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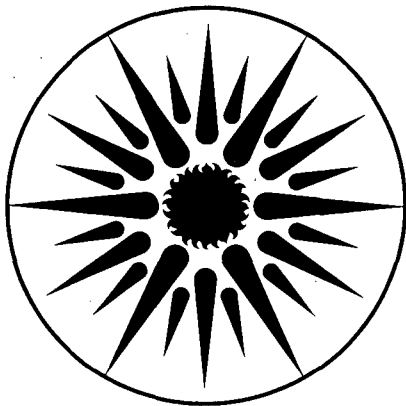
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**Metallo-Organic Geochemistry: Characterization and Comparison of Vanadyl and Nickel Compounds in Heavy Crude Petroleums and Asphaltenes by Reverse Phase and Size Exclusion HPLC-GFAA Analysis**

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**Abstract**

Vanadyl and nickel non-porphyrin rich fractions have been characterized in pyridine extracts of four heavy crude petroleums using reverse phase high performance liquid chromatography in combination with element-selective graphite furnace atomic absorption detection (RP-HPLC-GFAA). Based on rapid-scan uv-vis data that indicates a lack of Soret absorbance associated with separated vanadyl and nickel containing fractions, we have categorized the highly polar nickel compounds as non-porphyrin in Boscan, Cerro Negro, Wilmington and Prudhoe Bay heavy crude petroleums. The presence of lower polarity vanadyl non-porphyrin compounds, occurring primarily in Wilmington and Prudhoe Bay petroleums, have also been confirmed. Similar analysis of the n-pentane (40:1) precipitated asphaltenes of the four heavy crude petroleums has been accomplished. The vanadium histogrammic profiles, obtained using reverse phase HPLC-GFAA analysis for compounds extracted from the asphaltenes, were similar when compared to the above mentioned extracts from the heavy crude petroleums. In addition, size exclusion chromatography (SEC-HPLC-GFAA) was performed on the asphaltenes, maltenes, and asphaltene extracts of the above-mentioned heavy crude petroleums and these results were also compared to those found for the respective petroleums.

## Brief

The reverse-phase HPLC-GFAA analysis of pyridine extracts of Boscan, Cerro Negro, Wilmington and Prudhoe Bay heavy crude petroleums and their n-pentane precipitated asphaltenes provided information on the vanadyl and nickel non-porphyrin compounds present. In addition, size exclusion HPLC-GFAA analysis was performed on the asphaltenes, maltenes and pyridine extracts of the asphaltenes and the resulting vanadium and nickel compound content was also compared to those found for their respective heavy crude petroleums.

## Introduction

The presence of vanadyl and nickel non-porphyrin compounds in heavy crude petroleums has been the center of speculation for many years (1,2). Despite numerous studies directed towards the identification of vanadyl and nickel non-porphyrin compounds (3), as of yet, not a single molecular structure has been confirmed. The majority of these studies have been limited in effectiveness due primarily to the lack of a suitable metal detector. Since metallo-non-porphyrin compounds, unlike metallo-porphyrin compounds, do not have readily discernible uv-vis spectra, then the identification of these metallo-organic compounds requires novel separation and detection techniques.

The use of on-line, element-selective graphite furnace atomic absorption detection for high performance liquid chromatography systems (HPLC-GFAA) has recently proven highly effective with regard to the molecular characterization of trace-metal compounds in complex matrices such as oil shale, shale oil, oil shale retort waters and heavy crude petroleums (4-8).

In a previous paper (7), we described the use of an automatically coupled HPLC-GFAA combination to categorize, according to molecular weight and polarity, the vanadyl non-porphyrin and porphyrin compounds in heavy crude petroleums. This technique enabled us to profile or fingerprint as well as estimate the distribution of vanadyl compounds present in four petroleums and their extracts. Additionally, the molecular characterization of the vanadyl compounds in the petroleums was attempted by comparing the GFAA histogrammic retention behavior and rapid-scan uv-vis absorbance spectra of HPLC separated petroleum samples to that of known model vanadyl porphyrin and non-porphyrin standards.

In the present study, we report reverse-phase HPLC-GFAA analysis of the vanadyl and nickel compounds extracted, using pyridine as solvent, from four heavy crude petroleums; namely, Boscan, Cerro Negro, Wilmington and Prudhoe Bay. Although reverse phase separations of demetallated ligands have been dis-

cussed (9), to our knowledge, similar separation techniques with element-selective detection of metal-containing petroleum samples, have not been previously published. We also present, using size exclusion chromatography (SEC-HPLC-GFAA), vanadium profiles for the n-pentane precipitated asphaltenes, maltenes and asphaltene extracts of the four petroleums. Asphaltenes, the hydrocarbon insoluble fraction of petroleum, are an extremely abundant source of trace-metal compounds (10). However, asphaltenes also contain the majority of the high molecular weight, aromatic compounds and heteroatoms present in petroleums (11), which has made the structural characterization of vanadyl non-porphyrin compounds present in asphaltenes difficult to accomplish. We also compared the rapid scan uv-vis profiles, using reverse-phase separations, of the pyridine extracts of the four petroleums and their asphaltenes.

The molecular characterization of vanadyl and nickel non-porphyrin compounds, which are thought to account for approximately 50-80 percent of the metals present (1), is needed in order to design innovative trace-metal removal methods (12). In addition, knowledge of the molecular environment associated with both vanadium and nickel in heavy crude petroleums and asphaltenes is also required to provide an improved understanding of the biogeochemical mechanisms responsible for the inclusion of these metals during the diagenesis and maturation process of petroleum formation (1).

## **Experimental Section**

### **Materials**

Complete histories and descriptions of the four heavy crude petroleums have previously been reported (7).

HPLC grade methanol, tetrahydrofuran (THF), methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) and n-pentane were purchased from Burdick and Jackson (Muskegon, MI) and were filtered and degassed before use in the HPLC system. Extractions of polar compounds from the petroleums and their asphaltenes were performed with

reagent grade pyridine and xylene (Mallinckrodt; Paris, KY) and quartz-distilled water (also used in the HPLC system).

Synthesis of the majority of the standards shown in Chart 1 have been reported in reference (7). VOBZEN (13) and NiTMTADA (14) have been synthesized from the ligands. VO(acac)<sub>2</sub> was purchased from Alfa Products (Danvers, MA). The polystyrene standards were purchased from Altex (Berkeley, CA).

Reference solutions for the standards were made by dissolving the compounds in methylene chloride or methanol, for the SEC and ODS runs respectively, filtering using 0.45  $\mu$ m millipore filters (Bedford, MA) (used for all filtering in this study), and kept in the dark until needed. Ultraviolet-visible spectra of the standards and extracts were recorded using a Cary 219 (Varian, Palo Alto, CA) uv-vis spectrophotometer interfaced with an Apple II plus computer for data acquisition and storage.

#### **HPLC-GFAA Instrumentation**

The SEC separations used a previously described HPLC system (7). The ODS separations used an HPLC system (Schematic shown in Figure 1) consisting of two solvent delivery pumps (Beckman 112), a gradient programmer (Beckman 421) and a rapid-scan uv-vis detector (Beckman 165). Spectra from the rapid-scanning detector were stored on five inch floppy discs via an interfaced Apple II plus computer and printed on an Apple silent printer. A dual-pen strip chart (Kipp and Zonen) was used to record the single or dual wavelength uv-vis absorbances. GFAA instrument and coupling procedures have been previously reported (4). The GFAA histogrammic data was recorded using both the strip chart recorder and a digital integrator (Altex C-RIA).

HPLC separations were accomplished using a series combination of 50/100/1000 $\overset{\circ}{\text{A}}$   $\mu$ -spherogel columns (Altex, 8.0 mm I.D.\* 300 mm length) with swelled divinylbenzene as the packing for the SEC runs, or an octadecylsilane C-18, (ODS) column (Altex, 4.6 mm I.D.\* 250 mm length) with a self-packed guard



column (Waters, 3.2 mm I.D.\* 40 mm length) for the reverse phase separations.

### **Experimental Procedures**

**Asphaltene Preparation (11).** Asphaltenes were separated from the crude oils by precipitation with a 40 to 1 volume ratio of n-pentane. After adding n-pentane to the crude oil, the solution was gently agitated at 300 motions per minute for 24 hours. The asphaltenes were removed by filtering, washed with n-pentane until the wash solvent was colorless, and dried under vacuum. The coarse brown/black powder was then weighted to determine the percentage of precipitated asphaltenes in the petroleum. The pentane soluble maltenes and wash solvent were also collected and dried under vacuum. Approximately 95% by weight of the starting petroleum was recovered as asphaltenes and maltenes.

**Asphaltene Extraction (15).** Asphaltene extractions were accomplished by dissolving approximately 0.5 g of asphaltene in 40 ml of p-xylene and by extracting five consecutive times with a 50 ml solution of pyridine and water (4:1 v/v). In order to prevent reprecipitation of the asphaltenes, additional p-xylene (less than 100 ml) was added during extraction. The five extracts were combined and filtered to remove entrained asphaltene particles. The solvent was then removed under vacuum and the remaining material stored away from light.

**Chromatography Procedures.** The reverse-phase analyses were accomplished using an ODS column with the petroleum and asphaltene extracts dissolved in a pyridine/water (4:1) solution. The ODS separations were obtained with a solvent gradient consisting of an initial linear ramp from 100% methanol/water (3:1 v/v) to 30% THF from 1-3 minutes, a second linear ramp from 30% to 70% THF from 22-24 minutes, and a final linear ramp to 100% THF from 25-27 minutes, at a constant flow rate of 1.5 ml/min. Recalibration of the column after each run was accomplished by ramping to 100% methanol-water (3:1 v/v) over 3 minutes, and holding until a minimum of 10 column volumes of solvent had eluted.

Asphaltenes, maltenes, and the extracts were dissolved in methylene chloride and analyzed using the 50/100/1000Å SEC columns with a flow rate of 0.5 ml/min. The molecular weight calibration curve data has been previously published (7).

**Trace Metal Quantification.** Vanadium and nickel concentrations in the maltenes and asphaltenes were determined using x-ray fluorescence analysis performed by Robert Giaque of Lawrence Berkeley Laboratory.

**Method of Cup Analysis.** The vanadium concentration in the extracted asphaltenes was measured by GFAA single cup analysis (4,7,16). 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.

#### **Method of Quantification of Vanadium Histograms Obtained by SEC-HPLC-GFAA Analyses (7)**

The vanadium weight percentages appearing in Table 4 were obtained from the relevant vanadium histograms by measuring the area of each molecular weight category using the SEC calibration curve and the method of summing peak heights digitized with an integrator. The weight percentages were obtained by dividing these numbers by the total area of the pertinent vanadium histogram. The vanadium concentrations (ppm) in each molecular weight category were then calculated by multiplying the weight percentages by the total vana-

dium concentration found by either x-ray fluorescence or atomic absorption spectroscopy.

## Results and Discussion

### Reverse Phase HPLC-GFAA Analysis of the Heavy Crude Petroleum Extracts

Since our previously obtained HPLC-GFAA profiles, with SEC separated crude petroleum extracts, had indicated the presence of low molecular weight vanadyl compounds, <400 daltons, (7), we were interested in obtaining the reverse-phase HPLC-GFAA vanadium and nickel histogrammic distributions of the four petroleum pyridine extracts using various vanadyl and nickel standards (Chart 1) to verify retention times of classes of these compounds. Table 1 indicates the percentage of vanadium and nickel in each eluted peak via reverse-phase HPLC-GFAA analysis.

Figure 2 shows the HPLC-GFAA data, obtained using an octadecylsilane (ODS) column, for the standards and for the Boscan and Cerro Negro crude petroleum extracts. Each chromatogram consists of a conventional uv-vis absorbance trace (wavelength monitored as designated) and corresponding nickel (232 nm) and vanadium (318.4 nm) histogrammic profiles.

The model vanadium and nickel non-porphyrin standards (monitored at 320 nm) elute before the porphyrin standards (monitored at 408 nm) indicating the highly polar nature of these compounds. The nickel compounds extracted from the crude petroleum appear to be highly polar and definitely have non-porphyrin ligands. In comparison, the extracted vanadium compounds elute at moderate to low polarities as determined by the retention behavior of the various standards, and thus contain predominantly vanadyl porphyrins in the second band (~17.5 min), while the third band contains both metallo-porphyrin and non-porphyrin compounds.

Figure 3 shows similar ODS-HPLC-GFAA data for Wilmington and Prudhoe Bay petroleum extracts. These extracts also show a majority of the extracted

nickel compounds associated with the highly polar vanadyl standards of comparable structure; however, Wilmington extract also contains a sizable fraction of low polarity (possibly porphyrin derivatives) nickel compounds. Both extracts also show a majority of the vanadyl compounds at moderate to low polarity.

Although reverse phase separations of petroleum samples have been studied (3), we do not believe that the occurrence of these highly polar nickel compounds have been verified before. Figures 2 and 3 also indicate that reverse-phase separations of the pyridine extracts give improved resolution over that afforded using normal phase HPLC analysis (17,18). In fact these separations rival that reported for demetallated complexes (9) and question the usefulness of current demetallation procedures for the analysis of petroleum extracts.

**Rapid Scan Data for Heavy Crude Petroleum Extracts.** The use of a rapid scan uv-vis detector has increased our ability to differentiate between metallo-porphyrin and non-porphyrin compounds. Unfortunately, we were unable to scan the highly polar, ODS separated nickel compound (Figures 2 and 3) peaks due to the sharpness; a maximum scan rate of 20 nm/sec, in effect, sets a limit on the peak-width which can be scanned. The highly polar nickel fractions were, therefore, collected and uv-vis spectra were obtained off-line using a Cary 219 spectrophotometer. Maximum absorbances (above background) for these collected fractions were observed between 280 and 300 nm. The lack of any observable Soret absorbance associated with these fractions strongly suggests a predominance of nickel non-porphyrin compounds.

The fact that these nickel non-porphyrin fractions had not been previously found is not surprising. The majority of previous research involving the identification of metallo-porphyrins in crude petroleums used column chromatography with silica or alumina packing to isolate the porphyrins (3). The highly polar nickel compounds shown in Figures 2 and 3 would be irreversibly bound to the column packing during normal-phase elution (2). The use of solvent selective extraction is not common in recent research; but importantly, prevents the

loss of nickel non-porphyrins through interaction with a fractionating column (16).

Rapid scan data obtained for the ODS separated moderate and low polarity vanadium containing bands for Boscan and Cerro Negro extracts are shown in Figure 4. Rapid scan data for Boscan extract at 16 minutes shows a "relatively clean" vanadyl porphyrin spectra. However, the other three spectra show varying uv background absorbances at less than 400 nm, indicating the presence of distinctly non-porphyrinic species in these separated fractions. Similar rapid scan data obtained for Wilmington and Prudhoe Bay extracts are shown in Figure 5. The lack of any discernible Soret absorbance associated with these fractions strongly suggests the presence of vanadyl non-porphyrin compounds as major vanadium constituents in Prudhoe Bay and Wilmington crude petroleum extracts.

A majority of the extracted nickel compounds exist as highly polar non-porphyrin compounds, in contrast to vanadium which is associated primarily with moderate and low polarity compounds, and this fact has important processing implications with regard to catalyst deactivation studies (19). The majority of current catalyst deactivation modeling studies exclusively use vanadyl and nickel porphyrins (20). However, since metallo-porphyrins are known to account for only a limited portion of the two metals, the relevancy of these studies must be reexamined, especially with regard to the reactivity of acid unstable metallo- non-porphyrin ligands (1).

#### **Analysis of the n-Pentane Precipitated Asphaltenes**

Vanadium and nickel compound analyses of the heavy crude petroleum asphaltenes are presented in Table 2. Approximately, 49 - 77 percent of the vanadium compounds are precipitated with the asphaltenes, even though this fraction constitutes only 4 - 23 percent by weight of the petroleum. Similarly, a large fraction of the nickel compounds are also precipitated with the asphaltenes at concentrations constituting 39 percent to 78 percent of the nickel com-

pounds present in the petroleum sample.

The results from the extraction of the precipitated asphaltenes are presented in Table 3 and reveal that only 5 - 18 percent by weight of the vanadium compounds present in the asphaltenes have been extracted. This behavior is very different from that observed for the extraction of the crude petroleum (7), from which upwards of 50 percent of the vanadium compounds were removed. Previously, we had observed that a considerable percentage of vanadyl non-porphyrin compounds could be removed from the high molecular weight asphaltenic component of heavy crude petroleum using solvent selective extraction techniques (15). A significantly lower percentage of the vanadyl compounds is extracted from the n-pentane precipitated asphaltenes and this, as we will show, has importance with regard to the use of asphaltenes as starting materials for the identification of vanadyl porphyrin and non-porphyrin compounds in heavy petroleum.

#### **SEC-HPLC-GFAA Analyses of Asphaltenes**

Clearly a better understanding of the types and distribution of vanadyl and nickel compounds present in n-pentane precipitated asphaltenes is needed. We decided to analyze the n-pentane precipitated asphaltenes, the maltenes, and their pyridine extracts of each petroleum using the SEC-HPLC-GFAA technique.

Separations obtained for Boscan asphaltene, maltene, and polar extract using a 50/100/1000Å SEC column combination are shown in Figure 6. The visible absorbance was monitored at 408 nm corresponding to the Soret band of vanadyl porphyrins identified in crude oils (21) and the GFAA detector was set at 318.4 nm, specific for vanadium.

Molecular weight calibration (see experimental) for the low molecular weight regions was accomplished using the standards from Chart 1. In comparison to the more traditional use of polystyrenes (3), the use of vanadyl compounds as calibration standards should increase the accuracy of molecular weight determinations for vanadyl compounds present in heavy crude

petroleum. Polystyrene standards have, however, been used to calibrate the high molecular weights (>900 daltons), since no vanadyl compounds at these molecular weights were available.

Due to possible interactions, which may occur between the complex petroleum matrix and the SEC column (22), the designated molecular weight categories are not regarded as absolute, but are more useful for comparison purposes. Boscan asphaltene (Figure 6) registers continuous visible absorbances and vanadium profiles over the entire molecular weight region. The maximum absorbance for both visible and vanadium detection occurs in the lowest molecular weight range, corresponding to less than 400 daltons, with very little vanadium present at molecular weights greater than 10,000 daltons. As expected from the structural differences which exist between the maltene and asphaltene fractions (23), the maltene vanadium absorbances are skewed toward lower average molecular weights than the corresponding asphaltenes. Most notable is the deficiency of vanadium compounds present above 2,000 daltons as compared to the asphaltene profiles. The pyridine extract of Boscan asphaltene has a vanadium maximum corresponding to 380 daltons, which is too low to represent metallo-porphyrins with alkyl substituents. Thus, the majority of the metal compounds present in the extracts must be considered non-porphyrinic, based on the accuracy of the SEC calibration data for the standards in Chart 1.

Similar data for Prudhoe Bay asphaltene, maltene and polar extract, is shown in Figure 7. A significantly greater percentage of vanadium associated with Prudhoe Bay asphaltene is present above 2000 daltons as compared to Boscan asphaltene. However, Prudhoe Bay maltene, similarly to Boscan maltene, shows a trend towards lower average molecular weights and also registers a predominance of extractable low molecular weight (less than 400 daltons) vanadyl compounds. Data from Figures 6 and 7 as well as data for Cerro Negro and Wilmington crude petroleums (not reproduced here but similar to data shown in

Figures 6 and 7, respectively) are summarized in Table 4.

Table 4 lists the quantitative distribution of vanadyl compounds by molecular weight using a calibration curve previously reported by Fish and Komlenic (7) and categorizes the vanadyl compounds as greater than 9,000 daltons; 9,000-2,000 daltons; 2,000-900 daltons; 900-400 daltons; and less than 400 daltons. Values shown for the percent vanadium in Table 4 were determined by summing the peak heights automatically digitized using an integrator (see experimental). For each molecular weight category, the heights of the vanadium histograms were summed and then divided by the total vanadium peak height for the entire analysis.

Table 4 reveals that Wilmington and Prudhoe Bay asphaltenes have greater percentages of vanadium in the very high molecular weight region (>2,000 daltons) than do the asphaltenes of the two Venezuelan petroleums. Further, a comparison of the vanadium percentages associated with the four petroleums and maltenes shows that Boscan, Cerro Negro, and Prudhoe Bay maltenes contain proportionately less vanadium below 400 daltons than do the heavy crude petroleums. Wilmington maltene, in contrast, has proportionately less vanadium above 2000 daltons and has more vanadium in the metallo-porphyrinic molecular weight region (400-900 daltons) than the petroleum itself.

Interestingly, vanadyl compounds extracted from the asphaltenes of all four petroleums are present predominantly at the low molecular weights (less than 400 daltons), indicating vanadyl non-porphyrin compounds. Previously, we had found that low molecular weight vanadyl compounds (molecular weight < 900 daltons) could be extracted from high molecular weight fractions of each of the heavy crude petroleums (7). Table 4 confirms that these low molecular weight vanadyl complexes can also be extracted from the n-pentane precipitated asphaltenes of each petroleum as well. Each asphaltene shows a majority of the extractable vanadyl compounds having molecular weights less than 400 daltons; however, as Table 3 indicates, only 5 - 18 percent by weight of the vana-



dium was extractable, as compared to 50 - 87 percent by weight for heavy crude petroleums (7). Although vanadyl compounds of similar molecular weight are extracted from both petroleum and asphaltene sources, significant environmental differences must exist between vanadyl complexes present in the heavy crude petroleums and those found in the n-pentane precipitated asphaltenes.

#### **Reverse Phase HPLC-GFAA Analysis of the Asphaltene Extracts**

Figure 8 compares the ODS-HPLC-GFAA data for the standards and the Boscan asphaltene extract monitored at both 320 and 408 nm. Similar to Boscan whole crude petroleum extract, the majority of the nickel compounds elute with the highly polar standards, while the vanadyl compounds are primarily associated with the low to moderate polarity compounds. ODS-HPLC-GFAA analyses of Cerro Negro, Wilmington, and Prudhoe Bay asphaltene extracts show similar metal profiles to those obtained for the petroleum extracts and are, therefore, not reproduced here. Wilmington asphaltene extract, however, does show a fraction of non-polar nickel compounds, indicating that some nickel porphyrin compounds have been extracted. Table 5 provides percent vanadium and nickel distributions in the asphaltene extracts using reverse-phase HPLC-GFAA analysis. Rapid scan data for the moderate and low polarity bands for the Wilmington asphaltene and Prudhoe Bay asphaltene extracts are shown in Figure 9. In comparison to the rapid scan uv-vis spectra of the heavy crude petroleum extracts (Figures 4 and 5), the four asphaltene extracts generally show greater Soret absorbances, indicating increased concentrations of vanadyl porphyrin compounds in the asphaltene extract.

#### **Comparison of the Petroleum and Asphaltene Results**

The extraction of the precipitated asphaltenes removed only 5 percent to 18 percent of the vanadium present (Table 3), in comparison to the removal of 50 percent to 87 percent of the vanadium present in the heavy crude petroleum (7). The proposed existence of larger micelles in the precipitated asphaltenes could account for this difference in behavior, since asphaltenes are by definition

a solubility class and the choice of the precipitating solvent is known to have a noticeable effect on the mass and aromaticity of precipitated asphaltenes (16,24). Further, vapor pressure osmometry 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 (25).

An equilibrium apparently exists between the interactions of asphaltene molecules with each other and with the solvent. In the heavy crude petroleums, 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. Non-polar solvents such as p-xylene 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.

However, in order to make comparisons among the petroleum components, a solvent must be used that will prevent associations during the procedure used to separate the components. Thus, methylene chloride is a much more effective solvent for breaking up asphaltene micelles than xylene. This can be seen by comparing the 50/100/1000 $\text{\AA}$  SEC-HPLC-GFAA analysis of the heavy crude petroleums (7) with a similar analysis of the asphaltenes and maltenes reported in this study (Table 4). 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 heavy crude petroleum. Clearly, methylene chloride is sufficiently polar to overcome any intermicellar interaction, which may have occurred during the precipitation of the asphaltenes.

SEC-HPLC-GFAA analysis of the extracted asphaltenes shows an increase in the amount of vanadium present at molecular weights over 2000 daltons (Figure

10). This suggests that a rearrangement occurs and involves the reentrainment of low molecular weight vanadyl compounds into the high molecular weight asphaltenic fraction of the petroleum. The extracts have almost no vanadyl compounds at molecular weights over 900 daltons, which is consistent with extracts of the heavy crude petroleums. Rapid scan analysis of the precipitated asphaltene pyridine extracts by reverse phase HPLC-GFAA has shown the concentration of vanadyl porphyrins to be higher in the asphaltene extracts than in the extracts of whole crude petroleums. Despite studies which indicate that asphaltenes have higher concentrations of vanadyl non-porphyrins than do maltenes (26), the increased concentration of extractable vanadyl porphyrins in precipitated asphaltenes makes it more difficult to detect and isolate vanadyl non-porphyrin present in asphaltenes. Our work indicates that the precipitation of asphaltenes accomplishes a desired separation by selectively precipitating vanadyl porphyrins, thus, making the maltene component an excellent source of vanadyl non-porphyrin compounds (16) and this is an area we will pursue.

Because nickel is generally present in heavy crude petroleums at lower concentrations than vanadium, relatively little research has been directed at identifying nickel compounds in these complex matrices (3). In experiments in which column chromatography has been used to remove vanadyl porphyrins from the petroleum matrix, a light pink band eluting before 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.

The results of the reverse phase HPLC-GFAA analysis show that very little of the nickel compounds in the petroleum asphaltene extracts is actually present as nickel porphyrins (Figure 8). The Boscan, Cerro Negro, and Prudhoe Bay extracts clearly indicate that over 90 percent of the nickel compounds present are non-porphyrin. Wilmington is the exception, with one third of the nickel compounds eluting at a retention time consistent with nickel porphyrins. The high concentration of nickel porphyrins present in Wilmington petroleum and

asphaltene extracts could be a consequence of less severe aging compared to the other three petroleums. Nickel, because of its smaller size and greater symmetry, coordinates more readily with the porphyrin ring than does the vanadyl ion and nickel porphyrins could conceivably be formed in the early diagenesis of the petroleum (27). However, during maturation of the petroleum, the nickel is possibly replaced by vanadyl ion, which forms a more stable metallo-porphyrin complex (28). Wilmington is not the youngest or the least deeply buried petroleum of the four studied, but it does have the least severe combination of these two factors.

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 (20). Thus, most of the suspected non-porphyrin chelating systems are less stable with respect to demetallation than porphyrins, and these studies have failed to adequately model the deposition of nickel compounds on catalysts. Before modelling studies of nickel compound poisoning can be improved, it will be necessary to isolate and identify these nickel non-porphyrin compounds.

The identification of vanadyl and nickel non-porphyrins should also provide important biogeochemical information. Knowing the structures of these compounds should give insight into their sources in the petroleum feedstock. 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. In future work, it will be necessary to have a greater array of model metallo-non-porphyrin compounds. Among the compounds that should be considered are the hydrogenated vanadyl porphyrins. In the reducing environment of the crude petroleum reservoir (29), it is possible that the por-

pyrrole rings are hydrogenated, and there has been a report on the identification of non-metallated, hydrogenated porphyrin ligands in oil shale (30). If the pyrrole rings are sufficiently hydrogenated, the metallo-porphyrin will be susceptible to demetallation and decomposition (31). This may represent a mechanism by which porphyrins have been demetallated in older petroleum deposits.

### **Conclusions**

The relevant findings in this paper are that the preponderance of both vanadium and nickel compounds in the extracts of both the heavy crude petroleums and their asphaltenes have non-porphyrin ligands associated with the metal.

The more important question is the definitive identification of these metallo-non-porphyrin compounds. In this regard, we have recently preparatively separated fractions obtained using the reverse-phase HPLC technique and have submitted these for high resolution mass spectrometry and electron spin resonance spectroscopy analysis. We will report details of this analysis in the near future (32).

Obviously, the identification of vanadyl and nickel non-porphyrin compounds as biomarkers will have a profound effect on future exploration studies in addition to catalyst deactivation phenomena, where metallo-porphyrins have prevailed as models. Furthermore, future innovative removal methods will also be affected by the knowledge of the metallo-non-porphyrin structures. Our work continues in this exciting area of metallo-organic geochemistry.

### **Acknowledgements**

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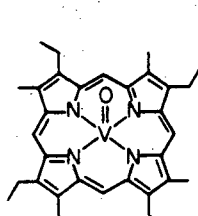
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**Credit**

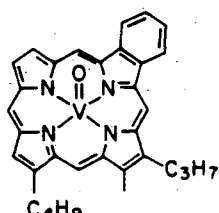
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### Chart Caption

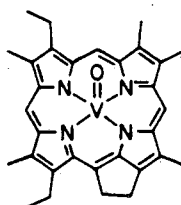
- (1) Model vanadyl and nickel porphyrin and non-porphyrin compounds used for the calibration curve and for comparisons with unknown components in the heavy crude petroleum and their asphaltenes.



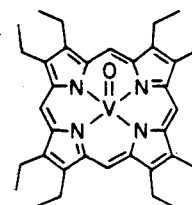
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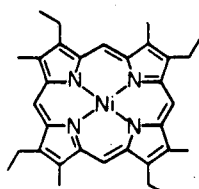
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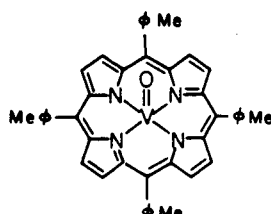
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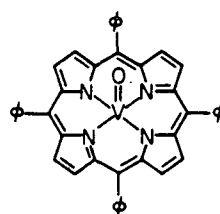
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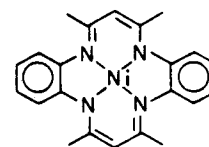
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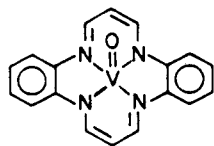
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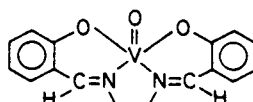
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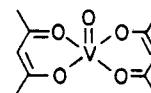
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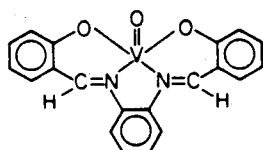
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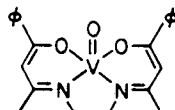
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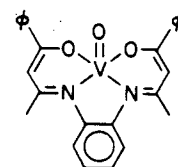
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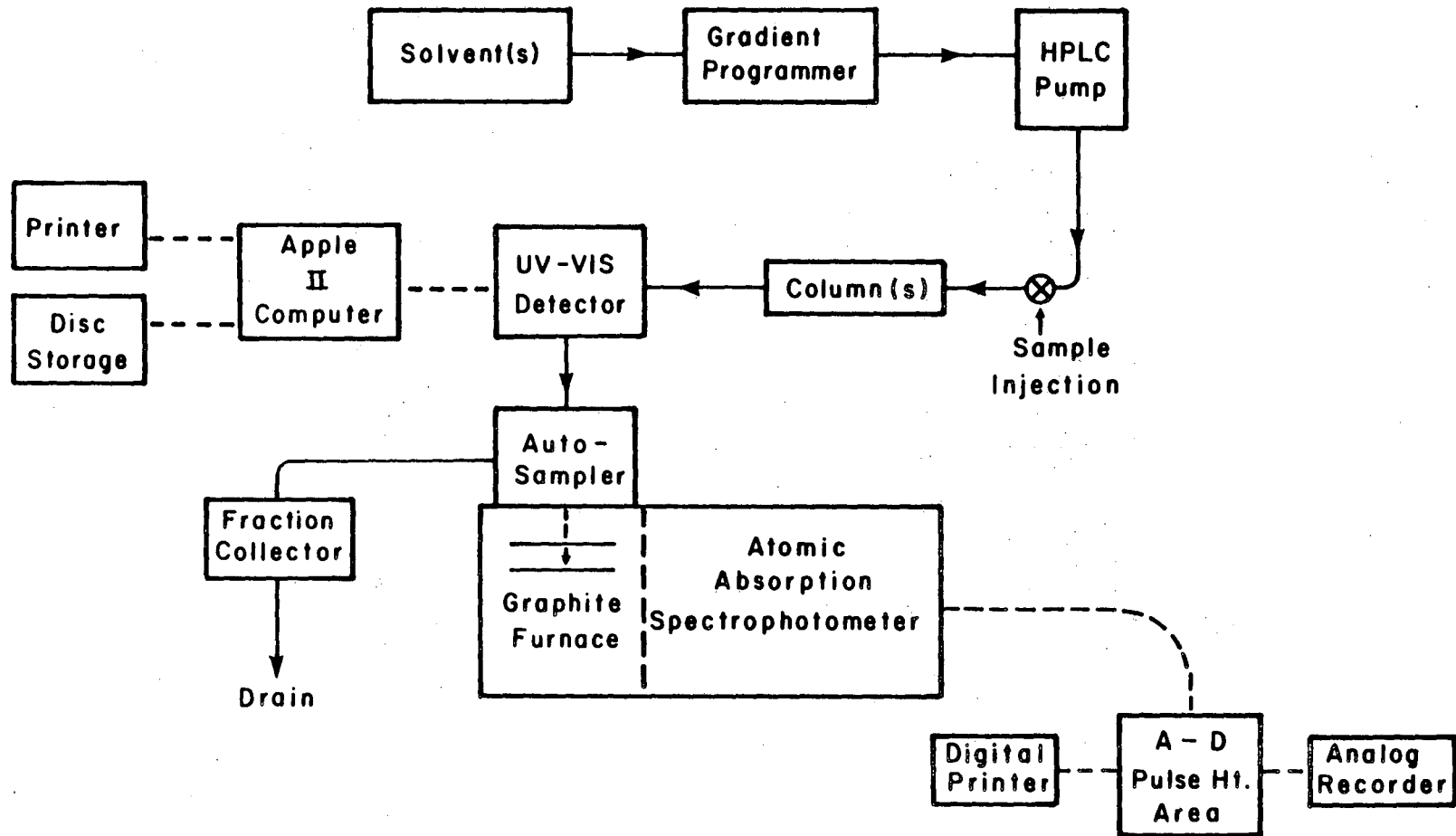
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## Figure Captions

- (1) Schematic of the automatically coupled HPLC-GFAA system incorporating rapid-scan UV-Vis detection.
- (2) ODS-HPLC-GFAA profiles for a) standards, b) Boscan petroleum extract, and c) Cerro Negro petroleum extract. AA (vanadium) at 318.4 nm and AA (nickel) at 232.0 nm.
- (3) ODS-HPLC-GFAA profiles for a) standards, b) Wilmington petroleum extract, and c) Prudhoe Bay petroleum extract. AA (vanadium) at 318.4 nm and AA (nickel) at 232.0 nm.
- (4) Rapid scan UV-Vis spectra for the reverse-phase separated Boscan and Cerro Negro petroleum extracts.
- (5) Rapid scan UV-Vis spectra for the reverse phase separated Wilmington and Prudhoe Bay petroleum extracts.
- (6) 50/100/1000<sup>o</sup>Å SEC-HPLC-GFAA profiles for a) Boscan asphaltene, b) Boscan maltene and c) Boscan asphaltene extract. Molecular weight calibration data from reference 7.
- (7) 50/100/1000<sup>o</sup>Å SEC-HPLC-GFAA profiles for a) Prudhoe Bay asphaltene, b) Prudhoe Bay maltene and c) Prudhoe Bay asphaltene extract. Molecular weight calibration data from reference 7.
- (8) ODS-HPLC-GFAA profiles for a) standards, b) Boscan asphaltene extract monitored for vanadium and c) nickel.
- (9) Rapid scan UV-Vis spectra for the reverse-phase separated Wilmington and Prudhoe Bay asphaltene extracts.
- (10) 50/100/1000<sup>o</sup>Å SEC-HPLC-GFAA profiles for a) Boscan, b) Cerro Negro, c) Prudhoe Bay, and d) Wilmington asphaltenes after pyridine extraction.

Figure 1

# High Performance Liquid Chromatography - Graphite Furnace Atomic Absorption - Rapid Scan UV-VIS Spectrophotometer



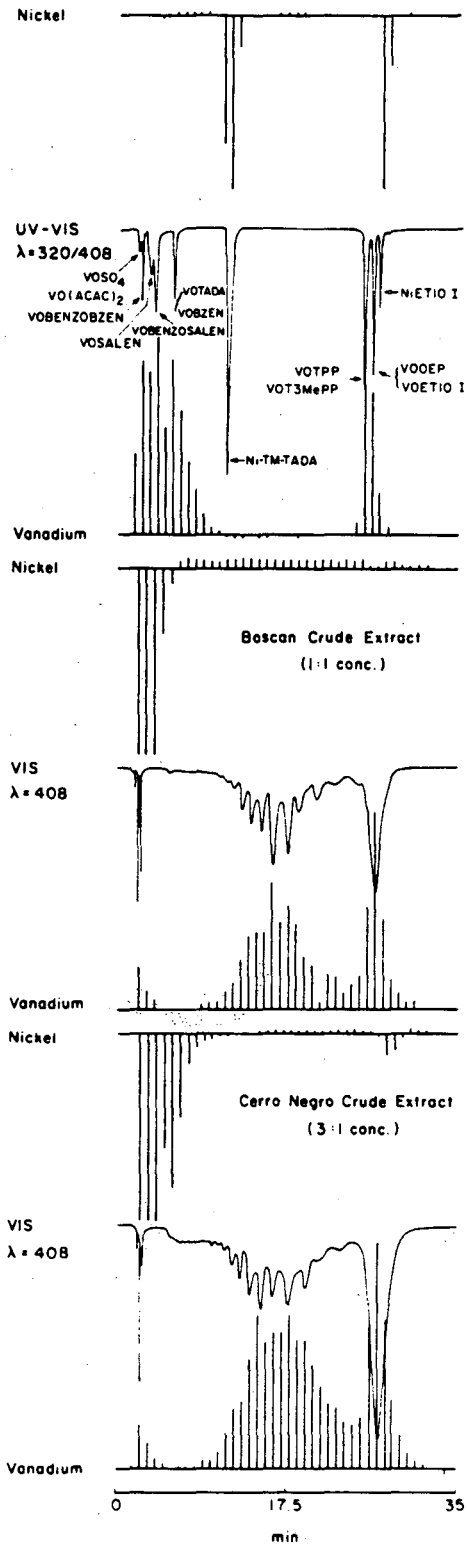
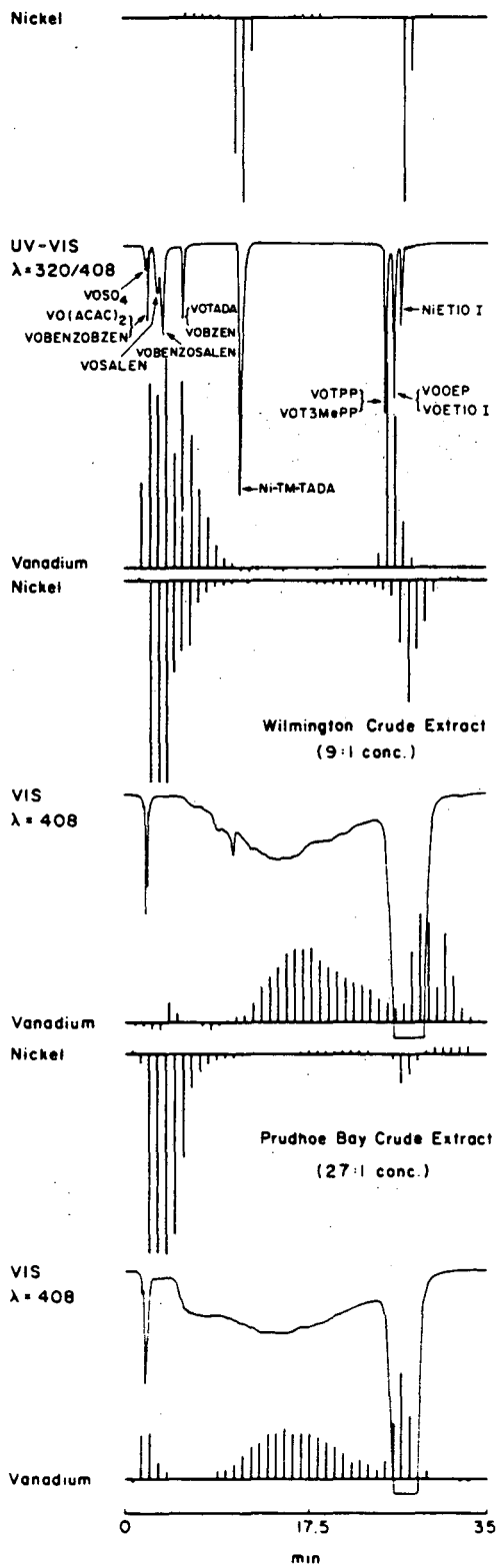


Figure 2

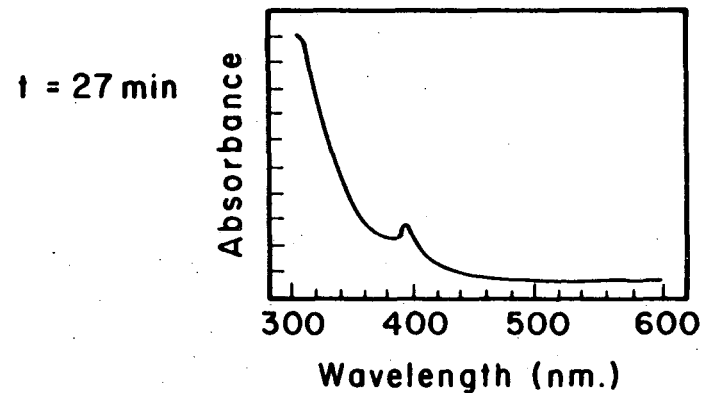
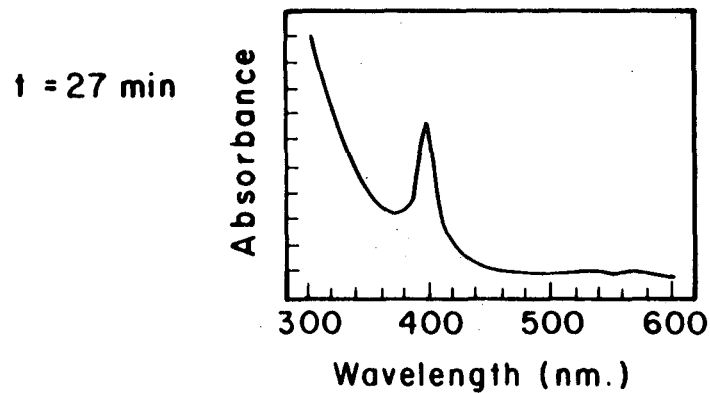
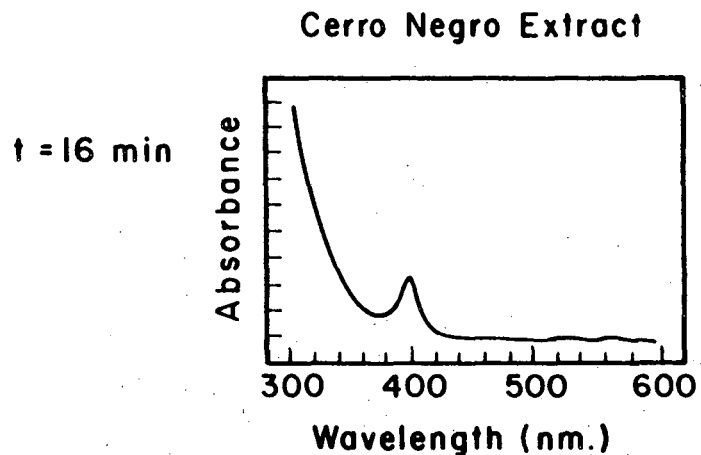
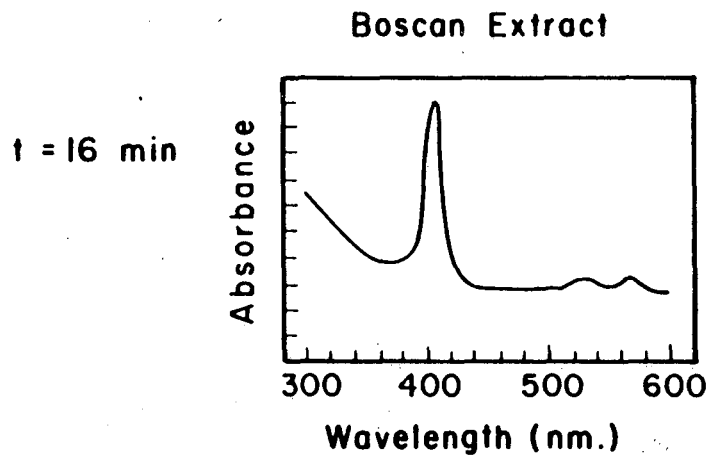


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Figure 3

# HPLC - Rapid Scan UV-VIS Analysis

Figure 4

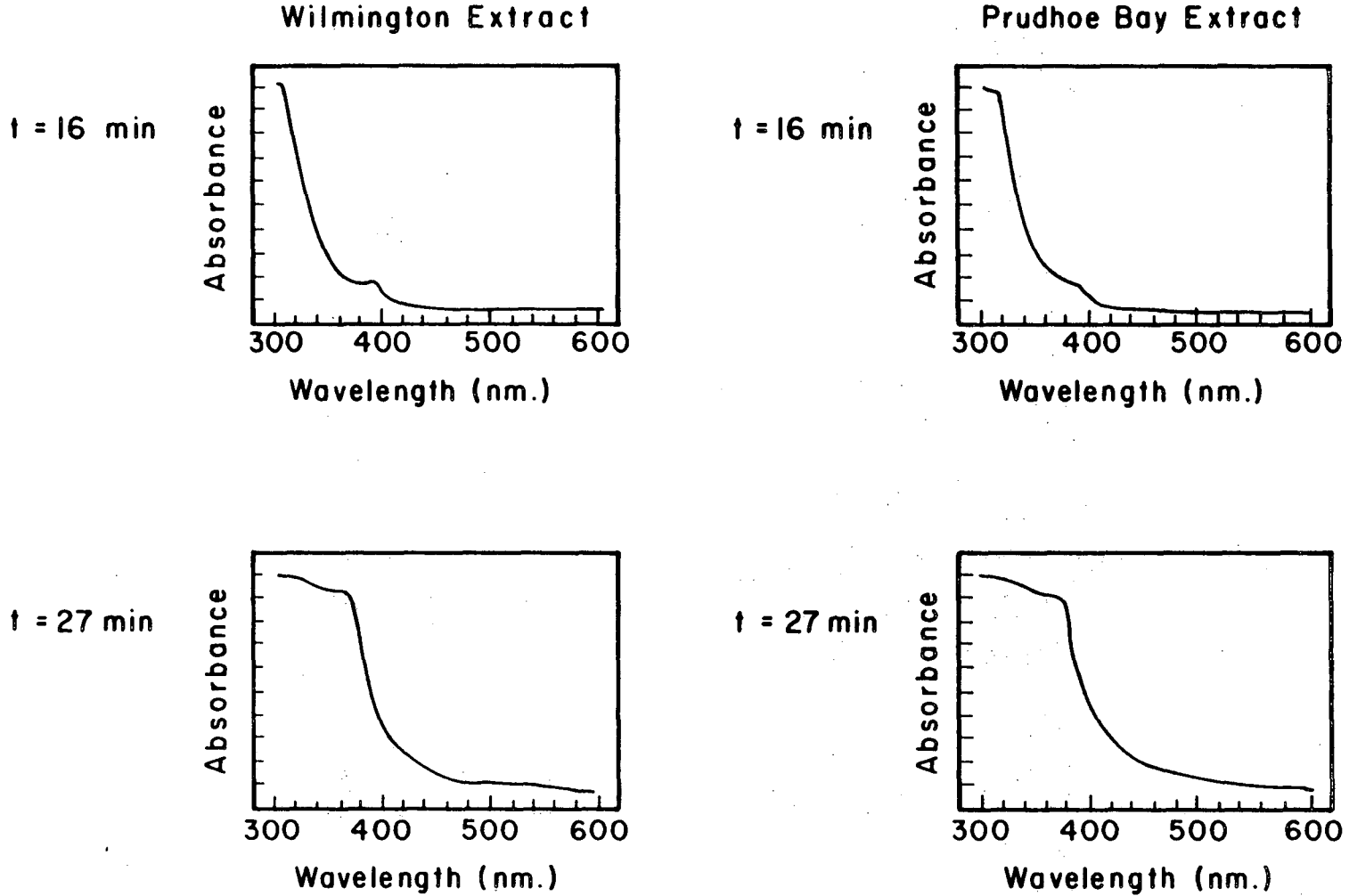


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# HPLC - Rapid Scan UV-VIS Analysis

Figure 5



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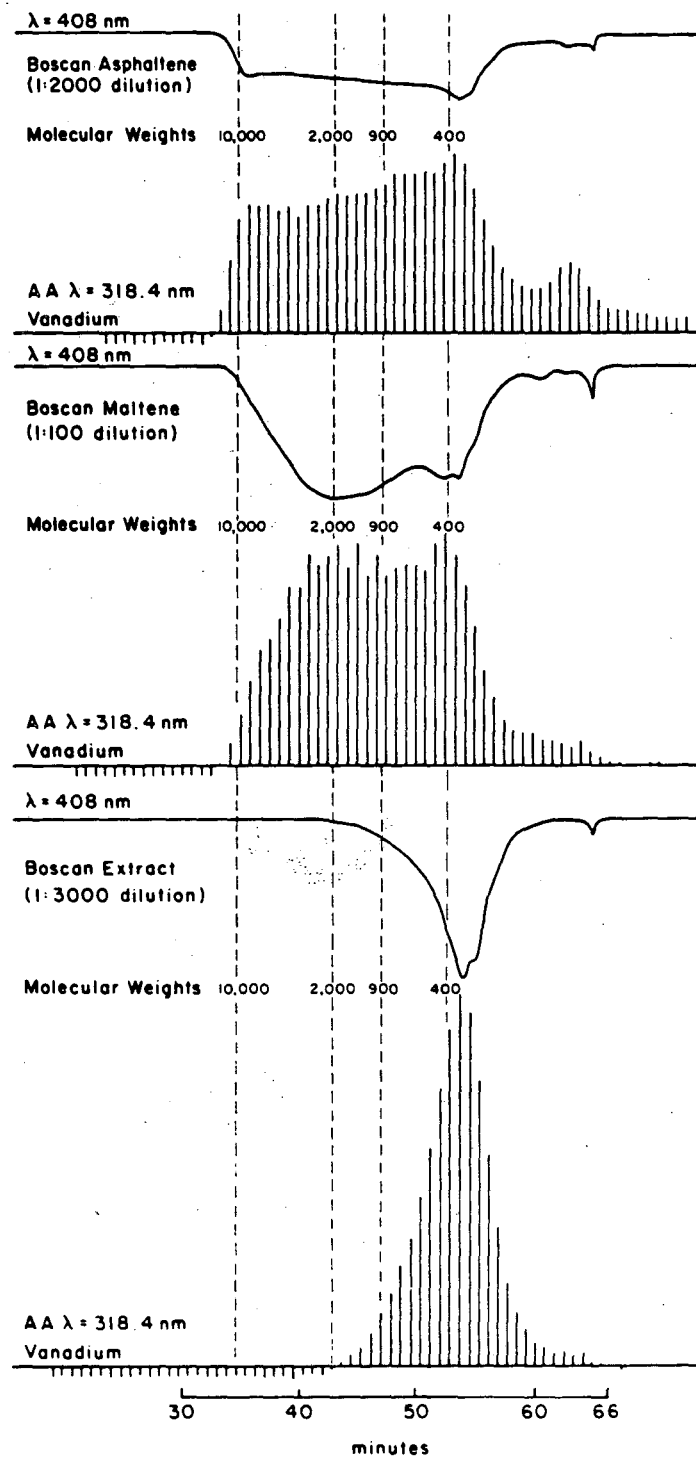


Figure 6

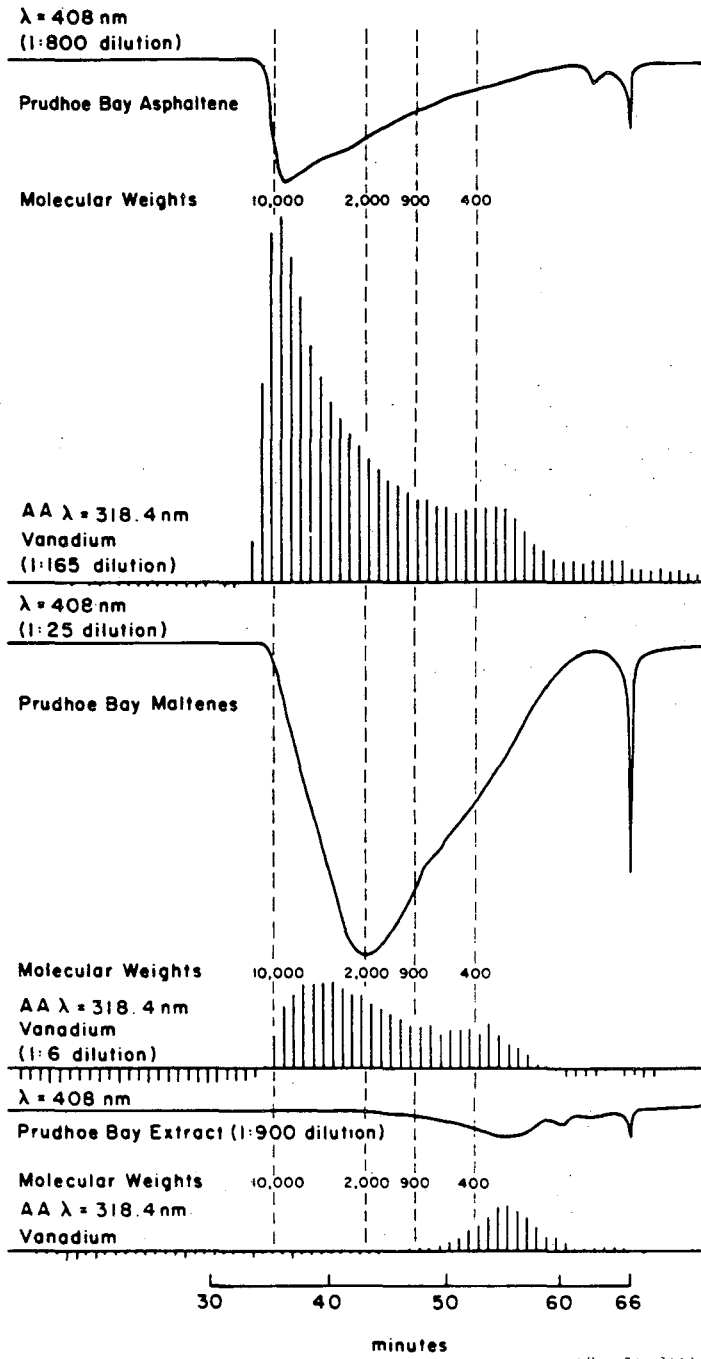


Figure 7

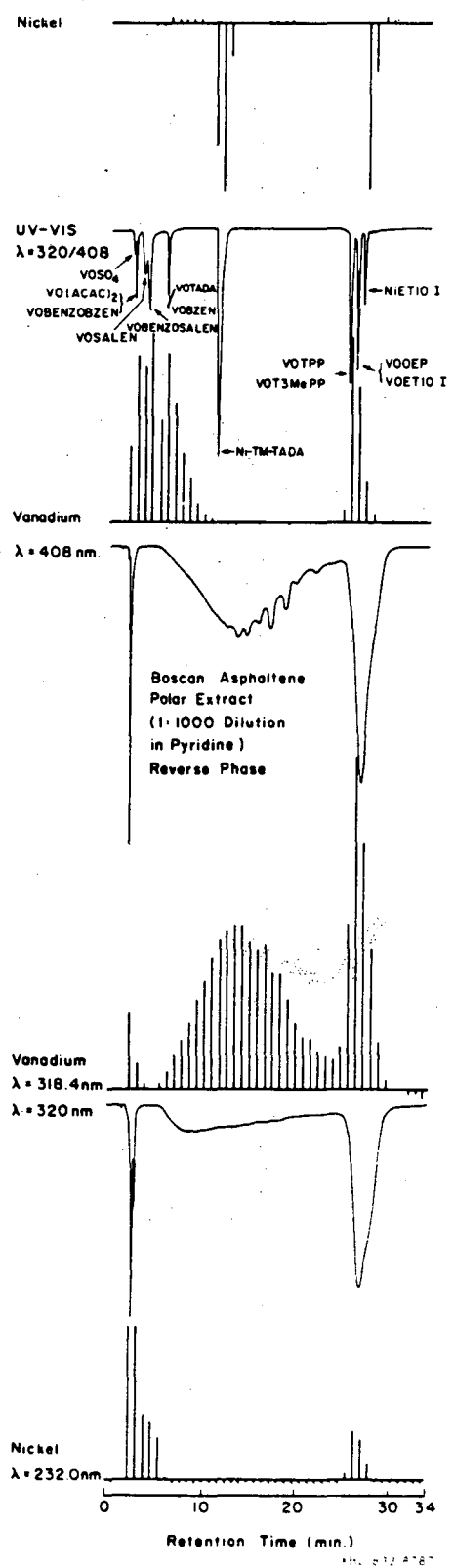
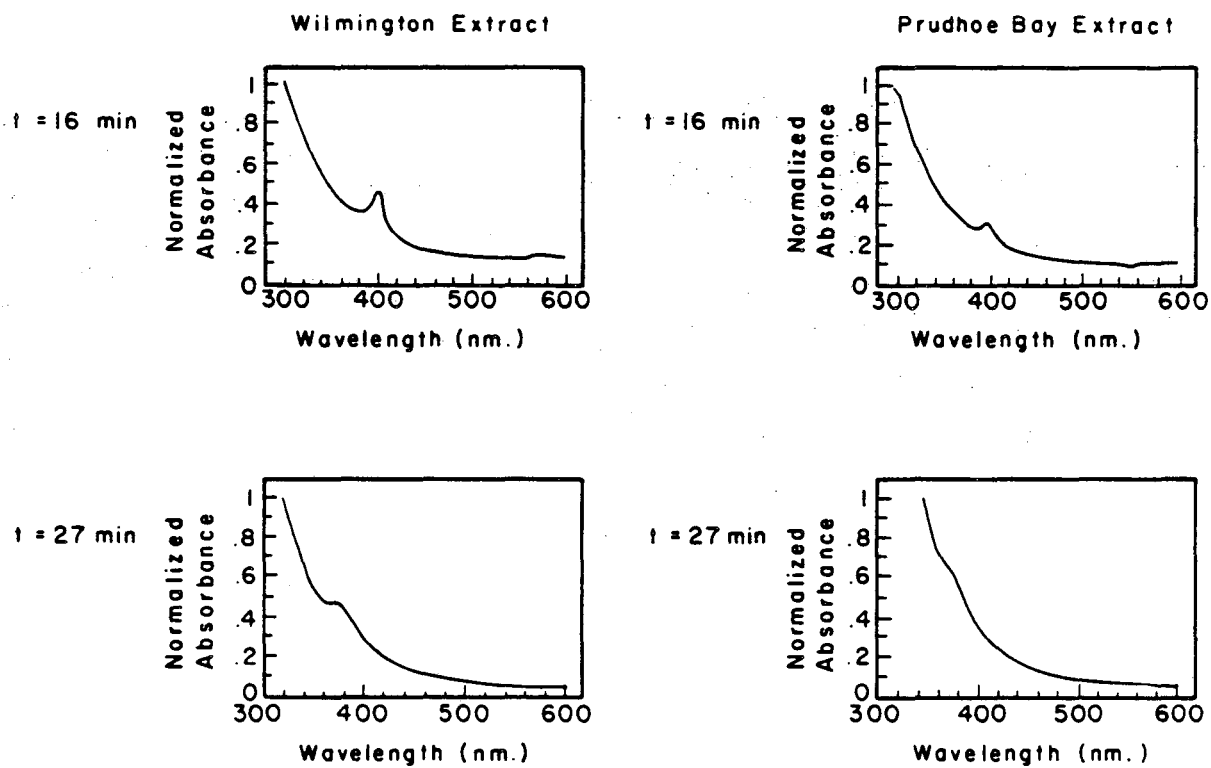


Figure 8

Reverse Phase HPLC -Rapid Scan UV-VIS Analysis  
of Polar Extracts from Asphaltenes



XBL 833-8739

Figure 9

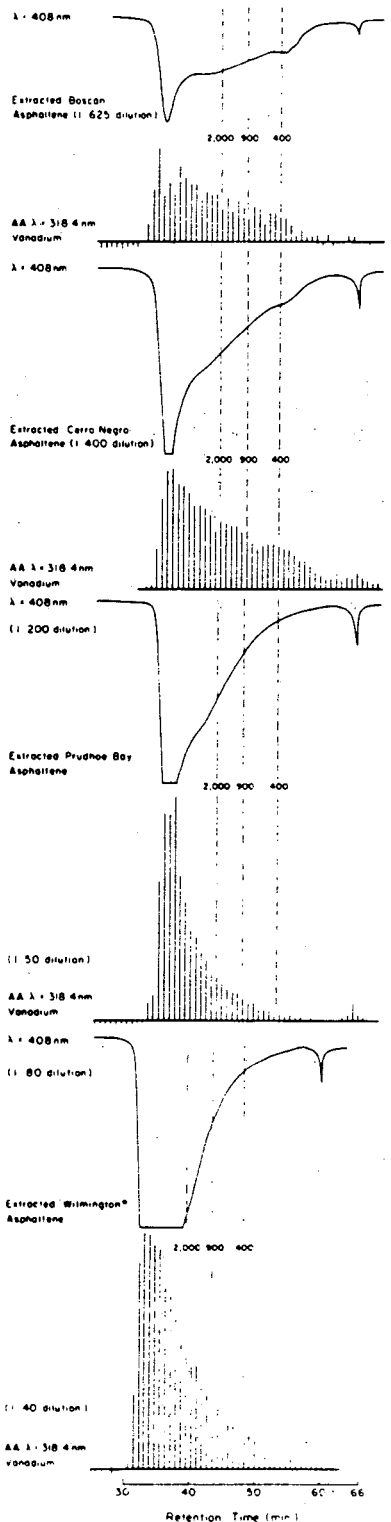


Figure 10

Table I

The Distribution of Vanadyl and Nickel Compounds in Heavy Crude  
Petroleum Extracts by Reverse-Phase HPLC-GFAA Analysis<sup>a,b</sup>

	Peak One <sup>c</sup> (High Polarity)		Peak Two <sup>d</sup> (Moderate Polarity)		Peak Three <sup>e</sup> (Low Polarity)	
	V	Ni	V	Ni	V	Ni
Boscan	5	100	60	0	35	0
Cerro Negro	3	98	74	2	23	0
Wilmington	2	78	59	0	39	22
Prudhoe Bay	12	95	59	0	29	5

- a) Percentage of total vanadium and nickel determined by method of summing peak heights digitized with an integrator for the elution peak designated.
- b) Due to concentration differences between runs these values are useful for comparison purposes only.
- c) t = 0 to 8 minutes.
- d) t = 8 to 24 minutes.
- e) t = 24 to 35 minutes.

Table II  
Vanadium and Nickel Concentrations in Precipitated Asphaltenes<sup>a</sup>

	ppm in <sup>b</sup> Crude Petroleum		ppm in <sup>b</sup> Asphaltene		ppm in <sup>b</sup> Maltene		Wt. % of <sup>c</sup> Asphaltene in Crude Petroleum	% of Total <sup>d</sup> metal in Asphaltene	
	V	Ni	V	Ni	V	Ni		V	Ni
	Boscan	1100	103	3700	350	280		30	23
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) n-pentane precipitated; (40:1) ratio.
- b) Determined by x-ray fluorescence spectroscopy.
- c) Grams of precipitated asphaltene divided by original grams of crude petroleum.
- d) (ppm metal in asphaltene) times (Wt. % asphaltene in crude petroleum) divided by (ppm metal in crude petroleum).



Table III

Solvent Selective Extraction of Precipitated Asphaltenes<sup>a</sup>

	ppm V in <sup>b</sup> Asphaltene	ppm V in <sup>c</sup> Extracted Asphaltene	Estimated <sup>d</sup> ppm V in Extract	Wt. % of Vanadium Extracted from Asphaltene
Boscan	3700	3500	8100	5
Cerro Negro	1600	1500	4200	7
Wilmington	360	340	470	4
Prudhoe Bay	250	210	440	18

- a) Pyridine-water (4:1 v/v).
- b) Determined by x-ray fluorescence spectroscopy.
- c) Determined by comparing GFAA cup analysis of asphaltene and extracted asphaltene.
- d) Calculated from weight removed by extraction and difference in vanadium concentration in the asphaltenes and extracted asphaltenes as determined in footnotes a) and b).

Table IV

The Percent Vanadium in Each Molecular Weight Category of Vanady Compounds  
in the Four Heavy Crude Petroleums and their Asphaltenes, Maltenes,  
Asphaltene Polar Extracts, and Extracted Asphaltenes by 50/110/1000  
A SEC-HPLC-GFAA Analysis<sup>a</sup>

Molecular Wt. <sup>b</sup>	BOSCAN				CERRO NEGRO				WILMINGTON				PRUDHOE BAY			
	>2000	<2000 >900	<900 >400	<400	>2000	<2000 >900	<900 >400	<400	>2000	<2000 >900	<900 >400	<400	>2000	<2000 >900	<900 >400	<400
Heavy Crude Petroleum	28	20	23	29	31	22	20	28	31	29	23	17	28	23	19	30
Asphaltene	33	19	19	29	34	16	18	34	37	18	17	30	58	15	12	17
Maltenes	29	24	27	21	33	26	25	16	18	32	32	17	23	34	30	13
Asphaltene Extract	0	4	31	65	0	5	28	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 a calibration curve (7).

b) Daltons.

Table V

The Distribution of Vanadyl and Nickel Compounds  
in the Precipitated Asphaltene Extracts  
by Reverse-Phase HPLC-GFAA Analysis<sup>a</sup>

	Peak One <sup>b</sup> (High Polarity)		Peak Two <sup>c</sup> (Moderate Polarity)		Peak Three <sup>d</sup> (Low Polarity)	
	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 and nickel determined by method of summing peak heights digitized with an integrator for the elution peak designated.
- b) t = 0 to 8 minutes.
- c) t = 8 to 24 minutes.
- d) t = 24 to 35 minutes.

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