

Note

Liquid chromatographic determination of planar aromatic sulphur compounds in crude oil

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Little data have been reported concerning the liquid chromatographic (LC) retention characteristics of polycyclic aromatic sulphur heterocycles (PASHs) presumably because of their low concentrations relative to polycyclic aromatic hydrocarbons (PAHs) in environmental samples and the lack of a suitable sulphur-specific LC detector.

No successful method to separate sulphur heterocycles as original compounds from the non-polar aromatic compound fraction has been reported. Adsorption chromatography using silica gel and/or alumina has been generally used as the first step for isolating PASHs. However, the isolation of the PASHs from PAHs has been difficult.

Organic sulphides are known to form adducts with metal cations and with many other substances¹. Complexation of organic sulphur compounds by means of copper, mercury, palladium and other metal salts is a well known technique and has been applied to coal extracts and coal products². Procedures using these salts have been effective for the isolation of aliphatic sulphides but are generally not applicable to the separation of thiophene compounds. Thiophene compounds can be separated on a silver nitrate-coated silica column³. Copper(II) chloride is a good complexing agent for aliphatic thioethers, and PdCl₂ for aromatic heterocycles^{1,4–7}.

The sulphone method described in the literature was applied for gas chromatographic (GC) determination and required reduction of the isolated sulphones back to heterocyclic sulphides^{8–14}. The aromatic fraction was treated in benzene–acetic acid (1:1) with H₂O₂ and then fractionated on a silica gel column. The unoxidized aromatic compounds were eluted with benzene and the sulphone/quinone fraction was collected with benzene–methanol (1:1) as the eluent. The latter fraction was reduced with LiAlH₄ in diethyl ether and the sulphides were separated from the hydroquinones by elution with hexane on a silica gel column.

The purpose of this study was to develop a method for the separation and determination of the PASHs in crude oil. The method was to be applied to environmental samples in oil residue analysis.

EXPERIMENTAL

Thin-layer chromatography (TLC)

TLC experiments were performed to see where the heterocyclic aromatic sulphur compounds could be separated from aromatic hydrocarbons in the non-polar aromatic compounds fraction of crude oil. The experiments were done according to the literature¹⁵. Silica gel (Merck, Kieselgel 60 F₂₅₄, 20 cm × 10 cm, 0.25 mm) and alumina (Merck, Aluminium oxid 60 F₂₅₄, Type E, 20 cm × 20 cm, 0.25 mm) plates with a fluorescence indicator were used.

The components tested were biphenyl, dibenzothiophene (DBT) and the non-polar aromatic fraction of a Russian crude oil. Biphenyl and dibenzothiophene were used to see how the addition of a sulphur atom to an aromatic hydrocarbon changes the R_F values in different solvent systems.

Ligand-exchange chromatography

Approximately 10 g of silica gel were mixed with 0.5 g of palladium chloride in an aqueous solution and dried at 140°C in an oven overnight. A 4-g amount was introduced into a glass column (20 cm × 5.0 mm I.D.) and about 200 mg of the non-polar aromatic fraction of the crude oil in 2 ml of hexane were added to the top of column. Hexane, chloroform and benzene were used as the eluents.

Oxidation of dibenzothiophenes to sulphones and analysis by high-performance liquid chromatography (HPLC)

A weighed sample of Russian crude oil was first fractionated into aliphatic hydrocarbons and non-polar aromatic compounds using column chromatography¹⁶. The non-polar aromatic fraction was oxidized by refluxing with an excess of 30% hydrogen peroxide in glacial acetic acid for 4 h. The mixture was allowed to stand overnight, then extracted with dichloromethane and washed with water to remove acetic acid. Silica gel column chromatography was used to separate the sulphones from the dichloromethane extract. The column contained 6 g of SiO₂. Non-oxidized compounds were eluted with 80 ml of hexane and sulphones with 40 ml of methanol.

Sulphones cannot easily be analysed by GC because they are highly polar, non-volatile and thermolabile¹⁷. Reversed-phase HPLC is a suitable method. The apparatus used was an Hitachi 655A-11 liquid chromatograph with a 655A variable wavelength UV monitor. An Spherisorb ODS2 column, 5 μm (25 cm × 4.6 mm I.D.), was used. Methanol–water and acetonitrile–water solutions were used as the eluents.

RESULTS AND DISCUSSION

TLC

From the results, it was concluded that the aromatic sulphur heterocycles cannot be separated as a group from aromatic hydrocarbons by TLC on silica gel or alumina plates. The only measurable differences in R_F values for biphenyl and dibenzothiophene on silica gel were detected when light petroleum (b.p. 40–60°C)–diethyl ether–acetic acid (80:15:5), light petroleum (b.p. 40–60°C)–ethyl acetate–acetic acid (80:15:5) or light petroleum (b.p. 40–60°C)–acetone–acetic acid was used as the eluent. Even then the separation was not complete. On alumina, biphenyl and DBT were successfully separated with light petroleum or hexane.

Ligand-exchange chromatography

The sulphur compounds were separated from the non-polar aromatic fraction of the crude oil using silica gel/PdCl₂ column chromatography. Hexane and benzene alone did not elute the compounds; rather hexane-chloroform or hexane when a little diethylamine was added.

The fraction obtained was analysed by GC-mass spectrometry (MS) and the presence of C₀₋₃DBT (dibenzothiophenes with 0-3 carbons in side chains) was confirmed by molecular ion mass fragmentography.

Oxidation

The methanol fraction obtained from the oxidation of crude oil was examined by

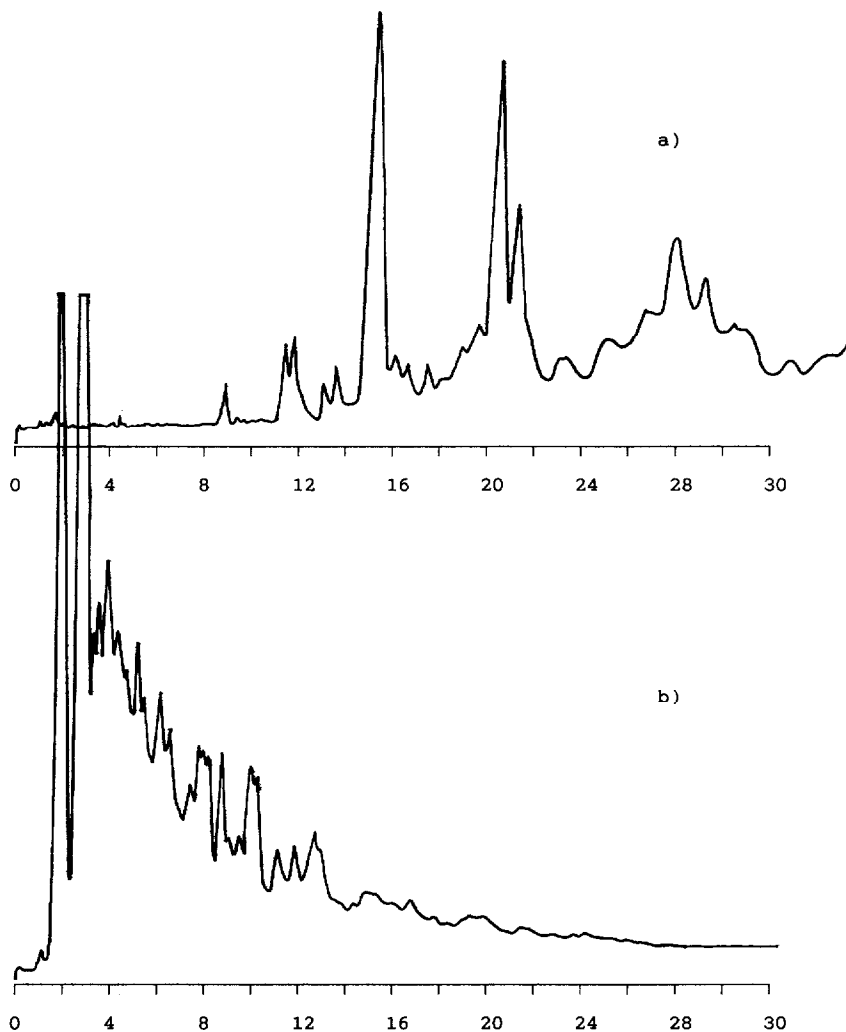


Fig. 1. HPLC chromatograms of (a) the non-polar aromatic compounds fraction of Russian crude oil (28.7 μg) and (b) the sulphone fraction of the same oil (13.8 μg). Column: Spherisorb 5 μm . Mobile phase: acetonitrile-water (60:40); flow-rate 1 ml/min. Detection: UV, 254 nm.

GC-MS using a short SE-54 column and found to contain mainly dibenzothiophene-5,5-dioxide and methylated analogues.

The procedure was also tested with dibenzothiophene, which was oxidized completely to dibenzothiophene-5,5-dioxide and recovered in 90–100% yield after silica gel column chromatography.

In reversed-phase HPLC, sulphones are eluted in a relatively short time when the eluent contains 33–45% water. The retention time of dibenzothiophene-5,5-dioxide was 5.60 min when acetonitrile–water (60:40) was used as the eluent. The sulphones from crude oil were all eluted before 15 min. The non-oxidized dibenzothiophenes and aromatic hydrocarbons have much longer retention times. When the eluent contains less than 35% water the sulphones are not eluted. When the eluent contains more than 45% water the retention times are longer than with 40% of water. The wavelengths used in the UV detection were 225, 231, 240 and 254 nm. At shorter wavelengths the sensitivity increases for sulphones. For example, at 231 nm it is ten times that at 254 nm, but there are disturbing peaks. Therefore the wavelength of 254 nm was chosen for the analysis. The HPLC chromatogram of the non-oxidized non-polar aromatic compound fraction of Russian crude oil and the chromatogram of the same fraction after oxidation and column chromatography are shown in Fig. 1.

CONCLUSIONS

Different TLC adsorbents like silica gel, aluminium oxide and amino silane did not allow the isolation of PASHs.

Column chromatography using silica gel impregnated with palladium chloride produced a moderate separation of PASHs, but the compounds were partly eluted as PASH-PdCl₂ complexes which cannot be analyzed by conventional methods.

The oxidation of dibenzothiophenes to the corresponding sulphones was found to be quantitative and the separation of the sulphones from oxidized and unoxidized PAHs was achieved by column chromatography. The oxidation time of 4 h used was long enough to oxidize all of the dibenzothiophenes to the corresponding sulphones, which can be analyzed as such or reduced back to the original sulphur compounds.

The non-polar aromatic fraction was about 28% of the Russian crude oil samples when weighed and the sulphone fraction about 20% of the non-polar aromatic compound fraction.

The sulphones were not determined quantitatively by HPLC because of the lack of a good internal standard. Diphenyl sulphone was tested but it was not sufficiently resolved from other sulphones. The synthesis of model compounds for the analysis of PASHs is underway in our laboratory.

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