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Short Communication

Separation of vanadyl and nickel petroporphyrins on an aminopropyl column by high-performance liquid chromatography

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ABSTRACT

The nickel(II) and vanadyl(II) petroporphyrins in fuel oil and crude oil samples are separated by normal-phase high-performance liquid chromatography on an aminopropyl column. Separation mechanisms presented include hydrogen bonding as well as Van der Waals interactions between the petroporphyrin and the amino group on the column surface. The method is simple and efficient for the fingerprinting of petroporphyrins in crude oils and oil products.

INTRODUCTION

Vanadyl [VO(II)] and nickel(II) petroporphyrins (PPs) were identified in fossil fuels as products derived from chlorophyll [1,2]. Since then, they have been used as biomarkers in the study of the origin and the formation of petroleum and as an important parameter for oil exploration [3]. However, the PPs have not been used as extensively as other biomarkers, probably because of the complexity of their chemical structure, the large number of closely similar isomers, and the lack of simple and accurate analytical techniques [3–5].

The interest for the PPs has increased in the last 10 years because the oil refinery industry is dealing with increasingly heavier crude oils. Vanadium and nickel are the most abundant metals found in crude oils [1–4], often in the form of petroporphyrins or other organic chelates. These metals can block the activity of the catalyst in the hydrogenation process by precipitation as metal sulphides [6,7]. Therefore, metal speciation in crude oils is important for the selection of refining methods and for the assessment of the quality of crude oils. In environmental studies, PPs are potentially useful as biomarkers for determining the origin of spills.

The PPs are a group of macrocyclic aromatic compounds consisting of a porphin ring, to which a metal ion is bound. There are eight alkyl substituents on the porphin ring (Fig. 1). The most abundant series found in crude oils are etioporphyrins (ETIOs) and deoxophylloerythroetioporphyrins (DPEPs) with the total carbon number from 29 to 39 [8]. Differences of the alkyl substituents and their steric structure lead to a large number of homologues and isomers which are characteristic of each

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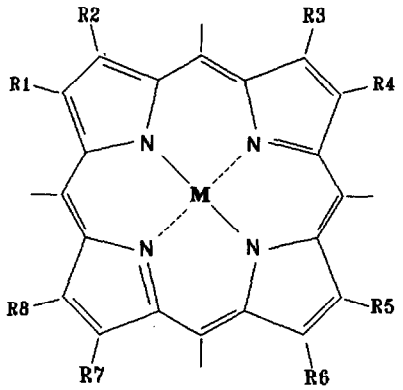

Fig. 1. Generalized chemical structure of petroporphyrins (R stands for an alkyl group with 1 to 8 carbon numbers). ETIO-I: $R_{1,3,5,7}$ = CH_3, $R_{2,4,6,8}$ = C_2H_5; ETIO-III: $R_{1,3,5,8}$ = CH_3, $R_{2,4,6,7}$ = C_2H_5; octaethylporphyrin: R_{1-8} = C_2H_5; DPEPs: the porphyrins bearing an isocyclic ring [8].

petroleum deposit. Thus, PPs are ideal as fingerprint chemicals.

Techniques for the analysis of PPs can be divided into two categories: indirect (after removal of the chelated metal) and direct. Amongst the indirect analytical techniques, the most efficient separation reported is by normal-phase high-performance liquid chromatography (HPLC). The analytical procedures involve isolation of the PPs by liquid chromatography, demetallation by acid, and finally separation of the demetallated porphyrins by HPLC [9–13]. This analytical procedure is time consuming and, moreover, the demetallation reaction may degrade the alkyl substituents on the porphin ring. However, the most significant drawback, is that the indirect analytical techniques cannot provide information on the original forms of metal chelates. Therefore, recent studies have focused on the development of direct analytical techniques. Several researchers have used size-exclusion chromatography (SEC) to separate the PPs [6,7], but the separation is limited by the poor resolution of the SEC. By using reversed-phase octadecylsilane columns or normal-phase silica columns, separation of the standard mixtures [Ni(II) and VO(II) octaethylporphyrins] has been achieved [14–16]. In oil samples, however, only VO(II)petroporphyrins could be sep-

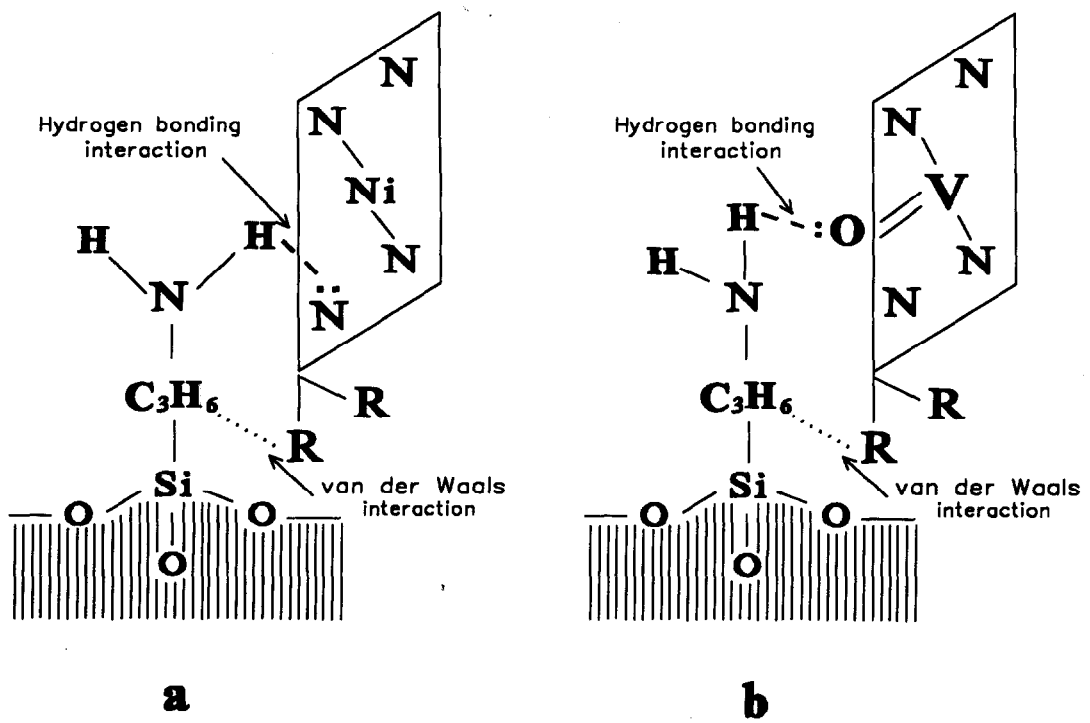

Fig. 2. Separation mechanisms of the PPs on the aminopropyl column: (a) Ni(II) petroporphyrin; (b) VO(II) petroporphyrin.

arated [15,16]. The resolution for Ni(II) petroporphyrins was very poor [16].

In the present study, separation of PPs was conducted by normal-phase HPLC because PPs are poorly soluble in methanol and acetonitrile. In contrast to the previous methods using silica columns, an aminopropyl column was chosen in this study in order to improve the selectivity for the PPs. Separation of the petroporphyrin homologues and isomers on the amino column is based on the differences in the adsorption energy of each. As shown in Fig. 2, two types of interactions between the porphyrin and the stationary phase may occur. The first is hydrogen bonding between the free electron pair from the nitrogen [in the case of Ni(II) petroporphyrins, Fig. 2a] or from the oxygen [VO(II) petroporphyrins, Fig. 2b] and the hydrogen of the amino group. The other is Van der Waals interaction between the alkyl substituents of the porphyrin and the propyl group on the stationary phase. Unger *et al.* [17] found a slight reversed-phase effect of diol bonded phase due to the influence of hydrophobic interactions between the long alkyl group of the diol bonded phase and solutes. The selectivity of the diol bonded phase as well as amino bonded phase was also improved for both acidic and basic compounds. Thus, chemical or steric differences in the alkyl substituents will lead to differences in adsorption energy by both hydrogen bonding and Van der Waals forces. Therefore, the homologues and isomers can be separated better on an aminopropyl column than on a silica column where only hydrogen bonding prevails.

This paper presents an improved method for the separation of the PPs directly on the aminopropyl column by HPLC. The method is applied to fuel oil and crude oil samples and fingerprints of these samples are compared.

EXPERIMENTAL

HPLC system and conditions

The HPLC system consists of a quaternary solvent delivery pump (600E; Waters, Milford, MA, USA), a Waters autoinjector (WISP 700), an UV–VIS detector (SP8440; Spectra-Physics), a fluorescence detector (470; Waters) and a computer work station. The UV–VIS detector was set at 400 nm for the analysis of metal porphyrin standards and at

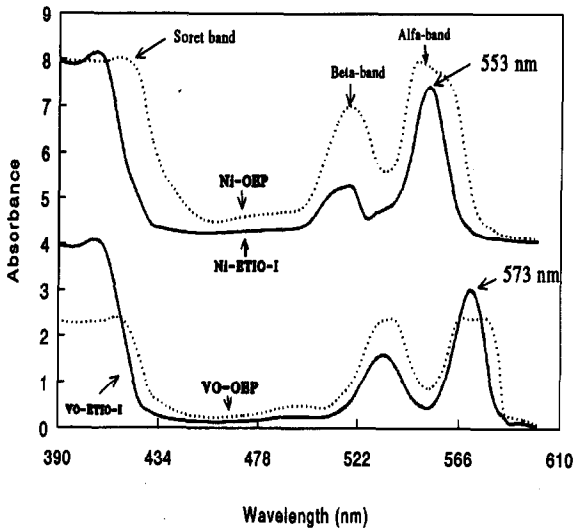

Fig. 3. Adsorption spectra of Ni-OEP, Ni-ETIO-I, VO-OEP and VO-ETIO-I in toluene.

400, 553 and 573 nm for the analysis of the oil samples. The wavelength of 553 nm and 573 nm was considered as an α-band for Ni(II) and VO(II) petroporphyrins, respectively (Fig. 3). The fluorescence detector was set at 400 nm for the excitation and at 620 nm for the emission to detect free base porphyrins in the oil samples.

A μBondapak-NH_2 column (300 × 3.9 mm) obtained from Waters was employed. The μBondapak-NH_2 column contained aminopropyl groups chemically bonded to irregular-shaped 10 μm porous silica.

Hexane, toluene and dichloromethane (DCM) were employed as mobile solvents. A mixture of hexane and toluene in the ratio of 55:45 was established in a linear gradient across the column and maintained for 10 min. This mixture was then modified to 30:20:50 of hexane, toluene and DCM respectively over a period of 15 min, maintained at this ratio for 20 min, and returned to the initial condition over a period of 5 min.

Preparation of standards

The standards employed included VO(II)-etioporphyrin-I (VO-ETIO-I) and Ni(II)-etioporphyrin-I (Ni-ETIO-I) (Midcentury Chemicals, Posen, USA), VO(II)-octaethylporphyrin (VO-OEP) and Ni(II)-octaethylporphyrin (Ni-OEP) (Porphyrin

Products, Logan, UT, USA). All standards were dissolved in toluene except for VO-ETIO-I, which was dissolved in DCM and then diluted with toluene. Absorption spectra of the standards were measured by a spectrophotometer (UV-260, Shimadzu) and shown on Fig. 3.

Preparation of sample

One fuel oil sample and four crude oil samples were analyzed. They included Bunker C oil from Venezuela, Alberta sweet mixed blend crude oil from western Canada, Atkinson crude oil from the Canadian North West Territories, Terra Nova crude oil and Avalon crude oil from off-shore exploration in the northern Atlantic. The samples (about 4 g) were extracted with 5 ml of pyridine–water–toluene (4:1:1) for four consecutive repetitions. The extract was then dried by evaporation, the residue dissolved in toluene (2 ml) and stored in the dark.

RESULTS AND DISCUSSION

The separation of Ni-OEP, Ni-ETIO-I, VO-OEP and VO-ETIO-I standards on the aminopropyl column by HPLC is shown on Fig. 4. The four standards were well separated with the retention time at 5.70, 7.17, 21.78 and 22.93 min for Ni-OEP, Ni-ETIO-I, VO-OEP and VO-ETIO-I, respectively.

The PPs in the Bunker C fuel oil sample from Venezuela were also well separated. The chromatograms of the fuel oil sample on the UV–VIS detector at the wavelength of 400, 553 and 573 nm, respectively, are shown on Fig. 5. Three Ni(II) petroporphyrin and four VO(II) petroporphyrin peaks were detected at the retention time from 8 to 11 and 23 to 27 min. There are no commercially available standards for many of these compounds.

The separations of VO(II) petroporphyrins in the four crude oil samples are shown on Fig. 6. Peaks at the retention time between 9 to 12 min are not attributable to Ni(II) petroporphyrins because of their lack of absorbance at 553 nm, a specific adsorption wavelength for Ni(II) porphyrins (Fig. 3). This indicates that the content of Ni(II) porphyrins is much less than VO(II) porphyrins in these Canadian crude oils.

In the first 7 min, there were also large unresolved peaks detected by both UV–VIS and fluorescence detectors in all samples. These peaks are probably due to the presence of carotenoids or flavonoids [18]. After 7 min there were porphyrin peaks detected by the UV–VIS detector but not by the fluorescence detector. Because free base porphyrins are fluorescent while metallated porphyrins are not, this result implies that the mature oils contain mainly the metallated porphyrins.

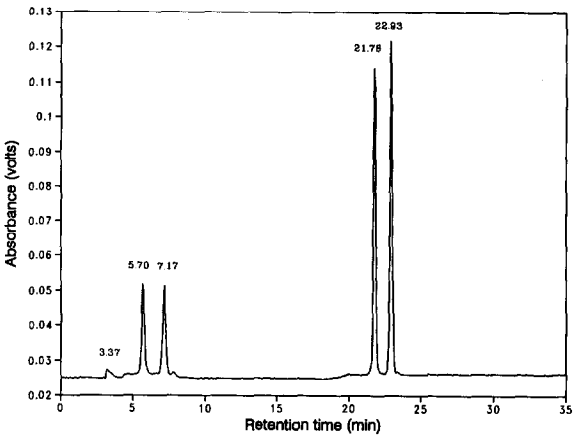

Fig. 4. HPLC chromatogram of Ni-OEP, Ni-ETIO-I, VO-OEP and VO-ETIO-I standards (134 ng each) on the aminopropyl column under normal-phase conditions (injection volume: 10 μl; flow-rate: 1.0 ml/min; UV–VIS detector: 400 nm).

It is interesting to note that the four crude oils show three types of PPs fingerprints based on their geographic locations. The Alberta crude oil from

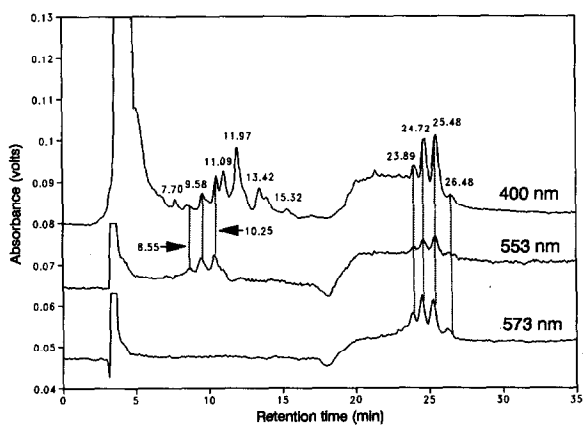

Fig. 5. HPLC chromatograms of Ni and VO petroporphyrins in Bunker C oil (Venezuela) on the UV–VIS detector [injection volume: 10 μl (2.8 mg fuel oil) at 400 nm and 50 μl (14 mg fuel oil) at 553 and 573 nm; other conditions as in Fig. 4].

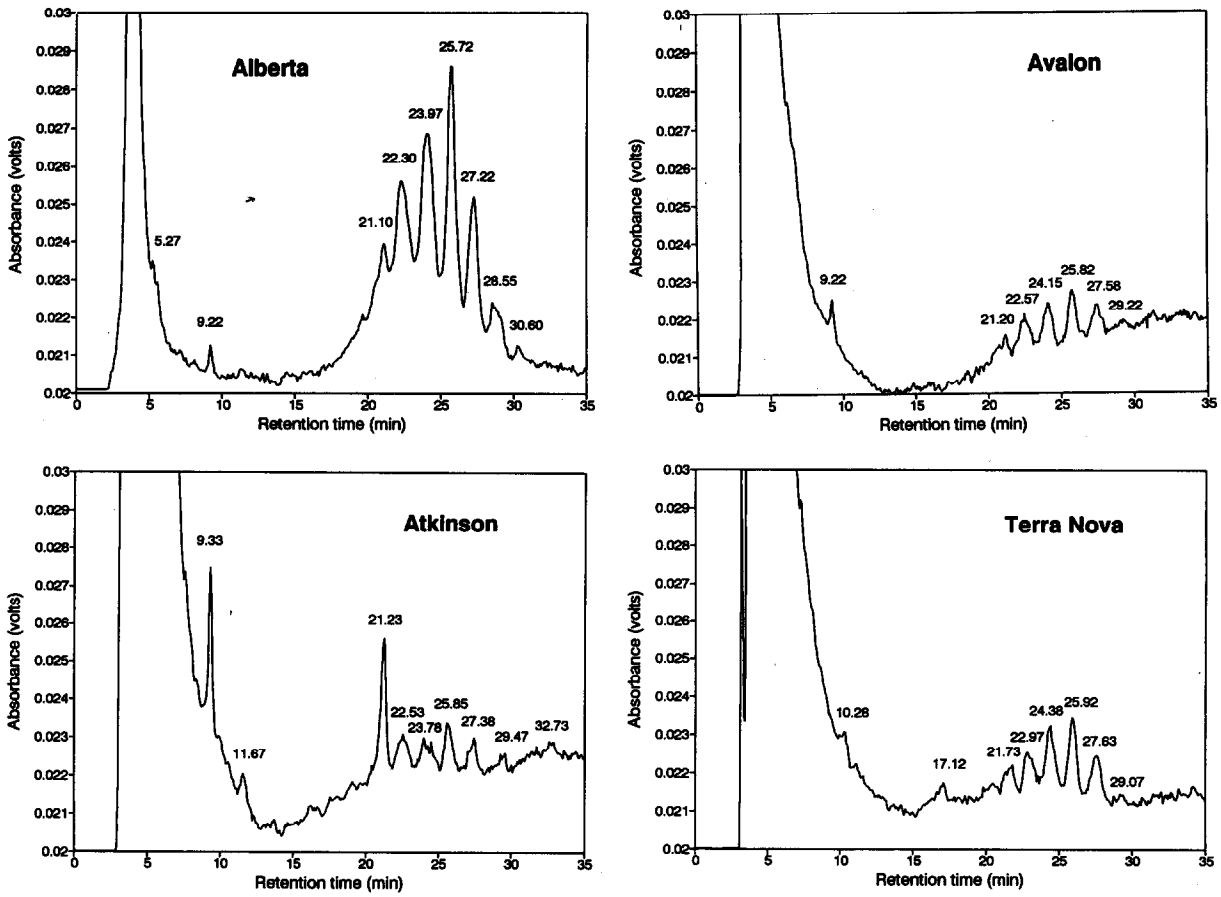

Fig. 6. HPLC chromatograms of VO petroporphyrins in the crude oil samples on the UV–VIS detector (400 nm) (injection volume: 20 μl, which is equal to 81, 153, 237 and 230 mg Alberta, Atkinson, Avalon and Terra Nova crude oils, respectively; other conditions as in Fig. 4).

western Canada contains seven peaks of PPs with a dominant peak at 25.72 min and the Atkinson crude oil from the Northwest Territories contains seven peaks with a dominant peak at 21.23 min. The Avalon and Terra Nova crude oils, offshore oils from the Canadian east coast, have a similar type of PPs fingerprints. The content of PPs decreases in the order of Alberta > Atkinson > Avalon ≈ Terra Nova.

The resolution of both VO(II) and Ni(II) petroporrphyrins in the present study is much better than that observed in previous studies using either silica columns or octadecylsilane columns [15,16]. This is expected because as discussed in the introduction, the aminopropyl column provides better selectivity for the PP isomers which often only differ in a few alkyl substituents.

CONCLUSION

The PPs can be directly separated on an aminopropyl column by HPLC. The possible mechanisms involved are interactions due to hydrogen bonding and the Van der Waals forces between the PPs and the aminopropyl group.

This method is valuable for fingerprinting PPs in crude oils and fuel oils, which is useful in oil exploration, assessment of oil quality for refining, and in environmental impact studies. The method is more straightforward and efficient than the previously published methods.

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