

Identification of Benzo[b]thiophene and its 2- and 3-Methyl Homologs in Wasson, Texas, Crude Oil

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THE SEPARATION and identification of sulfur compounds occurring in crude oils is part of the work of the Federal Bureau of Mines in cooperation with the American Petroleum Institute (API) Research Project 48 on the synthesis, properties, and identification of sulfur compounds. This paper reports the identification of benzo[b]thiophene (thianaphthene) and two of its homologs (2- and 3-methylbenzo[b]thiophene) in sulfur concentrates obtained from Wasson, Tex., crude oil distillates.

Birch and his coworkers have identified six individual alkylthiophenes in an acid sludge from a kerosine boiling-range distillate from mixed Iranian crude oils (1). However, to the authors' knowledge, only two individual dicyclic thiophenes have been reported in petroleum. These are benzo[b]thiophene, isolated by Richter, Williams, and Meisel (5) in Santa Maria Valley, California, crude oil, and 1,4,4-trimethyl-4,5,6,7-tetrahydrobenzo[c]thiophene (1,4,4-trimethyl-4,5,6,7-tetrahydroisothianaphthene), found by Birch and others, (2) in a kerosine-extract tar oil (boiling at about 250° C.) from Agha Jari crude oil. Six individual tricyclic and higher thiophenes have been identified in petroleum: 1,8-dimethyldibenzothiophene, found by Carruthers (3) in a 330° to 350° C. distillate from Kuwait crude oil, 1,2,6,7-tetramethyldibenzothiophene, 1,3,6,7-tetramethyldibenzothiophene, 1,3,6,8-tetramethyldibenzothiophene, 3-ethyl-6,8-dimethylnaphtho[1,2b] thiophene, and 9-thia-1,2-benzofluorene, reported by Carruthers and Douglas (4) in the same Kuwait crude oil. Identification of benzo[b] thiophene in a 200° to 250° C. fraction of

Wasson, Tex., crude oil and of 2- and 3-methylbenzo[b]thiophenes in a 220° to 225° C. distillate of the same crude oil is discussed herein. Although American Petroleum Institute Project 48 has identified thiophene and its two methyl homologs in another crude oil (7, 10) and has ample evidence from mass spectrometry (6, 8) that multiring thiophenes exist in Wasson crude oil, the benzo[b]thiophenes identified as described herein are the first definite compounds of this type that have been found during the Project's work with the Wasson oil.

PREPARATION OF CONCENTRATES

The 220° to 225° C. distillate, in which the methylbenzo[b]thiophenes were found, was obtained in a series of isothermal and fractional distillations as outlined in Figure 1. The all-glass, steam-heated, isothermal stripping unit previously described (8) was used to strip the distillate from the crude oil. The residence time of the residue in the heated zone in this equipment was less than 30 seconds. This mild treatment was designed to protect the sulfur compounds in the heavier portions of the crude oil from thermal breakdown. The distillates prepared from the crude oil then were fractionated in a 30-plate Oldershaw column, under reduced pressure to permit the desired separations to be made at relatively low pot temperatures. In general, pot temperatures were held below 100° C., although in the preparation of some of the higher boiling distillates it was necessary to go to temperatures as high as 162° C. for short periods of time. Frequent "stability" tests (heating

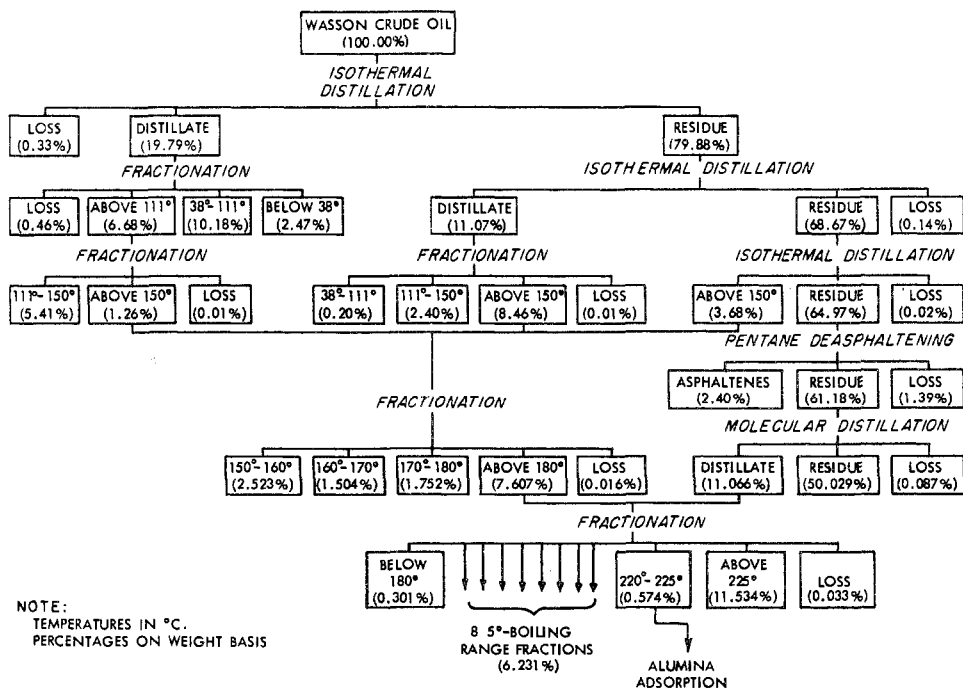


Figure 1. Processing of Wasson, Tex., crude oil

samples for 2.5-hour intervals at ascending temperature levels up to 205° C.) made on the distillates evidenced no breakdown of sulfur compounds. As indicated in Figure 1, the 220° to 225° C. distillate represented about 0.6 weight % of the original crude oil. Investigation of other fractions shown in the chart has resulted in the identification of 53 additional sulfur compounds (thiols and sulfides).

The 220° to 225° C. fraction (Figure 1) was percolated through H-41 alumina, of about 200-mesh, in a 12-mm. × 12.2-meter (40-foot) column having a volume of about 1350 ml. In this operation, a charge of 100 ml. of distillate was placed on top of the H-41 alumina and allowed to enter the column. After a small amount of the alumina was added as a "spacer," ethyl alcohol was added to the column to desorb the sample. As shown in Figure 2, three initial fractions totaling about 60 ml. of sulfur-free material were collected, followed by 26 fractions of about 1.5 ml. each. The final fraction (No. 27) consisted of material washed from the alcohol fractions emerging at the end of the percolation. In Figure 2, the drop in the sulfur content of the fractions coinciding with the rise in refractive index when 92% (fraction 20) of the charge had been eluted was caused almost entirely by the large quantity of naphthalenes (later identified as 1- and 2-methylnaphthalene) emerging at that point, but it also reflects a change in sulfur type.

A semiquantitative mass spectrometer-type analysis made on adsorption fractions 8 through 27 indicated that fraction 26 contained the highest concentration of methylbenzo[*b*]thiophenes (about 25%).

The 200° to 250° C. distillate, in which the benzo[*b*]thiophene was identified, was obtained from the crude oil by "topping" in several stages up to 300° C. in a manner essentially identical to that used to prepare the 220° to 225° C. distillate, again with precautions to prevent decomposition of the sulfur compounds. The 200° to 250° C. distillate was percolated through silica gel to effect a preliminary concentration of the sulfur compounds, and this concentrate then was treated (8) successively with NaOH and with sodium aminoethoxide to extract thiols and phenols. The 406-grams of thiol-free aromatic-sulfur compound concentrate, containing 2.25% of sulfur, was diluted with five volumes of pentane, filtered through a 15-foot × 2-inch column of H-41 alumina, and divided into 27 fractions as indicated in Figure 3.

Sulfur concentrate fractions, 19 to 26, from the alumina percolation of the 200° to 250° C. distillate were chilled in *n*-butane to remove solids (mostly naphthalenes), and the filtrates were treated with anhydrous HI at -78° C. to remove sulfides. The residues from this treatment were treated twice with trinitrobenzene to remove naphthalenes

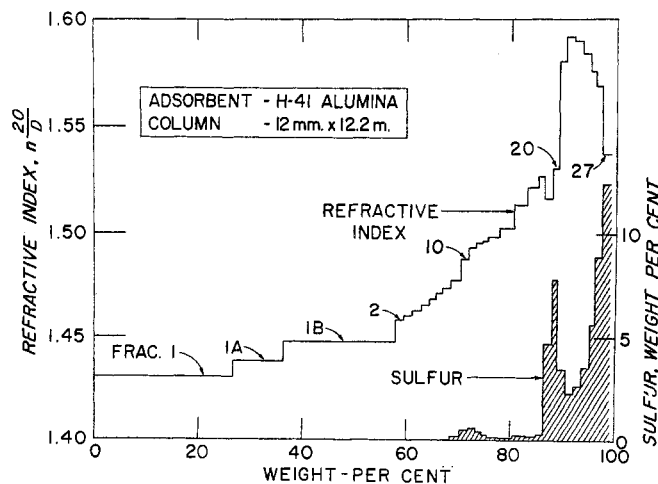


Figure 2. Adsorptogram of 220° to 225° C. Wasson distillate

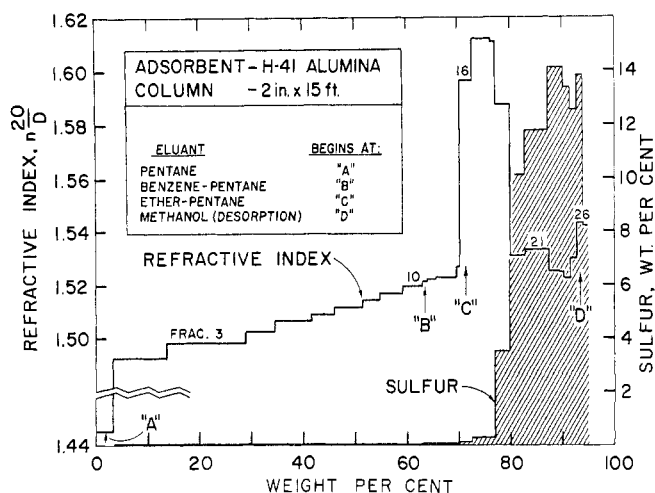


Figure 3. Adsorptogram of aromatic fraction of Wasson 200° to 250° C. distillate

and benzothiophenes as adducts, and the combined adducts were regenerated and distilled to separate the lowest boiling materials. The first fraction, containing predominantly naphthalene, was recrystallized from a butane-ethyl alcohol mixture and the filtrate was reserved for the identification of benzo[*b*]thiophene. The entire treatment is shown in Figure 4. Isolation and identification of benzo[*b*]thiophene in this distillate was but one object of the processing; as indicated in the figure, additional work on the various fractions is in progress.

ANALYSIS OF CONCENTRATES

All sulfur-containing fractions from the alumina percolation of the 220° to 225° C. concentrate (Figure 2) and the final filtrate from chemical treatment of the 200° to 250° C. concentrate (Figure 4) were analyzed by gas-liquid chromatography (Perkin-Elmer Model 154 with a 2-meter × 1/4-inch stainless steel column packed with 30- to 60-mesh firebrick impregnated with 25 weight % Dow-Corning 550 silicone oil. (Later G.L.C. work by the authors with Reoplex 400 and *m*-bis(*m*-phenoxy phenoxy)benzene as stationary phases showed good separations of methylbenzo[*b*]thiophenes from methylnaphthalenes.) The chromatograms of fraction 26, prepared from the 220° to 225° C. distillate, and of the final filtrate from the 200° to 250° C. concentrate are shown in Figure 5 (panels B and A, respectively) compared with the chromatograms of various dicyclic

Table I. Partial Mass Spectra of G.L.C. Fraction 2^a and of Pure Compounds

<i>m/e</i>	2-Methylbenzo[<i>b</i>]thiophene (1026 ^b)	2-Methylnaphthalene (855 ^b)	Peak Height	Intensity Relative to <i>m/e</i>
126	...	1.37	1.3	...
139	...	9.23	7.4	...
140	...	2.75	3.0	...
141	...	67.1	57.7	...
142	...	100.0	75.6	...
143	...	11.6	8.6	...
146	2.63	...	2.0	4.51
147	100.0	...	44.3	100.0
148	82.6	...	34.0	76.8
149	12.5	...	5.2	11.7
150	4.08	...	1.5	3.39
Approximate mole % (in trap) ^f				38 62

^a Figure 5. ^b A.P.I. mass spectra catalog number. ^c *m/e* 147 = base peak of methylbenzo[*b*]thiophene. ^d *m/e* 142 = base peak of methylnaphthalene. ^e Analytically insignificant intensity. ^f Using pure compound sensitivities.

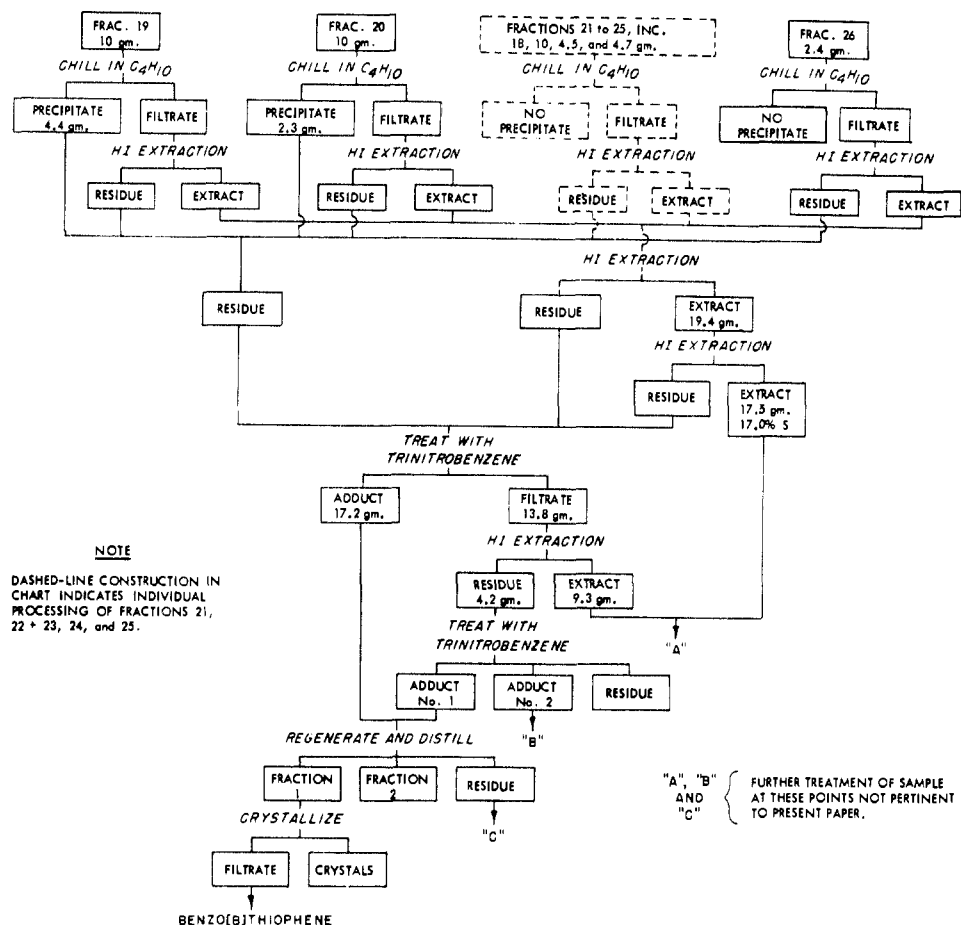


Figure 4. Treatment of Wasson 200° to 250° C. adsorption fractions

aromatic hydrocarbons and sulfur compounds (panel C). By means of the emergence times of the pure compounds and the mass spectrometer analyses of trapped fractions, as given in Tables I, II, and III, the following tentative identifications were made: benzo[*b*]thiophene and naphthalene, contained in fraction 1, panel A; 2-methylbenzo[*b*]thiophene and 2-methylnaphthalene, contained in fraction 2, panel B; and 3-methylbenzo[*b*]thiophene and 1-methylnaphthalene, contained in fraction 3, panel B.

To substantiate these tentative identifications, particularly with respect to differentiating isomers, the same material in these marked peak areas was retrapped by bubbling the gas stream through iso-octane or cyclohexane

(solvent choice dictated by subsequent analysis desired), and examined by infrared and ultraviolet spectrometry.

2-Methylbenzo[*b*]thiophene. To obtain the ultraviolet differential spectrum shown in Figure 6, a solution of 2-methylnaphthalene was prepared in concentration approximating that in the trapped gas-liquid chromatograph fraction 2, panel B, Figure 5. This was used in a variable-path-length cell of a Beckman DK-1 spectrophotometer

Table II. Partial Mass Spectra of G.L.C. Fraction 3^a and of Pure Compounds

<i>m/e</i>	3-Methylbenzo[<i>b</i>]thiophene (1027 ^b)	1-Methylnaphthalene (487 ^b)	Peak Height	Intensity Relative to <i>m/e</i>	
				147 ^c	142 ^d
126	...	1.31	0.9	...	1.57
139	...	9.79	6.2	...	10.8
140	...	5.82	2.0	...	3.49
141	...	69.1	45.8	...	79.9
142	...	100.0	57.3	...	100.0
143	...	11.0	6.5	...	11.3
146	2.66	...	0.5	5.10	...
147	100.0	...	9.8	100.0	...
148	76.0	...	7.1	72.4	...
149	11.7	...	1.4	14.3	...
150	3.64	...	0.4	4.08	...

Approximate mole % (in trap)^e

11 89

^a Figure 5. ^b A.P.I. mass spectra catalog number. ^c *m/e* 134 = base peak of benzo[*b*]thiophene. ^d *m/e* 128 = peak of naphthalene. ^e Using pure compound sensitivities.

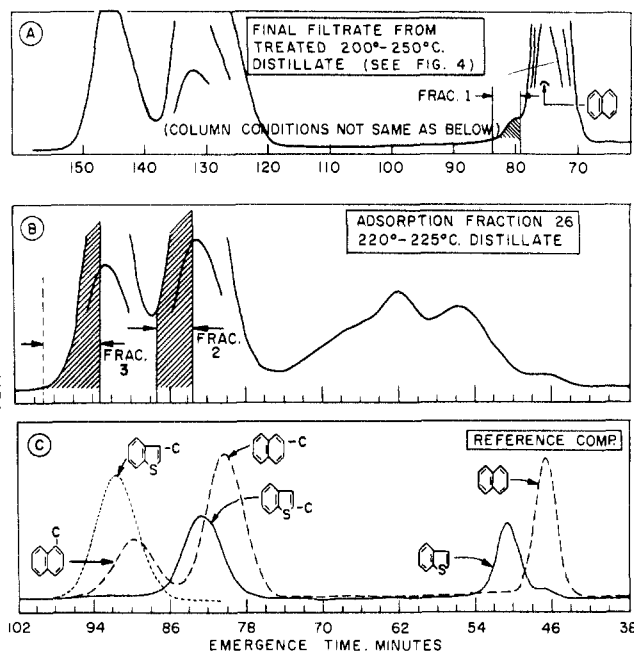


Figure 5. Gas-liquid chromatograms of Wasson fractions and of certain reference hydrocarbons and sulfur compounds

as a reference material. By slightly adjusting the path length, the adsorption of the 2-methylnaphthalene in the sample could be effectively nullified. The resulting differential spectrum is essentially duplicated by the spectrum of pure 2-methylbenzo[*b*]thiophene, also reproduced in Figure 6. This duplication points to the presence of the compound in the 220° to 225° C. fraction. Ultraviolet absorption spectra essentially identical to those illustrated

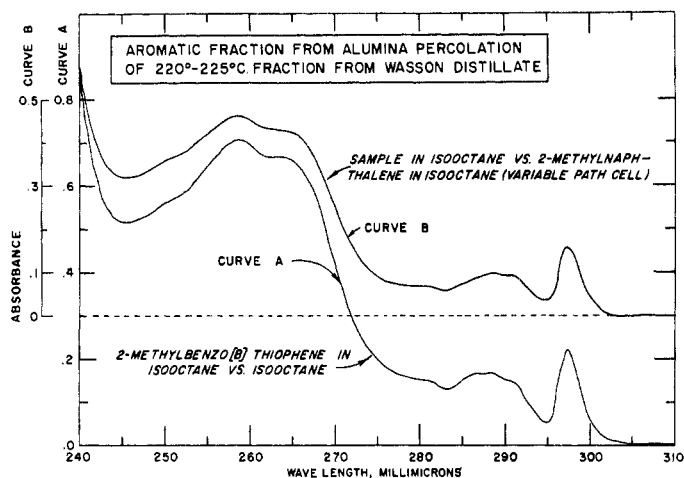


Figure 6. Ultraviolet spectrum of material from gas-liquid chromatographic separation of Wasson 220° to 225° C. fraction 26

in Figure 6 also were obtained upon examination of the residue from the HI treatment of adsorption fraction 21 (Figure 4) of the 200° to 250° C. Wasson thiol-free distillate.

As the ultraviolet spectra of many alkylbenzo[*b*]thiophenes are somewhat similar, such spectral evidence was considered insufficient for complete identification; therefore, infrared spectra of the trapped samples also were obtained. In Figure 7, center panel, the differential infrared spectrum (against cyclohexane) of trapped fraction 2 (panel *B*

Table III. Partial Mass Spectra of G.L.C. Fraction 1^a and of Pure Compounds

<i>m/e</i>	Benzo[<i>b</i>]-thiophene (917) ^b	Naphthalene (410) ^b	Peak Height	Intensity Relative to <i>m/e</i>	
				134 ^c	128 ^d
89	10.5	0.73	3.3	10.6	...
90	8.54	...	2.8	9.0	...
108	4.18	...	1.6	5.1	...
128		100.0	7.3	...	100.0
133	3.33		1.3	4.2	
134	100.0		31.0	100.0	
135	10.2		3.0	9.7	
136	4.16		1.7	5.5	

Approximate mole % (in trap)^e 81 19

^a Figure 5. ^b A.P.I. mass spectra catalog number. ^c *m/e* 147 = base peak of methylbenzo[*b*]thiophene. ^d *m/e* 142 = base peak of methylnaphthalene. ^e Using pure compound sensitivities.

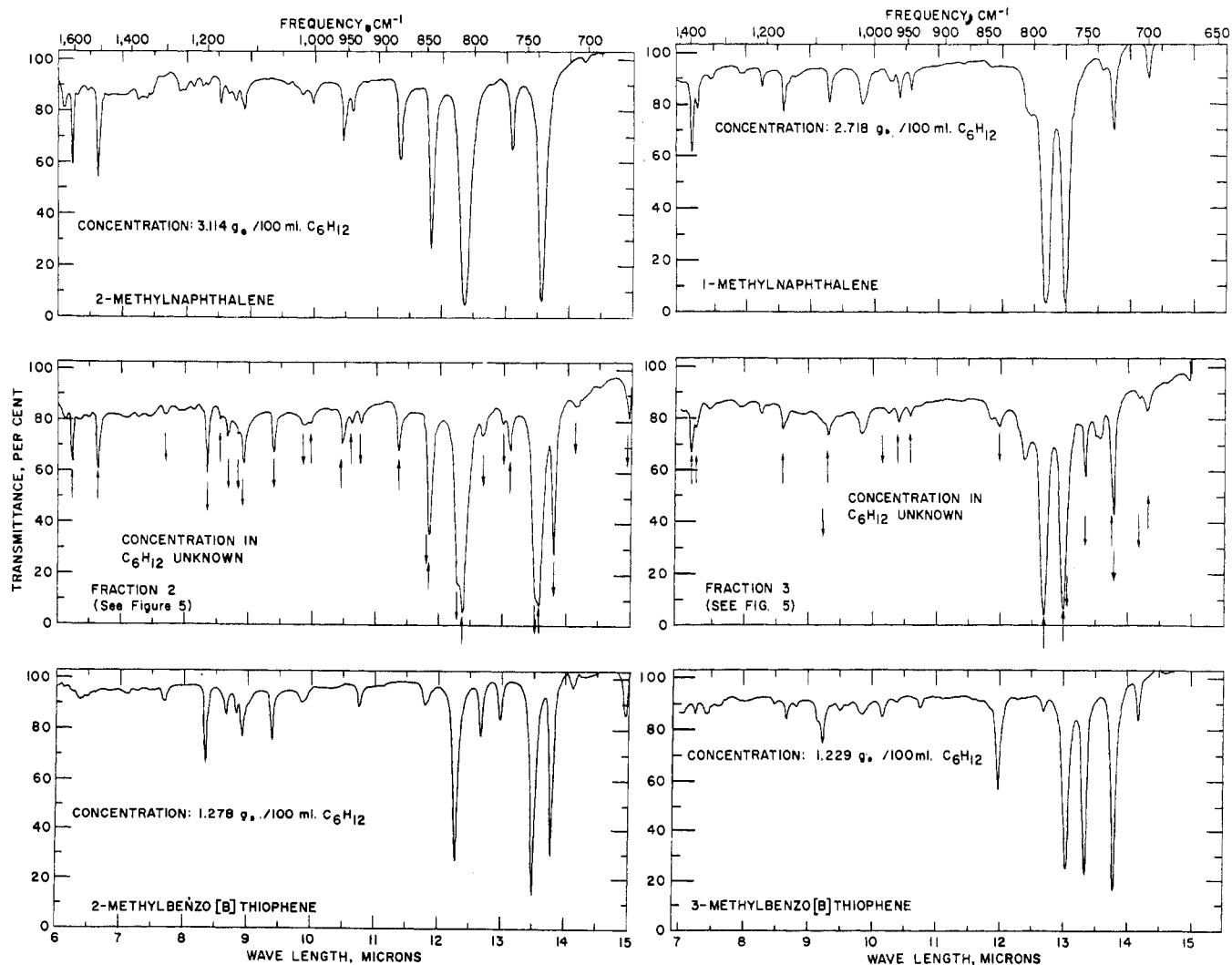


Figure 7. Comparison of infrared spectra

Figure 5) is compared with the infrared spectrum of 2-methylnaphthalene in the top panel and with the infrared spectrum of 2-methylbenzo[*b*]thiophene in the bottom panel. Essentially each band in the absorption spectrum of fraction 2 can be identified in one of the companion spectra. Calculations indicate that the two principal components of the sample, 2-methylbenzo[*b*]thiophene and 2-methylnaphthalene, are present in the ratio of 1 to 1.8.

3-Methylbenzo[*b*]thiophene. In a similar manner, the material emerging from the gas-liquid chromatographic column between 93 and 99 minutes (fraction 3, panel B, Figure 5) was trapped in cyclohexane and its differential absorption spectra against cyclohexane determined. Figure 7 shows the curve (center panel) compared with 3-methylbenzo[*b*]thiophene (bottom panel) and 1-methylnaphthalene (top panel). As the concentration of the 3-methyl isomer in the sample is lower than was that of 2-methylbenzo[*b*]thiophene in fraction 2, the evidence for the presence of 3-methylbenzo[*b*]thiophene is not as overwhelming as in the case of the 2-methyl isomer. The identification is considered definite, however, in view of the correspondence of major peaks in the sample spectrum with peaks in the spectrum of the reference compound. The band at 13.35 microns is particularly outstanding and convincing. Calculations indicate that the ratio of 3-methylbenzo[*b*]thiophene to 1-methylnaphthalene is about 1 to 8.

Benzo[*b*]thiophene. Fraction 1 (panel A, Figure 5) was treated in a manner analogous to that described above, and its differential infrared spectrum (against the solvent cyclohexane) is shown in Figure 8 compared with the spectra of benzo[*b*]thiophene and of naphthalene. All prominent absorption bands of the sample, except for the one at 13.8 microns, are accounted for by bands in the spectra of the two pure compounds.

GENERAL

It is of interest that all of the above identifications have been confirmed by the microdesulfurization technique described by Thompson, Coleman, Ward, and Rall (9). This supporting evidence for the identification of the two methyl derivatives is discussed in their article.

It is estimated that fraction 26 of the alumina filtration of the 220° to 225° C. distillate (Figure 5A) contains 2-methylbenzo[*b*]thiophene equivalent to 0.00063% on the crude oil basis and 0.00009% 3-methylbenzo[*b*]thiophene. These percentages are minimum values and cannot represent the entire amount present in the crude oil, as the distillate on either side of this 5° C. boiling range certainly contains these benzothiophenes as do the adsorption fractions on either side of fraction 26. Similar calculations of the amount of benzo[*b*]thiophene in the 200° to 250° C. fraction (Figure 5A) gives 0.00002% on the original crude oil. Here also this value is a minimum one as losses sustained in the chemical treatment of the final fractions precluded quantitative treatment.

CONCLUSION

Benzo[*b*]thiophene and two of its methyl homologs have been identified in distillates from Wasson, Tex., crude oil by isolation of the components by gas-liquid chromatography, followed by ultraviolet, infrared, and mass spectrometric examination of the trapped G.L.C. fractions.

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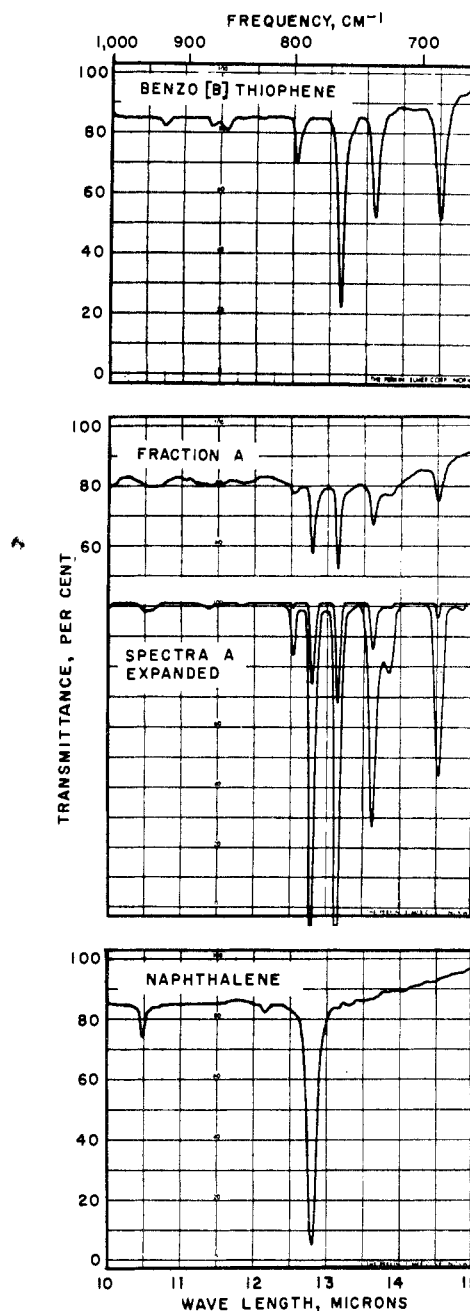


Figure 8. Infrared identification of benzo[*b*]thiophene in Wasson crude oil

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