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Vanadium and Nickel Complexes in Petroleum Resid Acid, Base, and Neutral Fractions

Topical Report

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Abstract

Acid and base fractions from petroleum vacuum resids with no detectable (by visible spectrophotometry) quantities of porphyrinic Ni or V complexes were hydrotreated under various conditions to determine if significant amounts of porphyrinic metals were released, via disassociation or other means, upon hydrotreating. No significant quantities were observed, thereby indicating that nonporphyrinic metals were not simply associated, complexed or otherwise masked (in terms of visible spectrophotometric response) porphyrinic metal complexes. However, it is possible that hydrotreating was simply not effective in breaking up these associates and/or that some porphyrinic forms of metal were in fact released but were rapidly destroyed by hydrotreating.

In addition, three liquid chromatographic (LC) separation methods were sequentially applied to Cerro Negro (Orinoco belt Venezüelan heavy crude) >700° C resid in an effort to separate and concentrate the metal complexes present. Nonaqueous ion exchange chromatography was used initially to separate the resid into acid, base and neutral types. A custom synthesized alkylpyridyl-bonded silica HPLC column packing was used in the intermediate separation step; plain silica was employed for the final step. Two concentrates containing 19,500 and 13,500 ppm total V, or an estimated 19 and 13 wt% V-containing compounds respectively, were obtained. The degree of enrichment of Ni compounds obtained was significantly lower. By visible spectrophotometry, using vanadyl etioporphyrin as a standard, each of the concentrates contained near a 1:1 ratio of porphyrinic:nonporphyrinic V complexes. Analogous separation behavior for porphyrinic versus nonporphyrinic metal forms was observed throughout much of the work, thereby suggesting that a comparable diversity of structures existed within each general class of metal compounds. However, strong acid and strong base fractions produced in the nonaqueous ion exchange separation contained largely nonporphyrinic metal complexes whereas the bulk of the measureable porphyrinic complexes partitioned into the weak base and neutral fractions. Also, nonporphyrinic forms of V tended to elute later in the other LC separations than porphyrinic forms. Thus, the behavior of porphyrinic versus nonporphyrinic complexes did not directly correspond, but appreciably overlapped. The generally wide dispersion of both Ni and V over the LC separation scheme suggests a structural variety of metal complexes that is comparable to that observed for other heteroatoms (N, S, O) in petroleum.

Introduction

Vanadium (V) and Nickel (Ni) are the most abundant trace metals in petroleum crudes and V levels from below 1 to 1200 ppm have been reported.[1] They cause problems in refining because they are catalyst poisons. A knowledge of the structure of Ni and V complexes in resids should aid in development of more efficient demetallation processes.

Ni and V occur in two forms in crude oil. Porphyrinic, which has been widely studied and categorized, and nonporphyrinic, (for lack of a better definition) into which category all of the V and Ni not determined to be porphyrinic is placed. The main forms of metalloporphyrins which have been found in petroleum[2] are shown in Figures 1a and 1b. These are respectively, deoxophylloerythroetioporphyrin (DPEP) and etioporphyrin; both are complexed in the vanadyl (VO) and Ni forms. Two other porphyrins found in trace amounts are RHODO-etio (figure 1c) and RHODO-DPEP (figure 1d). The RHODO-type porphyrins are more difficult to demetalate than other porphyrin types.[3] All types consist of a homologous series which range from ca. C_{25} to C_{39}[4-6] with one report of C_{50}[1]. In some situations, porphyrins are known to exist as dimers.[6,7]

Metalloporphyrins in petroleum are easily detected from their intense visible absorption spectra. VO etioporphyrin has an intense band at 410 nm (Soret band) and weaker bands at ca. 530 and 570 nm (β and α bands). Since the Soret band is often obscured by petroleum matrix absorption, metalloporphyrin concentrations are best determined by measuring the absorption above background of the α band, at 550 nm for Ni porphyrins and 570 nm for VO porphyrins. Calibration of molar absorptivity is usually by means of pure compounds; VO and Ni etioporphryins were employed as standards in this work. Because other porphyrinic types present may have different molar absorptivities and/or absorb at different wavelengths, the resulting estimates of porphyrinic content may be inaccurate.

Despite much research into the nature of metal complexes in petroleum, only the metalloporphyrins have been separated and unequivocally identified. The nonporphyrinic metals have been characterized by size exclusion chromatography/inductively coupled plasma atomic emission spectrometry (SEC/ICP),[8-12] which indicates that these metallocomplexes cover a range of molecular weights from thousands down to hundreds. No such compounds have ever been isolated and characterized. Recent work[13] demonstrated that when Ni porphyrins were added to asphaltenes in solution, the resultant SEC chromatograms showed Ni porphyrins to strongly associate with asphaltene species in all molecular weight ranges. Thus, SEC information concerning the molecular weight distribution of V and Ni may be erroneous due to the strong association of porphyrins with asphaltene materials. Yen[2] has speculated that nonporphyrin species include modified or very complex porphyrins, or are porphyrin degradation products. Several authors have studied the tetradentate ligands of nonporphyrinic V in asphaltenes by electron paramagnetic resonance spectroscopy (EPR).[14-16] However, others have concluded that EPR cannot unequivocally determine the ligand environment of V in asphaltenes.[17] Evidence that nonporphyrinic V and Ni may, in fact, be porphyrinic has been reported by several authors using a variety of analytical techniques.[18-20] Jacobs[21] has shown that at least a part of the nonporphyrin V in Athabasca asphaltenes was present as metalloporphyrin complexes. These studies suggest that much of the "nonporphyrinic" V content of asphaltenes comprises VO porphyrins, which are either strongly associated with the asphaltenes by π -π bonding, or are trapped in the micellar structure of the asphaltenes.[13]

In an earlier study,[22] two heavy petroleum resids were hydrotreated at differing severities. The whole resids were separated into acid, base and neutral (ABN) fractions before and after hydrotreating and analyzed for total V and Ni, and metalloporphyrins. In a number of fractions, the metal porphyrin level increased despite the fact that porphyrins are degraded by hydrotreating. It appeared that porphyrins were either released from association or modified so they were detected by UV-VIS absorption measurements. The molecular weight distribution of the V and Ni compounds in each acid or base fraction, by SEC/ICP, was the same as the distribution of the fraction itself. The total V and Ni levels showed V and Ni to be distributed over all ABN fractions, implying the nonporphyrins exhibited multiple chemical functionalities. Alternatively, the nonporphyrins may actually be porphyrin complexes associated with asphaltene-type molecules, and thus exhibit the characteristics which are typical of these very polar, high molecular weight, multifunctional molecules.

The present research continues the investigation of whether nonporphyrinic forms of V and Ni are really porphyrinic molecules. A two-pronged approach was used. The first was an attempt to decomplex or free the V and Ni molecules from their association with asphaltene molecules in the ABN fractions of heavy resids through hydrotreating. The second was based on liquid chromatographic (LC) techniques for concentrating V and Ni compounds from the ABN fractions of 700° C+ resid from a Venezuelan Orinoco Belt heavy oil (Cerro Negro). This resid contains 994 ppm V and 228 ppm Ni and represents 45.4 wt% of the whole crude.[23]

Experimental

Hydrogenation The best hydrogenation conditions (chosen from previously reported work[22]), resulting in the appearance of metalloporphyrins, were applied to a series of resid acid and base fractions. The fractions had been obtained previously using a nonaqueous ion exchange liquid chromatographic (NIELC) procedure[23,24] (see figure 2). The fractions were hydrotreated for 90 minutes at 375° C in 20 mL tube reactors. Hydrogen pressure was 1500 psi and a 40-80 mesh Co-Mo-Alumina presulfided catalyst was used, with sample to catalyst ratio of 70:1 and sample size of 1-2 grams. The reactor was extracted with 15 cc of toluene and minimal residue was left behind. Extracts were taken to dryness and dried in a vacuum oven at 65° C overnight. Total V and Ni, and metalloporphyrinic forms of each were determined for products using prior procedures.[22]

In a second series of experiments, hydrogenation with a homogeneous catalyst was carried out at varying temperatures. Portions of whole Cerro Negro 700° C+ resid were dissolved in cyclohexane to form a 10 percent solution which were hydrotreated in a 300 mL stirred reactor. The catalyst was molybdenum octenoate in 8 percent cyclohexane solution and was added to the sample solution in the ratio: 10 g of sample to 0.25 g molybdenum. The reactor was pressurized to

1200 psig with hydrogen (cold) and then heated to temperature. After hydrogenation, the reactor products were centrifuged to remove insolubles and the liquid products were stripped on a rotary evaporator and dried in a vacuum oven at 65° C overnight. The dried products were analyzed for total V and Ni and metalloporphyrins as before.

In the third series, portions of strong acid fractions from several resids and a Cerro Negro strong base fraction were hydrotreated using the same molybdenum liquid catalyst system and reactor. The samples were heated to 50° C and ultrasonicated until partly dissolved and partly dispersed (8 hrs.). They were hydrogenated at 350° C and 1200 psi cold hydrogen pressure. Sample size was 1 or 2 g in 100 mL of cyclohexane.

Liquid Chromatography. Figure 2 is a flow diagram depicting the LC procedures used to obtain metals-rich fractions from the Cerro Negro 700° C+ resid. Total metal and porphyrin contents of fractions were determined as before.[22] The sequence began with separation of the whole resid into ABN fractions using NIELC. The neutral and weak acid fractions were then chromatographed on a 25 x 2.5 (id) cm preparative scale HPLC column packed with (4-pyridyl)-ethyl silica which was made in house.[25] Conditions for separation of Cerro Negro neutrals into fractions were as follows. The chromatograph was a Spectra Physics (Santa Clara, CA) 8000 with an ISCO (Lincoln, NE) V4 UV-VIS detector and a 6-way valve for fraction collection. A wavelength of 400 nm was used for effluent monitoring and the flow rate was set at 30 mL/minute. Column temperature was 30° C. The mobile phase program used for separation of the neutrals is noted below. All gradient segments were linear. Mobile phase A was n-heptane, B was benzene, C was 70:30 benzene:ethanol. Figure 3 is a typical chromatogram from the Cerro Negro neutrals separation. The arrows mark the fraction cutpoints.

Separation of neutrals - pyridyl column

Time Minutes	Mobile Phase Composition %A	%B	%C
0	90	10	0
7	90	10	0
27	0	93	7
32	0	93	7
42	0	0	100
44	0	0	100
45	0	100	0
51	0	100	0
52	90	10	0
62	90	10	0

The weak acid fraction was separated on the same column and using the same mobile phases, flow rate and detector wavelength. A different mobile phase program was used, however, as shown below. Figure 4 is a typical chromatogram from separation of the weak acid fraction separated on the pyridyl column. The arrows mark the fraction cutpoints.

Separation of weak acids - pyridyl column

Time	Mobile Phase Composition		
Minutes	%A	%B	%C
0	90	10	0
20	0	93	7
25	0	93	7
35	0	0	100
50	0	0	100
51	0	100	0
57	0	100	0
58	90	10	0
68	90	10	0

Selected subfractions from separation of neutrals on the pyridyl column were further separated on silica (figure 2). A Rainin (Wolburn, MA) Dynamax silica column [25 x 2.14 (id)cm] with a guard column was used. Instrumentation and conditions were the same as used for pyridyl column separations, except for the mobile phases and mobile phase program. The following mobile phase program was used for the Cerro Negro neutral subfraction P2 (see figure 2). Mobile phase A was cyclohexane, B was methylene chloride, and C was 70:30 methylene chloride:ethanol.

Further separation of neutral P2 subfraction on silica

Time	Mobile Phase Composition		
Minutes	%A	%B	%C
0	100	0	0
5	100	0	0
30	0	100	0
40	0	67	33
46	0	67	33
47	0	100	0
55	0	100	0
56	100	0	0
76	100	0	0

Conditions for separation of neutral subfractions P3 and P4 were identical except for the mobile phase program, which is specified below. Figures 5-7 depict typical chromatograms from further separation of neutral P2, P3 and P4 subfractions on silica, respectively.

Further separation of neutral P3 and P4 subfractions on silica

Time	Mobile Phase Composition		
Minutes	%A	%B	%C
0	90	10	0
30	0	100	0
40	0	67	33
46	0	67	33
47	0	100	0
53	0	100	0
54	90	10	0
64	90	10	0

Results and Discussion

Hydrogenation Experiments. Table I shows data from the first hydrotreating series. Comparison of elemental composition for products versus the feeds indicates that the hydrotreating conditions were mild, as the H/C atomic ratio and nitrogen content were relatively unaffected. Sulfur reductions of 60-80% were obtained, which was expected because of the use of an hydrodesulfurization (HDS) catalyst. V and Ni levels were only moderately affected and in some cases rose, possibly due to production of light gases. The exception was the Cerro Negro weak acid fraction, where the metals were reduced by 67%. To summarize the behavior of the porphyrinic metals, six samples showed decreased or zero levels of V porphyrins while one sample (Cerro Negro strong acid) showed an increased level of V porphyrins.

Metal porphyrins are destroyed by hydrotreating and the low levels detected in the initial series of experiments potentially reflect a slow rate of disassociation (production) versus rapid destruction of free metal porphyrins. In order to determine if disassociation in fact occurs, alternate hydrotreating conditions were explored. Thus, a second series of hydrotreating experiments at different reactor temperatures was carried out using a homogeneous catalyst (molybdenum octenoate solution). To conserve the ABN fractions, whole resid was used. Table II gives the elemental analysis data of the feed and the hydrotreated products together with the operating conditions. The initial hydrogen pressure was the same (1200 psig) in each case, but the operating hydrogen pressure increased with temperature.

The major effect of this hydrotreating system was reduction of the level of metals at temperatures of 375° C and above. The V porphyrin levels were also reduced as the temperature increased, and in no case did the porphyrin metal increase. The H/C atomic ratio increased with temperature indicating that hydrogen was being added to aromatic sites. The reduction in nitrogen was greatest at the lowest temperature and was inversely proportional to the severity (temperature) of the hydrotreating. This is in keeping with previously reported work which indicates that hydrodenitrogenation requires mild temperatures to saturate aromatic rings which can then be successfully denitrogenated.[26]

Throughout this series of hydrotreating experiments, the porphyrinic V decreased from the levels in the feed and no clear cut, superior set of operating conditions was apparent. A temperature of 350° C was arbitrarily selected for the third series of experiments with acid and base fractions. With the whole resid, this temperature resulted in relatively mild hydrotreating and a one-third lower level of V porphyrins. Table III shows the elemental analyses for the products obtained. The molybdenum octenoate catalyst was most effective in reducing metals in the Maya strong acid (SA) fraction, and was least effective with the Merey SA fraction, which had virtually no change in V and only a 16% reduction in the Ni level. The Merey SA fraction had, however, the largest hydrogen uptake of all the hydrotreated fractions; this added hydrogen apparently was used in ring saturation and dealkylation reactions as opposed to mechanisms that would reduce metals. None of the acid or base fractions selected for hydrotreating exhibited detectable metal porphyrin bands in their visible spectra initially, but traces of porphyrins were detected in four fractions after hydrotreating. At these levels, the measurement precision is very poor, but a comparison of the spectral curves before and after hydrotreating does indicate that traces of metal porphyrins were present after hydrotreating. Obviously, the proportion of porphyrinic metals in any of the products is quite small in comparison to the total metals present.

Previous work indicated a significant increase in metal porphyrin levels in selected weak acid and weak base fractions after hydrotreating, potentially via conversion of nonporphyrinic metals to porphyrinic forms.[22] Based on the work reported here, those increases more likely resulted from physical enrichment via partial conversion of the feed resid to light gases, and in some cases solids, as well as chemical alteration of metal porphyrins present in other fractions in the feed (largely neutrals) causing them to elute into weak acid and weak base fractions of products. In that work, as well as as here, the concentration of metal porphyrins in the overall liquid products consistently decreased with hydrotreating severity. Thus, although the hypothesis that nonporphyrinic metals are actually metalloporphyrins in a bound or complexed state cannot be discounted from the available data, the present findings clearly work against it. This same conclusion was reached by Reynolds and Biggs,[11] who noted that low molecular weight V complexes which survived or were produced by thermal processing were exclusively nonporphyrinic types, and that porphyrinic metals were effectively removed by hydrotreating whereas significant proportions of nonporphyrinic forms survived.

Separation and Concentration of Metal Complexes. Table IV provides the mass balance from NIELC separation of whole Cerro Negro 700° C+ resid into ABN fractions. Absolute and relative total/porphyrinic V and Ni contents are also provided. As seen in the table, only 75% of the V and 91% of the Ni in the whole resid were recovered, as compared to 96.4% of the total mass. Based on visual assessment of the spent ion exchange resins after separation and extraction, the bulk of the losses occurred via incomplete extraction of resins used to trap strong acid and strong base fractions. The relative distributions of total mass, V, and Ni over the NIELC separation generally paralleled one another, except for the neutral fraction, which comprises one third of the total mass but contains only 9.4 and 11.6 % of the V and Ni, respectively. The distribution of porphyrinic V differed significantly from that of total V. Over 70% of the porphyrinic V partitioned into the weak base and neutral fractions which together contain only 15% of the total V. The broad distribution of metals over ABN types obtained for Cerro Negro is typical of other resids.[22,28] The preferential partitioning of porphyrinic forms of metals into weak bases and neutrals is also typical.

Mass balances and metal distributions from HPLC subfractionation of the neutral and weak acid fractions on the pyridyl column are reported in tables V and VI, respectively. Representative chromatograms from those separations were shown earlier in figures 3 and 4. Because of the different mobile phase programs used for separation of neutrals versus weak acids, timing for fraction cutpoints does not correspond directly between the two figures. Also, various chromatographic regions (e.g. subfraction P2) cover significantly different time spans in the two separations. However, based on elution of VO and Ni etioporphyrins and other pure compounds, fractions with the same number (P1, P2, etc.) from neutrals versus weak acids have roughly equivalent retention characteristics on the pyridyl column. Because of the lack of appreciable detector response beyond subfraction P5, subfraction P6 was not collected during subfractionation of neutrals.

In the case of neutral subfractions, the relative distributions of total versus porphyrinic V are quite similar. Both maximize at subfraction N-P3, which contains 57.2 % of the available porphyrinic V and 57.9 % of the total V. This subfraction contains 2030 ppm total V and an estimated 1000 ppm porphyrinic type V. Subfractions N-P2 and N-P4 contain lower proportions of total V and porphyrinic V, but the ratio of total/porphyrinic V is also near 2 for those subfractions, and for the whole neutrals as well. This correspondence between distributions of total versus porphyrinic V may indicate that the visible spectroscopic response factor used to determine porphyrinic V (based on VO etioporphyin), is high by about a factor of two, and that therefore essentially all V in the neutrals is of porphyrinic type. Alternately, if nonporphyrinic V is indeed present in the neutrals, it must exhibit analogous separation characteristics to that of the porphyrins present.

No Ni porphyrins were detected in any neutral subfractions or in the whole neutrals. However, the total Ni distribution maximized at subfraction N-P2, which corresponded with the elution time of pure Ni etioporphyrin. Thus, the situation with the majority of the Ni compounds is analogous to that of about one half of the V compounds; they exhibit LC retention characteristics of porphyrins, but do not show the characteristic porphyrin visible absorption bands. In the case of V compounds, this effect was explainable in terms of the probable inaccuracy of the visible spectroscopic method used for porphyrin estimation; since no Ni porphyrin bands were observed whatever, this hypothesis appears much less tenable in the case of Ni.

Overall, neutral Ni complexes were more weakly retained than V complexes on the pyridyl column, in keeping with the lesser retention of Ni etioporphyrin compared to VO etioporphyrin on this column. The relatively wide retention region (subfractions N-P1 - N-P5) spanned by both porphyrinic and nonporphyrinic V and Ni indicates a diversity of structures within both types of complexes. The degree of metal preconcentration obtained with this separation was significant (factor of 7.0 for V compounds in fraction N-P3 compared to whole neutrals, factor of 3.7 for Ni compounds in N-P2 compared to whole neutrals), but not sufficient to warrant a detailed analysis of any one subfraction.

The absolute (ppm) and relative (%) metal distributions obtained from subfractionation of weak acids (WA) (table VI) were considerably different than those obtained from the neutrals. The bulk of the WA metals eluted later (subfractions WA-P3 - WA-P6) than those in the neutrals and they were more evenly distributed, with the largest relative percentages of both V and Ni occurring in the same subfraction (WA-P3). The porphyrin content of all subfractions was low compared to total metals; the highest proportion of porphyrinic V was found in subfraction WA-P3 (140 ppm porphyrinic V out of 1110 ppm total V); this subfraction contained 70% (normalized) of the available porphyrinic V in the WA. No Ni porphyrins were detected in any subfractions or the whole WA.

Very little enrichment of either Ni or V was achieved through subfractionation of the WA (enrichment factor <2 for all subfractions). This, plus the fact that a longer elution time was required to completly elute the WA, indicates that WA contains a greater variety of metal complexes than the neutrals. The wide discrepancy between porphyrinic versus total metals in any subfraction leaves little doubt that the bulk of the WA V and Ni are of nonporphyrinic type. This finding lends additional weight to the argument that porphyrinic and nonporphyrinic metal complexes can exhibit equivalent LC separation behavior, since a substantial proportion of neutral porphyrins eluted over the same retention region as the bulk of the nonporphyrins in the WA (subfractions P2-P5). Whether or not equivalent LC separation behavior implies any similarity in structure between porphyrins and nonporphyrins in a given subfraction is not known.

Subfractions obtained from the pyridyl column clearly contained predominantly nonmetal species and a mixture of porphyrinic/nonporphyrinic types. In order to obtain improved metal preconcentration and resolution of the various metal complexes present, selected pyridyl column subfractions were further separated on silica.

Table VII lists retention times of selected pure components obtained on an analytical scale silica column of the same type and run under analogous conditions as those specified for preparative scale silica separations in the Experimental Section. Distinct resolution of aromatic hydrocarbons, Ni porphyrins, VO porphyrins, and polar compounds (except for l-naphthol) was observed. This selectivity is complementary to that of the pyridyl column, which tends to overlap nitrogen compounds and other types of polar nonmetal compounds with metal-containing species.

Only pyridyl column subfractions N-P2, N-P3 and N-P4 were further fractionated on silica because of time and funding constraints. These subfractions contained the bulk of the total and porphyrinic V present in the neutrals (table V). Example chromatograms from each of these separations were shown earlier in figures 5-7. Each of the pyridyl column subfractions gave rise to distinctly different chromatograms when further separated on silica. Tables VIII-X show the corresponding mass balances and metals data for each silica separation.

As noted in the Experimental Section, a different mobile phase program was used for silica separation of subfraction N-P2 as opposed to N-P3 and N-P4. The N-P2 separation required an initial period of elution with weak solvent to separate components of interest from the unretained matrix peak. Thus, the separation of the early eluting components is different from that of the N-P3 and N-P4 subfractions. For example, from N-P2, the third sub-subfraction is highest in V, while from N-P3 and N-P4, the second sub-subfraction is highest in V.

Highly V-enriched sub-subfractions were obtained from further separation of subfractions N-P3 and N-P4, sub-subfractions N-P3S2 and N-P4S2 respectively, but a corresponding degree of

V enrichment was not obtained from separation of N-P2. Assuming one V atom per molecule and an average molecular weight of 500 g/mole, sub-subfractions N-P3S2 and N-P4S2 contain 19 and 13 wt % V-compounds, respectively. This represents respective enrichment factors of 67 and 46 relative to the V content of the whole neutrals.

It is interesting to note that the ratio of the total/porphyrinic V is near 2 for both N-P3S2 and N-P4S2, the same as for the whole neutrals (table V). As mentioned earlier, this ratio is consistent with either a 1:1 porphyrin:nonporphyrin V-complex mixture, or use of a two-fold too high visible molar absorptivity for calculation of the VO-porphyrin content. An unknown band appears in the visible spectrum of a number of the silica sub-subfractions at 592 nm. It was also detected in spectra of pyridyl subfractions N-P3 and N-P4, and is strongest in fractions with higher levels of porphyrinic V. Compounds contributing to this band may be one of the RHODO-type porphyrins (see figure 1) since RHODO porphyrins are reported[1] to have α bands at or near 595 nm. Using the etioporphyrin molar absorptivity, the unknown band in N-P3S2 is equivalent to 1200 ppm V, which would account for only a small part of its "nonporphyrinic" V. However, this example illustrates the deficiencies in the current porphyrin content estimates. In order to resolve the question of nonporphyrins in the neutral fraction, one or more of the sub-subfractions with high total V content will be analyzed by high resolution mass spectrometry.

Relative total V distributions in tables VIII-X show major proportions of V in one or two sub-subfractions from each silica separation. V-compounds in subfraction N-P2 largely partitioned into sub-subfractions N-P2S3 and N-P2S6, those in N-P3 were concentrated into N-P3S2, and those in N-P4 into N-P4S2 and N-P4S5. The significant degree of V preconcentration achieved and the above groupings of V compounds demonstrate the complementary selectivities of the pyridyl versus silica HPLC columns. The preconcentration of V was achieved via separation of polar nonmetal components away from V-complexes, as predicted from pure compound retention data in table VII. Separation of one group of metal compounds eluting from the pyridyl column into two or more types on silica should improve their analysis by providing more homogeneous mixtures for spectroscopic examination.

Preconcentration of Ni compounds over the silica separations was less successful than for V. The most favorable results were obtained during sub-subfractionation of N-P3, where two sub-subfractions (N-P3S1 and N-P3S6) were obtained with 6-7 fold enrichment of Ni. Ni-compounds also tended to be more broadly distributed on a relative basis than V-compounds.

Conclusions

Hydrotreating acid and base fractions containing only nonporphyrinic V and Ni did not produce significant levels of free Ni or VO porphyrins. This finding, plus much of the literature evidence, indicates that nonporphyrinic forms of metals are not simply bound or complexed porphyrinic complexes with suppressed visible spectroscopic response. Similarly, no measureable release of bound metalloporphyrins was observed during the sequence of LC separations employed. Balances for VO porphyrins were generally within 100 ± 20% over any given separation step; Ni porphyrins were below levels of detection in all fractions. Considering the appreciable change in fraction composition occurring over the series of LC separations, and normal equilibria governing association phenomena, release of bound metal porphyrins over the separations should have occurred given a significant presence of such associates.

Throughout the various LC separation steps employed here, porphyrinic and nonporphyrinic forms of V largely partitioned over all fractions. However, in some cases the appearance of both porphyrins and nonporphyrins in a given fraction may simply reflect inaccuracy in estimates of VO porphyrin content. Also, strong acid fractions appeared to contain only nonporphyrinic metal complexes. But, in the majority of fractions, both types of complexes were clearly present. The parallel separation behavior of porphyrin and nonporphyrin complexes suggests similarity in their chemical behavior and/or structure. This is in turn consistent with EPR evidence indicating tetradentate coordination for both types of complexes, but variable heteroatom coordination for nonporphyrins.[14-16] For Cerro Negro crude specifically, both S_4 and NOS_2 coordination was indicated by EPR.[29] The wide dispersion of nonporphyrinic metals over all chromatographic fractions indicates that their structured variation may be as great as for the other heteroatoms present: N, S and O.

Two fractions with a significant degree of V enrichment were obtained from the separation scheme employed. They contain an estimated 19 and 13 wt% V-containing compounds, respectively comprising 4.6 and 0.5 percent of the total V in the Cerro Negro 700° C+ resid. They comprise essentially the same proportion of the V in the whole crude, due to the small proportion of V found in <700° C distillates.[23] Although neither the purity nor the proportion of total V contained in these fractions look particularly impressive, these results compare quite favorably to those from other separations--whenever adequate data have been reported to enable such a comparison.[30,31] A major fault of much of the reported work on isolation of metals from petroleum is the absence of material balances and assays for degree of enrichment obtained. For example, this subject was not even mentioned in a recent review of techniques for isolation of geoporphyrins.[32] Because of this, there is no means for assessing whether, even for the porphyrinic metal complexes, the components identified previously in the literature are representative of those present in a given crude.

Clearly, there is much room for improvement in techniques for isolation and speciation of metal complexes in petroleum. The initial NIELC separation employed here grouped the bulk of the nonporphyrinic metal into strong acid and strong base fractions, and the majority of porphyrinic metals into weak bases and neutrals. The proportion of porphyrinic versus nonporphyrinic metals in the weak acid fraction varies with crude source. While useful, the effectiveness of this separation may be no greater than distillation[1,11] or extractions with methanol[10] or dimethyl formamide,[31] which also partition nonporphyrinic versus porphyrinic metals. The combination of pyridyl and silica HPLC columns for further separation/isolation of metal complexes creates a large number of fractions requiring analysis. Creation of additional separation steps to improve the degree of metal enrichment is technically feasible, but probably exceeds practical limitations of manpower and funds in most cases.

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Table I. - Comparison of feeds and hydrotreated products at 375° and 1500 psi hydrogen

Fraction	Sample type	C wt%	H wt%	H/C Ratio	S wt%	N wt%	Total metals wt ppm		Porphyrinic metals wt ppm	
							V	Ni	V	Ni
Cerro Negro 700° C+ strong base	Feed	83.09	8.36	1.199	4.59	1.80	1310	343	110	<40
	HT-product	83.80	8.40	1.194	0.83	1.76	1185	303	68	<40
Cerro Negro 700° C+ strong acid	Feed	81.49	8.18	1.197	4.47	1.71	1270	275	<22	<22
	HT-product	83.74	8.15	1.160	1.35	1.43	1175	225	46	<22
Cerro Negro 700° C+ weak base I	Feed	81.86	9.02	1.313	5.33	1.33	913	240	220	<12
	HT-product	83.17	9.20	1.318	1.29	1.07	961	306	132	<12
Cerro Negro 700° C+ weak acid II	Feed	77.75	8.36	1.281	3.96	1.08	886	154	<10	<10
	HT-product	84.05	8.94	1.267	1.68	1.15	292	53	<10	<10
Wilmington 538° C+ strong base	Feed	82.84	9.73	1.390	2.23	2.12	94	130	<22	<20
	HT-product	84.81	8.95	1.257	0.50	2.71	162	264	<12	<12
Maya 496° C+ strong acid	Feed	81.25	7.76	1.138	5.36	1.42	1200	250	<19	<17
	HT-product	83.72	7.86	1.119	1.95	1.44	1200	254	<20	<20
Wilmington 538° C+ strong acid	Feed	81.63	8.78	1.281	2.23	2.13	170	220	<22	<21
	HT-product	85.20	8.82	1.233	0.76	2.35	205	296	<13	<13

Table II. - Elemental analyses for Cerro Negro 700° C+ resid after hydrotreating under varied conditions

Hydrotreating Conditions			H/C Ratio	N wt%	S wt%	Total Metals wt ppm		Porphyrinic metals wt ppm	
°C	H_2 Pressure	Time, min.				V	Ni	V	Ni
Feed			1.322	1.160	4.56	994	228	97	<10
300	2300	60	1.341	0.992	4.39	997	215	87	<11
325	2600	60	1.351	1.052	4.41	987	222	83	<16
350	2700	60	1.354	1.114	4.22	1073	198	66	<15
375	2900	60	1.366	1.126	3.94	674	143	28	<14
375	2800	120	1.379	1.148	3.92	569	127	<15	<17
400	2900	60	1.388	1.153	3.59	485	107	9	<10

Table III. - Elemental analyses of feeds and hydrotreated products at 350° C and 1200 psi hydrogen

Fraction	Sample type	C wt%	H wt%	H/C Ratio	S wt%	N wt%	Total metals wt ppm		Porphyrinic metals wt ppm	
							V	Ni	V	Ni
Cerro Negro 700° C+	Feed	83.09	8.36	1.199	4.59	1.80	1240	339	<9	<10
strong base	HT-product	83.87	8.54	1.213	4.17	1.80	1100	278	10	10
Cerro Negro 700° C+	Feed	81.49	8.18	1.197	4.47	1.71	1260	286	<9	<10
strong acid	HT-product	81.91	9.02	1.312	2.57	1.65	920	225	<10	<11
Lagomedio 510° C+	Feed	82.06	8.16	1.185	3.31	1.26	1500	149	<10	<11
strong acid	HT-product	84.34	8.53	1.205	3.36	1.12	1525	189	<8	<9
Merey 510° C+	Feed	83.22	7.86	1.126	3.86	1.58	1120	276	<12	<14
strong acid	HT-product	83.79	8.46	1.203	3.74	1.37	1115	234	17	<16
Wilmington 535° C+	Feed	80.06	8.62	1.283	2.36	1.16	157	209	<9	<10
strong acid	HT-product	82.38	8.98	1.299	3.72	1.27	124	205	18	<8
Maya 500° C+	Feed	80.36	7.68	1.139	6.00	1.43	1100	247	<9	<10
strong acid	HT-product	82.59	8.54	1.199	5.45	1.28	906	197	20	<9

Table IV. - Mass balance and metals data from NIELC separation of the Cerro Negro resid

	Whole	SA	WA	SB	WB	Neutral	Recovered
Mass balance, wt%	100	27.9	14.6	10.8	9.5	33.6	96.4
Metal contents, ppm							
Porphyrinic V	97	<22	57	110	220	145	90
Total V	1040	1250	1020	1170	602	291	779
Total Ni[a]	226	307	273	339	176	78	205
Relative metal recovery, %							
Porphyrinic V	-	<6	8.6	12.3	21.6	50.2	92.5
Total V	-	33.5	14.3	12.2	5.5	9.4	74.9
Total Ni	-	37.9	17.6.	16.2	7.4	11.6	90.7

[a] Ni porphyrins were not detected in the whole resid or any fraction.

Table V. - Mass balance and metals data from separation of Cerro Negro neutrals on the pyridyl column

	Subfraction number					Total
	N-P1	N-P2	N-P3	N-P4	N-P5	Recovered
Mass balance, wt%	57.2	11.9	8.3	12.1	2.2	91.7
Metal contents, ppm						
Porphyrinic V	15	161	1000	150	108	(145)[a]
Total V	63	396	2030	342	557	(291)
Porphyrinic Ni	<10	<15	<11	<12	<10	(<10)
Total Ni	51	292	104	60	117	(78)
Relative metal recovery, %						
Porphyrinic V	5.9	13.2	57.2	12.5	1.6	90.4
Total V	12.4	16.2	57.9	14.2	0.8	101.5
Total Ni	37.4	44.6	11.1	9.3	3.3	105.7

[a] Data for whole neutrals.

Table VI. - Mass balance and metals data from separation of Cerro Negro weak acids on the pyridyl column

	Subfraction number						Total
	WA-P1	WA-P2	WA-P3	WA-P4	WA-P5	WA-P6	Recovered
Mass balance, wt%	12.9	16.6	33.1	15.2	13.4	2.8	94.0
Metal contents, ppm							
Porphyrinic V	23	35	140	54	23	<18	(57)[a]
Total V	546	498	1110	1260	1760	1570	(1020)
Porphyrinic Ni	<13	<20	<20	<21	<20	<20	(<19)
Total Ni	144	123	188	234	375	321	(273)
Relative metal recovery, %							
Porphyrinic V	5.2	10.2	81.3	14.4	5.4	<0.9	116.5
Total V	6.9	8.1	36.0	18.8	23.1	4.3	97.2
Total Ni	6.8	7.5	22.8	13.0	18.4	3.3	71.8

[a] Data for whole weak acids.

Table VII. - Retention times of pure components on silica

Compound	Retention Time Min
2,3-benzfluorene	2.0
1,2-benzanthracene	5.2
1,2,3,4-dibenzanthracene	6.6
Nickel octaethylporphyrin	9.0
Nickel etioporphyrin	10.0
Nickel tetraphenylporphyrin	10.0
Vanadyl octaethylporphyrin	17.4
1-naphthol	18.0
Vanadyl etioporphyrin	18.5
Vanadyl tetraphenylporphyrin	20.0
1-azapyrene	39.2
4-azafluorene	38.8
2-naphthoic acid	39.0

Table VIII. - Mass balance and metals data from further separation of subfraction N-P2[a] on silica

	Sub-subfraction number						
	N-P2S1	N-P2S2	N-P2S3	N-P2S4	N-P2S5	N-P2S6	Total
Mass balance, wt%	7.5	19.0	14.6	12.9	5.8	32.8	92.6
Metal contents, ppm							
Porphyrinic V	<10	54	917	56	37	60	(161)[b]
Total V	39	143	1420	255	206	260	(396)
Porphyrinic Ni	<12	<10	<10	<10	<11	<11	(<15)
Total Ni	283	558	160	122	130	204	(292)
Relative metal recovery, %							
Porphyrinic V	<0.5	6.4	83.2	4.5	1.3	12.2	108.1
Total V	0.7	6.9	52.4	8.3	3.0	21.5	92.8
Total Ni	7.3	36.3	8.0	5.4	2.6	22.9	82.5

[a] See table V.

[b] Data for whole N-P2.

Table IX. - Mass balance and metals data from further separation of subfraction N-P3[a] on silica

	Sub-subfraction number					
	N-P3S1	N-P3S2	N-P3S3	N-P3S(4 +5)	N-P3S6	Total
Mass balance, wt%	5.0	7.7	8.6	78.9	3.4	103.6
Metal content, ppm						
Porphyrinic V	124	11,060	1780	112	101	(1000)[b]
Total V	869	19,500	4000	450	896	(2030)
Porphyrinic Ni	<10	<20	<21	<10	<11	(<11)
Total Ni	624	206	176	82	761	(104)
Relative metal recovery, %						
Porphyrinic V	0.6	85.2	15.3	8.8	0.3	110.2
Total V	2.1	74.0	16.9	17.5	1.5	112.0
Total Ni	30.0	15.2	14.5	62.2	24.9	146.8

[a] See Table V.

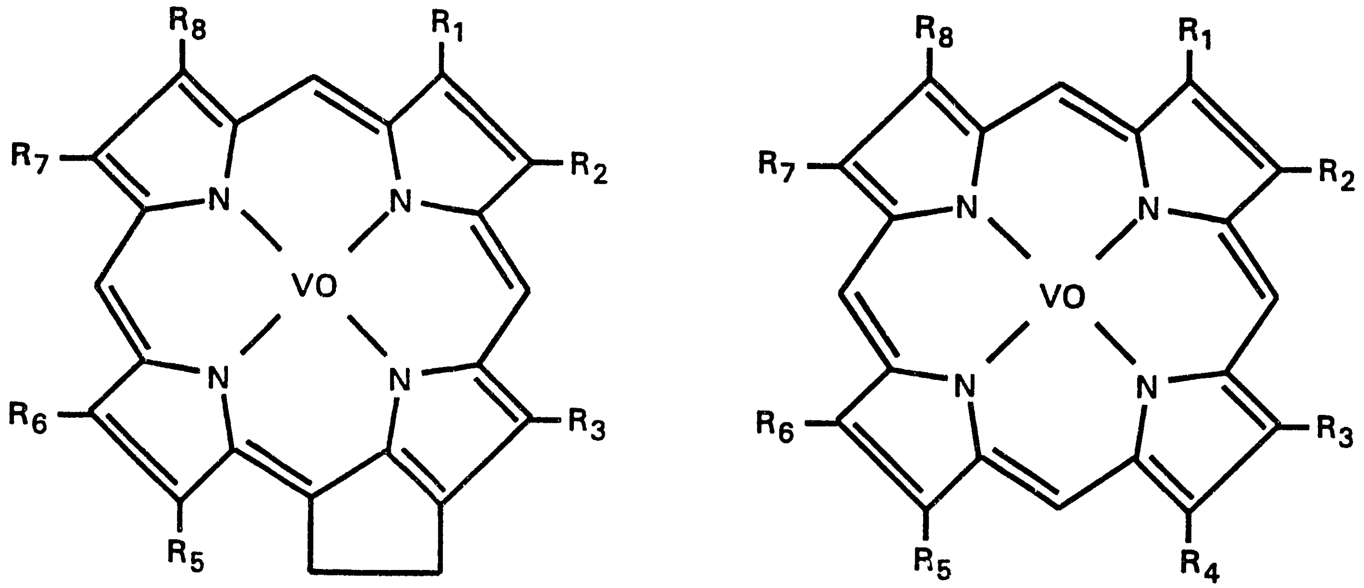
[b] Data for whole N-P3.

Table X. - Mass balance and metals data from further separation of subfraction N-P4[a] on silica

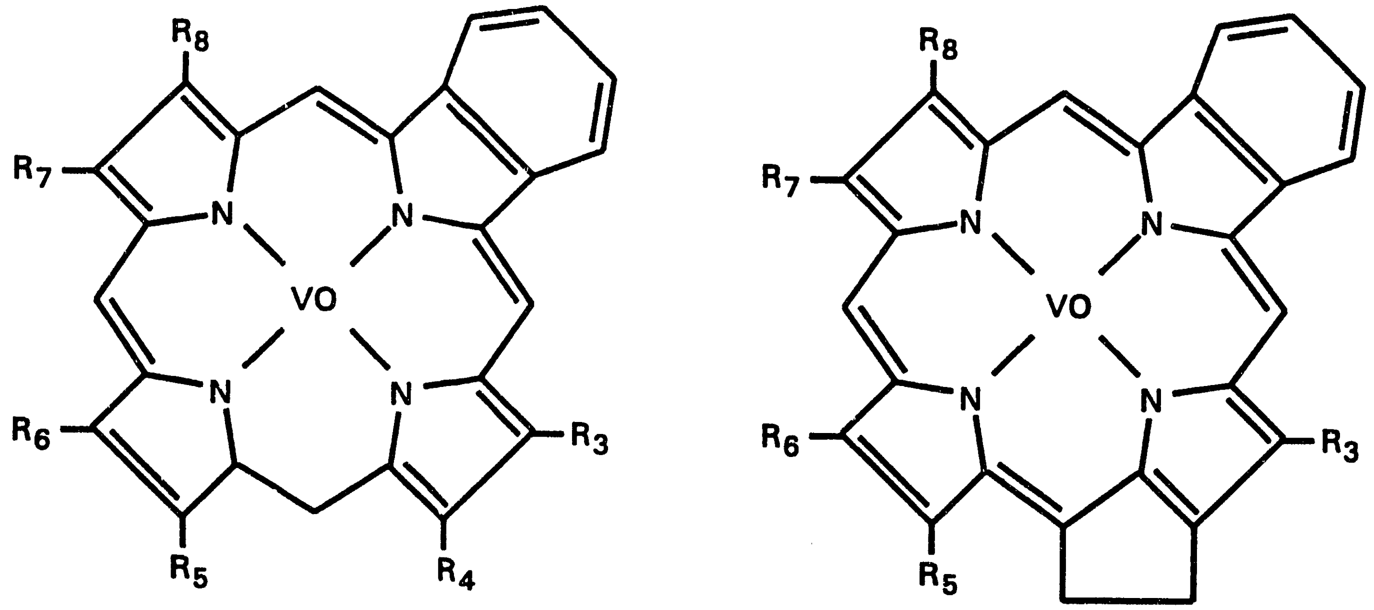
	Sub-subfraction number						
	N-P4S1	N-P4S2	N-P4S3	N-P4S4	N-P4S5	N-P4S6	Total
Mass balance, wt%	0.59	0.90	1.14	0.51	85.0	7.9	96.0
Metal content, ppm							
Porphyrinic V	44	6650	485	173	49	44	(150)[b]
Total V	773	13,500	2030	1290	251	302	(342)
Porphyrinic Ni	<12	<21	<19	<20	<9	<25	(<12)
Total Ni	161	148	145	149	55	157	(60)
Relative metal recovery, %							
Porphyrinic V	0.2	39.9	3.7	0.6	27.8	2.3	74.5
Total V	1.3	35.5	6.8	1.9	62.4	7.0	114.9
Total Ni	1.6	2.2	2.8	1.3	77.9	20.7	106.5

[a] See Table V.

[b] Data for whole N-P4.



(a) DPEP **(b) Etio**



(c) RHODO-etio **(d) RHODO-DPEP**

Figure 1. - Selected vanadyl porphyrin types.

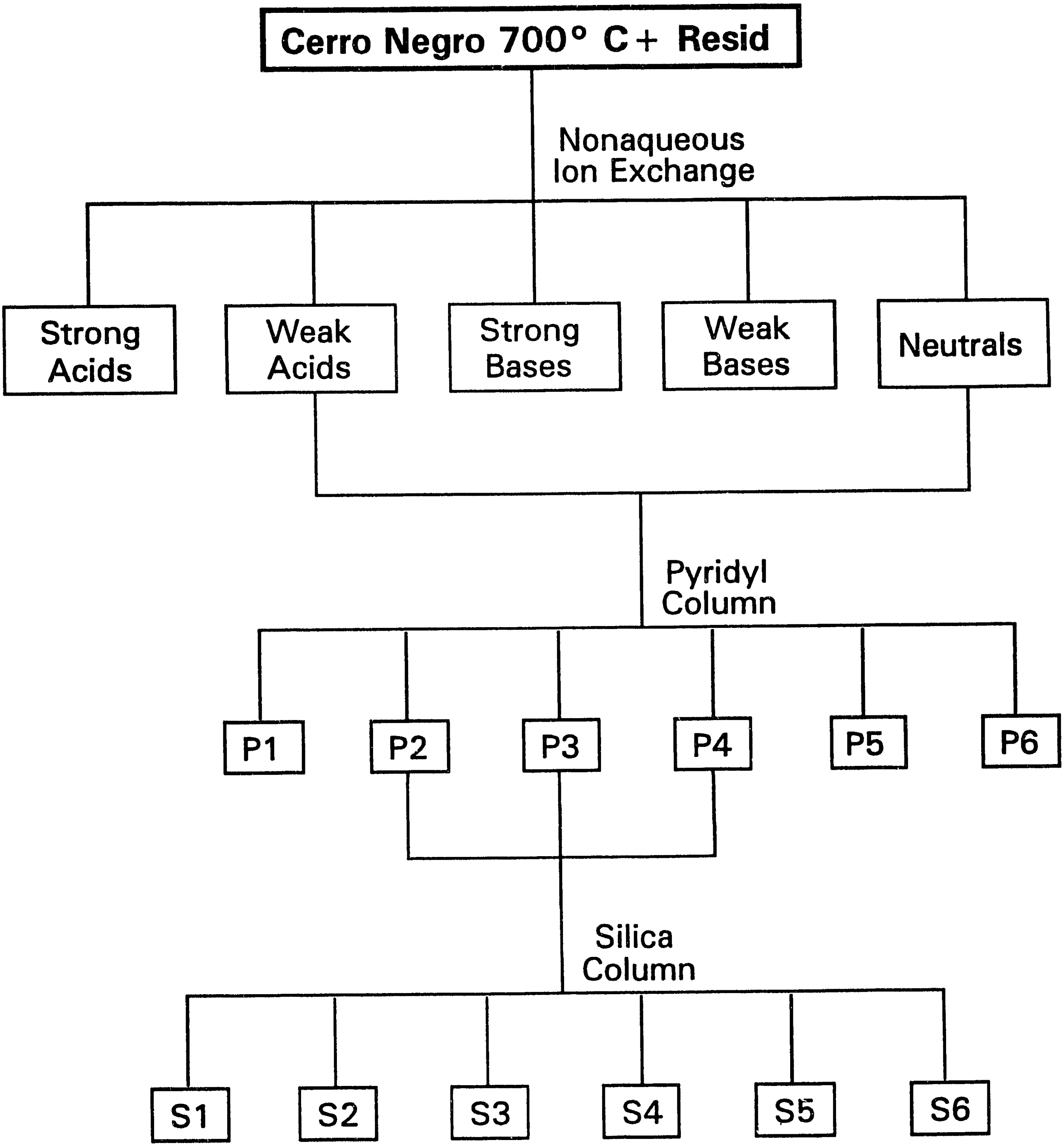


Figure 2. - Scheme for separation and concentration of metal complexes from Cerro Negro 700° C+ resid.

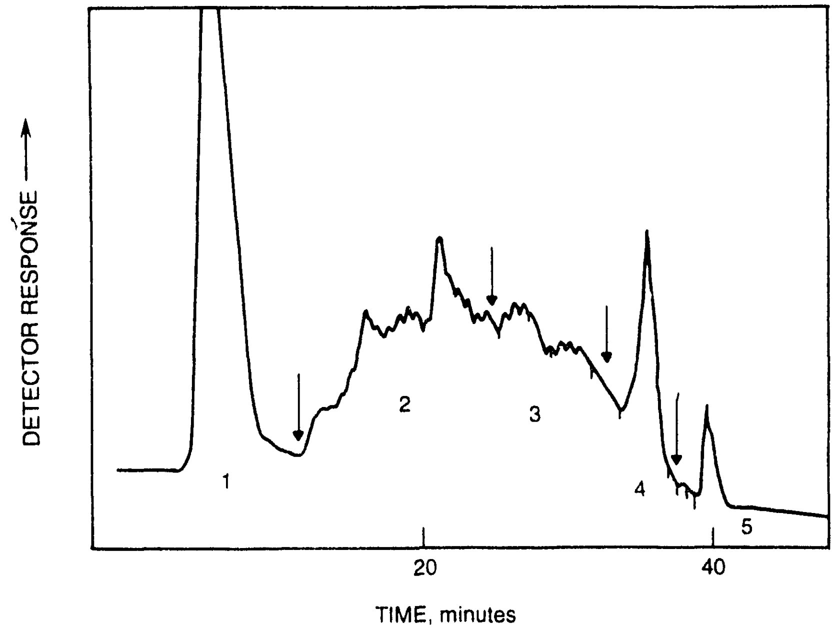


Figure 3. - HPLC chromatogram of the pyridyl column separation of Cerro Negro neutrals. The arrows mark the cutpoints of the fractions.

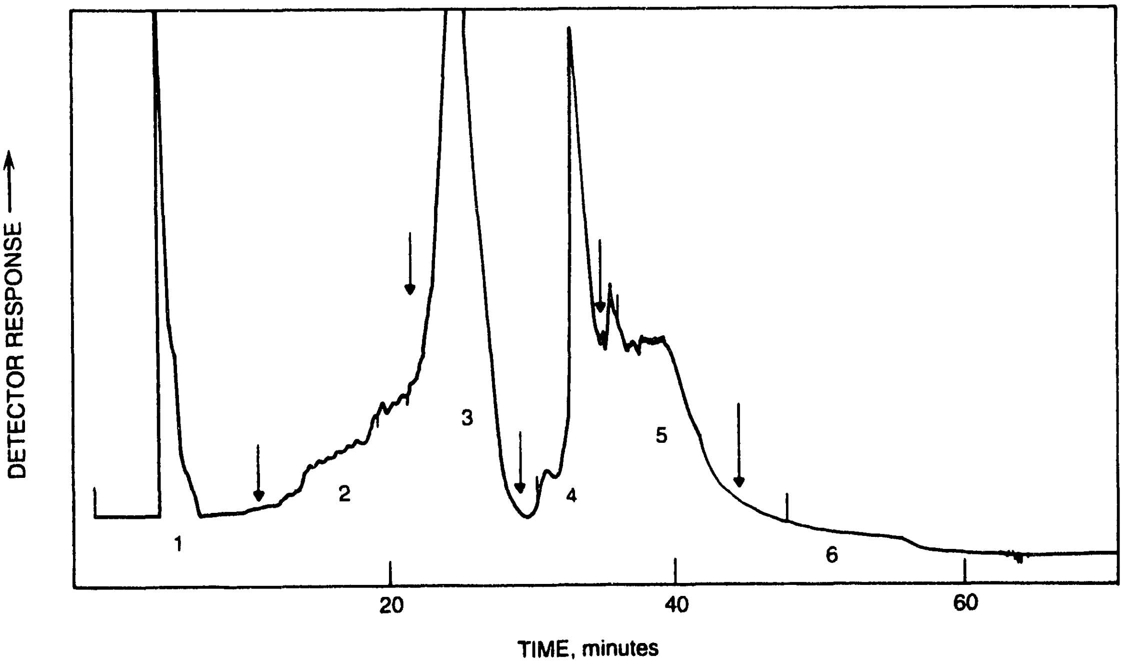


Figure 4. - HPLC chromatogram of the pyridyl column separation of Cerro Negro weak acids. The arrows mark the cutpoints of the fractions.

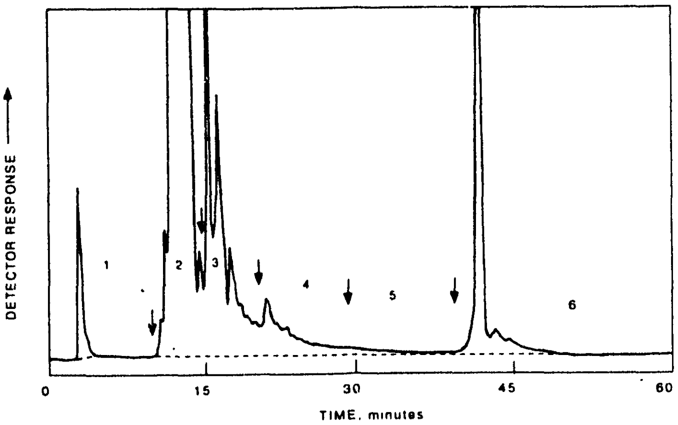


Figure 5. - HPLC chromatogram from further separation of neutrals subfraction N-P2 on silica. The arrows mark the cutpoints of the fractions.

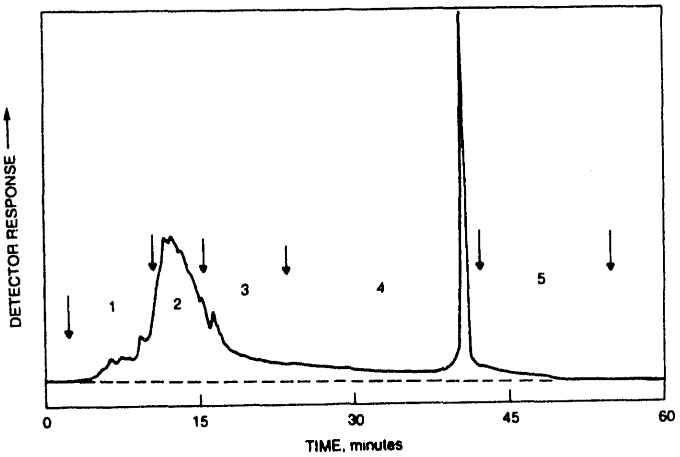


Figure 6. - HPLC chromatogram from further separation of neutrals subfraction N-P3 on silica. The arrows mark the cutpoints of the fractions.

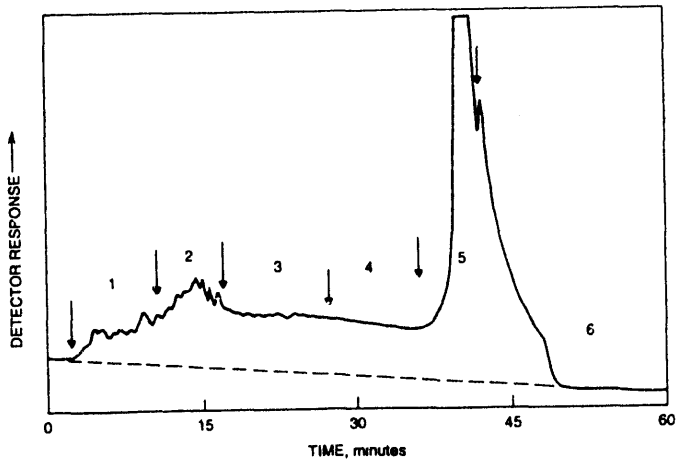


Figure 7. - HPLC chromatogram from further separation of neutrals subfraction N-P4 on silica The arrows mark the cutpoints of the fractions.

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