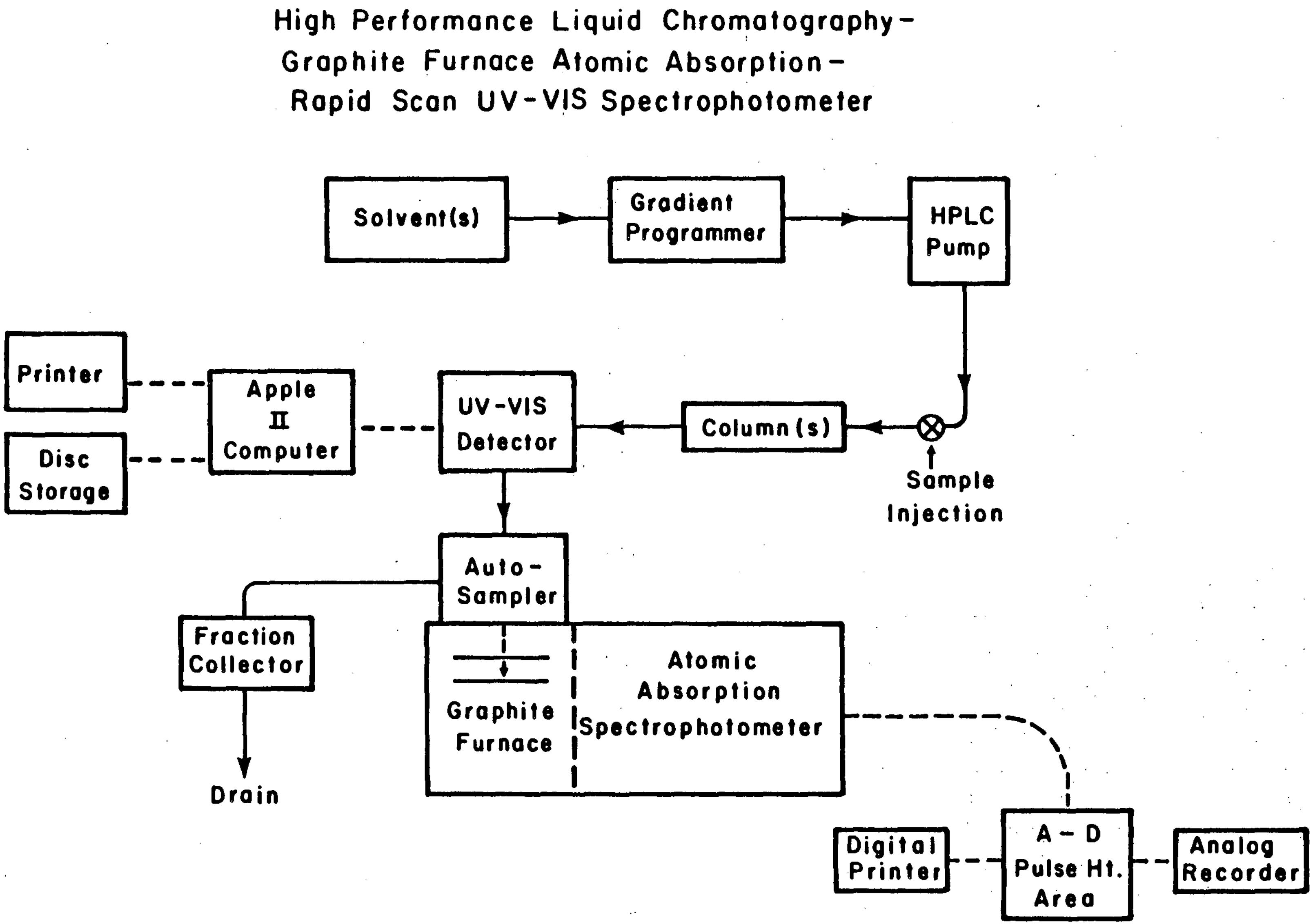

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Figure 26. Schematic of the Automatically Coupled HPLC-GFAA System.

injected 20 μL of sample into a Perkin-Elmer 4000 GFAA. Instrument parameters for the GFAA were: band width 0.2 nm; drytime 15 seconds; dry temperature 90°C; atomization time 7 seconds; and atomization temperature 2700°C. The detector wavelength was set at 318.4 nm for vanadium and 232.0 nm for nickel. Argon was used as the cooling gas.

Visible spectra from the UV-VIS detector and the histogramic output from the GFAA were recorded on a Kipp and Zonen dual-pen strip chart recorder. In addition, the GFAA data was recorded on an Altex C-RIA digital recorder.

For the normal phase and reverse phase work the gradient programmer was a Beckman-Altex 421 controller and the pumps were Beckman-Altex 112 solvent delivery modules. The normal phase column was an Altex Ultrasil-NH_2 with 10 micron particles (4.6 mm I.D. x 25 cm length) equipped with a 40 mm long guard column of the same packing. The reverse phase column was an Altex Ultrasphere-ODS with 5 micron particles (4.6 mm I.D. x 25 cm length) equipped with a 40 mm long C_8 guard column. The single wavelength detector was replaced with a Beckman-Altex 165 rapid scanning UV-VIS detector. This instrument is capable of taking complete UV-VIS spectra (300 to 600 nm) of eluting peaks. Data from the rapid scanning detector was stored on disk via an Apple II Plus interfaced with the detector. The GFAA system was similar to that used in the SEC analysis.

In addition to the HPLC-GFAA system, a Cary 219 UV-VIS spectrophotometer was interfaced with the Apple II Plus for off line analysis of standards, extracts, and fractions separated in the HPLC runs.

7 C. Procedures

7 C. 1. Precipitation of Asphaltenes

Asphaltenes were separated from heavy crude petroleums by precipitation from n-pentane (See Fig. 27). In the early SEC work, a ten to one volume ratio of solvent to petroleum was used. Later this work was repeated using asphaltenes precipitated with a forty to one volume ratio for the sake of consistency with the literature. All other analyses were performed using the forty to one ratio for the precipitation of asphaltenes. After adding the pentane to the crude petroleum, the solution was gently agitated at about 300 motions per minute for 24 hours. The asphaltenes were then removed by filtering over a 0.45 micron nylon 66 millipore filter, followed by washing with pentane until the wash solvent was colorless. The solid asphaltenes were then dried under vacuum and weighed to determine the percentage of asphaltenes in the petroleum. After drying, the asphaltenes were a coarse, brown to black powder. The pentane solubles, or maltenes, and the wash solvent were also collected and dried under vacuum. After removal of the pentane, the maltenes resembled the original whole petroleum. Typically about 95 percent of the starting material was recovered as asphaltenes and maltenes.

7 C. 2. Preparation of Polar Extracts

Polar extracts were prepared using an extraction procedure described by Baker for the removal of metal porphyrins from crude

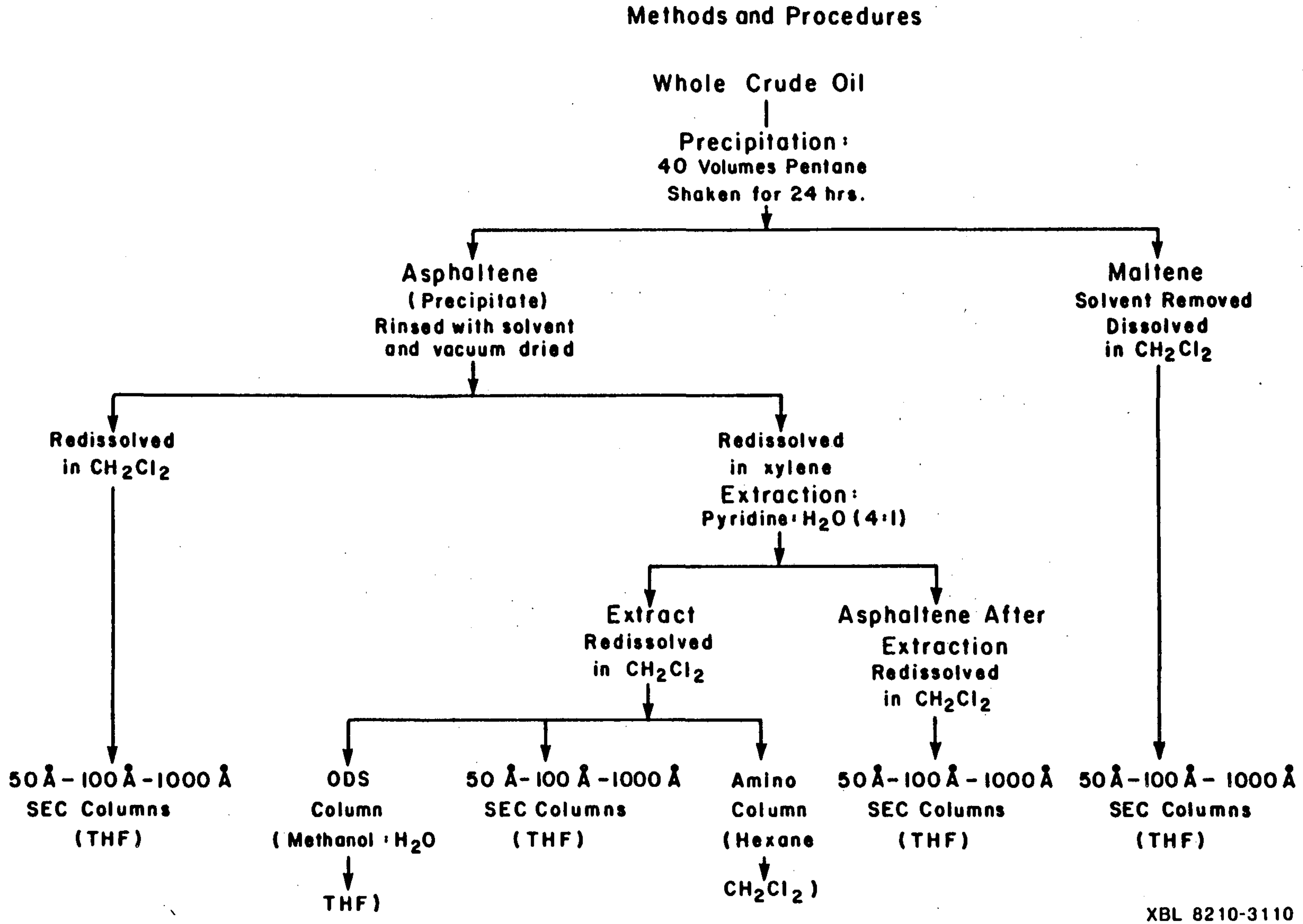

Figure 27, Methods and Procedures Outline.

petroleums (See Fig. 27).[70] About 0.5 g of asphaltene was dissolved in about 40 ml of xylene. This solution was then extracted in a separatory funnel with a solution of pyridine and water (4:1 v/v); the pyridine being capable of coordinating to vanadyl compounds with the lone pair electrons on the nitrogen. After the phases were separated and the colored pyridine phase removed, the extraction was repeated using another 50 ml of the pyridine-water solution and as much additional xylene as was necessary to keep the asphaltenes in solution. Usually the extraction was repeated five times. The polar solutions, which varied in color from wine red to yellow, depending on the particular asphaltene being extracted, were combined and then filtered over a 0.45 micron nylon 66 millipore filter to remove entrained asphaltenes. After filtering, the solvent was removed from the extract under vacuum and the remaining solid material was weighed and stored away from light.

For the final work with the Prudhoe Bay maltenes, a chromatographic extraction developed by Spencer and Rogers was used.[108] The maltene studied (3 grams) was dissolved in 30 ml of methylene chloride and then added to 30 ml of activated alumina. The alumina-maltene mixture was dried under nitrogen and packed in a 12mm by 30cm glass column, which had already been packed with 3 cm of activated alumina. The vanadyl "porphyrin rich" fraction was eluted with 200 ml of DMF and the vanadyl non-porphyrin fraction was eluted with an equal volume of chloroform. Some material was irreversibly adsorbed on the alumina. After collection, the solvents were removed from the fractions by vacuum distillation. This extraction procedure removed the visibly absorbing compounds much more efficiently than the pyridine extractions. An attempt to further extract the chromatographically derived vanadyl non-porphyrin compounds with pyridine-water showed that there were no further extractables present in that fraction.

7 C. 3. Metal Analysis

Vanadium and nickel concentrations in the heavy crude petroleums, maltenes, and asphaltenes were determined with x-ray fluorescence analysis by Robert Giauque of Lawrence Berkeley Laboratory. The vanadium concentration in the extracted asphaltenes was measured by GFAA single cup analysis. Asphaltene and extracted asphaltene samples were diluted in methylene chloride to give solutions of approximately 1 ppm vanadium and each sample was analyzed with the GFAA. The peak heights recorded by the digitizer were averaged over approximately 10 samplings to find the mean peak height of the sample. These mean peak heights were considered to be directly proportional to the vanadium content of the sample. The ppm vanadium in the extracted asphaltene was calculated by multiplying the ratio of the mean peak heights of the extracted asphaltene and the asphaltene by the ppm vanadium in the asphaltene as detected by x-ray fluorescence spectroscopy. The accuracy of this technique was tested with asphaltene samples of known concentrations and the experimental error was found to be less than five percent.

7 C. 4. High Performance Liquid Chromatography

Asphaltenes, maltenes, extracts, and extracted asphaltenes were all analyzed using one or both of the two SEC column configurations. Samples were dissolved in methylene chloride at concentrations sufficient to give good metal response on the GFAA. The system was run isocraticly, using a flow rate of 0.5 ml/min. For the normal phase runs the extracts were dissolved in pyridine. The solvent gradient used was a ramp from 100 % hexane to 10 % methylene chloride over the first 3 minutes, to 25 % methylene chloride at 10 minutes, and finally to 100 % methylene chloride at 20 minutes. All solvent gradient changes were made over 3 minutes. For the reverse phase work pyridine was also used as the injection solvent. The solvent gradient used was a ramp from 100 % methanol-quartz distilled water (3:1 v/v) at injection, to 30 % THF after 1 minute, to 70 % THF at 22 minutes, and finally to 100 % THF at 25 minutes. All solvent gradient changes were made over 2 minutes. Normal and reverse phase analysis were both run at a solvent flow rate of 2 ml/min.

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