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

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

John J. Komlenic*, Theodore Vermeulen,
and Richard H. Fish

(*M.S. Thesis)

December 1982

ENERGY
AND ENVIRONMENT
DIVISION

DISCLAIMER

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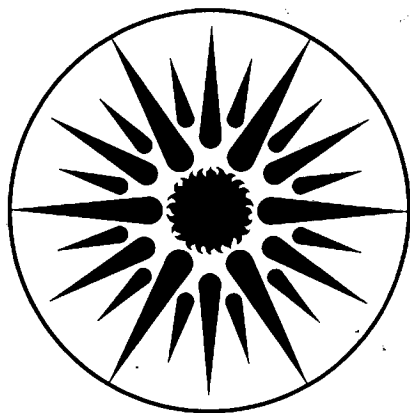HEAVY CRUDE PETROLEUMS USING HPLC-GFAA ANALYSIS

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and
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ABSTRACT

The identification of vanadyl compounds present in heavy crude petroleums provides important biogeochemical information regarding the diagenesis and maturation of these deposits, and should aid future removal of vanadium from processing feedstocks. In this study element-specific high performace liquid chromatography-graphite furnace atomic absorption (HPLC–GFAA) analysis has been used to molecularly characterize and classify vanadyl porphyrin and non–porphyrin compounds present in Boscan, Cerro Negro, Wilmington, and Prudhoe Bay heavy crude oils, containing 1,100, 550, 49, and 19 ppm vanadium, resepectively. The crude oils and pyridine extraction products have been analyzed using the HPLC–GFAA technique with steric exclusion chromatography (SEC) and polar amino–cyano (PAC) columns to yield molecular weight and polarity distributions respectively. This allowed comparisons between vanadyl compounds present in the heavy crude oils and synthesized vanadyl porphyrin and non–porphyrin model compounds.

Fifty percent of the vanadium present, in the form of low molecular weight vanadyl compounds, is extracted, primarily from the asphaltene fraction of each oil. HPLC–GFAA fingerprints reveal two classes of extracted vanadyl non–porphyrin compounds. One class, present in Cerro Negro, Wilmington, and Prudhoe Bay pyrdine extract, consists of relatively non–polar compound(s) with maximum UV–Vis aborbance at 300 nm, as determined using rapid scan spectroscopy (RSS). The other class, present in Boscan and Cerro Negro crude oils, consists of a more polar non–porphyrin compound(s) with maximum absorbance, determined using RSS,

of 265 nm. The two Venezuelan, high sulfur crude oils contain proportionally greater percentages of vanadyl porphyrin compounds, while the two North American, low sulfur crude oils contain predominantly vanadyl non-porphyrin and nickel porphyrin compounds. A correlation relating vanadium concentration and sulfur and asphaltene content has been observed, while correlations involving vanadium content and depth of burial or age of deposit were not apparent.

ACKNOWLEDGEMENTS

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I. INTRODUCTION

As reserves of light crude oil throughout the world decrease, and the nation switches to a more diversified and self-sufficient energy base, the processing of heavy crude petroleums and residuals will become increasingly important. Processing of heavy crude oil feedstocks has been limited in the past, due primarily to uneconomical catalyst poisoning effects known to be associated with naturally occurring trace metal compounds present in these oils.[1-7] Although the concentrations of these trace metals, primarily vanadium and to a lesser extent nickel, are small, usually at the part per million level, the harmful effects both to the processing catalyst and potentially, with increased useage, to the environment are severe.

In order to design processes capable of efficiently removing vanadium and nickel from heavy crude oil feedstocks prior to processing of the oils, it is essential to molecularly characterize or speciate the vanadium and nickel containing compounds present in these oils. Knowledge of the molecular environment associated with trace metal compounds in heavy crude oils will (1) enable the design of selective separation, removal, and recovery processes,[8,9] (2) aid in the exploration and processing for suitable heavy crude oil feedstocks, (3) serve as a means of identification for future oil pollution abatement efforts, and (4) provide important geochemical information regarding the origin and biogenesis of heavy crude oil deposits.[10]

A. The Chemical Nature of Heavy Crude Petroleums

Heavy crude oil differs from conventional light crude oil in three fundamental respects. Heavy crude oil contains, on the average, significantly larger aromatic asphaltic molecules, heterocyclic compounds containing nitrogen, oxygen, and sulfur, and trace metals such as vanadium and nickel.

1. Asphaltenes

Asphaltenes consist of that fraction of petroleum which is soluble in benzene and insoluble in straight chain hydrocarbons such as pentane.[11] This simple definition, however, belies the fact that asphaltenes are an extremely complex component of crude oils. Asphaltenes characteristically possess high aromaticity, large molecular weights, strong intermolecular forces, as well as low volatility. They also contain proportionally greater concentrations of both heteroatoms and metals than does the hydrocarbon soluble maltene fraction of the oil.[12,13]

Structurally, asphaltenes consist of stacked layers of planar aromatic molecules held together by $\pi-\pi$ interactions and H-bonding. Coordination of metals is possible when imperfections in the aromatic systems involving the heteroatoms nitrogen, sulfur and oxygen, occur near gaps or holes in the structured layers.[14] Metals can also be incorporated into asphaltenes as small planar aromatic molecules intercalated between the sheets of layers.[15] In the actual crude oils, these individual asphaltene clusters occur as colloidal mixtures, suspended in the lighter fractions of the oil. Asphaltenes from one oil may not be soluble in the maltenes of another oil, indicating significant structural

differences between asphaltenes isolated from crude oils.[15]

Intermolecular associations make the specific determination of asphaltene molecular weights difficult. However, molecular weights for clusters, discussed above, range from 4,000 to 10,000 daltons. Steric exclusion chromatography (SEC)[16-24] distributions for Canadian and Venezuelan asphaltenes, show molecular weights ranging from 1,000 to 50,000 daltons.[21]

2. Heteroatoms

The primary heteroatoms present in heavy crude petroleums are nitrogen, oxygen, and sulfur.[12] Although these atoms occur as heterocyclic compounds, in a variety of molecular forms, heteroatoms associated with vanadium can be categorized in terms of two classes.

The first category of heteroatom-containing vanadyl (VO^{+2}) compounds consists of low molecular weight tetradentate chelating systems, with the vanadium-oxygen bond perpendicular to the plane of the donor atoms, and with the sixth, axial coordination site of vanadium vacant. Molecules such as pyridine, with a pair of non-bonding electrons, are capable of acting as ligands with these metal coordination sites.[26-29] Electron spin resonance (ESR) has proven a valuable technique for studying the environment of vanadyl ion in these types of complexes.[22-25] The properties of oxovanadium (IV) complexes of porphyrins (four nitrogen donors)[30-32] and β-diketones (four oxygen donors),[33] as well as other vanadyl coordinating systems have been discussed. [34-40]

Several studies have demonstrated that heteroatoms are associated with both the asphaltenes and the metals present in crude oils.[12,13]

Tetradentate vanadyl compounds can complex to the planar asphaltenes via $\pi - \pi$ interactions and H-bonding. Vanadyl ion can also serve as a coordination site for large aromatic, heteroatom containing molecules present in the asphaltenes. Although axial coordination has been used to selectively extract vanadyl compounds from heavy crude oils and asphaltenes,[30] extraction of these highly conjugated vanadyl complexes using coordinating solvents is unlikely. Evidence suggesting that removal of these tightly bound vanadyl compounds is difficult, consists of studies which have shown that vanadyl compounds complexed to the asphaltenes in this manner can not be acid-demetallated.[41]

3. Trace Metals

The two most abundant trace metals present in heavy crude oil are vanadium, at concentrations ranging from 10 to 1,000 ppm (and up to 10,000 ppm in certain residues and asphaltenes), and nickel, usually present at concentrations less than 100 ppm. Vanadium present in heavy crude petroleums could originate from marine plant and animal life, and a diagenetic scheme, involving the conversion from chlorophyll "a" to several naturally occurring vanadyl porphyrin compounds, has been discussed.[42]

Currently, however, less than thirty percent of the vanadium present in heavy crude oils can be accounted for as vanadyl porphyrins.[43] Vanadyl non-porphyrin compounds, with vanadium known to occur in the 4+ oxidation state,[44] remain largely unidentified.

B. Previous Characterization of Heavy Crude Petroleums

1. Vanadyl Porphyrin Compounds

The first studies concerned with the speciation of vanadyl compounds from petroleum sources were performed by Triebs.[45-48] Using coordinating solvents to selectively extract a variety of petroleum products, Triebs was able to isolate and identify both vanadyl etio (VOEtio) and vanadyl deoxyphylloerthroetio (VODPEP) porphyrins as naturally occurring in heavy crude oils. Structures of these two vanadyl porphyrin compounds are shown in Figure 1. Triebs based his identification upon comparisons to known metallo-porphyrin ultraviolet-visible (UV-Vis) spectra, which consist of particularly strong Soret bands near 400 nm, and characteristically weaker bands in the 500-600 nm region.

Baker et al.,[49-51] using liquid chromatography/mass spectroscopy to analyze acid-demetallated porphyrins extracted from petroleum asphaltenes, have shown that vanadyl porphyrin compounds in crude oils actually exist as homologous series, (C_{28} to C_{38}) with alkyl chains of varying length and functionality peripherally attached to the central porphyrin ring structure.[52] Baker was also able to identify vanadyl rhodoporphyrin (VORhodo) as a third naturally occurring petroporphyrin (see Figure 1).

Both of these studies have demonstrated the usefulness of solvent selective extraction as a means of separating and characterizing vanadyl compounds present in petroleum sources. However, acid demetallation of the oil extracts may prohibit identification of certain classes of vanadyl compounds by completely degrading the ligand ring structure. Acid demetallation procedures also limit detection of biogeochemically

important differences between nickel and vanadyl compounds,[30] and may create artifacts that complicate rather than simplify analysis.[30,53]

2. Vanadyl Non-porphyrin Compounds

Studies by Branthaver et al.[54] and Sugihara et al.[53] using SEC to separate crude oils and asphaltenes into molecular weight fractions, have shown that significant quantities of vanadyl compounds remain in both heavy crude oils and asphaltenes, even after exhaustive extractions using a variety of coordinating solvents. These studies indicate that a fixed amount of both porphyrin (Soret absorbing) and non-porphyrin (non-Soret absorbing) vanadyl compounds remain in the high molecular weight, asphaltenic fractions. Based on these findings, they have suggested that extraction of these vanadyl compounds is precluded, due to solvent inaccesability to extractable vanadyl compounds, or to the presence of distinctly higher molecular weight, non-extractable vanadyl compounds complexed to the asphaltenes.

Yen et al.,[55-58] based on extensive studies of heavy crude oil asphaltenes, using UV-Vis spectroscopy, ESR, and mass spectroscopy, have found evidence for the presence of two types of vanadyl non-porphyrins. Based on the fractionation of a readily demetallated non-Soret absorbing vanadyl complex with an odd number of nitrogen atoms in the donor ring, as indicated using mass spectrosopy, Yen has proposed the presence of a class of vanadyl non-porphyrin compounds consisting of mixed nitrogen, oxygen, and sulfur tetradentate chelating systems. [56] Yen has also proposed a class of vanadyl non-porphyrin compounds consisting of altered porphyrin systems, with increased molecular weight and aromaticity, based on isolation of a fraction resistant to acid-demetallation

Dickson et al.[59,60] has studied this former class of vanadyl non-porphyrin compounds using UV-Vis and ESR detection to characterize fractions separated by gradient elution chromatography. By comparing ESR data obtained for separated fractions to those of synthesized model vanadyl non-porphyrin compounds, these researchers have found several possible environments, corresponding to N_2OS, S_2O_2, and N_3O, to be associated with vanadyl ion.

Although these studies have presented evidence for the presence of both high and low molecular weight vanadyl non-porphyrin compounds associated with the asphaltenes, the exact identification of a vanadyl non-porphyrin compound has not been achieved. Structural elucidation of this class of vanadyl compounds has been prevented, due to the lack of suitable separation and detection capabilities necessary for the isolation and identification of these compounds.

3. High Performance Liquid Chromatography (HPLC)

More recently, high performance liquid chromotography (HPLC) with visible absorbance detection has been used by Hajibrahim et al. to separate both metallo-petroporphyrin [61] and demetallated porphyrin[62] mixtures extracted from crude oils. Using gradient elution chromatography with silica packing, Hajibrahim was able to completely separate nickel porphyrins from the more polar and consequently later eluting vanadyl porphyrin compounds. Based on the unique profiles obtained for each oil analyzed, Hajibrahim includes a discussion of the potential of HPLC as a fingerprinting and identification technique for petroporphyrin mixtures.[61]

Barvise and Whitehead,[63] also using HPLC with visible detection to separate and detect vanadyl porphyrins obtained from petroleum residues, have been able to identify two new types of naturally occurring vanadyl porphyrin compounds. This paper also includes a discussion of the advantages of HPLC as applied to fingerprinting of vanadyl and nickel porphyrin compounds in crude oil and residua.

Spencer et al.,[64] has recently reported the fractionation of vanadyl non-porphyrins using UV-Vis absorbance and off-line graphite furnace atomic absorption (GFAA) to detect vanadium in fractions separated using liquid chromotography. This study demonstrates the potential usefulness of element-specific detection towards molecular identification of vanadyl non-porphyrin compounds in heavy crude oils. However, due to the paralleled absorbance between vanadyl non-porphyrins and other UV absorbing compounds present in the oils, the distinct separation and identification of vanadyl non-porphyrin compounds was not accomplished.

While these studies have demonstrated the potential of HPLC to analyze petroleum products for vanadyl compounds, the lack of a suitable detector for the vanadyl non-porphyrin compounds has prevented the molecular identification of this important class of vanadyl compounds. These studies have also indicated the need for model vanadyl non-porphyrin compounds, in order to compare retention properties, UV-Vis absorbance, ESR, and other molecular properties with those of fractionated components from the analyzed oil sample.

C. Speciation Using HPLC-GFAA

The automatic coupling of a high performance liquid chromatograph to a graphite furnace atomic absorption spectrometer (HPLC-GFAA)[65-68] offers much promise as a means of speciating the remaining, unidentified vanadyl compounds present in heavy crude oils. This coupling of instruments provides continuous, on-line element-specific detection of HPLC effluent peaks, combining the versatility, speed, and efficiency of HPLC with the selectivity and sensitivity of GFAA detection. The instrument coupling parameters have been described elsewhere.[65-68]

HPLC-GFAA has recently been used by Fish et al.[69] to speciate organoarsenic and inorganic arsenic compounds found in oil shale retort and process waters. This study has provided the first positive molecular characterization of any trace inorganic or organometallic substances in fossil fuel products.

Brinckman et al.[70] has used HPLC-GFAA to study the association of arsenic with iron, providing an understanding of the presence of these metals in a macromolecular (2,000 and 4,000 dalton) component of shale oils.

Weiss et al.[71] have recently correlated the logarithm of the chromatographic capacity factor with summations of structural substituent parameters for organoarsenicals and organotins. This type of correlation can accurately predict retention times for model compounds, enabling the structural elucidation of unknown components from experimentally determined retention data obtained for known reference compounds.

D. Model Vanadyl Porphyrin and Non-porphyrin Compounds

Speciation using the HPLC-GFAA technique requires obtaining a large collection of model compounds in order to compare and characterize the elution behavior of unidentified components in the analyzed sample.

Figure 1 shows VOEtio, VODPEP, and VORhodo porphyrin compounds which have been identified in heavy crude oils, as well as model vanadyl porphyrin and non-porphyrin compounds, used in this study. Porphyrin compounds consist of a sixteen member ring containing four nitrogen donor atoms located in four conjugated pyrrole groups. When vanadyl ion is incorporated into this structure, these systems are extremely stable. VOT3MePP and VOTPP represent synthetic vanadyl porphyrins (not occurring in nature) which due to the added conjugation of the peripherally attached phenyl rings are stable in strong acid solutions.

Vanadyl non-porphyrin compounds include a much broader classification of compounds, with ring size varying from twelve to sixteen members and with nitrogen, oxygen, and sulfur, in a variety of combinations, constituting the donating atoms. Although this class of vanadyl compounds gives characteristic absorbances in the UV region of the spectrum, absorbance in the visible region is possible, depending on the extent of ring conjugation. As opposed to vandyl porphyrin compounds, the majority of vanadyl non-porphyin compounds decompose readily in dilute acid solutions. VOBenzosalen, VOSalen, VOTADA, and VOBZEN represent vandyl non-porphyrin compounds which have yet to be identified in heavy crude petroleums. Table 1 summarizes and compares molecular characteristics of vanadyl porphyrin and non-porphyrin compounds referred to in this study.
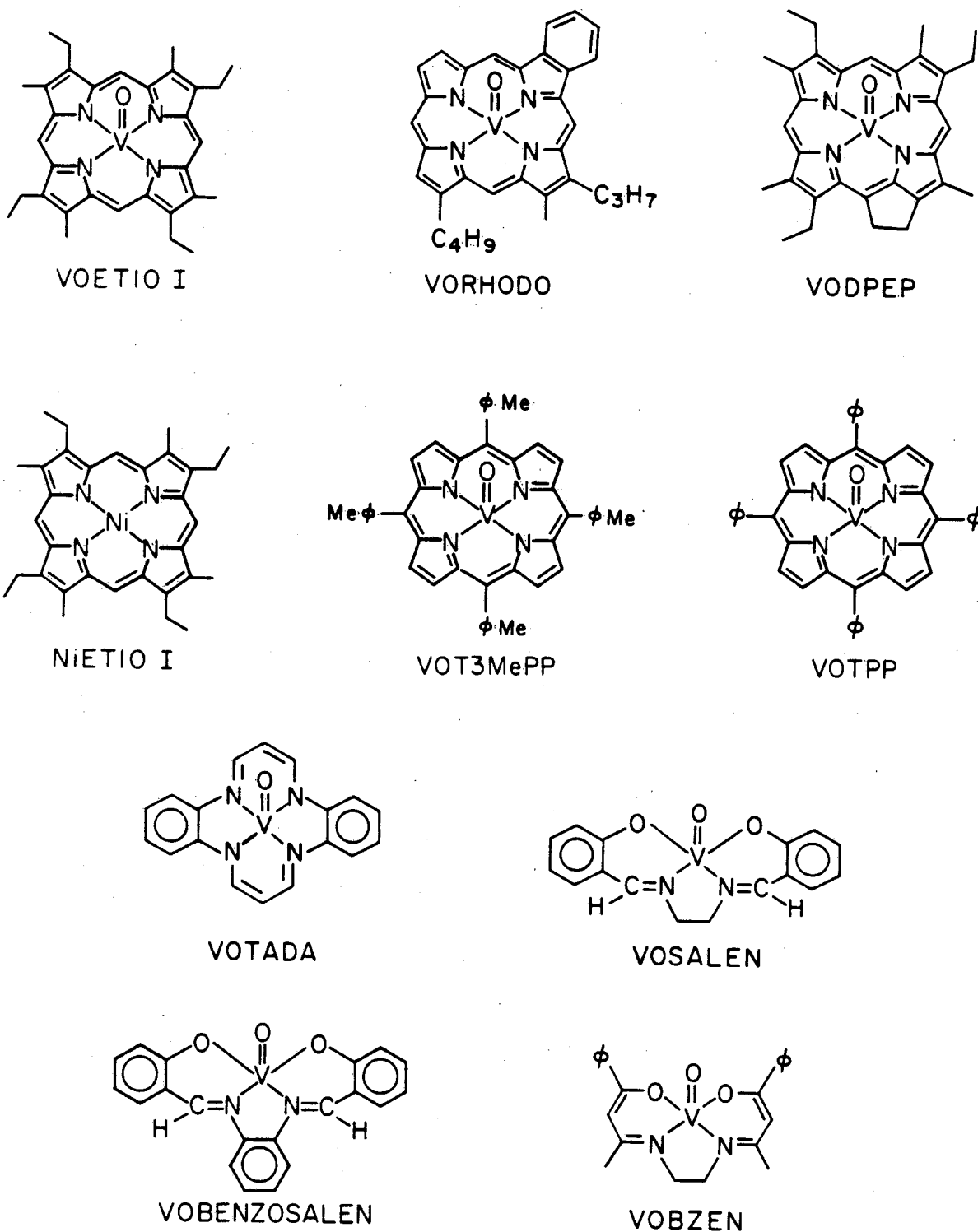
Figure 1. Model Porphyrin and Non-porphyrin Compounds.

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Table 1. Criteria for Vanadyl Porphyrin and Non-Porphyrin Compounds.

Parameter	Vanadyl Porphyrin	Vanadyl Non-Porphyrin
Ring size	16	12 - 16
Soret absorbance (400 nm)	yes	no
Donating atoms	N	N, O, S
Stability in dilute acids	stable	stable or unstable
Examples	VOETIO, VORHODO VOTPP, VODPEP	VOSALEN, VOTADA VOACEN, VOBZEN

E. Summation

The molecular identification of vanadyl porphyrin compounds present in heavy crude petroleums has received much attention and several molecular forms have been elucidated. The molecular identification of vanadyl non-porphyrin compounds, accounting for upwards of 70 percent of the total vanadium present in these oils, has received less attention to date, and molecular forms have yet to be elucidated.

The identification of vanadyl non-porphyrin compounds using conventional techniques has proven difficult, due to the lack of suitable detection capabilities. This is primarily due to the lack of a characteristic ultraviolet-visable spectra for the vanadyl non-porphyrin compounds.

HPLC-GFAA, which has been used recently to speciate arsenic compounds in shale oil[71,72] and and retort waters,[69] offers much promise as a means of molecularly characterizing and indentifying the vanadyl non-porphyrin compounds present in heavy crude petroleums. Identification of speciated molecules is accomplished by comparing retention and molecular properties of components in the analyzed sample to those of known standard compounds, as well as obtaining other spectroscopic data on collected fractions.

II. STATEMENT OF PURPOSE

The objectives of this study were (1) to explore the usefulness of HPLC-GFAA analysis in the characterization and fingerprinting of trace vanadyl compounds present in heavy crude petroleums, and (2) to characterize, according to molecular weight and polarity, the unidentified vanadyl compounds present in these oils, with specific emphasis on the vanadyl non-porphyrins.

The speciation of all vanadyl compounds contained in heavy crude oils could prove difficult, due to the complexity of the matrix itself, and the wide range of possible vanadyl non-porphyrin compounds. Therefore this study was concerned with the molecular characterization of the major classes of vanadyl complexes present, which account for a substantial portion of the total vanadium.

A. Background

The molecular identification of vanadyl compounds in heavy crude oils provides information necessary to the design and implementation of trace metal removal and recovery processing schemes. Knowledge of the molecular forms associated with vanadyl ion can also reveal important biogeochemical information, regarding the evolution of heavy crude petroleum deposits.

A majority of the vanadyl compounds in heavy crude petroleums, primarily the vanadyl non-porphyrin compounds, have proven difficult to identify using conventional techniques such as liquid chromatography, mass spectroscopy, ESR, and UV-Vis analysis. These techniques have pro-

ven inadequate, due to an inability to resolve single components from a complex environment of absorbing compounds.

Element-specific HPLC—GFAA detection provides a method whereby the relative amounts of vandium in eluting component peaks can quickly and accurately be determined, allowing the researcher to focus primary attention on vanadium rich fractions. HPLC—GFAA also offers the advantages of minimun artifact formation and sample destruction, since only two percent of the sample is needed for GFAA detection. This allows further characterization and analysis, based on the collection of isolated fractions.

B. Experimental Approach

In this study Boscan, Cerro Negro, Wilmington, and Prudhoe Bay crude petroleums, containing 1100, 550, 49, and 19 ppm vanadium respectively, have been analyzed by HPLC—GFAA analysis. These oils were chosen for study because they encompass nearly the entire range of vanadium and nickel concentrations normally associated with heavy crude petroleums. Boscan and Cerro Negro are extremely viscous Venezuelan crudes, which need to be heated in order to flow. Wilmington and Prudhoe Bay crudes, from California and Alaska respectively, are less viscous than the Venezuelan crude oils, and can readily be poured at room temperature.

Steric exclusion chromatography (SEC—HPLC—GFAA) has been used to yield molecular weight distributions for the vanadyl compounds present in these oils. Each of the oils has also been selectively extracted using the coordinating solvent pyridine, and the resulting extract and

extracted crude oils also analyzed using SEC–HPLC–GFAA analysis. Further, the pyridine extracts have been analyzed using a polar amino-cyano (PAC) column, which separates compounds according to molecular polarity. Rapid scan spectroscopy (RSS), which provides complete, on-line UV–Vis spectra (190 to 700 nm) of HPLC peaks, has also been used to characterize the PAC separated pyridine extracts.

Characterization of vanadyl compounds present in the heavy crude oils was accomplished by comparing the elution and molecular behavior of synthesized vanadyl porphyrin and non–porphyrin models, to that of vanadyl compounds present in the crude oils.

Although the primary emphasis in this study was directed at the characterization of vanadyl porphyrin and non–porphyrin compounds, one set of chromatograms comparing vanadium and nickel molecular weight distributions for each of the four crude oils has also been included to demonstrate both the versatility and broad applicability of element-specific HPLC–GFAA analysis.

EXPERIMENTAL APPARATUS, METHODS AND PROCEDURES

A. Reagents

The Cerro Negro, Wilmington, and Prudhoe Bay crude oils were pro-
vided by Dexter Sutterfield of Bartlesville Energy Technology Center.
The Boscan heavy crude oil was provided by Dr. J. Lubkowitz of INTEVEP,
Caracus Venezuela.

HPLC grade methylene chloride (CH_2Cl_2), tetrahydrofuran (THF), and
n-hexane were purchased from Burdick and Jackson (Muskegon, MI). All
solvents were filtered and degassed before use in the HPLC system.

Vanadyl tetra(3-methylphenyl)porphyrin (VOT3MePP), tetra(4-
carbomethoxy)phenylporphyrin (T4CMPP), vanadyl etioporphyrin I (VOE-
tioI), and nickel etioporphyrin I (NiEtioI) were purchased from Midcen-
tury (Posen, IL). Vanadyl tetraphenylporphyrin (VOTPP) was purchased
from Strem Chemicals (Newburyport, MA). Vanadyl salen (VOSalen) and
vanadyl benzosalen (VOBenzosalen) were prepared from free base ligands
according to the method of Bielig et.al.[73] VOBZEN, was synthesized
according to the method of Dilli and Patsalides,[34] while the VOTADA was
prepared from the free base ligand according to the procedure of Bur-
chill and Honeybourne.[74] The 3100 and 9500 molecular weight polystyrenes
were purchased from Altex (Berkeley, CA).

Reference solutions of all standards were made by dissolving each
standard in HPLC grade methylene chloride, filtering using 0.45 μm mil-
lipore filters (Bedford, MA) (used for all of the filtering in this
study), and stored away from light inorder to minimize decomposition.
Ultraviolet-visible spectra of the extracts and standards were recorded

using a Cary 219 UV-VIS spectrophotometer. The solvent selective extractions were performed using reagent grade pyridine and p-xylene (Mallinckrodt; Paris, Kentucky) and quartz-distilled water.

B. Apparatus

A schematic of the HPLC-GFAA instrumentation is shown in Figure 2. For a typical run, 250 μl of the sample to be analyzed was injected onto the column via a gradient-programmed solvent stream provided by two solvent delivery pumps (Altex 100 A) and a gradient programmer (Altex 420). Separations were accomplished using either a single or series combination of 50 and 100 Å spherogel columns (Altex, 8.0mm I.D. * 300mm length) with swelled divinylbenzene as the packing for the SEC runs, or a polar amino-cyano (PAC) column (Altex, 4.6mm I.D. * 250mm length) with a self-packed guard column (Waters, 3.2 mm I.D. * 40mm length) for the gradient elution runs.

After separation, the sample absorbance at a selected UV-Vis wavelength (nm) was read using a variable wavelength detector (Altex 155-40). The sample was then carried into a flowthrough Teflon receiving cup from which the HPLC effluent was automatically and continuously sampled for introduction into the GFAA (Perkin-Elmer 4000) at approximately 40 second intervals.

Instrument parameters for the GFAA were:

```
Band width  0.2 nm
Drytime  15 s
Atomization time  7 s
Detector wavelength  318.4 nm (vanadium)
                     232.0 nm (nickel)
Dry temperature  90°C
Atomization temperature  2700°C
```

HPLC - GFAA
High Performance Liquid Chromatography - Graphite Furnace Atomic Absorption Spectrophotometer
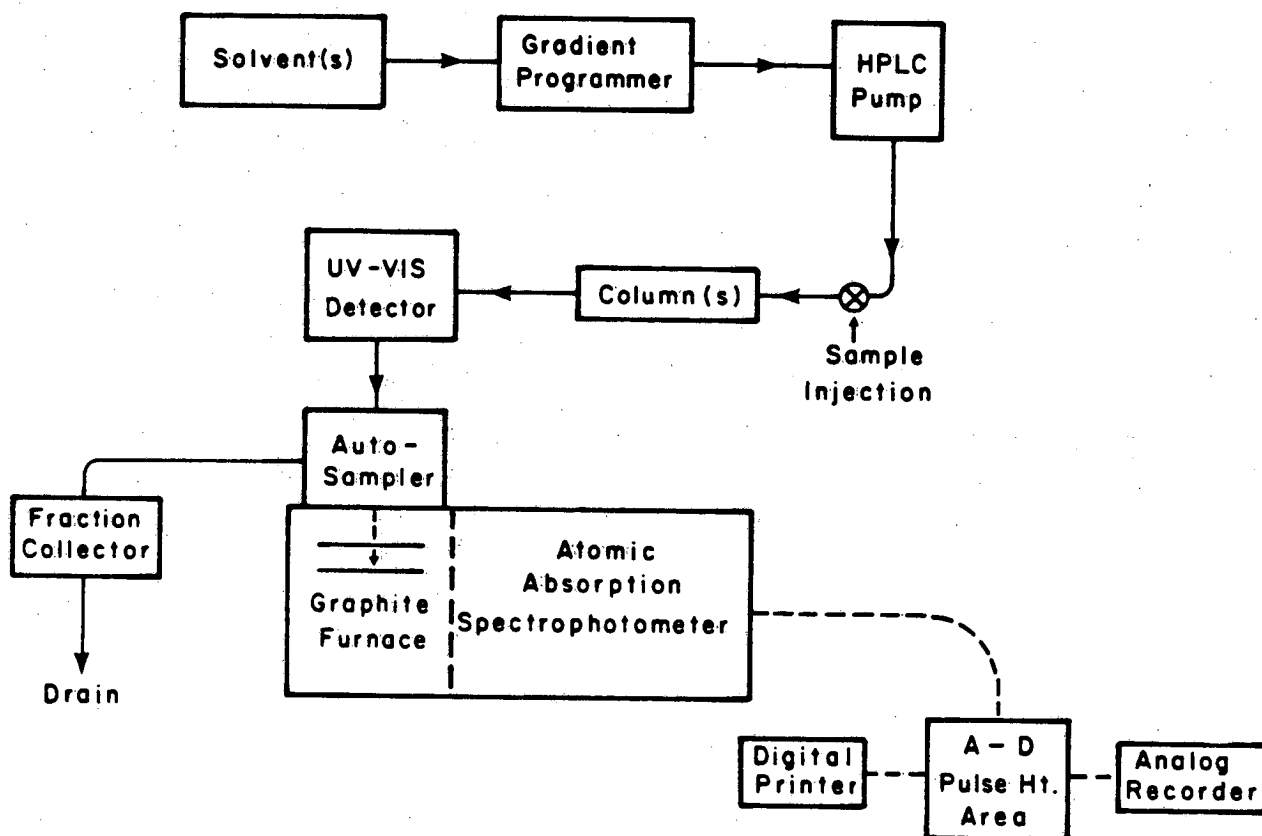
XBL 8210-3117

Figure 2. Schematic of the Automatically Coupled HPLC-GFAA System.

Cooling gas - argon

A dual-pen strip chart recorder (Kipp and Zonen) was used to record the single wavelength UV-Vis absorbances. The GFAA histogrammic data was recorded using both the strip chart recorder and a digital integrator (Altex C-RIA).

Rapid scan spectroscopy (RSS) analysis was accomplished using a variable wavelength detector (Altex 165). RSS was used to provide both UV-Vis (300 to 600 nm) spectra and UV maxima (250 to 350 nm) for the PAC-HPLC separated pyridine extracts.

C. Procedures

1. Extraction

A schematic of the overall separation procedure is shown in Figure 3. Five grams of each of the heavy crude oils was extracted five consequtive times with a mixture of pyridine (40 ml), H_2O (10 ml), and p-xylene (10 ml). Phase separations occured after approximately fifteen minutes, with separation time increasing slightly as the number of extractions increased. The extract phase was collected, filtered, and rotary-evaporated to remove any residual solvents. The extracts were then redissolved in HPLC-grade methylene chloride and stored in the dark until needed.

The four oils, after extraction, were also rotary-evaporated and submitted, along with the whole crude oils (before extraction) to x-ray fluorescence analysis. The crude oils, before and after extraction, were then diluted in HPLC-grade methylene chloride, filtered, and stored in

METHODS AND PROCEDURES

HEAVY CRUDE OIL
(Whole Oil) ~5 g

50/100 Å SEC
Column(s)
(THF)

EXTRACTION
Pyridine:H_2O (4:1)
200 ml total

OIL AFTER
EXTRACTION
Solvent Removed
~5 g

50/100 Å SEC
Column(s)
(THF)

EXTRACT
Redissolved in
CH_2Cl_2
200 ml

PAC
Column
Hexane ⟶
THF : CH_2Cl_2
(1:1)

50/100 Å SEC
Column(s)
(THF)

	V (ppm)
Boscan	1100
Cerro Negro	560
Wilmington	48
Prudhoe Bay	19
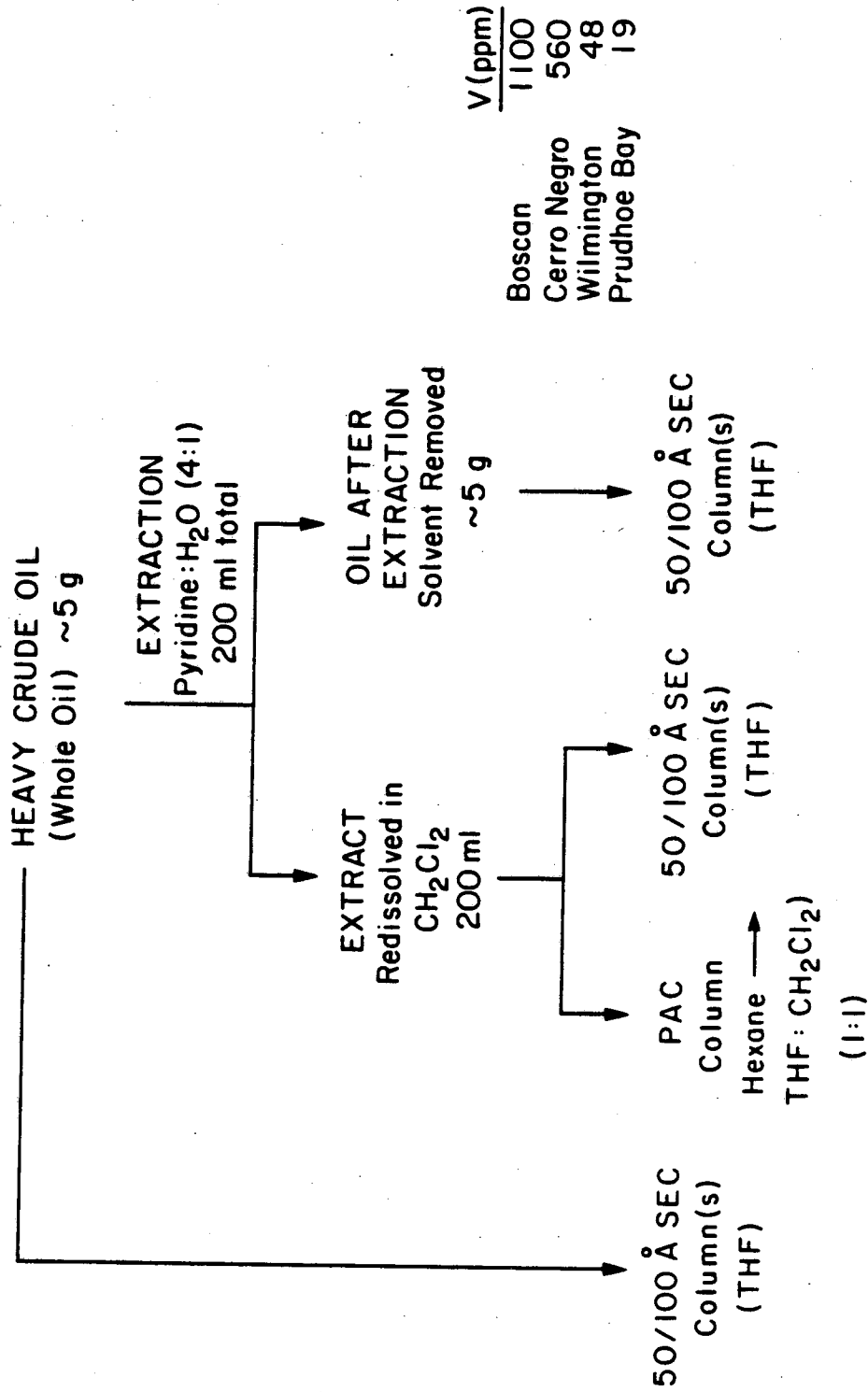
XBL 8210-3133

Figure 3. Methods and Procedures Outline.

the dark until needed.

2. Analysis

The x-ray fluorescence analyses were performed by Robert Giauque of Lawrence Berkeley Laboratory. The atomic absorption analyses was performed by the Microchemical Laboratory of the College of Chemistry, University of California, Berkeley.

3. Chromatography

The heavy crude oils, the extracted oils, and the extracts were all analyzed using both the 50 Å and the 50/100 Å columns. All SEC runs were performed with THF as the mobile phase at a flow rate of 0.5 ml/min.

Further, the four pyridine/water extracts were also analyzed using gradient elution chromatography with the polar-amino cyano PAC column. The PAC separations were obtained with a solvent gradient consisting of an initial linear ramp from 100 percent n-hexane to 25 percent methylene chloride - THF (1:1 v/v) from 0-3 min and a second linear ramp from 25 percent to 100 percent methylene chloride-THF (1:1 v/v) from 27-30 minutes at a flow rate of 2.0 ml/min.

Recalibration of the PAC column after each run was accomplished by ramping to 100 percent n-hexane over 3 minutes, and holding until a minimum of 10 column volumes of n-hexane had eluted.

IV. RESULTS

A. Extraction Results

The vanadium and nickel concentrations for Boscan, Cerro Negro, Wilmington, and Prudhoe Bay crude oils as determined using x-ray fluorescence and atomic absorption spectometry, are shown in Table 2. Although the amounts of nickel present in each of the oils is roughly equivalent, Boscan crude oil contains nearly twice as much vanadium as does Cerro Negro crude oil. While Wilmington crude oil contains slightly more nickel than vanadium, Prudhoe Bay crude oil contains approximately twice as much vanadium as nickel.

Since Boscan, Cerro Negro, and Prudhoe Bay crude oils contain more vanadium than nickel, and only Wilmington crude oil has less vanadium than nickel, attention in this study has been focused primarily on the characterization of the vanandium-containing compounds.

Table 2 also shows the vanadium concentrations for the four heavy crude oils after one and five extractions, as determined using x-ray fluorescence and atomic absorption spectroscopy, respectively. Boscan, Cerro Negro, and Wilmington crude oils show substantial vanadium removal after both one and five extractions, while Prudhoe Bay crude oil registers no vanadium removal after one extraction, and requires a full five extractions to effect significant removal. Vanadium removal after five extractions totals 51 percent for Boscan crude oil, 50 percent for Cerro Negro crude oil, 87 percent for Wilmington crude oil, and 50 percent for Prudhoe Bay crude oil.

Table 2. Vanadium Concentrations for the Four Heavy Crude Oils Studied, Before and After Extraction.

	Boscan		Cerro Negro		Wilmington		Prudhoe Bay	
	V	Ni	V	Ni	V	Ni	V	Ni
Whole Crude Oil[a]	1100[b]	103	560	118	48.5	60.4	18.7	9.3
Crude Oil after one extraction[a]	640	--	412	--	25.4	--	18.7	--
Crude Oil after[c] five extractions	540	--	280	--	6.4	--	9.3	--

[a]by x-ray fluorescence

[b]values in ppm

[c]by atomic absorption

The Boscan and Cerro Negro pyridine/water extracts were dark red in color, indicating the presence of vanadyl porphyrins. This was confirmed by the visible absorbance at 408 nm obtained using the Cary 219 UV-Vis spectrophotometer. These extracts also registered strong ultraviolet absorbances, indicating the possible presence of substantial quantities of vanadyl non-porphyrin compounds. Wilmington and Prudhoe Bay extracts were orange and yellow respectively, suggesting that these extracts were vanadyl porphyrin deficient. UV-Vis analysis of these samples showed proportionally less absorbance at 408nm and increased UV absorbance, confirming that these extracts contained less vanadyl porphyrins than the Venezuelen crude oils and possibly more vanadyl non-porphyrin compounds.

An unextractable fraction of vanadium remains in each heavy crude oil, indicating that pyridine was incapable of removing a fixed percentage of the vanadyl compounds present in the crude oils. This suggests that either pyridine was unable to contact a portion of the extractable vanadyl compounds contained in the asphaltenes, or non-extractable high molecular weight vanadyl compounds are incorporated into the structure of the asphaltenes.[54]

When the pyridine/water extractions were repeated, removal of vanadyl compounds after five extractions agreed within ten percent of the values listed in Table 2. Exact agreement was not achieved, owing possibly to such factors as the non-homogeneous nature of the oils, the separation and contact time differences, the temperature of the oils during exraction, and the irreversible mechanism of removal and incorporation of vanadyl compounds from the heavy petroleum asphaltenes.

B. SEC-HPLC-GFAA Analysis

1. 50 Å Column

The SEC calibration data for the 50 Å column using THF as the mobile phase is given in Figure 2. SEC separates on the basis of molecular size, with large molecules eluting first, due to the steric interaction which occurs between these molecules and the column pore structure. Small molecules, which spend proportionally more time traveling through the pore structure, elute later. Retention times shown in Figure 2 can readily be converted to retention volumes by multiplying the retention time by the flow rate of 0.5 ml/min.

Because the accuracy of SEC molecular weight determinations depends strongly on the choice of calibration standards, vanadyl porphyrin and non-porpyrin compounds were chosen in order to minimize error when assigning molecular weights for the oil samples. Although the 50 Å column gives good resolution at molecular weights between 200 and 900 daltons, above and below these values the resolving power of the column diminishes rapidly. Vanadyl porphyrins such as VOTPP, VOOEP, and VOT3MePP elute before the lower molecular weight vanadyl non-porphyrin compounds, VObenzosalen and VOsalen. Also shown is the retention time for the solvent, p-xylene.

Figure 5 shows SEC-HPLC-GFAA data obtained for Boscan crude oil, the oil after extraction, and the pyridine/water extracts separated using the 50 Å column. These chromatograms are composed of both a continuous visible absorbance reading (at 408 nm) in the upper portion of the chromatogram, and histogrammic GFAA vanadium output (318.4) in the lower portion.

CALIBRATION CURVE FOR 50 Å SEC COLUMN
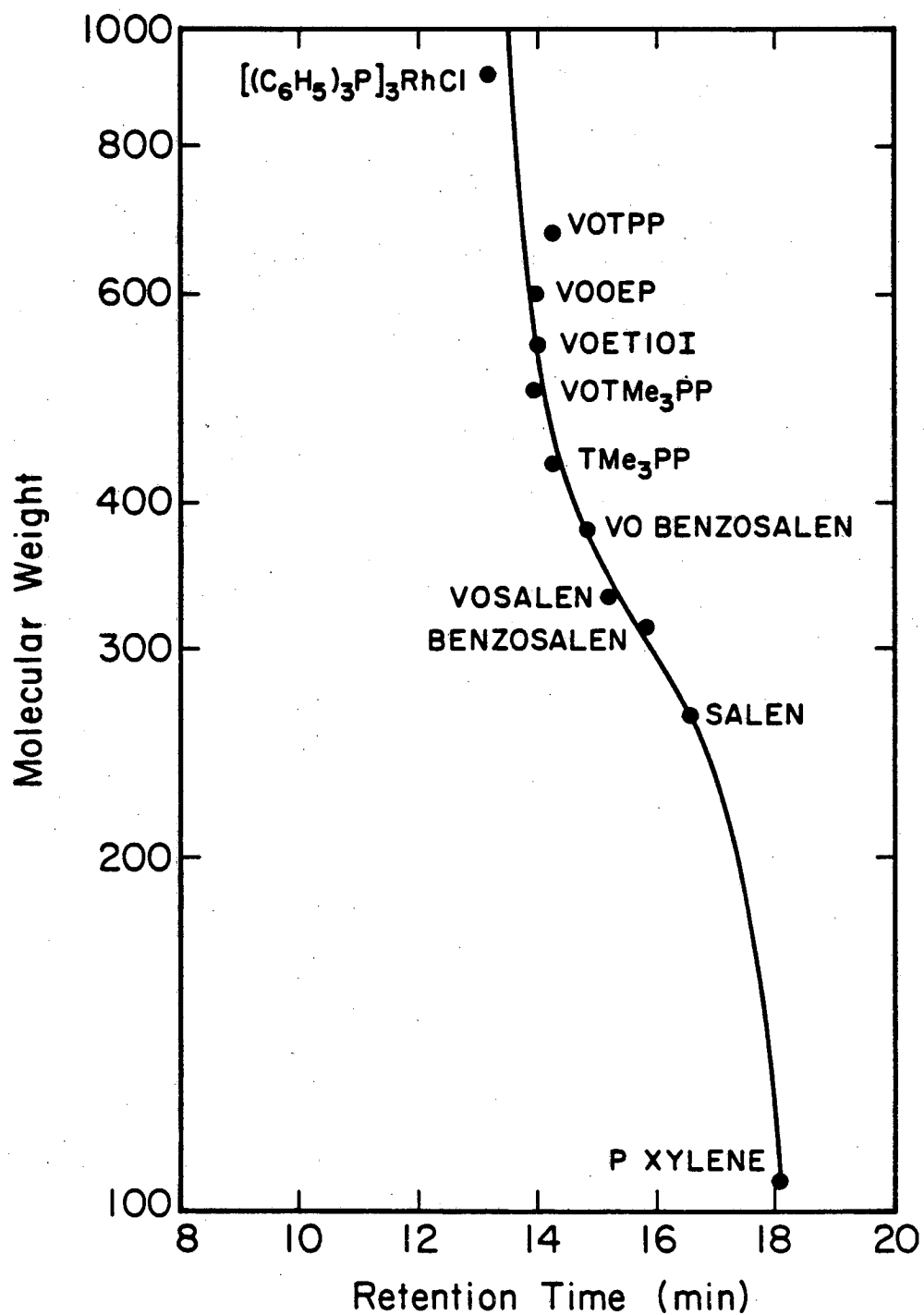
Figure 4. Plot of Log Molecular Weight Versus Retention Time for the 50 Å Column.

VIS

a) Boscan Crude Oil
(1:2000 dilution)

AA

VIS

b) Boscan Crude Oil
Extracted With
Pyridine/H_2O (4:1)
(1:2000 dilution)

AA

VIS

C) Boscan Crude Oil
Extract
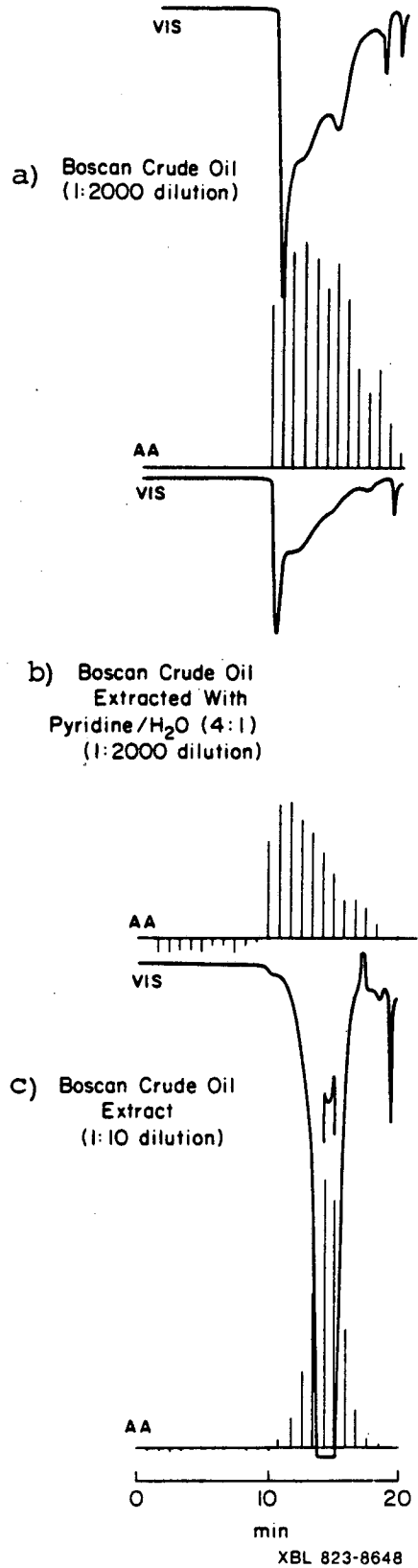(1:10 dilution)

AA

| 0 | 10 | 20 |

min

XBL 823-8648

Figure 5. 50 Å SEC-HPLC-GFAA Data for a)Boscan Crude Oil, b) Crude Oil After Extraction, and c)Crude Oil Extract.

Figure 5 (a) shows both visible and vanadium histograms for Boscan crude oil, diluted in methylene chloride, occurring from approximately ten to twenty minutes. The visible absorbance rises rapidly to a maximum value near ten minutes and then gives a series of peaks of decreasing absorbance over the next ten minutes. The vanadium histograms similarly increase rapidly to a maximum near twelve minutes, and give a series of decreasing peaks over the next eight minutes. However, both visible and atomic absorption outputs favor the more rapidly eluting molecules, with retention times less than thirteen minutes, which based on the calibration curve from Figure 4, correspond to molecular weights greater than 900 daltons. The final visible peak, evident in all of the chromatograms, is the methylene chloride solvent front.

Based on Figure 5 (a) and Figure 4, vanadyl compounds in Boscan crude oil can be assigned to either of three molecular weight categories. These categories include high molecular weight vanadyl compounds (molecular weights greater than 900 daltons), vanadyl porphyrin compounds (molecular weights greater than 400 daltons and less than 900 daltons), and low molecular weight vanadyl non-porphryin compounds (molecular weights less than 400 daltons). This first class could consist of extractable vanadyl porphyrin and non-porphyrin compounds complexed to the asphaltenes via hydrogen-bonding or $\pi-\pi$ interactions, or high molecular weight, non-extractable vanadyl compounds convalently bonded to the asphaltenes. Although Boscan crude oil shows vanadyl compounds present in all three molecular weight categories, the majority of these compounds exist in the asphaltenes, at molecular weights greater than 900 daltons.

Data for Boscan crude oil after five extractions are given in Figure 5 (b). Both visible and atomic absorption outputs have decreased over the entire range of retention times from ten to twenty minutes, indicating the extraction of vanadyl compounds from all three molecular weight categories. Figure 5 (c) shows similar data for the Boscan crude oil extract. This chromatogram, unlike the two previous ones, shows a single broad visible band and a broad series of vanadium histograms. These histograms, centered at elution times near fifteen minutes, corresponds to molecular weights of approximately 350 daltons.

Figure 5 (a), (b), and (c), in conjuncture, present strong evidence for the presence of extractable vanadyl porphyrin and low molecular weight vanadyl non-porphyrin compounds in the asphaltene fraction of the oil. This figure reveals that a certain percentage of the vanadyl compounds contained in the asphaltene fraction of the oil can be selectively extracted using the coordinating solvent pyridine.

Interestingly, vanadyl compounds in the pyridine extract occur at an average molecular weight of 350 daltons, lower than that normally associated with vanadyl porphyrins. Based on the accuracy of the calibration data obtained using the model vanadyl porphyrin and non-porphyrin compounds, the majority of the vanadyl compounds in the pyridine extracts can be assigned as vanadyl non-porphyrin compounds. The strong visible absorbance at these molecular weights could be due to non-Soret absorbance of vanadyl non-porphyrins compounds. In view of this finding, demetallation of crude oil extracts should be viewed as a hazardous operation, since the majority of the extractable vanadyl compounds present are capable of being entirely degraded using this pro-

cedure. Due to the absence of high molecular weight vanadyl compounds in the extracts, it can be postulated that these compounds either are not present, or are so tightly bound to the asphaltenes that extraction using pyridine is not achieved.

Similar data for Cerro Negro crude oil are shown in Figure 6. Cerro Negro crude shows a similar profile to Boscan crude, with the exception of a late eluting vanadium-containing peak at approximately nineteen minutes. Figure 6 (b) shows substantial vanadium removal from the high molecular weight fraction of the oil, while Figure 6 (c) shows that the extract contains only low to medium molecular weight vanadyl compounds. Again the visible absorbance and vanadium histogrammic output are centered at molecular weights of 350 daltons, indicating vanadyl non-porphyrin compounds predominate in the extract.

SEC-HPLC-GFAA data for Wilmington and Prudhoe Bay crudes are shown in Figures 7 and 8, repectively. These two figures indicate that relatively more vanadyl compounds exist in the asphaltenes for these two oils than for the Venezuelan crude oils. However, the vanadyl compounds in the extracts exist only at low molecular weights. Interestingly, Figures 7(c) and 8(c) show slightly broader visible absorbance and atomic absorption histograms than do the two Venezualen crude oil extracts. As Figure 8(c) indicates, some very high molecular weight (greater than 900 dalton) vanadyl compounds are present in Prudhoe Bay crude oil extract.

Comparisons of the 50 Å SEC-HPLC-GFAA visible absorbance and vanadium histogram fingerprints reveal that similar extraction behavior occurs for all four oils, although the concentration of vanadium in the

XBL 823-8649
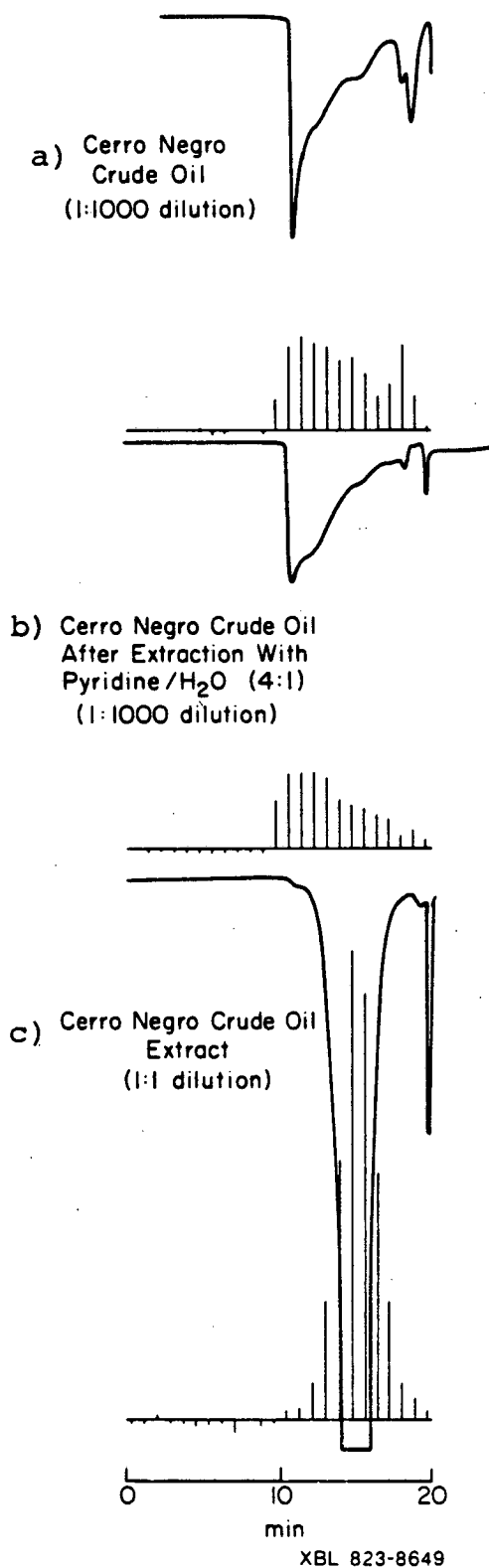
Figure 6. 50 Å SEC-HPLC-GFAA Data for a) Cerro Negro Crude Oil, b)Crude Oil After Extraction, and c) Crude Oil Extract.
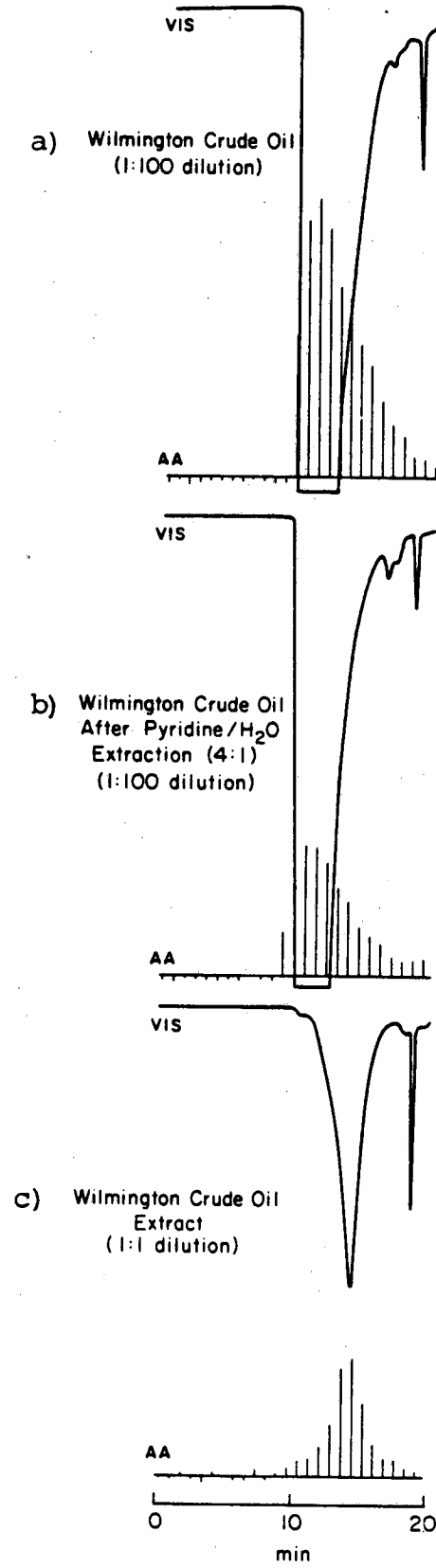
Figure 7. 50 Å SEC-HPLC-GFAA Data for a)Wilmington Crude Oil, b) Crude Oil After Extraction, and c) Crude Oil Extract.

VIS

a) Prudhoe Bay Crude Oil
       (1:50 dilution)

AA

VIS

b) Prudhoe Bay Crude Oil
       After Pyridine/H_2O
       Extraction (4:1)
       (1:50 dilution)

AA

VIS

c) Prudhoe Bay Crude Oil
           Extract
       (1:1 dilution)

AA

0   10   20
         min
        XBL 823-8647

Figure 8. 50 Å SEC-HPLC-GFAA Data for a) Prudhoe Bay Crude Oil,
b) Oil After Extraction, and c) Crude Oil Extract.

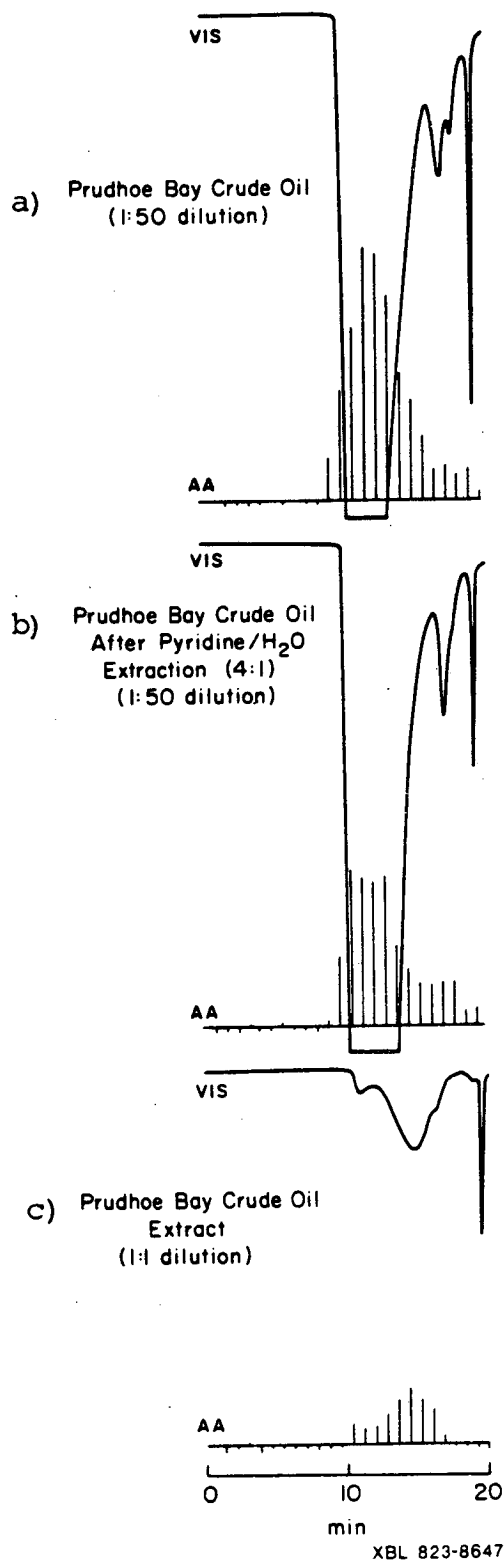individual oils varies dramatically. Each oil shows a preponderance of low molecular weight vanadyl non-porphyrin compounds being extracted from the high molecular weight asphaltene fraction of the oils. These fingerprints also reveal that a certain unextractable fraction of vanadium remains in each crude oil, concentrated in the asphaltene. Of the four oils analyzed, only Prudhoe Bay crude oil shows any high molecular weight vanadyl compounds being extracted from the crude oils.

2. 50/100 Å Column Combination

a. Vanadyl Compounds

Since the 50 Å SEC column proved incapable of differentiating molecular weights greater than 900 daltons, and much of the vanadium in each of the oils exists at molecular weights greater than this, as indicated using the 50 Å SEC column, a series combination of 50Å and 100 Å columns was subsequently used. This combination provided more accurate characterization of the the high molecular weight vanadyl compounds present in the asphaltenic molecular weight range (greater than 900 dalton).

The SEC calibration plot for the 50/100 Å column combination, which gives a linear working range from 100 to 3000 daltons, is shown in Figure 9. Vanadyl porphyrin and non-porphyrin compounds have again been used as calibration standards, to minimize error when assigning molecular weights to components in the petroleum samples. Polystyrene standards of 3100 and 9500 daltons have been used to calibrate the high molecular weights ranges, since no vanadyl compounds at these molecular weight ranges were available.

SEC CALIBRATION CURVE: 50 Å
AND 100 Å COLUMNS IN SERIES
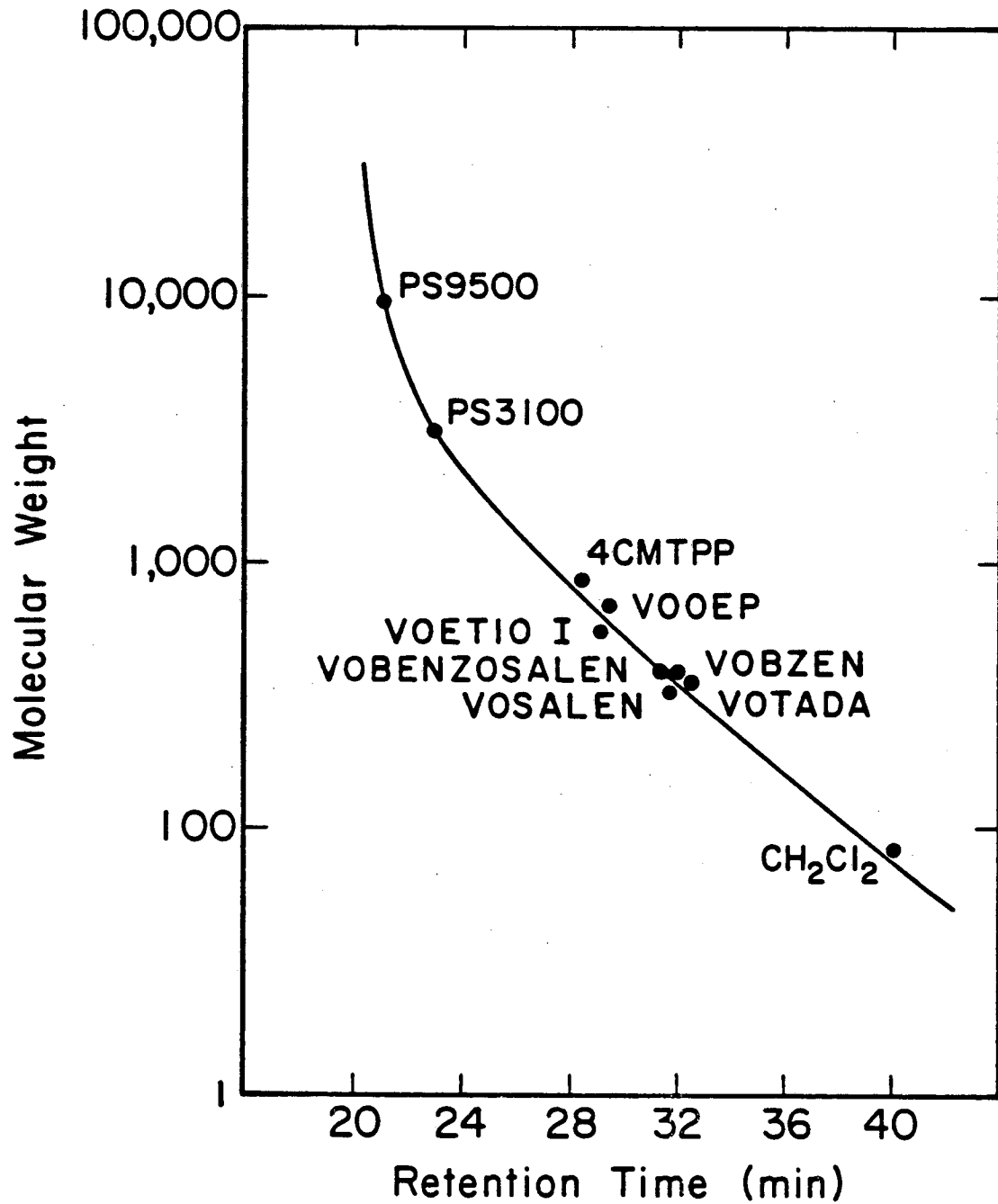
XBL 826-10469

Figure 9. Plot of Log Molecular Weight Versus Retention Time for the 50/100 Å Column Combination.

The 50/100 Å SEC-HPLC-GFAA data for the separation of several of the standards is shown in Figure 10 (a). The polystyrene standards were monitored at 254 nm, the vanadyl porphyrins and the metal-free porphyrin at 400 nm, and the vanadyl non-porphyrin compounds at 320 nm. The lower portion of Figure 10 (a) shows the GFAA vanadium histograms. The advantage of the added 100 Å column is increased resolution of molecules with molecular weights greater than 900 daltons, allowing for accurate determination from 100 to slightly greater than 2000 daltons. Due to the increased accuracy which this combination provides, all quantitative calculations contained in this study were based on the 50/100 Å column combination.

Based on Figure 9, vanadyl compounds in the heavy crude oils were assigned to either of four molecular weight categories. Vanadyl compounds with molecular weights less than 400 daltons were assigned as low molecular weight vanadyl non-porphyrin compounds. Similarly vanadyl compounds with molecular weights between 400 and 900 daltons were assigned as vanadyl porphyrin compounds. These molecular weights were chosen based on the definition of vanadyl porphyrin and non-porphyrin compounds from Table 1. Above molecular weights of 900 daltons, the definition of vanadyl porphyrins present in Table 1 does not hold, due to the increased ring conjugation which would be necessary at these high molecular weights. Vanadyl compounds with molecular weights between 900 and 2000 daltons were assigned as high molecular weight vanadyl compounds, while vanadyl compounds with molecular weights greater than 2000 daltons were assigned to very high molecular weight vanadyl compounds. These latter two molecular weight categories could include both low
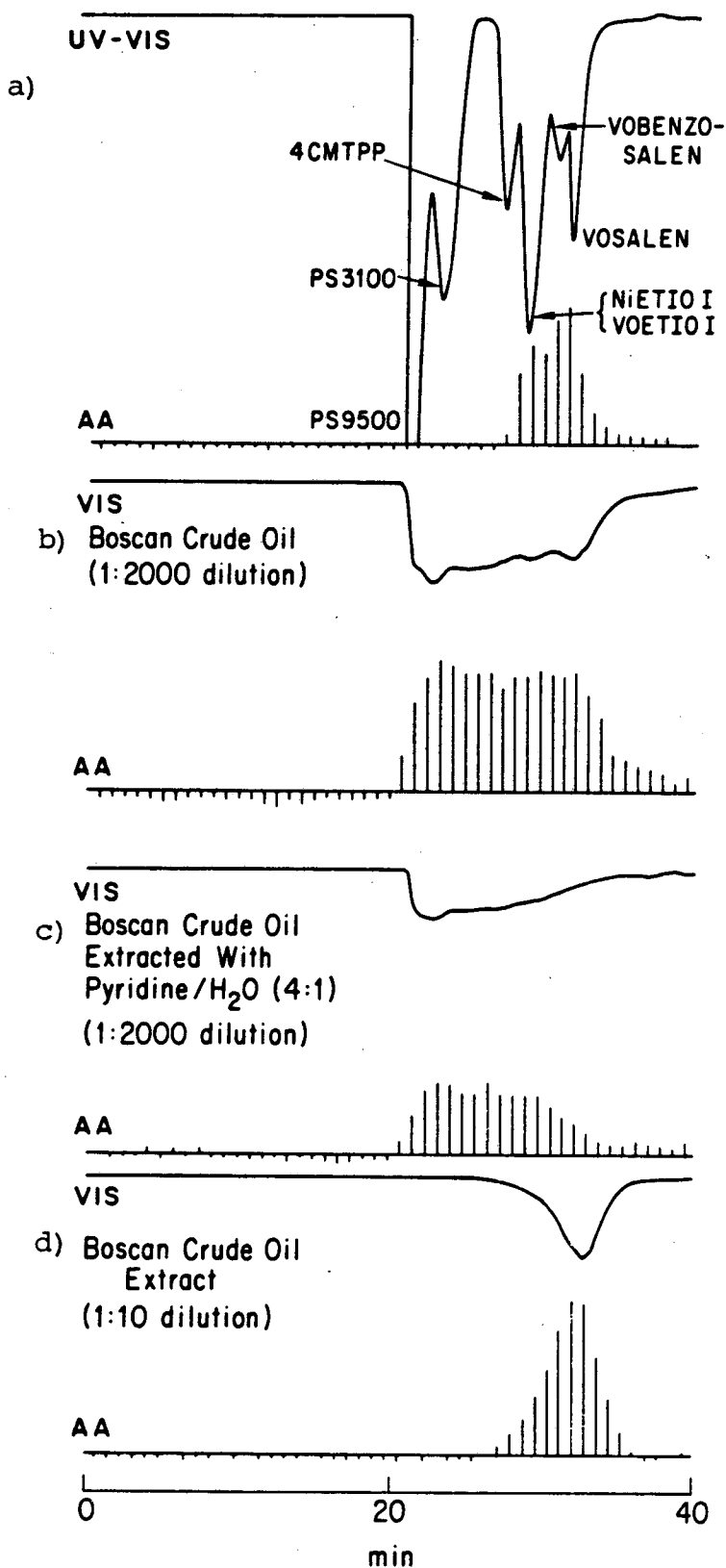
Figure 10. 50/100 Å SEC-HPLC-GFAA Data for a)Standards, b) Boscan Crude Oil After Extraction, and d) Crude Oil Extract.

molecular weight vanadyl porphyrin and non-porphyrin compounds inter-calated into the asphaltenes, and high molecular weight vanadyl porphy-rin and non-porphyin compounds existing as asphaltenes.

Although vanadyl porphyrin compounds are not normally associated with molecular weights greater than 900 daltons, complexation to the asphaltene fraction of the oil could drastically increase the apparent molecular weight of these vanadyl compounds. This encapsulation could change the physical and chemical properties of these compounds. Like-wise, low molecular weight vanadyl non-porphyrin compounds could be incorporated into the asphaltene fraction of the oil by $\pi - \pi$ interac-tion or hydrogen-bonding. This intercalation could drastically alter the stability and other spectroscopic properties, of these vanadyl non-porphyrin compounds.

Figures 10 (b), (c), and (d) show the 50/100 $\overset{\circ}{A}$ column combination data for Boscan crude oil, oil after extraction, and extract respec-tively. The upper portion of Figure 10 (b) shows the visible absorbance, measured at 408 nm, while the lower portion of the chromatogram gives the vanadium histogrammic output. The location of the vanadium histo-grammic peaks shows vanadium in Boscan crude oil eluting at retention times from twenty to forty minutes, corresponding to molecular weights ranging from greater than 10,000 to 100 daltons. Interestingly, the HPLC-GFAA output shows that Boscan crude oil contains nearly equivalent percentages of vanadyl compounds in all four molecular weight categories.

Figure 10 (c) shows similar data for Boscan crude oil after extraction. This figure shows vanadyl compounds being removed from the

entire molecular weight range of the crude oil. However, as evidenced in Figure 10 (d), only vanadyl compounds with retention times greater than 28 minutes and centered at 32 minutes, corresponding to a molecular weight of 350 daltons, exist in the extract. Thus, although vanadyl compounds have been extracted from molecular weights greater than 900 daltons, in the extract only low molecular weight (less than 400 dalton) vanadyl non-porphyrin compounds and vanadyl porphyrin compounds are present. Based on the accuracy of the calibration data from Figure 9, the majority of the vanadyl compounds present in the extract can be assigned as vanadyl non-porphyrin compounds. The fact that no high molecular weight vanadyl porphyrin or non-porphyrin compounds are present in the extracts, indicates that these vanadyl compounds are not removed using pyridine. This raises important questions regarding the chemical nature of the non-extractable vanadyl compounds remaining in the asphaltenes.

Figure 11 shows SEC-HPLC-GFAA data for Cerro Negro crude oil. Figures 11 (b), (c), and (d) show vanadyl compounds being extracted from molecular weight ranges corresponding to 100 to 10,000 daltons, with only low to medium molecular weight (less than 900 daltons) vanadyl compounds present in the extract. Similar data for Wilmington and Prudhoe Bay crude oils are given in Figures 12 and 13 respectively. While these two oils show proportionally more vanadyl compounds being removed from the high molecular weight ranges, the extracts register only vanadyl compounds with molecular weights less than 900 daltons. Prudhoe Bay crude oil extract shows small amounts of high molecular weight vanadyl compounds (greater than 900 daltons) being extracted.

Figure 11. 50/100 Å SEC-HPLC-GFAA Data for a) Standards, b) Cerro Negro Crude Oil, c) Crude Oil After Extraction and d) Crude Oil Extract.
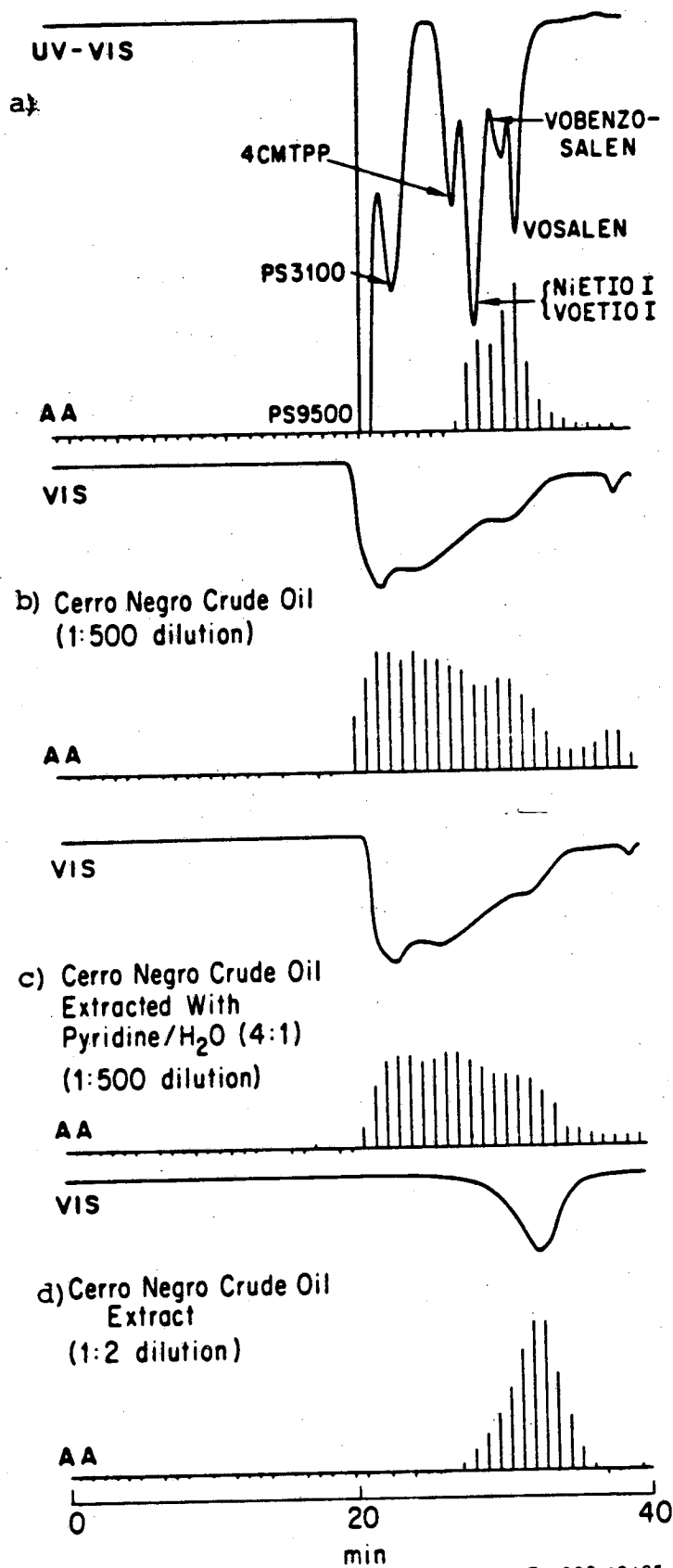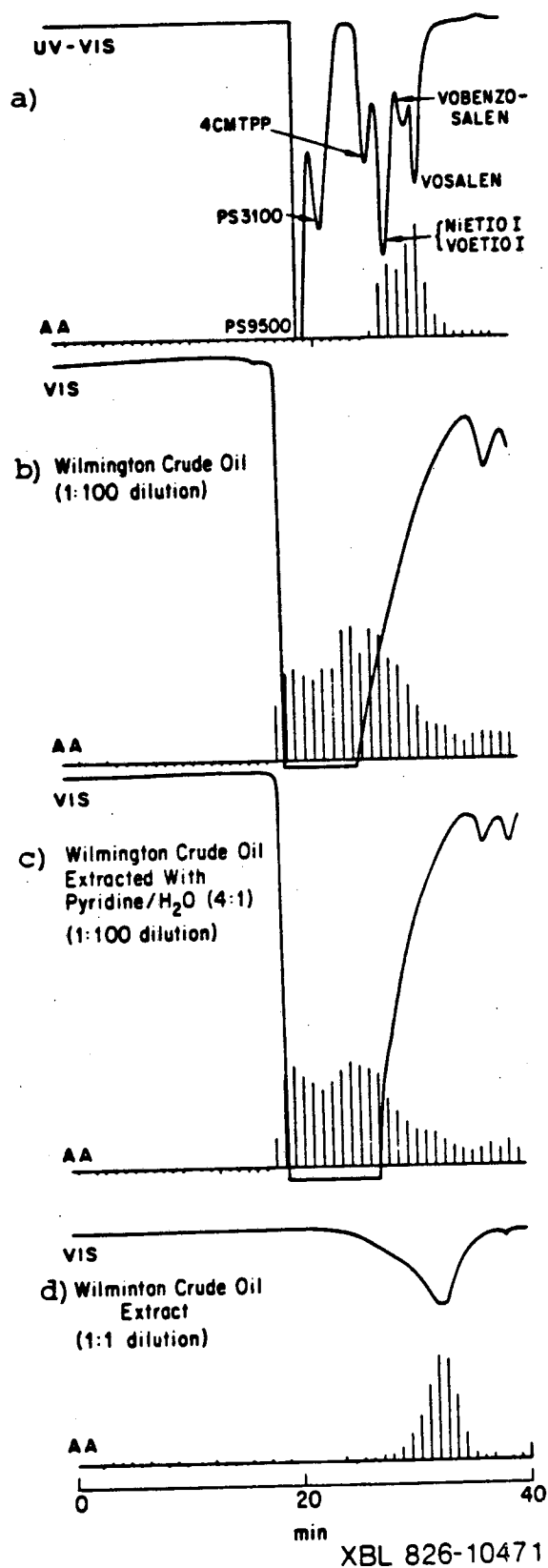
XBL 826-10471

Figure 12. 50/100 Å SEC-HPLC-GFAA Data for a) Standards, b) Wilmington Crude Oil, c) Crude Oil After Extraction, and d) Crude Oil Extract.
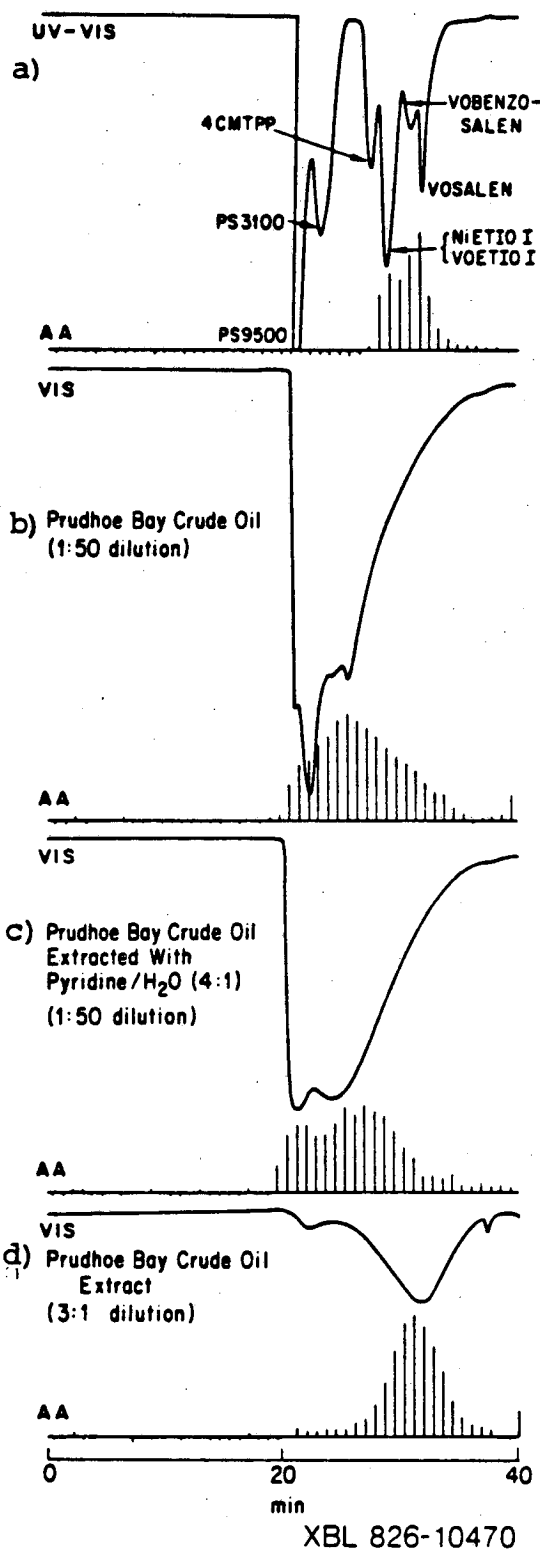
Figure 13. 50/100 Å SEC-HPLC-GFAA Data for a) Standards, b) Prudhoe Bay
Crude Oil, c) Crude Oil After Extraction, and d) Crude Oil Extract.

Comparisons of the four oils, based on the SEC-HPLC-GFAA finger-prints from selective solvent extraction experiments, reveal several important features. Although the concentration of vanadium present in the four crude oils varies widely, each of the oils contains nearly similar percentage in each of the four molecular weight categories. Geochemically this is of importance, because it suggests that a similar mechanism involving incorporation and competition for ligand sites occurs for the four oils. Also, vanadyl compounds remaining in the oils after extraction are evenly distributed between the greater than 2,000 dalton range, and the greater than 900 dalton, less than 2,000 dalton range. This suggests that vanadyl compounds present in these high molecular weight categories are similarly complexed. Of the three oils studied, only Prudhoe Bay crude oil shows any high molecular weight vanadyl compounds present in the extracts, this could be accounted for by a difference in the biogenesis and maturation of this relatively ancient Alaskan heavy crude petroleum.

Molecular weight data for the four heavy crude oils using the 50/100 Å SEC column combination have been summarized in Table 3. This table shows the vanadium concentration (ppm) and percentage distributions for the whole crudes, the oils after extraction, and the extracts in terms of the four molecular weight categories, (i.e., greater than 2000 daltons, between 900 and 2000 daltons, between 400 and 900 daltons, and less than 400 daltons).

Table 3 shows the vanadium percentages for the heavy crude oils, the oils after extraction, and the extracts in lines two, four and eight respectively. These values were calculated using the 50/100 Å SEC cal-

Table 3. Molecular Weight Distributions of Vanadyl Compounds Present in Heavy Crude Oils, Oils After Extraction, and the Extracts as Determined by 50/100 Å SEC-HPLC-GFAA Analysis.

	Molecular Weight	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 oil	V (ppm)	307.[a]	229.	257.	315.	175.	123.	114.	148.	13.8	11.1	9.3	14.3	5.8	5.3	4.3	3.3
	V (%)	27.9[b]	20.0	23.4	28.7	31.3	21.9	20.4	26.4	28.5	22.9	19.1	29.5	31.1	28.6	22.9	17.4
Oil after extraction	V (ppm)	176.	128.	127.	109.	106.	93.0	55.7	25.2	2.6	1.8	1.1	0.9	3.2	2.8	2.1	1.1
	V (%)	32.6	23.7	23.6	20.1	37.9	33.2	19.9	9.0	40.2	28.3	16.8	14.7	34.6	30.6	22.9	11.9
Removed	V (ppm)	131.	92.	130.	206.	69.0	30.0	58.3	123.	11.2	9.3	8.2	13.4	2.6	2.5	2.2	2.2
	V (%)	42.3	41.8	50.7	65.4	39.4	24.4	51.1	83.0	81.1	83.8	88.2	93.7	44.8	47.2	51.1	66.7
Extract	V (ppm)	--	6.0	136.	418.	--	--	74.0	206.	0.3	0.8	7.5	33.5	0.5	0.5	3.1	5.4
	V (%)	--	1.1	24.3	74.6	--	--	26.4	73.6	0.8	1.9	17.8	79.5	5.0	5.0	32.9	57.1

[a] Concentration of metal present at molecular weights greater than 2000 daltons.

[b] Percentage of total metal present at molecular weights greater than 2000 daltons.

bration data from Figure 9, and the digitally recorded histogrammic outputs from Figures 10-13. Figure 9 was used to ascertain retention times for eluting species in each of the four moleclar weight categories. Vanadium percentages were then calculated by summing the histogrammic vanadium outputs in each molecular weight category and dividing by the total histogrammic vanadium output for each oil summed over all four molecular weight categories. The vanadium concentrations (in ppm) were then calculated by multiplying each percentage by the total amount of vanadium present in the heavy crude oils and the oils after five extractions to give lines one and three respectively. The vanadium concentrations for the extracts, appearing in line seven of Table 3 were calculated based on the amount of vanadium removed by extraction from each heavy crude oil. Values for vanadium removal appearing in line five of Table 3 were calculated by subtracting vanadium concentrations after extraction from those concentrations before extraction for each molecular weight category. Percentage appearing on line six of Table 3 were calculated by dividing the vanadium concentration for each molecular weight category by the total vanadium extracted from each crude oil.

Although the total amount of vanadium present in Boscan, Cerro Negro, and Wilmington crude oils varies substantially, the percentages of vanadyl compounds present in each of the four molecular weight categories are very similar. As the second line of Table 3 indicates, these oils have nearly equal percentages of vanadyl compounds in the greater than 2,000 and less than 400 dalton range, and they also contain nearly equivalent percentages of vanadyl compounds with molecular weights between 900 and 2,000 daltons and between 400 and 900 daltons.

These three oils have approximately ten percent less vanadium in the two intermediate molecular weight fractions than in both the greater than 2,000 and less than 400 dalton molecular weight categories. Prudhoe Bay crude oil, unlike the other three crude oils, has increasing percentages of vanadyl comounds with increasing molecular weight for all four molecular weight categories.

As the data on the third and fourth lines of Table 3 show for the crude oils after extraction, the percentages of vanadyl compounds with molecular weights greater than 2,000 daltons increased for all four crude oils. The increases for this molecular weight category ranged from 11 percent for Prudhoe Bay crude oil to 41 percent for Wilmington crude oil, with and average increase of 22 percent for the four oils. The percentages of vanadyl compounds between 900 and 2,000 daltons also increased, ranging from 7 percent for Prudhoe Bay crude oil to 52 percent for Cerro Negro crude oil, while the average increase in this molecular weight category was 25 percent. The percentages for vanadyl compounds with molecular weights between 400 and 900 daltons has decreased by 2 and 12 percent for Cerro Negro and Wilmington crude oils respectively, but remained equal for Prudhoe Bay crude oil and increased by 1 percent for Boscan crude oil. The percentages of vanadyl compounds with molecular weights less than 400 daltons decreased for all four crude oils, ranging from 30 percent for Boscan crude to 66 percent for Cerro Negro crude oil, with an average decrease of 44 percent.

The fifth line of Table 3 shows the weight percentages of vanadyl compounds which have been removed from the four molecular weight categories for each of the four crude oils. While each of the oils shows

a trend towards increased removal at decreased molecular weights (especially less than 400 daltons), Wilmington crude oil shows significantly more vanadium removal over all four molecular weight categories.

The fact that extraction of vanadyl compounds from the low molecular weight categories was greater than that from the high molecular weight categories is not surprising. Vanadyl porphyrin and non-porphyrin compounds in the low molecular weight, maltene fraction of the crude oils occur freely suspended, and are therfore more likely to form ligational complexes. Vanadyl compounds in the high molecular weight, asphaltene fraction can be strongly complexed to the asphaltenes, making removal more difficult and and in some cases impossible.

Lines seven and eight appearing in Table 3 show the amounts and percentages of vanadyl compounds present in the four molecular weight categories for each of the crude oil extracts. As the last line of Table 3 indicates, the majority of the vanadyl compounds occurring in each extract exist at molecular weights less than 400 daltons. Cerro Negro crude oil extract contains no vanadyl compounds above molecular weights of 900 daltons. Of the other three crude oil extracts, only Prudhoe Bay extract has significant amounts of vanadyl compounds at molecular weights greater than 900 daltons.

This finding is important because it reveals that although vanadyl porphyrin compounds are present in the heavy crude oil extracts, they account for only 18 to 33 percent of the total vanadium present. The majority of the vanadyl compounds in the extracts are present as low molecular weight vanadyl non-porphyrin compounds. Demetallation of the pyridine extracts conceivably prohibits identification of these

compounds due to their instability in dilute acid solutions.

The lack of high molecular weight vanadyl compounds in the crude oils extracts, with the exception of Prudhoe Bay crude oil, suggests that if in fact distinct species are present, removal of these highly conjugated molecules using coordinating solvents will be difficult.

b. Nickel Compounds

Data comparing HPLC–GFAA vanadium and nickel distributions for Boscan and Cerro Negro crude oils is shown in Figure 14. Although the primary emphasis in this study was placed on characterization of the vanadyl compounds, these sets of chromatograms are included both to compare vanadyl and nickel compound distributions and to demonstrate the versatility of element-specific HPLC–GFAA analysis.

The elution behavior of the standards on the 50/100 Å column combination is repeated in Figure 14 (a). Figure 14(b) compares the nickel and vanadyl compound molecular weight profiles for Boscan crude oil obtained using the 50/100 Å column combination. This figure shows separations for Boscan crude oil, with visible absorbance monitored at 408 nm, and with vanadium and nickel GFAA histograms (monitored at 318.4 nm and 232.0 nm respectively) as indicated. While nickel gives a rather symmetric profile, the vanadyl compound profile extends into both the higher and lower molecular weight ranges, with predominantly more vanadium associated with the asphaltenes. The nickel and vanadyl compound profiles for Cerro Negro crude oil are compared in Figure 11 (c). Cerro Negro crude oil similarly registers significantly more nickel at low molecular weights. However, the profile does indicate that Cerro Negro crude oil contains some very high molecular weight nickel
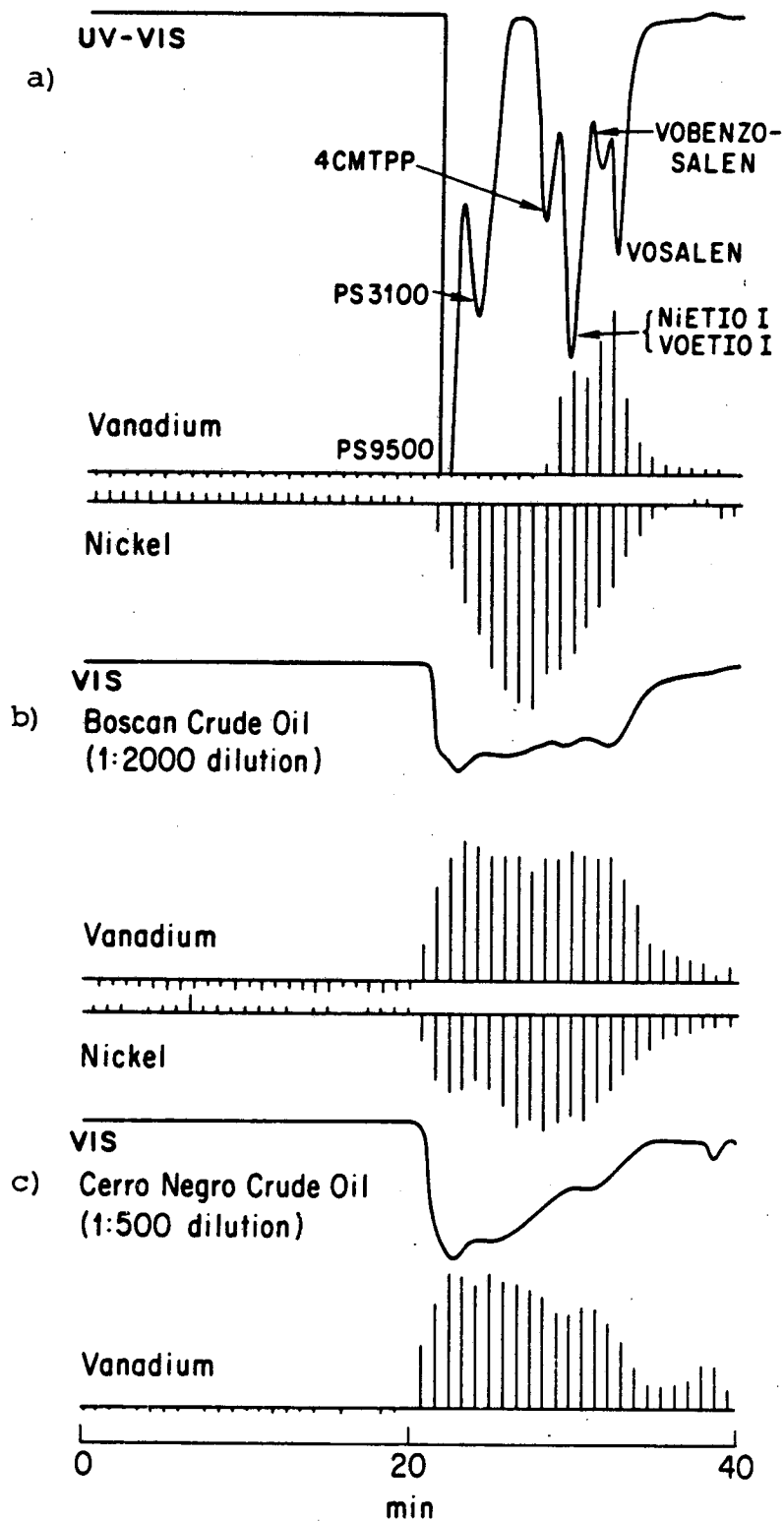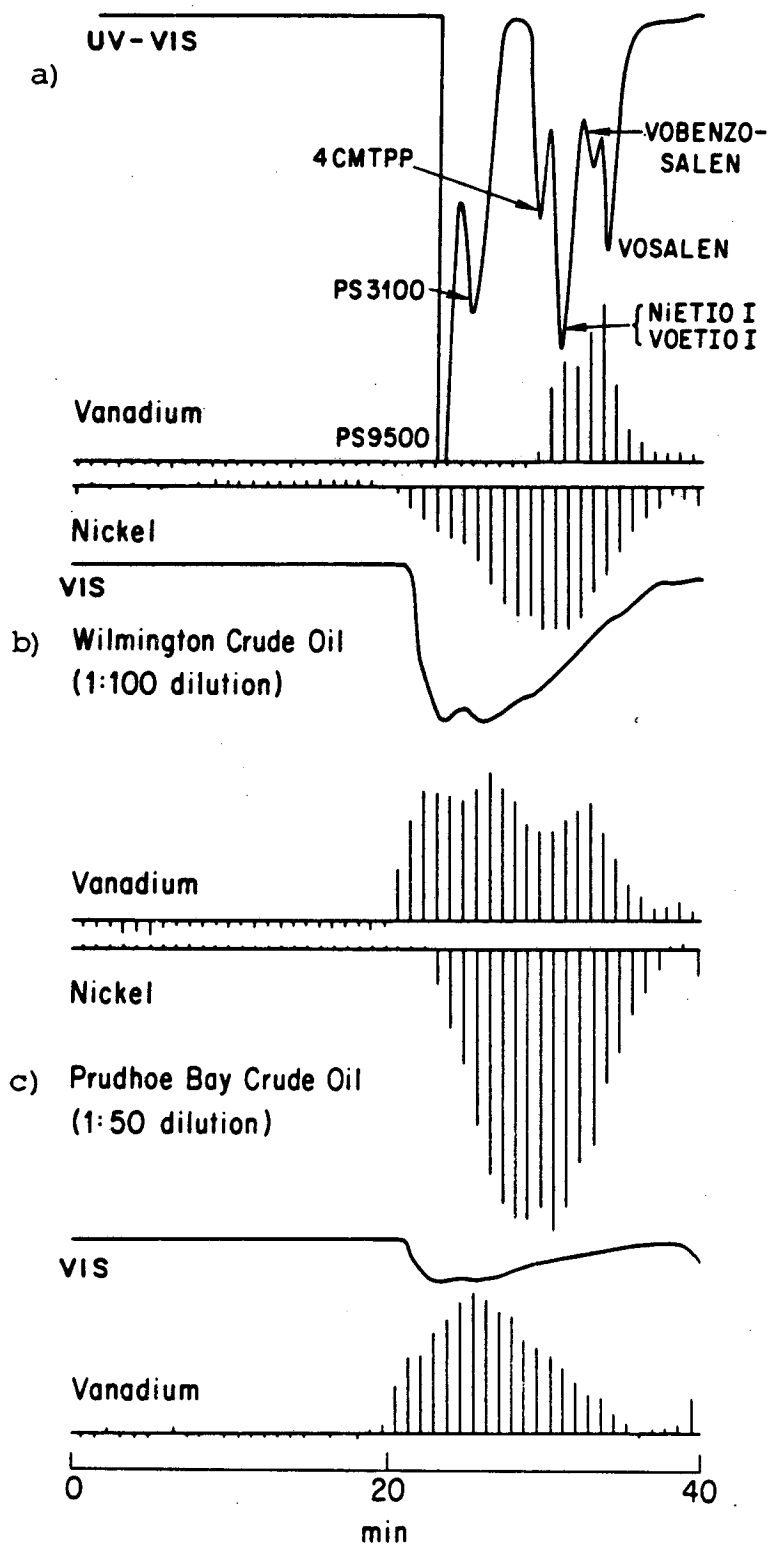
Figure 14, 50/100 Å SEC-HPLC-GFAA Data comparing Vanadium and Nickel Distributions for a) Standards, b) Boscan Crude Oil, and c) Cerro Negro Crude Oil.

compounds absent from Boscan crude oil. This figure demonstrates that these two oils contain proportionally more nickel compounds at molecular weights normally associated with metallo-porphyrins.

Similar data comparing Wilmington and Prudhoe Bay crudes are shown in Figure 15 (a) and (b) respectively. These chromatograms indicate that vanadyl compounds elute over a much broader time period, favoring the higher molecular weights, while the nickel profiles show a much smaller range of eluting times, centered at lower molecular weights.

Table 4 summarizes this data in terms of the percentages of vanadium and nickel with molecular weights greater than and less than 900 daltons. These values have been calculated by multiplying the fraction of the histogrammic GFAA outputs with retention times greater than and less than 900 daltons, as determined using the model vanadyl porphyrin and non-porphyrin compounds (Fig. 9), by the total amount of vanadium or nickel present in the crude oil.

With the exception of Boscan crude oil, all of the oils contain greater percentages of vanadyl compounds at molecular weights above 900 daltons and proportionally more nickel compounds at molecular weights less than 900 daltons. Prudhoe Bay crude oil shows the greatest separation between nickel and vanadyl compounds, with over 70 percent of the nickel occurring at molecular weights less than 900 daltons, and nearly 60 percent of the vanadyl compounds at molecular weights above 900 daltons. This table also reveals that as the concentrations of vanadium in the crude oil decreases, the percentage of nickel at molecular weights less than 900 daltons increases. This could indicate a competition for porphyrin sites, or preferential bonding of vanadyl ion to sulfur

Figure 15. 50/100 Å SEC-HPLC-GFAA Data Comparing VAnadium and Nickel Distributions for a) Standards, b) Wilmington Crude Oil, and c) Prudhoe Bay Crude Oil.

Table 4. Molecular Weight Distributions of Vanadyl and Nickel Compounds Present in Heavy Crude Oils by 50/100 Å SEC-HPLC-GFAA Analysis.

Molecular Weight	Boscan		Cerro Negro		Wilmington		Prudhoe Bay	
	>900	<900	>900	<900	>900	<900	>900	<900
Vanadium (ppm)	527 [a]	573	298	262	24.9	23.6	11.1	7.6
(%)	47.9 [b]	52.1	53.2	46.8	51.4	48.6	59.7	40.3
Nickel (ppm)	56.5 [a]	48.5	52.0	66.0	24.4	36.0	2.6	6.7
(%)	53.8 [b]	46.2	44.1	55.9	40.4	59.6	23.8	71.7

[a] Concentration of metal present at molecular weights greater than 900 daltons.

[b] Percentage of total metal present at molecular weights greater than 900 daltons.

present in the asphaltenes, and preferential bonding of nickel to nitrogen ligands as has been reported.[75]

C. PAC-HPLC-GFAA

Because Table 3 indicates that nearly all of the vanadyl compounds present in the pyridine/water extracts have molecular weights less than 900 daltons, further characterization of this fraction was accomplished. Gradient elution chromatography, which separates molecules according to polarity, has been used to molecularly characterize and fingerprint the heavy crude petroleum pyridine extracts. In practice, increasingly polar solvent gradients were pumped through the column, with less polar compounds eluting first, due to the interaction of polar functional groups with the solute molecules.

Initially a silica packed column was used; however, a polar amino-cyano (PAC) column provided both improved separation and quicker equilibration times. Therefore, all separations reported in this study were accomplished using the PAC column.

The PAC-HPLC-GFAA data obtained for Boscan crude extract are shown in Figure 16. Figure 16 (a) indicates where several of the model vanadyl porphyrin and non-porphyrin compounds elute. The non-polar NiEtio I and VOT3MePP elute before the slightly more polar VOTPP and VOEtio I porphyrins, while the polar vanadyl non-porphyrins, VOTADA, VOBZEN, and VOBenzosalen, elute between 30 and 35 minutes. The vanadyl porphyrin complexes were monitored at 400 nm, while the vanadyl non-porphryrin complexes were monitored at 320 nm. The earliest eluting peak evident in all of the chromatograms represents the solvent, methylene chloride.
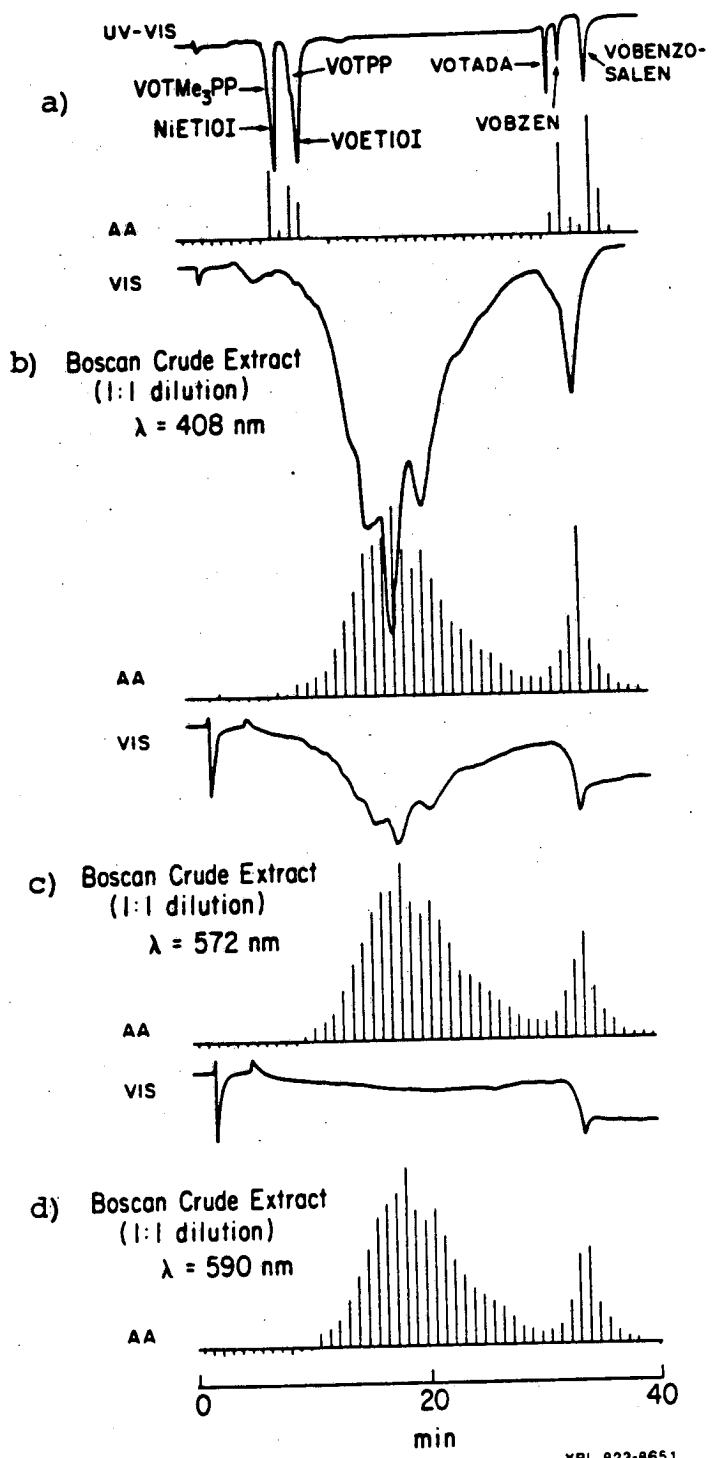
a)

UV-VIS

VOTMe₃PP →
NiETIOI →
VOTPP
VOETIOI
VOTADA →
VOBZEN
VOBENZO-SALEN

AA

VIS

b) Boscan Crude Extract
(1:1 dilution)
$\lambda = 408$ nm

AA

VIS

c) Boscan Crude Extract
(1:1 dilution)
$\lambda = 572$ nm

AA

VIS

d) Boscan Crude Extract
(1:1 dilution)
$\lambda = 590$ nm

AA

0   20   40
min

XBL 823-8651

Figure 16. PAC–HPLC–GFAA Data for a) Standards, b) Boscan Crude Oil Extract Monitored at 408 nm, c) at 572 nm, and d) at 590 nm.

The lower portion of Figure 16 (a) shows the histogrammic vanadium outputs. With the exception of NiEtio I porphyrin, all the other standards register vanadium histograms.

Figures 16 (b), (c), and (d) show PAC-HPLC-GFAA fingerprints for Boscan crude oil extract, with visible absorbance measured at 408 nm, 572 nm, and 590 nm respectively. Figure 16 (b) indicates substantial metallo-porphyrin compounds present in the extract, based on the visible absorbance at 408 nm. These elute from approximately 10 to 30 minutes, with a late eluting peak occurring near 35 minutes. Also shown in the lower portion of Figure 16 (b) is the vanadium histograms of Boscan crude oil extract separated using the PAC column. The paralleled visible absorbance and vanadium histograms suggest the presence of vanadyl porphyrins in the extract. This is confirmed by Figure 16 (c), since VOEtio, VODPEP, and VORhodo porphyrins are known to have characteristic absorbances at 572 nm. However, as Figure 16 (c) indicates, only one peak occurs at a wavelength of 590 nm. Of the three vanadyl porphyrin classes, only VORhodo porphyrin absorbs at this wavelength. Thus, this latter eluting peak can be assigned to VORhodo pophyrin, while the VOEtio and VODPEP porphyrins can be assigned to the earlier eluting vanadyl porphyrin peaks. This confirms HPLC obtained results for VOEtio and VODPEP porphyrins.[43,63] The HPLC identification of VORhodo porphyrin in crude oil extracts has not been reported.

The vanadyl non-porphyrin compounds, VOBZEN, VOTADA, and VOBenzosalen, could conceivably be present in Boscan crude oil extract, since they elute in the vicinity of VORhodo porphyrin. All of the vanadyl porphyrin standards elute before the bulk of the VOEtio and VODPEP porphy-

rins contained in the extract, suggesting that the model vanadyl porphy-rins are less polar than the vanadyl porphyrin compounds present in the extract. The broad peak shapes observed in the extracts are due to the presence of various peripherally substituted functionalities attached to the porphyrin ring structure. These also account for the increased polarity of the vanadyl porphyrin compounds present in the extracts.[63]

Data comparing Boscan and Cerro Negro crude oil extracts are shown in Figures 17 (b) and (c) respectively. Figure 17 (a) repeats the standard compound data from the previous figure. Based on a comparison to the Boscan PAC-HPLC-GFAA fingerprint, it can be stated that Cerro Negro crude oil extract also contains VOEtio, VODPEP, and VORhodo porphyrins. However, unlike Boscan extract, Cerro Negro extract shows an early eluting vanadyl compound peak at 5 minutes, and a nickel porphyrin[43] visible peak at 7 minutes, clearly distinguishing the two extracts.

Data comparing Prudhoe Bay and Wilmington crude oil extracts are shown in Figures 18 (b) and (c). Evident in Figure 18 (b) is the fact that Prudhoe Bay extract contains no VODPEP, VOEtio, and VORhodo porphyrins. However, it does contain an early eluting vanadyl compound peak, accounting for all of the vanadium present in the extract, followed by a broad nickel porphyrin peak. Figure 18 (c) shows similar peaks for Wilmington crude oil extract, which registers an early eluting vanadyl compound peak, followed by a broad peak containing the extracted nickel porphyrins. This extract also shows the presence of VOEtio and VODPEP porphyrins; however, due to the lack of vanadium histograms near 35 minutes, VORhodo porphyrins do not appear to be present. The visible absorbance shown for Wilmington and Prudhoe Bay crude oils near 35
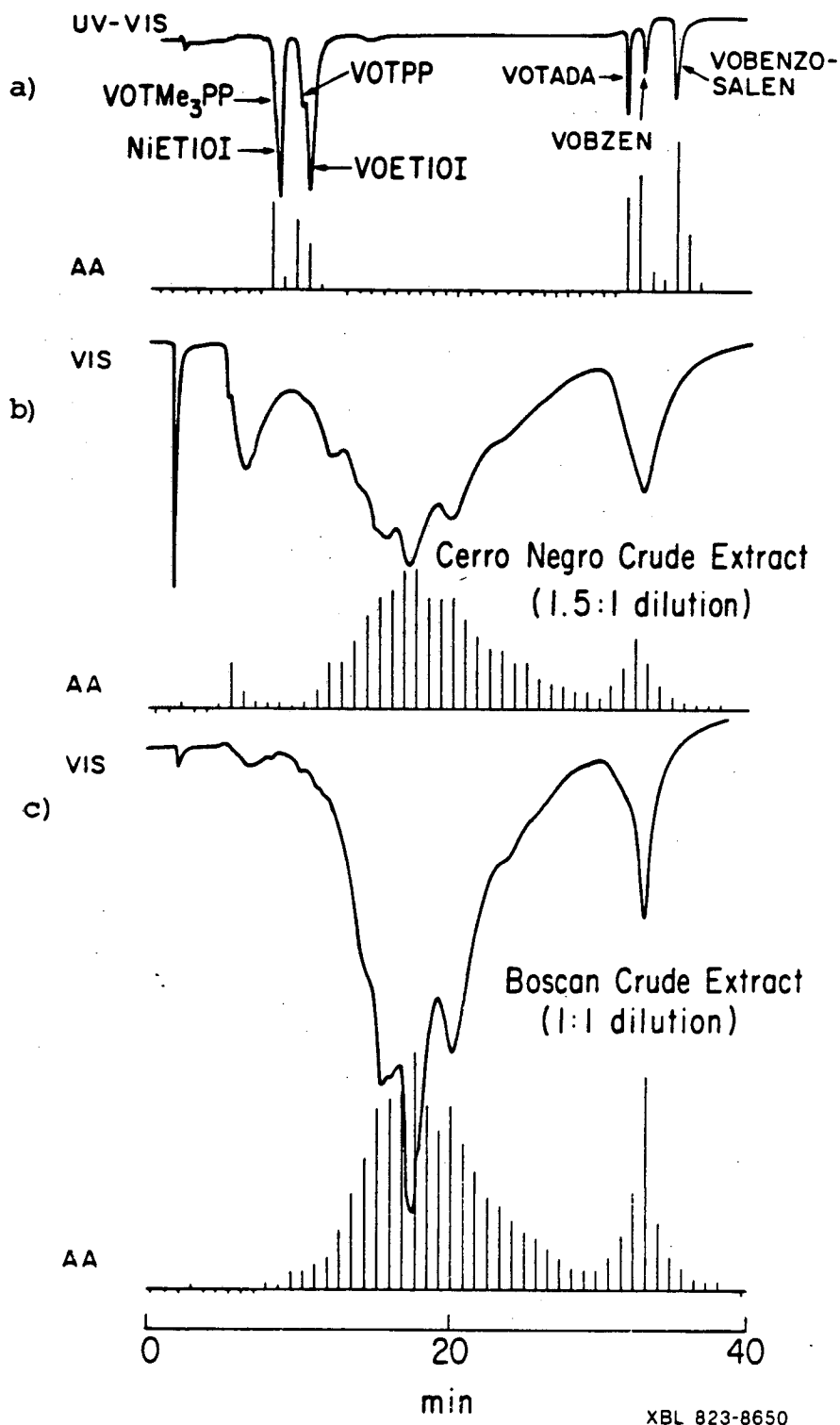
Figure 17. PAC-HPLC-GFAA Data for a) Standards, b) Cerro Negro Crude Oil Extract, and c) Boscan Crude Oil Extract.
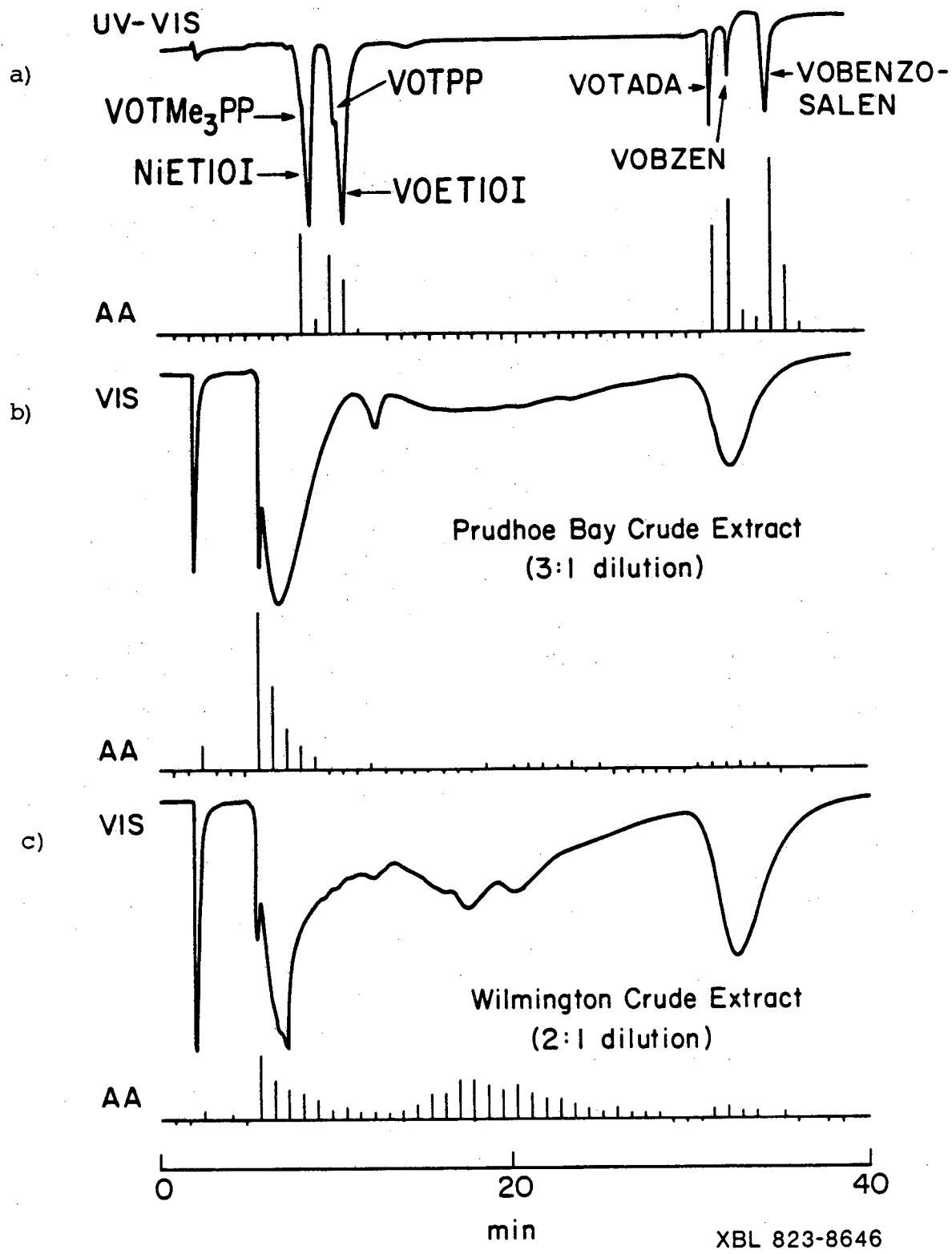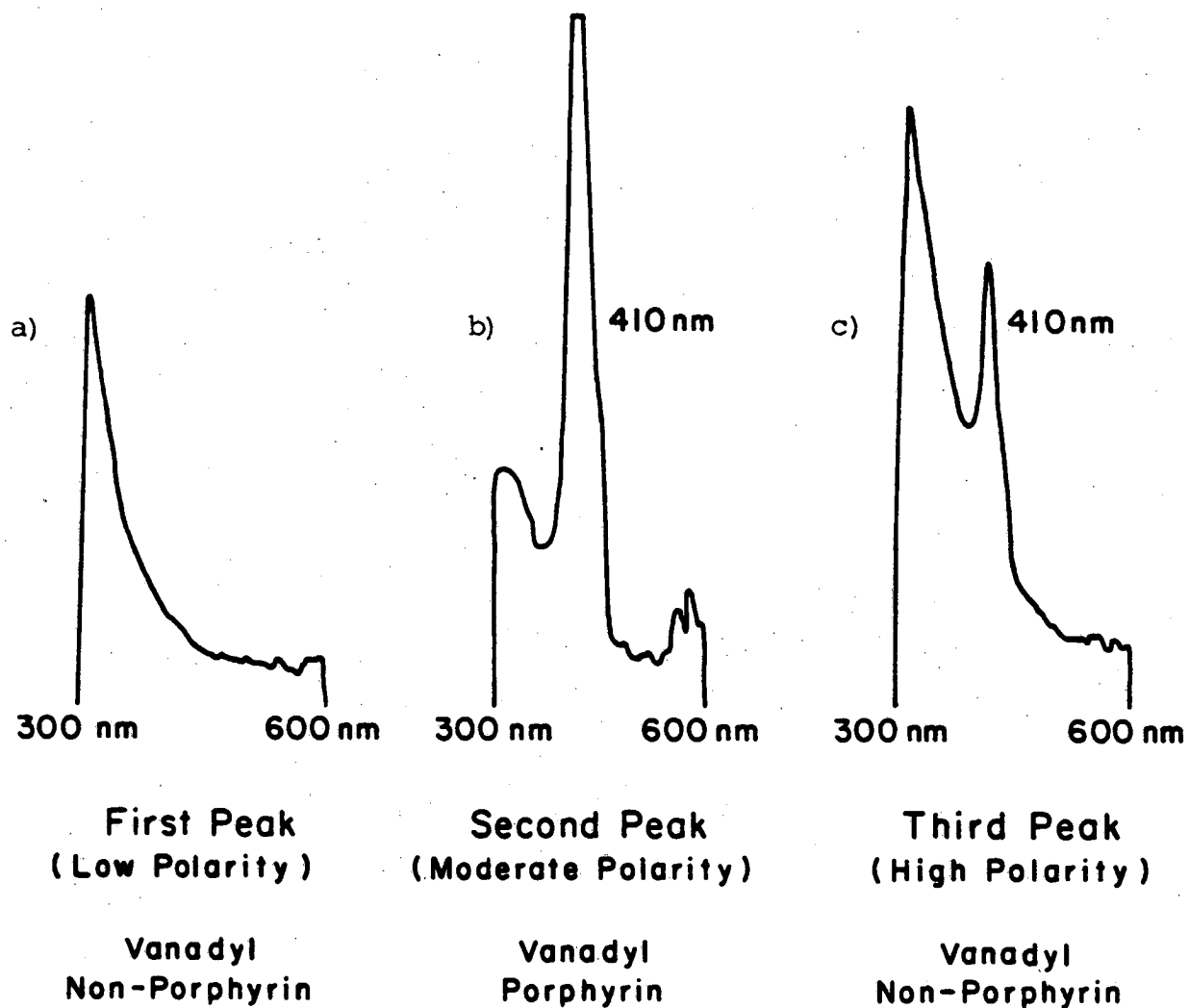
Figure 18. PAC-HPLC-GFAA Data for a)Standards, b) Prudhoe Bay Crude Oil Extract, and c) Wilmington Crude Oil Extract.

minutes is probably due to nickel porphyrin and non-porphyrin compounds.

The extraction of non-polar vanadyl compound has been reported in the literature. Dickson,[59,60] using ESR to characterize crude oil fractions separated by liquid chromatography, has found an environment corresponding to $(VO)S_4$ to be associated with an early eluting vanadyl non-porphyrin compound. Further, metallo-porphyrin demetallation procedures were not successful with this fraction, indicating that vanadyl ion was coordinated to a system other than typical porphyrin ligands.

Rapid-scan spectroscopy (RSS) UV-Vis analysis of this early eluting vanadyl compound peak indicates that the maximum absorbance occurs at 300 nm, confirming the presence of vanadyl non-porphyrin compounds in Cerro Negro, Wilmington, and Prudhoe Bay crude oil extracts. Figure 19 (a) shows HPLC-RSS data, from 300 to 600 nm obtained for this early eluting peak. RSS analysis of the vanadyl porphyrin peaks eluting from 10 to 30 minutes, shown in Figure 19 (b) reveals only characteristic vanadyl porphyrin spectra, and no other UV absorbing vanadyl non-porphyrin compounds. Similarly, RSS-UV-Vis analysis, shown in Figure 19 (c), of the peak occurring near 35 minutes reveals that this peak consists of a mixture of both vanadyl porphyrin (maximum absorbance 410 nm) and vanadyl non-porphyrin (maximum absorbance 265 nm) compounds. This class of compounds conceivably has an environment corresponding to $(VO)N_2O_2$ or $(VO)N_4$.

Thus, RSS has demonstrated the presence of at least two classes of extractable vanadyl non-porphyrin compounds. One class consists of a relatively non-polar vanandyl non-porphyrin compound(s) with maximum UV-Vis absorabce at 300 nm. This non-porphyrin was found to be present

a) First Peak
(Low Polarity)

Vanadyl
Non-Porphyrin

b) 410nm
Second Peak
(Moderate Polarity)

Vanadyl
Porphyrin

c) 410nm
Third Peak
(High Polarity)

Vanadyl
Non-Porphyrin

XBL 8211-11950

Figure 19. Representative Rapid Scan Spectroscopy (RSS) Data Obtained for the PAC-HPLC-GFAA separated pyridine extracts.

in Cerro Negro, Wilmington, and Prudhoe Bay crude oil extracts. The other class consists of a relatively polar vanadyl non-porphyrin compound with maximum UV-Vis absorbance occurring at 265 nm, and present in both Boscan and Cerro Negro crude oils.

The apparent deficiency of vanadyl non-porphyrin compounds in Boscan and Cerro Negro crude oil extracts is interesting. Table 3 indicates that both of these extracts should contain nearly three times more vanadyl non-porphyrin than vanadyl porphyrin compounds. However, from the PAC-HPLC-GFAA chromatograms and UV-Vis rapid-scan analysis, this is not apparent. This discrepancy could be due to irreversible loss of polar vanadyl non-porphyrin compounds on the PAC column. VOSalen eluted at retention time of 60 minutes, much later than that of the other vanadyl non-porphyrin compounds. If more polar vanadyl compounds are present in the extracts, irreversible binding to the PAC column may have occurred. Column degradation over a period of approximately six months suggests that some of the more polar vanadyl compounds were retained on the column.

Studies have indicated that irreversible loss of vanadyl compounds from petroleum samples using gradient elution chromatography with strongly polar solvents can range to 20 percent.[59,60] When polar solvents such as isopropanol were pumped through the column after each extract injection, no vanadyl compounds eluted. However, after a series of extract injections, broad UV absorbing, vanadium containg bands were observed. These very polar vanadyl non-porphyrin compounds may deposit on the column in a manner similar to that of deposition on processing catalyst. Molecular identification of these very polar vanadyl non-

porphyrin compounds is highly important in this respect.

V. DISCUSSION

A. Biogeochemical Information

Studies have indicated that crude oils which are rich in vanadium have high asphaltene contents.[13,25] Figure 20 shows that for the oils analyzed in this study, vanadium concentration increases exponentially with asphaltene content. Interestingly, this curve does not level off at asphaltene concentrations of 20 to 25 percent, suggesting that asphaltenes have an unsaturated capacity to complex vanadyl ion. A plot of nickel concentration versus asphaltene content does not show similar behaviour. Above 10 to 15 percent asphaltene concentration, nickel content does not increase. This indicates that asphaltenes have a much greater capacity to coordinate vanadyl ion, and that nickel saturation of asphaltenes occurs more readily.

HPLC–GFAA comparisons of the vanadyl and nickel component profiles shown in Figures 14 and 15 and summarized in Table 4, reveal that most of the nickel is associated with porphyrinic molecular weights, while the most of the vanadium is associated with asphaltenic molecular weights. The capacity of asphaltenes to incorporate vanadyl ion has been investigated. Erdman and Harju[41] have demonstrated that asphaltenes in benzene solutions can incorporated inorganic vanadyl salts, in amounts bearing no relationship to the original vanadium concentration. Retention of nickel (II) was found to be negligible in comparison.

Figure 21 shows a plot of sulfur percent versus asphaltene content for the oils analyzed. Linearity indicates that sulfur and asphaltene content are strongly related. This suggests the presence of sulfur
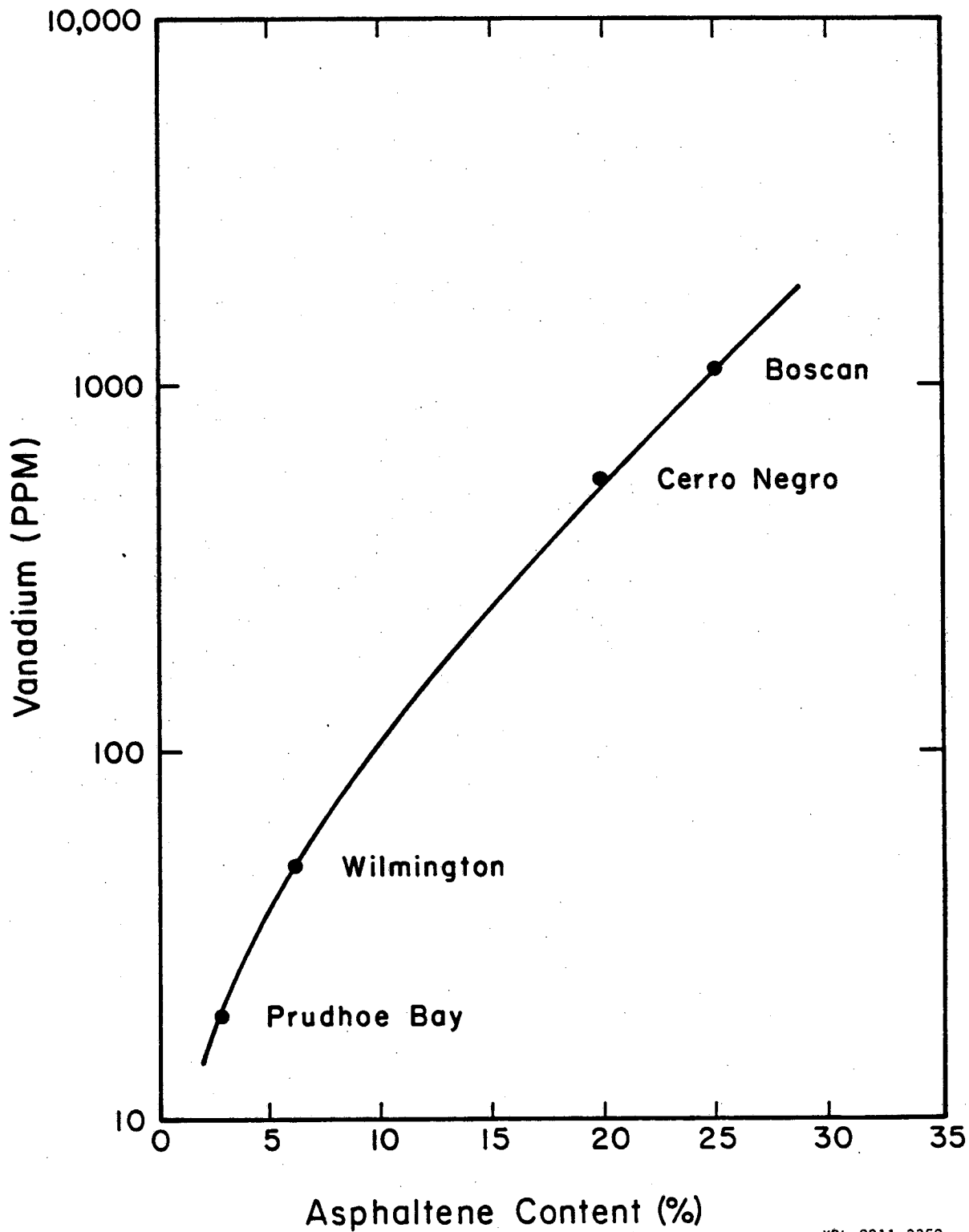
XBL 8211-3359

Figure 20. Plot of Log Vanadium Concentration (ppm) Versus Asphaltene
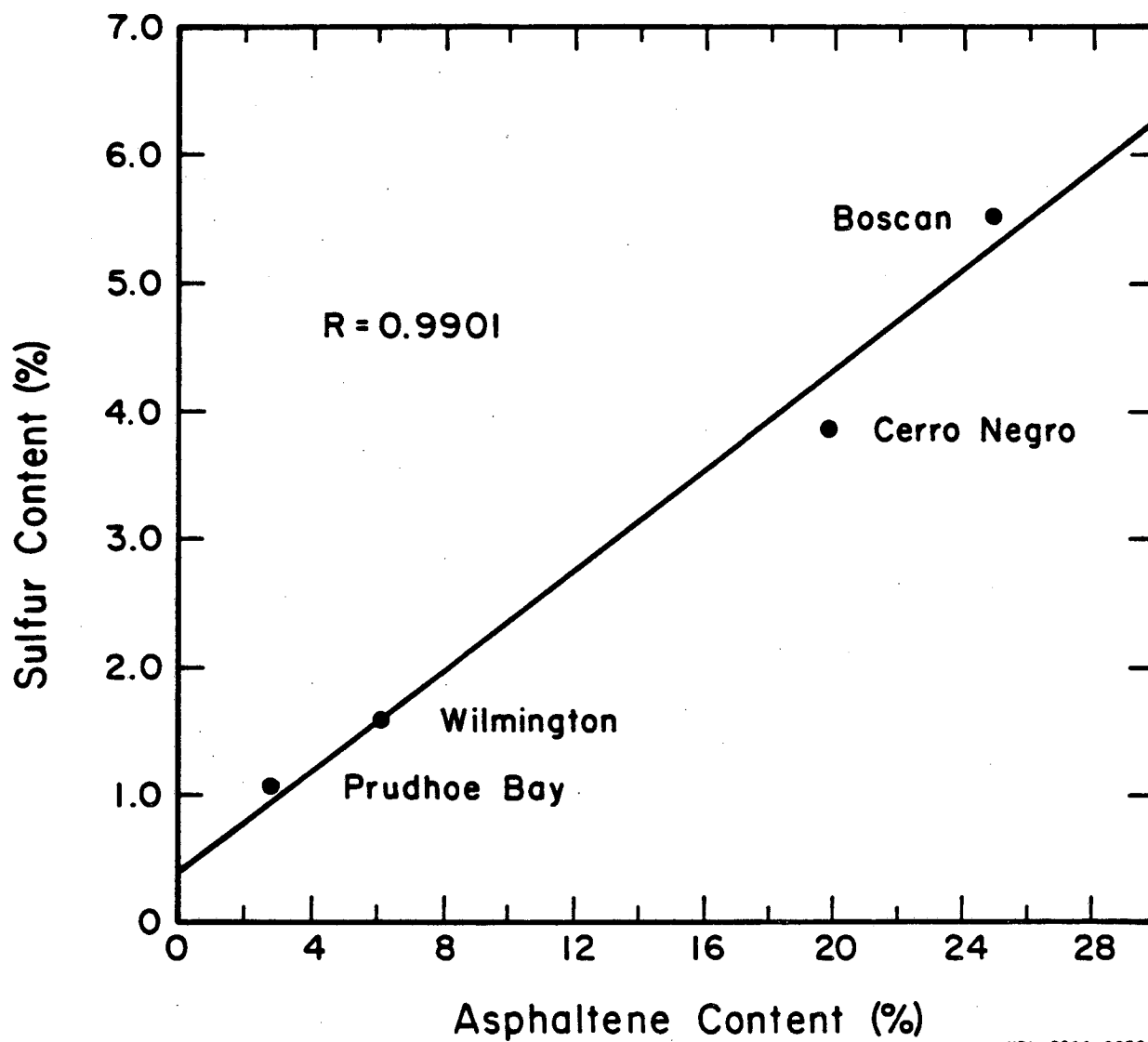Content, for Boscan, Cerro Negro, Wilmington, and Prudhoe Bay Crude Oils.

Figure 21. Plot of Sulfur Content Versus Asphaltene Content for Boscan, Cerro Negro, Wilmington, and Prudhoe Bay Crude Oils.

coordination sites in asphaltenes which selectively coordinate vanadyl ion, rather than nickel ion. Recent studies[12,76] have indicated that petroleum asphaltenes, irrespective of the origin, possess a sulfur polymeric framework, with 65 to 90 percent of the sulfur present as sulfide bonds.[12]

Radchenko[75] has compared vanadyl and nickel porphyrin concentrations in high and low sulfur crude oils, and has found that low sulfur crude oils contain proportionally greater percentages of nickel porphyrins, while high sulfur crude oils contain proportionally more vanadyl porphyrins. Data presented in Table 4, coupled with the PAC-HPLC-GFAA chromatograms from Figures 17 and 18, confirm this finding. Boscan crude oil (5.50 percent sulfur) has been shown to be rich in vanadyl porphyrins, while Prudhoe Bay crude oil (1.06 percent sulfur) is deficient in vanadyl porphyrins and relatively rich in nickel porphyrins.

Based on this type of analysis, Radchenko has concluded that genesis of vanadyl and nickel porphyrins occur by different methods. Radchenko has proposed that only the nickel porphyrins are of primary origin, and has suggested that the vanadyl porphyrins are secondary products, formed during the maturation of the petroleum deposit.

A proposed route which allows for the late incorporation of vanadyl ion, suggests that vanadium, heteroatoms, and asphaltenes arise through the action of aerobic, sulfate-reducing bacteria in the reservoir.[12,76-78] This theory has the advantage of explaining the association between vanadyl non-porphyrin compounds, sulfur, and asphaltenes, and excludes difficult reactions required in the traditional diagenetic scheme. Excess vanadyl non-porphyrin compounds could then

serve as metallating reagents for the porphyrins,[54] derived from chloro-
phyll "a" as proposed,[42] or synthesized from bacteria.[78]

Another proposed mechanism [75] involves the residual enrichment of
heavy fractions resulting from the migration of light components during
maturation. This would account for the increases of both asphaltene and
sulfur content. Vanadium could then be incorporated from marine organ-
isms or through acid depolymerization of polymeric vanadates present in
the crust of the earth.[41,54]

Regardless of the method of incorporation, vanadyl complexes
present in the asphaltenes must be regarded as more stable than vanadyl
porphyrins. Complexation to the asphaltenes either increases the sta-
bility of the low molecular weight vanadyl non-porphyrin compounds, or
prevents competition with other coordinating ligands present in the
oils. This study has indicated that substantial quantities of these low
molecular weight vanadyl compounds can be extracted from the asphal-
tenes. The identity and stability of the extractable and non-
extractable complexes is important both technologically and geochemi-
cally.

This study indicates that vanadyl compound molecular weight distri-
butions are independent of vanadium concentration. However, the types
of vanadyl complexes present in each oil have been shown to vary consid-
erably. This suggests vanadyl compounds may possibly serve as important
biogeochemical markers. Molecular identification of the two types of
extractable vanadyl non-porphyrin compounds should aid in the clarifica-
tion of bio-evolutionary processes affecting heavy crude petroleum depo-
sits.

Table 5[79,80] summarizes biogeochemically important parameters for the four heavy crude oils. Correlations involving geological age and depth of burial with vanadium concentration are inconsistent, confirming previous findings,[41] and suggesting that a mechanism other than strictly time and temperature is repsonsible for incorporation of vanadyl ion into heavy crude petroleums.

B. Identification of Oil Spills by HPLC-GFAA Analysis

Both infrared spectroscopy[81,82] and gas chromatography[83,84] have been widely used for oil spill characterization in the marine environment. However, weathering often results in the partial dissolution and evaporative loss of the light components of the oil, altering the spectral and chromatographic patterns of the spilled oils. Positive identification in cases of severe weathering (more than nine days at sea) is currently doubtful.[85]

A more direct approach depends on the analysis of oils and pollutants for trace metal content.[86] Because the majority of the trace metals are associated with the heavy components of the oils and these are not seriously affected by weathering, trace metal analysis has been shown to be a useful technique for oil spill identification.[87] This suggests that HPLC-GFAA fingerprinting is a potentially useful technique for matching weathered oil samples with unweathered oils.

This study has demonstrated that each heavy crude oil has a unique HPLC-GFAA trace metal fingerprint. If a large library of these fingerprints is assembled, this method could potentially be used to ascertain the age, depth of burial, and exact field of origin of both weathered

Table 5. Biogeochemically Important Parameters Involving Heavy Crude Oil Diagenesis and Maturation.

Oil	Vanadium Concentration (ppm)	Asphaltene Content (ppm) [a]	Sulfur Content (%) [b]	Geological Age [c]	Date of Origin (x10^6 years)	Depth (m) [c]
Boscan	1100	25.0	5.50	Ogliocene/Eocene	26 – 54	840
Cerro Negro	550	20.0	3.85	Miocene/Pliocene	2.5 – 26	1800
Wilmington	49	6.2	1.55	Miocene/Pliocene	2.5 – 26	900
Prudhoe Bay	19	2.9	1.06	Paleogene/Cretaceous	65 – 136	900

[a] Reference 79

[b] Reference 80

[c] Reference 75

and un-weathered petroleum samples.

C. Applications Utilizing SEC-HPLC-GFAA Analysis

1. Removal of Trace Metals from Processing Feedstocks

Several findings in this study have direct application to current problems involving catalyst deactivation, and trace metal removal. SEC-HPLC-GFAA analysis has shown that the majority of the extractable vanadyl non-porphyrins occurring in heavy crude oils have molecular weights less than that of the vanadyl porphyrins. It is probable that a percentage of these low molecular weight vanadyl non-porphyrin compounds are less stable than the vanadyl porphyrins. This finding is important because it implies that competition experiments, based on the use of polymeric ligands capable of selectively removing vanadyl ion from its indigenous state, are worth investigating.[8]

Although the chemical nature of the non-extractable vanadyl non-porphyrins remaining in the asphaltenes has not been elucidated, it is likely that a substantial percentage of these compounds exist as "trapped" low molecular weight vanadyl non-porphyrin compounds as has been suggested.[53] If these "trapped" vanadyl non-pophyrin compounds can be released from coordination to the asphaltenes, selective removal of vanadyl ion from heavy crude petroleums will become a more likely possibility.

SEC-HPLC-GFAA analysis should prove useful for continous, on-line characterization of heavy crude oil and residual desulfurization, denitrogenation, and cracking process streams. Currently SEC is used to provide saturate, aromatic, resins, and asphaltene ratios, for the

optimization of processing conversions.[76] In a similar manner, SEC-HPLC–GFAA analysis can be used to monitor, on-line, the molecular weight distributions of vanadyl compounds present in the various stages of processing. Further, HPLC–GFAA analysis provides a rapid, sensitive, and non-destructive detection method for the laboratory study of sulfur/vanadium association. Reaction mixtures can be quickly and accurately analyzed to give the amounts and classifications of vanadyl compounds of interest.

2. Exploration of Petroleum Deposits

Of the four oils analyzed, Wilmington crude oil contained the greatest percentages of low molecular weight vanadyl non-porphyrin compounds. This fact was reflected in the highest percentages of vanadyl compound removal using pyridine. HPLC–GFAA fingerprints should provide useful information with regard to prospecting for suitable heavy crude petroleum feedstocks. If a large percentage of certain vanadyl compounds signifies less catalyst deactivation, this criteria could be used to select prefered heavy crude oil feedstocks. Thus, HPLC–GFAA analysis should provide important and useful information relating to the exploration of heavy crude oil deposits.

VI. CONCLUSIONS

A. Summary

Element-specific HPLC–GFAA analysis provides a convenient and sensitive technique for the molecular characterization of vanadyl compounds present in heavy crude petroleums. Molecular weight and polarity separations reveal unique fingerprints for each oil analyzed, and allow characterization, based on comparisons to model vanadyl compounds, of vanadyl porphyrin, and more importantly, vanadyl non-porhyrin compounds. A major advantage of HPLC–GFAA analysis is the non-destructive nature of this technique, which preserves important differences between vanadyl and nickel compounds, and does not contribute to the creation of complicating artifacts. The HPLC–GFAA technique should prove extremely useful in the eventual identification of vanadyl non-porphyrin compounds.

B. Conclusions

In conclusion, the major findings of this study include:

(1) Although the concentration of vanadium in the four oils varies dramatically, molecular weight distributions, from 100 to greater than 2,000 daltons, are similar for each of the oils.

(2) Low molecular weight vanadyl porphyrin and non-porphyrin compounds are selectively extracted, using pyridine, from the asphaltenes of each oil.

(3) No high molecular weight vanadyl compounds are extracted. These compounds conceivably account for a significant percentage of the non-extractable vanadyl non-porphyrin compounds present in the oils.

(4) PAC-HPLC-GFAA fingerprints reveal that the distribution of vanadyl compounds present in the four extracts varies greatly. Boscan extract contains predominantly vanadyl porphyrin compounds, while Cerro Negro and Wilmington extracts contain both vanadyl porphyrin and non-porphyrin compounds. Prudhoe Bay crude oil extract, having no vanadyl porphryrin compounds, contains a non-polar vanadyl non-porphyrin compound(s) with UV-Vis absorbance maximum at 300 nm, as determined using RSS.

(5) The two high sulfur crude oils (Boscan and Cerro Negro) contained proportionally more vanadyl porphyrin compounds than the two low sulfur crude oils (Wilmington and Prudhoe Bay), which had greater concentrations of both vanadyl non-porphyrin and nickel porphyrin compounds.

(6) A correlation involving vanadium, sulfur, and asphaltene concentration was observed for the four analyzed oils. Unlike nickel concentration, which reached a maximum value at 10 to 15 percent asphaltene concentration, vanadium concentration did not reach saturation levels, even at asphaltene concentrations of 20 to 25 percent.

(7) Correlations between vanadium concentration and geological age or depth of burial are not apparent, suggesting that asphaltenes hold the key to understanding the biogeochemical origin of vanadium in heavy crude petroleum deposits.

(8) HPLC-GFAA analysis provides an extremely convenient and useful technique for the identification and fingerprinting of trace metal compounds in heavy crude petroleums. Direct applications include: oil spill identification, monitoring of heavy crude oil and residual

processing streams, and exploration of suitable heavy crude oil deposits.

C. Recommendations for Future Work

This initiatory study has demonstrated the potential of HPLC-GFAA analysis with regard to the identification of vanadyl non-porphyrin compounds in heavy crude petroleums. Recommendations for future work include: (1) analysis of the heavy crude oil asphaltenes, to determine the role of sulfur atoms in coordinating vanadyl ion. (2) Furthur separation and identification of vanadyl compounds found in the pyridine extracts using HPLC-GFAA and HPLC-RSS analysis. (3) Synthesis of a wider variety of vanadyl non-porphyrin compounds, especially those incorporating sulfur into the ring structure. (4) Better characterization of the non-extractable vanadyl compounds remaining in the asphaltenes, to determine the molecular nature of these vanadyl compounds.

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