IDENTIFICATION OF SOME NATURALLY OCCURRING ALKYL-THIOPHENES IN WILMINGTON, CALIF., CRUDE OIL BY USE OF A SERIES OF GAS-LIQUID CHROMATOGRAPHY STATIONARY PHASES

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INTRODUCTION

Knowledge of the natural occurrence of alkylthiophenes in petroleum is important, not only to the practical chemist interested in the separation, identification, and removal of sulfur compounds from petroleum distillates, but also to the fundamental chemist and geologist concerned with the origin of petroleum.

Early researchers[1,2] reported the presence of thiophene and some of its alkyl homologs in products of pyrolytic origin such as coal tars, shale oils, and "cracked" petroleum. BIRCH[3] in 1953 described the identification of four alkylthiophenes in an acid extract of an Iranian distillate. In 1956 THOMPSON et al.[4] identified thiophene and 2-methylthiophene in a specially prepared, unpyrolyzed distillate. The use of gas chromatography as a separation tool for thiophene and its homologs[5-8] resulted in additional identifications[9,10].

This paper describes in detail the systematic liquid–solid- and gas–liquid-chromatographic procedures used for the concentration and identification of eight alkylthiophenes in a Wilmington, Calif., crude oil distillate having a boiling range of 111° to 150°, and presents quantitative data for each of the identified thiophenes.

EXPERIMENTAL

Preparation of sulfur-compound concentrate

A major obstacle in separating and identifying any particular sulfur compound from a crude oil is the minute quantity usually present. The processing and sulfur-compound concentrating steps applied to the crude oil, preparatory to separating and identifying individual alkylthiophenes, included isothermal distillation, vacuum fractionation, and liquid–solid chromatography.

Isothermal distillation. Fig. 1 shows the sequence of steps used in processing 165.37 kg (approximately 50 gallons) of Wilmington, Calif., crude oil to yield the concentrates for sulfur-compound identifications. The initial step consisted of passing the crude oil through an all-glass falling film flash still, heated by steam to 100°. With a crude oil input of 30 to 40 ml per min, a sample contact time on the rotating glass drum of less than 30 sec, and a helium sweep rate of 9 l per min, this isothermal still, at atmospheric pressure, produced a distillate containing all the material
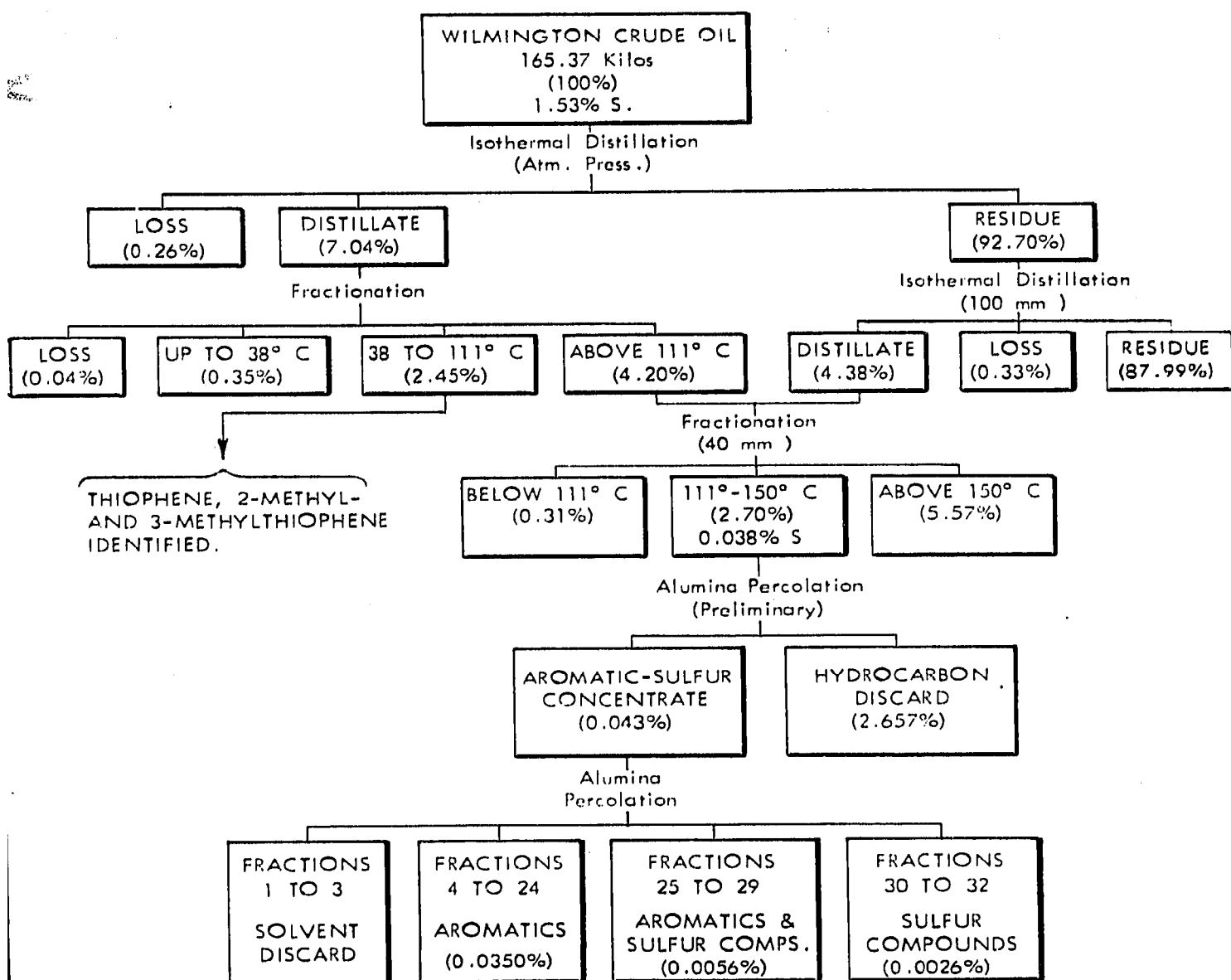
Fig. 1. Summary of the processing of Wilmington crude oil.

boiling below 111°. A second pass through the isothermal still at 100 mm pressure, removed all distillate boiling below 150°. A paper by RALL et al.[11] not only gives a working drawing of the complete still but also provides more detail with respect to associated auxiliary apparatus, operating conditions, and distillate production.

Vacuum fractionation. The next step was the application of vacuum fractionation to the distillates mentioned above and shown in Fig. 1 as encompassing the 111° to 150° boiling range. Fractionation at reduced pressure avoided exceeding an arbitrary 100° temperature limitation on the stillpot while procuring a distillate sample boiling 111° to 150°. The 100° temperature limitation represented an additional precaution for avoiding thermal degradation, although the most unstable components of the crude oil were confined to the residuals. The vacuum fractionation step provided a limited molecular weight range fraction comprising 2.70 % of the original crude oil and containing only 0.038 % sulfur.

Liquid–solid chromatography. Liquid–solid or adsorption chromatography on either silica gel or alumina gel concentrates organic compounds by types; however, alumina gel accomplishes a better resolution between aromatics and sulfur compounds than does silica gel. Published literature[12–15] contains some general adsorption techniques applicable to sulfur-containing mixtures.

The preliminary alumina adsorption step (denoted as alumina percolation in Fig. 1) for concentrating sulfur compounds in 2.3 kg aliquot portion of the 111° to 150° distillate consisted of four small (750 ml) batch runs. The method used for each of these four individual adsorption runs included the following: Dilution of the distillate with an equal volume of *n*-pentane; introduction of the *n*-pentane diluted sample to a 225 cm long glass adsorption column containing 1,500 ml of alumina; elution with *n*-pentane (2,500 ml) until the refractive index approaches that of *n*-pentane; introduction of ethyl alcohol to effect complete sample displacement; collection of the sulfur and aromatic compound concentrate as one fraction and a sulfur containing alcohol portion as another fraction; recovery of sulfur compounds from the alcohol fraction by *n*-pentane dilution, water washing, and a micro adsorption run; and combining both sulfur compound concentrates for further testing.

This preliminary adsorption accomplished a volume concentration of 63 times (now 0.043 % of the crude oil) and gas–liquid chromatographic (GLC) analyses combined with microdesulfurization proved the presence of sulfur compounds. However, the high aromatic content of the resulting sulfur and aromatic compound concentrate interfered with GLC separation and identification of individual sulfur compounds. Therefore, further concentration by alumina adsorption was desirable. The second adsorption step, indicated in Fig. 1, included the following procedures: Dilution of 28 + g of sulfur and aromatic-compound concentrate from the preliminary adsorption step with 38 g of isooctane; introduction of the diluted sample to a 12-mm × 12.2-m (40-ft.) column containing 1350 ml of alumina; addition of a small amount of fresh alumina at the top of the column as a "spacer" following complete sample entry into the alumina column; introduction of ethyl alcohol to effect complete sample displacement; and collection of small (0.7 to 1.5 g) fractions eluting from the bottom of the adsorption column.

Factors influencing the fraction collection included volume of fraction, the observance of schlieren (an optical effect caused by a sharp change of refractive index of the eluate or effluent material over that already accumulated in the test tube), visible boundary shadings of the liquid on alumina and noticeable odor changes of effluent, particularly for the later fractions containing sulfur compounds.

This final alumina adsorption run not only reduced the amount of extraneous aromatic compound contamination by a factor of five based on the overall weight of sulfur-containing fractions 25 to 32 (see the two blocks of bottom right portion of Fig. 1) but also produced some fractions completely free of aromatic compound contamination (fractions 30 to 32). These latter fractions contain only cyclic sulfides, and another related paper will describe the identification of individual compounds in this class.

Analysis of sulfur compound concentrate

The limited amount of available sample in each fraction (0.7 to 1.5 g) discouraged the determination of refractive index or the sulfur percentage by the lamp

or bomb methods. Thus, GLC, because of its versatility and small sample requirement, augmented by microdesulfurization and infrared spectroscopy, provided the means of identifying individual alkylthiophenes.

Gas–liquid chromatography (GLC). The narrow boiling range of fractions, considered in this study, permitted use of isothermal GLC analysis. The gas chromatographs used included both Perkin-Elmer Model 154 D[*] and Barber-Colman Model 20. Although this investigation included the use of many columns of various lengths and column packing, the column used for the analysis shown in Fig. 2 consisted of a $1/4$ in. $\times$ 40 ft. aluminum column packed with the specially selective Reoplex 400 (polypropylene glycol adipate)[16, 17] on 30–42 mesh GC-22 Super Support (20/100 wt. ratio) operating at 120° with a helium flow rate of 60 ml per min.

The chromatograms of fractions 26 to 29 inclusive, shown in Fig. 2, and GLC analysis of the fractions preceding No. 26 indicated differences of adsorptive strength on alumina, not only for the alkylthiophenes identified in this paper, but also for a number of aromatic hydrocarbons. Some general observations with respect to the aromatics include the following: C_3 substituted benzenes, such as isopropyl-, *n*-propyl-, and the methyl, ethyl isomers occur only in the earlier fractions; 1,2,3-trimethylbenzene, a high-boiling strongly adsorbed C_3 substituted benzene, present only because of azeotropic effects, and then only in trace amounts, occurs in adsorption fractions 10 to 27; ethylbenzene reaches peak concentration in fraction 10, followed slightly later by *m*-xylene and both, though decreasing in concentration, remain as minor contaminants in the analyses for alkylthiophenes present in fractions 26 to 28 of Fig. 2; *p*-xylene, present in the earliest fractions, rapidly decreases to extinction; *o*-xylene, representing the most strongly adsorbed C_2 substituted benzenes, appears in the middle fractions and continues to increase through fraction 26 to cause considerable contamination troubles in the alkylthiophene-containing fractions; toluene makes a very late appearance and reaches its maximum concentration in fraction 27; and the benzene occurs entirely in fractions 27, 28 and 29, shown in Fig. 2.

The chromatograms of Fig. 2 trace the relative retentions on activated alumina gel for the various alkylthiophenes resolved by the Reoplex column. Thiophenes with alkyl substitution next to the sulfur atom elute first, as evidenced by the early appearance of 2-*n*-propyl-, 2-ethyl-, 2,3-dimethyl-, and 2,5-dimethylthiophene as compared with the late appearance of 3,4-dimethylthiophene in fraction 26. Also, both the alkyl chain length involved in the substitution in the 2-position and alkyl substitution in the 2- and 5- positions significantly influence relative retention values. Fig. 2 indicates a difference of relative retentions on alumina gel with respect to substitution in the 2- and 2,5-positions through peak size changes for 2,5-dimethyl-thiophene and 2-ethylthiophene in fractions 26 to 28. These data indicate 2-ethyl-thiophene adsorbs more strongly on alumina than does 2,5-dimethylthiophene.

Fig. 3 shows quantitative relationships for four selected alkylthiophenes in the various alumina adsorption fractions and provides a general picture of their relative retention on activated alumina, as mentioned in the text above. These data indicate the order of adsorptivity as follows: 3,4-dimethylthiophene > 3-ethylthiophene > 2-ethylthiophene > 2,5-dimethylthiophene. Additional data, not included in Fig. 3

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[*] Reference to specific brand names is made to facilitate understanding and does not imply endorsement of such brands by the Bureau of Mines.
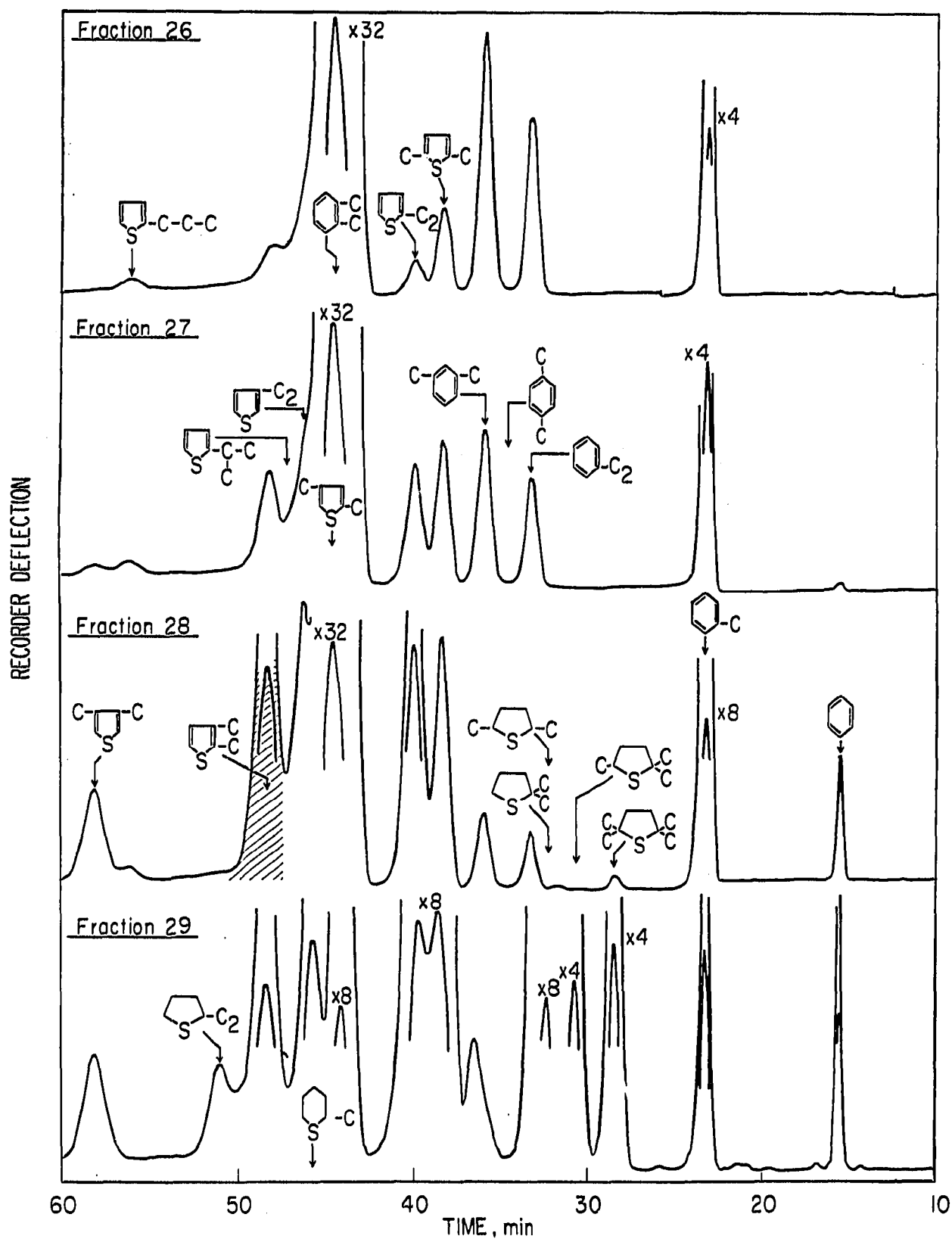
Fig. 2. Gas–liquid chromatograms showing changing concentrations of thiophenes, aromatics, and cyclic sulfides in alumina adsorption fractions 26 through 29.

because of possible crowding conditions, show that 2,3-dimethylthiophene is more strongly adsorbed than 2,4-dimethylthiophene which, in turn, is more strongly adsorbed than 2-ethylthiophene. 2-Isopropyl- and 2-n-propylthiophene, present in this boiling range only because of azeotropic effects, and then only in trace amounts, begin emerging from the adsorption column even before 2,5-dimethylthiophene. SNYDER[14] mentions many of these same adsorption differences occurring in slightly differing order in linear elution chromatography on hydrated alumina.
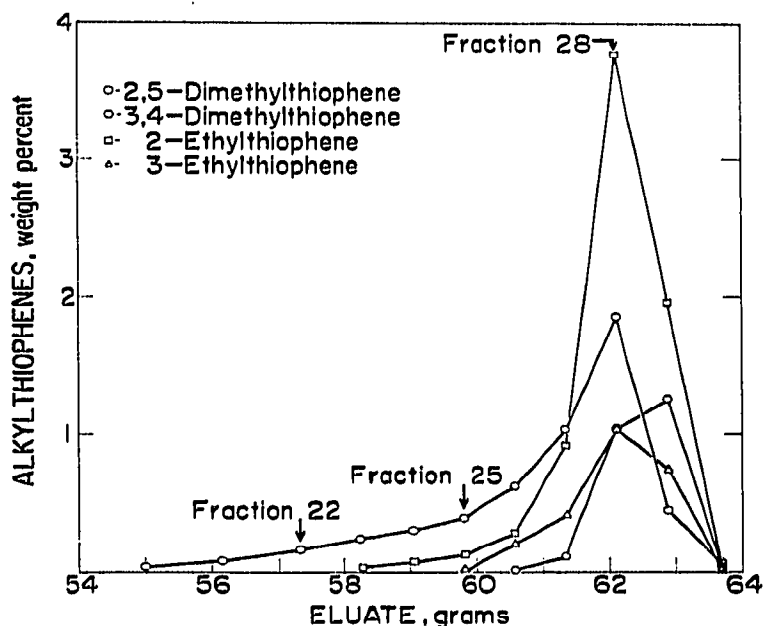

Fig. 3. Quantitative distribution curves for selected alkylthiophenes in alumina adsorption fractions.

The chromatograms of Fig. 2 indicate an increasing alkylthiophene content through fraction 28. Thus, fraction 28 represented the optimum choice for further separation and identification studies, especially since in fraction 29 the alkylthiophenes decrease sharply, and cyclic sulfides appear as a complicating factor.

GLC analysis of fraction 28 with the Reoplex column achieved satisfactory resolution for identifying all the alkylthiophenes present in the Wilmington, Calif., 111° to 150° distillate, except 2-isopropyl- and 2,4-dimethylthiophene. The 2-isopropyl isomer represented but a small constituent, smaller than even 2-n-propylthiophene. 2-Isopropylthiophene, with a retention time falling between 3-ethylthiophene and 2,3-dimethylthiophene, occurred as a trace contaminant with the isolated 2,3-dimethylthiophene (see crosshatched peak in fraction 28 of Fig. 2). A major component in fractions 26 to 29, o-xylene, completely obscured the presence of 2,4-dimethylthiophene because of identical retention times on the Reoplex column. Although not used in this study, microcoulometric sulfur detection, as reported in a publication by MARTIN AND GRANT[18], provides quantitative detection of such sulfur compounds despite the occurrence of a hydrocarbon contaminant at the same retention time. However, reliance on a conventional thermal conductivity (thermistor) detector required the use of different GLC stationary liquids, not only to separate and identify each individual alkylthiophene, but also to establish quantitative relationships.

Fig. 4. Chromatograms showing resolution of thiophenes and aromatics in fraction 28 achieved with various GLC stationary liquids.

Extensive experimentation with different GLC stationary liquids established retention time relationships for all the possible alkylthiophenes and alkylbenzenes in the 111° to 150° boiling range petroleum distillate. Fig. 4 shows four chromatograms (pertinent retention time indicated) obtained on the alkylthiophene concentrate fraction 28 with four selected GLC columns containing differing stationary phases. The legend in the upper left corner of each chromatogram lists the stationary phase for each column and conditions of column operation. The GLC columns consisted of $^1/_4$ in. × 40 ft. aluminum tubing packed with 30 to 42 mesh GC-22 "Super Support" carrying 20 g of stationary liquid to 100 g of solid support, except in the column containing the Dow Corning 550 silicone oil. In this silicone oil column, an increase to 35 g of this relatively nonpolar liquid on 100 g of solid support lessens polar side effects of the solid support.

The top chromatogram of Fig. 4 shows that polyepichlorohydrin, as a stationary phase, separates only 2,3-dimethylthiophene as an individual component while leaving 2-ethyl- and 2,5-dimethylthiophene together as a single peak, 2-n-propyl- and 3,4-dimethylthiophene together as a single peak, and 3-ethyl- and 2,4-dimethylthiophene together as an unresolved shoulder on the leading edge of the large o-xylene peak. The second chromatogram shows that sucrose acetate isobutyrate (SAIB) as a stationary phase satisfactorily resolves five individual thiophenes, including 2,4-dimethylthiophene, a compound unresolved by all of the other stationary phases. This column was important only for the resolution of 2,4-dimethylthiophene as it failed to separate 3-ethylthiophene and 2,3-dimethylthiophene from o-xylene. The third chromatogram shows separations obtained with Reoplex 400 in which the separation at 90° compares with that obtained at 120° as illustrated in Fig. 2. Since 2,4-dimethylthiophene with a retention time identical to o-xylene on Reoplex 400 constituted the main separation problem, use of both the SAIB column and the Reoplex-400 column separates all thiophenes in this Wilmington distillate. The fourth panel shows the chromatogram obtained with a DC-550 silicone oil column. This column produced only two distinct separations, namely 3,4-dimethylthiophene and 2-n-propylthiophene. 2-Ethyl- and 2,5-dimethylthiophene emerge as a mixture under one peak as does 2,4-dimethyl- and 3-ethylthiophene at a slightly later time and 2,3-dimethylthiophene emerges from the GLC column at the retention time of o-xylene. Such binary mixtures may be trapped from the silicone column and rerun on a different column, such as the SAIB or Reoplex-400 column, for separation and identification.

The chromatograms of Fig. 4 indicate that no one of the four stationary liquids separates each thiophene as an individual "peak". However, the chromatograms and the discussion related to them indicate that a selected combination of two columns will resolve all peaks. The use of such a technique provided the necessary means to separate and identify both qualitatively and quantitatively each alkylthiophene listed in Table I and Fig. 3.

Microdesulfurization. Microdesulfurization of GLC fractions constitutes a recent important development in the art of structure characterization[19-21]. Although the qualitative analysis of the materials forming peaks in the chromatograms of Figs. 2 and 4 included the use of microdesulfurization, this paper describes only its application to the crosshatched peak labeled 2,3-dimethylthiophene in Fig. 2. Desulfurization of the material emerging over the 47.5 to 50 min time interval produced

TABLE I

ALKYLTHIOPHENES IDENTIFIED IN WILMINGTON, CALIF. DISTILLATE BOILING 111° TO 150°

Name	Boiling point (°C)	Weight % in crude oil
2-Ethylthiophene	134.0	0.000080
3-Ethylthiophene	136.0	0.000027
2,5-Dimethylthiophene	136.7	0.000061
2,4-Dimethylthiophene	140.7	0.000058
2,3-Dimethylthiophene	141.6	0.000094
2-Isopropylthiophene	142.0	0.000006 (Est.)
3,4-Dimethylthiophene	145.0	0.000028
2-n-Propylthiophene	158.5	0.000009*

* Some 2-n-propylthiophene possibly present in next higher boiling range.

3-methylpentane and a trace of 2-methylhexane (determined with a stainless steel capillary column [0.01 in. × 185 ft.] coated with squalane and a beta ionization detector). Only 2,3-dimethylthiophene and 2-isopropylthiophene can fulfill the retention time and structural requirements of precursors of the identified hydrocarbon products of desulfurization.

Infrared spectroscopy. Final proof of identification of all thiophenes listed in Table I consisted of comparing the infrared spectrum of a reference compound with that of the isolated material trapped as effluent from a GLC column. Spectra were determined on a Perkin-Elmer Model 21 spectrophotometer using a cavity cell of 0.05 mm path length and a 4 × beam condenser. Fig. 5 shows a comparison of the
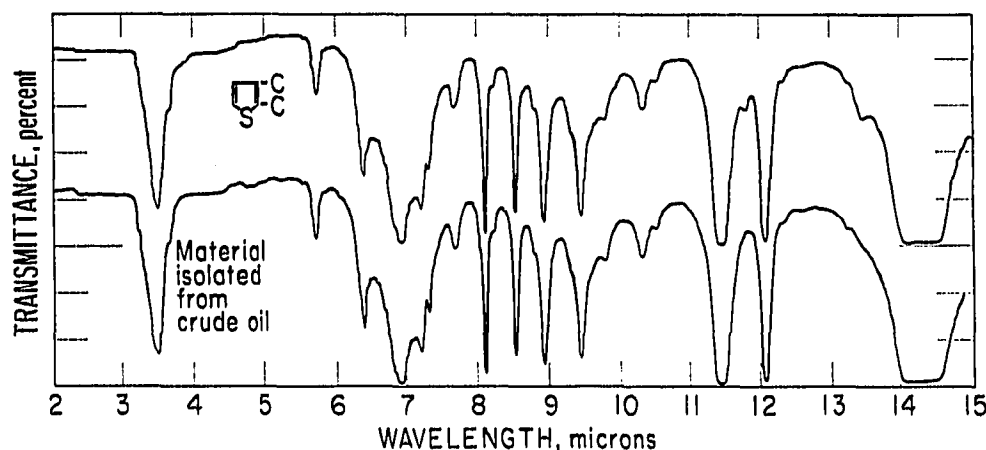

Fig. 5. Comparison of infrared spectrum of 2,3-dimethylthiophene with spectrum of material isolated from Wilmington, Calif. crude oil.

infrared spectrum of reference 2,3-dimethylthiophene with the infrared spectrum of material collected from the GLC column over the 47.5 to 50 min time interval denoted by the crosshatched peak in Fig. 2. In addition to the firm identification of 2,3-dimethylthiophene derived from the marked similarity of spectra, the very small absorption band at 11.81 μ represents the contribution of a trace of 2-isopropylthiophene, and the small band at 13.48 μ represents an even smaller quantity of o-xylene.

SUMMARY

The firm identification of eight alkylthiophenes in a pyrolysis-free Wilmington, Calif., 111° to 150° distillate required the application of several processing steps including the use of more than one gas–liquid chromatography stationary phase. The systematic procedures employed for both qualitative and quantitative evaluation of each alkylthiophene present in the original crude oil included isothermal distillation, vacuum fractionation, liquid–solid chromatography (alumina adsorption), gas–liquid chromatography, microdesulfurization, and infrared analysis.

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