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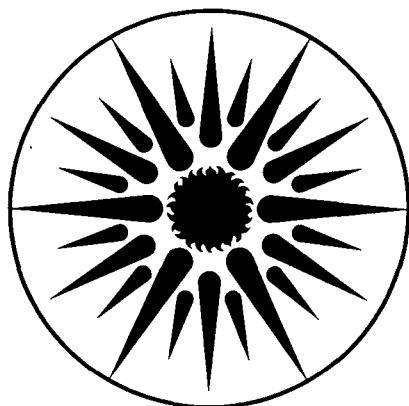
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METAL COORDINATION CHEMISTRY: REMOVAL AND RECOVERY  
OF METAL COMPOUNDS FROM HEAVY CRUDE AND SHALE OIL  
WITH MULTIDENTATE LIGANDS  
Annual Report, October 1983-October 1984

R.H. Fish

April 1985

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**Metal Coordination Chemistry:  
Removal and Recovery of Metal Compounds  
From Heavy Crude and Shale Oil with  
Multidentate Ligands**

**Annual Report  
October 1983 - October 1984**

**by**

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## SUMMARY

The removal and recovery of trace-metal compounds in complex matrices, such as heavy crude petroleums and shale oils, is a basic problem in the general area of fundamental petroleum chemistry. We are developing innovative methods to remove arsenic compounds from shale oil and vanadium and nickel compounds from heavy crude petroleums. This involves placing ligands onto polymers that will react with the trace-metal compounds present in these matrices. As well, studies directed toward the molecular characterization of the trace-metal compounds in the above-mentioned petroleums allows selective methods to be utilized in the polymer pendant ligand experiments designed to remove these trace-metals.

In this annual report, we will demonstrate the use of polymer pendant catechol ligands in removal and recovery studies using arsenic compounds that were characterized in Green River Formation oil shale and its pyrolysis products. In addition, the evaluation of a new ligand for arsenate removal will also be discussed. The molecular characterization of metallo-non-porphyrin compounds of vanadium and nickel in petroleums and their asphaltenes will also be addressed to clearly demonstrate the need to understand these complex mixtures and to use this knowledge for exploration, catalyst poisoning and removal studies that will directly benefit the petroleum industry.

## INTRODUCTION

Transformations and bioaccumulation of trace metals and metalloids, especially arsenic, are well known to occur in modern microorganisms, including the bacteria<sup>1,2</sup> molds,<sup>3</sup> and marine plankton or algae.<sup>4,5</sup> Such microflora demonstrate capacities for uptake of both inorganic and organic forms of elements, and in some instances, are shown to involve biomethylation of inorganic substrates which result in cellular incorporation of organometal(loid)s, e.g., methylarsonic acid or dimethylarsonic acid.<sup>5</sup> Arsenic is known to bioaccumulate in higher marine organisms to a substantial degree,<sup>6,7</sup> where it resides in some shellfish tissues as arsenobetaine.<sup>8</sup>

Similar considerations for ancient metal(loid) uptake or transformations appear quite reasonable for primordial microflora, especially the algae which account for the present ubiquitous distribution of kerogen in shale rocks.<sup>9,10</sup> In general, the fossil deposition record suggests that substantial metal(loid) accumulation also occurred in higher plants which underwent diagenesis to form modern petroleum and coal deposits.<sup>11,12</sup> In many instances, various present-day species of plants are known to both selectively and extensively hyperaccumulate various metal(loid)s to such a degree that geochemical prospection is feasible by correlating metal concentration profiles with local flora.<sup>13</sup> It is not unexpected, therefore, to discern characteristic concentration patterns for trace elements in various fossil deposits - whether we regard these as essential or toxic to life - and to expect that gross differences in the profiles between the three main types: coal, kerogen, and petroleum, as summarized in Table I.<sup>14-18</sup> Similarly expected, though far more subtle, we might anticipate that element distributions for these three main fossil sources also depend upon specific sites, and reflect their terrestrial or marine origins, subsequent geochemical history, and maturation.<sup>19-21</sup>

The molecular forms of trace metal(loid)s in fossil deposits is doubtless complex, probably consisting of varying proportions of inorganic, metallo-organic (no covalent element-carbon bonds), and true organometallic chemical species residing in unspecified sites within the carbonaceous matrix. Over the years a very substantial



solvent differentiation methodology has emerged,<sup>22-24</sup> which greatly aids the analyst in assessing the broad matrix categories of fossil materials, and produces reproducible information concerning possible ligation, elements present, and approximate molecular size (weight) of soluble components.

The determination of the molecular forms of trace metal(loid)s in fossil materials ideally requires a technique with extreme selectivity, lack of interferences, sensitivity to the sub-ppm level, and the ability to deal with heterogeneous samples. The state-of-the-art analytical methods which are capable of meeting these criteria to varying degrees, without extensive sample preparation, are quite limited and have only recently been applied to limited types of fossil samples.

The coupling of chemical separations, which provide selectivity and reduce interferences, with instrumental techniques, which are capable of providing further selectivity and the necessary sensitivity, has been an active area of analytical research, being performed in both off-line and on-line modes. The recent emergence of a number of on-line "hyphenated" techniques,<sup>24</sup> GC-MS, MS-MS, LC-ESD (including variable- and scanning UV, IR, NMR, GFAA, FAA and electrochemical detectors) appears to be the most effective and versatile method to quantitate organic, inorganic, organometallic and metallo-organic compounds in complex matrices. Among these, automated coupling of high performance liquid chromatography (HPLC) in normal, reverse phase, ion exchange, or size exclusion modes with element-selective detectors appears most promising for the characterization of metal(loid) containing molecules in complex matrices.<sup>25</sup>

Reports of on-line, element-selective detection of chromatographic effluents of fossil materials have appeared more recently and offer the advantages of increased resolution and easier chromatographic optimization because of the real time acquisition of elemental distributions during the chromatographic run. Recently, Brinckman et al.<sup>26</sup> have coupled a graphite furnace atomic absorption (GFAA) spectrometer to a high performance liquid chromatograph, which has been applied by Fish et al.<sup>27-30</sup> and Weiss et al.<sup>31</sup> to the analysis of arsenic compounds in Green River Formation oil shale, shale oil,

retort waters and vanadium and nickel compounds in heavy crude petroleums and their asphaltenes. The molecular characterization studies described above were a prelude to the utilization of polymer pendant ligands for the eventual removal of these speciated trace-metal(s) from fossil fuels. In this annual report, we will describe our progress in polymer pendant ligand chemistry and as well our new results in defining the metallo-non-porphyrin compounds in heavy crude petroleums and their asphaltenes. The new results on the analysis of Paraho shale oil will also be presented to unequivocally demonstrate the presence of inorganic and organoarsenic compounds in that matrix.

**POLYMER PENDANT LIGAND CHEMISTRY: REACTION OF ORGANOARSONIC ACIDS  
AND ARSENIC ACID WITH CATECHOL LIGANDS BONDED TO POLYSTYRENE-  
DIVINYLBENZENE AND REGENERATION OF THE LIGAND SITE BY A  
SIMPLE HYDROLYSIS PROCEDURE**

The use of polymer-supported pendant ligands for metal ion removal is a well developed field.<sup>32a,b</sup> More recent studies have focused on the selective reactions of these polymer-bonded ligands and include separations of biological substrates,<sup>33a</sup> protein fractionation,<sup>33b</sup> racemates,<sup>33c</sup> and transport of cations through membranes.<sup>33d</sup> Interestingly, very few of the reported, selective methods incorporate a chemical reaction that forms discrete metal-heteroatom bonds for the metal ion removal step; but rather, they usually entail an ion exchange or binding phenomena for reaction to occur.<sup>34a,b</sup>

Additionally, an important area concerning processing of complex matrices such as synthetic fuels and petroleum crudes, for the removal and recovery of metal compound contaminants, has received little or no attention in this field.<sup>35</sup> From an environmental and economic standpoint, new and innovative methods for removal and recovery of trace-metal compounds, would be useful.

We wish to report on a novel method for reactions of organoarsenic acids and arsenic acid, known to be present in oil shale and its pyrolysis products,<sup>28,36,37</sup> with catechol ligands bonded to either 2% or 20% cross-linked methylated polystyrene-divinylbenzene (PS-DVB) resins.

The bonded catechol ligands were reacted with phenylarsonic acid, **1**, and methylarsonic acid, **2**, in benzene or with arsenic acid, **3**, in 90% aqueous ethanol to provide the corresponding polymer bonded 1:2, **1** and **2**, (Eq. 1) or 1:3, **3**, arsenic

catecholates.<sup>38a,b</sup>

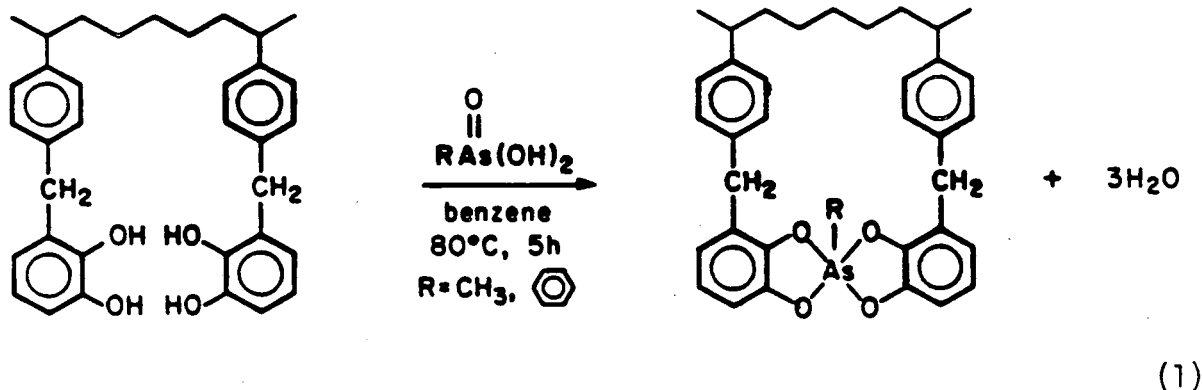


Table II provides the concentrations (mmole As/g of resin) of 1-3 removed from solution, while comparing the 2% cross-linked resin to the 20% analogue. It is evident from the results in Table II that high percentages of compounds 1-3 are removed from solution with both the 2% and 20% cross-linked catechol bonded resins. We verified the 1:2 and 1:3 ratios of arsenic to catechol for 1, 2 and 3, respectively, by varying the ratio of the two reactants and finding the maximum percentages removed at the above mentioned stoichiometries.

In addition, we attempted to verify structures of the polymer-bonded arsenic catecholates by comparing the infrared spectrum (KBr) of the polymer-supported catechol resin with those resins containing compounds 1-3 after reaction with the bonded catechol ligands. Unfortunately, IR bands due to As-O stretching frequencies,  $\sim 680-700\text{ cm}^{-1}$ , were masked by PS-DVB aromatic C-H deformations and as well by those of the catechol ligands. However, we did see dramatic changes in the IR spectra of the bonded arsenic catecholates. For example, IR bands at 1250, 1115 and  $870\text{ cm}^{-1}$ , attributed to the OH deformations of the bonded catechol ligands, disappeared in the IR spectra of the bonded arsenic catecholates. We feel that this result substantiates reactions of 1, 2 and 3 with the bonded catechols to provide the bis-catecholates (Eq. 1) and the triccatecholate arsenic anion for 3.

The equilibrium values of removal from solution of compounds 1-3 were ascertained by plotting mmoles of arsenic per gram of resin (20%) versus time and is illustrated in Figure 1. From the results in Figure 1, compound removal values at equilibrium are  $1 > 2 > 3$  for the 20% cross-linked resin, while the initial rate ratio for 1/2 is  $\sim 7.3$ . This latter initial rate ratio for 1 and 2 could not be readily compared to 3, because of solvent and molar ratio differences in their respective reactions, i.e., benzene for 1, 2 and aqueous ethanol for 3 and arsenic to catechol ratios of 1:2 and 1:3 respectively.

It is also apparent from Table II that the 2% cross-linked swellable resins contain the higher concentration of catechol and consequently can remove almost twice the concentration of arsenic compounds, 1-3, from solution. However, for this application, we found the macroreticular 20% cross-linked resins easier to handle in filtrations and constant reuse; thus we preferred to use these resins in both removal and regeneration experiments.

In this regard, the ligand site could be easily regenerated by a simple hydrolysis procedure using a solution of sodium carbonate ( $6.3 \times 10^{-2}$  M) in either 63% aqueous ethanol or quartz distilled water at 65 °C for 1h. Figure 2 demonstrates the rapid ligand regeneration reaction for the 20% cross-linked resins containing the arsenic catecholates. Importantly, from 40 to 85% of the arsenic compounds, 1-3, are recovered after approximately the first 10 min of hydrolysis with rates of hydrolysis being  $2 > 1 > 3$ . Further arsenic compound hydrolysis is provided after 1hr (5-10%) by reaction with a sodium bicarbonate solution ( $7 \times 10^{-2}$  M, 1h, 65 °C), which also regenerates the catechol site for reuse. It is then important for continued reuse to wash the catechol bonded resins with hot water and methanol to remove carbonates and finally dry the resin under vacuum (95 °C, 1h) to remove water. The above mentioned removal (uptake) and hydrolysis procedures were repeated at least three times for compounds 1-3 with consistent results (Table II).

Clearly, these polymer-pendant ligand reactions with organometallic and inorganic compounds have the potential of being highly selective, as with the arsenic compounds discussed, especially in non-polar solvents where, for example, 1 and 2 are benzene

soluble and **3** is not. We are continuing our studies on polymer-pendant ligand chemistry directed toward metal compound removal from synthetic fuels and petroleum using appropriate compounds found in the above mentioned complex matrices as well as other bonded ligands.

**SYNTHESIS OF AN ENCAPSULATED ARSENIC ANION VIA  
REACTION OF ARSENIC ACID WITH A LINEAR CATECHOLAMIDE-  
N,N',N"-TRIS(2,3-DIHYDROXYBENZOYL)-1,5,1-TRIAZADECANE**

The molecular characterization of inorganic and organometallic compounds present in fossil fuel precursors and their products has become increasingly more important as our synthetic fuel industry develops. The chief reasons for this are that these compounds are thought to be responsible for the poisoning of process catalysts and their presumed effects on man and his environment.<sup>31</sup>

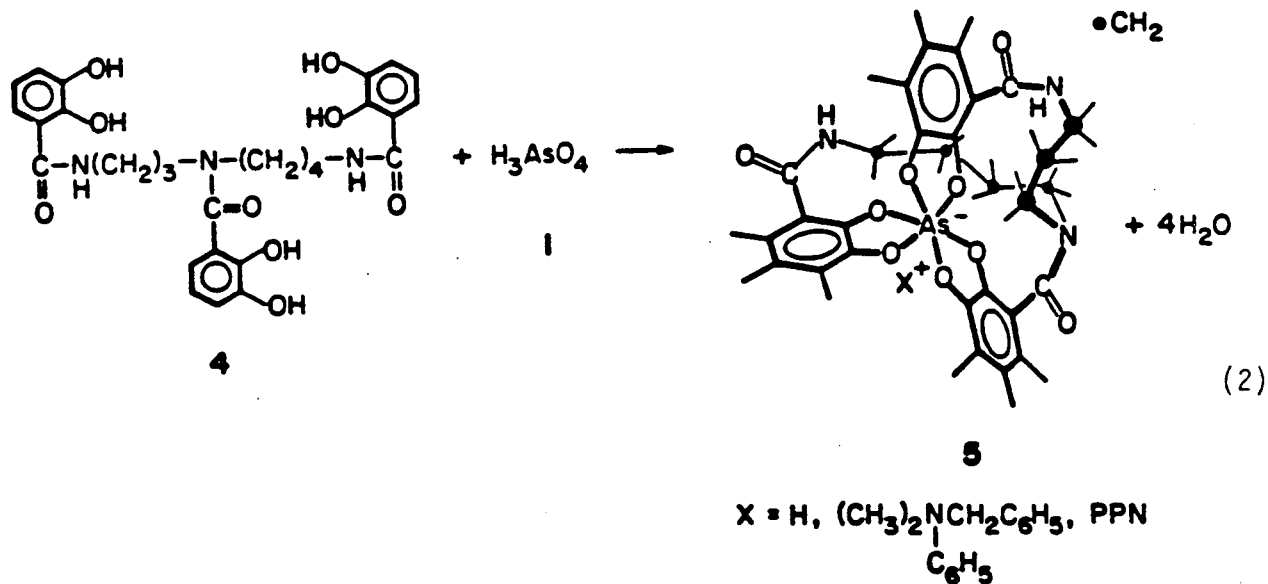
We have recently characterized inorganic arsenic and organoarsenic compounds in oil shale,<sup>28</sup> shale oil,<sup>37</sup> and oil shale retort waters.<sup>27</sup> These studies have provided evidence that arsenate  $\text{AsO}_4^{-3}$ , **1** and methyl- and phenylarsonic acids, **2** and **3**, are present in the above mentioned fossil fuel precursor and products.

While the molecular characterization of these arsenic compounds is an important first step in understanding their biogeochemical origin and their presence in fossil fuel products, the ultimate aim of removing them from these complex matrices utilizing innovative methods is also a predominate goal of our program. In this regard, we recently reported on a novel method that used substituted catechols as models for the above-stated goals with the characterized organoarsenic compounds, **2** and **3**.<sup>38a</sup>

Similar reactions with **1** have focused on a class of linear catecholamide compounds (LICAM) synthesized by Raymond et al.<sup>39a-i</sup> to be used eventually for the removal of iron and actinide metal ions in clinical applications. We were particularly interested in N,N',N"-tris(2,3-dihydroxybenzoyl)-1,5,10-triazadecane(3,4-LICAM), **4**,<sup>39b</sup> a ligand with three catechols on a linear amide chain, that could potentially coordinate in an octahedral configuration around an arsenic anion and that could be placed in a polymeric backbone for eventual removal of **1** from complex matrices.

We report on the reaction of 3,4-LICAM, **4**, with **1** to provide a novel encapsulated

arsenic anion, 5 (X=H), (Eq. 2).



The ligand, 4, reacted with 1 in an aqueous ethanol solution and after work-up gave a white powder (83%) which had a decomposition point at 275-276 °C. The material was analyzed spectroscopically by  $^{13}\text{C}$  nmr, IR, UV, FAB-MS as well as elemental analysis to provide evidence for the structure designated as, 5 (X = H), in Equation 2. A tetraammonium salt (X = benzyldimethylphenylammonium) and the bis(triphenylphosphoranylidene)ammonium (PPN) salt were also prepared; but unfortunately, were not found to be suitable for single crystal x-ray studies.

The  $^{13}\text{C}$  nmr spectrum of the acid (X = H), 5, is shown in Figure 3 along with the ligand 4. The arsenic anion appears to have a less complicated  $^{13}\text{C}$  nmr spectrum than the ligand, 4. The carbonyl region, ~160-170 ppm, should contain three carbonyl resonances, however, 4 has more carbonyl lines (~6-8) indicative of a possible role of geometrical isomers (syn and anti isomers with eight possible carbonyl resonances). Thus, upon arsenic coordination, the carbonyl region of 5 appears somewhat simplified as compared to 4 (3-4 carbonyls) with resonances at 163.6, 164 (shoulder), 168, and 169.6 ppm. The aromatic carbons with hydroxyl groups in the ligand, 4, (~140-152 ppm) should show six resonances; however, many more are evident, while the arsenic compound, 5, has six phenolic carbons at 140, 143, 143.4, 144, 145, and 150 ppm. The remaining aromatic carbons are in the 110-135 ppm range (12) for 5, while the



methylene carbons (0-50 ppm, not shown in Fig. 3) were somewhat masked by the solvent, dimethylsulfoxide- $d_6$ .

The UV spectra of both 4 and 5 are shown in Figure 4, and indicate that on formation of the arsenic anion a pronounced shift from 314 nm ( $\epsilon = 6,576$ ) for 4 to 304 nm ( $\epsilon = 9,001$ ) for 5 (X = H) occurs. A similar occurrence was observed by Raymond et al.<sup>39b,g</sup> in the coordination of ferric ion with a sulfonated 3,4-LICAM, where the extinction coefficient rises and the wave length decreases upon complexation of all six phenolic oxygens. The fast atom bombardment (FAB) mass spectrum (glycerol) of 5 (X = H) provides confirmatory evidence for the molecular weight with a small parent ion at  $m/e$  623 (2.5%) and ions at 625 (M+2, 5%) and 626 (M+3, 16%), while IR data (KBr) indicates As-O stretching frequencies at 650-720  $cm^{-1}$ .

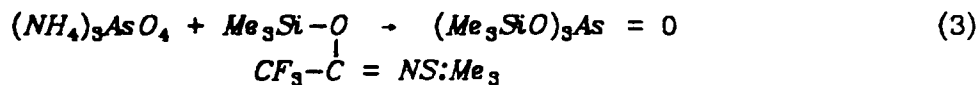
The above mentioned data is strongly supportive of structure, 5, with a presumed octahedral configuration around the arsenic, and represents the first isolated encapsulated arsenic anion structure yet reported. The only other synthesis of a catechol-arsenic anion compound was for catechol itself,<sup>40</sup> and a single crystal x-ray study provided unequivocal evidence for the distorted octahedral symmetry around arsenic.<sup>41</sup> While we were unable to prepare a suitable crystalline derivative for unequivocal, structural x-ray analysis of 5, a Drieding model clearly indicates that the triscatecholate coordination of 4 around arsenic can readily occur.

Finally, in recent experiments we have placed 4, and catechol itself, on a polymer support (10% cross-linked chloromethylated polystyrene-divinylbenzene) and have been able to quantitatively remove arsenate, 1, from an aqueous ethanol solution, which verifies the usefulness of this approach in possible synthetic fuel applications.<sup>42</sup>

**THE MOLECULAR CHARACTERIZATION OF INORGANIC ARSENIC AND  
ORGANOARSENIC COMPOUNDS IN PARAHO SHALE OIL**

Recently, we tentatively identified methylarsonic acid, phenylarsonic acid, and arsenate in a Paraho shale oil sample.<sup>31</sup> In order to unequivocally characterize these arsenic compounds in this shale oil, we decided to use our derivatization techniques on fractions that were isolated from the oil via size exclusion chromatography.<sup>28</sup>

Figure 5 shows the arsenic profile of Paraho shale oil obtained using a 50/100/1000Å SEC column combination and a previously generated calibration curve for molecular weight determinations. The interesting aspect of these arsenic profiles is the dramatic differences between the sample initially dissolved in benzene (top) and that in tetrahydrofuran (THF). The benzene solution of the Paraho shale oil has an arsenic profile from MW 210 to 6600 Daltons, while that for the THF dissolved oil had a profile from 1200 to 6600 Daltons with the peak at 4700 Daltons. We preparatively collected the arsenic compounds in the 210 to 500 Dalton region with the SEC column and then added 3-methylcatechol to derivatize the organoarsenic compounds present. Figures 6 and 7 clearly show the presence of methylarsonic acid; however, we could not identify phenylarsonic acid. The arsenate anion was verified by extraction of the Paraho shale oil with a 0.2 M solution of ammonium carbonate followed by liophilization and then derivatization with a trimethylsilylating reagent (Eq. 3).



The GC-MS analysis gave the correct ions at m/e 207, 343 and 358 consistent with an authentic sample that was prepared for comparison to the isolated arsenate.

This represents the first unequivocal identification of arsenic compounds in any shale oil; but clearly demonstrates the fact that other arsenic compounds are complexed to higher molecular weight ligands and may be difficult to identify. This area should be pursued in future investigations.

**CHARACTERIZATION AND COMPARISON OF VANADYL AND NICKEL COMPOUNDS  
IN HEAVY CRUDE PETROLEUMS AND ASPHALTENES BY REVERSE PHASE AND  
SIZE EXCLUSION LIQUID CHROMATOGRAPHY / GRAPHITE FURNACE  
ATOMIC ABSORPTION SPECTROMETRY**

The presence of vanadyl and nickel non-porphyrin compounds in heavy crude petroleum has been the center of speculation for many years.<sup>43,44</sup> Despite numerous studies directed towards the identification of vanadyl and nickel non-porphyrin compounds,<sup>45</sup> as of yet, not a single molecular structure has been confirmed. The majority of these studies have been limited in effectiveness due primarily to the lack of a suitable metal detector. Since metallo-non-porphyrin compounds, unlike metallo-porphyrin compounds, do not have readily discernible uv-vis spectra, then the identification of these metallo-organic compounds requires novel separation and detection techniques.

The use of on-line, element-selective graphite furnace atomic absorption detection for high performance liquid chromatography systems (HPLC-GFAA) has recently proven highly effective with regard to the molecular characterization of trace-metal compounds in complex matrices such as oil shale, shale oil, oil shale retort waters and heavy crude petroleum.<sup>27,28,36,29,46</sup>

In a previous paper,<sup>29</sup> we described the use of an automatically coupled HPLC-GFAA (Figure 8) combination to categorize, according to molecular weight and polarity, the vanadyl non-porphyrin and porphyrin compounds in heavy crude petroleum. This technique enabled us to profile or fingerprint as well as estimate the distribution of vanadyl compounds present in four petroleum and their extracts. Additionally, the molecular characterization of the vanadyl compounds in the petroleum was attempted by comparing the GFAA histogrammic retention behavior and rapid-scan uv-vis absorbance spectra of HPLC separated petroleum samples to that of known model vanadyl porphyrin and non-porphyrin standards.

In the present study, we report reverse-phase HPLC-GFAA analysis of the vanadyl and nickel compounds extracted, using pyridine as solvent, from four heavy crude petroleums; namely, Boscan, Cerro Negro, Wilmington and Prudhoe Bay. Although reverse phase separations of demetallated ligands have been discussed,<sup>47</sup> to our knowledge, similar separation techniques with element-selective detection of metal-containing petroleum samples, have not been previously published. We also present, using size exclusion chromatography (SEC-HPLC-GFAA), vanadium profiles for the n-pentane precipitated asphaltenes, maltenes and asphaltene extracts of the four petroleums. Asphaltenes, the alkane insoluble fraction of petroleum, are an extremely abundant source of trace-metal compounds.<sup>48</sup> However, asphaltenes also contain the majority of the high molecular weight, aromatic compounds and heteroatoms present in petroleums,<sup>49</sup> which has made the structural characterization of vanadyl non-porphyrin compounds present in asphaltenes difficult to accomplish. We also compared the rapid scan uv-vis profiles, using reverse-phase separations, of the pyridine/water extracts of the four petroleums and their asphaltenes.

The molecular characterization of vanadyl and nickel non-porphyrin compounds, which are thought to account for approximately 50-80 percent of the metals present,<sup>43</sup> is needed in order to design innovative trace-metal removal methods.<sup>38a</sup> In addition, knowledge of the molecular environment associated with both vanadium and nickel in heavy crude petroleums and asphaltenes is also required to provide an improved understanding of the biogeochemical mechanisms responsible for the inclusion of these metals during the diagenesis and maturation process of petroleum formation.<sup>43</sup>

## **Results and Discussion**

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

Since our previously obtained HPLC-GFAA profiles, with SEC separated crude petroleum extracts, had indicated the presence of low molecular weight vanadyl compounds, < 400 daltons,<sup>29</sup> we were interested in obtaining the reverse-phase HPLC-GFAA vanadium and nickel histogrammic distributions of the four petroleum pyridine extracts using various vanadyl and nickel standards (Chart I) to verify retention times

of classes of these compounds. Table III indicates the percentage of vanadium and nickel in each eluted peak via reverse-phase HPLC-GFAA analysis.

Figure 9 shows the HPLC-GFAA data, obtained using an octadecylsilane (ODS) column, for the standards and for the Boscan and Cerro Negro crude petroleum extracts. Each chromatogram consists of a conventional uv-vis absorbance trace (wavelength monitored as designated) and corresponding nickel (232 nm) and vanadium (318.4 nm) histogrammic profiles.

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

Figure 10 shows similar ODS-HPLC-GFAA data for Wilmington and Prudhoe Bay petroleum extracts. These extracts also show a majority of the extracted nickel compounds associated with the highly polar vanadyl standards of comparable structure; however, Wilmington extract also contains a sizable fraction of low polarity (possibly porphyrin derivatives) nickel compounds. Both extracts also show a majority of the vanadyl compounds at moderate to low polarity.

Although reverse phase separations of petroleum samples have been studied,<sup>45</sup> we do not believe that the occurrence of these highly polar nickel compounds have been verified before. Figures 9 and 10 also indicate that reverse-phase separations of the pyridine extracts give improved resolution over that afforded using normal phase HPLC analysis.<sup>54,55</sup> In fact these separations rival that reported for demetallated complexes<sup>47</sup> and question the usefulness of current demetallation procedures for the analysis of petroleum extracts.

### *Rapid Scan Data for Heavy Crude Petroleum Extracts*

The use of a rapid scan uv-vis detector has increased our ability to differentiate between metallo-porphyrin and non-porphyrin compounds. Unfortunately, we were unable to scan the highly polar, ODS separated nickel compound (Figures 9 and 10) peaks due to the sharpness; a maximum scan rate of 20 nm/sec, in effect, sets a limit on the peak-width which can be scanned. The highly polar nickel fractions were, therefore, collected and uv-vis spectra were obtained off-line using a Cary 219 spectrophotometer. Maximum absorbances (above background) for these collected fractions were observed between 280 and 300 nm. The lack of any observable Soret absorbance associated with these fractions, as well as the fact that they are much more polar than our known porphyrin standards, indicates a predominance of nickel non-porphyrin compounds.

The fact that these nickel non-porphyrin fractions had not been previously found is not surprising. The majority of previous research involving the identification of metallo-porphyrins in crude petroleums used column chromatography with silica or alumina packing to isolate the porphyrins.<sup>45</sup> The highly polar nickel compounds shown in Figures 9 and 10 would be irreversibly bound to the column packing during normal-phase elution.<sup>44</sup> The use of solvent selective extraction is not common in recent research but, as demonstrated here, circumvents the loss of nickel non-porphyrins by interaction with a fractionation column using silica or alumina packings.<sup>53</sup> More importantly, typical metal recoveries using the ODS column were in excess of 97 percent.

Rapid scan data obtained for the ODS separated moderate and low polarity vanadium containing bands for Boscan and Cerro Negro extracts (Figure 9) are shown in Figure 11. Rapid scan data for Boscan extract at 16 minutes shows a "relatively clean" vanadyl porphyrin spectrum. However, the other three spectra show varying uv background absorbances at less than 400 nm, indicating the presence of distinctly non-porphyrinic species in these separated fractions. Similar rapid scan data obtained for Wilmington and Prudhoe Bay extracts are shown in Figure 12. The lack of any discernible Soret absorbance associated with these fractions indicates the presence of vanadyl

non-porphyrin compounds as major vanadium constituents in Prudhoe Bay and Wilmington crude petroleum extracts.

A majority of the extracted nickel compounds exist as highly polar non-porphyrin compounds, in contrast to vanadium which is associated primarily with moderate and low polarity compounds, and this fact has important processing implications with regard to catalyst deactivation studies.<sup>56</sup> The majority of current catalyst deactivation modeling studies exclusively use vanadyl and nickel porphyrins.<sup>57</sup> However, since metallo-porphyrins are known to account for only a limited portion of the two metals, the relevancy of these studies must be reexamined, especially with regard to the reactivity of acid unstable metallo-non-porphyrin ligands.<sup>43</sup>

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

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

The results from the extraction of the precipitated asphaltenes are presented in Table V and reveal that only 5-18 percent by weight of the vanadium compounds present in the asphaltenes have been extracted. This behavior is very different from that observed for the extraction of the crude petroleum, <sup>29</sup> from which upwards of 50 percent of the vanadium compounds were removed. Previously, we had observed that a considerable percentage of vanadyl non-porphyrin compounds could be removed from the high molecular weight asphaltenic component of heavy crude petroleum using solvent selective extraction techniques.<sup>52</sup> A significantly lower percentage of the vanadyl compounds is extracted from the n-pentane precipitated asphaltenes and this, as we will show, has importance with regard to the use of asphaltenes as starting materials for the identification of vanadyl porphyrin and non-porphyrin compounds in heavy petroleum.

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

Clearly a better understanding of the types and distribution of vanadyl and nickel compounds present in n-pentane precipitated asphaltenes is needed. We decided to analyze the n-pentane precipitated asphaltenes, the maltenes, and their pyridine extracts of each petroleum using the SEC-HPLC-GFAA technique. Separations obtained for Boscan asphaltene, maltene, and polar extract using a 50/100/1000Å SEC column combination are shown in Figure 13. The visible absorbance was monitored at 408 nm corresponding to the Soret band of vanadyl porphyrins identified in crude oils<sup>58</sup> and the GFAA detector was set at 318.4 nm, specific for vanadium.

Molecular weight calibration (see experimental section) for the low molecular weight region (< 900 daltons) was accomplished using the porphyrin and non-porphyrin standards from Chart I. In contrast to the more traditional use of polystyrenes,<sup>45</sup> the use of vanadyl compounds as calibration standards should improve the accuracy of molecular weight determinations for vanadyl compounds present in heavy crude petroleum samples. Polystyrene standards have, however, been used to calibrate the high molecular weight region (> 900 daltons), since vanadyl compounds at these molecular weights were not available.

Because of differences involving the particle size of petroleum asphaltenes and polystyrene standards, and since interactions between the petroleum matrix and the SEC column are possible,<sup>59</sup> the designated molecular weight categories should not be regarded as absolute, but are more useful as comparison references.

Boscan asphaltene (Figure 13) registers continuous visible absorbances and vanadium profiles over the entire molecular weight region. The maximum absorbance for both visible and vanadium detection occurs in the lowest molecular weight range, corresponding to less than 400 daltons, with very little vanadium present at molecular weights greater than 10,000 daltons. As expected from the structural differences which exist between the maltene and asphaltene fractions,<sup>24</sup> the maltene vanadium absorbances are skewed toward lower average molecular weights than the corresponding asphaltenes. Most notable is the deficiency of vanadium compounds present above 2000



daltons as compared to the asphaltene profiles. The pyridine extract of Boscan asphaltene has a vanadium maximum corresponding to 380 daltons, which is too low to represent metallo-porphyrins with alkyl substituents. Thus the majority of the metal compounds present in the extracts, based on the accuracy of the SEC calibration data for the standards in Chart I, must be considered non-porphyrinic.

Similar data for Prudhoe Bay asphaltene, maltene and polar extract, is shown in Figure 14. A significantly greater percentage of vanadium associated with Prudhoe Bay asphaltene is present above 2000 daltons as compared to Boscan asphaltene. However, Prudhoe Bay maltene, similarly to Boscan maltene, shows a trend towards lower average molecular weights and also registers a predominance of extractable low molecular weight (less than 400 daltons) vanadyl compounds. Data from Figures 13 and 14 as well as data for Cerro Negro and Wilmington crude petroleums (not reproduced here but similar to data shown in Figures 13 and 14, respectively) are summarized in Table VI.

Table VI lists the quantitative distribution of vanadyl compounds by molecular weight using a calibration curve previously reported by Fish and Komlenic<sup>29</sup> and categorizes the vanadyl compounds as greater than 9000 daltons; 9000-2000 daltons; 2000-900 daltons; 900-400 daltons; and less than 400 daltons. Values shown for the percent vanadium in Table IV were determined by summing the peak heights automatically digitized using an integrator (see experimental). For each molecular weight category, the heights of the vanadium histograms were summed and then divided by the total vanadium peak height for the entire analysis.

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

itself.

Interestingly, vanadyl compounds extracted from the asphaltenes of all four petroleums are present predominantly at the low molecular weights (less than 400 daltons), indicating vanadyl non-porphyrin compounds. Previously, we had found that low molecular weight vanadyl compounds (molecular weight < 900 daltons) could be extracted from high molecular weight fractions of each of the heavy crude petroleums.<sup>29</sup> Table VI confirms that these low molecular weight vanadyl complexes can also be extracted from the n-pentane precipitated asphaltenes of each petroleum as well. Each asphaltene shows a majority of the extractable vanadyl compounds having molecular weights less than 400 daltons; however, as Table VI indicates, only 5-18 percent by weight of the vanadium was extractable, as compared to 50-87 percent by weight for heavy crude petroleums.<sup>29</sup> Although vanadyl compounds of similar molecular weight are extracted from both petroleum and asphaltene sources, significant environmental differences must exist between vanadyl complexes present in the heavy crude petroleums and those found in the n-pentane precipitated asphaltenes.

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

#### *Extracts*

Figure 15 compares the ODS-HPLC-GFAA data for the standards and the Boscan asphaltene extract monitored at both 320 and 408 nm. Similar to Boscan whole crude petroleum extract, the majority of the nickel compounds elute with the highly polar standards, while the vanadyl compounds are primarily associated with the low to moderate polarity compounds. ODS-HPLC-GFAA analyses of Cerro Negro, Wilmington, and Prudhoe Bay asphaltene extracts show similar metal profiles to those obtained for the petroleum extracts and are, therefore, not reproduced here. Wilmington asphaltene extract, however, does show a fraction of non-polar nickel compounds, indicating that some nickel porphyrin compounds have been extracted. Table V provides percent vanadium and nickel distributions in the asphaltene extracts using reverse-phase HPLC-GFAA analysis. Rapid scan data for the moderate and low polarity bands for the Wilmington asphaltene and Prudhoe Bay asphaltene extracts are shown in Figure 16. In

comparison to the rapid scan uv-vis spectra of the heavy crude petroleum extracts (Figures 11 and 12), the four asphaltene extracts generally show somewhat greater Soret absorbances, indicating increased concentrations of vanadyl porphyrin compounds in the asphaltene extract.

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

The extraction of the precipitated asphaltenes removed only 5 percent to 18 percent of the vanadium present (Table V), in comparison to the removal of 50 percent to 87 percent of the vanadium present in the heavy crude petroleum.<sup>29</sup> The proposed existence of larger micelles in the precipitated asphaltenes could account for this difference in behavior, since asphaltenes are by definition a solubility class and the choice of the precipitating solvent is known to have a noticeable effect on the mass and aromaticity of precipitated asphaltenes.<sup>53,60</sup> Further, vapor pressure osmometry studies of asphaltene molecular weights have demonstrated that the degree of association between asphaltene molecules is strongly influenced by the polarity and functionality of the solvent used in the measurements.<sup>61</sup>

An equilibrium apparently exists between the interactions of asphaltene molecules with each other and with the solvent. In the heavy crude petroleum, the resins form a very complex solvent in which the asphaltenes are dispersed. When asphaltenes are precipitated, the asphaltene-resin interactions become weakened and the asphaltene-asphaltene interactions dominate, forming larger micelles. Non-polar solvents such as p-xylene are ineffective in breaking up the large micelles in precipitated asphaltenes and many vanadyl compounds which are entrapped during the precipitation are inaccessible to extraction.

However, in order to make comparisons among the petroleum components, a solvent must be used that will prevent associations during the procedure used to separate the components. That methylene chloride is an effective solvent for breaking up asphaltene micelles can be seen by comparing the 50/100/1000Å SEC-HPLC-GFAA analysis of the heavy crude petroleum<sup>29</sup> with a similar analysis of the asphaltenes and maltenes reported in this study (Table VI). Methylene chloride was used as the injection

solvent for all of these analyses and a mass balance of the vanadium present in each molecular weight region shows that the vanadium in the maltenes and asphaltenes of a given region sum to the vanadium present in the same region of the heavy crude petroleum. Clearly, methylene chloride is sufficiently polar to overcome the intermolecular interaction which may have occurred during the precipitation of the asphaltenes.

SEC-HPLC-GFAA analysis of the asphaltene raffinate (after extraction) show an increase in the amount of vanadium present at molecular weights over 2000 daltons (Figure 17). This suggests that a rearrangement occurs in the non-extractable asphaltenes and involves the reentrainment of low molecular weight vanadyl compounds into the high molecular weight asphaltenic fraction of the petroleum. The extracts have almost no vanadyl compounds at molecular weights over 900 daltons, which is consistent with extracts of the heavy crude petroleum. Rapid scan analysis of the precipitated asphaltene pyridine extracts by reverse phase HPLC-GFAA has shown the concentration of vanadyl porphyrins to be higher in the asphaltene extracts than in the extracts of whole crude petroleum. Despite studies which indicate that asphaltenes have higher concentrations of vanadyl non-porphyrins than do maltenes,<sup>62</sup> the increased concentration of extractable vanadyl porphyrins in precipitated asphaltenes makes it more difficult to detect and isolate vanadyl non-porphyrins present in asphaltenes. Our work indicates that the precipitation of asphaltenes accomplishes a desired separation by selectively precipitating vanadyl porphyrins, thus, making the maltene component an excellent source of vanadyl non-porphyrin compounds<sup>53</sup> and this is an area we will pursue.

Because nickel is generally present in heavy crude petroleum at lower concentrations than vanadium, relatively little research has been directed at identifying nickel compounds in these complex matrices.<sup>45</sup> In experiments in which column chromatography has been used to remove vanadyl porphyrins from the petroleum matrix, a light pink band eluting before the bright red vanadyl porphyrin band has generally been assumed to contain nickel porphyrins, but little work has actually been done to identify

the constituents of this band.

The results of the reverse phase HPLC-GFAA analysis show that very little of the nickel compounds in the petroleum asphaltene extracts is actually present as nickel porphyrins (Figure 15). The Boscan, Cerro Negro, and Prudhoe Bay extracts clearly indicate that over 90 percent of the nickel compounds present are non-porphyrin. Wilmington is the exception, with one third of the nickel compounds eluting at a retention time consistent with nickel porphyrins. The high concentration of nickel porphyrins present in Wilmington petroleum and asphaltene extracts could be a consequence of less severe aging compared to the other three petroleums. Nickel, because of its smaller size and greater symmetry, coordinates more readily with the porphyrin ring than does the vanadyl ion and nickel porphyrins could conceivably be formed in the early diagenesis of the petroleum.<sup>63</sup> However, during maturation of the petroleum, the nickel is possibly replaced by vanadyl ion, which forms a more stable metallo-porphyrin complex.<sup>64</sup> Wilmington is not the youngest or the least deeply buried petroleum of the four studied, but it does have the least severe combination of these two factors.

The discovery of large amounts of nickel non-porphyrins has a direct bearing on current research studying refinery catalyst poisoning by trace metals. Since it has generally been accepted that a substantial fraction of the nickel present in heavy crude petroleums is coordinated in porphyrin rings, studies of the poisoning mechanisms have used nickel porphyrins to model the naturally occurring nickel compounds.<sup>57</sup> Thus, most of the suspected non-porphyrin chelating systems are less stable with respect to demetallation than porphyrins, and these studies have failed to adequately model the deposition of nickel compounds on catalysts. Before modelling studies of nickel compound poisoning can be improved, it will be necessary to isolate and identify these nickel non-porphyrin compounds. The identification of vanadyl and nickel non-porphyrins should also provide important biogeochemical information. Knowing the structures of these compounds should give insight into their sources in the petroleum feedstock. Reverse-phase analyses showed that most of the extracted vanadyl non-porphyrins were not comparable to the model vanadyl non-porphyrins available in this

study.

In future work, it will be necessary to have a greater array of model metallo-non-porphyrin compounds. Among the compounds that should be considered are the hydrogenated vanadyl porphyrins. Since hydrogenation of the metallo-porphyrin ring structure significantly decreases Soret absorbance, hydrogenated metallo-porphyrins could account for the lack of a Soret band noted in several of our fractions. In the reducing environment of the crude petroleum reservoir,<sup>65</sup> it is possible that the porphyrin rings are hydrogenated, and there has been a report on the identification of non-metallated, hydrogenated porphyrin ligands in oil shale.<sup>66</sup> If the pyrrole rings are sufficiently hydrogenated, the metallo-porphyrin will be susceptible to demetallation and decomposition.<sup>67</sup> This may represent a mechanism by which porphyrins have been demetallated in older petroleum deposits.

## Conclusions

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

We have based this finding on the lack of a Soret absorbance associated with our separated vanadyl and nickel containing fractions. The non-presence of a distinct Soret absorbance has traditionally been used to discern the occurrence of non-porphyrin compounds.<sup>45</sup>

More important, however, is the definitive molecular identification of these metallo-non-porphyrin compounds. In this regard, we have recently preparatively separated fractions obtained using the reverse-phase HPLC technique and have submitted these for high resolution mass spectrometry and electron spin resonance spectroscopy analysis. We will report details of this analysis in the near future.<sup>68</sup>

Obviously, the identification of vanadyl and nickel non-porphyrin compounds as biomarkers will have a profound effect on future exploration studies in addition to catalyst deactivation phenomena, where metallo-porphyrins have prevailed as models.

Furthermore, future innovative removal methods will also be affected by the knowledge of the metallo-non-porphyrin structures. Our work continues in this exciting area of metallo-organic geochemistry.

## EXPERIMENTAL

### *Materials and Instrumentation*

The 400 MHz nmr spectrometer for the  $^{13}\text{C}$  (at 100 MHz) nmr spectra was located at the NBS-NML high field nmr facility located at NBS, Gaithersburg, MD. A Cary 219 UV-VIS spectrophotometer - Apple II computer combination was used for the ultraviolet spectra and a Perkin-Elmer 1330 for infrared spectra. The FAB-MS of **5** (suspended in glycerol) was obtained on a Kratos MS-50 mass spectrometer located in the Department of Chemistry, U.C. Berkeley. Elemental analyses were also obtained from the Chemistry Department's microanalytical laboratory. The 3,4-dihydroxybenzoic acid, thionyl chloride, boron tribromide and spermidine were purchased from Aldrich Chemical CO.

Complete histories and descriptions of the four heavy crude petroleums have previously been reported.<sup>29</sup>

HPLC grade methanol, tetrahydrofuran (THF), methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) and n-pentane were purchased from Burdick and Jackson (Muskegon, MI) and were filtered and degassed before use in the HPLC system. Extractions of polar compounds from the petroleums and their asphaltenes were performed with reagent grade pyridine, and p-xylene (Mallinckrodt; Paris, KY) and quartz-distilled water (also used in the HPLC system).

Synthesis of the majority of the standards shown in Chart I have been reported in reference.<sup>29</sup> VOBZEN<sup>50</sup> and NiTMTADA<sup>51</sup> have been synthesized from the ligands. VO(acac)<sub>2</sub> was purchased from Alfa Products (Danvers, MA). The polystyrene standards were purchased from Altex (Berkeley, CA).

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



### *HPLC-GFAA Instrumentation*

The SEC separations used a previously described HPLC system.<sup>29</sup> The ODS separations used an HPLC system (schematic shown in Figure 8) consisting of two solvent delivery pumps (Beckman 112), a gradient programmer (Beckman 421) and a rapid-scan uv-vis detector (Beckman 165). Spectra from the rapid-scanning detector were stored on five inch floppy discs via an interfaced Apple II plus computer and printed on an Apple silent printer. A dual-pen strip chart (Kipp and Zonen) was used to record the single or dual wavelength uv-vis absorbances. GFAA instrument and coupling procedures have been previously reported.<sup>27</sup> The GFAA histogrammic data was recorded using both the strip chart recorder and a digital integrator (Altex C-RIA).

HPLC separations were accomplished using a series combination of 50/100/1000Å  $\mu$ -spherogel columns (Altex, 8.0 mm I.D. x 300 mm length) with swelled divinylbenzene as the packing for the SEC runs, or an octadecylsilane C-18, (ODS) column (Altex, 4.6 mm I.D. x 250 mm length) with a self-packed guard column (Waters, 3.2 mm I.D. x 40 mm length) for the reverse phase separations.

### *Synthesis of Polymer Pendant Catechol Ligands*

Synthesized by reaction of catechol with 2% or 20% chloromethylated polystyrene-divinylbenzene resins in the presence of stannic chloride to provide an 11% by weight (2%) and 6% by weight (20%) incorporation of catechol in the polymer. See Warshawsky, A., and Kahana, N., *J. Am. Chem. Soc.* **1982**, 104 2663. and Iwabuchi, S., Nahahira, T., Fukushima, Y., Saito, O., and Kojima, K.; *J. Polym. Sci.*, **1981**, 19, 785, for similar synthetic routes to bonded catechol.

### *A Modified Procedure for the Preparation of Ligand, 4<sup>39b</sup>*

In a 100 ml flask equipped with a drying tube was placed 4.55 g (25 mmole) of 2,3-dimethoxybenzoic acid and 24.5 g (0.206 moles) of thionyl chloride. The reaction mixture was stirred at room temperature for 2 hr., after which the solution was rotary evaporated to give a white solid. The solid was then dissolved in benzene (30 ml, thrice) and rotary evaporated to give the benzene soluble acid chloride. The acid chloride was

dissolved in 20 ml tetrahydrofuran along with 3.5 g (34.6 mmole) of triethylamine and 1.66g (11.4 mmoles) of spermidine. The reaction mixture was refluxed for 20 hr. under nitrogen (important to exclude both air and water) and then rotary evaporated to give an oil that was dissolved in chloroform. The chloroform solution was washed with 50 ml of 0.1 N hydrochloric acid, 50 ml of deionized water and 50 ml of 10% sodium hydroxide and then again with deionized water and hydrochloric acid. The chloroform layer was dried over anhydrous magnesium sulfate, filtered and rotary evaporated.

The oil was then dissolved in 75 ml of methylene chloride and placed in a round bottom flask equipped with a stirring bar, a nitrogen inlet and a dropping funnel containing 6 ml of boron tribromide in 50 ml of methylene chloride. The boron tribromide was added slowly and after addition the reaction mixture was stirred at room temperature overnight under nitrogen. To the reaction mixture was added slowly 50 ml of deionized water with stirring for 3 hr. The precipitate was washed with deionized water and diethylether and attempted recrystallized from methanol/water gave an oil that was redissolved in methanol and rotary evaporated (thrice). The oil was washed well with diethylether and dried under vacuum ( $P_2O_5$ ) to give a solid, amorphous material (3.5 g, 55%), m.p. 267-270 °C [lit 267-270].<sup>39b</sup> The UV spectrum (DMSO) ( $1 \times 10^{-4}$  M) shows absorptions at 314 nm ( $\epsilon = 6,576$ ) and 291 nm ( $\epsilon = 4,948$ ).

#### *Preparation of 5 (X=H)*

In a 25 ml two-neck flask equipped with a reflux condenser with drying tube and a nitrogen gas inlet was placed 26 mg (0.11 mmoles) of arsenic pentaoxide along with 0.5 ml of water. This was refluxed for a few minutes to form arsenic acid, 1, ( $H_3AsO_4$ ), and to this was added 373 mg (0.67 mmoles) of 4 in 15 ml 100% ethanol and the reaction mixture refluxed for 20 hr. The work-up included solvent evaporation and washing the resulting solid throughly with methanol and with diethylether to provide 118 mg (83% yield) of a white powder which was dried under vacuum ( $P_2O_5$ ) and had a mp of 275-276 °C (dec).

A  $^{13}C$  nmr spectrum (DMSO- $d_6$ ) at 100 MHz gave the following resonances: (C=O), 169.7, 168, 164.3 (shoulder) and 163.6. (Aromatic C-OH), 149.7, 145.4, 144.4, 143.4, 143,

140. (Aromatic C) 118.7, 117.5, 117, 116.3, 115, 113.8, 112.5, 111.3, 110, 109, 108, (CH<sub>2</sub>) 0-50? The UV spectrum of 5 (X = H) in DMSO ( $7 \times 10^{-5}$  M) had a maximum absorption at 304 nm ( $\epsilon = 9,001$ ) and a minimum at 291 nm ( $\epsilon = 7,480$ ), while infrared (KBR) bands were found at 2950, 2880, 1642, 1486, 1453, 1384, 1310, 1220, 1145, 1115, 995, 900, 850, 790, 748, 720-650, 600, 415, 335, 320, and 310 cm<sup>-1</sup>.

The fast atom bombardment mass spectrum (MS-50, glycerol) provided ions at  $m/e$  623 (M; 2.5%) 625 (M+2, 5%) and 626 (M+3, 16%). Anal. Calcd. for C<sub>28</sub>H<sub>26</sub>O<sub>9</sub>N<sub>3</sub>As.H<sub>2</sub>O (monohydrate): C, 52.40; H, 4.57; N, 6.55. Found: C, 52.39, H, 4.67; N, 6.50.

#### *Preparation of the Benzyldimethylphenylammonium Salt of 5*

In a round-bottom flask was placed 200 mg (0.362 mmoles) of 4, 67.3 mg (0.362 mmoles) sodium arsenate and 269 mg (1.03 mmoles) of benzyldimethylphenylammonium chloride dissolved in 60 ml of 50% aqueous ethanol. The reaction mixture was refluxed for 24 hr. and then the solvent was reduced to half its volume and refrigerated. The precipitate that formed was filtered and the filtrate was again reduced in volume and refrigerated. This method produced 100 mg (33%) of product. Attempts to obtain suitable crystals of the tetraammonium salt for x-ray studies were unsuccessful. The infrared (KBR) spectrum provided the following bands at 1650, 1505, 1490, 1480, 1245, 1215, 1115, 1060, 995, 887, 842, 790, 770, 750, 685, 595, 570 and 415 cm<sup>-1</sup>. Anal. Calcd. for C<sub>43</sub>H<sub>44</sub>N<sub>4</sub>O<sub>9</sub>As.2.5 H<sub>2</sub>O. C, 52.64; H, 5.57; N, 6.36. Found C, 52.57; H, 5.67; N, 6.64.

#### *Preparation of the Bis(triphenylphosphoranylidene)ammonium Salt of 5 (X = PPN)*

In a round-bottom flask was placed 50 mg (.08 mmoles) of 5 (X=H) and 48 mg (.08 mmoles) of bis(triphenylphosphoranylidene)ammonium chloride dissolved in 10 ml of dimethylsulfoxide and stirred for 2 hr. The DMSO was removed under vacuum and the remaining precipitate was dissolved in methylene chloride and filtered. Removal of the methylene chloride was followed by a benzene and methanol wash to give 25 mg (25%) of product. All attempts to obtain crystals for x-ray analysis were met with failure. The infrared (CH<sub>2</sub>Cl<sub>2</sub>) provided the following bands at 3630, 3060, 2953, 2844, 1645, 1580,

1550, 1486, 1450, 1440, 1252, 1222, 1120, 1024, 682, 550, 539  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{64}\text{H}_{56}\text{N}_4\text{O}_9\text{P}_2\text{As}\cdot 4\text{H}_2\text{O}$ , C, 62.29; H, 5.19; N, 4.54; P, 5.03. Found: C, 62.29; H, 4.75; N, 4.61; P, 4.81.

#### *Asphaltene Preparation*<sup>49</sup>

Asphaltenes were separated from the crude oils by precipitation with a 40 to 1 volume ratio of n-pentane. After adding n-pentane to the crude oil, the solution was gently agitated at 300 motions per minute for 24 hours. The asphaltenes were removed by filtering, washed with n-pentane until the wash solvent was colorless, and dried under vacuum. The coarse brown/black powder was then weighed to determine the percentage of precipitated asphaltenes in the petroleum. The pentane soluble maltenes and wash solvent were also collected and dried under vacuum. Approximately 95% by weight of the starting petroleum was recovered as asphaltenes and maltenes, with the remaining 5 percent presumably lost as volatiles.

#### *Asphaltene Extraction*<sup>52</sup>

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

#### *High Performance Liquid Chromatography Procedures*

The reverse-phase chromatography was accomplished using an ODS column with the petroleum and asphaltene extracts dissolved in a pyridine/water (4:1) solution. The ODS separations were obtained with a solvent gradient consisting of an initial linear ramp from 100% methanol/water (3:1 v/v) to 30% THF from 1-3 minutes, a second linear ramp from 30% to 70% THF from 22-24 minutes, and a final linear ramp to 100% THF from

25-27 minutes, at a constant flow rate of 1.5 ml/min. Restoration of the column after each run was accomplished by ramping to 100% methanol-water (3:1 v/v) over 3 minutes, and holding until a minimum of 10 column volumes of solvent had eluted.

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

#### *Trace Metal Quantification*

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

#### *Method of Cup Analysis*

The vanadium concentration in the extracted asphaltenes was measured by GFAA single cup analysis.<sup>27,29,53</sup> Asphaltene and extracted asphaltene samples were diluted in methylene chloride to give solutions of approximately 1 ppm vanadium and each sample was analyzed with the GFAA. The peak heights recorded by the digitizer were averaged over approximately 10 samplings to find the mean peak height of the sample. These mean peak heights were considered to be directly proportional to the vanadium content of the sample. The ppm vanadium in the extracted asphaltene was calculated by multiplying the ratio of the mean peak heights of the extracted asphaltene and the original asphaltene by the ppm vanadium in the original asphaltene as detected by x-ray fluorescence spectroscopy. The accuracy of this technique was tested with asphaltene samples of known concentrations and the experimental error was found to be less than five percent.

#### *Method of Quantification of Vanadium Histograms Obtained by SEC-HPLC-GFAA Analyses<sup>29</sup>*

The vanadium weight percentages appearing in Table IV were obtained from the relevant vanadium histograms by measuring the area of each molecular weight

category using the SEC calibration curve and the method of summing peak heights digitized with an integrator. The weight percentages were obtained by dividing these numbers by the total area of the pertinent vanadium histogram.

### **FUTURE DIRECTIONS**

The identification of vanadium and nickel non-porphyrin compounds in heavy crude petroleums is now a top priority and we are presently isolating these compounds for ESR and MS studies in collaboration with Dr. John Reynolds and Dr. Emilio Gallegos of the Chevron Research Corporation, Richmond, CA. The utilization of polymer pendant catechol ligands for the removal and recovery of vanadyl and nickel compounds from solution has been initiated by Dr. Alejandro Izquierdo, a post-doctoral fellow, and we find that this method works well, however, selectivity, rates of removal, compounds that enhance removal and recovery studies need to be carried out in FY 85.

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**CHART I:** Model vanadyl and nickel porphyrin and non-porphyrin compounds used for the calibration curve and for comparisons with unknown components in the heavy crude petroleums and their asphaltenes.

**Table I**

Comparison of Selected Elemental Concentrations<sup>a</sup> in  
Petroleum, Coal, and Oil Shale

Element	Petroleum	Petroleum	Coal	Oil Shale
As	0.111	0.263	15	44.3
Be	--	--	2.0	--
Cd	--	--	1.3	0.64
Cr	0.093	0.008	15	34.2
Fe	10.8	40.7	1.6%	2.07%
Ge	--	--	0.71	--
Hg	0.051	3.236	0.18	0.089
Ni	9.38	165.8	15	27.5
S	0.83%	1.31%	2.0%	0.573%
Se	0.052	0.530	4.1	2.03
Si	--	--	2.6%	15%
U	--	0.060	1.6	4.5
V	13.6	87.7	20	94.2

a) Concentrations in ppm except as noted.

**Table II**

Concentration of Arsenic Compounds, 1-3, Removed From Solution Using Both 2% and 20% Cross-Linked, Catechol Bonded PS-DVB Resins <sup>a</sup>				
Arsenic Compd	2% <sup>b,c</sup> Conc (mmole As/g)	% Removed	20% <sup>b,c</sup> Conc (mmole As/g)	% Removed
1	0.503 <sup>d</sup>	100	0.232	86
2	0.307	62	0.20	74
3	0.212	64	0.124	69

- a) 100 mg of catechol bonded resin, 2% or 20% cross-linked, containing 1.0 mmole/g, 11% by weight of catechol or 0.538 mmole/g, 5.92% by weight of catechol respectively.
- b) Reaction conditions for compounds 1 and 2 : initial arsenic to catechol concentration is 1:2 at 80° C for 18 hr. in benzene (10 ml) under nitrogen.
- c) Reaction conditions, for compound 3 : initial arsenic to catechol concentration is 1:3, 81° C, 17 hr, 90% ethanol (10 ml) under nitrogen.
- d) After reaction, the beads were filtered and washed well with hot methanol, quartz water and again with methanol. The washings were added to the filtered solution and analyzed for arsenic by single cup graphite furnace absorption spectrometry.

**Table III**

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

	peak one <sup>c</sup> (high polarity)		peak two <sup>d</sup> (moderate polarity)		peak three <sup>e</sup> (low polarity)	
	V	Ni	V	Ni	V	Ni
Boscan	5	100	60	0	35	0
Cerro Negro	3	98	74	2	23	0
Wilmington	2	78	59	0	39	22
Prudhoe Bay	12	95	59	0	29	5

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

**Table IV**

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

	ppm in crude petroleum <sup>b</sup>		ppm in asphaltene <sup>b</sup>		ppm in maltene <sup>b</sup>		wt % of asphaltene in crude petroleum <sup>c</sup>	% of total metal in asphaltene <sup>d</sup>	
	V	Ni	V	Ni	V	Ni		V	Ni
	Boscan	1100	103	3700	350	280		30	23
Cerro Negro	560	118	1600	360	110	26	21	60	64
Wilmington	49	60	360	430	17	32	6.9	51	49
Prudhoe Bay	19	9	250	96	10	4	3.7	49	39

a) n-Pentane precipitated (40:1) ratio.

b) Determined by X-ray fluorescence spectroscopy.

c) Grams of precipitated asphaltene divided by original grams of crude petroleum.

d) (ppm of metal in asphaltene) times (wt % asphaltene in crude petroleum) divided by (ppm of metal in crude petroleum).

**Table V****Solvent Selective Extraction of Precipitated Asphaltenes<sup>a</sup>**

	ppm V in asphaltene <sup>b</sup>	ppm V in extracted asphaltene <sup>c</sup>	estimated ppm V in extract <sup>d</sup>	wt % of vanadium extracted from asphaltene
Boscan	3700	3500	8100	5
Cerro Negro	1600	1500	4200	7
Wilmington	360	340	470	4
Prudhoe Bay	250	210	440	18

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

Table VI

The Percent Vanadium in Each Molecular Weight Category of Vanadyl Compounds in the Four Heavy Crude Petroleums and their Asphaltenes, Maltenes, Asphaltene Polar Extracts, and Extracted Asphaltenes by 50/100/1000 Å SEC/HPLC/GFAA Analysis<sup>a</sup>

	>2000 <sup>b</sup>	Boscan			Cerro Negro				Wilmington				Prudhoe Bay			
		<2000 >900	<900 >400	<400	>2000	<2000 >900	<900 >400	<400	>2000	<2000 >900	<900 >400	<400	>2000	<2000 >900	<900 >400	<400
heavy crude petroleum	28	20	23	29	31	22	20	26	31	29	23	17	28	23	19	30
asphaltene	33	19	19	29	34	18	18	34	37	18	17	30	58	15	12	17
maltenes	29	24	27	21	33	26	25	16	18	32	32	17	23	34	30	13
asphaltene extract	0	4	31	65	0	5	26	69	9	14	25	52	0	0	13	87
extracted asphaltene	58	18	15	11	59	15	12	14	80	10	8	2	85	8	4	4

a) Percentage of total vanadium determined by method of summing peak heights digitized with an integrator for the molecular weight region designated. The molecular weight regions were determined by a calibration curve. <sup>29</sup>

b) Daltons.

**Table VII**

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

	peak one <sup>b</sup> (high polarity)		peak two <sup>c</sup> (moderate polarity)		peak three <sup>d</sup> (low polarity)	
	V	Ni	V	Ni	V	Ni
Boscan	4	92	66	0	30	8
Cerro Negro	17	98	68	1	15	1
Wilmington	9	67	66	0	25	33
Prudhoe Bay	18	99	58	0	24	1

- a) Percentage of total vanadium and nickel determined by method of summing peak heights digitized with an integrator for the elution peak designated.
- b) t = 0-8 min.
- c) <sup>c</sup> t = 8-24 min.
- d) t = 24-35 min.



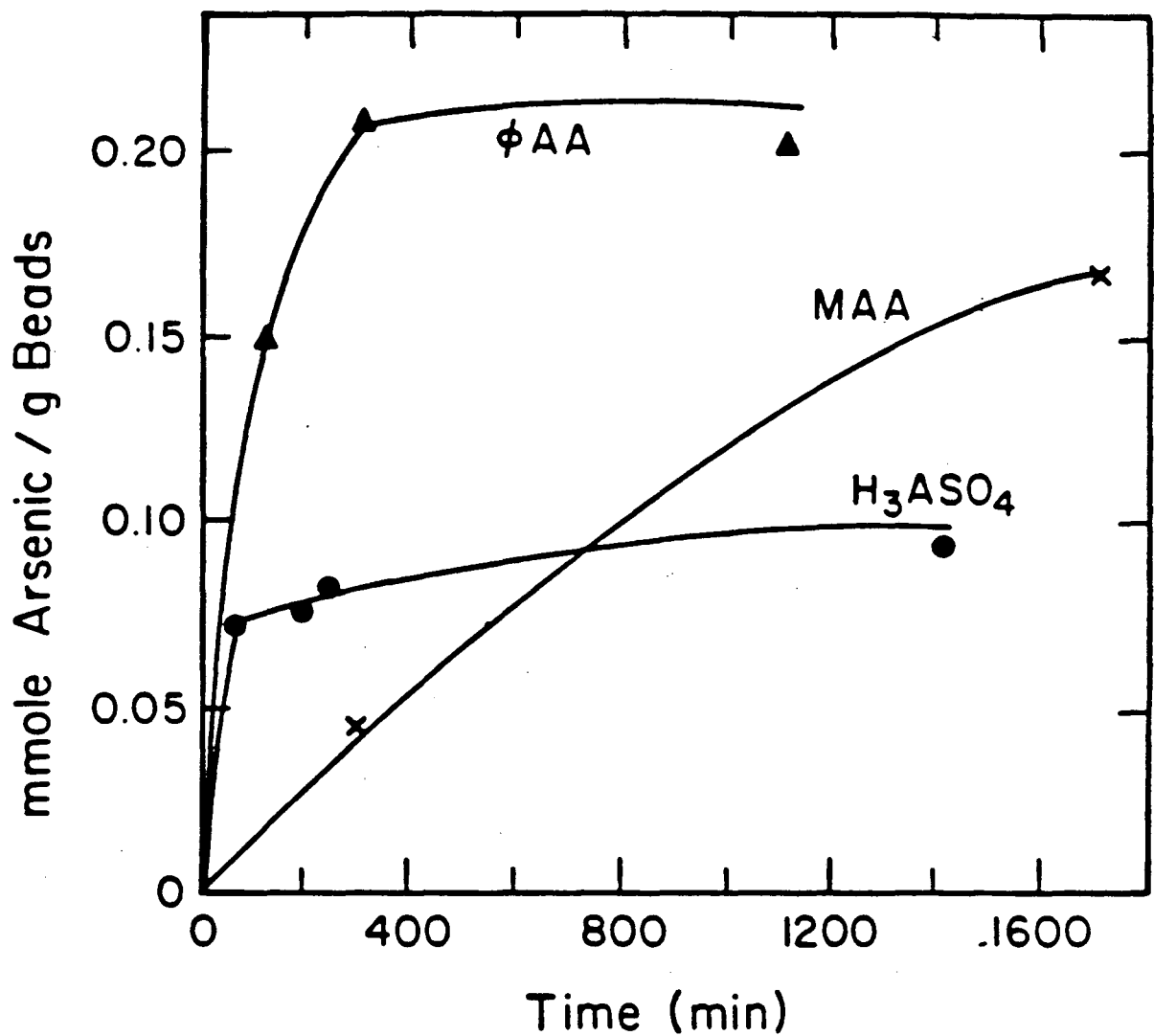


Figure 1

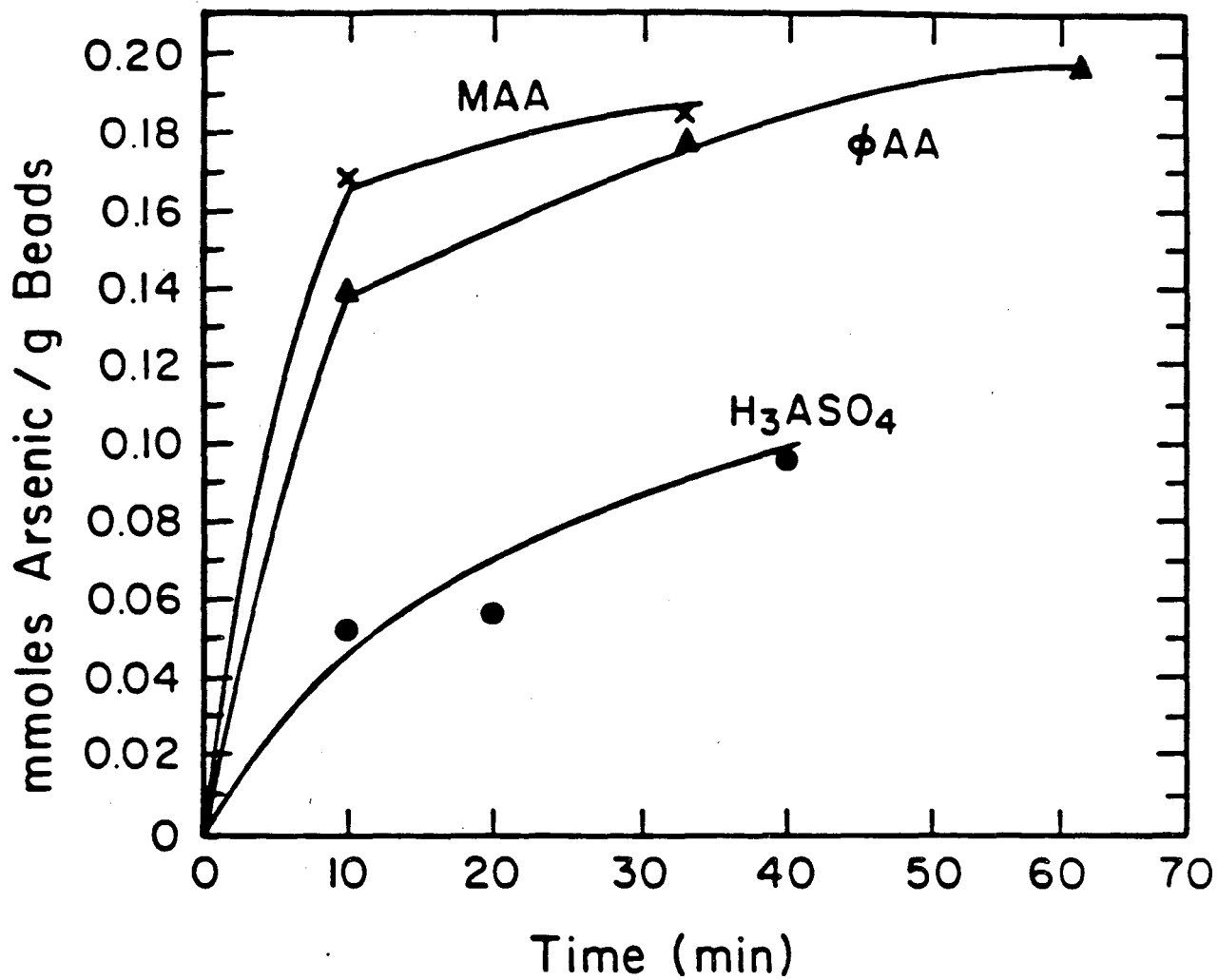


Figure 2

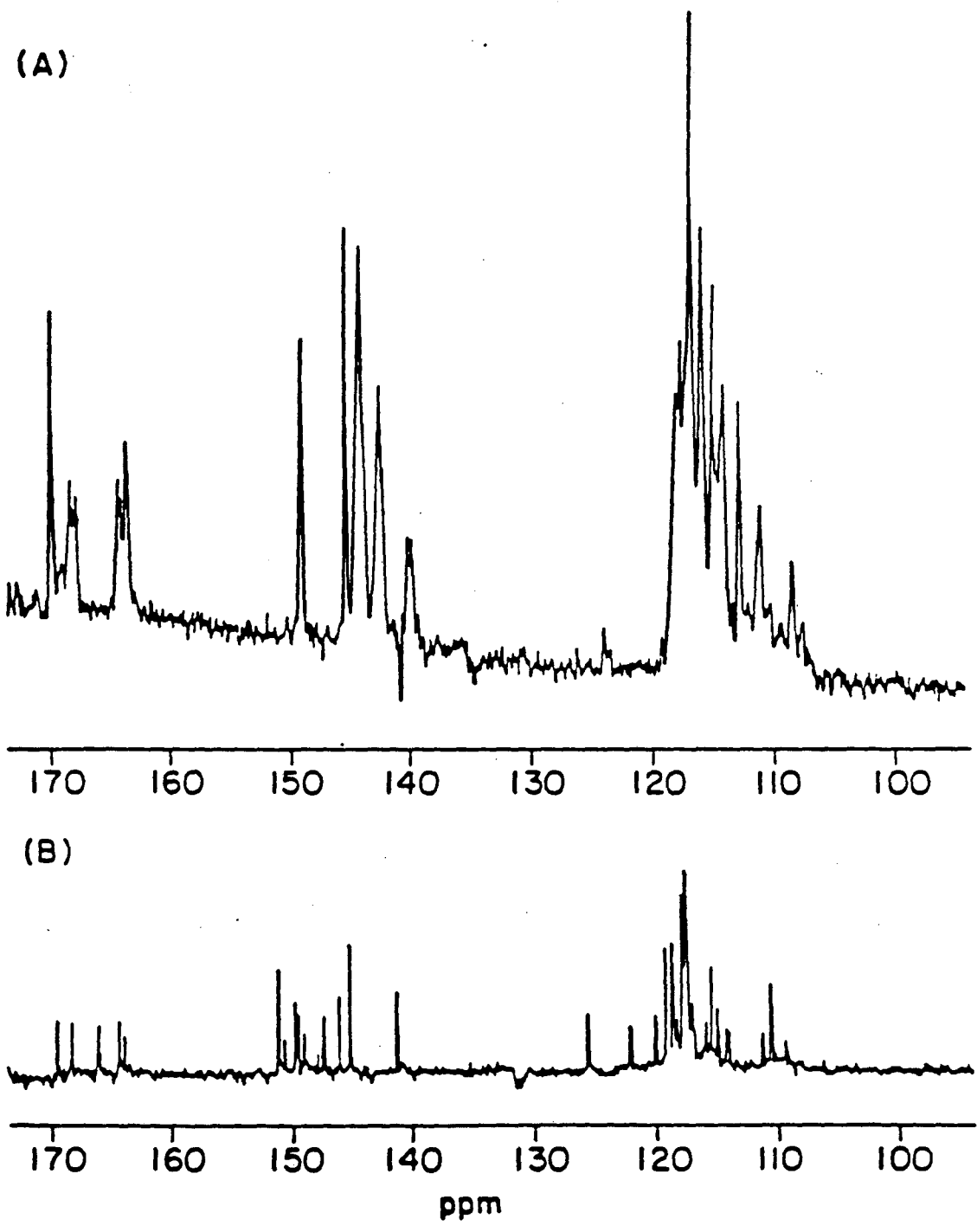


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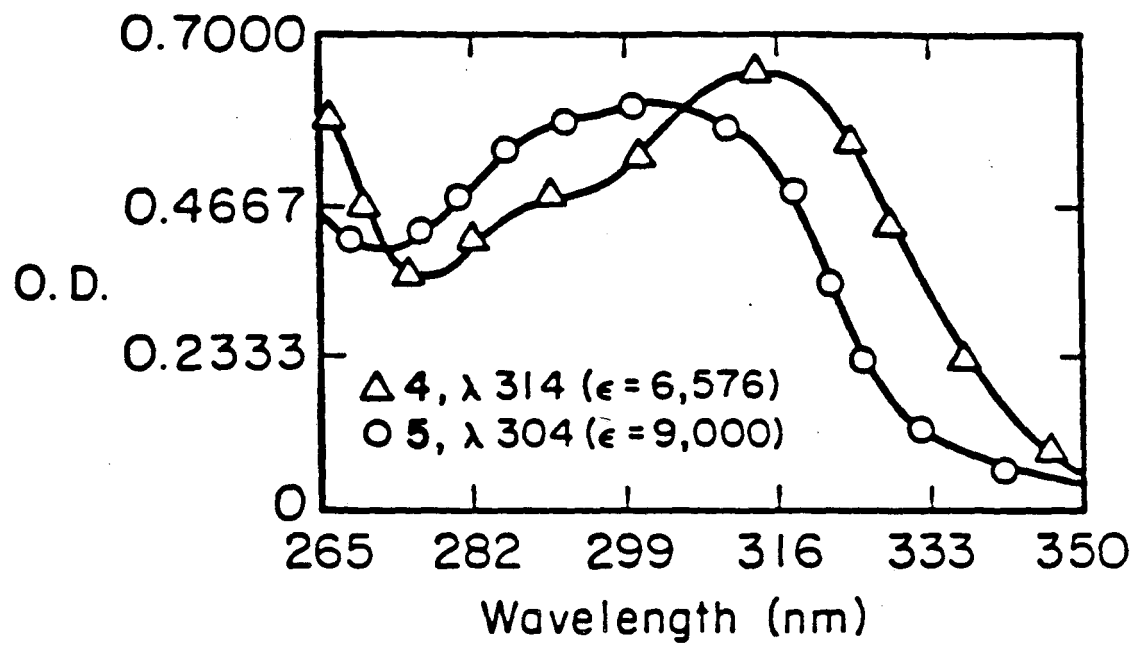


Figure 4

Arsenic Profile on 50/100/1000 Å SEC Column, AA at  
193.7 nm, THF Mobile Phase

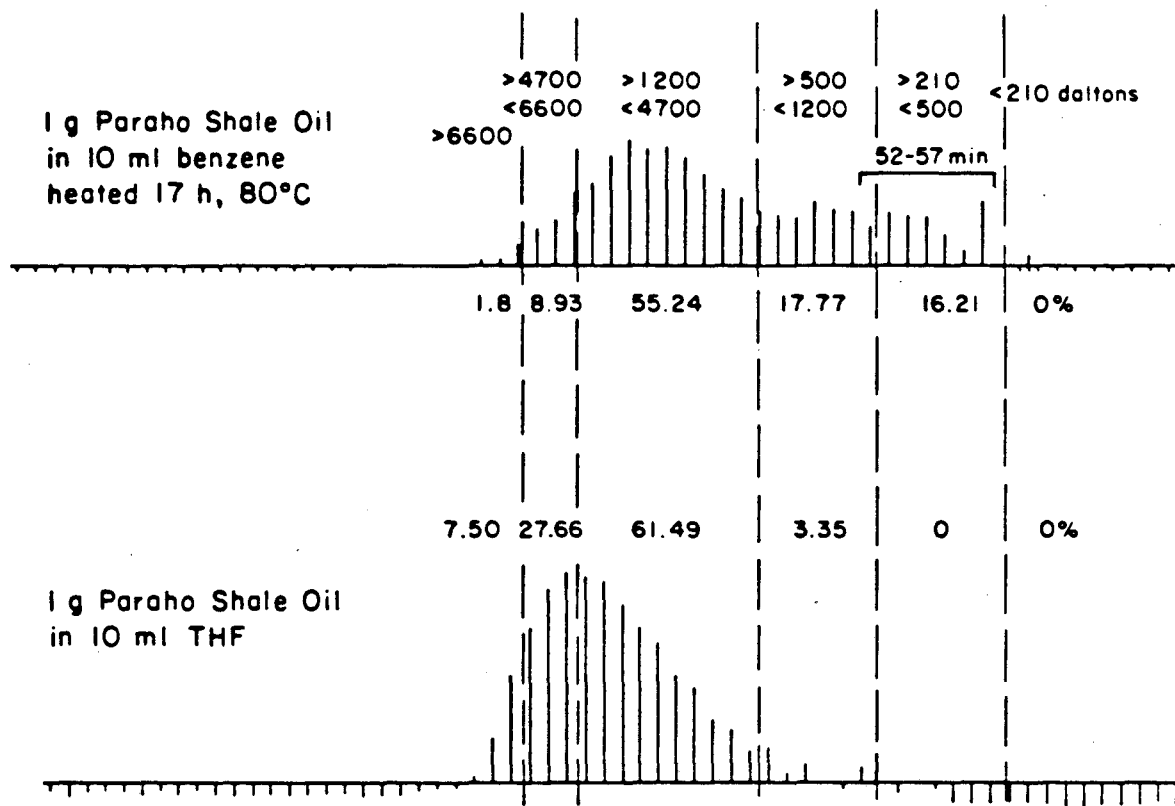


Figure 5

ANALYSIS BY GC-MS

Reconstructed Ion Chromatogram of Fraction 210-500 daltons (52-57 min)  
Isolated by Preparative HPLC with a SEC Column Followed by Derivatization  
with 3-Methylcatechol

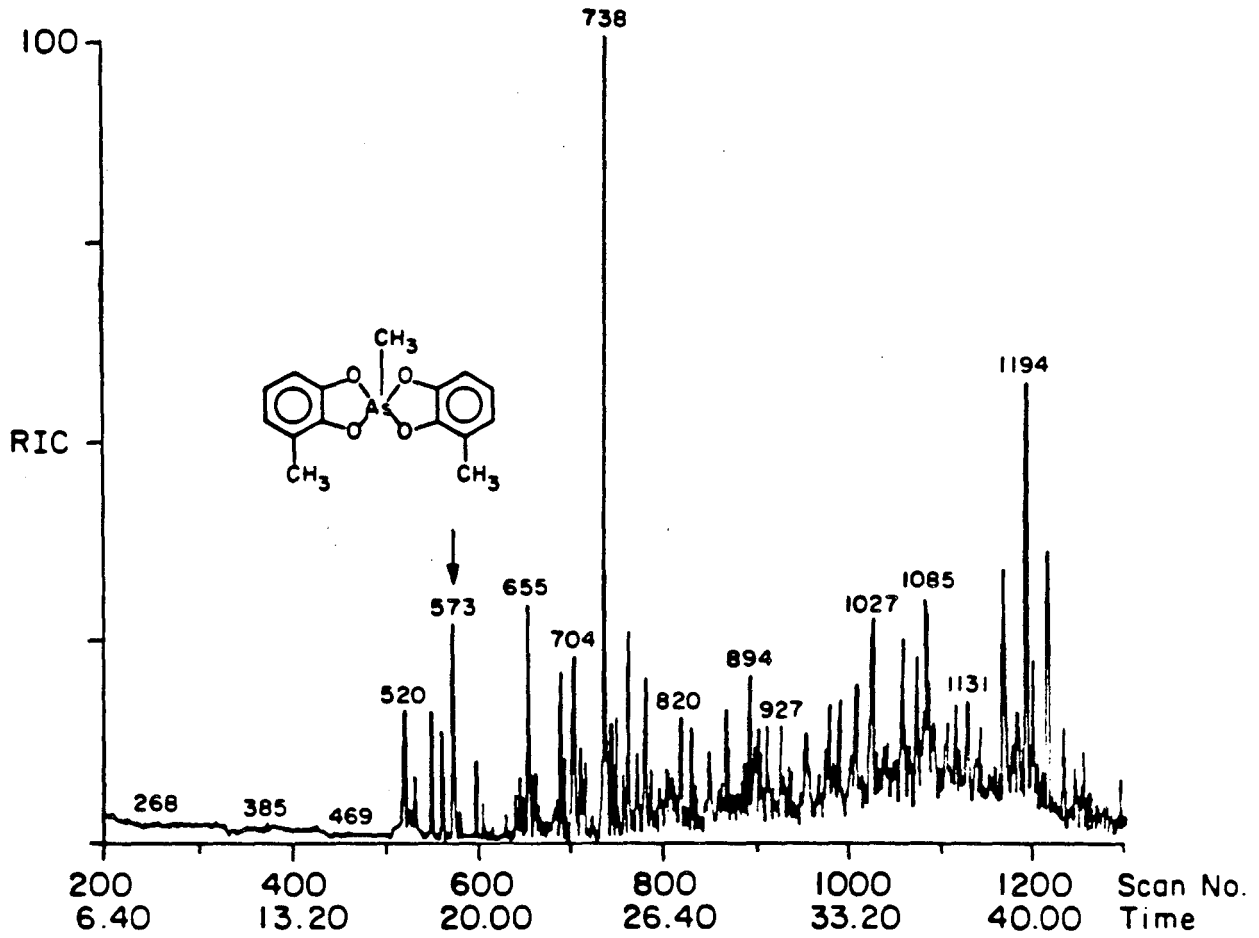


Figure 6

Reconstructed Ion Chromatograms and Single Ion Chromatograms of Isolated,  
Derivatized Paraho Shale Oil Sample

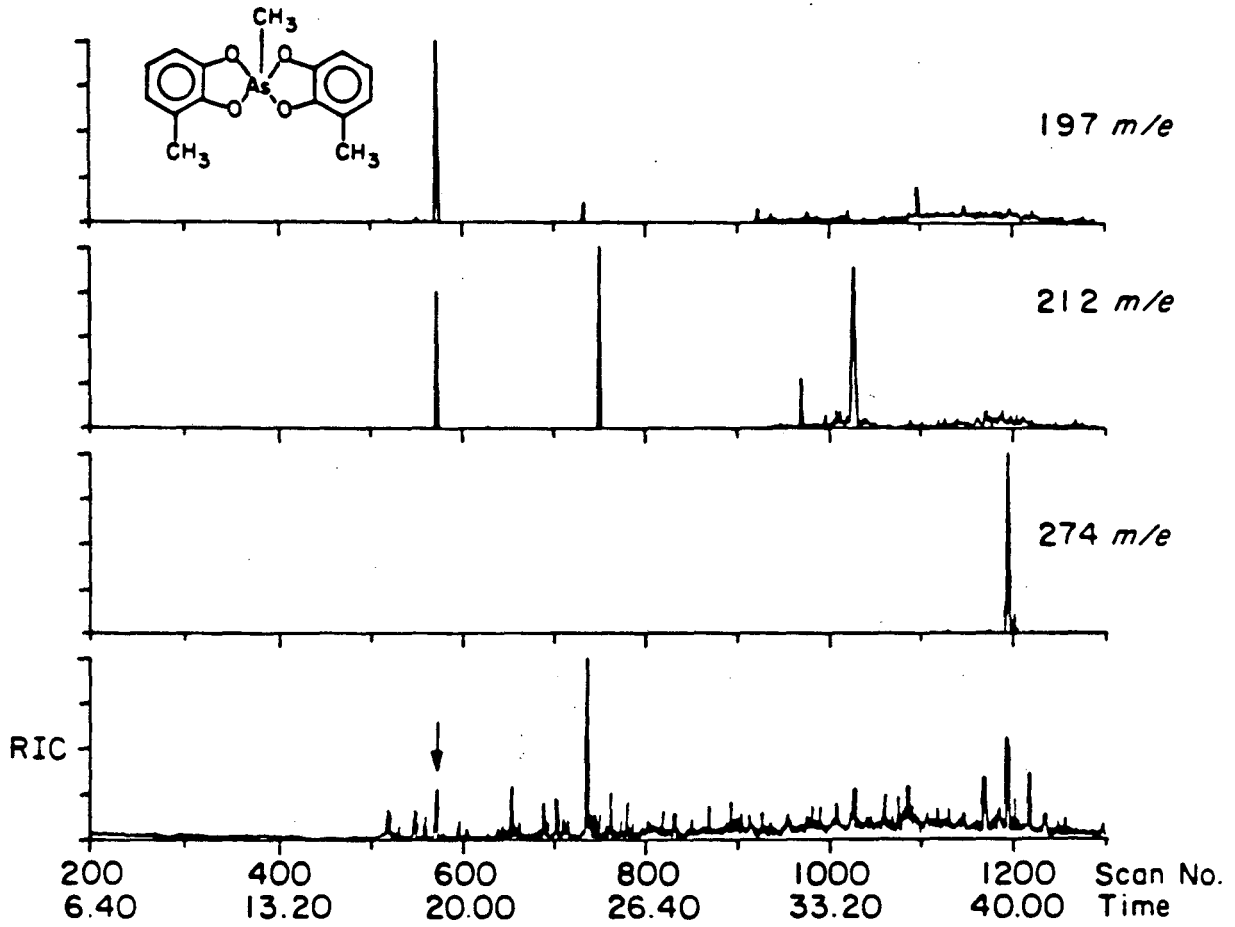


Figure 7

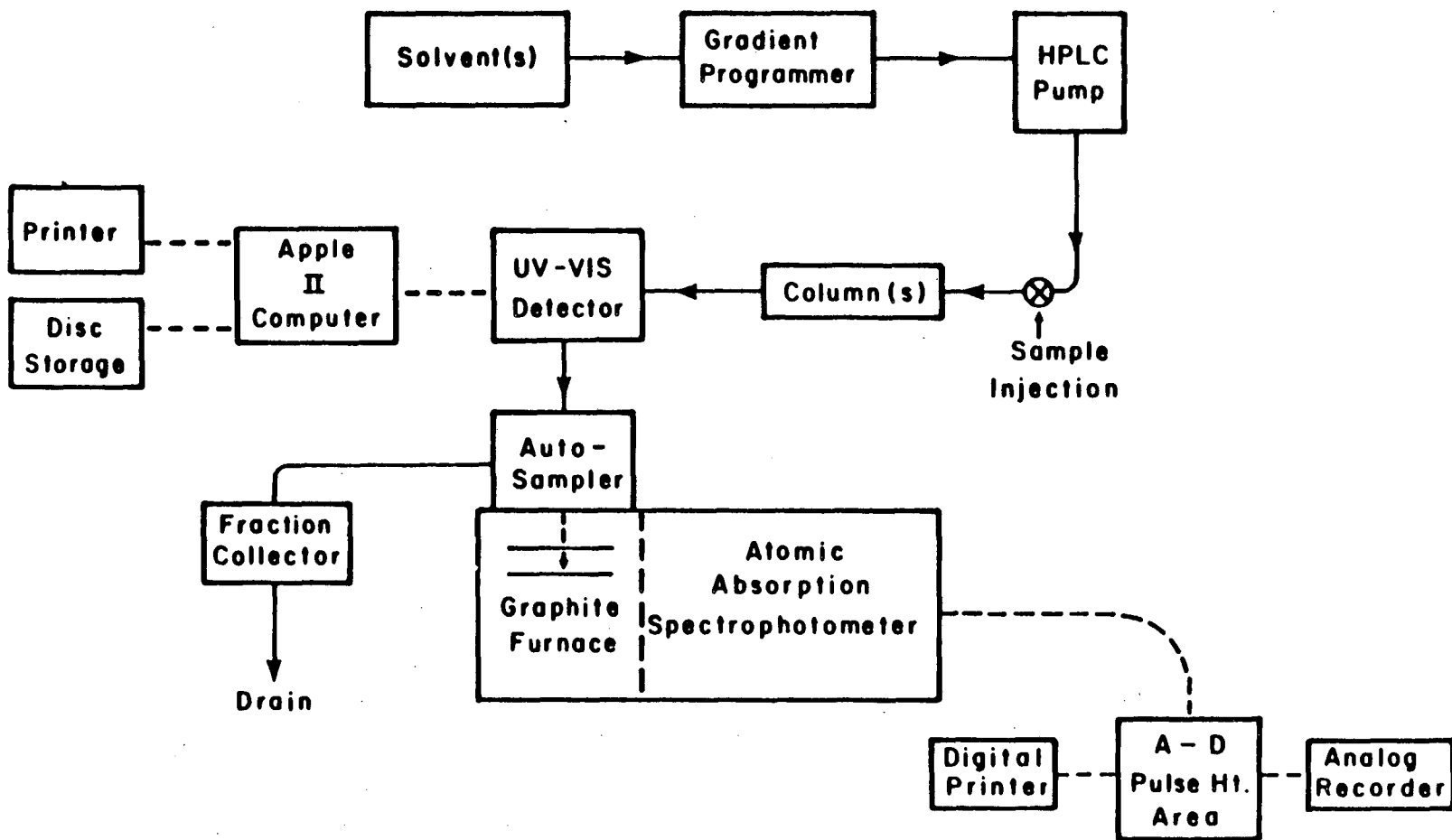


Figure 8



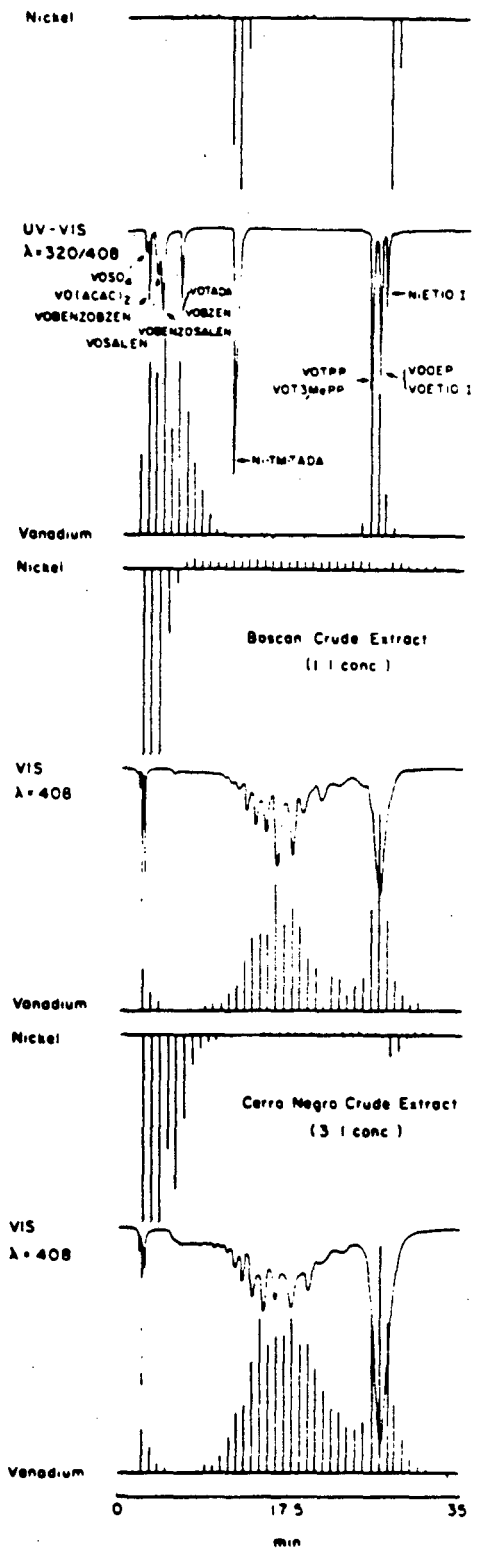


Figure 9

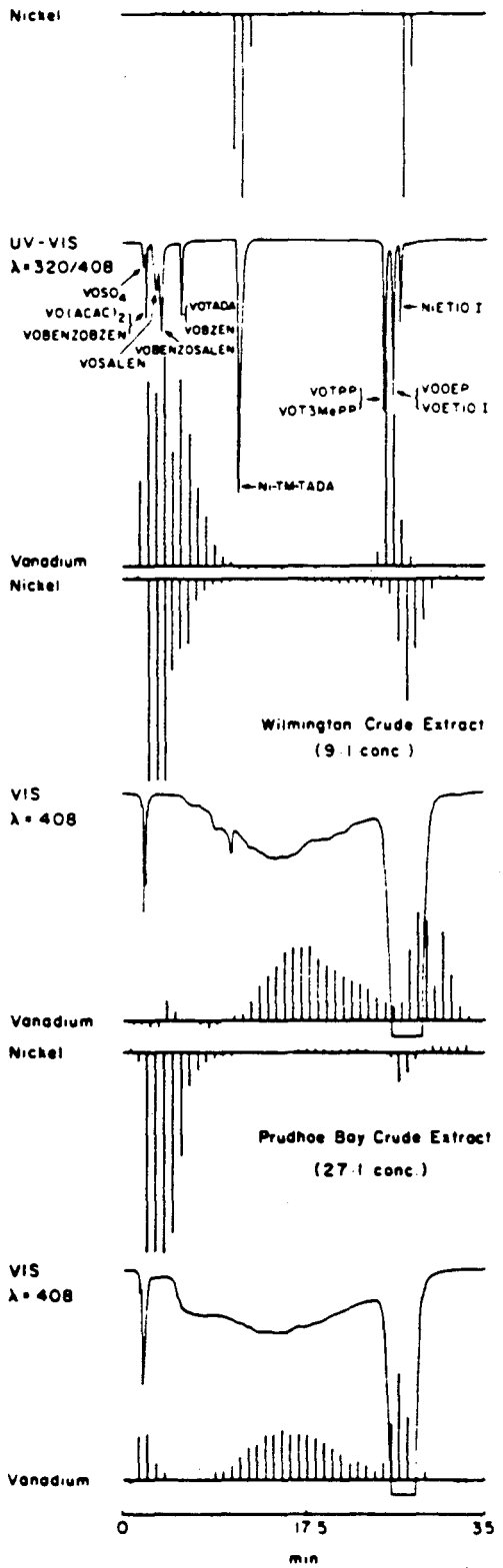
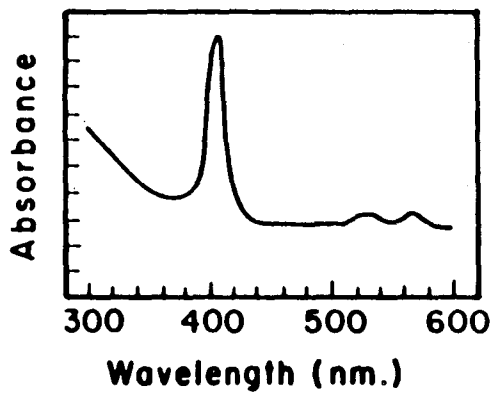


Figure 10

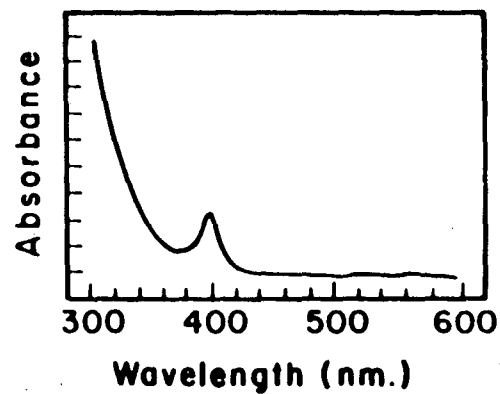
**Boscon Extract**

**t = 16 min**

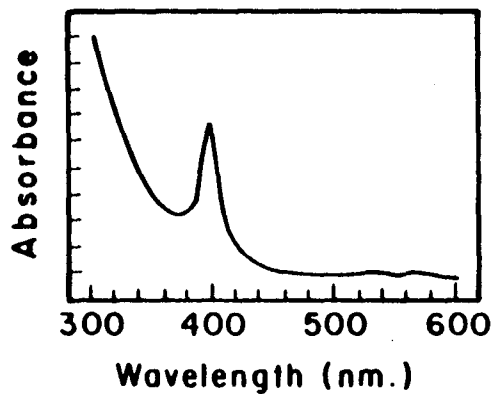


**Cerro Negro Extract**

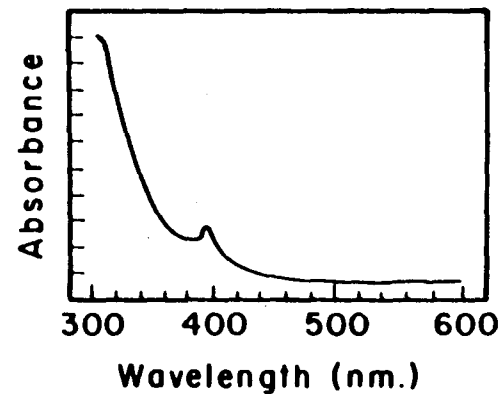
**t = 16 min**



**t = 27 min**

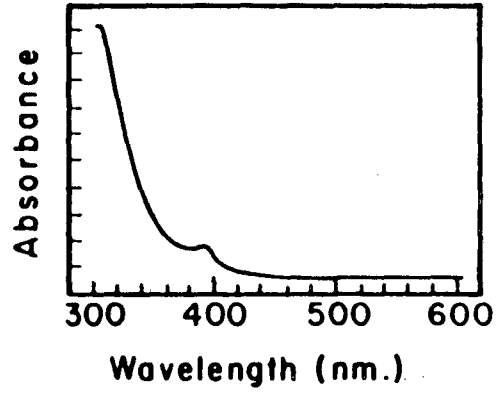


**t = 27 min**



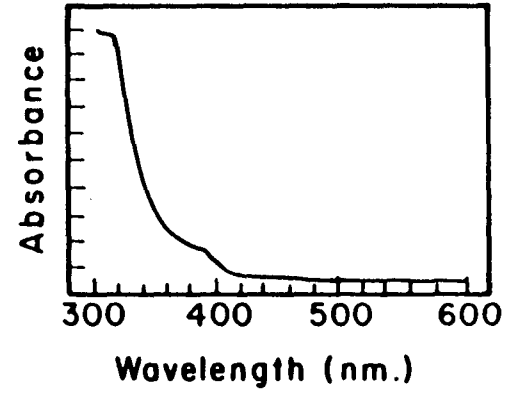
Wilmington Extract

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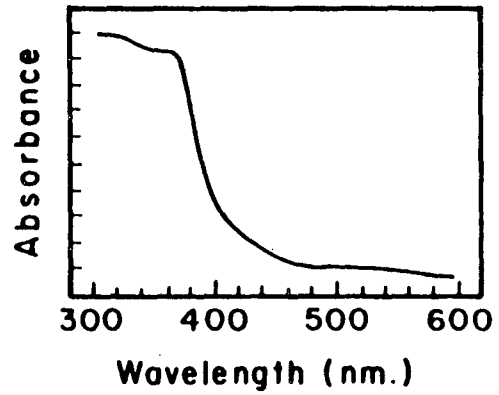


Prudhoe Bay Extract

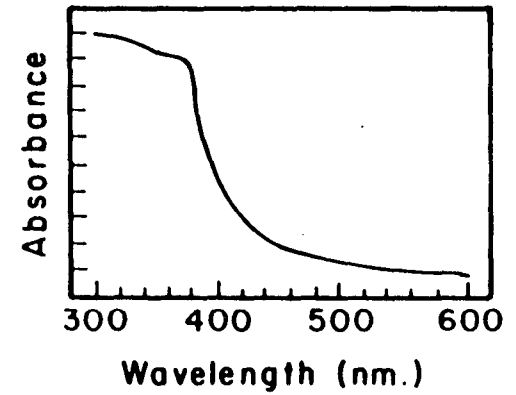
t = 16 min



t = 27 min



t = 27 min



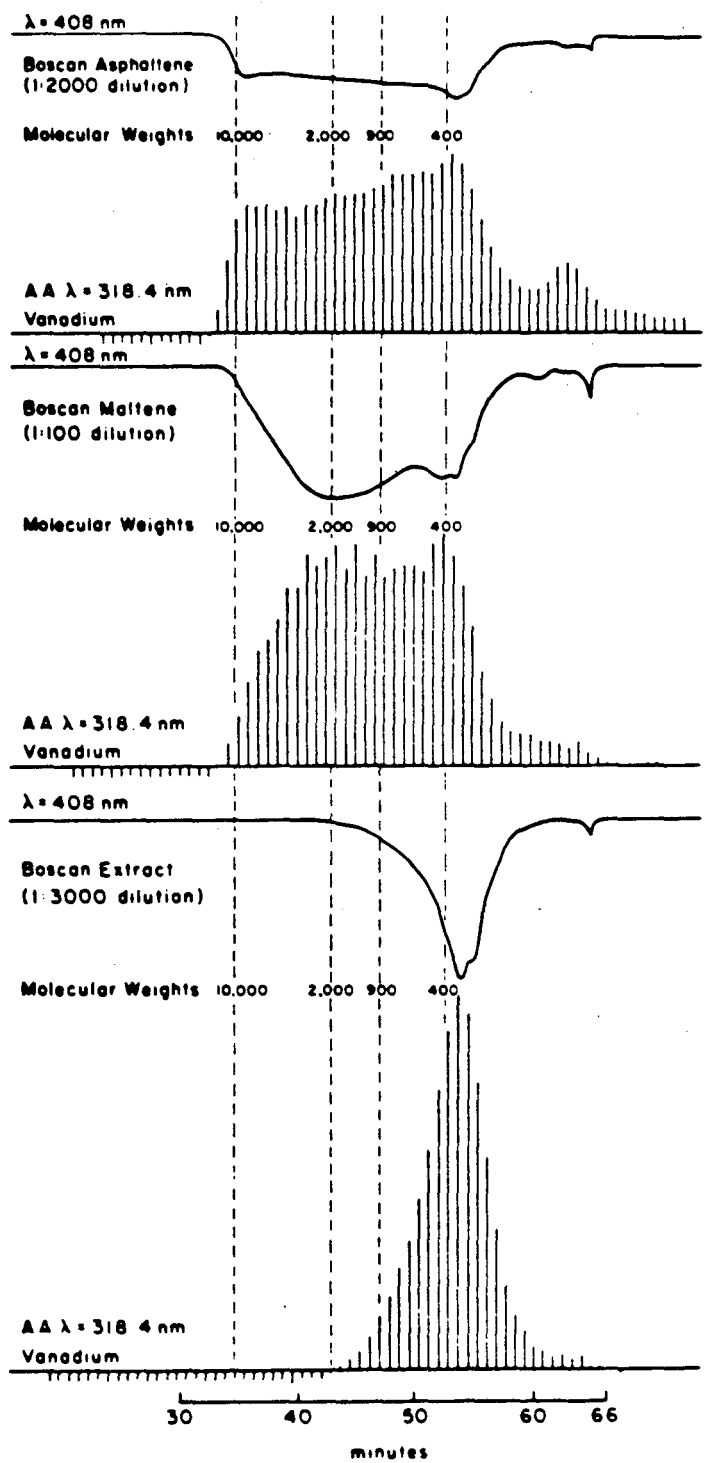


Figure 13

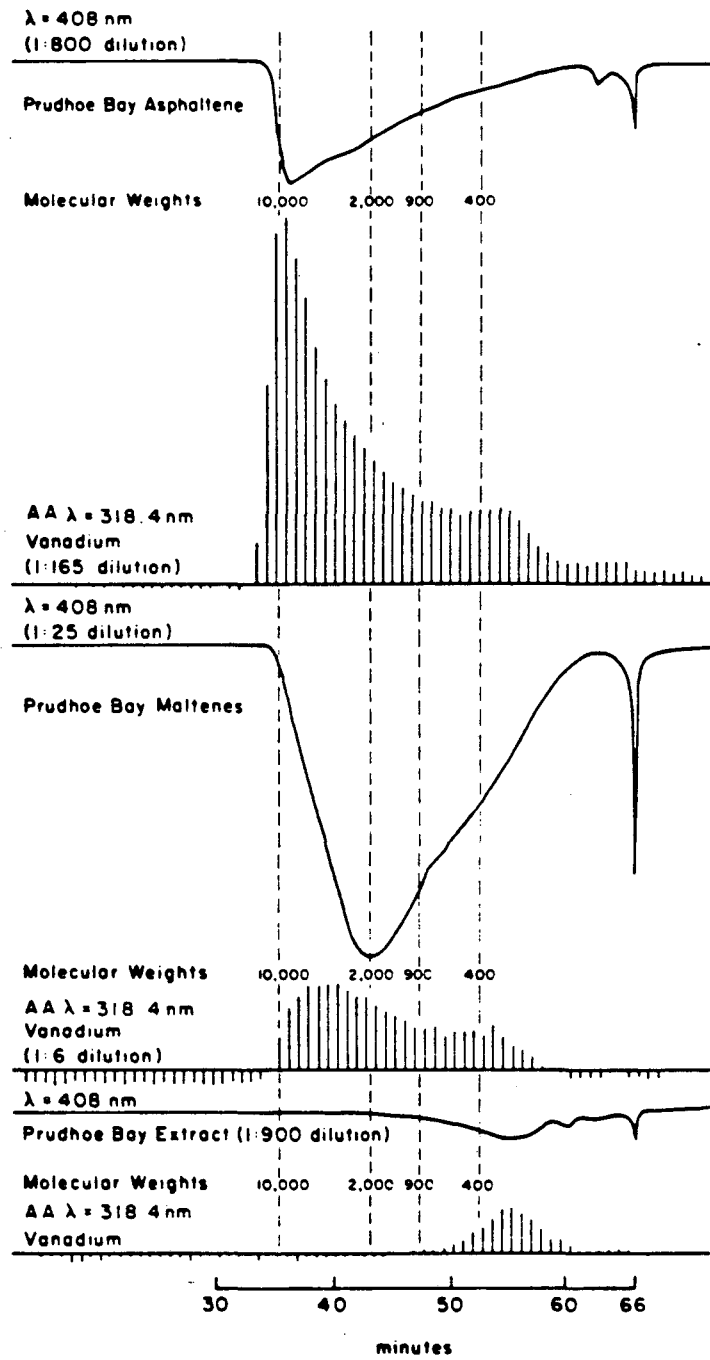


Figure 14

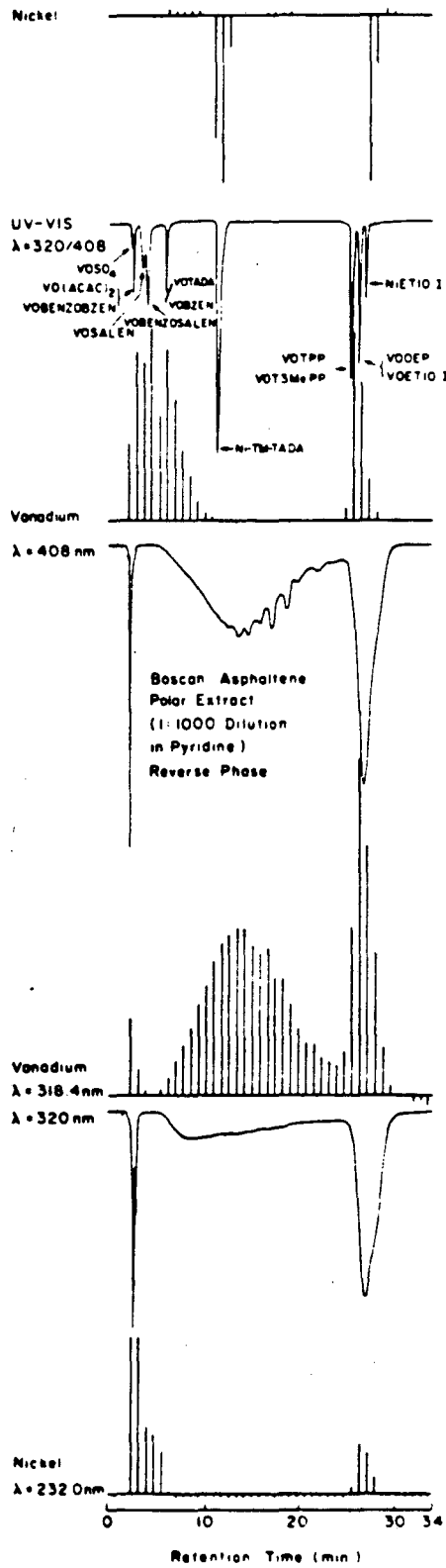


Figure 15

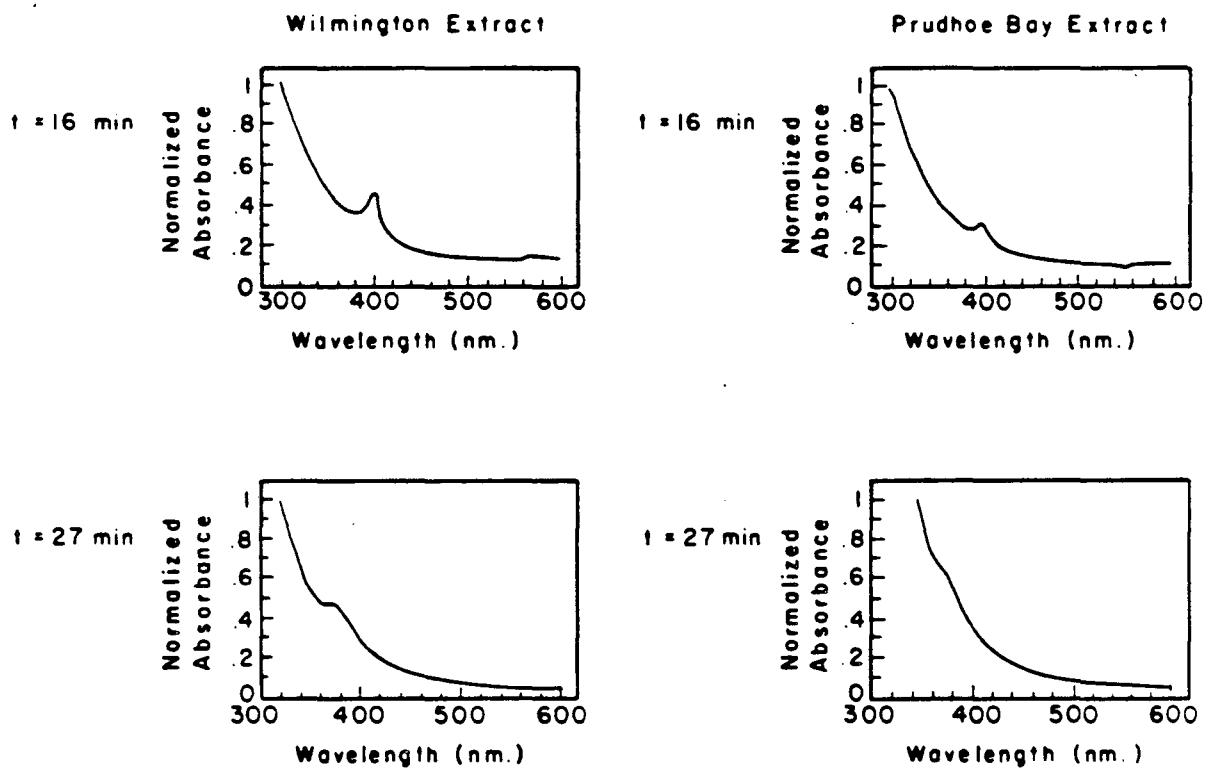


Figure 16



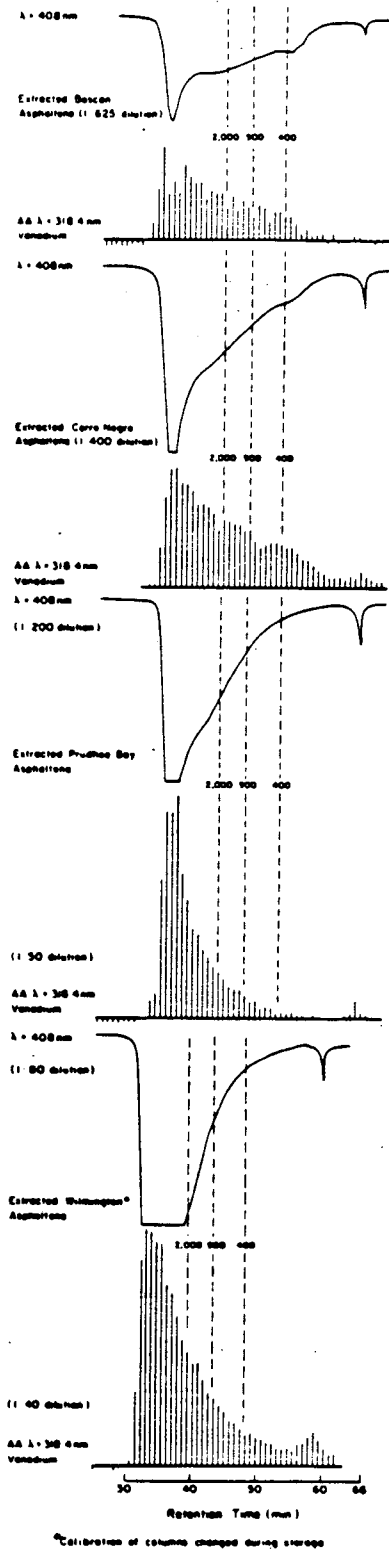
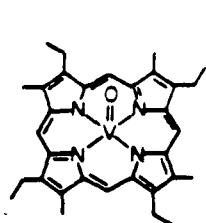
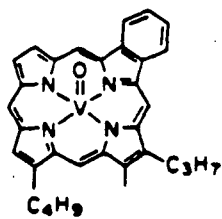


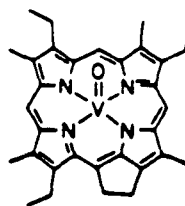
Figure 17



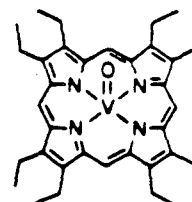
VOETIO I



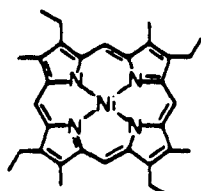
VORHODO



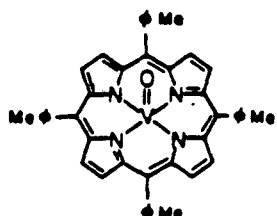
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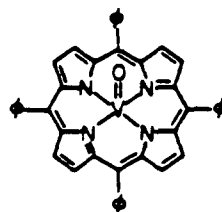
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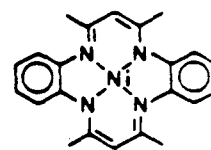
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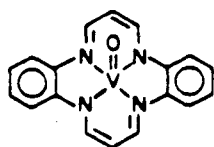
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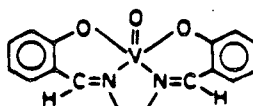
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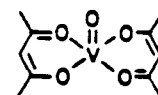
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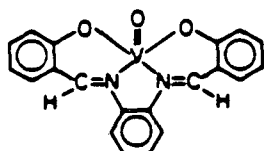
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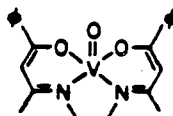
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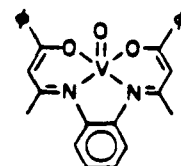
VOACAC



VOBENZSALEN



VOBZEN



VOBENZOBZEN

Chart I

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