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1). Introduction

The molecular characterization of vanadium and nickel compounds in heavy crude petroleums has been the subject of current research. Prior studies have shown porphyrins as being the only metal coordination site for both V and Ni (1), but newly developed analytical methods, such as high performance liquid chromatography (HPLC) combined with element-selective detection (ESD), such as inductively coupled plasma (ICP) (2) and graphite furnace atomic absorption (GFAA) spectrometry (3), have shown a considerable percentage (50 to 80) as metallo-non-porphyrin compounds. Application of electron paramagnetic resonance (EPR) spectroscopy also shows the probable existence of other types of coordination spheres for V (4-6), such as S, O, N combinations.

Arabian Heavy (AH), Maya (Ma), Boscan (Bo), Cerro Negro (CN), Prudhoe Bay (PB), Wilmington (W), Beta (Be), Kern River (KR), and Morichal (Mo) crude petroleums have been examined. Fractions from D 2007 separations (4), porphyrin extractions (2), and solvent selective extraction (3) with reversed phase (RP) column separations of these petroleums have been studied thoroughly by EPR (4-6). Experimental details are reported elsewhere (2-6).

2). Results and Discussion

The molecular size profiles of Bo, CN, W, and PB crudes were examined by SEC-HPLC-GFAA analyses to delineate characteristic metal profiles (3). These profiles were then matched with fully characterized model compounds examined under identical conditions. Figure 1 shows the V fingerprint with the element-specific detector at 318.4 nm, and the visible detector at 408 nm (Soret) for Bo. Model V compounds and polystyrene (PS)standards are also shown. Table 1 lists the distribution of V by PS equivalent molecular weight (MW) of the above crudes, using these methods of analyses (3).

Table 1: V Distribution by Molecular Weight

MW Range	Boscan	Cerro Negro	Wilmington	Prudhoe Bay
>9000	3.5%	4.2%	4.9%	7.2%
<9000,>2000	28.0%	38.3%	37.2%	47.8%
<2000,>900	17.2%	19.5%	15.5%	17.4%
<900,>400	20.5%	18.0%	16.6%	14.3%
<400	30.8%	20.0%	25.8%	13.3%

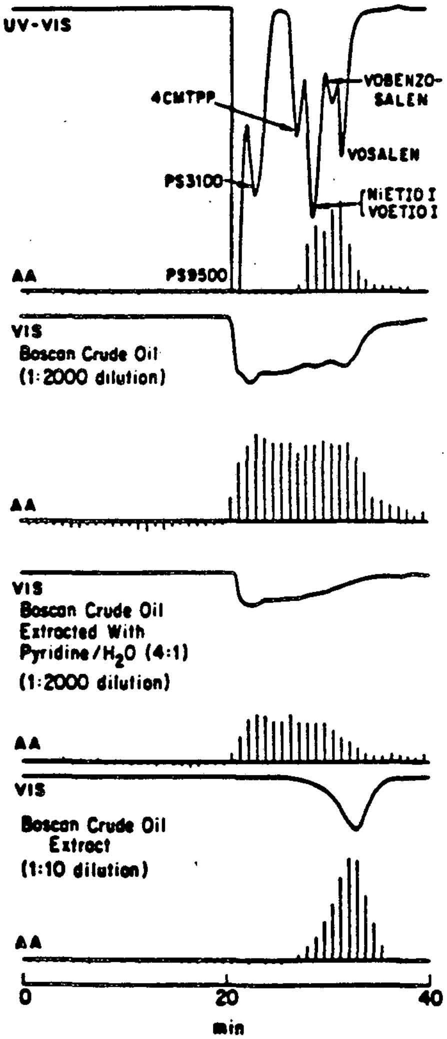

Figure 1. 50/100 Å SEC-HPLC-GFAA profiles for a) standards, b) Boscan crude oil, c) crude oil after extraction, and d) crude oil extract.

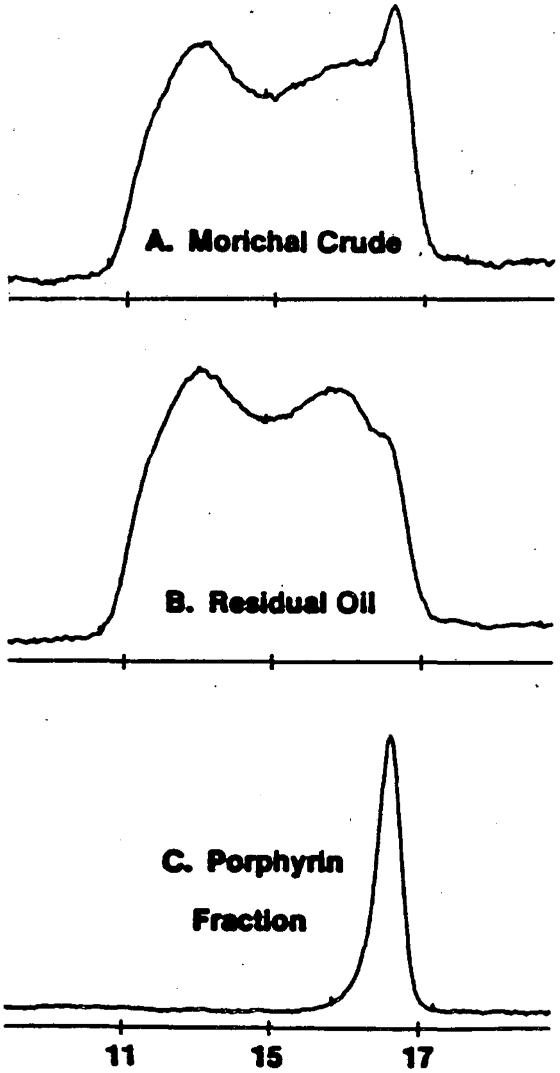

Figure 2. SEC-HPLC-ICP profiles for a) Morichal crude oil, b) crude oil after porphyrin extraction, c) porphyrin extract.

From the V profiles the following can be summarized: 1). For the crudes studied, 30-50% of the V compounds have MW <900. 2). Only 3-7% of the total V has MW >9000. 3.) Model compounds indicate V non-porphyrin compounds are predominant (50-80%). The results from Figure 1 and Table 1 illustrate the need for better separations for further characterization. A number of methods were employed for the direct purpose of speciating the metallo-non-porphyrin compounds.

AH, Bo, Ma, Be, and Mo crudes were separated into porphyrin and non-porphyrin fractions and examined by SEC-HPLC-ICP (2). The SEC profiles were different for each of the crudes studied, but some general features were similar. Figure 2 shows the V SEC profile of Mo crude from 24000 to 300 daltons as an example. The % V extracted for the crudes was: Be, Bo, Mo, Ma, AH; 28, 24, 21, 13, 6. Examination of Figure 2 and the other separation profiles (not shown) reveal the following features: 1). The extraction removes a sharp, low MW fraction centered around 800 daltons. The UV-vis data shows this separation removes almost all the metallo-petroporphyrins. 2). The unextracted material, the residual oil, is left virtually unchanged by the extraction, and is of higher MW than the corresponding extracted fraction. 3). The non-extracted material, which is considered to be metallo-non-porphyrin in nature, has a much broader SEC profile.

Ma, AH, Be, and KR atmospheric residua (AR) were characterized by the modified D 2007 and asphaltene separation. The organic portions of the four fractions (saturate, aromatic, resin, and asphaltene) have been analyzed in detail (4). The metals distribution of the separated fractions of the above residua allows several generalities to be made: 1). The saturate and aromatic fractions contain almost no detectable metals. 2). The majority of the metals are found in the asphaltene fractions except for KR. Comparable results have been found elsewhere (7,8).

Some work has been done on the fate of the porphyrins in the D 2007 separation. From absorption data, the majority of the porphyrins have been found in the resin fraction (9,10). This contradicts fingerprinting using RPC-HPLC-GFAA, where the V profiles of the maltene and the asphaltene extracts (pyridine/water) show the majority of the V petroporphyrins associate into the asphaltenes (7).

The extracts of Bo, PB, CN, and W were also examined by RPC-HPLC-GFAA. Three fractions were isolated where F1 is the most polar, and F3 is the least polar. Figure 3 shows the V and Ni profile of Bo. The following conclusions were made for the crudes: 1). The extraction removes V and Ni

Figure 3. Reversed Phase HPLC-GFAA profiles for a) standards and b) Boscan crude oil extract.

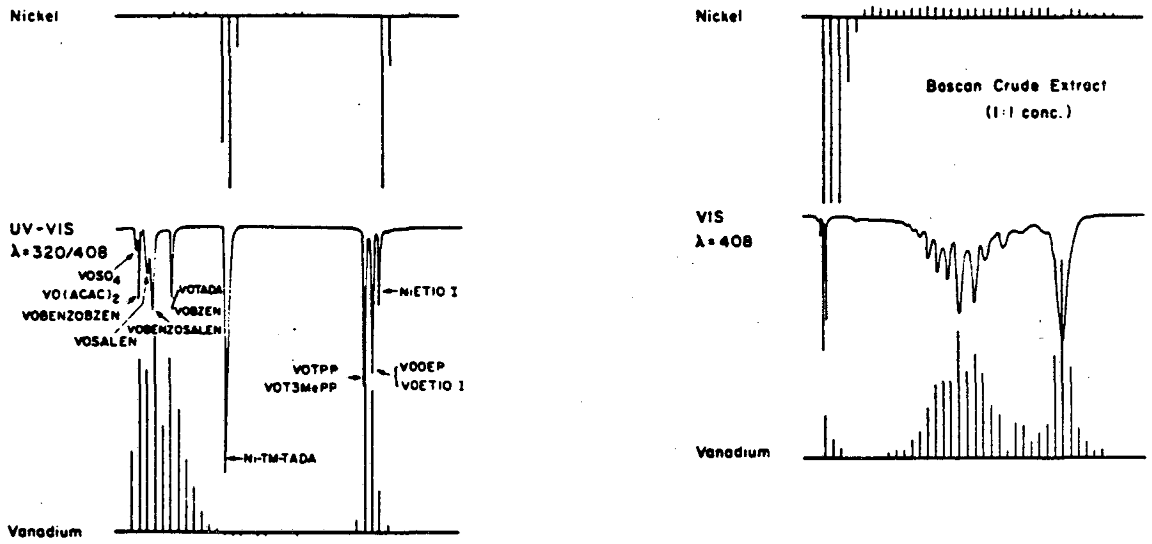

Table 2: EPR Parameters and Derived Coordination Spheres

Sample	g iso	a iso	Coordination	Temp.°C
		Resins		
Maya	1.9783	97.0 g	N O 2S	165
Arabian Heavy	1.9798	97.0 g	4N, 3N S	165
Beta	1.9786	97.0 g	4N, N O 2S	190
Kern River	1.9790	96.9 g	4N	165
		Asphaltenes		
Maya	1.9784	97.5 g	N O 2S, 4N	255
Arabian Heavy	1.9781	97.5 g	N O 2S	262
Beta	1.9792	97.3 g	4N	231
Kern River	1.9783	97.4 g	N O 2S	255
		Non-porphyrins		
Beta	1.9779	97.1 g	N O 2S	252
Boscan	1.9791	97.0 g	4N	252
Morichal	1.9787	96.9 g	4N, N O 2S	241
Maya	1.9772	97.4 g	N O 2S *	253
Arabian Heavy	1.9786	97.5 g	4N, N O 2S	254
		Reversed Phase Separations		
Boscan F2**	1.9801	95.6 g	4N, 3N S	RT
Boscan F3***	1.9789	95.3 g	4N	RT
Prudhoe Bay F2	1.9801	94.1 g	4N	RT
Prudhoe Bay F3	1.9800	93.7 g	4N, 3N S	RT
Cerro Negro F2	1.9819	94.2 g	4S	RT
Cerro Negro F3	1.978	94.2 g	4N, N O 2S	RT
Wilmington F2	1.9813	94.6 g	4S, 3S N	RT

*2N O S, 2S 2O, 3N O are also possible.

** F2 is moderate polar fraction.

*** F3 is low polar fraction.

compounds from all MW ranges. Compounds in MW ranges >2000 appear to have MW <400. This strongly implies that a considerable percentage of the V non-porphyrin compounds are complexed to the large MW asphaltic components and can be removed by extraction. 2). Bo, CN, and W have V porphyrin and non-porphyrin compounds; PB has virtually no porphyrins. 3). Bo, CN, PB have virtually no Ni porphyrins, while W has some Ni porphyrins.

The above fractions were examined by EPR and MS spectroscopy to further characterize V non-porphyrin compounds. Table 2 lists the EPR parameters calculated and the coordination spheres correlated for the above fractions.

The predominant coordination spheres indicated for the V non-porphyrin species are the 4N (i.e. possibly chlorins, phthalocyanines, aza-[14]-annulenes), N O 2S (no model compounds have been characterized), and 4S (dialkyldithiocarbamates, thiophenic type). High resolution MS has been performed on the RPC fractions. Unfortunately, due to overwhelming organic composition, no metallo-non-porphyrin complexes have yet been identified.

3). Conclusion

Important structural aspects are emerging from the presented data: 1). There are non-porphyrin metal complexes in the crude petroleums. 2). They appear to be smaller molecules with MW <400 which are liberated when the tertiary structure of the large asphaltics is denatured. 3). The first coordination spheres of this class of compounds are possibly 4N, N O 2S, and 4S.

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