

Separation of a Quinolone-Enriched Fraction From SHRP Asphalts

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ABSTRACT

A method originally designed to separate a carboxylic acid concentrate from asphalts has been modified so that quinolone concentrates also can be extracted from asphalts. The quinolone concentrates are high in molecular weight and contain large amounts of oxygen, nitrogen, and sulfur. Infrared spectra of the quinolone concentrates are similar to those obtained from petroleum distillates by a multistep separation scheme. Some of the sulfur atoms associated with the quinolones are readily oxidizable.

INTRODUCTION

The rheological properties of asphalts are believed to be influenced by associative interactions of polar, polyfunctional molecules in a non-polar hydrocarbon matrix (1). The identities of some of the functional groups involved in associative interactions in asphalts are carboxylic acids, phenols, pyridines, and quinolones. Other heteroatom-containing functional groups are probably involved. Compounds containing one or more of these groups have been identified in petroleum.

Asphalts contain non-volatile constituents of petroleum, which are also the largest and most polar components. The isolation of individual compounds, and even compound types, from asphalts for special study is a formidable task. This is because of the existence of large numbers of multifunctional compounds and extended methylene homologues in these residua.

As mentioned above, quinolones are one of a number of polar, associating species in asphalts, and thus may be major viscosity-controlling components of asphalts. Therefore the isolation and study of these compounds would be of interest. Quinolones were identified in petroleum by Copelin (2), who concentrated them from a gas oil fraction using a separation scheme involving hydrochloric acid treatment, ion exchange separation, and alumina chromatography. The quinolone fraction was characterized by a prominent peak at 1655 cm⁻¹

in the infrared spectrum. Based on a comparison with infrared spectra of model compounds, Copelin deduced that the quinolones were 2-quinolones and not 4-quinolones. Snyder et al. (3) detected the same materials in gas oil fractions of other crude oils. Petersen et al. (4) observed the 1655 cm^{-1} peak in the infrared spectrum of asphalts, and assigned the peak to 2-quinolones. These workers observed that asphalts contain molecules that are too large to be typical pyridones. They showed that the 1655 cm^{-1} peak was unaffected by treatments with hydrochloric acid or sodium hydroxide solutions, but disappeared when asphalts were treated with hexamethyldisilazane, which reacts with the enol form of the quinolones. Lithium aluminum hydride treatment of asphalts also resulted in loss of the 1655 cm^{-1} peak in the infrared spectrum of treated asphalts. In this reaction, carbonyl groups are reduced.

The work of Petersen et al. (4) identifies 2-quinolones as probable constituents of asphalts. The complex separation schemes of Copelin (2) and Snyder et al. (3) are not easily applied to asphalts, due to irreversible adsorption of asphalt components on alumina and difficulties in extracting asphalts with acids. However, separation of highly polar carboxylic acids from asphalts using base-treated silica gels have been reported by Ramljak et al. (5). In this report, a modification of the Ramljak et al. (5) separation scheme was developed as a rapid method for the concentration of 2-quinolones from asphalts.

EXPERIMENTAL

Asphalts used in this study were obtained from the Materials Reference Library of the Strategic Highway Research Program (SHRP).

The modified silica gel was prepared according to the procedure of Ramljak et al. (5). A typical preparation consists of slurring 400 g silicic acid (BIO-SIL A, 100-200 mesh, Bio-Rad Labs) in 4.0 L dichloromethane and then adding in portions a solution of 40 g potassium hydroxide (J.T. Baker) in 800 mL 2-propanol (J.T. Baker). After stirring the mixture for 30 minutes, it was poured onto a Buchner funnel having a sintered glass disc (C porosity) and washed with another 500 mL 2-propanol. Then the filter cake was washed with dichloromethane to remove alcohol.

The isolation of carboxylic acid concentrates was performed according to the procedure of Ramljak et al. (5), except that chromatographic columns were employed in place of extractors. In order to successfully concentrate quinolones, carboxylic acids must be removed from asphalts first. A flow sheet for the separation of asphalts into carboxylic acid concentrate, quinoline concentrates, and quinolone-free material is illustrated in Figure 1.

After the adsorption of the carboxylic acid concentrate on the modified silica gel, chloroform was removed from the eluted fraction on a rotary evaporator. The flask containing the chloroform solution was immersed in a hot water bath, and a vacuum of about 2 Torr was applied to remove the last of the chloroform. Approximately 20 g of this eluted fraction, which comprises 95% or more of the parent asphalt, was dissolved in 80 mL dichloromethane (Omni Solv, HPLC Grade). This solvent was poured onto the top of a column 2.5 cm i.d. x 100 cm filled about three-fourths full with modified silica gel. A small layer of sand was placed in the bottom of the column before adding the modified silica gel. In filling the

column, dichloromethane was poured into the column and then the gel slurry was added while the column stopcock was opened. Gel was added to fill the column with a well-packed bed to the 75 cm level. Flow rates for the separation were set by opening the column stopcock fully. About 4.0 L dichloromethane were required to complete the separation. Eluates were divested of solvent as described above, and designated the quinolone-free fraction. The modified silica gel and adsorbate were transferred to a Buchner funnel (M porosity) and a mixture of 20% formic acid (Aldrich Chemical Co.) and 80% dichloromethane was poured onto it to desorb the quinolone concentrate. These eluates were dried on a rotary evaporator as described above and then redissolved in dichloromethane and again filtered to remove potassium silicate associated with the quinolone concentrate. It may be necessary to use benzene as solvent for the quinolone concentrate in order to remove residual formic acid on the rotary evaporator.

Infrared Spectra of films of the quinolone concentrates were obtained on a Perkin-Elmer 983 Spectrophotometer. Molecular weights were determined by vapor phase osmometry using ASTM method D 2503 using toluene (60°C; 140°F) as solvent.

Elemental analyses were performed by the Analytical Research Division of Western Research Institute using standard methods.

RESULTS AND DISCUSSION

The Strategic Highway Research Program (SHRP) has designated eight asphalts for special study. Four of these asphalts, AAA-1, AAD-1, AAG-1, and AAK-1 were separated on modified silica gel to collect carboxylic acid concentrates and quinolone concentrates. The asphalts contain about 0.01 to 0.02 M/L of quinolones (Table 1), based on the infrared functional group analysis of Petersen (6). Recoveries of material range from 96-98% in each step, so that the two concentrates are small in amount compared with the whole asphalts. The replication of the separation for AAK-1, using two different operators was not good, but this does not affect the utility of the method in concentrating quinolones.

Elemental analyses and number-average molecular weights of the parent asphalts and the quinolone concentrates (Table 2) show that in each case, the quinolone concentrates are more aromatic and contain more nitrogen, oxygen, and sulfur than the parent asphalts. Large sulfur contents in quinolone concentrates in distillates were observed by Copelin (2), who claimed that substantial amounts of thioquinolines were present in the materials he studied. Number-average molecular weight (\bar{M}_n) values of the asphalt quinolone concentrates determined by vapor phase osmometry (VPO) in toluene at 60°C (140°F) are much higher than those reported by Copelin (2), which were about 300 Daltons. These materials were derived from 340-450°C (644-842°F) distillates. Evidently quinolones occur in crude oils over a large molecular weight range. The \bar{M}_n value of the quinoline concentrate of AAK-1 also was determined by VPO in pyridine at 60°C (140°F). This value is about half that of the \bar{M}_n value determined in toluene, which demonstrates that quinolones have strong tendencies to associate. In contrast, \bar{M}_n values for whole asphalts are similar in pyridine and toluene.

Infrared spectra of quinolone concentrates of asphalts are shown in Figures 2-5. Copelin (2) identified the peak at about 1650 cm^{-1} as the carbonyl peak of the quinolone amide

function. This peak is prominent in Figures 2-5. The quinolone concentrate of AAG-1 (Figure 4) is contaminated by some carboxylic acids, as shown by the presence of a peak at about 1705 cm^{-1} . No peak corresponding to thioquinolones is observed in any of the asphalt quinolone concentrates. Instead, large sulfoxide peaks ($\sim 1020\text{ cm}^{-1}$) are observed. The quinolones contain (or possibly are associated with) readily oxidizable sulfur functionalities.

In another study, the quinolone concentrate of AAD-1 was further separated into fractions using a column of modified silica gel (7). Retention times of most of the components of the concentrates were similar to those of model compounds having 2-pyridone or 2-quinolone structural units.

It is possible to collect both carboxylic acids and quinolones by eliminating the initial step and directly separating the original asphalt on activated silica with dichloromethane. Yield of the combination of quinolones and acids for AAA-1 is 4.8 wt %.

CONCLUSIONS

Quinolones can be concentrated from four asphalts by a modification of a method originally developed to concentrate carboxylic acids from asphalts. The quinolone concentrates are characterized by a prominent peak in their infrared spectra at about 1650 cm^{-1} . Nitrogen, oxygen, and sulfur concentrations in these materials also are high. The sulfur functionality associated with the quinolone concentrates is readily oxidizable. The number-average molecular weights of the quinolone concentrates are approximately twice those of the parent asphalts.

The method used to concentrate quinolones from asphalts is rapid and simple and it presumably can be extended to other petroleum-derived fractions. It is estimated that quinolones are concentrated about ten- to twenty-fold by this method based on concentrations of these compounds in parent asphalts. The concentrates can be further purified by other separation methods (7).

DISCLAIMER

The contents of this report reflect the views of the authors, who are solely responsible for the facts and accuracy of the data presented. The contents do not necessarily reflect the official view or policies of the Strategic Highway Research Program (SHRP) or SHRP's sponsors. The results reported here are not necessarily in agreement with the results of other SHRP research activities. They are reported to stimulate review and discussion within the research community. This report does not constitute a standard, specification, or regulation. Mention of specific brands of materials does not imply endorsement by SHRP or Western Research Institute.

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TABLE 1
Yields of Quinolone Concentrates from Four Asphalts

Asphalt	Yield of Quinolone Concentrate, wt % of Asphalt
AAA-1	2.6
AAD-1	6.7
AAG-1	2.7
AAK-1	5.0; 6.8

TABLE 2

Elemental Analyses and Number-Average Molecular Weights of Four Asphalts and Their Quinolone Concentrates

Substrate	Element, wt %					H/C	\bar{M}_n (Daltons) toluene pyridine
	C	H	N	O	S		
Asphalt AAA-1	84.2	10.5	0.48	0.6	5.5	1.48	790
AAA-1 Quinolone Concentrate	-	-	0.90	2.8	8.4	-	1,400
Asphalt AAD-1	81.4	10.8	0.77	0.9	6.9	1.58	700
AAD-1 Quinolone Concentrate	78.5	9.3	1.50	2.9	8.6	1.41	1,500
Asphalt AAG-1	85.6	10.5	1.10	1.1	1.3	1.46	710
AAG-1 Quinolone Concentrate	-	-	1.57	3.6	1.9	-	1,360
Asphalt AAK-1	80.7	10.2	0.71	0.8	6.5	1.51	860
AAK-1 Quinolone Concentrate, run 1	79.6	8.5	1.20	2.7	7.2	1.27	1,800
AAK-1 Quinolone Concentrate, run 2 ¹	76.6/76.3	9.0/9.0	1.1/1.2	3.9/3.9	8.3/8.4	1.40	2,172
							1,113

¹ Replicate elemental analyses were performed for this sample

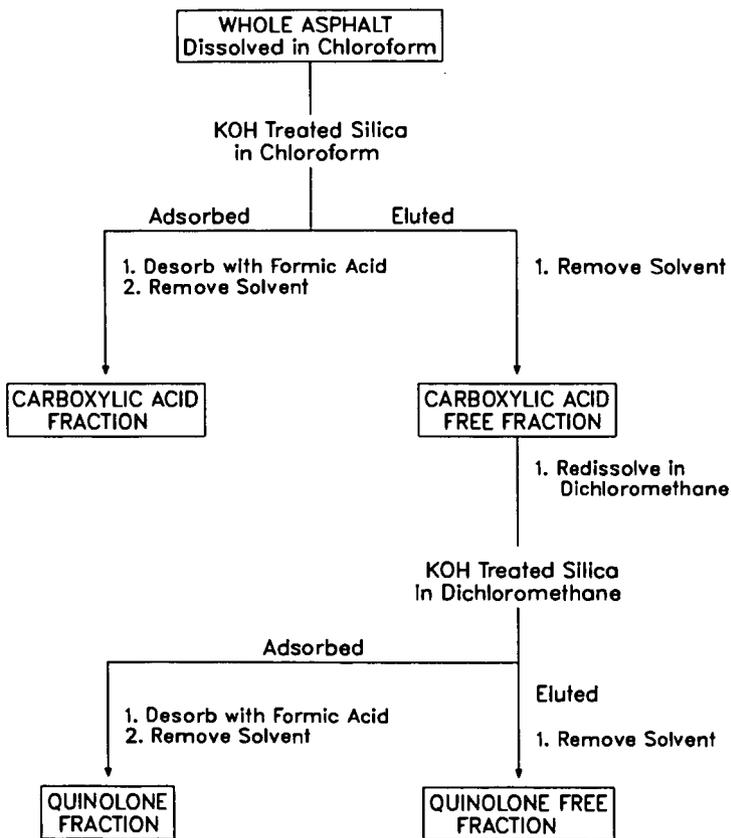


Figure 1. Flow Scheme for the Isolation of Quinolones

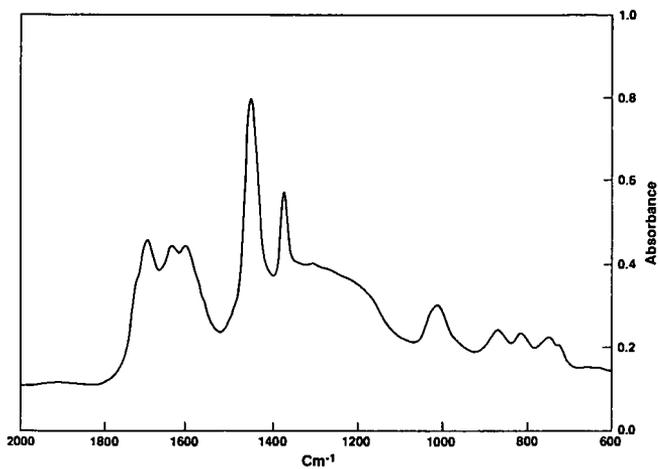


Figure 4. Quinolone Concentrate from AAG-1

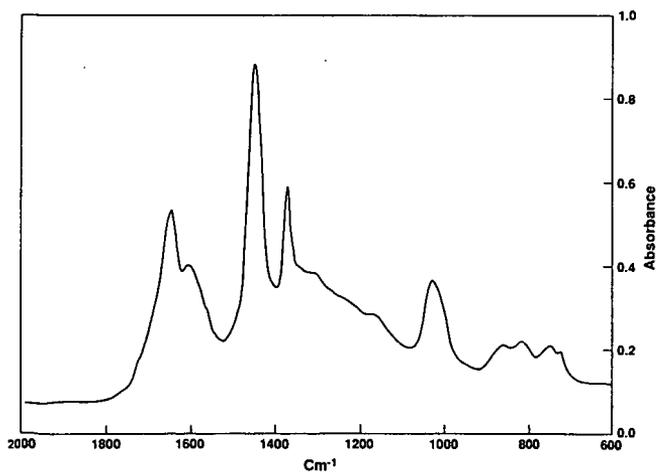


Figure 5. Quinolone Concentrate from AAK-1

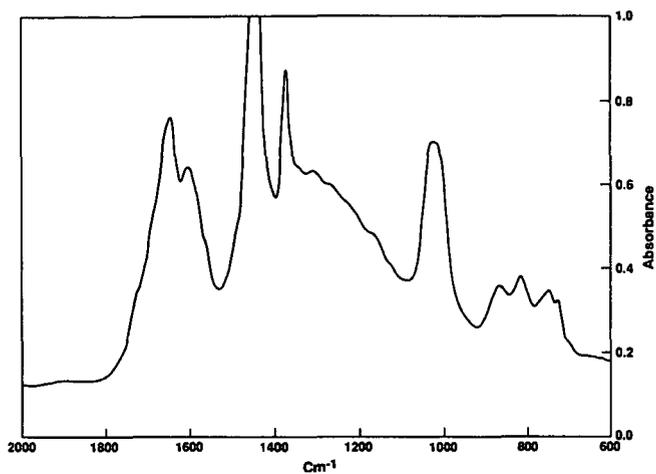


Figure 2. Quinolone Concentrate from AAA-1

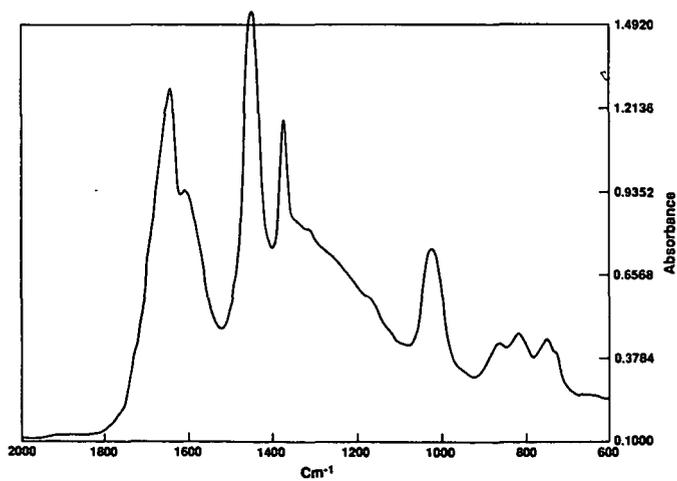


Figure 3. Quinolone Concentrate from AAD-1