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Separation Science and Technology

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Isolation and Characterization of Metalloporphyrins from a Heavy Crude Oil by Soxhlet Adsorption Chromatography and HPLC-SEC

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To cite this Article Ysambertt, F. , Marquez, N. , Rangel, B. , Bauza, R. and De La Cruz, C.(1995) 'Isolation and Characterization of Metalloporphyrins from a Heavy Crude Oil by Soxhlet Adsorption Chromatography and HPLC-SEC', Separation Science and Technology, 30: 12, 2539 — 2550

To link to this Article: DOI: 10.1080/01496399508021400

URL: http://dx.doi.org/10.1080/01496399508021400

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SEPARATION SCIENCE AND TECHNOLOGY, **30**(12), pp. 2539–2550, 1995

Isolation and Characterization of Metalloporphyrins from a Heavy Crude Oil by Soxhlet Adsorption Chromatography and HPLC-SEC

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ABSTRACT

An extraction and purification method for the isolation of metalloporphyrins from a heavy crude oil is reported. The metalloporphyrins are extracted from a Boscán crude oil by a Soxhlet extraction method and monitored by UV-Vis and graphite furnace atomic absorption (GFAA) spectroscopies. The first fraction is extracted with methanol and the second one with acetonitrile; both fractions are purified by adsorption chromatography using hexane/benzene and dimethylformamide/benzene mixtures to isolate the metalloporphyrin species according to their polarities. HPLC fractionation and SEC molecular weight distribution techniques are combined to characterize these fractions.

Key Words. Soxhlet extraction; Heavy crude oil; Metalloporphyrins; Adsorption chromatography

INTRODUCTION

Vanadium and nickel usually occur in high amounts in heavy crude oils from different regions of the world (1, 2). They are found as chelated complexes with porphyrins as well as nonporphyrins (3–5). These com-

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pounds are known to cause unfavorable effects during standard refinery operations.

Some authors (6–8) have reported that high performance liquid chromatography (HPLC) on silica gel columns allows for the separation of porphyrin mixtures and results in "fingerprinting" of the distribution of these compounds in nature. HPLC has also been combined with graphite furnace atomic absorption (GFAA) spectrometry by Fish et al. (9) to provide both a vanadium fingerprint and a molecular weight characterization of vanadyl-porphyrin and nonporphyrin compounds occurring in heavy crude oils. An alternate method for the separation and molecular weight characterization of these compounds is by the size exclusion chromatography (SEC) technique. However, the application of SEC to this field has been basically restricted to the gathering of information about organic components (10–12).

A new method for extracting and separating vanadium and nickel porphyrins from heavy crude oil is reported here. Soxhlet extraction and adsorption chromatography are used to separate several fractions, which are then characterized by HPLC, SEC, and GFAA spectrometry.

EXPERIMENTAL

Material

The heavy crude oil (10.3° API gravity) comes from the Boscán Field near Maracaibo, Venezuela. All solvents were of the highest purity available.

Separation Method

A sample of heavy crude oil was first dissolved in 30 mL chloroform; this solution was used to impregnate 20 g neutral alumina (80–200 mesh, Fisher) to form a slurry which was dried by blowing nitrogen through the bed. The resultant powder was placed in a cellulose thimble (30 × 80 mm Whatman 2800308) of a Soxhlet extractor (37 × 250 mm, Corning 3840-M). The first extraction, which was performed with methanol (J. T. Baker), yielded an orange fraction (Fraction 1). The second extraction, which was carried out with acetonitrile (ACN) (J. T. Baker), yielded a dark purple fraction (Fraction 2). The complete experimental procedure is showed schematically in Fig. 1. Both fractions were characterized by using a Perkin-Elmer Lamda 3B UV-Vis Spectrophotometer and a Varian AA-475 Graphite Furnace Atomic Absorption Spectrophotometer (2).

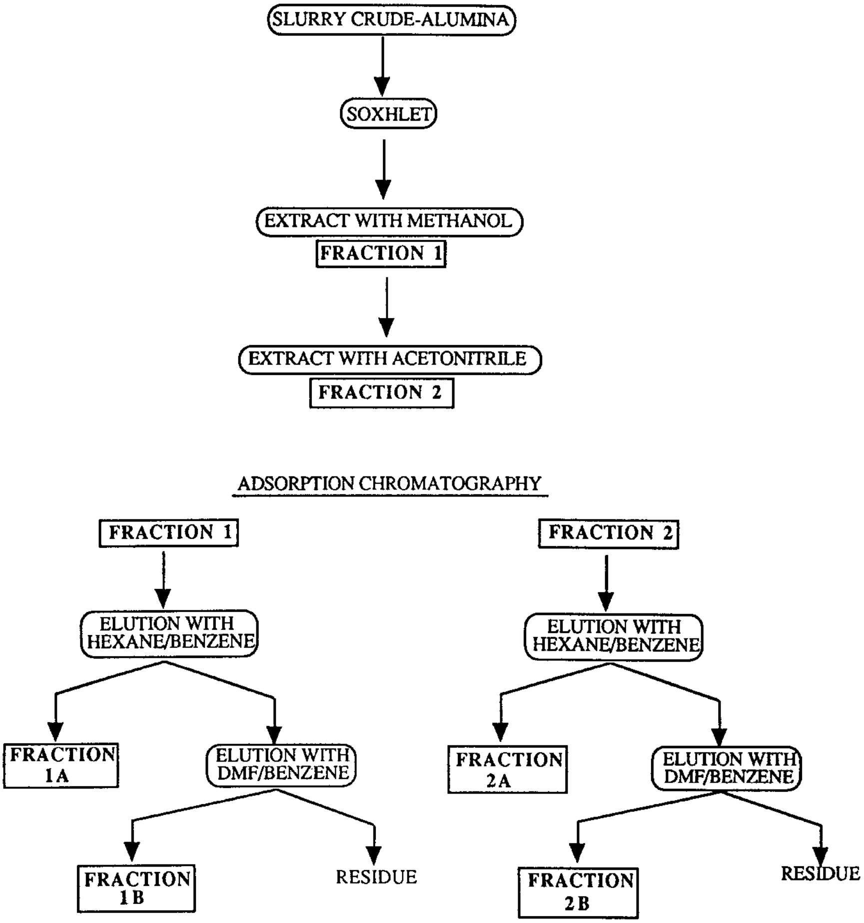


FIG. 1 Separation and purification procedure for petroporphyrins.

Purification Method

Fractions 1 and 2 were purified by adsorption chromatography using a glass column (300 × 2.2 mm, Pyrex 2145) packed with Silica gel S (70–230 mesh, Riedel-De Haën). Fraction 1 was extracted with a 80:20 v/v hexane/benzene mixture (solvent polarity: 0.62); this extract is called Fraction 1A. It was then washed with a 20:80 v/v dimethylformamide (DMF)/benzene mixture (solvent polarity: 5.66); this fraction is called Fraction 1B. The same procedure was followed for Fraction 2 to yield Fractions 2A and

2B. All extracts were dried, redissolved in acetonitrile, and allowed to stand for 24 hours in order to separate maltenes (13). Finally, the solutions were filtered on a 0.22-μm Millipore membrane.

HPLC and SEC Analyses

HPLC and SEC separation techniques were carried out with Waters equipment which included a universal U6K injector, a 510 solvent delivery pump, a 484 UV-Vis detector, and a 745B integrator. The stationary phase for HPLC was provided by a μ-Bondapack C_{18} column (25 cm × 4.6 mm, 10 μ), while the mobile phase was either a mixture of ACN/methanol (MeOH) 70:30 or a mixture of ACN/water 85:15. SEC analysis were performed with Ultrastyragel columns (100 and 500 Å, 7.8 mm × 30 cm), also manufactured by Waters, and a Zorbax-PSM 60S silica column (25 cm × 6.2 mm). The carrier solvent was HPLC-grade tetrahydrofuran (THF). The molecular weight calibration was carried out using polystyrene standards (Waters-Millipore, USA; MW: 418, 550, 946, 2300, 4075, and 10,200 daltons). They were prepared as 0.1% p/v in THF (Merck, HPLC grade).

RESULTS AND DISCUSSION

Soxhlet Extraction

Soxhlet extraction from impregnated alumina leads to the quick and unexpensive separation of several extracts with different polarities. It is worth noting that the transfer of oil on an alumina powder through the slurry drying step enhances the performance of the Soxhlet extraction procedure. This result is probably related to good solvent–crude contact. As a matter of fact, this method allows for the separation of our Fractions 1 and 2 which are extracted with methanol and ACN, respectively.

The UV-Vis spectra of the different extracts exhibit several characteristics: a Soret band at about 410 nm, a typical feature of all porphyrin compounds, and α and β bands at 570 and 530 nm, respectively, which are associated with the porphyrin divalent metal coordination link (14).

The ACN extracts exhibit stronger bands than the methanol extracts, which indicates that the former contains more metalloporphyrin than the latter. This difference is supported by the Ni/V analyses carried out by GFAAS, as reported in Table 1.

Adsorption Chromatography

The hexane/benzene fraction from the methanol extract (Fraction 1A in Fig. 1) is yellow while the one coming from the ACN extract (Fraction

TABLE 1
Vanadium (V) and Nickel (Ni) Content in Crude Oil and the Different Fractions Analyzed by GFAAS

Sample	Ni (ppm)[a]	V (ppm)[a]
Soxhlet—MeOH	2.5	74.4
Soxhlet—ACN	1.6	118.0
Fraction 1A	5.6	7.5
Fraction 2A	9.9	103.1
Fraction 1B	4.7	58.9
Fraction 2B	19.0	485.2
Crude oil	64.0	1150.0

[a] ppm = mg/kg crude oil.

2A) is dark yellow. The DMF/benzene fraction from the methanol extract is red (Fraction 1B) while the one coming from the ACN extract is an intense dark purple (Fraction 2B), a characteristic of porphyrin-vanadium complexes. GFAA analyses of these fractions indicate that the extraction is not fully quantitative. However, it is selective, with 74% vanadium and 68% nickel extracted.

HPLC Analyses

Preliminary trials with methanol and ACN as the mobile phase exhibited poor resolution in the separation of the components of Fractions 1 and 2. Enhanced resolution was attained by incorporating water in the solvent mixtures. Optimum results were reached with a 85 : 15 ACN/water mixture at a flow rate of 1 mL/min. Figure 2 shows the chromatogram resulting from the analyses of Fraction 1 (Fig. 2A) and Fraction 2 (Fig. 2B). Figure 2(B) exhibits stronger characteristic features of the vanadium-porphyrins than does Fig. 2(A). This is supported by the analysis of V and Ni (see Table 1). Moreover, Fig. 2 indicates that the methanol extract contains a less polar fraction which elutes after 15 minutes than does the ACN extract. This is probably due to the presence of both vanadium and nickel porphyrins in Fraction 1, with the more polar vanadium-porphyrins eluting first. This order of elution was found to apply (15, 16) to polar solvents elution on a reverse phase C_{18} column and GFAA analyses of the separated porphyrins.

As far as purification is concerned, it was first thought that Fractions A (1A and 2A) would contain mostly nickel-porphyrins since they are eluted by the less polar solvent mixture, i.e., 80:20 hexane/benzene, while

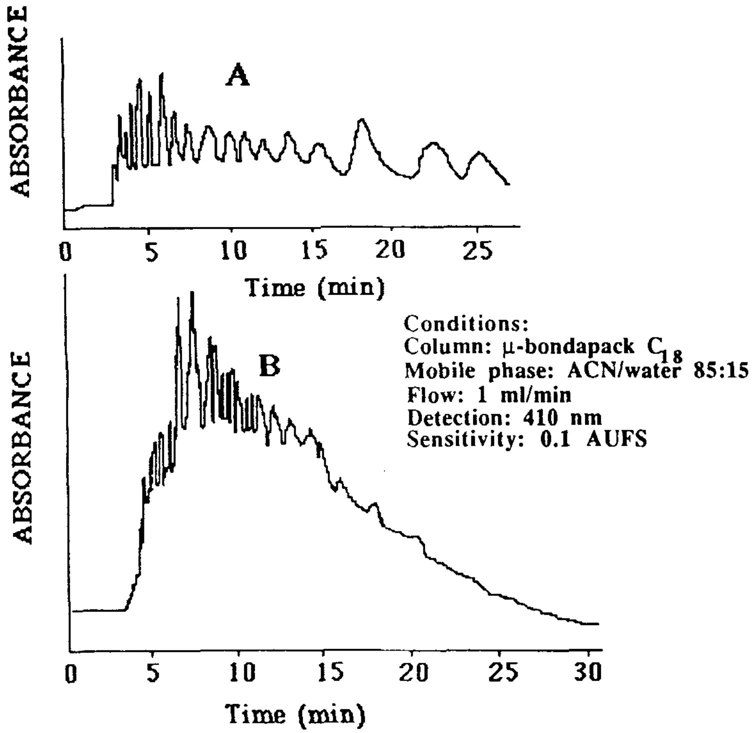


FIG. 2 HPLC fractionation of petroporphyrins extracted by Soxhlet: (A) with methanol, (B) with acetonitrile.

Fractions B (1B and 2B) would contain mostly vanadyl-porphyrins since they are eluted by the most polar solvent, i.e., 80:20 DMF/benzene mixture. In order to detect both types of porphyrin complexes, the spectrophotometric detection was carried out at both 397 and 410 nm, which are respectively the absorption maxima for nickel- and vanadium-porphyrin compounds.

The first runs on the four fractions were carried out with a 85:15 ACN/water solvent mixture; they did not exhibit good resolution but instead gave wide absorption bands. Since acetonitrile is the solvent of higher selectivity, it was kept and the polarity was reduced by substituting water with methanol.

The best separation was attained for Fractions 1B and 2B by using a 30:70 methanol/acetonitrile solvent mixture; the corresponding chromatograms are shown on Figs. 3(A) and 3(B). These figures indicate the clear

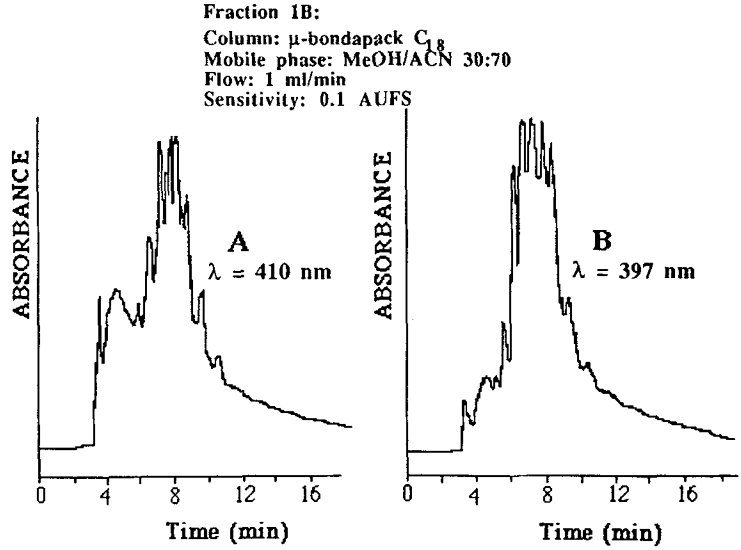


FIG. 3 HPLC fractionation of Fraction 1B. Detection: (A) 410 nm, (B) 397 nm.

separation of two fractions, one which elutes in less than 6 minutes while the other requires between 6 and 10 minutes to exit the column. When the detection wavelength was switched from 410 nm (Chromatogram A) to 397 nm (Chromatogram B), the signal from the first eluted fraction was reduced while that from the other fraction was increased. Figure 4 exhibits essentially the same features, although the fraction separation is even better than in Fig. 3.

Both results can be compared with the GFAA data. In effect, Table 1 indicates that the nickel/vanadium concentration is highest in Fraction 2B; as a consequence, it can be said that acetonitrile extraction is more selective, especially for vanadyl-porphyrin compounds. On the other hand, comparison of Figs. 2(B) and 4(B) shows that the separation with DMF/benzene in the adsorption column allows for the best purification of the Soxhlet extract products.

SEC Analysis

The best molecular weight distribution (MWD) was attained by using a 60S-100 Å two columns set which leads to a symmetrical distribution. Calibration curves were established with the standards previously mentioned. They showed an exclusion volume of about 10 mL and a permea-

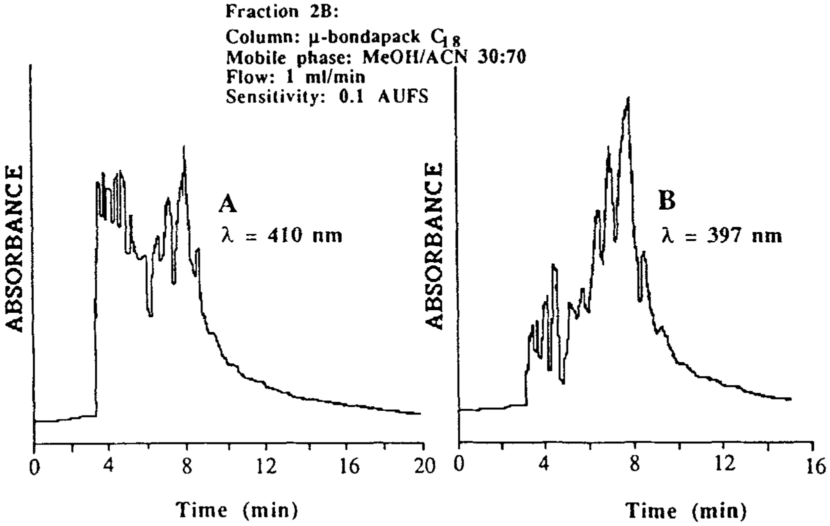


FIG. 4 HPLC fractionation of Fraction 2B. Detection: (A) 410 nm, (B) 397 nm.

tion volume of 16 mL. The latter was calculated from a run in which a *n*-tetradecane standard was injected.

The data of Fig. 5 on the molecular weight (MW) of fractions eluted with DMF/benzene exhibit good agreement with the reported results (9) of about 400 daltons as for calibration carried out with polystyrene standards. However, it is important to point out that the molecular weights of Fractions 1A and 1B eluted by hexane/benzene are rather low when they are compared with literature data; this may be due to the presence of nonporphyrin low molecular weight compounds which are extracted by the less polar solvent. Previous mass spectroscopic data corroborate this interpretation (17).

Figure 6, which gathers the MWD of the different fractions, leads us to formulate the following comments.

1. The more symmetrical and higher signal distributions correspond to fractions with the high vanadium content.
2. Fractions 1A and 2A, which come from elution with hexane/benzene, exhibit a widespread MWD, an indication of the lack of purification.
3. Fraction 1A is actually a mixture according to its bimodal MWD, while Fraction 2A exhibits a widespread but symmetrical distribution. These results are again in good agreement with the GFAA data (Table

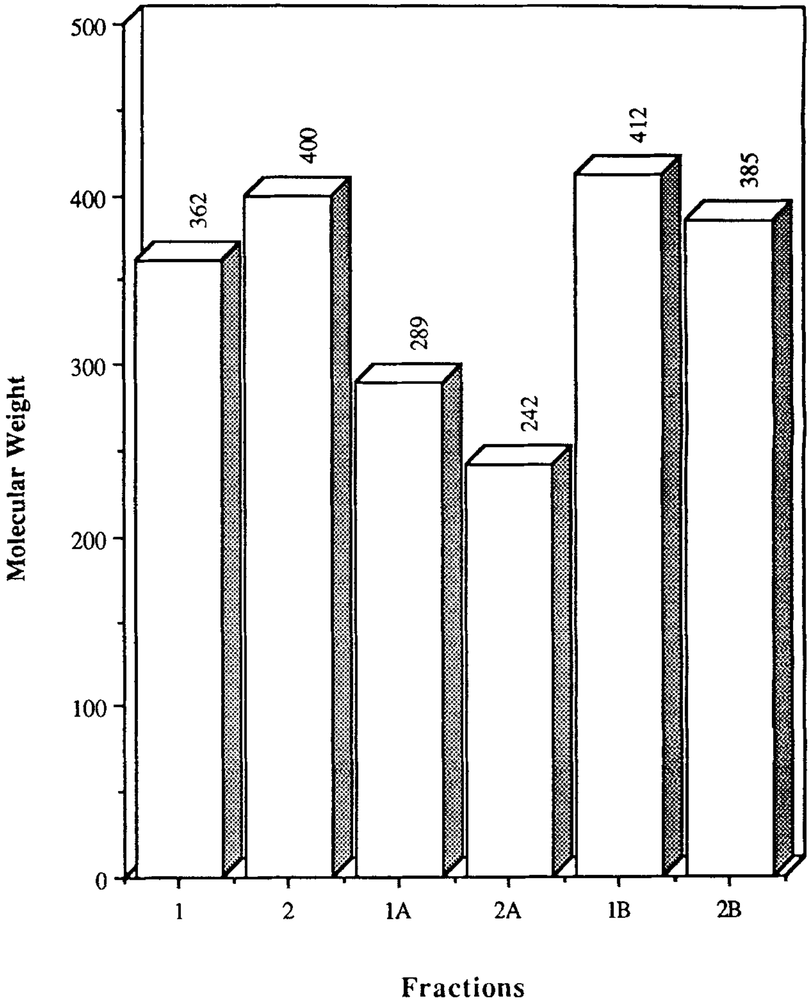
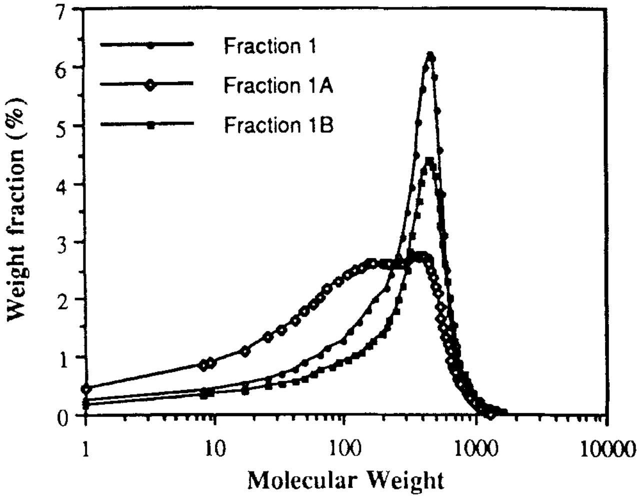


FIG. 5 Molecular weights of the different fractions found by SEC.

1), where it is seen that Fraction 1A contains roughly equal amounts of vanadium and nickel while Fraction 2A does not. All these results point to the better efficiency of acetonitrile as an extraction solvent of the vanadyl-porphyrins.

4. Both the average MW and MWD of Fraction 2B closely match the results reported by Fish et al. from work on an asphaltenic extract from Boscán crude oil. Since Fish et al. used a vanadium-specific



Conditions:
Columns: Zorbax 60S-Ultrastyragel 100Å
Mobile phase: THF
Flow: 1 ml/min
Detection: 400 nm
Sensitivity: 0.1 AUFS

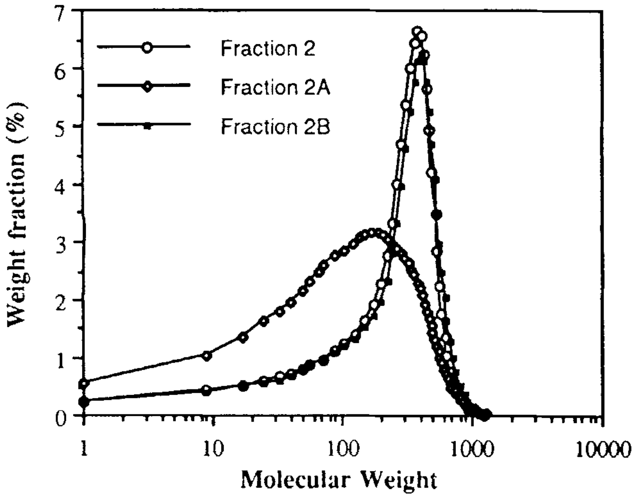


FIG. 6 Molecular weight distributions of the differents fractions found by SEC.

detector on their SEC system, it can be concluded that purification with DMF/benzene on an adsorption column is efficient for the separation of vanadyl-porphyrin compounds.

CONCLUSIONS

The reported method, which combines preparation of an alumina slurry, Soxhlet extraction, and chromatography adsorption, is found to lead to good extraction and separation of the vanadium and nickel porphyrins coming from a heavy crude oil.

Reversed-phase HPLC separation of most polar extracts was carried out efficiently with a 30:70 methanol/acetonitrile mobile phase and a C_{18} stationary phase.

SEC analysis provided several interesting features which allowed us to observe mixtures and selective extracts by using acetonitrile for the polar fractions, which are believed to be the vanadyl-porphyrins.

The MWD and average MW of porphyrins compounds found in this study are in good agreement with those previously reported.

ACKNOWLEDGMENTS

The authors would like to thank the University of Zulia Research Council (CONDES-LUZ) and the National Research Council (CONICIT) for providing financial support for this research.

REFERENCES

1. M. A. Braie and J. Eppolito, in *The Role of Trace Metals in Petroleum* (T. F. Yen, Ed.), Ann Arbor Science Publishers, Ann Arbor, Michigan, 1975.
2. N. Márquez, C. Gall, C. Tudares, J. Paredes, and C. De La Cruz, *Prepr. Symp. Anal. Chem. Heavy Oils/Resids, Div. Pet. Chem., Am. Chem. Soc.*, *34*, 292–296 (1989).
3. E. Osorio, E. Angulo, S. Segovia, F. Ysambertt, N. Márquez, and C. De La Cruz, *Acta Cient. Venez.*, *45*, 1–8 (1994).
4. J. S. Flynn and D. H. Freeman, *J. Chromatogr.*, *386*, 111–121 (1987).
5. L. A. Spencer, J. F. Galobardes, M. Curtis, and L. B. Rogers, *Sep. Sci. Technol.*, *17*, 797–819 (1981).
6. K. Hajibrahim, P. J. C. Tibbetts, C. D. Watts, J. R. Maxwell, and G. Eglinton, *Anal. Chem.*, *50*, 549–553 (1978).
7. K. Hajibrahim, P. J. C. Tibbetts, C. D. Watts, J. R. Maxwell, and G. Eglinton, *Ibid.*, *56*, 2452–2460 (1984).
8. R. H. Fish and J. J. Komlenic, *Ibid.*, *56*, 510–517 (1984).
9. R. H. Fish, J. J. Komlenic, and B. K. Wins, *Ibid.*, *56*, 2452–2460 (1984).
10. H. H. Kiet, L. P. H. Blanchard, and S. L. Malhotra, *Sep. Sci.*, *12*, 607–634 (1977).
11. J. Reynolds and W. Biggs, *Acc. Chem. Res.*, *21*, 319–326 (1988).

12. W. A. J. De Waal, C. C. H. M. Kniper, F. J. M. J. Maessen, and J. C. Kraak, *J. Chromatogr.*, *462*, 115–135 (1989).
13. N. Márquez, Magister Science These, University of Georgia at Athens, 1984.
14. J. Paredes, E. Angulo, N. Márquez, and C. De La Cruz, *Soc. Venez. Quím.*, *14*(2), 15–19 (1991).
15. J. S. Flynn and D. H. Freeman, *J. Chromatogr.*, *386*, 111–121 (1987).
16. S. K. Hajibrahim and H. Colin, *Anal. Chem.*, *50*(4), 549–553 (1978).
17. N. Márquez, G. Litwinski, and L. B. Rogers, *Rev. Téc. Ing., Univ. Zulia*, *13*(2), 89–94 (1990).

Received by editor July 18, 1994