

Separation of Sulfur Compounds in Straight-Run Naphtha

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Sulfur-containing compounds in straight-run naphtha were separated from coexisting hydrocarbons by means of open-column chromatography. Elution with hexane was continued after outflow of saturated hydrocarbons in the original sample, and aromatic hydrocarbons eluted gradually without any accompanying sulfur-containing compounds. When aromatic hydrocarbons ceased to be observed in the effluent, hexane was changed to benzene. A mixture of thiophenes, disulfides, and thiols then began to elute, followed ultimately by a mixture of sulfides and thiacycloalkanes. The obtained sulfur-containing compounds contained very small amounts of hydrocarbons other than the elution solvent, and their mass spectra could be observed by means of gas chromatograph-mass spectrometry.

For environmental protection reasons, the production of low-sulfur fuel oils is becoming increasingly important. Structural analysis of sulfur-containing compounds is an effective technique for identifying less reactive sulfur species to assist hydrodesulfurization (HDS) and for designing HDS operating conditions as well as HDS catalysts. Light fuel oils, such as gasoline and naphtha, usually contain very small amounts of sulfur-containing compounds, suggesting that, to identify the molecular weights and mass spectra of individual sulfur species, it is important to separate them from coexisting hydrocarbons. Various methods to separate the sulfur species have been reported. Thiols, sulfides, and disulfides have been separated from aromatic hydrocarbons by ligand-exchange thin-layer chromatography on mercury-loaded silica gel, but the thiols are irreversibly adsorbed and cannot be recovered.[1,2] Sulfides and thiacycloalkanes have been separated, and good recoveries have been obtained by liquid–liquid chromatography with an aqueous stationary phase consisting of concentrated zinc chloride.[3] Sulfur species have been oxidized to sulfones, separated from the hydrocarbons, and subsequently reduced to the starting material.[4] Sulfur species present in naphtha in fairly large amounts have been separated by gradient elution liquid chromatography on a silica gel alumina column; however, some aromatic hydrocarbons have been found in the sulfur compound concentrate.[5] Up to now, to the best of our knowledge, no method has been developed for analyzing all of the sulfur species in light fuel oil. This report describes a procedure for separating all of the sulfur-containing compounds from coexisting hydrocarbons by chromatography on a silica-gel column.

Experimental

Materials. The feedstock used in this investigation was petroleum straight-run naphtha. Its properties are shown in Table 1. Hexane, benzene, dodecane, tetralin, and methanol, used as eluents, were commercially available special-grade reagents. A number of commercial reagents and synthesized compounds were used to identify the sulfur species. The commercial reagents used were thiophene, 2-ethylthiophene, 1- and 2-butanethiol, 1-pentanethiol, cyclohexanethiol, diethylsulfide, butyl ethyl sulfide, dimethyl disulfide, diethyl disulfide, and tetrahydrothiophene. Tetrahydro-2-methylthiophene, tetrahydro-3-methylthiophene, tetrahydro-3-ethylthiophene, tetrahydro-2,3-dimethylthiophene, and tetrahydro-2,5-dimethylthiophene were prepared by hydrogenation of corresponding thiophenes on a nickel–molybdenum/alumina catalyst.[6,7]

Table 1. Properties of Straight-Run Naphtha

	Composition/vol %
Straight paraffins	33.5
Branched paraffins	30.7
Naphthenes	22.5
Olefins	0.16
Aromatics	13.2
Total sulfur/S-ppm	242
Density/g cm^{-3} (at 15 °C)	0.735
Distillation temperature/°C	
IBP	89.5
10%	97.6
50%	119.0
90%	145.7
95%	151.1
FBP	156.4

Chromatographic Separation System. The column was a glass tube with an i.d. of 0.90 cm and a length of 100 cm, packed with 25 g of Wakogel C-200 (75–150 μL) silica gel after calcination at 200 °C for 24 h. The bottom end of the column was plugged with glass wool.

Naphtha (10 mL) was poured on the top of the column, and hexane was gradually passed though the column. The eluent was changed from hexane to benzene after no aromatic hydrocarbons were detectable in the effluent. Lastly, a benzene–methanol mixture (1:1) was passed through. The fractions of the column effluent were collected in glass sample tubes 1.5 mL at a time. A similar operation used dodecane and tetralin, instead of hexane and benzene, to identify low-boiling-point sulfur-containing compounds.

Gas Chromatography. The effluents were identified using a gas chromatograph (HP 6890N) with a flame-ionization detector (GC-FID), a gas chromatograph (HP 1530A) with a chemiluminescence sulfur detector (Sievers 355, GC-SCD), and a gas chro-

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Table 2. Operating Conditions of Gas Chromatography

GC-SCD	
Detector	Chemiluminescence sulfur detector
Sample injector temperature	250 °C
Column stationary phase	HP-1 (Crosslinked methyl siloxane)
Column dimensions	30 m × 0.25 mm × 0.25 μm film
Liquid sample volume	1 μL
Split ratio	1:26.7
Column flow	He, 2.2 mL min^{-1}
Oven temperature program	
Initial temperature	50 °C for 5 min
Program temperature	5 °C min^{-1}
Final temperature	250 °C, 15 min
GC-FID	
Detector	Flame-ionization detector
Sample injector temperature	250 °C
Column stationary phase	HP-1 (Crosslinked methyl siloxane)
Column dimensions	30 m × 2.25 mm × 0.25 μm film
Liquid sample volume	1 μL
Split ratio	1:26.7
Column flow	He, 2.2 mL min^{-1}
Oven temperature program	
Initial temperature	50 °C for 5 min
Program temperature	5 °C min^{-1}
Final temperature	250 °C, 15 min
GC-MSD	
Detector	Mass spectrometer
Ionization voltage	70 eV
Sample injector temperature	280 °C
Column stationary phase	Ultra 1 (Crosslinked methyl siloxane)
Column dimensions	50 m × 0.20 mm × 0.11 μm film
Liquid sample volume	1 μL
Split ratio	1:60
Column flow	He, 1 mL min
Oven temperature program	
Initial temperature	50 °C for 1 min
Program temperature	5 °C min^{-1}
Final temperature	300 °C, 9 min

matograph (HP 6890) with a mass spectrometer (HP 5973, GC-MSD). The chromatographic conditions are summarized in Table 2.

Results and Discussion

Figure 1 shows the elution of hydrocarbons and sulfur-containing compounds in relation to the fraction sample number. The *y*-axis refers to the concentrations of alkanes, cycloalkanes, alkylbenzenes, and sulfur species relative to the fraction with maximum concentrations. Alkanes and cycloalkanes were eluted in fraction (Fr.) 1 to 8 with no accompanying

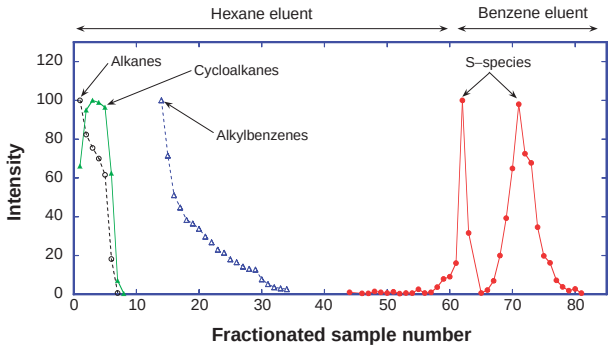

Fig. 1. Open-column chromatographic separation of straight-run naphtha.

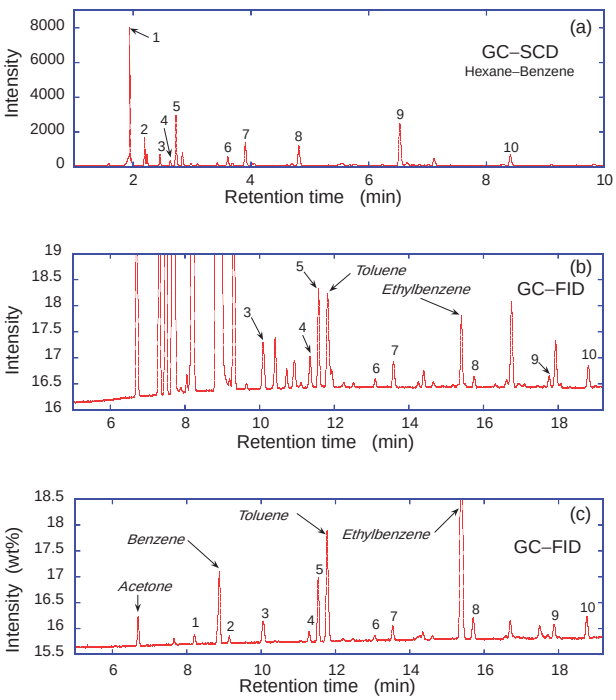

Fig. 2. GC-SCD and GC-FID chromatograms of Fractions 62. (a), (b); hexane/benzene eluent, (c); dodecane/tetralin eluent.

aromatic hydrocarbons or sulfur-containing compounds. Aromatic hydrocarbons were present in Fr. 12, after which their content decreased gradually. Almost no sulfur-containing compounds were eluted when hexane was used as the eluent. Hexane was changed to benzene at Fr. 61, after which numerous sulfur species were eluted. The eluted sulfur species showed two maxima at fractions 62 and 71. Elution with a benzene–methanol mixture was started at Fr. 85, and no hydrocarbons or sulfur species were observed in this fraction.

To analyze the mass spectra of sulfur-containing compounds, the amounts of hydrocarbons need to be lower than those of sulfur species. The GC-SCD chromatogram and GC-FID chromatogram of Fr. 62 when hexane and benzene were used as eluents are shown in Figs. 2a and 2b respectively. The GC-SCD chromatogram (Fig. 2a) had more than thirty peaks with ten major peaks counted. The GC-FID chromato-

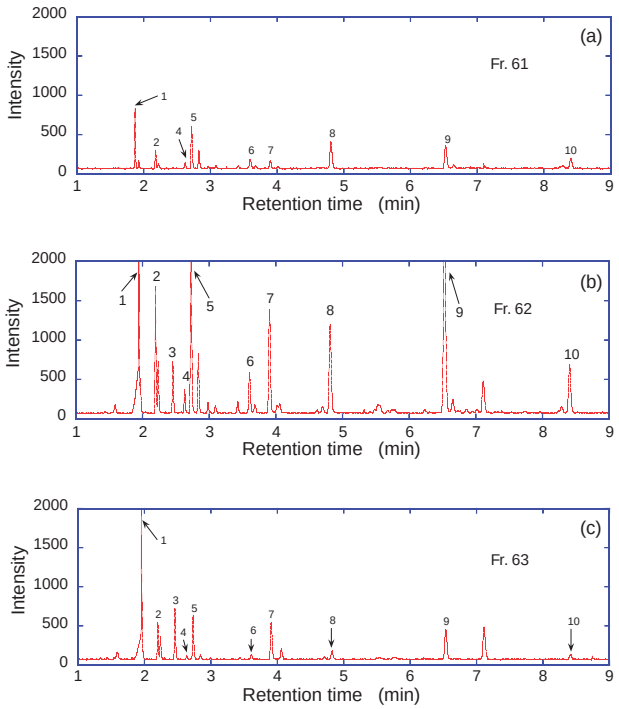

Fig. 3. GC-SCD chromatograms of Fractions 61, 62, and 63.

gram (Fig. 2b) shows that sulfur species with retention times of longer than ten minutes can be assigned by using GC-MS analysis, although sulfur species with retention times shorter than ten minutes are difficult to assign by interruption of impurities included in the eluents. The GC-FID chromatogram of Fr. 62 for elution with dodecane and tetralin is presented in Fig. 2c. This figure shows that sulfur species with a retention time of shorter than ten minutes can be assigned.

The GC-SCD chromatograms of Frs. 61, 62, and 63 are compared in Figs. 3a, 3b, and 3c, and the results of the assignment are listed in Table 3. Peaks 3, 8, and 10 were determined to be dimethyl disulfide, ethyl methyl disulfide, and diethyl disulfide, respectively, and compounds with more carbon atoms appear in earlier fraction. Peaks 2, 4, 5, and 7 were 1-butanethiol, 3-methyl-2-butanethiol, 2-pentanethiol, and 1-pentanethiol, respectively. Peak 1 was assigned to thiophene and 2-butanethiol. Fraction 61 had a large quantity of thiophene, and Fr. 63 had a large amount of 2-butanethiol.

The GC-SCD chromatograms of Frs. 71, 72, and 74 are presented in Fig. 4, and the major 19 peaks are numbered. These sulfur species were assigned by GC-MS using a mass spectra library and are presented in Table 3. In these fractions, tetrahydrothiophenes, tetrahydrothiopyrans, and cyclohexanethiols were the major compounds, and sulfides were minor components. Peaks 24 and 28 were assigned to tetrahydro-C3-thiophene or tetrahydro-C2-thiopyran; however they could not distinguished. Peaks 11, 12, 13, and 14 were determined to be methyl isopropyl sulfide, diethylsulfide, methyl propyl sulfide, and ethyl isopropyl sulfide, respectively.

As mentioned above, all the sulfur species in straight-run naphtha could be concentrated. However, the eluted sulfur species showed two maxima, and thiols appeared in earlier fraction. In addition, sulfides appeared in the latter fraction. We

Table 3. Sulfur Species Included in Fr. 62 and Fr. 72

Peak No.	Compound
1	Thiophene, 2-Butanethiol
2	1-Butanethiol
3	Dimethyl disulfide
4	3-Methyl-2-butanethiol
5	2-Pentanethiol
6	Hexanethiol isomer
7	1-Pentanethiol
8	Ethyl methyl disulfide, 3-Methyl-3-pentanethiol
9	2-Ethylthiophene, 3-Hexanethiol
10	Diethyl disulfide
11	Methyl isopropyl sulfide
12	Diethyl sulfide
13	Methyl propyl sulfide
14	Ethyl isopropyl sulfide
15	Ethyl isobutyl sulfide, Tetrahydrothiophene
16	Tetrahydro-2-methylthiophene
17	Tetrahydro-3-methylthiophene
18	Tetrahydrothiopyran
19	Tetrahydro-*trans*-2,5-dimethylthiophene
20	Tetrahydro-*cis*-2,5-dimethylthiophene
21	Tetrahydromethylthiopyran, Butyl ethyl sulfide
22	Tetrahydromethylthiopyran
23	Tetrahydromethylthiopyran
24	Tetrahydro-C3-thiophene/Tetrahydro-C2-thiopyran
25	Cyclohexanethiol
26	Tetrahydro-*cis*-2,3-dimethylthiophene
27	Tetrahydro-*trans*-2,3-dimethylthiophene
28	Tetrahydro-C3-thiophene/Tetrahydro-C2-thiopyran
29	Tetrahydro-3-ethylthiophene

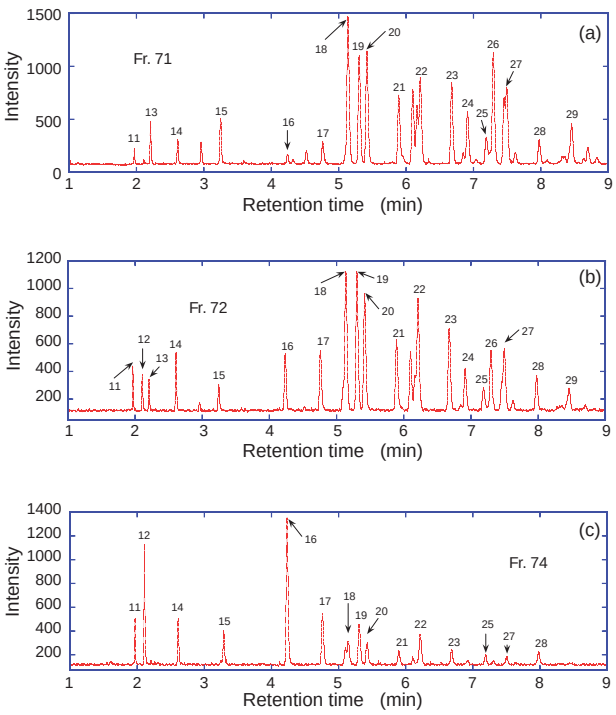

Fig. 4. GC-SCD chromatograms of Fractions 71, 72, and 74.

could not explain the reason why thiols elute earlier than sulfides. In this study, 25 g of silica gel were used for treating of 10 mL of naphtha and about 85 mL of hexane were passed through the column to separate aromatic compounds from sulfur species. The conditions depend on samples, especially the amount and the composition of the aromatic fraction. Because of low sulfur content of straight-run naphtha, a considerable amount of feed naphtha was needed in order to assign the sulfur species after separation. The aromatic fraction in the feed should also act as an eluent for the sulfur species during elution in the column. Therefore, a fair amount of silica gel and hexane are needed to separate the sulfur species from aromatic compounds.

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