Title

METAL COORDINATION CHEMISTRY: REMOVAL AND RECOVERY OF METAL COMPOUNDS FROM HEAVY CRUDE AND SHALE OILS WITH MULTIDENTATE LIGANDS. ANNUAL REPORT - OCT. 1981 TO OCT. 1982.

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ANNUAL REPORT - OCTOBER 1981 TO OCTOBER 1982

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INTRODUCTION

It is now highly important for our nation to scrutinize all fossil fuel alternatives and develop those that appear promising both commercially and environmentally. Amongst several possibilities, one that emerges as extremely viable is the recovery of shale oil from our substantial domestic deposits of oil shale.[1]

Shale oil is recovered from oil shale kerogen by a controlled pyrolysis at 500°C using surface and *in situ* technologies. These produce, along with the shale oil, considerable amounts of process waters which originate from mineral dehydration, combustion, groundwater seepage, and steam and moisture in the input gas. Since the waters are in intimate contact with raw and partially retorted shale and shale oils, they constitute a leachate of these products.[2]

Several possible process and environmental problems are recognized in the formation and disposal of these retort process products. Firstly, the shale oils and retort waters contain a host of trace organic compounds[2,3] as well as a large array of trace metals and metalloids that poison process catalysts and are potentially toxic in certain forms to aquatic biota and man.[4-6] Secondly, in order to evaluate the latter contaminants for their process and environmental impacts, the key inorganic and organometallic forms associated with these toxic metals or metalloids (e.g., arsenic, cadmium, mercury,

selenium, etc. must ultimately be identified and their molecular features characterized or speciated.[7]

Recent advances, since the introduction of a high performance liquid chromatograph (HPLC) automatically coupled to a graphite furnace atomic absorption spectrometer as a detector (GFAA),[8] permit element-specific characterization of environmentally important trace inorganic and organometallic compounds. These advances provide an effective tool that allows direct separation and identification of these types of compounds in oil shale precursors and process products.[8-13] We will report on the separation and identification by HPLC-GFAA analysis of inorganic and organocarsenic compounds occurring in oil shale retort and process waters, shale oils and Green River Formation oil shale.

Arsenic was selected for the present investigations because of its widely acknowledged toxicity in groundwaters,[14,15] its effect on hydroprocessing catalysts, and because previous work indicates that total arsenic concentrations in oil shale process waters ranges from 5 to 15 ppm, shale oil 20-40 ppm and oil shale 20 ppm.[4]

The removal of the speciated inorganic arsenic and organoarsenic compounds from the shale oils and retort waters for various process and environmental problems is an extremely important research area. We will report on the model compounds we prepared for such future removal studies. This entails the use of substituted catechols as ligands capable of reacting with the speciated inorganic arsenic and organoarsenic compounds found in shale oil and retort water.

Additionally, the use of polymer-bonded catechols may have practical applications in these latter mentioned studies and our progress in preparing these catechol bonded polymers will be discussed.

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.[16-22] 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 usage, 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 petroleum and their asphaltents will (1) enable the design of selective separation, removal, and recovery process;[23,24] (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;[4] and provide important geochemical information regarding the origin and biogenesis

of heavy crude petroleum deposits.[25]

We have addressed these crucial areas of fossil energy research with the theme that by understanding the types of inorganic, metallo-organic and organometallic compounds in these complex matrices will allow a more rational approach to removal and recovery methods as well as help establish the biogeochemical origin of these compounds.

SPECIATION OF INORGANIC ARSENIC AND ORGANOARSENIC COMPOUNDS IN RETORT WATERS, SHALE OIL AND GREEN RIVER FORMATION OIL SHALE

Peak Identification in Oil Shale Retort and Process Waters

Figures 1 and 2 compare the arsenic-specific GFAA chromatograms obtained for the seven retort or process waters described.

Conventional chromatograms, taken with an ultraviolet (254 nm) detector in series with the GFAA detector, are shown superimposed (solid traces) on the arsenic-selective outputs; these clearly reveal the intensity and complexity of the organic matrix, and the analytical limitations of non-selective detectors. Each time we ran a sample, we also ran five authentic arsenic standards (as 10 ng As in each peak) combined into one solution. These included sodium arsenite, dimethylarsenic acid, methylarsonic acid, phenylarsonic acid and sodium arsenate. We regarded each GFAA chromatographic peak as "positively" identified (Table 1) if its retention volume matched that of the mean value of the calibration peak for each As species within two standard deviations of RSD < 5 percent t_R').[8,9] "Tentative" assignments were given to those peaks outlying 2σ, although spiking the field samples with authentic arsenic compounds (see below) yielded the same (increased) single chromatographic peak for both positively and tentatively, identified species.

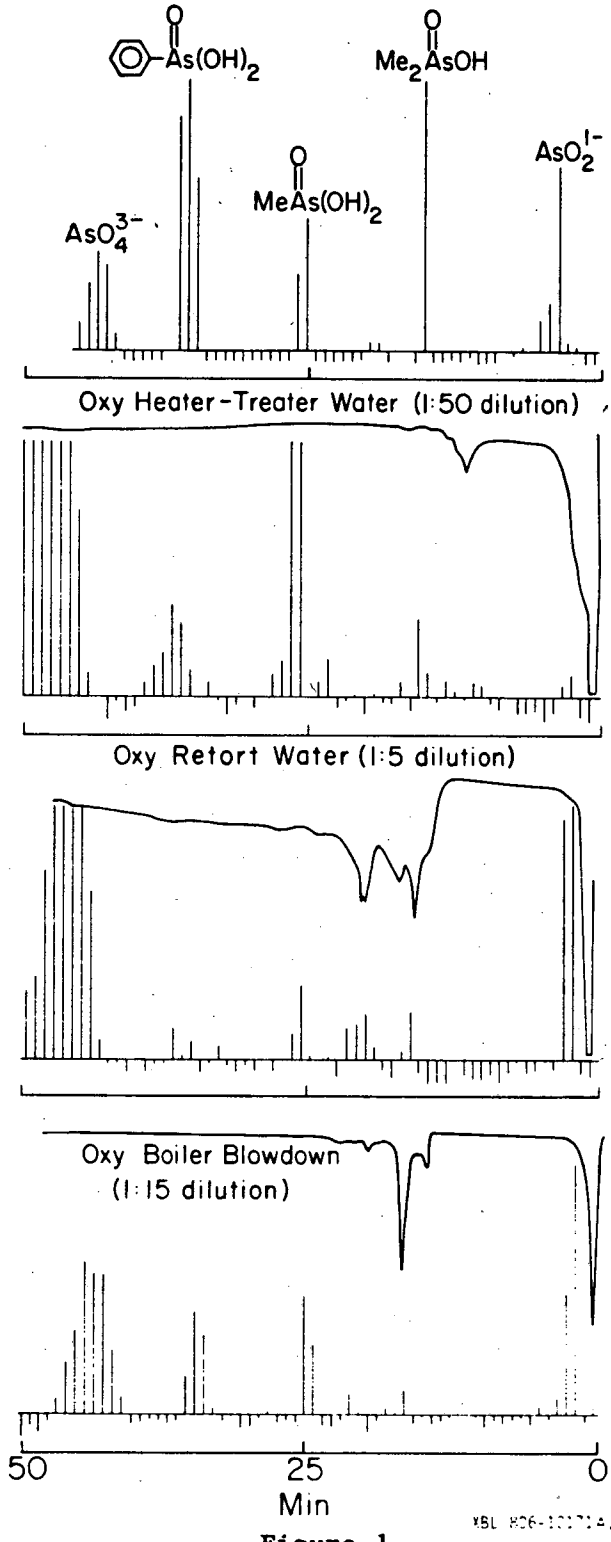


Figure 1

Element-specific chromatograms or arsenic species fingerprints obtained by HPLC-GFAA (bottom of each sample set) and associated UV detector chromatograms (continuous trace shown at top of each set, inverted) are compared against authentic arsenic standards for three water samples taken at different stages of the Occidental Modified In-Situ Process, Retort 6, Logan Wash, Colorado. The chromatogram of the aqueous calibration solution shown at top identified each of the five arsenicals present at a concentration of 10 ng mL^{-L} (as As).

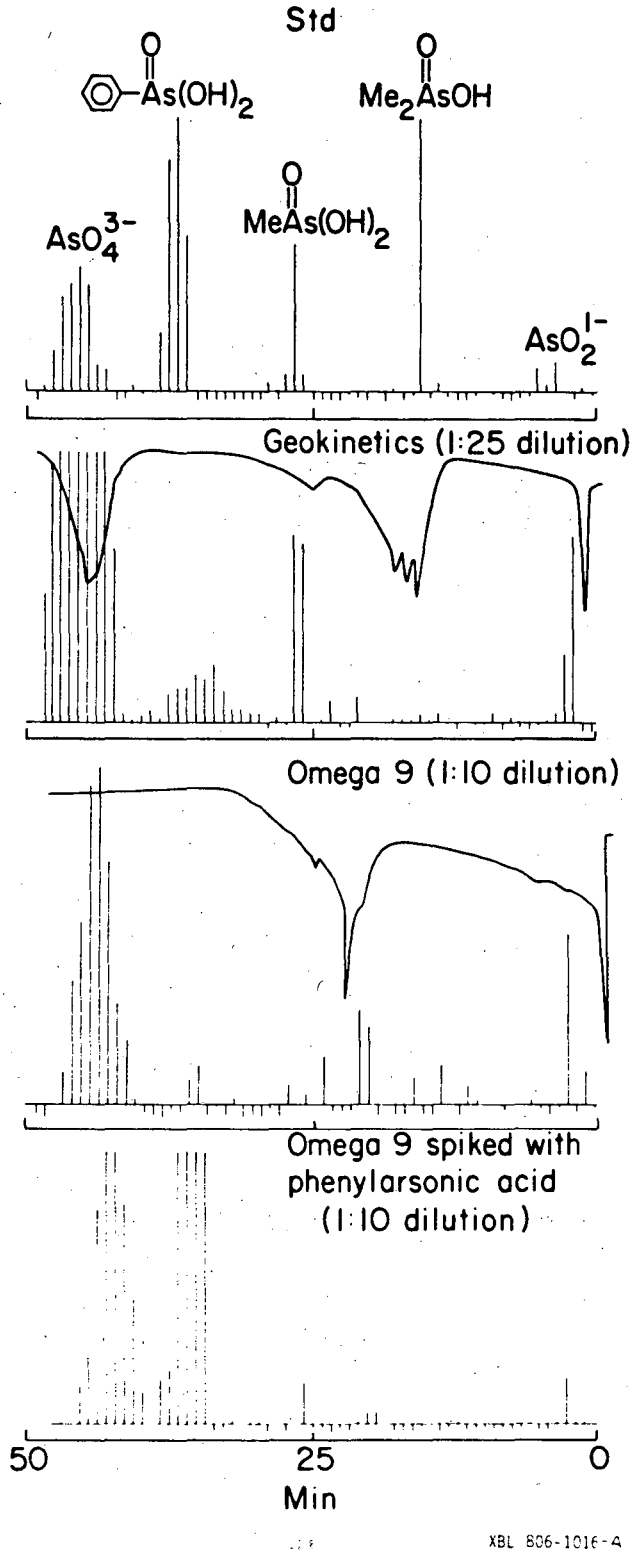


Figure 2

Arsenic fingerprints and corresponding UV chromatograms are compared, as in Fig. 1, against authentic arsenicals for two retort water samples derived from Geokinetics and Omega-9 true in-situ processes.

Sample	Retention Times[a] (min), $t_R \pm \sigma$ Sodium Arsenite $NaAsO_2$	Cacodylic Acid $(CH_3)_2As(O)(OH)$	Methylarsonic Acid $CH_3As(O)(OH)_2$	Phenylarsonic Acid ϕ-$As(O)(OH)_2$	Sodium Arsenate Na_3AsO_4	Unknown
CALIBRATION SOLUTIONS[b]	2.1 ± 0.4	16.3 ± 1.8	25.4 ± 0.4	35.7 ± 0.4	44.8 ± 1.1	---
SIMULATED IN-SITU RETORTS[c]						
L-2 Retort Water	---	---	25.2 (+)	35.6 (+)	42.9 (+)	1.0
150-Ton Retort Water	---	---	23.8 (±)	---	43.9 (+)	0.5
FIELD IN-SITU RETORTS[c]						
Omega-9 Retort Water	---	---	25.2 (+)	34.9 (+)	43.7 (+)	1.4 20.4
Geokinetics Retort Water	---	---	26.0 (+)	33.3 (±)	44.5 (+)	1.1 20.4
Occidental Heater-Treater Water[c]	---	---	25.1 (+)	36.4 (+)	46.8 (+)	1.0 14.6
Occidental Boiler Blowdown Water	---	---	24.9 (+)	34.6 (±)	44.2 (+)	0.8
Occidental Retort Water	---	---	24.6 (+)	35.9 (+)	44.8 (+)	0.5 15.0

[a] A dash (---) signifies that the species was not detected. A (+) signifies that the species was tentatively identified. The numerical values are the retention times at which the species or unknown peaks were detected.

[b] Mean ± standard deviation of five or more scattered runs.

[c] Positive identification (+) fell within ± 2σ (2 - 5 % RSD) for calibration runs taken in sequence with unknown runs.

Table 1

Tentative Identification of Inorganic Arsenic and Organoarsenic Compounds by HPLC-GFAA in Various Oil Shale Retort or Process Waters

Moreover, our spiking results confirmed that peak enhancement occurred for only those arsenic compounds spiked, without affecting the peak area of other arsenicals in the matrix. This result is in contrast to other workers who observed a methanol-dependent change in retention time for arsenate when dissolving the sample in methanol.[15] This methanolic arsenate derivative could have interfered with phenylarsonic acid, since it had a similar retention time.

Quantitation of Identified Arsenic Species

The representative figures clearly demonstrate that each retort or process water has a distinctive "fingerprint" and that substantial but variable quantities of arsenate, methylarsonic acid and phenylarsonic acid are present, while arsenite and dimethylarsinic acid are probably absent, or at best, marginally detected. Estimated detection limits and sensitivities for each arsenic species were found to vary, mainly a consequence of the alkaline organic matrix and the fixed GFAA atomization program. Consequently, we compared each sample chromatogram against that of a standard solution of authentic arsenicals in distilled water. Reliable retention times discussed above were obtained this way, as were approximate concentrations of major arsenic species in retort or process waters.

In order to more fully assess matrix effects on t_R and concentrations of minor components, we also ran authentic arsenicals as spikes in several process waters. For example, as shown in Figure 3 in Occidental retort water (diluted 1:10) HPLC-GFAA system detection limits at 95 percent confidence level using standard additions of 0,

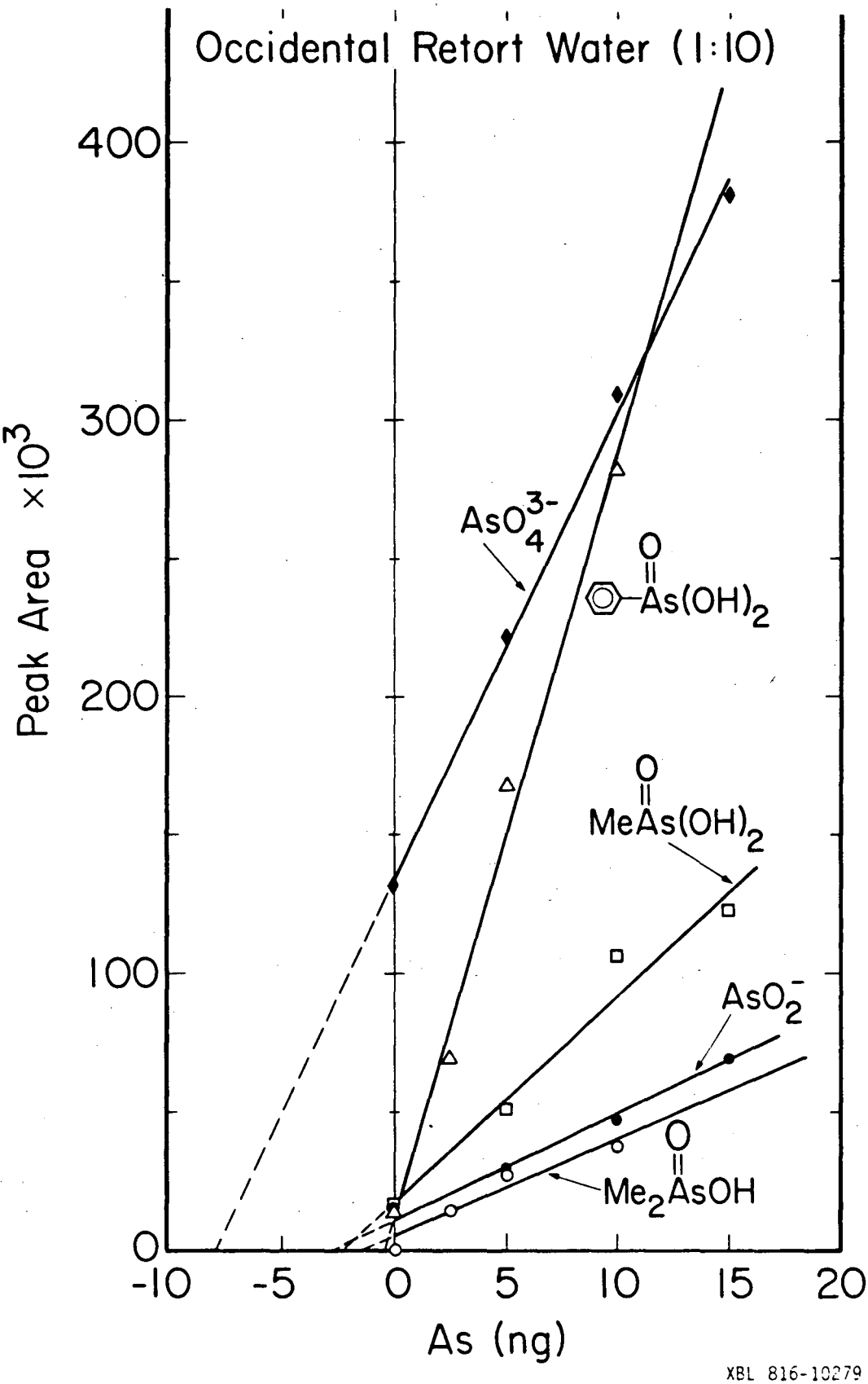


Figure 3

Plots of chromatographic peak areas versus standard additions of individual arsenicals to diluted (1:10) Occidental Retort Water showing relative concentrations

2.5, 5, 10 or 15 ng of analyte were: arsenite, 8.2; dimethylarsinic acid, 20.4; methylarsonic acid, 20.1; phenylarsonic acid, 7.4; and arsenate, 5.2 ng mL^{-1} (as As), respectively. The arsenical concentrations in the Occidental retort water were estimated to be: arsenite, 0.13 0.08; dimethylarsinic acid, 0.049 0.20; methylarsonic acid, 0.096 0.20;phenylarsonic acid, 0.018 0.074, and arsenate, 0.32 0.05 g mL^{-1}. Clearly from these results and Figure 1 this was a worst-case analysis, although AsO^{3-}, and AsO^{-} appeared to give reasonable error limits. For the remaining samples more favorable error limits and concentrations prevailed, as illustrated in Figs. 1 and 2, and summarized in Table 2. presence in the seven sample waters at $< 0.1 \pm 0.06$ ppm; for dimethylarsinic acid, we tentatively place an upper limit of $< 0.05 \pm 0.20$ ppm.

Comparisons Between the Retort and Process Waters

Tables 1 and 2 correlate the identified arsenic species and their estimated concentrations with the corresponding retort or process waters. Arsenate is by far the major (0.6-10 ppm) arsenical component identified in all of the samples studied, but the variable concentrations of the other species suggest quantitative diagnostics for monitoring widely different production sites. It is interesting to note that Occidental's retort and process waters (Fig. 1) all contain methylarsonic acid, phenylarsonic acid, arsenate, and one or several neutral or weakly ionized arsenicals, possibly in the molecular R_3As or R_3AsO classes. Generally, neutral or weakly ionized molecules elute with the solvent front (at t_o min) or with only

Process Water	Compound[a]	µg mL^{-1}[b] (ppm)	
Occidental Retort Water	Unknown organoarsenic compound	-	(-)
	Arsenite	-	(0.13)
	Methylarsonic Acid	0.16	(0.10)
	Phenylarsonic Acid	< 0.003	(0.02)
	Arsenate	0.46	(0.32)
Occidental Heater-Treater Water	Unknown organoarsenic compound	-	
	Methylarsonic Acid	<2.0	
	Phenylarsonic Acid	<0.42	
	Arsenate	~10	
Occidental Boiler Blowdown Water	Unknown Organoarsenic compound	-	
	Methylarsonic Acid	0.58	
	Phenylarsonic Acid	0.15	
	Arsenate	0.63	
LETC 150-Ton Water	Unknown organoarsenic compound	-	
	Methylarsonic Acid	<1.5	
	Arsenate	<3.0	
LLL L-2 Water	Unknown organcarsenic compound	-	
	Methylarsonic Acid	0.63	
	Unknown inorganic or organo-arsenic compound	-	
	Phenylarsonic Acid	0.31	
	Arsenate	>2.0	
Geokinetic Retort Water	Unknown organoarsenic compound	-	
	Methylarsonic Acid	<2.0	
	Phenylarsonic Acid	<0.38	
	Arsenate	>10	
LETC Omega-9 Water	Unknown organoarsenic compound	-	
	Methylarsonic Acid	<0.18	
	Phenylarsonic Acid	<0.02	
	Arsenate	<1.6	

[a]Determination of identified compounds by retention times with known authentic compounds, Table 2.

[b]Each standard 10 ng as As. Area under each peak estimated by method of summing peak heights digitized with an integrator (9-11) and comparison with calibration solutions in deionized water or method of additions (22) with spikes in sample solutions (in parentheses).

Table 2

Estimation of Inorganic and Organic Arsenic Compounds Separated and Detected by HPLC-GFAA Analyses

slight retention (at t_R min) in well-behaved ion exchange columns where $k' \sim 1/\mu$; $k' = (t_R - t_o)/t_o$ and μ = ionic strength.

The two true in situ retort waters, Geokinetic and Omega-9, also display (Fig. 2) early peaks and contain methyl and phenylarsonic acids, arsenate and another unknown ionic arsenic species eluting at 20.4 min. Important in a different way, both simulated in situ process waters, 150-Ton and L-2 were distinguished by a significant diagnostic feature involving, respectively, absence of detectable [< 0.002 ppm] phenylarsonic acid in the 150-Ton sample, whereas L-2 water contains . 0.3 ppm of this species. Beyond this, both 150-Ton and L-2 samples contained methylarsonic acid, arsenate, and the neutral component which suggested their similarity to Omega-9. These distinguishable fingerprints may reflect different operating parameters used in the controlled pyrolysis reaction possible with the 150-Ton and L-2 facilities. The similarities last noted may well indicate that basic chemical phenomena are the same in certain laboratory and field retorts, and imply that HPLC-GFAA fingerprinting may serve as a monitoring tool for correlating such operations.

Biogeochemical or Process Origins of Organoarsenicals

The origin of these observed organoarsenic compounds, at this time, is not understood. Kerogen, generally regarded as a biogeochemical creation, large fromlipid fractions of ancient algae,[2] forms the ubiquitous oil source matrix in shales. Thus, it is conceivable that these methyl- and phenylarsonic acids occur naturally following original biosynthesis or bioaccumulation[26] and subsequent

mineralization in oil shale and are released with little decomposition upon pyrolysis, ending up as leachates in the process water after intimate contact with the shale oil. Ample evidence is available for both terrestrial and marine biomethylation of inorganic arsenic(v) by modern microorganisms and marine algae[26] to produce both dimethylarsinate and methylarsonate species;[27] no analogous biophenylation is reported as far as we know. The negligible amounts of dimethylarsinate or arsenite in our sample waters may result, from oxidative loss of the latter in aged sample, or from oxidative pyrolysis of both species in aerobic retorts, selective rates of formation during original biogenesis, or an alternative purely abiotic synthesis forming methyl- or phenylarsenic bonds in the hot reaction zone of the retort. This last pathway seems quite reasonable for the methylarsonic acid observed, since it parallels the long-known Meyer reaction between alkyl halides and arsenite salts.[28] In boiling aqueous solution both alkylarsonic and dialkylarsinic acids can form, but arylarsonic acids are not similarly obtained, thereby suggesting that the phenylarsonic acid observed may arise from other sources.[29] Finally, we cannot rule out formation of these organoarsenic compounds after the retort or process water reaches at the exit of the retort. For example, biomethylated arsenicals could be introduced with boiler feedwater (Occidental boiler blowdown) or by groundwater seepage into <u>in situ</u> retorts (Omega-9 and Geokinetic retort waters) and converted to the observed arsonic acids under conditions of high temperatures and pH.

Conclusions

The significant environmental implications of our study are that potentially toxic inorganic arsenic and organoarsenic compounds in varied mixtures at appreciable concentrations are either released or synthesized during oil shale retorting processes representing present-day technology. The methods applied by us presage similar efforts with other toxic elements. The possibility of their bioaccumulation in soils, water, and edible biota at appreciable distances from the retorting site *via* disposal of retort leachate waters containing bioactive forms may represent potential health hazards for humans as well as a threat to aquatic species. Suggested bioleaching of petroliferous shales[30] as an energy-conserving alternative to pyrolysis, must now be regarded with new concerns for rerelease or biotransformation of arsenicals entrapped in kerogen, and this should guide research on other metals as well. A more immediate consequence of low-level exposure of workers in these future retort process plants to such inorganic and organoarsenic compounds will require monitoring, since there is not presently a complete understanding of *in vivo* mechanisms of arsenic and other heavy metal toxicity.

We believe this to be the first positive molecular characterization of any trace inorganic or organometallic substances in such fossil fuel recovery products. Since the HPLC-GFAA technique is shown to be broadly applicable to a wide variety of elements in many molecular classes, with great freedom from usual matrix interferences, we

envision similar utility for speciating other toxic metal-containing molecules in oil shale products. Among these prospects, mercury, selenium and lead are important because of their known biotransformations and presence in kerogen pyrolysates. Since the HPLC-GFAA method permits use of a large variety of non-ionic separation columns, we are also examining the shale oils as well as oil shale kerogens with the aim of establishing the molecular form of hydrophobic or macromolecular organoarsenicals not readily partitioned into retort waters. It is hoped that current qualitative survey work of this type can later offer quantitative bases for optimizing retort process parameters while minimizing impacts of speciated metal toxicants.

Shale Oil Speciation Studies

Even though the presence of arsenic in shale oil has necessitated the development of dearsenation processes to protect hydrotreating catalysts during shale oil processing, the molecular speciation of arsenic in shale oil has not been reported. Curtin et al.[31] found that arsenic was present throughout various boiling range fractions including a fraction obtained below 205°C. The development of methods for the molecular speciation of arsenic in shale oil would be invaluable to further optimize dearsenation processes as well as process monitoring in support of dearsenation catalysts.

The analysis of NBS shale oil SRM 1580, certified or organics only, is presented in Figure 4 and exemplifies the dual element selective chromatographic detection. The arsenic is eluted with a

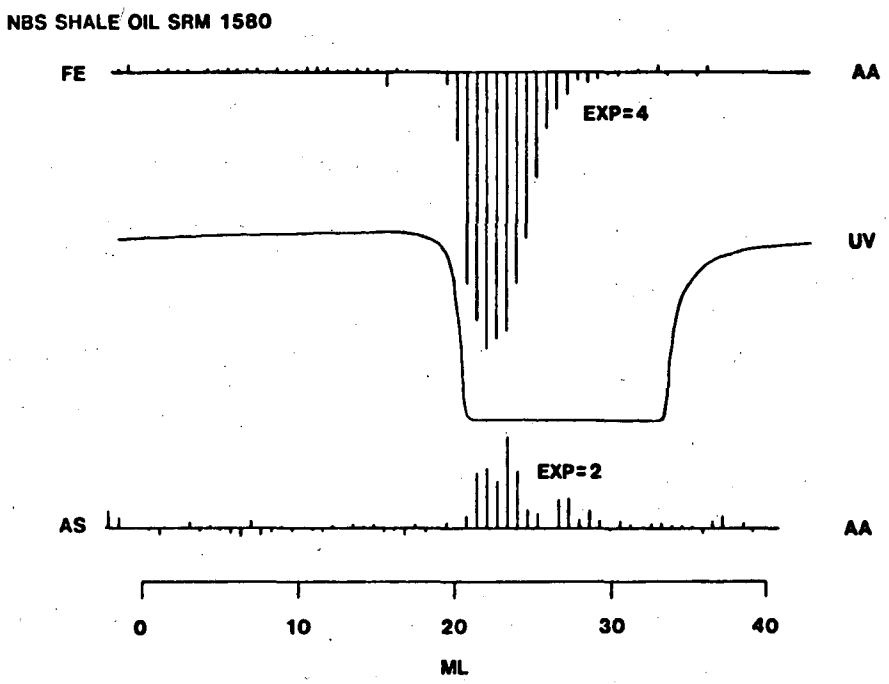


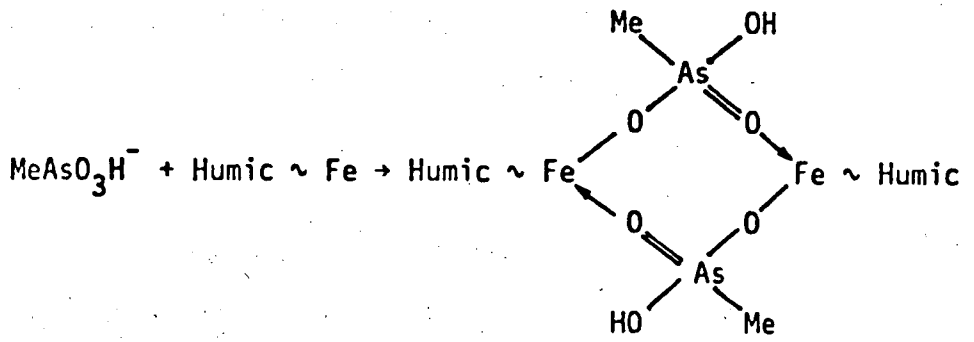
Figure 4

Dual Element-Selective Detection for iron and arsenic of the size exclusion chromatogram for NBS Shale Oil SRM1580

retention volume corresponding to a molecular species of close to 2,000 daltons, as is the iron. The arsenic also appears to be distributed among species of various molecular weight. In the NBS oil, the arsenic and iron compounds coelute with a molecular species having an apparent molecular weight greater than 2,000 daltons. In the ORNL centrifuged oil, the arsenic was distributed towards lower molecular weights and the iron has a bimodal distribution with elution volumes corresponding to about 12,000 and 2,000 daltons.

The primary difficulty in trying to speciate metals in oils is in finding appropriate standards for macromolecular compounds. This is evidenced by the reporting of the distributions of metals without the necessary standards for chemical speciation.[32,33] Our experimental approach was to spike the Paraho shale oil with methylarsonic acid. The methylarsonic acid was ligated by the molecular weight compounds of 2,000 daltons, again coeluting with iron. We postulate that this association of arsenic with iron in macromolecules is analogous to the association of orthophosphate and metals such as chromium and iron via oxygen bonding in polymers. We envision iron complexes of humic acids, the precursors of many fossil fuels, ligating the anionic forms of arsonic acids via Fe-O-As bonding.

This may indicate the competitive chemistry occurring in iron oxide guard beds used for the commercial dearsenation of shale oil. Our continuing arsenic speciation studies can provide information for innovative methods of removal of arsenate, methyl and phenylarsonic



acids from shale oils. For example, one method we are studying involves reaction of alkyl and arylarsonic acids with polymer-bond catechols. Recent model compound reactions suggest that this method has exciting possibilities.[23]

The definitive molecular speciation of arsenic is possible in some cases; however, macromolecular arsenic-containing species, evident in size exclusion chromatograms of various shale oils, must be evaluated in terms of: heteroatom content, correlations among a variety of elements, the extent and nature of the complexing capacity of the matrix for arsenic and the stability of these arsenic containing compounds. The conclusions drawn during this study are: (1) HPLC-GFAA permits the chemical speciation of arsenic in process fluids from oil shale retorting; (2) the association of arsenic with iron provides a preliminary chemical basis for understanding the presence of metals and metalloids in the macromolecular components of fossil fuels; (3) the anionic nature of arsenic may explain its

unique behavior with respect to other elements' cationic behavior; (4) studies based on the uptake of alkyl and arylarsonic acids by the macromolecular compounds in shale oil may provide beneficial insights for optimizing the removal of arsenic from shale oil.

Speciation Studies in Green River Formation Oil Shale

The molecular characterization of organometallic compounds which occur as natural products in fossil fuel precursors is becoming a significant area to research due to the importance of these compounds in emerging synthetic fuel processes as well as their impact on the environment.

Recently, we identified, using a high performance liquid chromatograph coupled to a graphite furnace atomic absorption spectrometer as an element-selective detector (HPLC-GFAA), methyl- and phenylarsonic acids as well as arsenate in oil shale retort waters.[34] We also have analyzed the shale oils produced by pyrolysis of oil shale and have found that the above-mentioned organoarsonic acids also occur, but in association with iron-containing macro-molecules with molecular weights in the range of 2,000-4,000 daltons.[35,36]

In order to discern whether these compounds were natural products in the precursor of the shale oil and the retort waters or were formed during pyrolysis, we examined a Green River Formation oil shale. Oil shale from the Green River Formation is a fine-grained sedimentary rock, which contains appreciable quantities of organic material. It consists of three fractions - kerogen, bitumen and an

inert substance. Kerogen and bitumen, which constitutes the organic material, generally are regarded as biogeochemical fossil products, emanating largely from lipid fractions of ancient algae and forming the ubiquitous oil source matrix in shales.

The Green River Formation oil shale sample (10 g) was crushed and Soxhlet extracted with 500 mL of methanol for 48 hours. This effectively removed about 20% of the total arsenic contained in this oil shale such as freshwater marine algal mats as well as other biogeochemical samples. Following evaporation (25 mL) and filtration, we speciated the extract by HPLC, using a Dionex anion exchange column with 0.2M ammonium carbonate in water/methanol (85:15) as the eluting solvent. The arsenic compounds were detected via automatic GFAA analysis at 197.3 nm.

Figure 5 gives the arsenic-specific chromotogram of the compounds we identified as methylarsonic acid, phenylarsonic acid, and arsenate, based on retention times of the authentic arsenic compounds. An unknown neutral organoarsenic compound eluted with the solvent front.

We recently have studied the reactions of methyl- and phenylarsonic acids with substituted catechols, and established that they provide five-coordinate organoarsenic catecholates.[23] Since many of these organoarsenic catecholates could be gas chromatographed on fused silica capillary columns and characterized by electron impact mass spectroscopy (GC-EIMS), we decided to apply this derivitization technique for the unequivocal identification of methyl- and

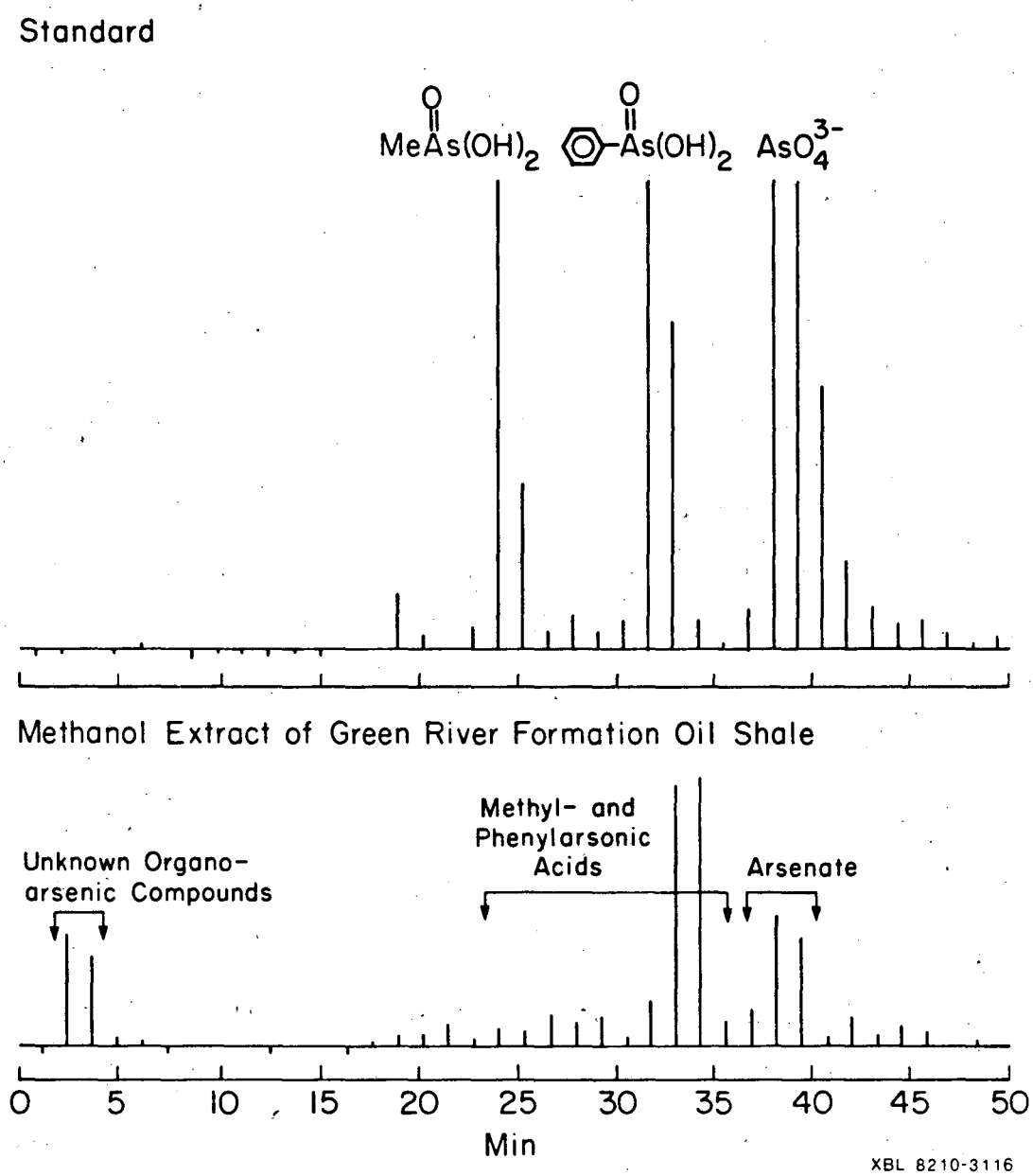


Figure 5

The HPLC-GFAA analysis of Green River Formation oil shale extracted with refluxing methanol. The GFAA detection of arsenic was at 193.7 nm. The HPLC column was a Dionex anion exchange column with 0.2M $(NH_4)_2CO_3$ in aqueous methanol as the eluting solvent. The bracketed areas were isolated by preparative HPLC.

phenylarsonic acids present in the oil shale extract.

The methanol extract was purified by preparative HPLC (the area from 22 to 35 min. was collected, see Figure 1), lyophilized and dissolved in benzene. To this solution was added excess 3-methylcatechol and the reaction mixture was refluxed for 5 h and worked up to remove the excess 3-methylcatechol. A concentrated sample was subjected to GC-EIMS analysis to provide spectra and scan numbers (retention times) that were identical to the known samples of the 3-methylcatecholates of both methyl- and phenylarsonic acids.

Figure 6(A) shows the reconstructed ion chromatogram of the two standards, 3-methylcatecholates of methyl- and phenylarsonic acids, and the single ion chromatograms show pertinent fragments of interest at m/e 197 and 212 for the methylarsonic acid derivative (Figure 6 B,C) and m/e 197 and 274 for the phenylarsonic acid derivative (Figure 6 B,D). Figure 7(C) shows the region we purified by HPLC containing the organoarsonic acids, which were derivatized, and the expanded sections of this chromotogram containing the organoarsenic catecholates with the important ions, m/e 197, 212 and 274, clearly evident for the 3-methylcatecholates of methyl- (Figure 7 A) and phenylarsonic (Figure 7 B) acids. Additionally, the inorganic anion, arsenate (AsO_4), was verified in a similar fashion (preparative HPLC of the region from 35.5-41 min) by preparation of the tris(trimethylsilyl-) derivative of the ammonium salt of arsenate and analyzing the purified extract by GC-EIMS for ions at m/e 207, 343, and 358.[37] The organoarsenic compound(s) that elutes with the solvent

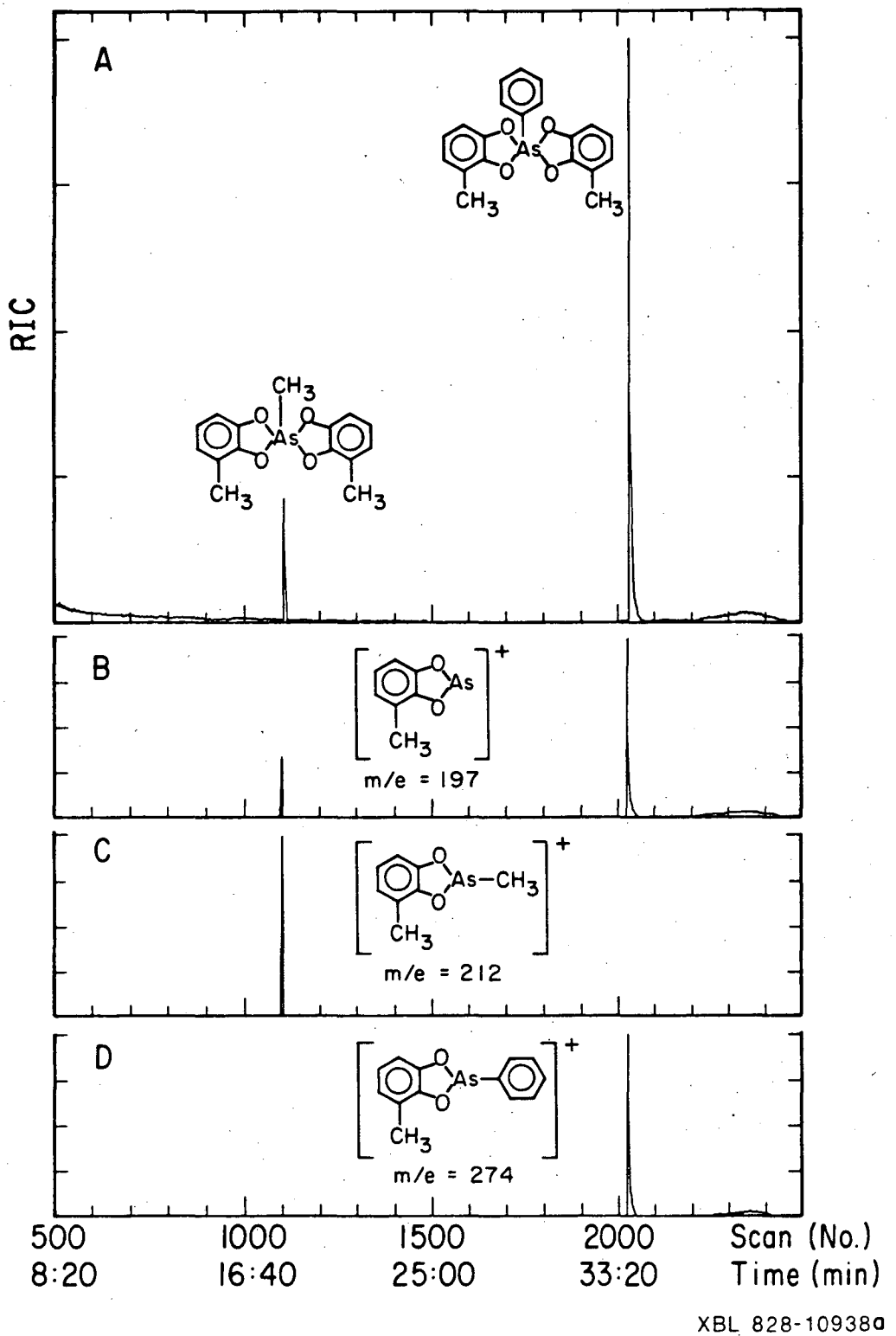


Figure 6

GC-EIMS analysis of the 3-methylcatecholates of methyl- and phenylarsonic acids. (A) Reconstructed ion chromatogram of known methyl- and phenylarsonic acids derivatives of 3-methylcatechol. (B) Selected ion chromatogram showing m/e 197 for each derivative. (C) Selected ion chromatogram for methylarsonic acid-3-methylcatecholate at m/e 212. (D) Selecetd ion chromatogram for phenylarsonic acid-3-methylcatecholate at m/e 274.

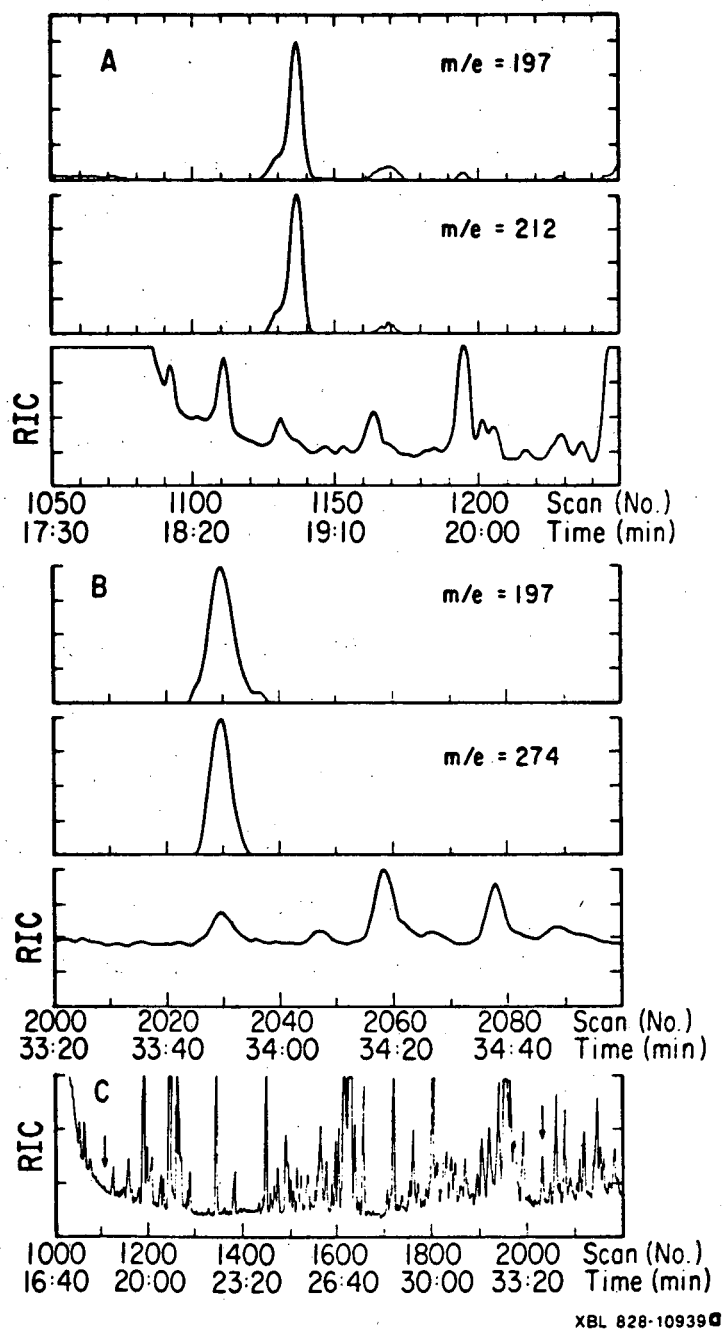


Figure 7

GC-EIMS analysis of the derivatized, HPLC purified, methanol extract. (A) Selected ion chromatograms near Scan 1137 for m/e 197 and m/e 212 confirming the identification of the 3-methylcatecholate of methylarsonic acid in the expanded reconstructed ion chromatogram. (B) Selected ion chromatograms near Scan 2030 for m/e 197 and m/e 274 confirming the identification of the 3-methylcatecholate of phenylarsonic acid in the expanded reconstructed ion chromotogram. (C) Reconstructed ion chromatogram of HPLC purified methanol extract with arrow on left designating methylarsonic acid-3-methyl catecholate and arrow on right designating phenylarsonic acid-3-methyl catecholate.

front (Figure 5) has not been as yet identified and further work is in progress to verify its structure.

We believe these identifications of the organoarsonic acids to be the first such molecular characterizations of trace organometallic compounds to be reported for any fossil fuel precursors and initiates the area of organometallic geochemistry, a field that has hitherto-fore been totally unexplored.[36,38]

The implications are that these organoarsonic acids are natural products and hence have a biogeochemical origin in the oil shale taphonomy process. It is also interesting to note that no examples of biophenylation have been reported, whereas biomethylation of arsenic compounds is a well known reaction.[27] How the phenylarsonic acid forms will have to be answered with the examination of precursors to the oil shale such as freshwater marine algal mats as well as other biogeochemical samples.

Finally, the fact that these organoarsonic acids are released upon oil shale pyrolysis has important implications in the various synthetic fuel processes where the role of organometallic compounds in poisoning process catalysts and contribute to environmental problems is paramount.

SYNTHESIS OF ORGANOARSENIC AND INORGANIC ARSENIC CATECHOLATES AS MODELS FOR REMOVAL OF ORGANOARSENIC AND INORGANIC ARSENIC COMPOUNDS FROM RETORT RECOVERY PRODUCTS SUCH AS SHALE OIL AND RETORT WATER

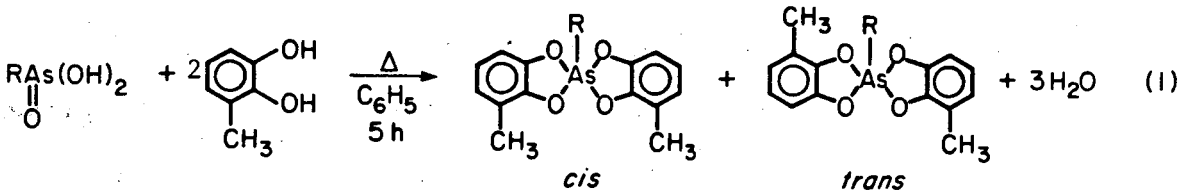
Recently, we have been investigating the speciation or molecular characterization of organoarsenic compounds thought to be present in biogeochemical materials such as oil shale kerogen and the products of the pyrolysis of oil shale kerogen, those of the shale oils and the retort waters. These studies led to the identification, for the first time, of methyl and phenylarsonic acids in these precursors and products.[34-38]

In view of these discoveries, we have initiated studies to find innovative methods for the removal of these compounds and other organometallics from fossil fuel products.[23] In this regard, we have been experimenting with a method that utilizes substituted catechols as potential ligands that could be placed in a polymeric matrix for the future removal of organoarsenic compounds from the above mentioned products.

Surprisingly, we found very few references on the reactions of catechols with alkyl or arylarsonic acids[39a-f] and none on similar reactions with substituted catechols.[23,40] Thus, we reported our initial results on the synthesis, structural elucidation and stereochemistry of the five-coordinate organoarsenic catecholates we prepared

as model compounds for the above mentioned purposes.[23]

Chart 1 shows the catechols, 1-4, we utilized in the reactions with methyl or phenylarsonic acid, 5 and 6 Compound 1 reacts with either 5 or 6 to provide a mixture of cis and trans five-coordinate organoarsenic catecholates, 7 - 10 (Eq. 1).



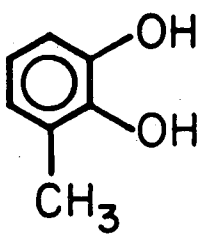
5 R = CH_3
6 R = Ph

7-10

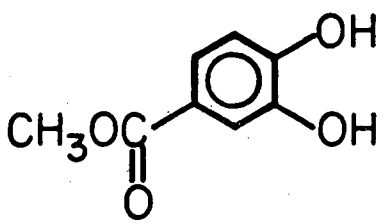
XBL 823-8459

Compounds 7-10 were characterized by a combination of nuclear magnetic resonance spectroscopy (NMR), mass spectrometry (MS), infrared spectroscopy (IR) and elemental analysis. The 250 MHz ^1H NMR spectrum provided definitive evidence that compound 1 reacted with either 5 or 6 to give a mixture of cis and trans isomers (7, 8 R= CH_3 and 9, 10 R = Ph). Thus, compounds 7 and 8 showed two methyl resonances (catecholate ring) at 2.21 and 2.19 ppm (benzene-d_6, TMS) and two methyl resonances for groups bonded to arsenic at 1.33 and 1.32 ppm in the ratio of 53:47. The corresponding cis and trans compounds, 9 and 10, where R=Ph, had methyl resonances at 2.26 and 2.12 ppm (benzene-d_6, TMS) in the ratio of 90:10. The complexity of the phenyl region at 250 MHz did not allow a separation of catecholate protons and phenylarsenic protons and thus the ^1H NMR spectrum was obtained at 400 MHz. The 400 MHz ^1H NMR spectrum of 9, 10 (benzene-

Catechols used in the synthesis of five coordinate organoarsenic catecholates



1



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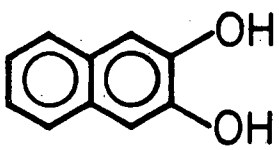

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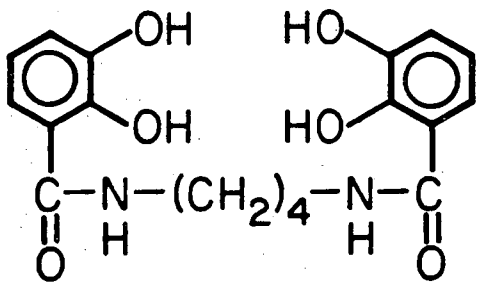


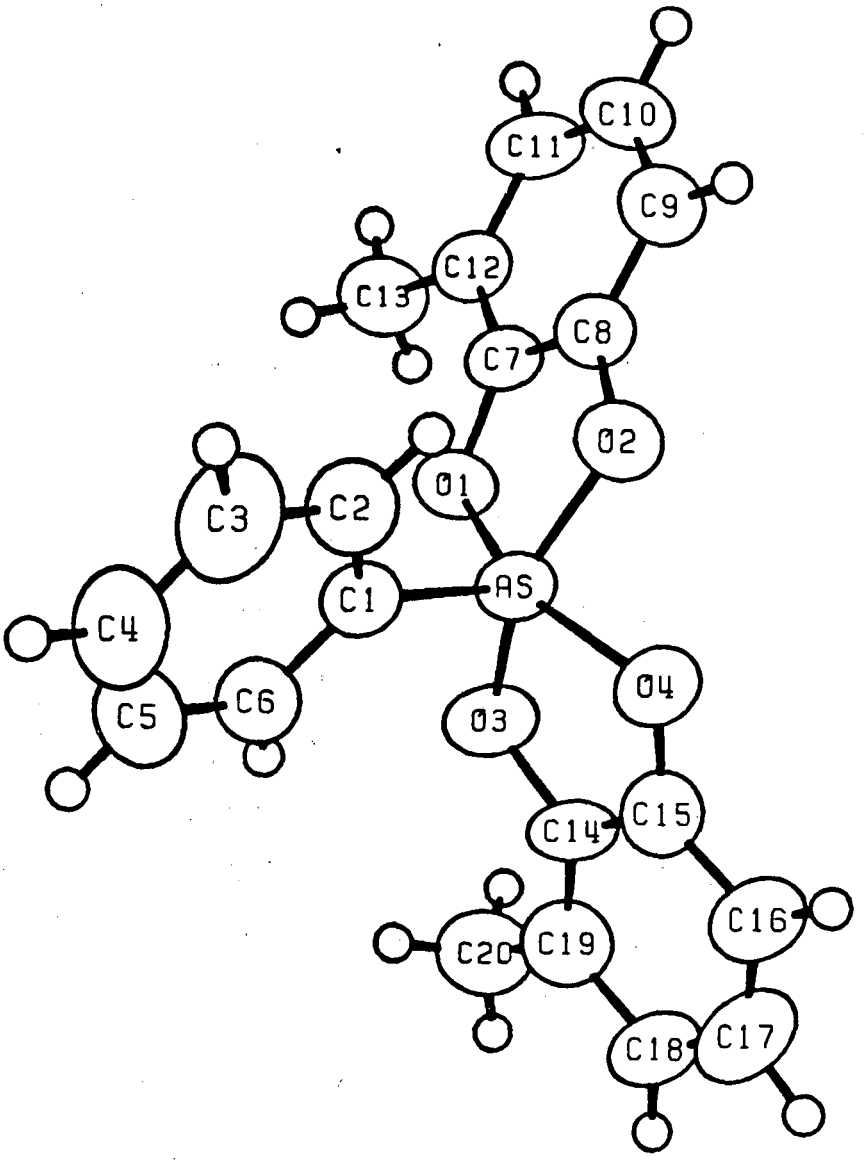
4

XBL 823-8458

Chart 1

d_6, TMS) showed resonances at 7.81 (doublet, J=8.3Hz); 6.83 (multiplet) and 6.74 ppm (overlapping triplets J=8.3Hz) for the phenylarsenic protons in the ratio of 2:1:2. The catecholate protons were found at 6.56 (doublet of doublets, J_{ortho} 7.8 Hz, J_{meta} 1.4 Hz); 6.65 (overlapping triplets, J=7.8 Hz), 6.93 (triplet, J=7.8 Hz) and the methyl groups at 2.24 ppm (singlet) in the ratio of 2:2:2:6. The complexity of the phenyl region, where protons on the phenyl group attached to arsenic appeared to be all non-equivalent, provided tentative evidence for the cis isomer, 9, rather than the trans isomer, 10, as the major product in this reaction.

In order to unequivocally ascertain the stereochemistry of the major isomer, either 9 (cis) or 10 (trans), we obtained a single-crystal x-ray analysis. Figure 8 shows the ORTEP drawing of the major isomer, 9, with the methyl groups clearly cis to each other and the geometry around the arsenic, essentially rectangular pyramidal (95%), while the axial phenyl group is twisted so that it lies in the same plane as oxygen 2 and oxygen 3. The angle between the carbons 1 through 6 on the phenyl group attached to arsenic and the oxygen-arsenic-oxygen plane is 4.7°. (See Table 3 for pertinent bond angles and lengths). Recently, Day et al.,[41] reported on the crystal structure of a product from the reaction of phenylarsonic acid and catechol. This five-coordinate organoarsenic catecholate was also found to have a rectangular pyramidal geometry around arsenic. Our study represents the first stereochemical assignment to be made on a five-coordinate organoarsenic catecholate and has implications in the



XBL 823-8156

Figure 8

ORTEP diagram of cis $(3\text{-}CH_3\text{-}C_6H_3O_2)_2AsC_6H_5$, 9 , showing 50% Probability ellipsoids.

Selected Bond Lengths and Angles for

cis $(3\text{-}CH_3\text{-}C_6H_3O_2)_2AsC_6H_5$, 9[a]

Atoms	Bond Length	Atoms	Angle, Deg
$As\text{-}O_1$	1.806 (1)	$O_1\text{-}As\text{-}O_2$	87.93 (7)
$As\text{-}O_2$	1.799 (2)	$O_1\text{-}As\text{-}O_3$	85.43 (7)
$As\text{-}O_3$	1.784 (2)	$O_1\text{-}As\text{-}O_4$	150.84 (9)
$As\text{-}O_4$	1.825 (2)	$O_2\text{-}As\text{-}O_3$	149.85 (9)
$As\text{-}C_1$	1.899 (2)	$O_2\text{-}As\text{-}O_4$	82.71 (8)
$C_7\text{-}O_1$	1.365 (3)	$O_3\text{-}As\text{-}O_4$	88.95 (9)
$C_8\text{-}O_2$	1.370 (3)	$O_1\text{-}As\text{-}C_1$	105.5 (8)
$C_{14}\text{-}O_3$	1.413 (3)	$O_2\text{-}As\text{-}C_1$	104.99 (9)
$C_{15}\text{-}O_4$	1.345 (3)	$O_3\text{-}As\text{-}C_1$	105.12 (9)
$C_{12}\text{-}C_{13}$	1.474 (4)	$O_4\text{-}As\text{-}C_1$	103.59 (9)
$C_{19}\text{-}C_{20}$	1.410 (4)	$As\text{-}O_1\text{-}C_7$	111.12 (13)

[a] Estimated standard deviations in parenthesis

Table 3

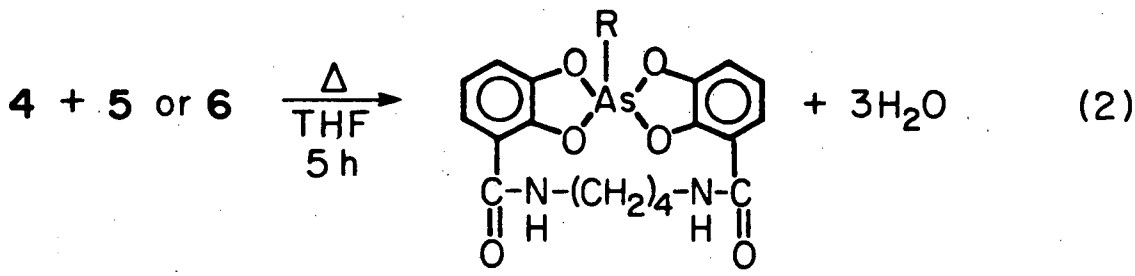
Selected Bond Lengths and Angles for cis $(3\text{-}CH_3\text{-}C_6H_3O_2)_2\ AsC_6H_5$, 9[a]

mechanism of formation of these compounds, which will be discussed in a future full account of this work.

Compound 2 reacted with 5 to provide a compound, 11, with a single methylarsenic resonance at 1.92 ppm (^{1}H, 250MHz, DMSO-d_6, TMS) and a single methoxyl resonance at 3.78 ppm and is indicative of one isomer, which we presume to have cis stereochemistry as in 9. Compound 2 also reacts with 6 to provide a mixture of compounds, 12 and 13, with two methoxyl signals (^{1}H, 250 MHz, DMSO-d_6, TMS) at 3.76 and 3.74 ppm in the ratio of 95:5. Again, as with 11, we presume cis stereochemistry for the major isomer. Compound 3, a benzo-substituted catechol, reacted with 5 or with 6 to give the five-coordinate organoarsenic compounds 14 and 15 respectively. While no stereochemistry is involved in the formation of either 14 or 15, it is important to note that substitution on the naphthyl ring is certainly possible for future attachment of this type of compound to a polymeric backbone. The pertinent ^{1}H NMR data (250 MHz, DMSO-d_6, TMS) provided an upfield shift, as with the NMR spectra of compounds 7-13, for the catechol ring protons of 14 and 15 when compared to 3. Thus, 14 had the catechol protons (singlet) at 7.09 ppm, 15 at 7.10 and 3 at 7.12 ppm indicative of the arsenic atoms influence on shifting, to higher fields, protrons on catechol rings. A similar NMR result was obtained by Raymond et al.[42] for some gallium and rhodium catecholate complexes.

Our final ligand of interest, 4 was important to study, since it represented a model for a recently reported polymer of potential use

for our future applications.[43] We chose 4 (4-LICAM) after making Dreiding models that clearly showed the central cavity being able to accommodate an arsenic atom (~3.58 to 3.63 A, see Figure 8). Reaction of 4, with either 5 or 6, provided the intramolecular five-coordinate organoarsenic derivatives, 16 and 17 (Eq. 2).



(2)

16 R = CH_3
17 R = Ph

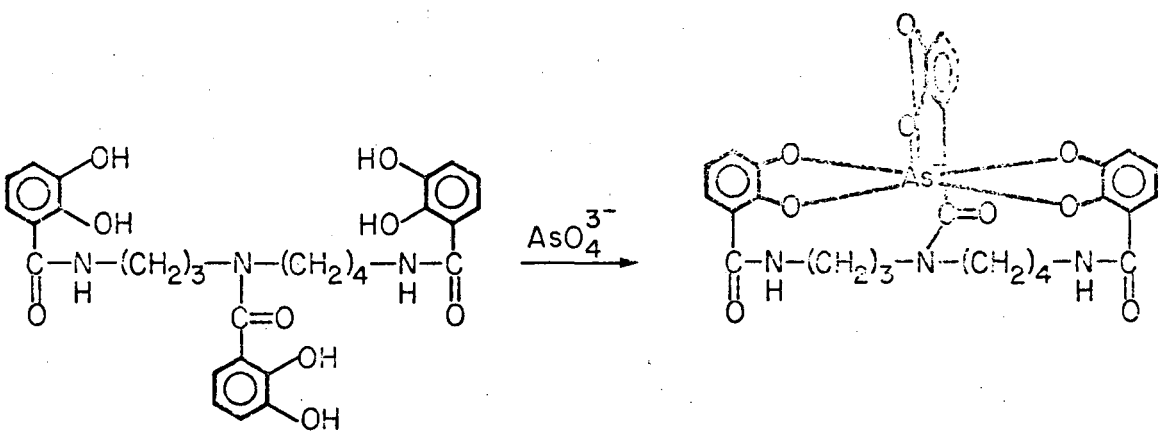
The 250 MHz ^1H NMR and 70 ev MS (solid probe) data were consistent with the structures assigned. Notably, the mass spectra provided the parent ion and an ion resulting from a loss of the catechol group with a carbonyl attached. This was followed by a fragmentation of the $-CH_2CH_2-NH$ groupings. For example, with 17 the MS ions of interest were: m/e 508 ($M^{+\cdot}$); 373 ($M-C_7H_{13}N_2O_3$); 331 ($M-C_9H_8NO_3$); and 287 ($M-C_{11}H_{13}N_2O_3$).

A typical procedure for the preparation of a five-coordinate organoarsenic catecholate derivative is described as follows for 9.

In a 50 ml flask, equipped with condenser, drying tube, and dean-stark trap for water removal, was placed 1.29g (10.42 mole) of phenylarsonic acid and 1.05 g (5.21 mmole) 3-methylcatechol (freshly sublimed) in 30 ml of benzene. The reaction mixture was refluxed for

5h. The benzene was removed on a rotary evaporator and the compound recrystallized from carbon tetrachloride/methanol and dried under vacuum to give 1.88g (91% yield) of 9, mp, 134-135°C. Calculated for $C_{20}H_{17}O_4As$; C, 60.6; H, 4.3, Found: C, 60.39; H, 4.46; EIMS (70 ev, solid probe) m/e 396 ($M^{+\cdot}$), 274, 197, 151, 106.

The inorganic anion, AsO^{3-}, (arsentate) was reacted with a polymer model compound 3, 4-LICAM to form the octahedrel arsenic anion complex. This arsenic anion complex is the first isolated metal complex of these tricatecholate linear amides and enhances the notion that these types of ligands can be placed in a polymeric matrix for future removal of these inorganic arsenic compounds from fossil fuel products.[44]



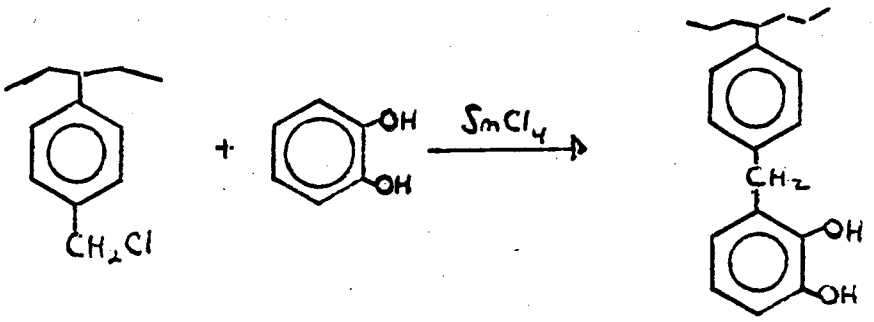
3,4-LICAM

XBL 818-10973

PREPARATION OF POLYMER-BONDED CATECHOLS FOR REACTION STUDIES WITH ORGANOARSENIC AND INORGANIC ARSENIC COMPOUNDS

We have reported on the speciation of inorganic arsenic and organoarsenic compounds in shale oil and retort waters in the previous section.[34-38] In view of these very interesting and exciting results, we are now implementing another stage in our program to find innovative methods to remove the speciated organoarsenic and inorganic arsenic compounds from the shale oil and possibly from the retort waters. In a study to determine the feasibility of using polymer-bonded catecholes for this purpose, we have initiated an experiment to determine whether 3-methylcatechol can remove methyl- and phenylarsonic acids from their association with Fe and ligands of molecular weight in the 2,000 dalton range in Parahoe shale oil.[36] The results of this experiment are not complete and we will report them in the next quarterly. In addition, synthesis of polymer-bonded catechol has also been implemented for studies with authentic organoarsonic acids, i.e., methyl- and phenylarsonic acids. This synthetic method includes reaction of chloromethylated polystyrene-divinylbenzene polymer (20 % cross-linked) with catechol in the presence of stannic chloride (Eq. 3)

This polymer has been prepared and experiments are underway to evaluate its reactivity with methyl- and phenylarsonic acids.



(13)

MOLECULAR CHARACTERIZATION AND FINGERPRINTING OF VANADYL PORPHYRIN AND NON-PORPHYRIN COMPOUNDS FOUND IN VARIOUS HEAVY CRUDE PETROLEUMS AND THEIR ASPHALTENES

Previous Characterization of Heavy Crude Petroleums

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 9. 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

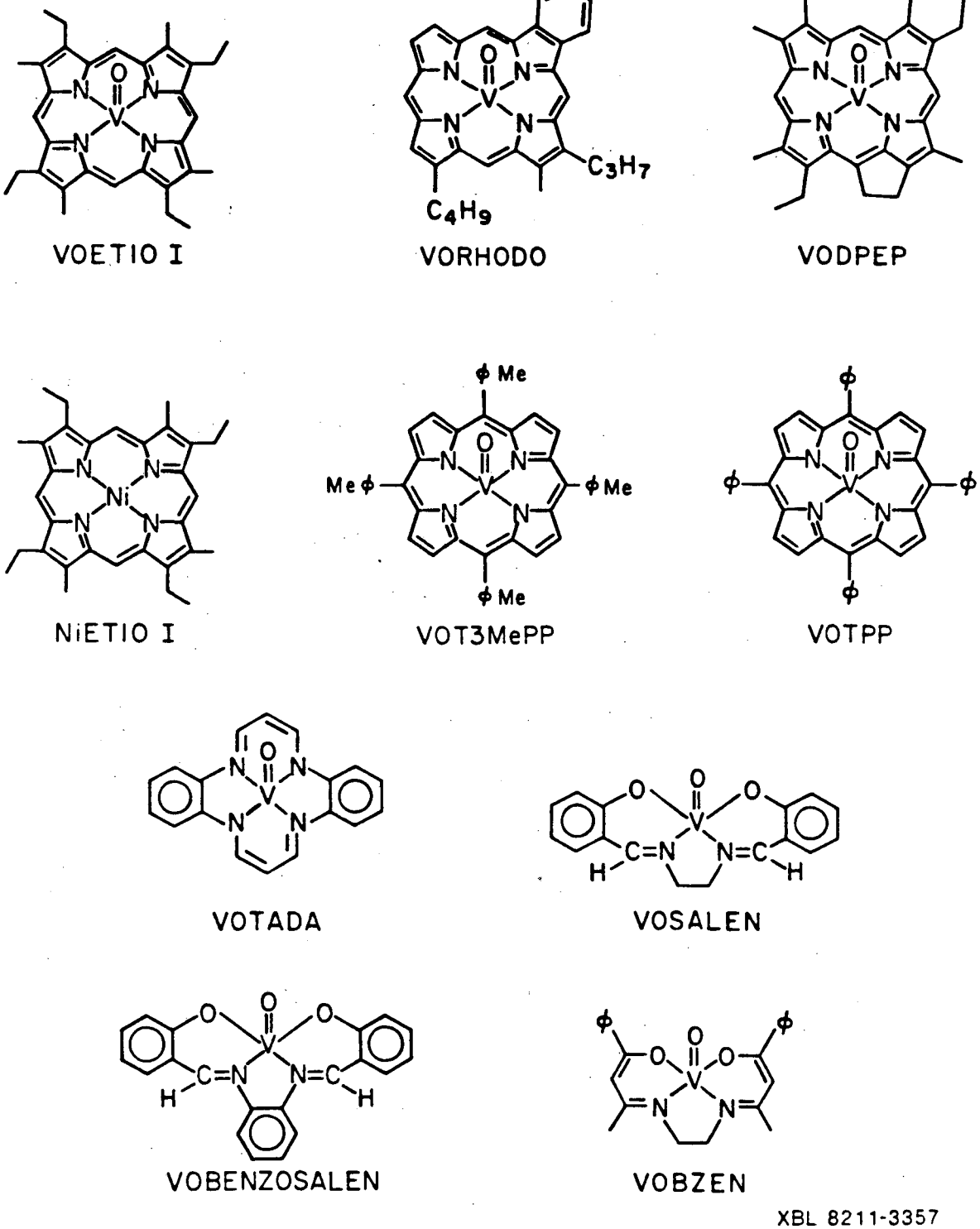


Figure 9

Model Vanadyl Porphyrin and Non-porphyrin Compounds

the central porphyrin ring structure.[52] Baker was also able to identify vanadyl rhodoporphyrin (VORhodo) as a third naturally occurring petroporphyrin (see Figure 9).

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, and may create artifacts that complicate rather than simplify analysis.[53]

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 inaccesibility 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 spectroscopy, 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 procedures.

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.

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 porphyrins in crude oil and residue.

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-porphyrins 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) 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.[8-10]

HPLC-GFAA has recently been used by Fish et al.[34] 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.[36] 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.[65] 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.

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 9 shows VOEtio, VODPEP, and VORhodo porphyrin compounds which have been identified in heavy crude oils, as well as model vanadyl porphyrin and non-porphyrins used in this study. Porphyrin compounds consist of a sixteen member ring containing four nitrogen donor atoms located in four conjugated pyrole 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 vanadyl porphyrins, the majority of vanadyl non-porphyrin compounds decompose readily in dilute acid solutions. VOBenzosalen, VOSalen, VOTADA, and VOBZEN represent vanadyl non-porphyrin compounds which have yet to be identified in heavy crude petroleums. Table 4 summarizes and compares molecular characteristics of vanadyl porphyrin and non-porphyrin compounds referred to in this study.

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.

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

Table 4

Criteria for Vanadyl Porphyrin and Non-Porphyrin Compounds

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[36] and and retort waters,[34,35] offers much promise as a means of molecularly characterizing and identifying 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.

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.

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 proven 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.

Experimental Approach

In this study Boscan, Cerro Negro, Wilmington, and Prudhoe Bay crude petroleums, containing 1,100, 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.

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 spectrophotometry, are shown in Table 5. 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 5 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

	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

Table 5

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

crude oil, 50 percent for Cerro Negro crude oil, 87 percent for Wilmington crude oil, and 50 percent for Prudhoe Bay crude oil.

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 Venezuelan 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 5. 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 extraction, and the irreversible mechanism of removal and incorporation of vanadyl compounds from the heavy petroleum asphaltenes.

SEC-HPLC-GFAA Analysis

50 Å Column

The SEC calibration data for the 50 Å column using THF as the mobile phase is given in Figure 10. 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 10 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-porphyrin 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.

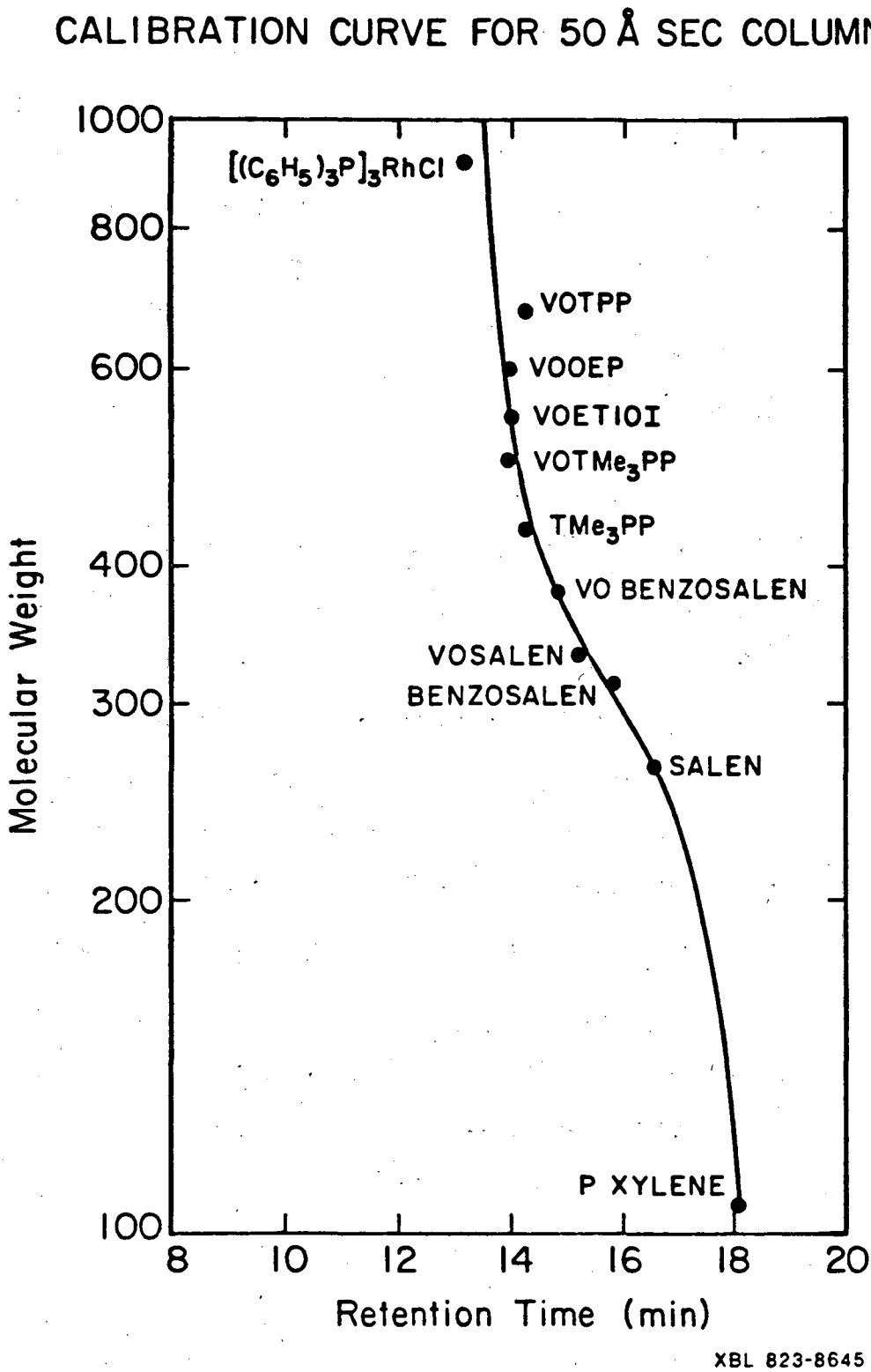


Figure 10

Plot of Log Molecular Weight Versus Retention Time for the 50 Å Column

Figure 11 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 histogramic GFAA vanadium output (318.4) in the lower portion.

Figure 11 (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 11, 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 11 (a) and Figure 10, 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-porphyrin

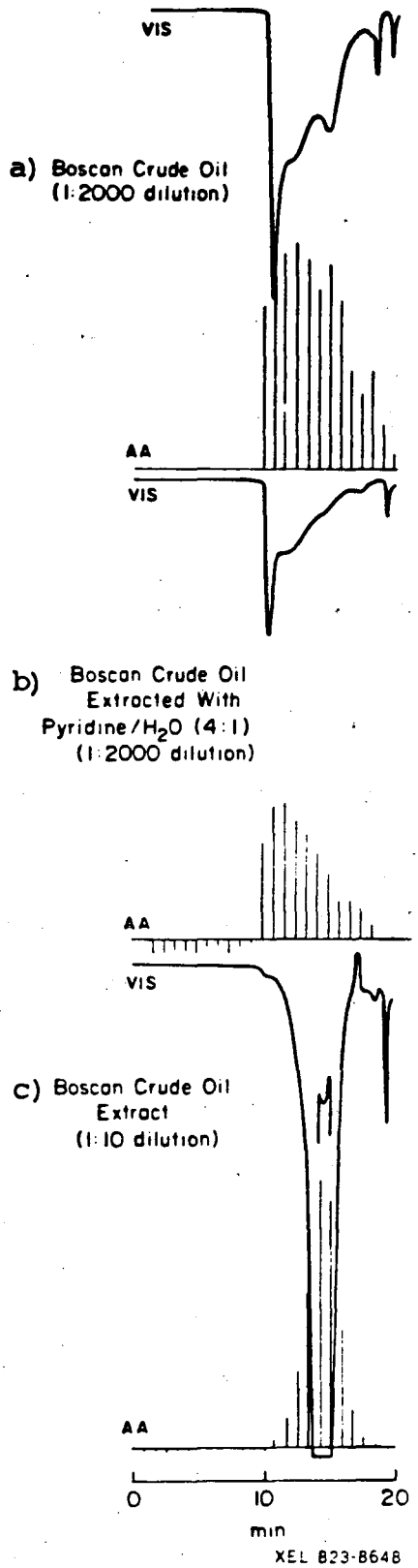


Figure 11

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

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 11 (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 11 (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 11 (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 procedure. 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 12. 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 12 (b) shows substantial vanadium removal from the high molecular weight fraction of the oil, while Figure 12 (c) shows that the extract contains only low to medium molecular weight vanadyl compounds. Again the visible absorbance and vanadium histogramic output are centered at molecular weights of 350 daltons, indicating vanadyl non-porphyrin compounds predominate in the extract.

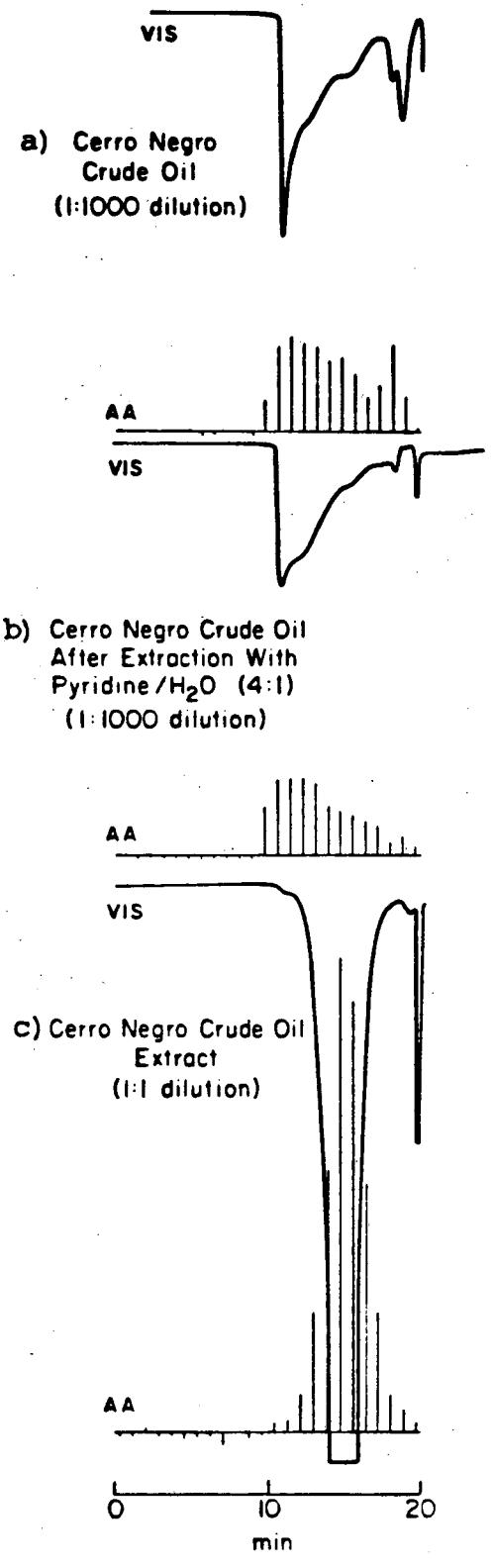


Figure 12

50 Å SEC-HPLC-GFAA Data for a) Cerro Negro Crude Oil, b) Crude Oil After Extraction and c) Crude Oil Extract

SEC-HPLC-GFAA data for Wilmington and Prudhoe Bay crudes are shown in Figures 13 and 14, respectively. 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 13(c) and 14(c) show slightly broader visible absorbance and atomic absorption histograms than do the two Venezuelan crude oil extracts. As Figure 14(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 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.

50/100 Å Column Combination

Vanadyl Compounds

Since the 50 Å SEC column proved incapable of differentiating molecular weights greater than 900 daltons, and much of the vanadium

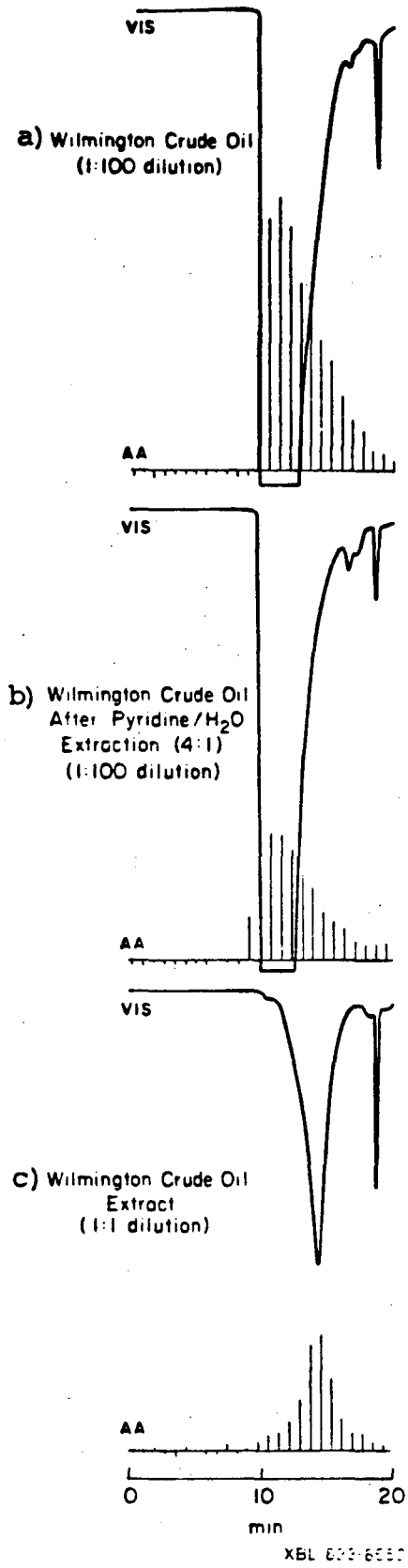


Figure 13

50 Å SEC-HPLC-GFAA Data for a) Wilmington Crude Oil, b) Crude Oil After Extraction and c) Crude Oil Extract

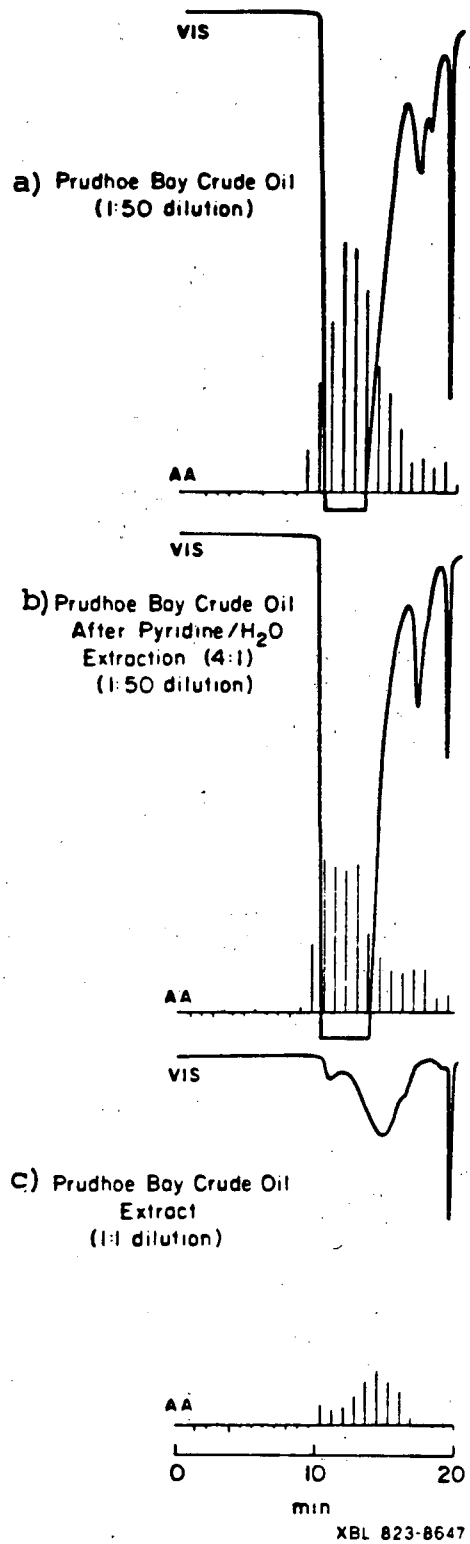


Figure 14

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

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 15. 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.

The 50/100 Å SEC-HPLC-GFAA data for the separation of several of the standards is shown in Figure 16 (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 16 (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.

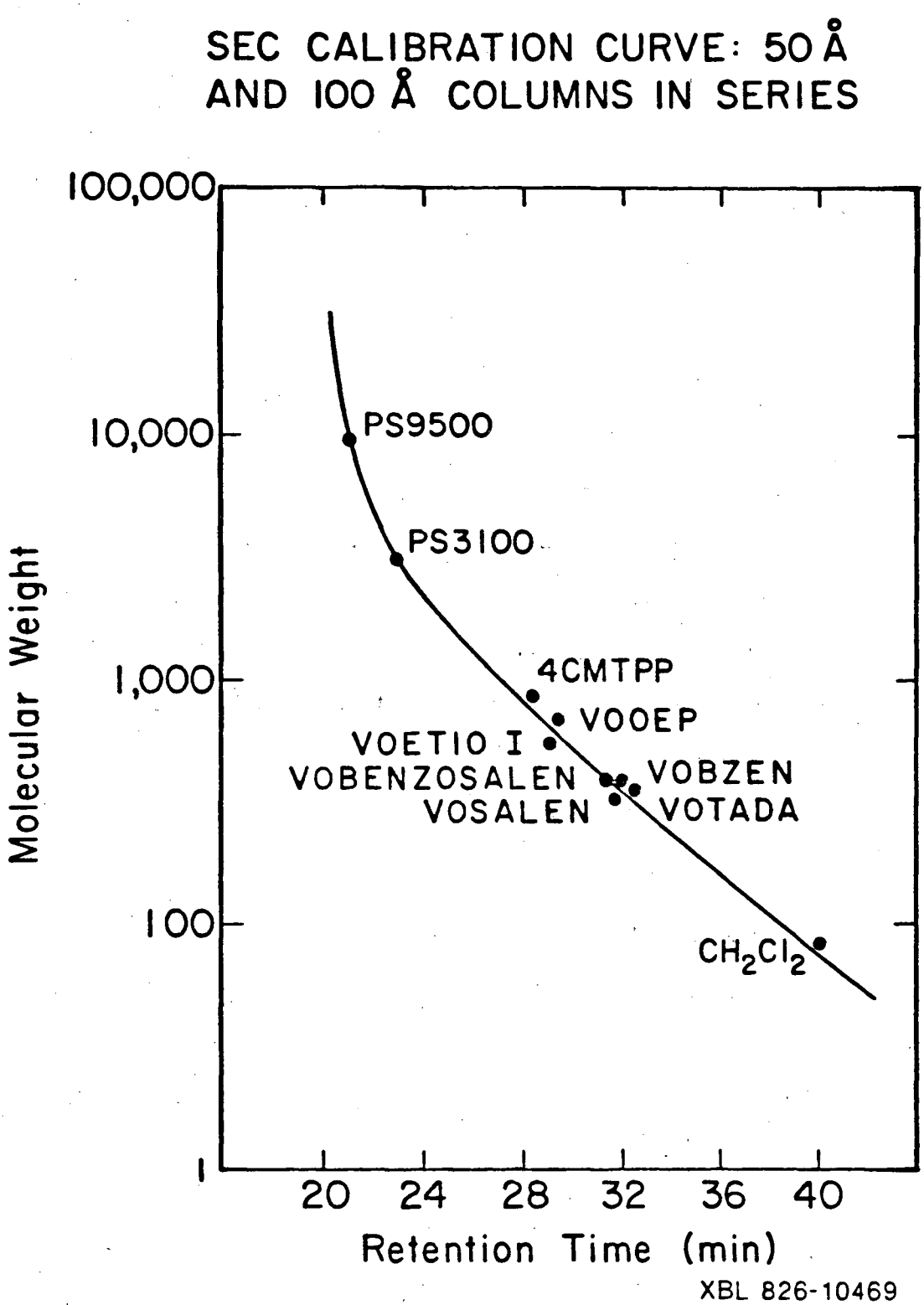


Figure 15

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

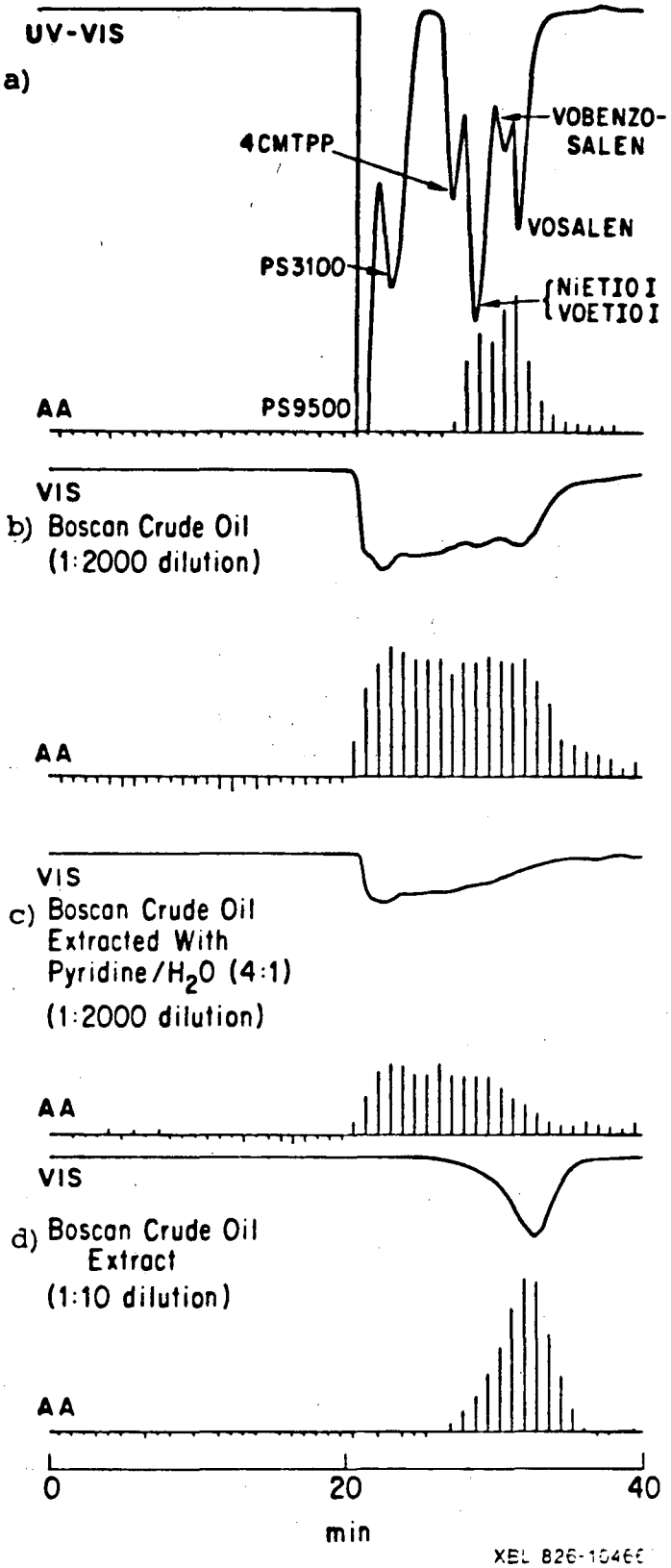


Figure 16

50/100 Å SEC-HPLC-GFAA Data for a) Standards, b) Boscan Crude Oil, c) Crude Oil After Extraction, and d) Crude Oil Extract

Based on Figure 15, 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 4. Above molecular weights of 900 daltons, the definition of vanadyl porphyrins present in Table 4 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 molecular weight vanadyl porphyrin and non-porphyrin compounds intercalated into the asphaltenes, and high molecular weight vanadyl porphyrin and non-porphyrin 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. Likewise, low molecular weight vanadyl non-porphyrin com-

pounds could be incorporated into the asphaltene fraction of the oil by π-π interaction or hydrogen-bonding. This intercalation could drastically alter the stability and other spectroscopic properties, of these vanadyl non-porphyrin compounds.

Figures 16 (b), (c), and (d) show the 50/100 Å column combination data for Boscan crude oil, oil after extraction, and extract respectively. The upper portion of Figure 16 (b) shows the visible absorbance, measured at 408 nm, while the lower portion of the chromatogram gives the vanadium histogramic output. The location of the vanadium histogramic 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 16 (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 16 (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 cali-

bration data from Figure 15, 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 17 shows SEC-HPLC-GFAA data for Cerro Negro crude oil. Figures 17 (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 18 and 19 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.

Comparisons of the four oils, based on the SEC-HPLC-GFAA fingerprints 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

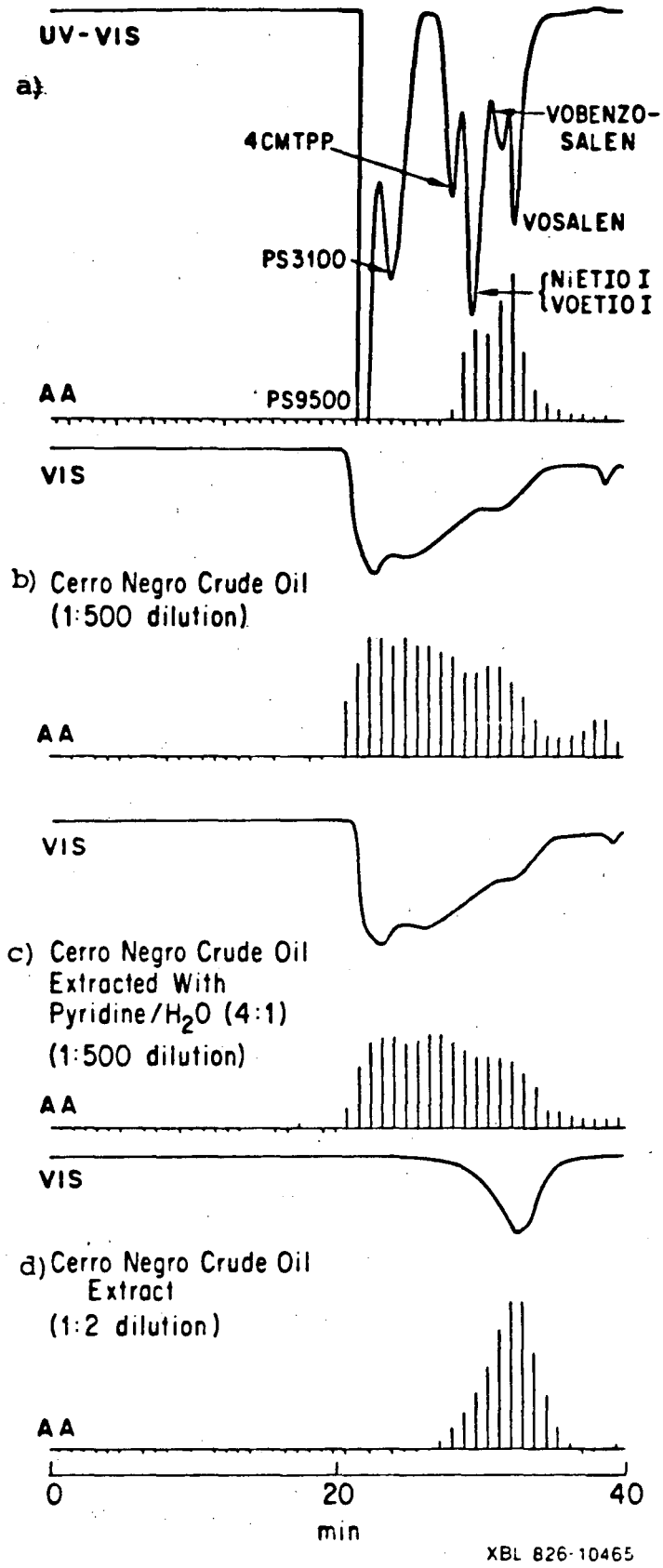


Figure 17

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

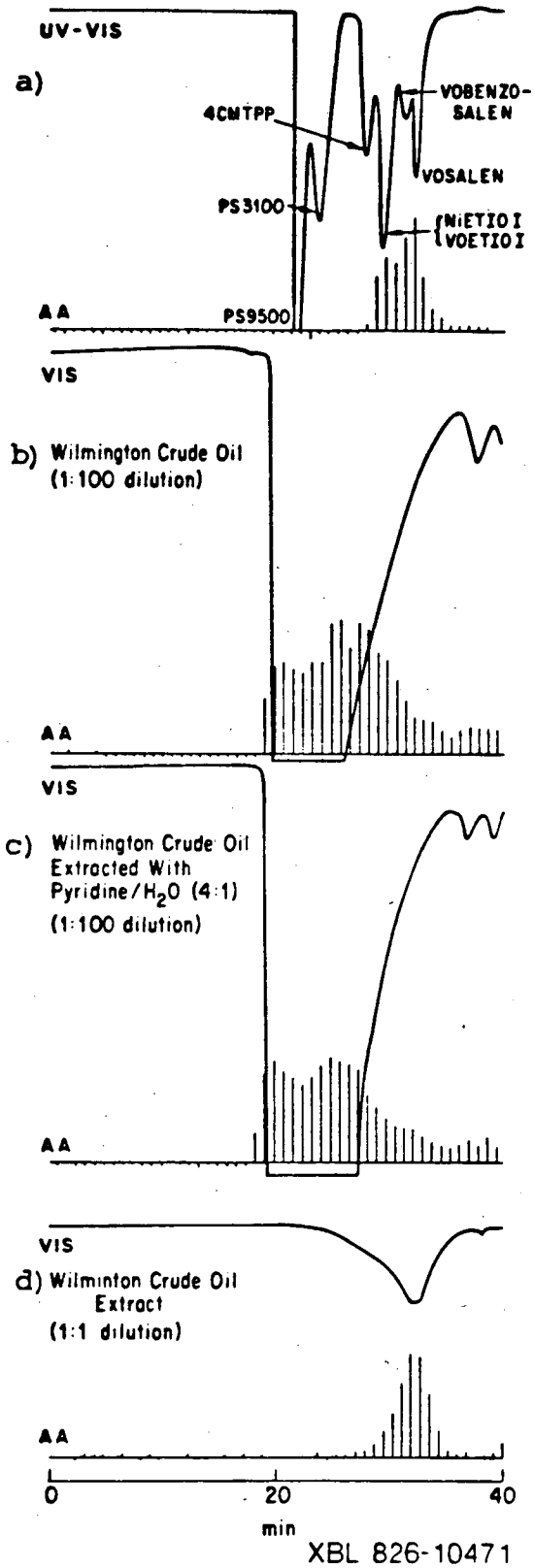


Figure 18

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

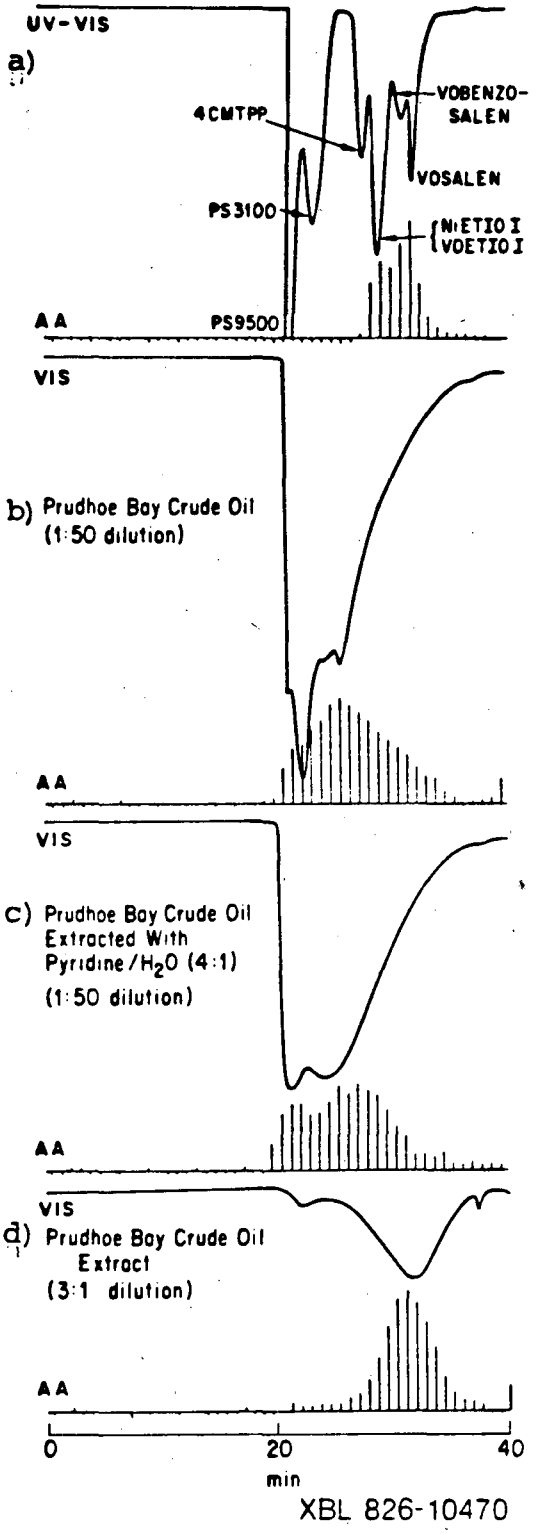


Figure 19

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

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 6. 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 6 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 calibration data from Figure 15, and the digitally recorded histogramic outputs from Figures 16-19.

Figure 15 was used to ascertain retention times for eluting species in each of the four molecular weight categories. Vanadium percentages were then calculated by summing the histogramic vanadium

	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.

Table 6

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

outputs in each molecular weight category and dividing by the total histogramic 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 6 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 6 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 6 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 6 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 compounds with increasing molecular weight for all four molecular weight categories.

As the data on the third and fourth lines of Table 6 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 6 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 therefore 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 6 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 6 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.

Nickel Compounds

Data comparing HPLC-GFAA vanadium and nickel distributions for Boscan and Cerro Negro crude oils is shown in Figure 20. 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 20 (a). Figure 20(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

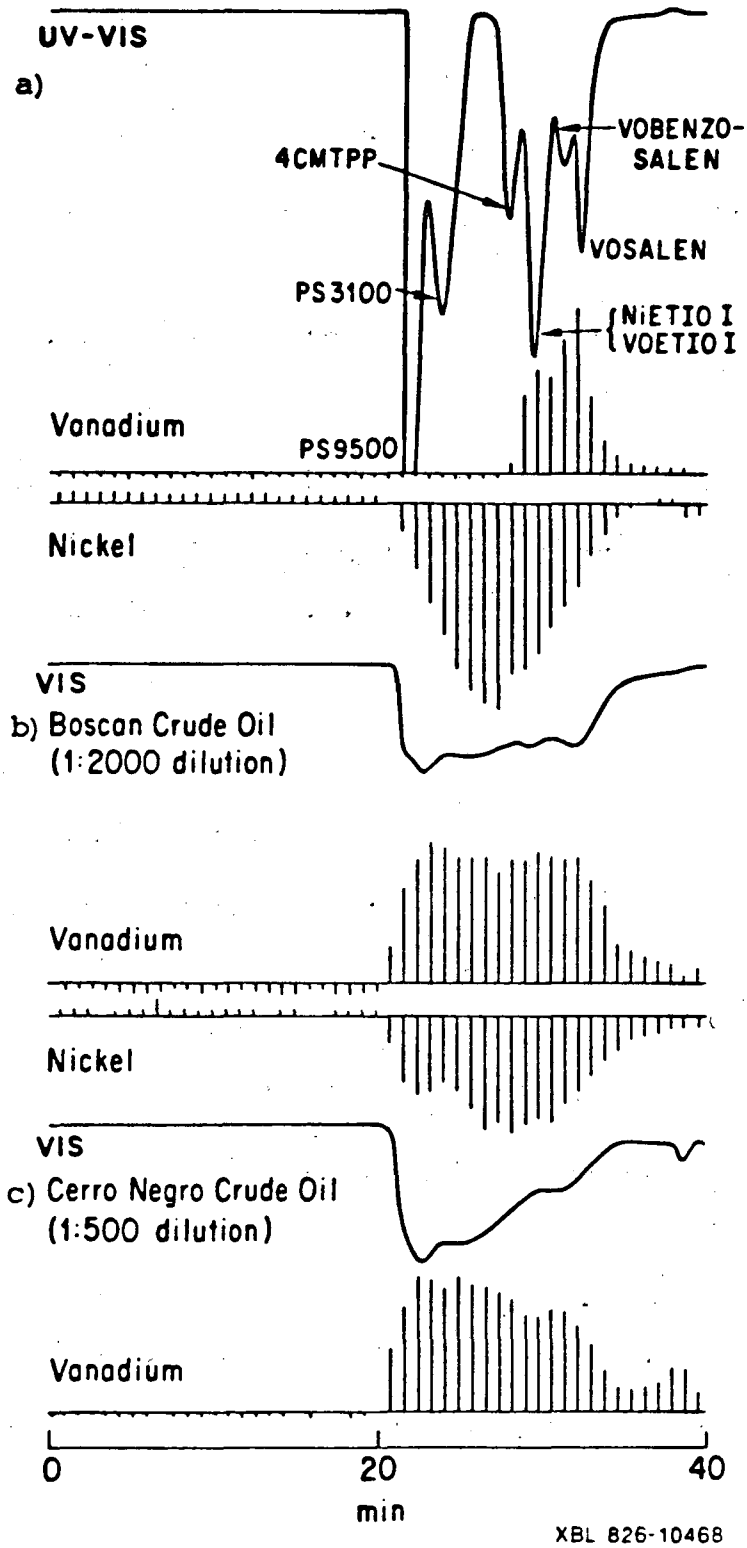


Figure 20

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

nickel and vanadyl compound profiles for Cerro Negro crude oil are compared in Figure 17 (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 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 21 (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 7 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 histogramic GFAA outputs with retention times greater than and less than 900 daltons, as determined using the model vanadyl porphyrin and non-porphyrin compounds (Fig. 15), 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

Table 7. Molecular Weight Distributions of Vanadyl and Nickel Compounds Present in Heavy Crude Oils by 50/100 Å SEC-HPLC-GFAA Analysis.

	Boscan		Cerro Negro		Wilmington		Prudhoe Bay	
Molecular Weight	>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.

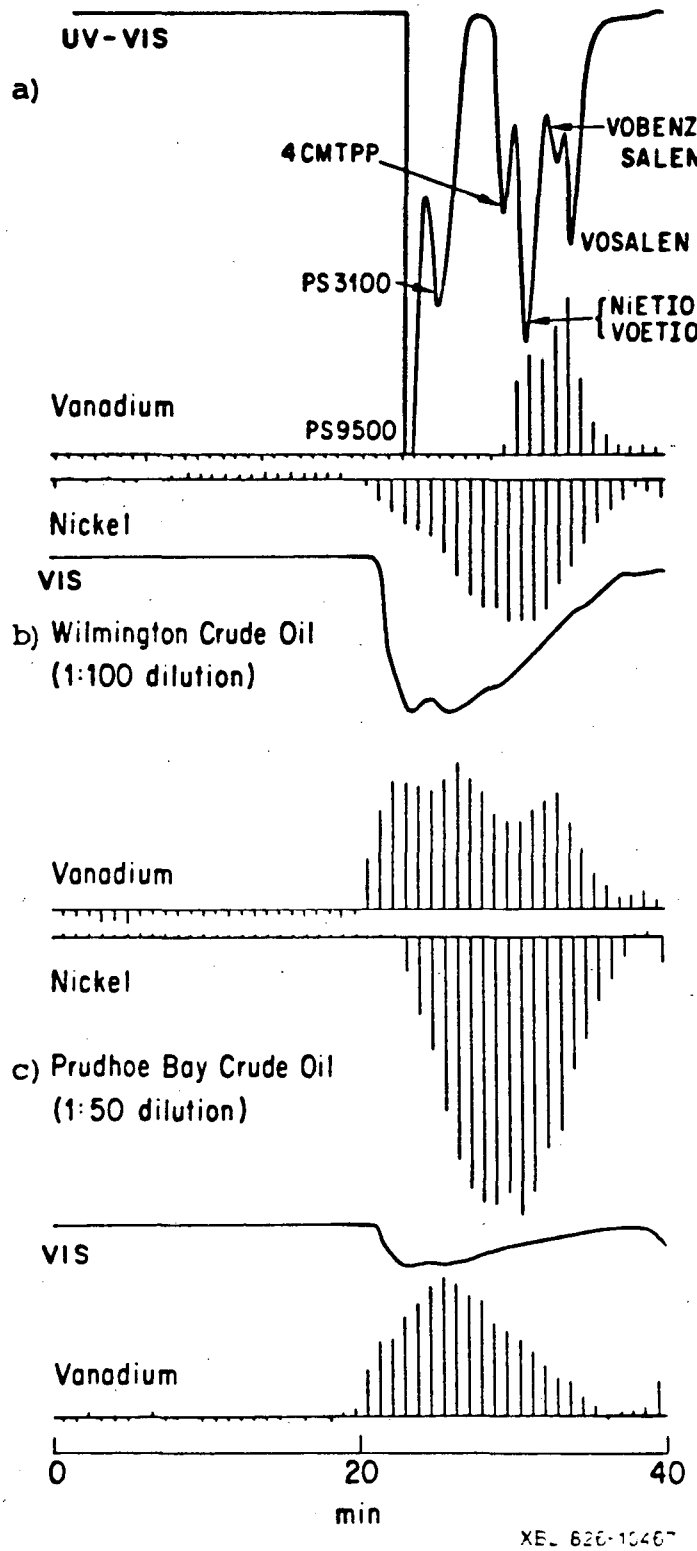


Figure 21

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

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 present in the asphaltenes, and preferential bonding of nickel to nitrogen ligands as has been reported.[66]

PAC-HPLC-GFAA

Because Table 6 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 22. Figure 22 (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-porphyrin complexes were monitored at 320 nm. The earliest eluting peak evident in all of the chromatograms represents the solvent, methylene chloride. The lower portion of Figure 22 (a) shows the histogramic vanadium outputs. With the exception of NiEtio I porphyrin, all the other standards register vanadium histograms.

Figures 22 (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 22 (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 22 (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 22 (c), since VOEtio, VODPEP, and VORhodo porphyrins are known to have characteristic absorbances at 572 nm. However, as Figure 22

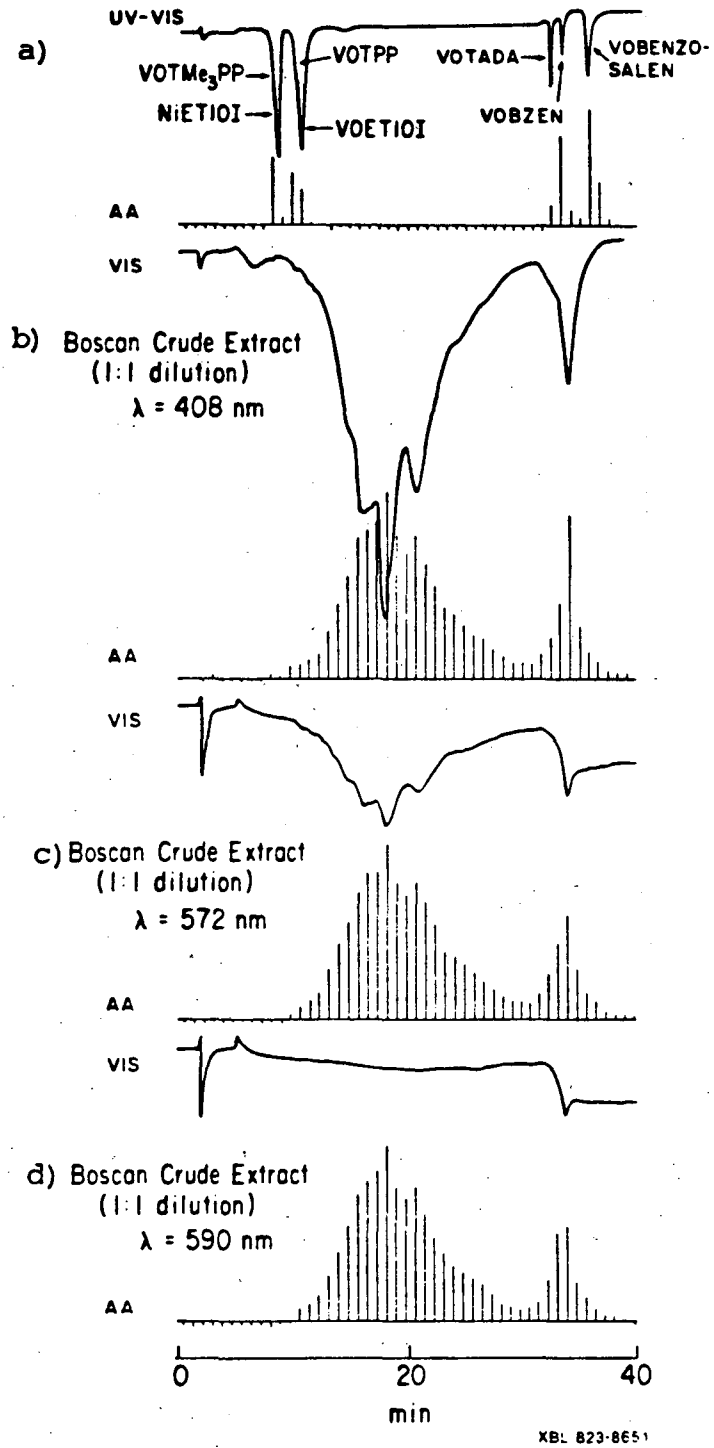


Figure 22

PAC-HPLC-GFAA Data for a) Standards and Boscan Crude Oil Extract at b) 408 nm, c) 572 nm, and d) 590 nm

(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 porphyrin, while the VOEtio and VODPEP porphyrins[63,67] can be assigned to the earlier eluting vanadyl porphyrin peaks. This confirms HPLC obtained results for VOEtio and VODPEP porphyrins. 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 porphyrins contained in the extract, suggesting that the model vanadyl porphyrins 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 23 (b) and (c) respectively. Figure 23 (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

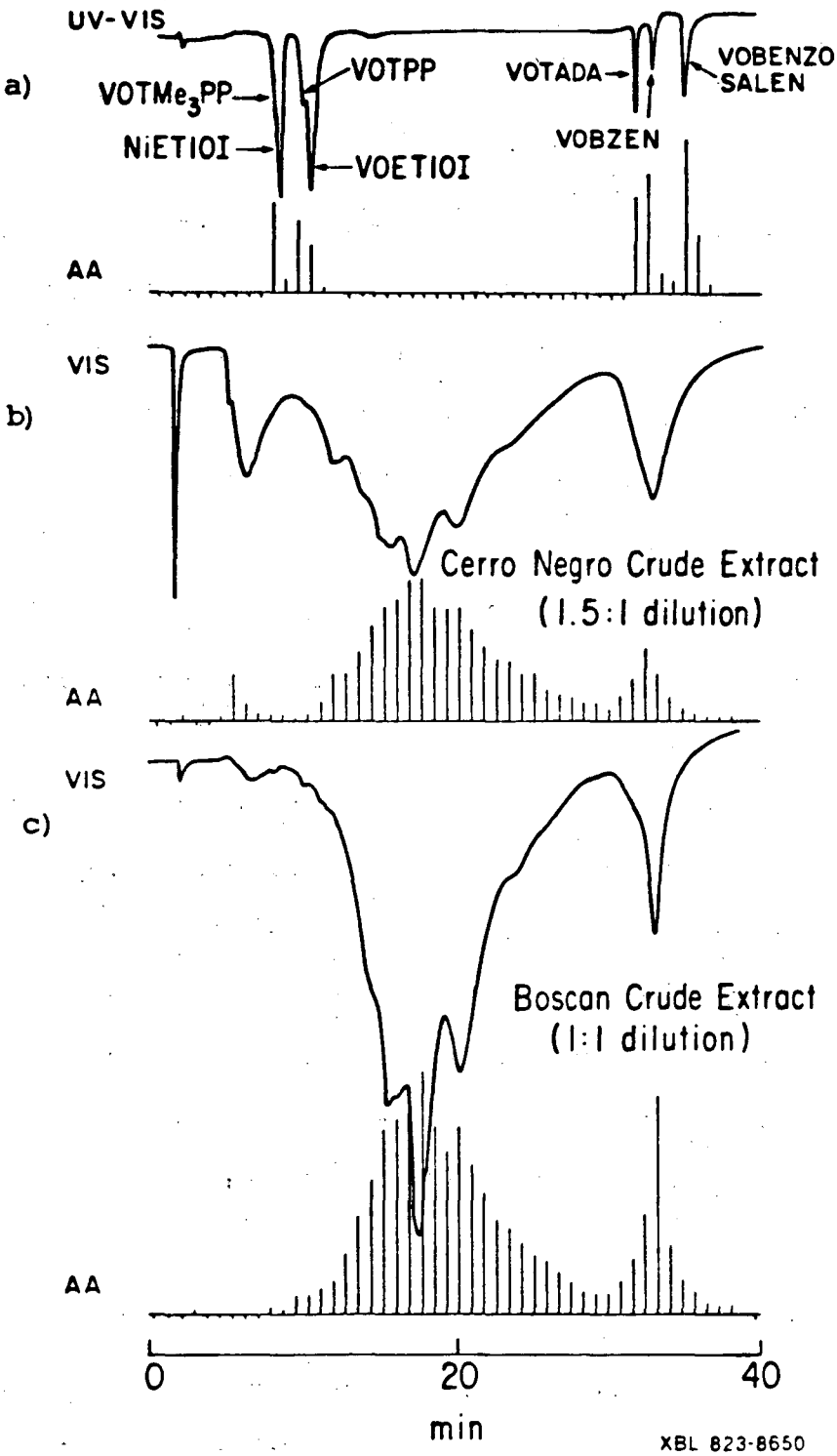


Figure 23

PAC-HPLC-GFAA Data for a) Standards, b) Cerro Negro Crude Oil Extract and c) Boscan Crude Oil Extract

extract shows an early eluting vanadyl compound peak at 5 minutes, and a nickel porphyrin visible peak at 7 minutes, clearly distinguishing the two extracts.

Data comparing Prudhoe Bay and Wilmington crude oil extracts are shown in Figures 24 (b) and (c). Evident in Figure 24 (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 24 (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 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.

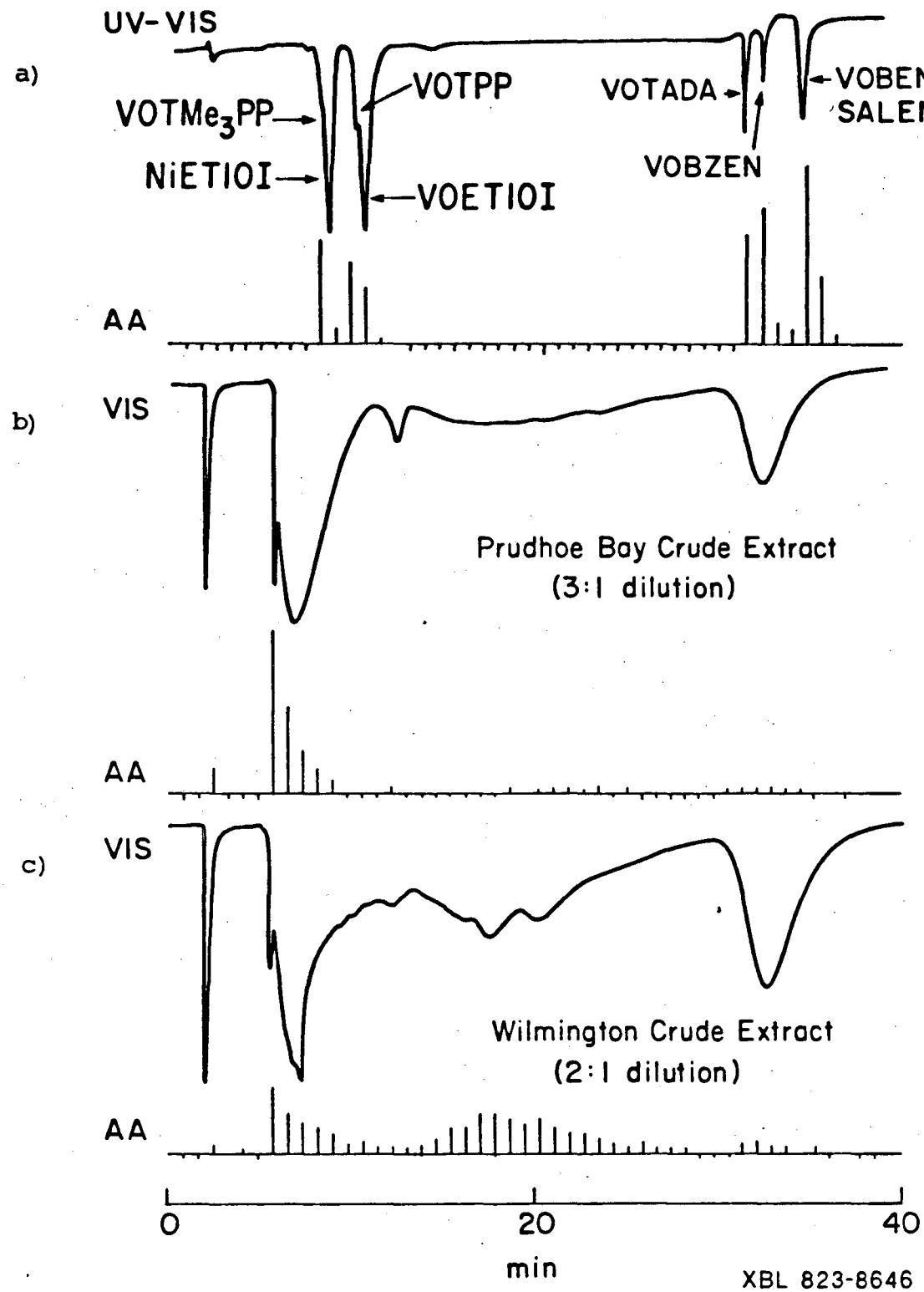


Figure 24

PAC-HPLC-GFAA Data for a) Standards, b) Prudhoe Bay Crude Oil Extract, and c) Wilmington Crude Oil Extract

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 25 (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 25 (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 vanadyl non-porphyrin compound(s) with maximum UV-Vis absorbance at 300 nm. This non-porphyrin was found to be present 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 6 indicates that both of these extracts should contain nearly three

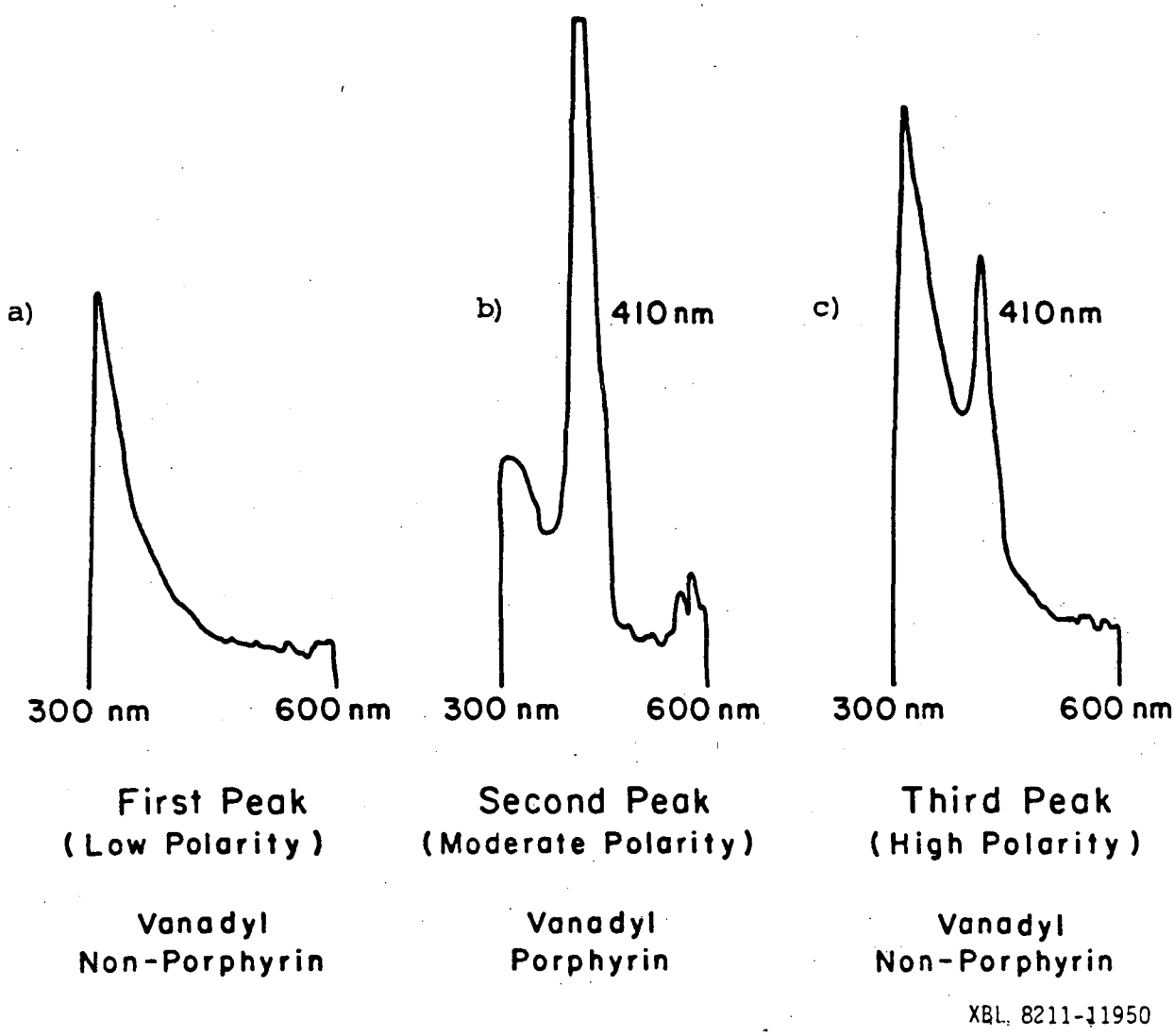


Figure 25

Representative Rapid Scan Spectroscopy (RSS) Data Obtained for PAC-HPLC-GFAA Separated Pyridine Extracts

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 containing 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.

DISCUSSION

Biogeochemical Information

Studies have indicated that crude oils which are rich in vanadium have high asphaltene contents.[68,69] Figure 26 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 behavior. 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 20 and 21 and summarized in Table 7, 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[70] have demonstrated that asphaltenes in benzene solutions can incorporate 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 27 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 coordination sites in asphaltenes which selectively coordi-

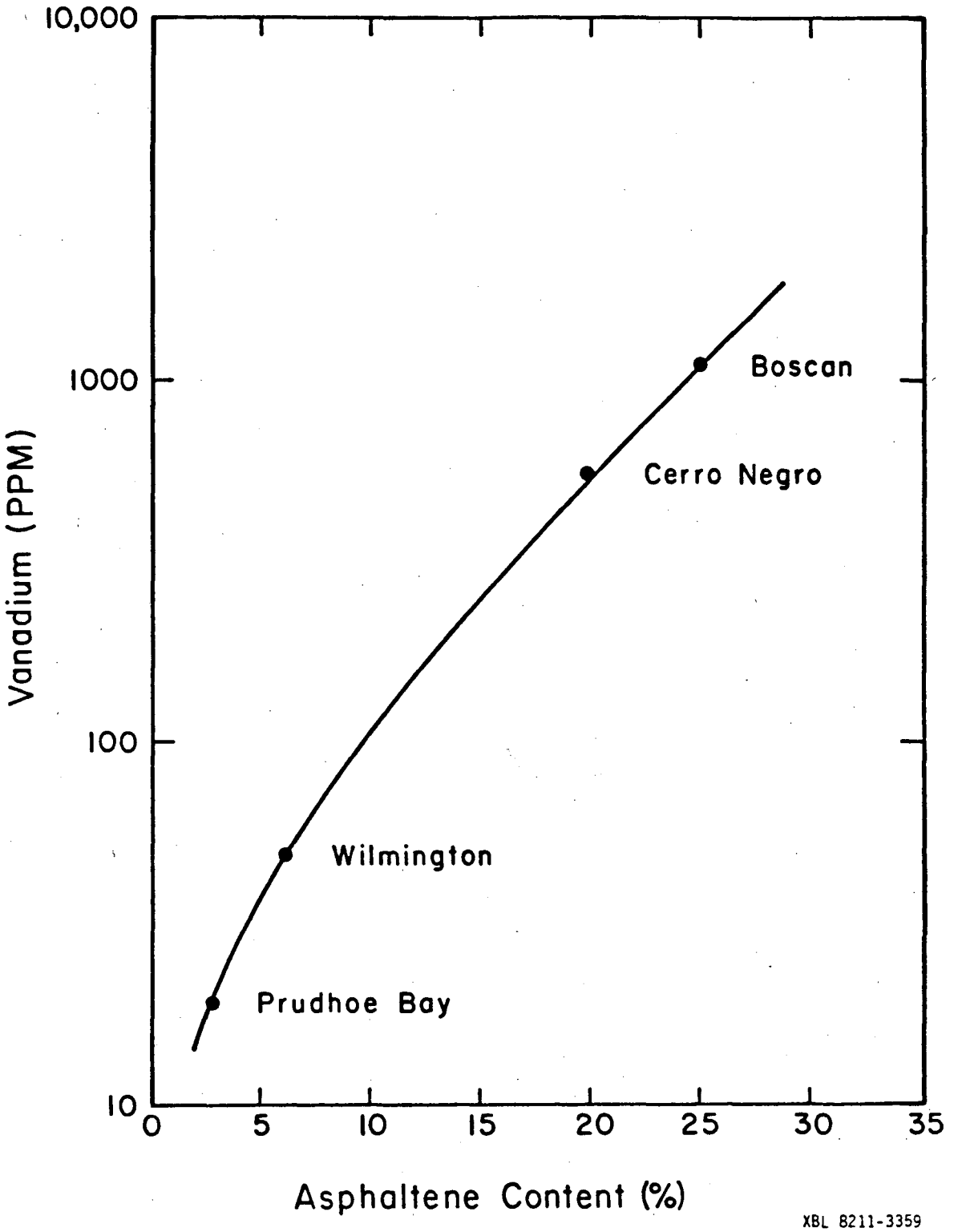


Figure 26

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

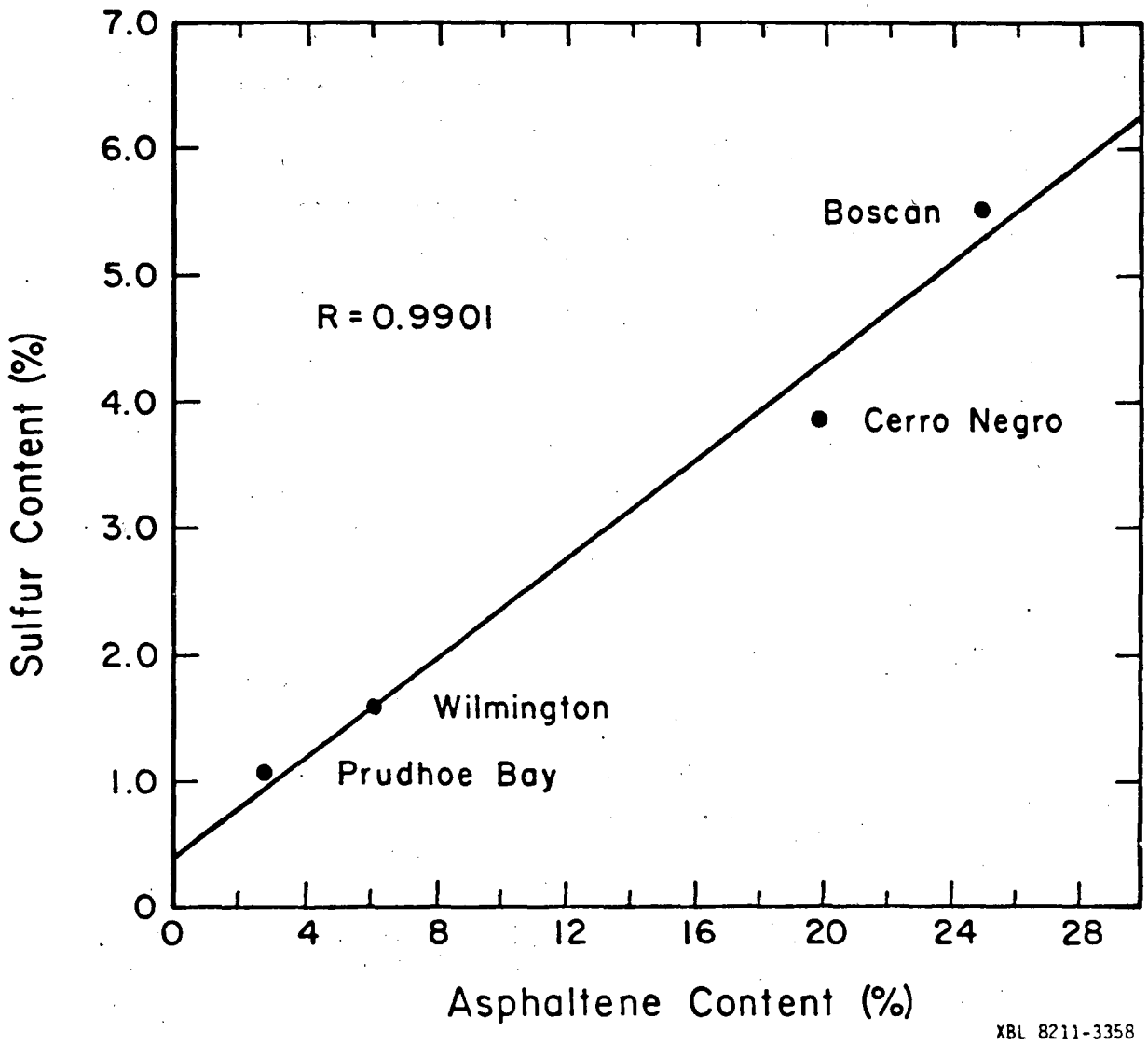


Figure 27

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

nate vanadyl ion, rather than nickel ion. Recent studies[71,72] 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.[71]

Radchenko[66] 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 7, coupled with the PAC-HPLC-GFAA chromatograms from Figures 23 and 24, 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.[66] 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.[66]

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.[71-74] 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 chlorophyll "a" as proposed,[75] or synthesized from bacteria.[74]

Another proposed mechanism[66] 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 organisms or through acid depolymerization of polymeric vanadates present in the crust of the earth.[70,54]

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 stability 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 asphaltenes. The identity and stability of the extractable and non-extractable complexes is important both technologically and geochemically.

This study indicates that vanadyl compound molecular weight distributions are independent of vanadium concentration. However, the types of vanadyl complexes present in each oil have been shown to vary considerably. 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 clarification of bio-evolutionary processes affecting heavy crude petroleum deposits.

Applications Utilizing SEC-HPLC-GFAA Analysis

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.

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-porphyrin 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 continuous, 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. 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.

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.

SEC-HPLC-GFAA Analysis of Heavy Crude Asphaltenes

The asphaltenes in the heavy crude oils contain a significant percentage of the vanadium, and thus examination of their vanadyl compound content for porphyrin and non-porphyrin compounds by HPLC-SEC-GFAA analysis would be critical. Additionally, extraction of the asphaltenes with a pyridine/H_2O solution would be helpful in learning more about non-porphyrin vanadyl compounds complexed to the macromolecular structure of the asphaltenic fraction.

During this quarter, work has continued with the asphaltenes of Boscan, Cerro Negro, Wilmington, and Prudhoe Bay heavy crude oils. Separation of the oils is achieved by agitating samples of oil in 10 volumes of pentane at about 300 motions per minute for 24 hours. Separations have also been made using heptane as the solvent, but these samples have not yet been analyzed. The asphaltenes are separated from the pentane solubles with a 0.45 micron millipore filter, washed with pentane and stored under nitrogen. X-ray fluorescence analysis for vanadium has been performed and compared with earlier results for whole crude oils (Table 8). A significant percentage of the vanadium in the oils is contained in the asphaltenes. The percentage of vanadium in the asphaltenes is not directly proportional to the amount of asphaltenes present in an oil and although the asphaltenes represent less than 3 percent of the weight of a crude they still account for almost half of the vanadium present.

	ppm V in Crude Oil	ppm V in Asphaltene	Wt. % of Asphaltene in Crude	% of Total V in Asphaltene
Boscan	1100	4310	25	98
Cerro Negro	560	1680	20	60
Wilmington	49	422	6.2	53
Prudhoe Bay	19	280	2.9	43

TABLE 8

Concentrations of Vanadium in Heavy Crude Oils and Asphaltenes

Samples of the asphaltenes are redissolved in methylene chloride and analyzed by HPLC-SEC-GFAA using 50Å and 100Å SEC columns in series with element-specific vanadium detection at 318.4 nm. The visible detector was set at 408 nm to detect the soret bands of vanadyl porphyrins. The extraction and analysis procedure was repeated three times for each oil. Figures 28-31 show typical SEC results and Figure 32 is a calibration curve for the HPLC-GFAA. Following the usual procedure the asphaltenes were separated into four fractions by molecular weight: greater than 2000, less than 2000 but greater than 900, less than 900 but greater than 400, and less than 400. The third fraction is assumed to be rich in vanadyl porphyrins. Table 9 shows the asphaltenes compared with the whole heavy crude. It can be seen that the percentage of vanadium in the less than 900, greater than 400 molecular weight fraction is much lower for the asphaltenes. This does not mean that there are less porphyrins in the asphaltenes, but may indicate that the asphaltenic porphyrins are incorporated into larger complexes since there is intense visible absorption in the highest molecular weight fraction.

The pentane soluble, malthene, fractions of the oils were vacuum distilled to remove the pentane and then dissolved in methylene chloride for HPLC-SEC-GFAA analysis. The bottom line of Table 9 shows the molecular weight distribution of vanadium in the malthenes. Figures 28-31 show typical vanadium distributions for the malthenes of the four oils. By comparing the asphaltenes and malthenes with their whole oils, it can be observed, in general, that the asphal-

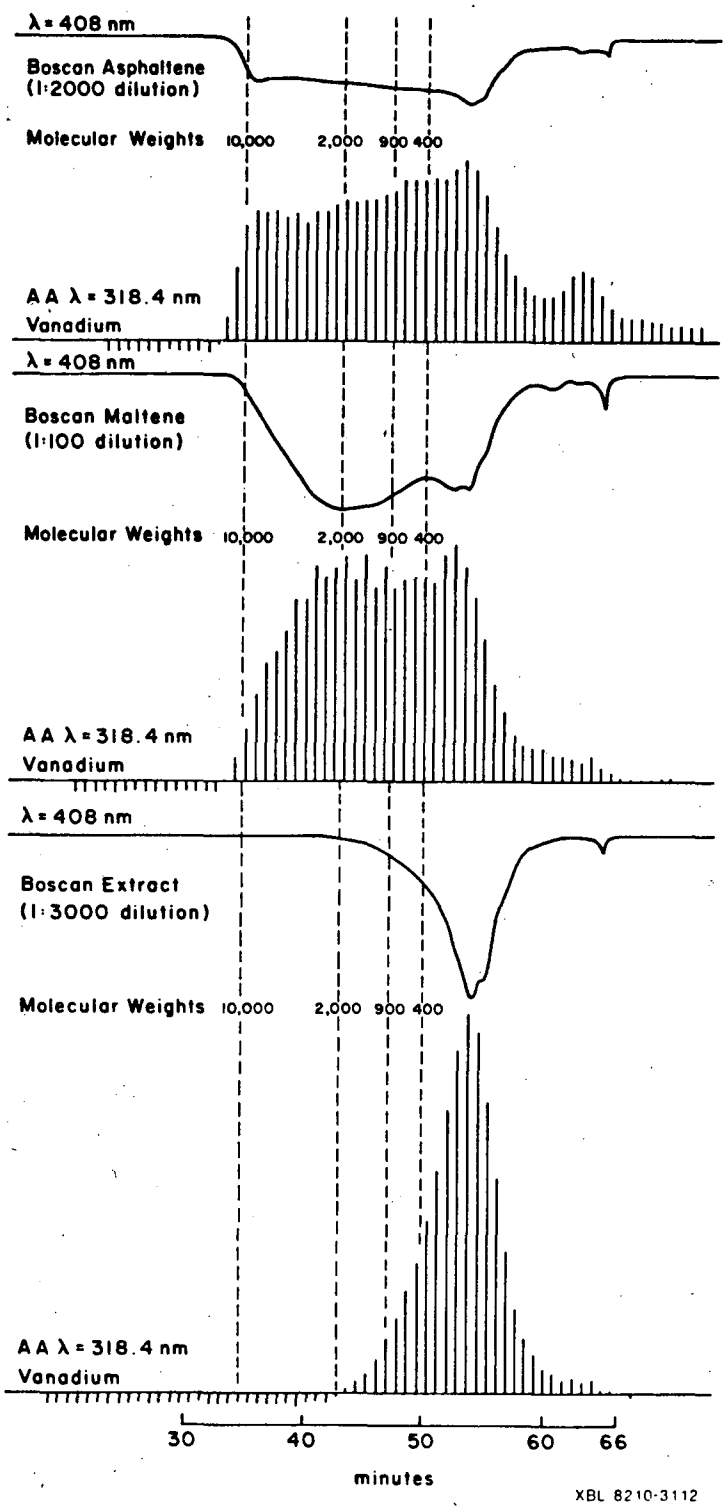


Figure 28

50/100/1000 Å SEC-HPLC-GFAA analysis of Boscan Asphaltene, Maltene and Asphaltene Extract

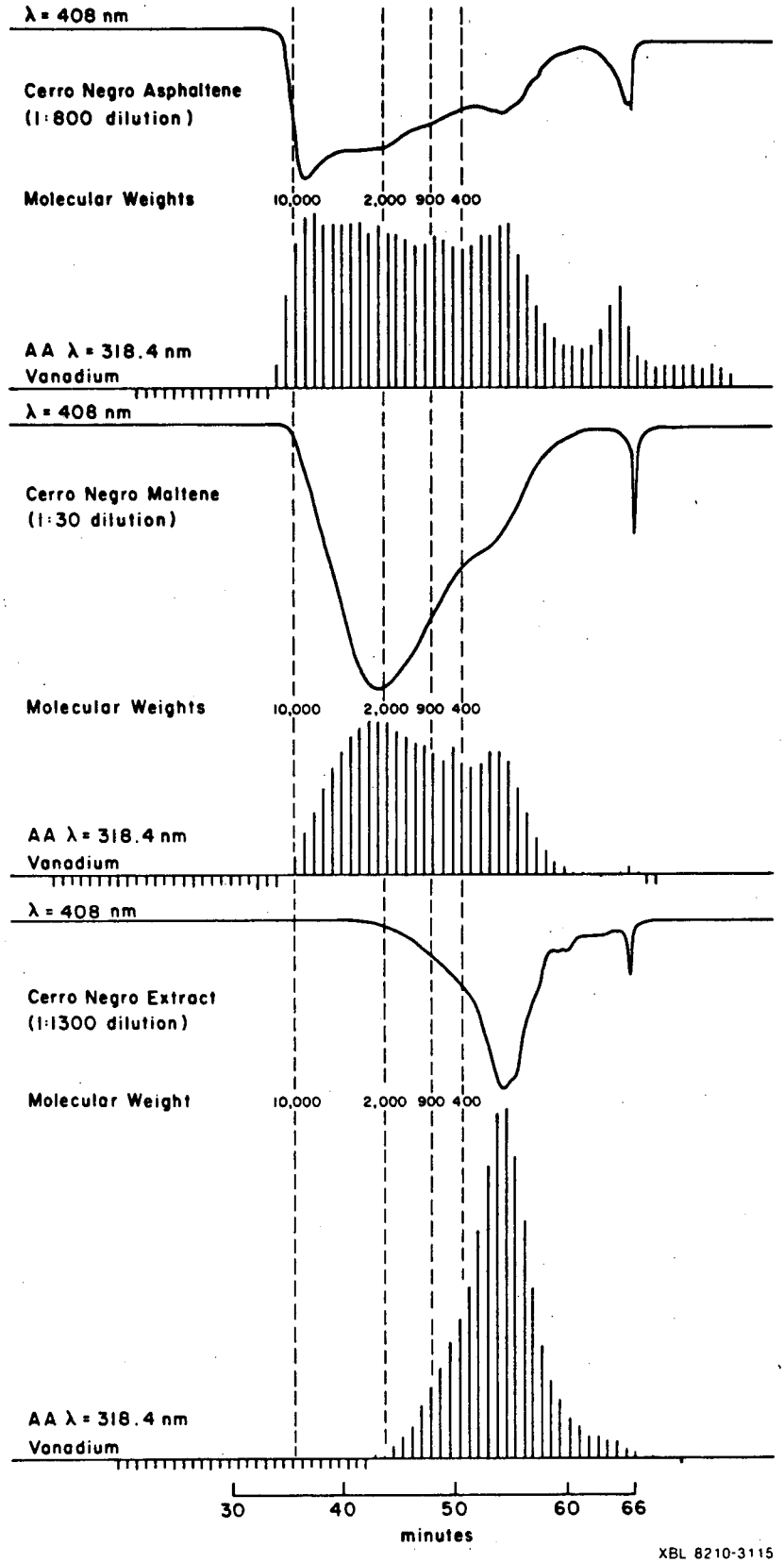


Figure 29

50/100/1000 Å SEC-HPLC-GFAA analysis of Cerro Negro Asphaltene, Maltene and Asphaltene Extract

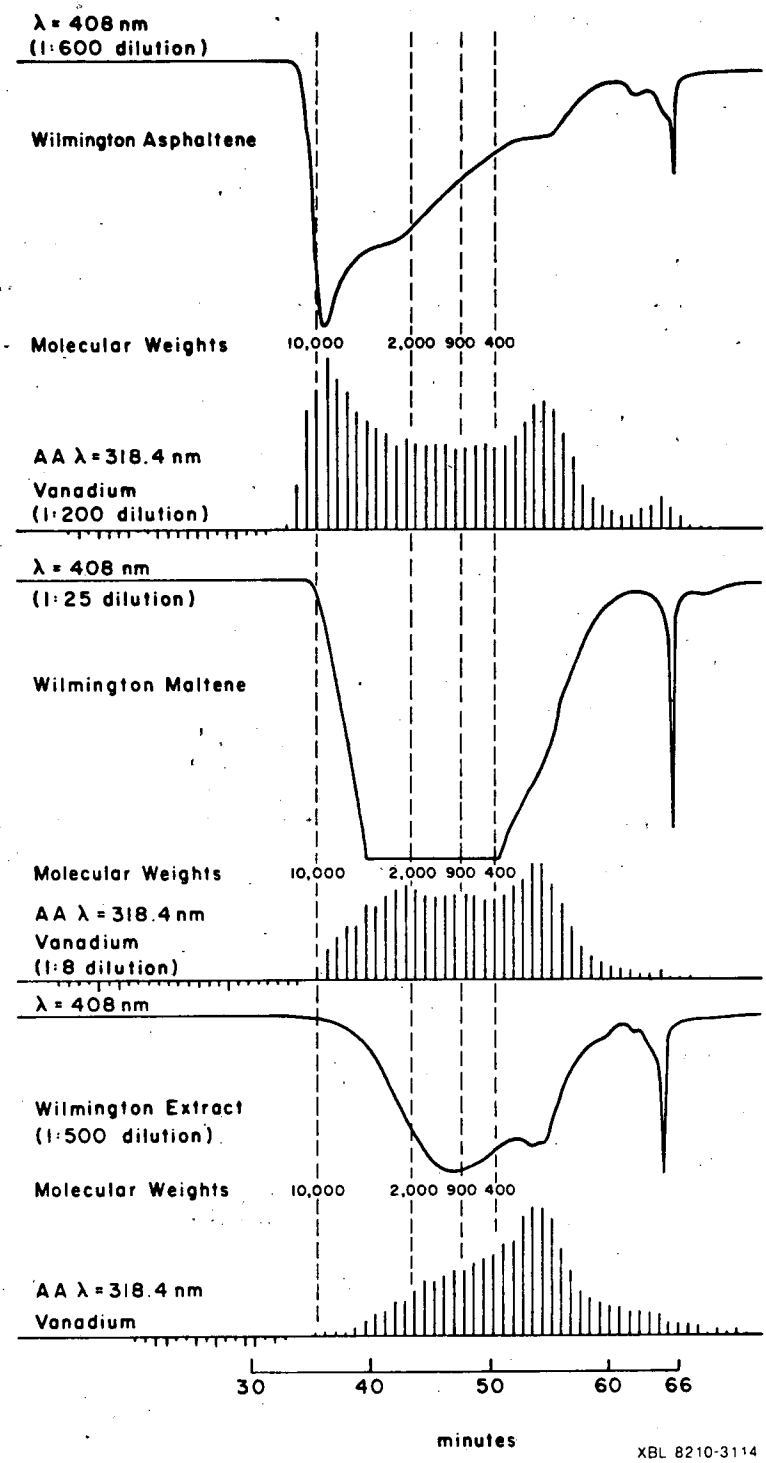


Figure 30

50/100/1000 Å SEC-HPLC-GFAA analysis of Wilmington Asphaltene, Maltene and Asphaltene Extract

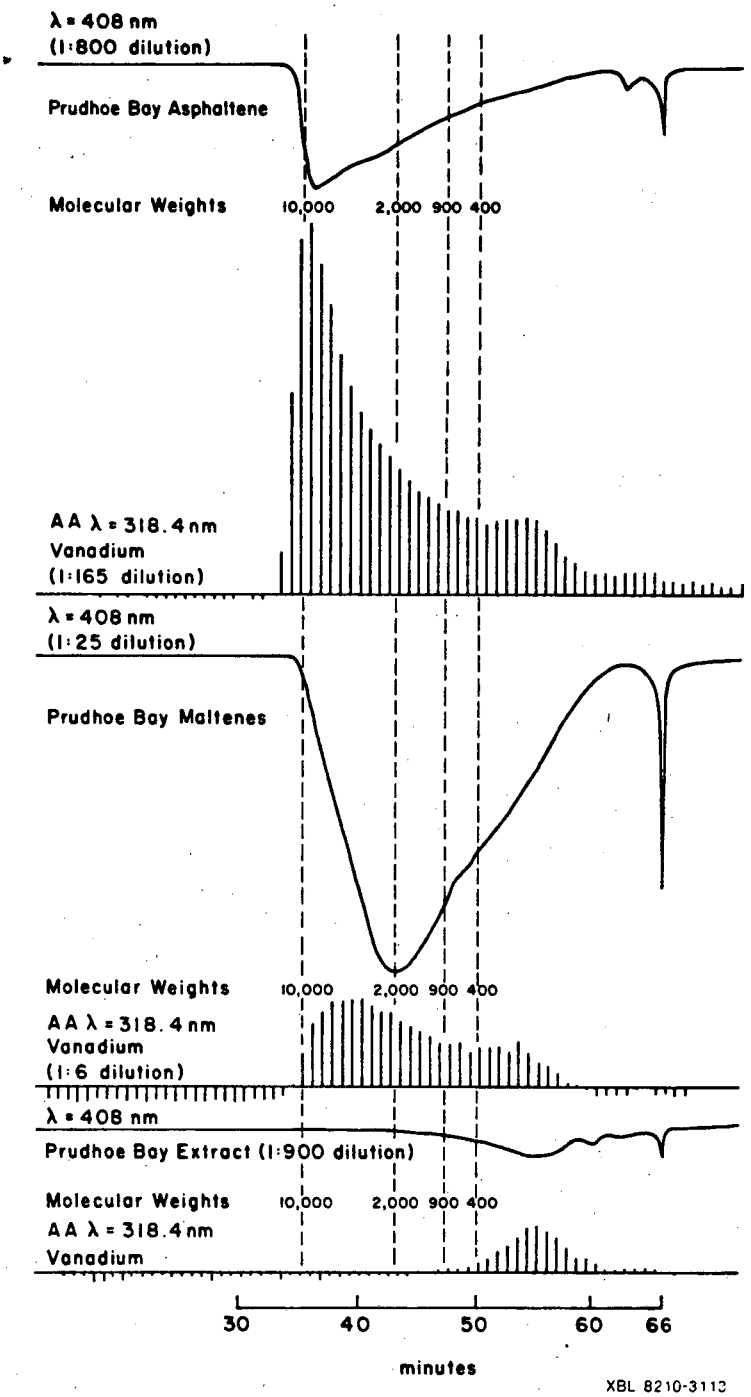
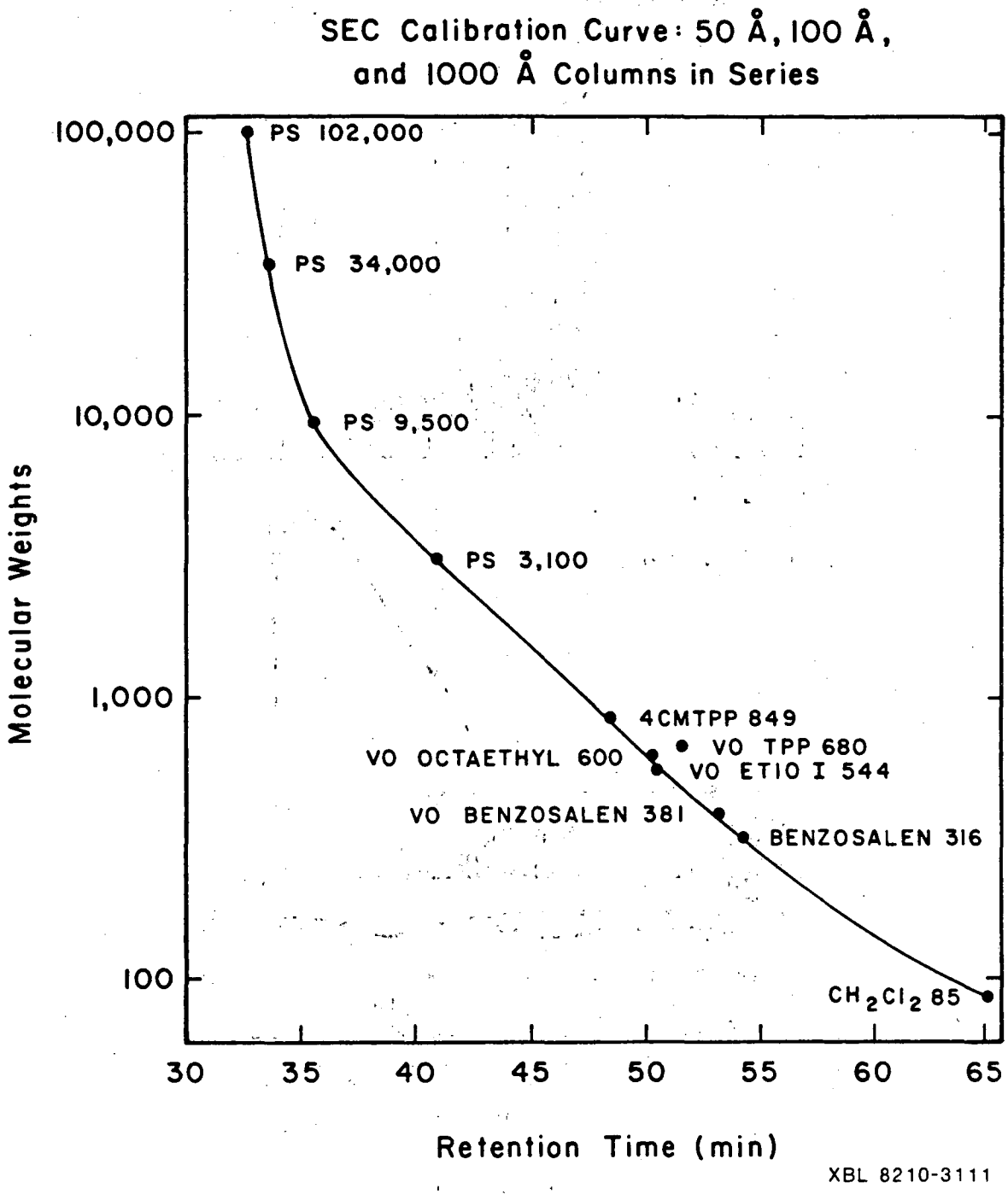


Figure 31

50/100/1000 Å SEC-HPLC-GFAA analysis of Prudhoe Bay Asphaltene, Maltene and Asphaltene Extract

Figure 32


SEC Calibration Curve: 50 Å, 100 Å, and 1000 Å Columns in Series
100,000
10,000
1,000
100
Molecular Weights
PS 102,000
PS 34,000
PS 9,500
PS 3,100
4CMTPP 849
VO TPP 680
VO OCTAETHYL 600
VO ETIO I 544
VO BENZOSALEN 381
BENZOSALEN 316
CH2Cl2 85
30
35
40
45
50
55
60
65
Retention Time (min)
XBL 8210-3111

	BOSCAN				CERRO NEGRO				WILMINGTON				PRUDHOE BAY			
	>2000[a]	2000 900	900 400	<400	>2000	2000 900	900 400	<400	>2000	2000 900	900 400	<400	>2000	2000 900	900 400	<400
Whole Crude Oil	28[b]	20	23	29	31	22	20	26	31	29	23	17	28	23	19	30
Asphaltene	33	19	19	29	34	16	26	34	37	16	27	30	56	15	12	17
Malthene	29	24	27	21	33	26	25	16	18	32	32	17	23	34	30	13

[a] molecular weight

[b] % of Vanadium in whole sample

Table 9

Vanadium Distribution in Whole Crude Oils, Asphaltenes, and Malthenes

tenes are richer in the high molecular weight vanadium compounds and the malthenes are richer in vanadium in the two middle molecular weight ranges. The heavier vanadium concentrations in the very highest and very lowest molecular weight fractions of the asphaltenes conforms well with the concept of asphaltenes as large molecules with smaller molecules encapsulated within them. It is also interesting to note that Boscan crude, which has the highest asphaltenic vanadium concentration of the four oils studied, has an asphaltenic vanadium distribution which is very similar to the vanadium distribution of the whole crude oil. The four oils can also be divided into two groups: high asphaltene oils, including Boscan and Cerro Negro, and low asphaltene oils, including Wilmington and Prudhoe Bay. The high asphaltene oils have similar molecular weight distributions of vanadium in their asphaltenes and whole oils and have similar percentages of vanadium in the highest and lowest molecular weight ranges of the asphaltenes. The low asphaltene oils have more extreme variations in vanadium distribution between the asphaltenes and the whole oils and have significantly greater vanadium concentration in the greater than 2000 range than in the less than 400 range. The second feature is especially pronounced in the lowest asphaltene oil, Prudhoe Bay, which has 57 percent of its vanadium in the greater than 2000 range and only 17 percent in the less than 400 range.

Work has also been done on attempts to isolate vanadyl porphyrins from the asphaltenes. Following a procedure similar to that used by several other researchers, the asphaltenes were dissolved in

xylene and extracted with a pyridine-water solution (Figures 28-31). The extracts have a strong absorbance at 408 nm, which is typical for vanadyl porphyrins. Of the four crude oils, only Boscan and Cerro Negro gave extracts with sufficiently large vanadium concentrations to make GFAA analysis possible. Analysis using the HPLC-SEC-GFAA combination showed that a substantial portion of the vanadium compounds present in these two extracts were at a molecular weight too small for porphyrins (Table 10). Further analysis with a second HPLC system equipped with an amino-cyano column and a rapid scanning UV-VIS detector has established the presence of several vanadyl non-porphyrin compounds in the pyridine-water extract and future work will emphasize characterizing these vanadyl non-porphyrin compounds.

Vanadium distribution by MW (% of total V)

Sample	>2000	<2000 >900	<900 >400	<400
Boscan Extract	4	18	39	39
Cerro Negro Extract	4	20	36	40
Boscan Filtrate	54	24	12	10

Table 10

Vanadium Distribution in Pyridine-Water Extracts of Asphaltenes

SYNTHESIS OF MODEL VANADYL NON-PORPHYRIN COMPOUNDS FOR COMPARISON TO THOSE FOUND IN VARIOUS HEAVY CRUDE PETROLEUMS

The identification of Vanadyl non-porphyrin compounds, known to be present in heavy crude oils, is of the utmost importance if we are to use multidentate ligands to remove vanadyl ion from these oils. Additionally, these compounds may be responsible for the poisoning of catalysts used to upgrade these future fuel sources.

With this approach in mind, we needed to have a variety of vanadyl non-porphyrin compounds for the speciation studies. Thus we initiated a synthesis program to generate these compounds and the following vanadyl non-porphyrin compounds were synthesized. (Chart 2)

These compounds are being tested to determine if they are constituents in the heavy crude oils Cerro Negro, Boscan, Wilmington and Prudhoe Bay via HPLC-UV-Vis Fast Scan analysis. This detector, for our HPLC separated vanadyl compounds, is able to give UV-Vis spectra in the range of 190-700 nm for any compound or cluster of compounds eluting from an HPLC column.

We have used the fast scan detector to tentatively identify two vanadyl non-porphyrin compounds present in Prudhoe Bay and Boscan crude oils. By comparing the retention times of the authentic vanadyl non-porphyrin compounds, 1 and 2, with those in the crude oils and also comparing their respective UV-Vis spectra, we have been able

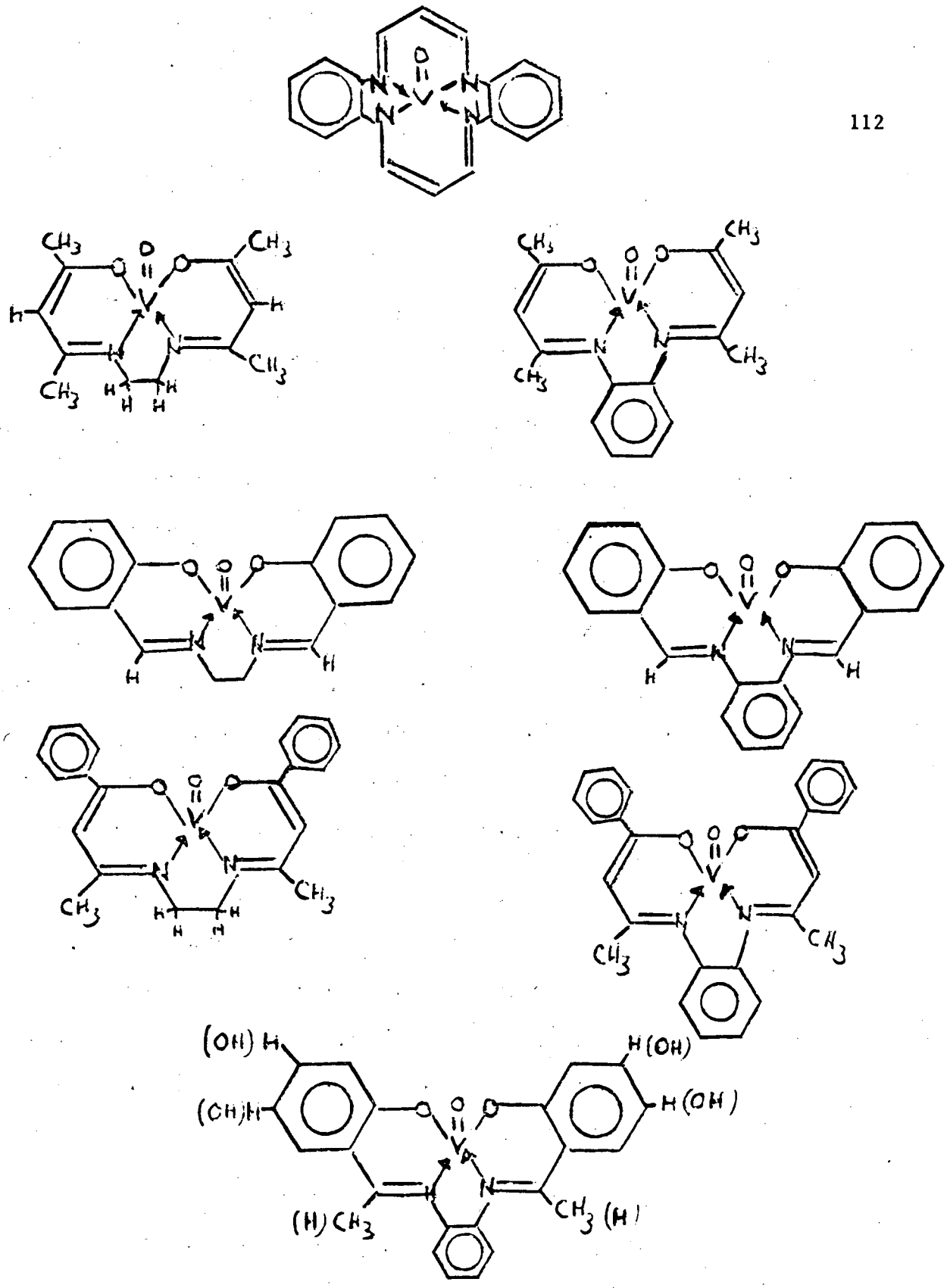
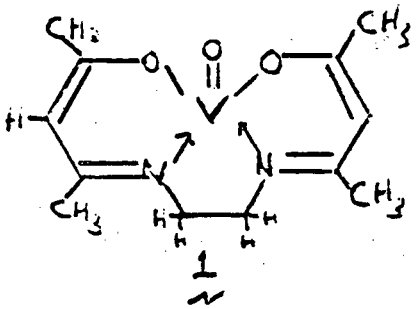


Chart 2

Vanadyl Non-Porphyrin Compounds Synthesized for Speciation Studies

to ascertain their possible presence in these heavy crude oils.



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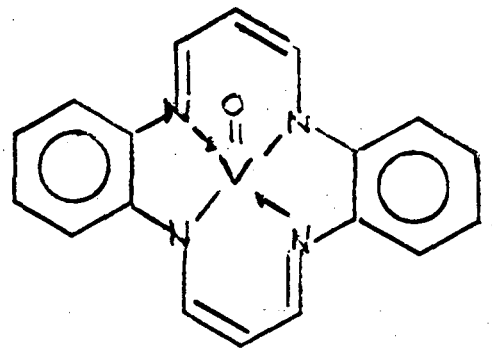

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The obvious importance of this HPLC detector in future speciation studies can be seen in these preliminary results. In addition, we have connected the fast scan detector to the Apple II computer for on-line acquisition of the recorded UV-Vis spectra and will report on this in subsequent papers.

Experimental

Apparatus for Speciation Studies in Retort Waters and Shale Oils

Two Perkin-Elmer graphite furnace atomic absorption spectrometers, Models 4000 and 460, were used as arsenic-specific detectors for hgh performance liquid chromatographs (Altex Model 100A). Additionally, each setup has an Altex 153 ultraviolet detector, which was used at 254 nm to monitor the organic matrix and to measure solvent fronts (t_o). Experimental parameters for coupling the HPLC to the GFAA detector, and optimization of arsenic speciation, have been previously described.[8,10,34]

The size exclusion chromatographic separations for the shale oils and oil shale extract were performed on both rigid and non-rigid

polystyrene divinyl benzene packings using THF as the mobile phase. The rigid μ-Styragel columns [2(1000Å) and 1(100Å) columns] are capable of separating compounds of differing molecular size, by comparison with polystyrene calibration standards, from less than 600 to greater than 19,000 daltons.

Oil Shale Retort Water Samples and Shale Oils Studied

Seven important in situ oil shale retort and process water samples were examined, including three waters from Occidental's Logan Wash modified in situ process (retort, boiler blowdown, and heater treated waters); Laramie Energy Technology Center's Rock Springs Site 9 true in situ experiment Omega-9 water; and two large-scale simulated, modified in situ retort waters: one run, L-2 from Lawrence Livermore Laboratory's 6,000 kg retort, and one from Laramie Energy Technology Center's 150-ton retort. These materials were warmed to room temperature, filtered (0.45μm, Millipore), appropriately diluted with deionize water, and directly injected (100-250 μL) into the HPLC-GFAA systems.

The shale oils investigated during this study were: Paraho shale oil, National Bureau of Standards SRM 1580, and Crude Shale Oil A and Centrifuged Shale Oil number 4101 (Fossil Fuels Research Materials Facility, Oak Ridge National Laboratory). The oils were diluted with THF to concentrations near ten percent, centrifuged where necessary and filtered through a 0.45 μm filter prior to injection into the HPLC-GFAA system.

Chromatographic Procedures for Analysis of Retort Waters

Several available gradient compositions were used for the HPLC speciation or arsenicals in the basic (pH ~9.2) retort and process waters, a very effective combination being that of a commercial anion exchange column (Dionex) with an eluent composition recommended by Woolson and Aharonson.[13] This method used a step gradient starting 10 minutes after injection from 100 percent water-methanol (80:20 v/v) to 100 percent 0.02 M $(NH_4)_2CO_3$ in water-methanol (85:15 v/v) at 5 percent min^{-1}, with a flow rate of 1.2 mL min^{-1}. The HPLC eluent was automatically sampled from a specially designed[8] flowthrough teflon cup for periodic graphite furnace atomic absorption detection at 193.7 nm for arsenic.

Each chromatogram consisted of a series of histogramic peaks which, in combination, represented an individual eluting chromatographic peak. We then summed the individual histogram comprising each arsenical species peak over the range of $t_R \pm \sigma$ to determine total chromatographic peak areas.

Procedure for Isolation and Identification of Arsenic Compounds from Green River Formation Oil Shale

The sample of Green River Formation was crushed and extracted with a soxhlet apparatus. After examination by SEC-HPLC-GFAA analysis, as previously described, it was deuwatized with 3-methyl catechol and analyzed by gas chromatography-mass spectrometry. The GC-MS analyses were run on a Finnigan 4023 mass spectrometer system

with a 30 m x 0.3 mm DB-5 (J&W) capillary column, conditions: 55° (3 min.) - 300°C at 4°/min. Data analysis and preparation were performed using the INCOS Data system.

Experimental Apparatus, Methods and Procedures for Analysis of Heavy Crude Petroleums and Their Asphaltenes

The Cerro Negro, Wilmington, and Prudhoe Bay crude oils were provided 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 (VOEtioI), and nickel etioporphyrin I (NiEtioI) were purchased from Midcentury (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.[76] VOBZEN, was synthesized according to the method of Dilli and Patsalides,[71] while the VOTADA was prepared from the free base ligand according to the procedure of Burchill and Honeybourne.[78] 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 m millipore filters (Bedford, MA) (used for all of the filtering in this study), and stored away from light in order 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.

A schematic of the HPLC-GFAA instrumentation is shown in Figure 33. 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.

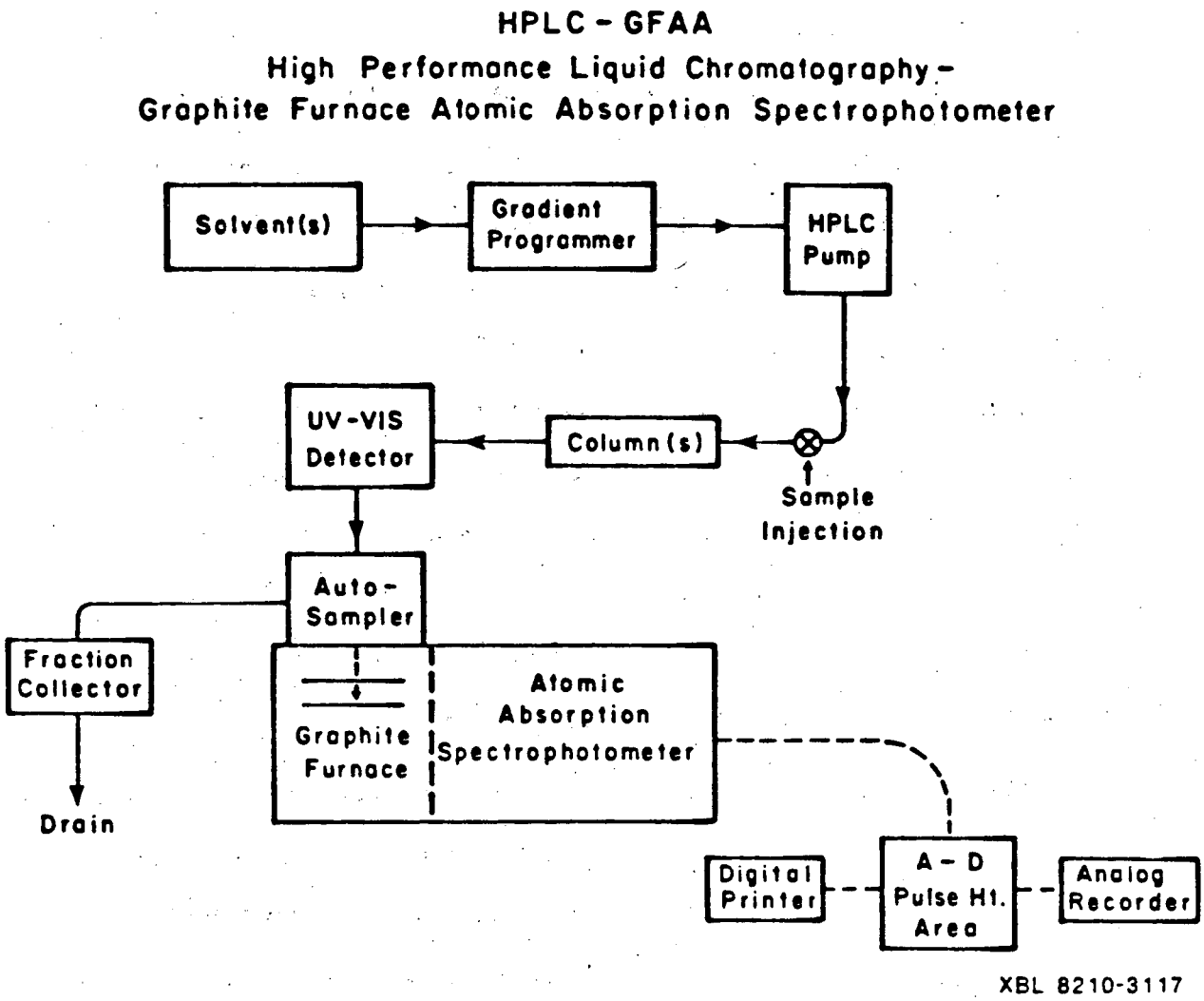

Figure 33

Schematic of the Automatically Coupled HPLC-GFAA System

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
Cooling gas - argon

A dual-pen strip chart recorder (Kipp and Zonen) was used to record the single wavelength UV-Vis absorbances. The GFAA histogramic 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.

A schematic of the overall separation procedure is shown in Figure 34. Five grams of each of the heavy crude oils was extracted five consecutive times with a mixture of pyridine (40 ml), H_2O (10 ml), and p-xylene (10 ml). Phase separations occurred 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-

METHODS AND PROCEDURES

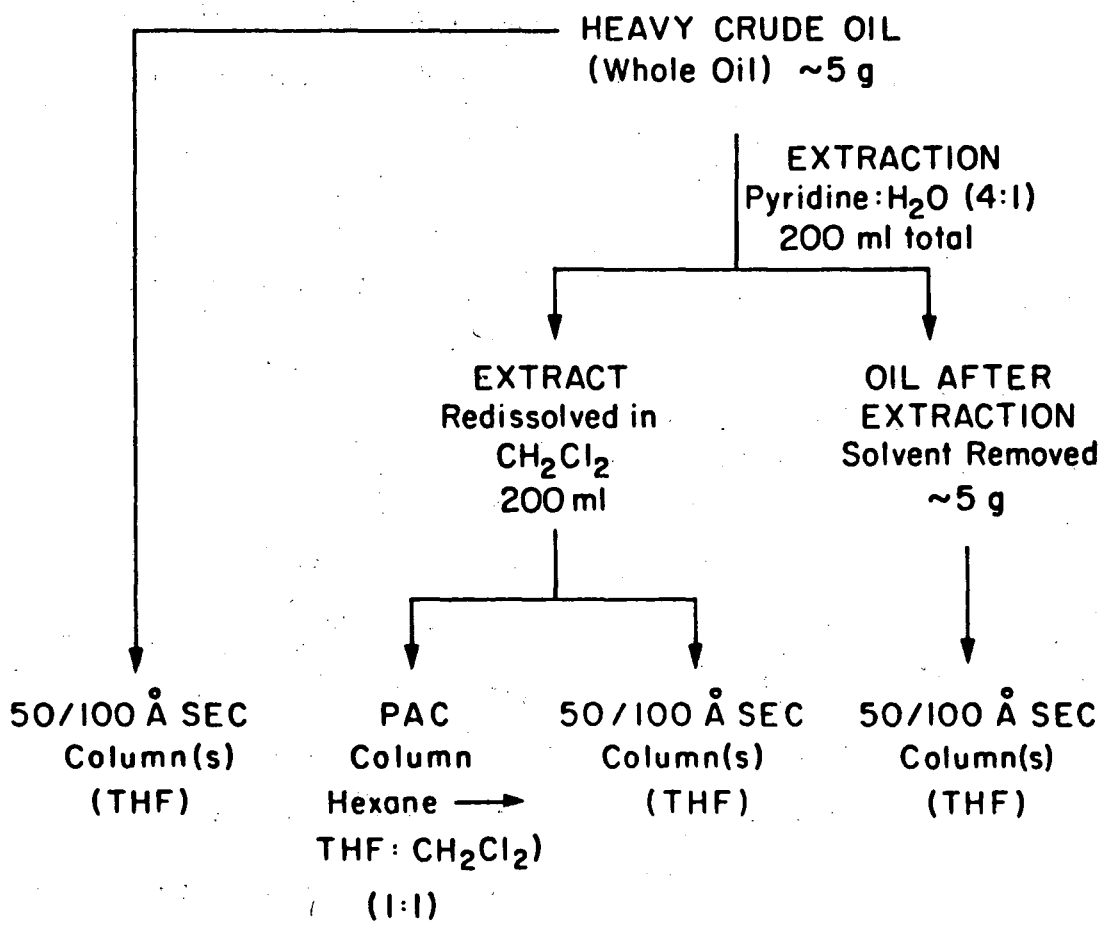

Figure 34

Separation Methods and Procedures Outline

ray fluorescence analysis. The crude oils, before and after extraction, were then diluted in HPLC-grade methylene chloride, filtered, and stored in the dark until needed.

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.

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.

The asphaltenes of the four previously studied heavy crude petroleums were analyzed, as just described above for the oils, by the methods and procedures shown in Figure 35.

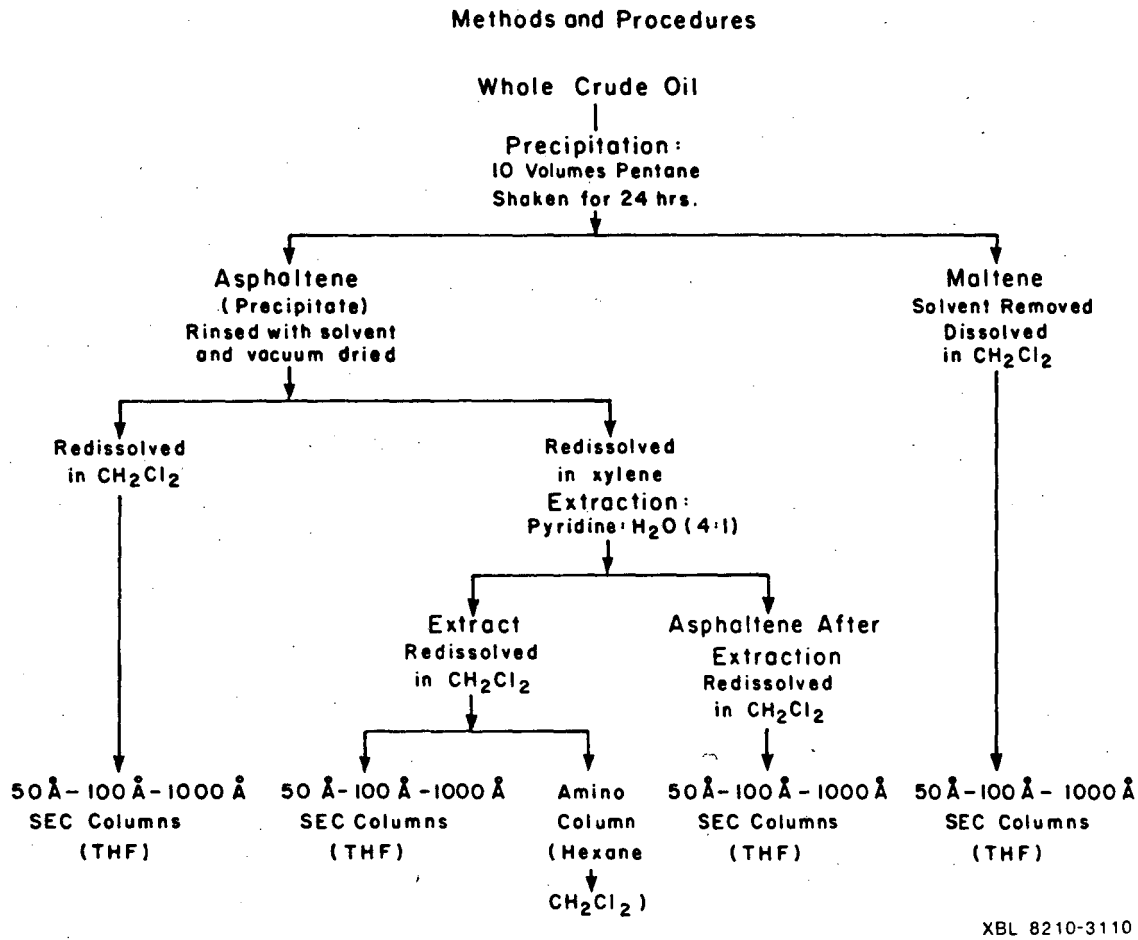

Figure 35

Asphaltene Isolation and Analysis for Heavy Crude Petroleum

FUTURE STUDIES

The speciation of arsenic compounds in oil shale precursors and products has defined that the arsenic compounds are released upon pyrolysis. In view of these facts, we will now concentrate on reactions of 3-methylcatechol with the organoarsonic acids known to be coordinated to macro-molecules in the shale oil. This will allow us to ascertain whether we can remove these compounds from their sites of coordination in this complex matrix. Additionally, reactions with methyl-and phenylarsonic acids with the synthesized polymer bonded catechols will be attempted to verify the reactivity of these ligands bonded to a polymer backbone.

The speciation of vanadyl non-porphyrin compounds in heavy crude petroleums and their asphaltenes are important to continue, since they may lead to rational removal methods and contribute to understanding catalyst poisoning phenomena.

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