

# Isolation of Thiophenic Compounds by Argentation Liquid Chromatography

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**A liquid chromatographic method for the isolation of thiophenic compounds from aromatic shale oil fractions is described. Separate one-ring and two-ring aromatic fractions were first obtained by two stages of silica adsorption chromatography. Thiophenic compounds were then separated by class from these fractions by argentation chromatography on a silver nitrate coated silica column. Fractions were examined by capillary gas chromatography with flame ionization and flame photometric detection to follow the sulfur profiles of the enriched eluates. Virtually complete separation was achieved for one ring thiophenes, and benzothiophenes were enriched by about 96% in comparison to naphthalenes. Comparisons are drawn between the method developed and sulfuric acid extraction and sulfoxide/sulfone oxidation.**

The presence of sulfur compounds in shale oil is undesirable for several reasons. They are deleterious to oil refining because they poison catalysts and cause corrosion, if used directly in a fuel they give noxious sulfur dioxide emissions, and in themselves they are suspected mutagens and/or carcinogens. It is desirable to identify individual sulfur compounds in shale oil because different isomers may have drastically different health effects, their identification may also aid in the development of methods for removal of sulfur compounds from shale oil.

Approximately 80% of the organic sulfur in shale oil occurs as thiophenic compounds with the remainder as thiols, sulfides, and disulfides (1). Since thiophenes are present at the greatest level and also are the most difficult to remove, they are probably the most important class of sulfur compounds to study. The purpose of this study was to develop a procedure by which they could be isolated without discrimination or alteration of the compounds initially present.

Dean and Whitehead reviewed chemical and physical separation and identification methods for sulfur compounds in petroleum and shale oil (2). The chemical methods were extraction with sulfuric acid, formation of additional compounds with mercury salts, and formation of sulfoxides and/or sulfones. These methods generally suffer drawbacks from either partial decomposition or alteration of the sample or discrimination between different isomers. Sulfuric acid extraction will cause side reactions such as alkylation by alkenes also present in shale oil. The optimum conditions for the mercury addition method vary for different thiophenes and an adduct cannot form if no hydrogens are present on the thiophene ring. Oxidation at the sulfur atom to form sulfoxides and/or sulfones is fairly nondiscriminatory, but regeneration of the original thiophene is difficult. The sulfones formed on oxidation are very stable and a strong reducing agent such as lithium aluminum hydride must be used to accomplish reduction back to the original thiophene. This procedure is known to reduce benzothiophene 1,1-dioxide at the double bond before reducing the sulfur (3). Drushel and Sommers tried to overcome this by oxidizing only to the sulfoxide, which is more easily reduced than the sulfone, but

this reaction is difficult to control since the sulfoxide is more easily oxidized than the original thiophene (4). Despite these drawbacks it has been demonstrated more recently by Lee that thiophene-rich fractions may be obtained by this oxidation-reduction pathway (5, 6).

Physical methods for isolation of thiophenes include distillation and liquid chromatography on various adsorbents. Distillation obviously does not isolate a whole class of compounds, and liquid chromatography has not been used to do more than isolate the thiophenes within a fraction which contains all the aromatics also.

In this study, a method was developed to isolate thiophenic compounds by liquid chromatography. One- and two-ring aromatic fractions were first obtained from shale oil by liquid chromatography on silica and then the thiophenic compounds were separated from the aromatics by liquid chromatography on a silver nitrate coated silica column. The fractions obtained were then examined by capillary gas chromatography with flame ionization and flame photometric detectors to confirm that the integrity of the thiophenes was maintained.

## EXPERIMENTAL SECTION

**Liquid Chromatography.** The pumping system consisted of a single Constametric III pump (Laboratory Data Control Inc., Riviera Beach, FL). Samples were injected on the 4 mm i.d. columns by a Model 7125 sample injection valve (Rheodyne Inc., Cotati, CA) equipped with a 100- $\mu$ L sampling loop. A Teflon sample injection valve equipped with a 2-mL loop was used with the glass column.

Liquid chromatographic eluents were monitored with a Refractomonitor I refractive index detector (Laboratory Data Control, Inc.).

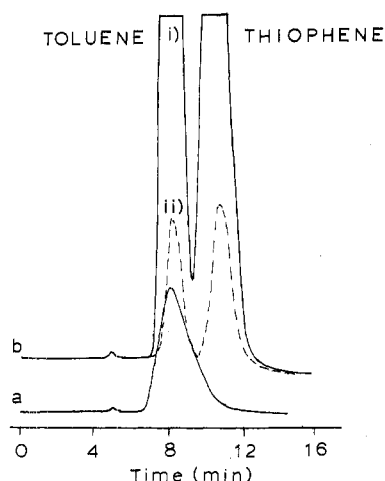
Liquid chromatographic columns used were a 30 cm  $\times$  10 mm Pyrex column packed with 32-63  $\mu$ m Woelm silica, a 30 cm  $\times$  4 mm stainless steel column packed with 32-63  $\mu$ m Woelm silica, and a 60 cm  $\times$  4 mm stainless steel column packed with 32-63  $\mu$ m Woelm silica which was impregnated with 20% silver nitrate according to the procedure of Heath et al. (7).

**Gas Chromatography.** Gas chromatography was carried out on a Model 2760 instrument (Varian, Palo Alto, CA) equipped with a flame ionization detector and a Model 18805A flame photometric detector (Hewlett-Packard Corp., Avondale, PA). A 40 m  $\times$  0.4 mm Pyrex glass column coated with 0.5  $\mu$ m OV-101 prepared by the method of Grob was used (8).

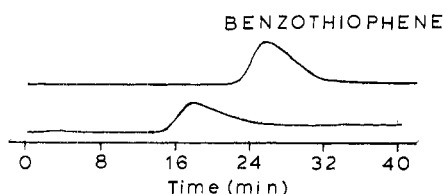
**Liquid Mobile Phase.** Reagent grade hexane obtained from the Fisher Scientific Co. (Fairlawn, NJ) was used after distillation.

**Shale Oil.** Shale oil was obtained from a modified in situ (below ground) process (Department of Energy, Laramie Energy Technology Center, Laramie, WY) (boiling range 76.3% below 480  $^{\circ}$ C).

**Separation of Shale Oil into One-Ring and Two-Ring Aromatic Classes.** Asphaltenes were removed from the shale oil by filtration after dissolving 5 g of oil in 20 mL of hexane. The hexane was removed by passing nitrogen over the sample. Two milliliters of this sample was injected onto a preparative Pyrex glass column and eluted with hexane at 5 mL/min. Fractions were collected at times predetermined by the retention time of standards (benzene, naphthalene) and were then evaporated down to about 200  $\mu$ L. Each fraction was then rechromatographed on a 30 cm  $\times$  4 mm stainless steel column packed with 32-63  $\mu$ m Woelm silica; 175  $\mu$ L of each fraction was injected onto this column



**Figure 1.** Preparative liquid chromatographic separation of thiophene from one-ring aromatics: column 60 cm  $\times$  4 mm i.d. stainless steel, 20%  $\text{AgNO}_3$  on 32–63  $\mu\text{m}$  silica (Woelm), hexane eluent at 2 mL/min; (a) (lower trace) one-ring aromatics, (b) (upper traces) toluene and thiophene (10-fold attenuation difference between i and ii).



**Figure 2.** Preparative liquid chromatography separation of benzothiophene from two-ring aromatics, column as in Figure 1, hexane eluent at 3 mL/min: (a) (lower trace) two-ring aromatics, (b) (upper trace) benzothiophene.

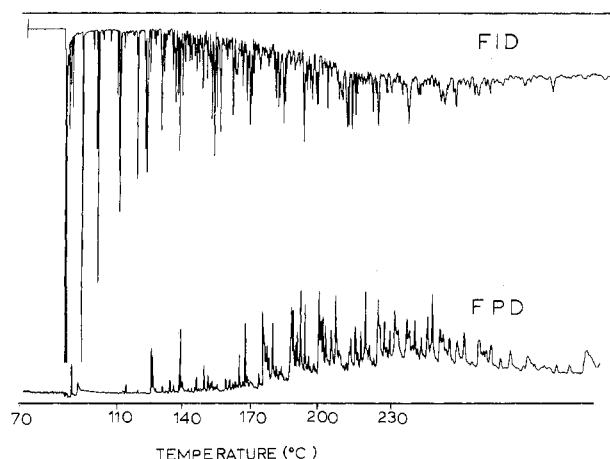
with a flow rate of 3 mL/min. Fractions were again collected at times predetermined by the retention time of the same standards. These fractions were then concentrated to about 200  $\mu\text{L}$ .

#### Separation of Thiophenic Compounds from Aromatics.

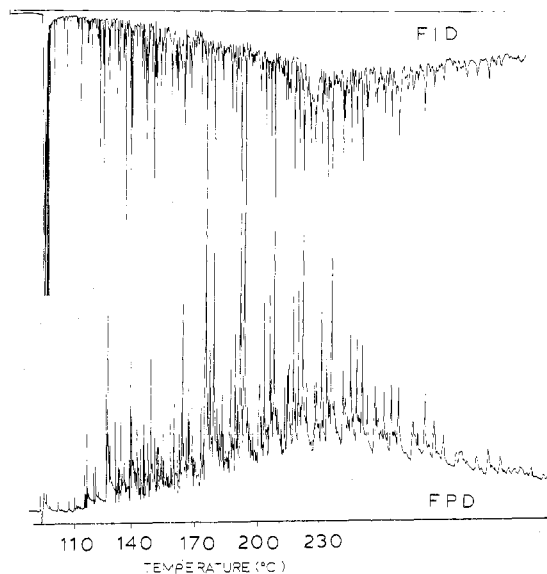
The thiophenes were separated from the aromatics by injecting 100  $\mu\text{L}$  of the aromatic concentrate onto a 60 cm  $\times$  4 mm stainless steel column of silica coated with 20% silver nitrate (Figures 1 and 2). Elution was with hexane at 2 mL/min for the one-ring aromatics and at 3 mL/min for the two-ring compounds. The fractions were collected at times predetermined by the retention time of standards (thiophene and benzothiophene), and were evaporated down to 100–200  $\mu\text{L}$  volumes. The whole one-ring and two-ring aromatics and one-ring and two-ring thiophenes were then compared by capillary gas chromatography (Figures 3–6).

Thiophenic compounds were also isolated by two other methods for comparison to separation by argentation chromatography: extraction with sulfuric acid and formation of sulfones. The extraction with sulfuric acid was a relatively simple procedure. A 1-mL aliquot of an in situ aromatic concentrate was shaken with 1 mL of 90% sulfuric acid at approximately 0  $^{\circ}\text{C}$ . The organic layer was separated and then the acid layer was washed several times with 5-mL aliquots of toluene. While the vial containing the 90% sulfuric acid was maintained in an ice bath, ice was added until the volume of the acid solution was approximately doubled. It was then back-extracted with one 1-mL aliquot of hexane. This sample was used to generate the chromatogram of thiophenic compounds obtained by sulfuric acid extraction (Figure 7).

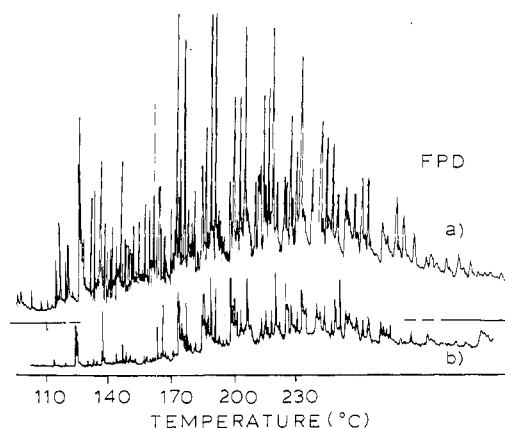
Isolation of thiophenic compounds by formation of sulfones was carried out following a procedure described by Lee (5) which is outlined as follows: (1) Aromatics from whole oil were isolated by liquid chromatography. (2) The thiophenic compounds were oxidized to sulfones by refluxing in 50/50 benzene/glacial acetic acid while adding 30%  $\text{H}_2\text{O}_2$  over a period of 1 h. Refluxing was then continued for 16 h. (3) Excess  $\text{H}_2\text{O}_2$  and acetic acid was then removed by washing with distilled water. The oxidized material was then separated from nonoxidized material by liquid chromatography. (4) The sulfones were then reduced back to thio-



**Figure 3.** Dual detector capillary gas chromatogram of one-ring aromatic fraction from argentation LC: column, 40  $\times$  0.4 mm i.d. Pyrex; 0.5  $\mu\text{m}$  thickness OV-101; temperature program 70–235  $^{\circ}\text{C}$  at 6  $^{\circ}\text{C}/\text{min}$ ; (a) (lower trace) flame photometric detector (FPD) at  $10^{-7}$  AFS square root circuit applied, (b) (upper trace) flame ionization detector (FID) at  $16 \times 10^{-11}$  AFS.

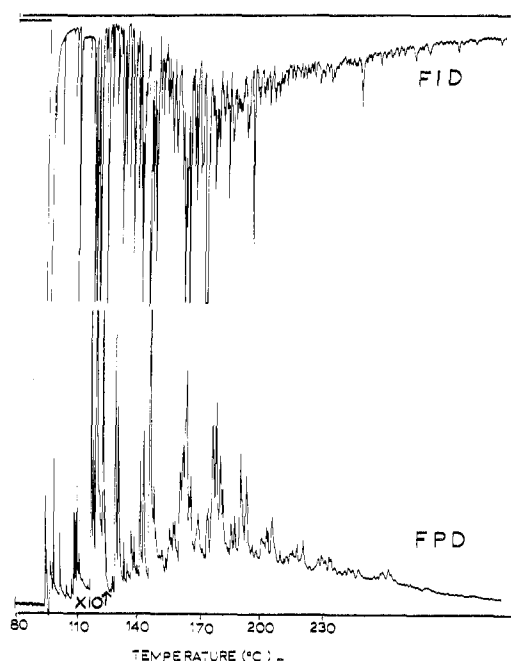


**Figure 4.** Gas chromatogram of one-ring thiophenic fraction from argentation LC, column and conditions as in Figure 3: (a) (lower trace) FPD at  $10^{-7}$  AFS, (b) (upper trace) FID at  $4 \times 10^{-11}$  AFS.

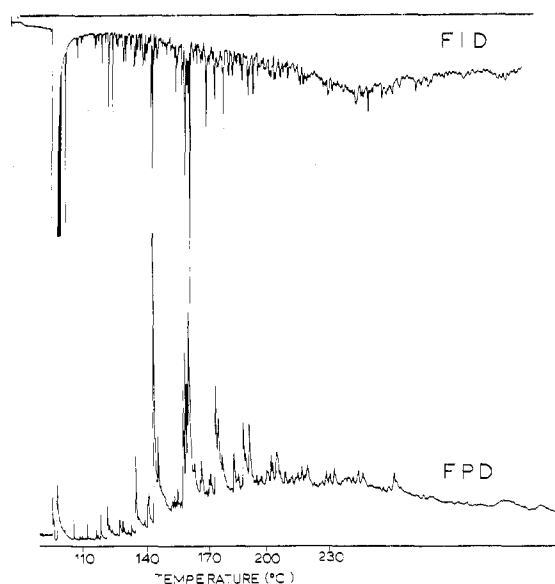


**Figure 5.** Flame photometric detection chromatograms of (a) one-ring thiophenic fraction and (b) one-ring aromatic fraction from argentation LC. Column and conditions are the same as those given in Figure 3.

phenic compounds by adding the sulfone solution over a period of 1 h to a refluxing suspension of  $\text{LiAlH}_4$  in ether. Refluxing was then continued for 2 h and excess  $\text{LiAlH}_4$  decomposed by the



**Figure 6.** Gas chromatogram of two-ring aromatic fraction from argentation LC, column as Figure 3, temperature program 80–235 °C at 6 °C/min: (a) (lower trace) FPD at  $10^{-7}$  AFS and  $10^{-8}$  AFS as noted; (b) (upper trace) FID at  $8 \times 10^{-11}$  AFS.

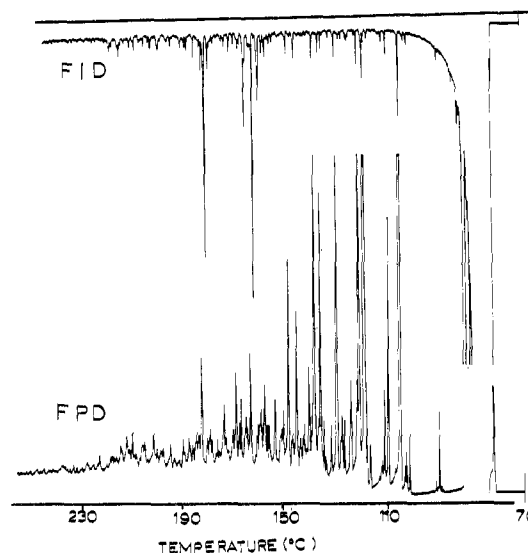


**Figure 7.** Gas chromatogram of two-ring thiophenic fraction from argentation LC, column and conditions as in Figure 6: (a) (lower trace) FPD at  $10^{-7}$  AFS, (b) (upper trace) FID at  $4 \times 10^{-11}$  AFS.

addition of water. (5) The thiophenic compounds were then separated from the polar compounds, remaining after reduction, by liquid chromatography on silica. A capillary chromatogram with flame ionization and flame photometric detectors was run of this fraction (Figure 8).

## RESULTS AND DISCUSSION

The isolation of thiophenic compounds required three liquid chromatographic steps for each fraction, the first two using the same silica stationary phase. The second step was carried out to ensure that no two-ring aromatics were present in the one-ring fraction and no three-ring aromatics were present in the two-ring fraction and also to ensure that no alkenes were present in the one-ring fraction. If two-ring aromatics or alkenes were present in the one-ring fraction they could contaminate the thiophene fraction on carrying out the final



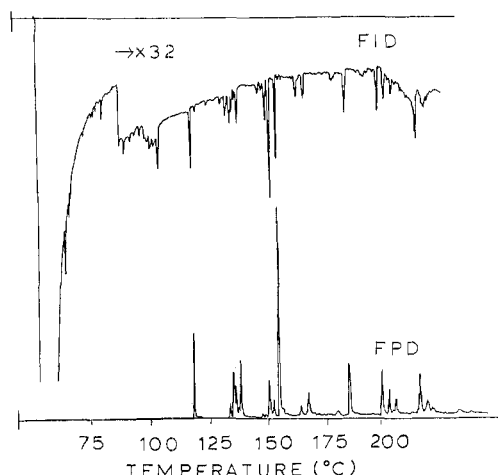
**Figure 8.** Gas chromatogram of thiophenic compounds extracted from in situ shale oil by 90%  $H_2SO_4$ , column and conditions as in Figure 3: (a) (lower trace) FPD at  $5 \times 10^{-8}$  AFS, no square root circuit applied; (b) (upper trace) FID at  $8 \times 10^{-11}$  AFS.

separation by argentation chromatography. Three ring-aromatics would contaminate the benzothiophene fraction in the final step. When the two-ring fraction was rechromatographed on silica, the cut points were selected to ensure no three-ring compounds were collected, but there was no concern about one-ring aromatics as these would be eliminated in the final step.

The capillary chromatogram of the one-ring thiophene fraction shows that most of the peaks contain sulfur (Figure 4), the majority of non-sulfur compounds being found at the beginning of the chromatogram. Comparison with the chromatogram of whole one-ring aromatics (Figure 3) shows a high degree of enrichment in sulfur. A direct comparison of sulfur specific detection of the one-ring thiophene and one-ring aromatic fractions is made in Figure 5, the lower trace (b) of the latter being acquired at a sample level four times that of the former (a). The fingerprint of sulfur compounds in these two chromatograms is not identical but is similar enough for the pattern to be recognized. The differences are attributed to an apparent loss of some sulfur compounds in the last liquid chromatographic separation and also to different gas chromatographic behavior in the absence of a relatively large amount of aromatics.

The capillary chromatograms of the two-ring fractions show that the benzothiophenes were collected essentially unaltered (Figures 6 and 7). The compounds eluting before benzothiophene in the whole two-ring fraction (Figure 6) are one-ring thiophenic compounds that should not be found in the final fraction. The benzothiophene fraction has more contamination by non-sulfur compounds than does the one-ring thiophene fraction, but by comparison of the ratio of peak heights on the FID for naphthalene and benzothiophene, an enrichment by a factor of about 16 was found. The homologous series of peaks present in this fraction suggests benzothiophenes with up to eight carbons attached are present.

The chromatogram of thiophenes obtained by extraction shows that the lower molecular weight compounds are recovered efficiently although a few compounds are discriminated against (Figure 8). As the molecular weight increases the recovery decreases due to the decreasing solubility of the thiophenes in sulfuric acid, due to long alkyl chains present, even if sulfonated. If the concentration of sulfuric acid is increased, then higher molecular weight thiophenes may be extracted and even benzothiophenes will be extracted, but



**Figure 9.** Gas chromatogram of thiophenic compounds isolated from in situ shale oil by oxidation-reduction scheme, column as in Figure 3, temperature program 50–220 °C at 8 °C/min: (a) (lower trace) FPD at  $10^{-8}$  AFS, (b) (lower trace) FID at  $64 \times 10^{-12}$  AFS.

alkylation will take place and the thiophene recovery will actually decrease.

A thiophene-rich fraction was obtained by the oxidation-reduction procedure, but the recovery was low and there was apparently a high level of discrimination (Figure 9). The procedure is lengthy and complicated by comparison with argentation chromatography, and while it might be made more effective it was felt the simpler argentation procedure was advantageous.

The one-ring thiophenes were almost completely separated from non-thiophenes and the benzothiophenes enriched by about 96% in comparison to naphthalenes. This was done without any chemical reaction so there was no danger of

compounds being chemically altered. The benzothiophenes were recovered with essentially no discrimination and the thiophenes were recovered with a small degree of discrimination.

The ultimate goal of this research was to provide a simple means of recovering from shale oil thiophene fractions sufficiently enriched to allow identification of individual isomers by capillary gas chromatography/mass spectrometry.

This study was restricted to the isolation of one-ring and two-ring thiophenes as shale oil has greater concentrations of one-ring thiophenes with lower amounts of two-ring thiophenes and even lower amounts of higher ring number thiophenes. This procedure could be extended to isolation of thiophenes with higher numbers of aromatic rings by allowing longer retention on the third liquid chromatographic step or by using a mobile phase of higher polarity.

**Registry No.** Silver nitrate, 7761-88-8.

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## Laser Modulated Electron Capture Detection for Gas Chromatography

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Three distinct mechanisms have been demonstrated for laser modulated electron capture detection wherein the sensitivity of electron capture detection is combined with the selectivity of absorption spectrometry. In the first mechanism, direct vibrational excitation, a vibrationally excited population is formed by absorption of laser radiation. This vibrationally excited population has a different electron capture cross section than the ground state. In the second mechanism, bulk gas heating, the temperature within the cells is modulated by absorption of laser light by some molecule within the cell followed by radiationless relaxation. The temperature variation modulates the electron capture cross section of the absorbing molecule or some other molecule within the cell. In the third mechanism, photodetachment, absorption of a photon of energy greater than the ionization potential of an ion formed in the electron capture process results in the liberation of an electron.

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In gas chromatography, the most selective detectors employed are those which provide data of sufficient dimensionality to allow identification of eluted species (1). Information from these multidimensional detectors may also be used for resolution of overlapped components (2). An additional class of gas chromatographic detectors are referred to as semiselective. They provide one-dimensional data but only have high sensitivity for a limited group of molecules. This restricted sensitivity is of value when a complex mixture must be analyzed for components from the limited group. However, neither identification of eluted compounds nor resolution of overlapped peaks is possible from a single chromatogram by using a semiselective detector. Hence, it would be advantageous to increase the selectivity of this detector by a method which provides data of increased dimensionality. In this paper, we demonstrate three distinct mechanisms for the laser modulation of an electron capture detector's response wherein spectroscopic information is combined with electron capture detection.

The electron capture detector is a popular semiselective gas chromatographic detector of high sensitivity. It relies upon