Polarographic Estimation of Thiophenes and Aromatic Sulfides in Petroleum

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► A procedure has been developed for the estimation of thiophenes and aromatic sulfides in molecular distillates of chromatographic fractions derived from crude oil; this method has also been applied to straight-run kerosine and fuel oil distillates. Some pure thiophene dioxides and aromatic sulfones have been synthesized and studied polarographically. The effect of molecular weight upon the rate of diffusion of these compounds in the solvent-electrolyte has been evaluated, and conditions required for oxidation of the sulfur compounds in petroleum fractions have been established. Interpretation of the polarograms of oxidized petroleum fractions was based upon the polarographic behavior of the pure sulfones. This and one other procedure accounted for at least 90% of the total sulfur in most of the samples examined.

DEPLETION of high-grade crude oil reserves has forced the petroleum industry to use crudes having increasingly higher sulfur contents. This has added impetus to fundamental studies on the nature of the sulfur compounds in petroleum. Such studies should provide valuable information in understanding desulfurization mechanisms and the behavior of sulfur compounds in refinery operations.

Petroleum refinery chemists have been concerned for so many years with the thermal degradation products of sulfur compounds in refinery processes and their deleterious effects that they have overlooked, perhaps through necessity, the true nature of the sulfur compounds present in crude oil. Recent work has shown that, instead of hydrogen sulfide, thiols, and disulfides (or polysulfides), the major types of sulfur compounds in petroleum are aliphatic sulfides, condensed thiophenes, and aromatic sulfides (and perhaps elemental sulfur in some cases). For example, Thompson et al. (32) presented mass spectrometric data on the analysis of a series of chromatographic fractions from a topped, deasphalted sample of Wasson, Tex., crude oil. They found that benzo- and dibenzothiophenes were the predominant sulfur types while aliphatic sulfides were present in moderate amounts. Free sulfur, thiols, disulfides, and polysulfides were not detected. Hastings and others (15, 25)obtained similar results from an investigation of the constituents in heavy gas oils (600° to 1000° F.). Drushel and Miller (8) applied the iodine complex method originally proposed by Hastings (13, 14) to crude oils and observed that aliphatic sulfides account for a large proportion (as much as 50% in some cases) of the total sulfur in a crude oil. Elemental sulfur may be present in quantity or completely absent (9, 10).

This paper describes a polarographic procedure for the estimation of condensed thiophenes and aromatic sulfides. The sulfur compounds are oxidized to the sulfones with hydrogen peroxide, then reduced at the dropping mercury electrode.

Previous data on the polarography of sulfones are rather meager. Smith and others (30) studied the reduction of benzothiophene 1-dioxide and halogenated derivatives and concluded that, if the reduction is to take place, the benzothiophene derivative must contain a double bond in the 2,3 position and a dioxide group at the 1 position. Mairanovskiĭ and Neiman (26) investigated the polarography of methyl phenyl sulfone, phenyl sulfone (plus some halogenated derivatives), and phenyl sulfoxide, but their interpretation of the electrode reaction disagrees with chemical behavior.

Later, Levin and Shestov (23) proposed a more feasible mechanism for the reduction of phenyl sulfone at the dropping mercury electrode. Johnson (19) observed that the wave for methyl vinyl sulfone was pH independent and concluded that the double bond, not the sulfone group, was reducible. This corroborates the work of Smith and coworkers (30), who found that 2,3-dihydrobenzothiophene 1-dioxide was not reducible. Recently, Elliott (11) described the electrochemical determination of some sulfones.

In the present work, various sulfones have been synthesized from the parent sulfur compound by oxidation with hydrogen peroxide. Their polarographic reduction has been investigated and the effect of molecular weight upon the diffusion current estimated. Sulfone structure and half-wave potentials have been correlated. Sulfur concentrates from crude oils were separated into fractions of narrow molecular weight range by molecular distillation. The fractions were oxidized, to convert the sulfur compounds to sulfones, with hydrogen peroxide under a controlled set of conditions. From a knowledge of the polarographic behavior of the synthesized sulfones, the polarograms of the oxidized samples were interpreted and the percentage of thiophene sulfur and aromatic sulfide sulfur was calculated.

EXPERIMENTAL

Apparatus. A Leeds & Northrup Electro-Chemograph, Type E, was used throughout. The dropping mercury electrode (Leeds & Northrup Catalog No. 7733-C) had a capillary constant $(m^{2/3}t^{1/6})$ of 1.77 mg.^{2/3} second^{-1/2} (m = 1.70 mg. per second and t = 3.73 seconds), for an open circuit with the electrode immersed in the solvent-electrolyte solution described below. A Precision Scientific Co. circulating constant-temperature bath was used to circulate water at $25.0^{\circ} \pm 0.1^{\circ}$ C. through a 2-liter container (acting as a bath for the polarographic cell), mounted on a vibrationfree Leeds & Northrup polarographic stand having a rubber base.

Reagents. Benzene, fuming sulfuric acid-washed (obtained from the United States Steel fellowship, Mellon Institute).

Methanol, Fisher certified reagent grade.

Tetra-n-butylammonium iodide, polarographic grade (Southwestern Analytical Chemicals).

Nitrogen, high purity, dry (Linde Air Products Co.).

Hydrogen peroxide, 30% (J. T. Baker Chemical Co.).

Acetic acid, glacial, 99.5%, B & A quality (General Chemical Co.).

Solvent-Electrolyte Solution. A 0.2M solution of tetra-n-butylammonium iodide in methanol was prepared as a stock solution. Ten milliliters of this solution were pipetted into a 25-ml. volumetric flask, an appropriate aliquot of the oxidized sample (or pure sulfone) dissolved in benzene was added, and the solution diluted to the mark with benzene. The final solution was therefore 0.08M in tetra-n-butylammonium iodide, and the benzene-to-methanol ratio was 3 to 2 (by volume).

Table	۱.	Data	on	S	ynthesis	of	Some	Sulfones
				-		•••		

	Source of Parent	Solvent Used for Recrys-	Melting Po	int, ° C.
Compound	Sulfur Compound	tallization	Corrected	Lit. value
Benzothiophene 1-di- oxide	Kopper's Fellowship Mellon Institute, m.p. 31° C.	50% EtOH	142-143.5	142 (27)
Dibenzothiophene 5- dioxide	Eastman	95% EtOH	236-237	230 (17)
Thianthrene 5,10-tet- roxide	Eastman	Xylene	337.5 - 340	325 (7)
Di-tert-butylthiophene- 1-dioxide ^a	Socony-Vacuum	70% EtOH	127.5-128.5	127 (12)
Di-tert-octylthiophene- 1-dioxide ^a	Socony-Vacuum	70% EtOH	118.5-121	
Benzyl sulfone 6a,11b-Dihydro- naphtho [2,1-b]benzo- [d]thiophene 7-di-	Eastman	95% EtOH Acetone	$\frac{152 - 154}{184 - 185}$	151 (<i>16</i>) 183–184 (4)

oxide

- 72 1 1 1 1

^a Probably substituted in 2,5-positions.

^b Synthesized (4) and recrystallized by R. T. Wendland, Mellon Institute.

Table I	l. Elemer Su	ntal An Ifones ^a	alysis a	of Two
		W	Veight %	,
		\overline{C}	Н	ŝ
Di-tert-o phe oxid Theor Found Thianth	etylthio- ne 1-di- de y i, average rene 5,10- oxide	$70.51 \\ 70.28$	10.65 10.47	$9.41 \\ 9.55$
Theor Found	y i, average	$\begin{array}{c} 51.37 \\ 51.56 \end{array}$	f 2 , 88 3 , 36	$\frac{22.88}{22.69}$
^a Perf Institut	ormed by e.	J. R.	Kerns,	Mellon

Polarographic Procedure. Sufficient mercury to serve as an anode was placed in a single-compartment polarizing cell (Leeds & Northrup Catalog No. 7733-E, designed for use with the mercury pool anode or an external electrode). The solventelectrolyte solution containing the sample (or pure sulfur compound) was poured into the cell, the cell and contents were immersed in the constant temperature bath, and the nitrogen line was connected to the polarographic cell. The solution was degassed for 15 minutes, during which time the cell and contents came to thermal equilibrium with the bath. The nitrogen stream, which was presaturated with solvent vapors (3 to 2 benzene-methanol by volume), was then diverted to blanket the solution with an atmosphere of nitrogen. Polarograms were re-corded between -0.6 and -2.4 volts (vs. Hg pool).

The mercury pool anode was more satisfactory than a saturated calomel reference electrode. One advantage was the reasonably low cell resistance of 2000 ohms, which is ordinarily difficult to achieve with the solventelectrolyte used. Also, the mercury could be re-used in consecutive runs by merely rinsing it with water. In fact, the residual current curve improved between the first and second runs as a result of washing the mercury with distilled water.

Synthesis of Sulfones. The sulfones used in this study were prepared by oxidizing the parent sulfur compound with hydrogen peroxide in acetic acid (18, 28, 33). The synthesis of dibenzothiophene 5-dioxide, described below, is typical of the procedures used to synthesize the other sulfones.

Eastman White Label grade dibenzothiophene (7.22 grams of 0.0392 mole) was dissolved in 200 ml. of glacial acetic acid. The solution was placed in a three-necked flask of 500-ml. capacity fitted with a reflux condenser, a separatory funnel, and a stirrer. The solution was heated to 65° C. with a heating mantle (Glascol heater), then 9.8 ml. (0.1095 mole) of hydrogen peroxide (assayed at 38% H₂O₂ by two different methods) was added over a $^{1/2}$ -hour period. The temperature was slowly raised to 95° C. over a 1-hour period.

1.2

08

0.4

8° 0.0

-0;

-0.8

-16

After the solution was allowed to cool, it was poured into 1 liter of distilled water. The crystalline product was filtered on a Büchner funnel, washed thoroughly with distilled water, and dried at 100° C. The crude product was recrystallized twice from hot ethyl alcohol.

Table I summarizes some data concerning the synthesis of the sulfones used in this study. Samples of phenyl sulfone, butyl sulfone, and p-tolyl sulfone were obtained from Eastman Kodak Co. and recrystallized from ethyl alcohol. A sample of 6a,11bdihydronaphtho [2, 1 - b] benzo [d] thiophene 7-dioxide was synthesized by the Diels-Alder self-condensation of benzothiophene 1-dioxide (4). Two of these synthesized sulfones were analyzed for carbon, hydrogen, and sulfur (Table II).

The structures of some of these compounds are shown below as an aid to subsequent discussion:



-1.8

 $E_{d.e.}$ (Volts vs. Hg Pool) Figure 1. Plots of log $\frac{i}{i_d - j}$ vs. $E_{d.e.}$

POLAROGRAPHY OF SULFONES

In order to interpret the cathodic polarograms of crude oil fractions which have been oxidized with hydrogen peroxide, an understanding of the nature of the electrode processes for the reduction of some pure sulfones is desirable.

Reversibility of Electrode Process. For irreversible electrode reactions, the following relationship between the current and the potential has been found experimentally (22):

$$i = kC^{\circ} \exp\left(\frac{\alpha n_a EF}{RT}\right) \tag{1}$$

where α is the transfer coefficient, n_a is the number of electrons transferred in the rate-determining step, C° is the concentration of the electroactive substance at the surface of the electrode, and R, T, and F retain their usual electrochemical significance. In this case, the polarographic equation becomes

$$E_{\rm d.e.} = E_{1/2} + \frac{RT}{\alpha n_a F} \ln \frac{i}{(i_d - i)}$$
 (2)

where $E_{\text{d.e.}}$ is the potential of the dropping mercury electrode, *i* is the polarographic current, and *i_d* is the diffusion current. For reversible reactions, αn_a is replaced by *n*, an integer, which represents the number of electrons transferred in the over-all electrode reaction.

$$E_{\rm d.e.} = E_{1/2} + \frac{0.059}{n} \log \frac{i}{(i_d - i)}$$
 (3)

Values of αn_a were calculated using plots of $E_{d.e.}$ vs. log $i/(i_d - i)$ (Figure 1) for polarograms of several of the



Curve Compound Mmoles/Liter Benzothiophene 1-dioxide 1.340 2 Dibenzothiophene 5-dioxide 0.818 3 6a,11b-Dihydronaphtho[2,1-b]benzo[d]thiophene 7-dioxide 0.660 4 5 Di-tert-octylthiophene 1-dioxide 0.309 Thianthrene 5,10-tetroxide 0.253 6 p-Tolyl sulfone 0.720 Methyl p-tolyl sulfone Unknown

sulfones (Figure 2). The polarograms were corrected for the effect of ohmic potential prior to applying Equation 2. These calculations revealed the following values for αn_a : di-*tert*-octylthiophene 1-dioxide, 0.83; 6a,11b-dihydronaphtho [2,1 - b]benzo [d]thiophene 7dioxide, 0.63; p-tolyl sulfone, 0.91; and benzothiophene 1-dioxide, 1.17. All polarograms begin near zero current, but have been shifted with respect to the ordinate for convenience in Figures 2, 8, and 9.

The average value of αn_a is probably near 0.8 or 0.9 for the reduction of sulfones of the type studied, indicating that the electrode reaction is irreversible. Levin and Shestov (23) also found the reaction to be irreversible for phenyl sulfone with αn_a equal to 0.84.

Number of Electrons Transferred. Levin and Shestov (23) attributed the wave for phenyl sulfone in 0.05M tetraethylammonium iodide (in 50% ethanol) to a 2-electron reduction.

$$C_{6}H_{5} \longrightarrow SO_{2} \longrightarrow C_{6}H_{5} + 2H_{2}O + 2e \rightarrow$$

$$C_{6}H_{5} \longrightarrow SO_{2}H + C_{6}H_{6} + 2OH^{-} \quad (4)$$

This is similar to reduction with metallic sodium in boiling xylene.

$$2C_{6}H_{5} \longrightarrow C_{6}H_{5} + 2Na \rightarrow$$

$$2C_{6}H_{5} \longrightarrow SO_{2}Na + C_{6}H_{5} \longrightarrow C_{6}H_{5} \quad (5)$$

The number of electrons transferred was calculated from the relative wave heights of the waves for diphenyl sulfone and benzophenone, for which n was taken as 2 electrons.

The relative wave heights for the dioxides of benzothiophene and the dialkylthiophenes indicate that n for these compounds is also 2. Only dibenzothiophene 5-dioxide exhibited a wave height of sufficient magnitude to represent a transfer of 4 electrons. Bordwell and McKellin (2) obtained a smooth and rapid conversion of benzothiophene 1-dioxide to 2,3-dihydrobenzothiophene 1-dioxide by catalytic low pressure hydrogenation with palladiumon-charcoal catalyst. Bordwell and coworkers (4) also found that the compound 6a, 11b - dihydronaphtho [2, 1 - b]benzo[d]thiophene 7-dioxide could be reduced to the corresponding 5,6,6a,11btetrahydro-derivative by reduction with hydrogen using a palladium-on-charcoal catalyst. A similar reaction was observed by Challenger and Clapham (5), who used zinc and sodium hydroxide for the reduction. Therefore, the electrode reaction for these compounds probably involves reduction in the 2,3 position which would involve 2 electrons. Transfer of 4 electrons for dibenzothiophene 5-dioxide suggests the presence of two such reaction sites.

To confirm these conclusions, some of these reactions were investigated by coulometry at controlled potential.





Figure 4. Plots of log i vs. log P for some sulfones

a 0.5M aqueous lithium sulfate solution. The center compartment was also filled with 0.5M aqueous lithium sulfate. The external reference electrode was a small mercury pool connected by a salt bridge containing some of the catholyte. To ensure accurate potential control, the capillary tip of the reference electrode was positioned very close to the mercury pool working electrode. A line-operated Leeds & Northrup pH meter was interposed between the controller of the potentiostat and the reference electrode-working electrode pair.

Table III lists the number of electrons transferred for the reduction of certain sulfones in these studies. Isolation and identification of the products are still in progress and the results will be reported later.

Controlling Process in Electrode Reaction. Karchmer and Walker (20) determined whether a wave was diffusion-controlled, kinetically controlled, or governed by adsorption by studying the effect of the mercury pressure (mercury column height), P, upon the wave height. The value of the exponent, x, in the relationship

$$i = kP^{x} \tag{6}$$

should signify the type of current involved in the polarographic wave. The value of x may be obtained easily by graphical solution of the equation

$$\log i = \log P + \log k \tag{7}$$

where x is the slope of the line. A value of x near 0.5 would indicate that the current is diffusion-controlled. Values of x near 0 or 1 would suggest

Table III. Number of Electrons Transferred in Electrode Reaction

(Coulometry at co	ntrolled pot	ential)
	Control Potential.	
	Volts vs. Hg Pool	
Compound	Ref.	$n_{\rm total}$
Phenyl sulfone Benzothiophene	-1.70	1.85
1-dioxide Dibenzothiophene	-1.00	1.95
5-dioxide	-1.60	4.18
naphtho[2,1-b]-		
penzo [<i>a</i>]thiophene 7-dioxide	-1.65	1.91

A modified Lingane-Jones type potentiostat altered to provide a total direct current output of about 120 volts was used. Current-time curves for each electrolysis experiment were obtained by recording the potential drop across a precision resistance shunt (connected in series with the electrolysis circuit) with a 1-mv. Leeds & Northrup quantity of electricity consumed was measured by integrating the currenttime curve graphically. A three-compartment cell with sintered-glass disk separators was employed. The cathode was a large mercury pool and the catholyte was 0.1M tetra-*n*-butylammonium iodide in methanol. The anode was a platinum cylinder; the anolyte

Table IV. Polarographic Currents at Various Mercury Column Heights for a Number of Sulfones

		Volta	ge of		<i>i^a, µ</i> a.		
Compound	Mmoles/ Liter	$\frac{Measur}{Lower}$	ement Upper	At 27.8 cm. Hg	At 39.3 cm. Hg	At 56.7 cm. Hg	x
<i>p</i> -Tolyl sulfone	0.720	-1.50	-1.95	3.69	4.43	5.28	0.52
Benzothiophene 1-dioxide	${1.340 \atop 1.340}$	$-0.70 \\ -1.70$	$-1.30 \\ -2.10$	$\begin{array}{c} 8.79 \\ 7.01 \end{array}$	$\begin{array}{c}10.58\\8.34\end{array}$	$\begin{array}{c} 12.99 \\ 9.93 \end{array}$	0.57 0.53
Dibenzothiophene 5-dioxide	$\begin{array}{c} 0.818 \\ 0.818 \end{array}$	-1.20 - 1.90	$^{-1.70}_{-2.20}$	$\frac{8.58}{3.44}$	$\begin{array}{c}10.34\\3.44\end{array}$	$\substack{12.47\\3.91}$	$\begin{array}{c} 0.54 \\ 0.39 \end{array}$
6a,11b-Dihydronaphtho $[2,1-b]$ benzo $[d]$ thiophene 7-dia oxide	- 0.660	-1.40	-1.95	3.78	4.58	5.47	0.55
Thianthrene 5,10-tetroxide	$\begin{array}{c} 0.386 \\ 0.386 \\ 0.386 \end{array}$	-0.80 -1.15 -1.40	-1.15 -1.40 -1.80	$1.49 \\ 0.69 \\ 1.91$	$1.74 \\ 0.90 \\ 2.24$	$\substack{1.99\\1.16\\2.71}$	$\begin{array}{c} 0.41 \\ 0.77 \\ 0.51 \end{array}$
Phenyl sulfone	1.041	-1.40	-1.85	5.49	6.42	7.86	0.52
Di- <i>tert</i> -octylthiophene 1-dioxide	0.215	-0.80	-1.40	1.138	1.340	1.615	0.51
^a Corrected for residual cur	rrent.						



Figure 5. Estimated variation of i_d/c with molecular weight of some sulfones

8.

Benzothiophene 1-dioxide 6a,11b-Dihydronaphtho [2,1-b] benzo [d] 6. 2. Di-tert-butylthiophene 1-dioxide thiophene 7-dioxide 3. Dibenzothiophene 5-dioxide 7.

4. Phenyl sulfone

5.

p-Tolyl sulfone

Thianthrene 5,10-tetroxide Di-tert-octylthiophene 1-dioxide



Figure 6. Estimated variation of diffusion coefficients of sulfones with molecular weight

Methanol-benzene (40-60) solvent system at 25.0° C.



that the currents are kinetic or adsorption currents, respectively.

Data from polarograms of the sulfones at different mercury pressures, as well as values of the exponent, x, are shown in Table IV. Plots according to Equation 7 are reproduced in Figures 3 and 4. The mercury pressure, P, was corrected for surface tension (back pressure) in these plots by subtraction of the correction term $3.1/(mt)^{1/3}$ cm.

Most of the waves examined represent diffusion-controlled processes for which the exponents, x, are near 0.5 (Table IV). One exception is the second wave for dibenzothiophene 5dioxide $(E_{1/2} = -2.08 \text{ volts } vs. \text{ Hg}$ pool; Figure 2) which has an x value of 0.39, indicating that the current is partly diffusion- and partly rate-controlled. This wave occurs at a very negative potential and is of no concern in the analytical method. Another possible exception is thianthrene 5,10tetroxide (Figure 2) which has an xvalue of 0.41 for the first wave $(E_{1/2} =$ 1.01 volts) and 0.77 for the second wave $(E_{1/2} = -1.23 \text{ volts})$. Deviation from 0.5, in this case, may be a result of the difficulty in measuring the wave heights of these two waves which are not too distinctly separated. Each wave probably represents the transfer of only one electron. If these two waves are considered as a single 2electron wave, the value of x is 0.53, indicating diffusion control. The third wave $(\bar{E_{1/2}} = -1.63 \text{ volts})$ is diffusioncontrolled (Table IV). Other sulfones yield waves which appear to be composite (Figure 2, dibenzothiophene). Mairanovskiĭ and Neiman (26) report two waves in the polarogram of phenyl sulfone.

Variation of Diffusion Coefficients with Molecular Weight. As it has been shown that the electrode processes of interest are diffusion-controlled, it should be possible to calculate apparent diffusion coefficients from the Ilkovič equation by neglecting the irreversibility of the process.

$$i_d = 607 \ n D^{1/2} c m^{2/3} t^{1/6} \tag{8}$$

Half-wave potentials, i_d/c values, and apparent diffusion coefficients for the investigated sulfones are listed in Table V. The first two waves for thianthrene 5,10-tetroxide were combined and considered one wave for the calculation of D. Hereafter, D will be used to indicate the apparent diffusion coefficient.

Figure 7. Effect of reflux time on Kuwait No. 2 fuel oil (5.24 grams per liter)

Table V.	Apparent Diffusion	Coefficients	of Some	Sulfones	in 3 to	2 (by	Vol-
	ume) Benze	ne-Methanol o	at 25.0°	\pm 0.1 ° C			

Commound	Mal We	$E_{1/2},$ Volts $vs.$	$i_d/c^a, \mu a$	D, (Sq. Cm./Sec.)
Compound		ng Pool	Liters/ Winole	X 10°
<i>p</i> -Tolyl sulfone	246.3	-1.74	6.15	8.2
Benzothiophene 1-dioxide	166.2	$-0.97 \\ -1.93$	7.89	13.5
Dibenzothiophene 5-dioxide	216.2	$-1.42 \\ -2.08$	12.64	8.6
6a,11b-Dihydronaphtho $[2,1-b]$ - benzo $[d]$ thiophene 7-dioxide	268.3	-1.68	6.94	10.4
Thianthrene 5,10-tetroxide	280.3	-1.01 -1.23	$\begin{array}{c} 4.51 \\ 2.33 \\ 5.80 \end{array} 6.84$	10.1
		-1.03	0.80	1.0
Phenyl sulfone	218.3	-1.65	6.17	8.2
Di- <i>tert</i> -octylthiophene 1-dioxide	340.6	-1.16	6.23	8.4
Di- <i>tert</i> -butylthiophene 1-dioxide	228.4	-1.09	7.80	13.10
$^{a} m^{2/3} t^{1/6} = 1.77 \text{ mg.}^{2/3} \text{ sec.}^{-1/3}$	2.			

	Table	VI.	Effect	of	Excess	Peroxide
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	(Kuwait	: No. 2 fuel oil, 1	.08% S)	
Molar Ratio	Between -0.8 a	nd -1.4 Volts	Between -1.4 a	and -1.85 Volts
of Peroxide of Total Sulfur	i _d , μa., minus residual current	Calcd. as % thiophene sulfur	i _d , μa., minus residual current	Calcd. as % diaryl sulfide sulfur
2:1 3:1 5:1 10:1 50:1	5.44 5.98 6.56 7.91 9.27	$\begin{array}{c} 0.46 \\ 0.51 \\ 0.55 \\ 0.67 \\ 0.78 \end{array}$	1.982.633.123.634.74	$\begin{array}{c} 0.14 \\ 0.19 \\ 0.23 \\ 0.26 \\ 0.35 \end{array}$

The value of n was taken as 2, except for dibenzothiophene 5-dioxide, for which n was taken as 4 electrons.

Values of i_d/c were plotted against the molecular weight of the sulfone (Figure 5) and a curve was then drawn to represent the average variation of i_d/c with molecular weight (for the particular dropping mercury electrode used). By means of Equation 8, a similar relationship between the apparent diffusion coefficient and molecular weight was constructed (Figure 6). Knowledge of the effect of molecular weight upon the rate of diffusion of the sulfone in the solvent-electrolyte made it possible to interpret polarograms of oxidized petroleum molecular distillates.

Other Sulfones. Polarograms of *n*-butyl sulfone and benzyl sulfone showed no waves up to -2.4 volts. This is not surprising, because aliphatic sulfones and even phenyl ethyl sulfone and thiacyclohexane 1-dioxide are extremely difficult to reduce with lithium aluminum hydride (3). The cathodic polarogram of methyl *p*tolyl sulfone (prepared by oxidation of the Eastman grade sulfide), however, does show a wave ($E_{1/2} = -1.84$ volts).

In summary, aliphatic sulfides would be converted, by reaction with hydrogen peroxide, to aliphatic sulfones which would not be reduced polarographically.

Alkyl thiophenes and benzothiophenes would be converted to the corresponding dioxides which would produce waves between -1.0 and -1.3 volts $(E_{1/2})$. Diaryl sulfides would yield diaryl sulfones exhibiting half-wave potentials near -1.7 volts. Mixed sulfones (alkyl aryl) would be reduced at slightly more negative potentials. Dibenzothiophenes would form dioxides reducible at potentials intermediate between benzothiophene dioxides and diaryl sulfones. Unfortunately, pure compounds were not available to study the effect of alkyl substitution on the behavior of dibenzothiophene dioxides, but it seems likely that such compounds would behave like diaryl sulfones as far as the potential required for reduction is concerned.

ANALYSIS OF PETROLEUM SAMPLES

The first experiments to oxidize crude oils with hydrogen peroxide in benzene-acetic acid mixtures were unsuccessful. Too large an excess of hydrogen peroxide was employed and hydrophilic groups were produced. A stable emulsion formed when extraction with water to remove the acetic acid and excess peroxide was attempted. Polarograms showed no definite waves, only a large, gradually increasing current. Therefore, in studying the effect of excess peroxide and reflux time, **a** sample free of asphaltic or other possible interfering material was chosen. This was No. 2 fuel oil from a Kuwait crude oil.

Effect of Reflux Time. Exactly 2 ml. (1.637 grams) of Kuwait No. 2 fuel oil (containing 1.08% total sulfur) was dissolved in 10 ml. of high-purity, thiophene-free benzene (washed with fuming sulfuric acid). To this solution were added 20 ml. of glacial acetic acid and 0.188 ml. of hydrogen peroxide solution. This corresponds to 1.66 mmoles of hydrogen peroxide, which is three times the molar quantity of total sulfur in the sample (stoichiometrically, 2 moles are required for complete reaction). The solution was then refluxed using a Glascol heater.

After the reflux period was completed, the reaction mixture was cooled with tap water and transferred quantitatively, using several small portions of benzene, to a 125-ml. separatory funnel. The benzene solution containing the oxidized sample was extracted (being careful not to shake too vigorously) with 5 75-ml. portions of distilled water to remove acetic acid and traces of hvdrogen peroxide. The washed benzene solution was quantitatively transferred and filtered through a Whatman No. 30 filter paper into a 25-ml. volumetric flask and diluted to the mark with benzene.

A known volume of this final benzene solution (in this case, 2.00 ml.) was pipetted into a clean 25-ml. volumetric flask, 10 ml. of 0.2M tetra-*n*-butyl-ammonium iodide stock solution was added, and the solution was diluted to the mark with pure benzene. The cathodic polarogram of this solution was then recorded from -0.60 to -2.4 volts (vs. Hg pool).

This entire procedure was then repeated several times using various reflux times. The results are depicted in Figure 7. A polarogram of the oxidized No. 2 fuel oil is included in Figure 8 (for these polarograms the reflux time was 2 hours). It was concluded from Figure 7 that a reflux time of 2 hours was sufficient. Longer refluxing would probably permit undesirable side reactions, which would result in inferior polarograms.

Effect of Excess Peroxide. The above procedure was used, except that the reflux time was fixed at 2 hours and the molar ratio between hydrogen peroxide and total sulfur varied. The findings are listed in Table VI. With a very large excess of hydrogen peroxide (greater than 5 to 1), the polarograms indicated the presence of considerable quantities of undesirable reducible materials which tended to mask the two waves being measured. On the basis of these results, it was concluded that the molar ratio of peroxide to sulfur should be about 3 to 1 for the best results.



	Concn.,
	G./Liter
Unoxidized kerosine	5.12
Oxidized kerosine	11.08
Unoxidized No. 2 fuel oil	5.24
Oxidized No. 2 fuel oil	5.78

Discussion. From the above results, if it is assumed that No. 2 fuel oil is representative of the samples to be analyzed, the best conditions for oxidation of the sulfur compounds involve a reflux time of 2 hours and a 3-to-1 molar ratio of hydrogen peroxide to total sulfur.

Polarograms of oxidized Kuwait kerosine and oxidized Kuwait No. 2 fuel oil are compared in Figure 8. The waves at -2.1 volts in the case of the unoxidized samples (Figure 8) have not been thoroughly investigated. However, study of the effect of mercury pressure upon the wave height showed that the polarographic current for these waves in the unoxidized samples is diffusion-controlled. Other analytical data characterizing these samples are given in Table VII. A well-defined wave appears at -1.18volts in the polarogram of the kerosine sample. The half-wave potential for the corresponding wave in the case of the No. 2 fuel oil is 0.02 volt more negative (possibly caused by a difference in average molecular weight). This wave appears nearest the half-wave potentials for the dioxides of the two alkyl thiophenes, di-tert-butyl- and di-tert-octylthiophene ($E_{1/2} = -1.09$

and -1.16 volts). Alkyl-substituted benzothiophene dioxides might also be reduced at these potentials.

A second wave $(E_{1/2} = -1.62 \text{ volts})$ appears in only the polarogram of the No. 2 fuel oil. This is near the halfwave potentials observed for diarvl sulfones (Table IV). From the distillation data in Table VII, diphenyl sulfide (boiling point 296° to 297° C.) would not be expected to be present in the kerosine distillate, which has an end point of 505° F. (263° C.), but could be present in the fuel oil. Benzothiophene and derivatives might be present in the kerosine distillate, however. Dibenzothiophene, which boils at 332° to 333° C., would be absent in the kerosine and its presence would be doubtful in the No. 2 fuel oil. Certainly, in the absence of azeotropic effects, the higher homologs of dibenzothiophene are absent in these samples. It should not be necessary to correct for the late wave of benzothiophene dioxides in measuring the second wave in the samples, as the half-wave potential for the late wave of benzothiophene 1-dioxide is about 0.3 volt more negative than the second wave of the samples.

The weight percentages of thiophene

Table VII. Analytical Data° for Kuwait Distillates					
Type of Analysis	Kerosine ^b	No. 2 Fuel Oil			
Gravity, °API	44.3	38.8			
Sulfur, %, GRM 1123	0.45	1.08			
Mercaptan sulfur, %, GRM 1119	0.020	0.018			
Nitrogen, %, GRM 1121 A	0.0007	0.006			
Hydrocarbon type, vol. %, ASTM D 1319 Olefins Aromatics Saturates	5.0 19.1 73.9	$3.0 \\ 23.7 \\ 73.3$			
Bromine No., ASTM D 1159-52T	2.7	9.0			
Distillation, gas oil ASTM D 158- 54, °F. Over point	354	372			
End point 10% 30% 50% 70% 90%	505 402 416 432 445 464	642 433 471 510 551 602			
^a Obtained from Development Co.	Gulf Res	earch and			

^b Kerosine cut is IBP-47% by volume of full-range No. 2 fuel oil.



Figure 9. Polarograms of oxidized and unoxidized petroleum molecular distillates

Table VIII. Summa Two Kuwait	ry of Ro Distillates	esults on
	Weight 9	% Sulfur
Sulfur Type	Kerosine	No. 2 fuel oil
Thiol ^a Aliphatic sulfide ^b Thiophene Diaryl sulfide Total Total, by direct deter- mination	$\begin{array}{c} 0.020 \\ 0.29 \\ 0.12 \\ \hline 0.43 \\ 0.45 \end{array}$	$\begin{array}{c} 0.018\\ 0.39\\ 0.51\\ 0.17\\ \overline{1.09}\\ 1.08 \end{array}.$
^a From Table VII. ^b Spectrophotometric method (8).	ic iodine	$\operatorname{complex}$

sulfur and diaryl sulfide sulfur were calculated by means of the following equation:

ments were performed to determine the extent of oxidation of some of the pure sulfur compounds under the conditions established for the procedure (3-to-1 molar ratio of hydrogen peroxide to sulfur and a reflux time of 2 hours). The concentration of sulfur compound in the reaction mixture was very low, approximately 5 mM, to conform more closely to the conditions used for the samples. The percentages converted to the sulfone are as follows: phenyl sulfide, 83; dibenzothiophene, 41; di-tert-butylthiophene, 5; and benzothiophene, 0. Benzothiophene and di-tert-butylthiophene were studied in the presence of Kuwait kerosine. Oxidation of benzothiophene by refluxing for 3 hours at a peroxide-to-sulfur molar ratio of 26 to

Wt.
$$\mathcal{C}_{c}$$
 thiophene (or diaryl sulfide) sulfur $= \frac{\binom{i_{d}}{(0.032)(100)}}{\binom{i_{d}}{(i_{d}/c)_{\text{std.}}(c)}}$ (9)

where i_d is the diffusion current, $(i_d/c)_{\text{std.}}$ is a constant having the units μ a.liters per mmole derived from polarograms of the pure sulfones, and c is the concentration of sample in grams per liter. The samples were also analyzed for aliphatic sulfides by the iodine complex method (8) (Table VIII). The total weight percentage of sulfur by summation of the individual types agrees remarkably well with the total sulfur found by direct determination.

Rate of Oxidation. Some experi-

 $\frac{0.032}{(c)_{\text{std.}}(c)}$ (9) $\frac{0.032}{(c)_{\text{std.}}(c)}$ The

1 produced 70% conversion. The choice of 3-to-1 peroxide-to-sulfur molar ratio for the analytical procedure was based upon the behavior of an actual sample (Kuwait fuel oil) rather than upon the conversion values mentioned above. These pure compounds are probably not representative of the sulfur compounds in crude oil with respect to reactivity with hydrogen peroxide to form sulfones.

The low results for di-*tert*-butylthiophene may be attributed to stearic hindrance. The ease of oxidation of the remaining compounds is predictable from theoretical considerations. As the ease of sulfone formation roughly parallels the dipole moment (β), phenyl sulfide, which has a high dipole moment compared to benzothiophene, should readily form a sulfone. For the purpose of comparison, the dipole moments of some sulfur compounds are tabulated in Table IX. In general, the ease of oxidation of the sulfur compounds should show the following order:

$\begin{array}{l} {\rm RSR} > {\rm RSAr} > {\rm ArSAr} > {\rm dibenzothio-} \\ {\rm phene} > {\rm benzothiophene} \end{array}$

The relative order for the first three members in the series could be established more easily from the relative stabilities of the iodine complexes of representative sulfur compounds (indicating the electron availability at the sulfur atom).

The rather rapid rate of conversion of the sulfur compounds in Kuwait kerosine and fuel oil to sulfones (Figure 7) may provide a clue to the structure of the sulfur compounds involved. If the sulfur type represented by the first wave $(E_{1/2} = -1.2 \text{ volts})$ is indeed some type of thiophene, one must conclude that the electron availability is considerably greater than in thiophene, benzothiophene, or even dibenzothiophene to exhibit such a pronounced reactivity toward hydrogen peroxide. A high degree of alkyl substitution might be the most plausible explanation for such behavior.

A similarly high degree of reactivity was reported by O' Donnell (28), who oxidized the sulfur compounds in molecular distillates from a California coastal asphalt. Three times the theoretical amount of hydrogen peroxide, based on the sulfur content, was added to an acetic acid solution of the oil. This was heated to 70° C. and stirred 8 hours. The efficiency of this oxidation procedure is indicated by a drop in the total sulfur from 6.4 to 0.1% upon removal of the resulting sulfones by chromatography. The nearly quantitative conversion of the sulfur compounds to sulfones described by O'Donnell supports the use of hydrogen peroxide in the procedure presented in this paper.

Application to Molecular Distill-ates. Molecular distillates obtained from sulfur-rich chromatographic fractions derived from crude oils were analyzed by the proposed procedure. The samples were oxidized with hydrogen peroxide according to the procedure described above. Wave heights measured from polarograms of the oxidized samples were corrected for currents caused by background reducible material. These background currents were obtained from cathodic polarograms of the sample before oxidation (at the same concentration in the solvent-electrolyte as the oxidized sample) in a way completely analogous to the measurement of residual cur-rents. The weight percentage of sulfur (thiophene sulfur for the first wave and diarvl sulfide sulfur for the second) was derived from the relationship in Figure 5 and the molecular weight of the sample-the molecular weight ranges of the samples were considered

Table IX. Dipole M Sulfur Com	oments c pounds	of Some
(Arranged in order of it	ncreasing :	moment)
Compound	Dipole Moment, D	Refer- ence
2,5-Dimethylthiophene Thiophene Tetraphenylthiophene Benzothiophene 2-Methylthiophene Dinaphthylenethio-	$\begin{array}{c} 0.51 \\ 0.53 \\ 0.60 \\ 0.62 \\ 0.67 \end{array}$	$(6) \\ (21) \\ (6) \\ (6) \\ (21) \\ (21)$
phene Dibenzothiophene Methyl naphthyl sulfide Phenyl o-tolyl sulfide Phenyl sulfide Phenyl sulfide	$\begin{array}{c} 0.8 \\ 0.83 \\ 1.27 \\ 1.34 \\ 1.40 \\ 1.47 \end{array}$	(6) (6) (24) (29) (31) (1)
Propyl sulfide <i>n</i> -Butyl sulfide <i>n</i> -Amyl sulfide Phenyl <i>m</i> -tolyl sulfide Phenyl <i>p</i> -tolyl sulfide 3.3-Dimethylthiacyclo-	$ \begin{array}{r} 1.55 \\ 1.57 \\ 1.58 \\ 1.62 \\ 1.76 \\ \end{array} $	(31) (31) (31) (29) (29)
butane p-Tolyl sulfide Thiacyclopentane	$1.8 \\ 1.97 \\ 1.97$	$(31) \\ (29) \\ (6)$

sufficiently narrow to make this valid. If pure sulfones are not available in other laboratories for the standardization of a dropping mercury electrode, the relationship of D with molecular weight (Figure $\hat{6}$) may be used to estimate $(i_d/c)_{\rm std}$. from the Ilkovič equation (Equation 8).

Results of the analysis of some of these molecular distillates are arranged in Table X. Sample 2 is a chromatographic fraction which is aliphatic in nature-i.e., it was collected during the early stages of elution (the eluent was n-pentane containing progressively increasing amounts of benzene). The samples became more aromatic as the sample number increased. Representative polarograms of an oxidized sample of aliphatic character (from the early stages of elution) and an oxidized sample of aromatic character (from the

Table X. Summary of Results from Cathodic Polarography of Oxidized Molecular Distillates

(Derived from Light Mara, Venezuela, crude oil)

				$\iota_d{}^a, \mu$	а.				
				From	From	$(i_d/c)_{\rm std}$.			
				-0.8 to	-1.4 or	Used.			
				-1.4 or	-1.5 to	48	Weigh	nt $\%\mathrm{S}$ –	
			Concn	-1.5	-1.85	Liters/	Thio-	Diarvl	
	Sample	Mol. Wt.	G./Liter	volts	volts	Mmole	phene	sulfide	
~	ounipic .		<i>ai</i> , bi	10100	10100		phone	2000	
2		221			0.04	0.00	0.00	0.17	
	Fraction 2	221	0.5592	4.65	0.24	8.00	3.33	0,17	
	3	283	0.6159	4.86	0.34	7.28	3.47	0.24	
	· · · · · · · · · · · · · · · · · ·	332	0.6374	3.67	0.36	6.76	2.72	0.27	
	Residue	629	2.110	5.91	0.92	4.75	1.89	0.29	
3									
0	Fraction 1	185	0.6162	5 43	0.34	8 42	3 35	0.21	
	2	245	0.7201	6 62	0.47	7 75	3 80	0.27	
	3	330	0.7762	5 90	0.63	6 78	3 59	0.38	
	4	400	0 8011	4 30	0.54	6 10	2.82	0.35	
	Residue	731	1 443	4 34	0.01 0.74	4 000	$\frac{2}{2}$ $\frac{3}{40}$	0 41	
	10051000	101	1.110	1.01	0.11	1.00	- .10	0.11	
4									
	Fraction 2	299	0.6576	3.22	4.67	7.11	2.20	3.20	
	3	367	0.7590	2 .99	3.61	6.42	1.96	2.37	
	- 4	457	0.9652	3.71	3.26	5.60	2.20	1.93	
	Residue	855	1.305	3.05	2.20	3.8°	1.97	1.42	
5									
Č	Fraction 2	310	0.7964	4 52	6 11	7 00	2.60	3 51	
	4	465	0 5541	2 69	1 84	5 55	2 80	1 92	
	Residue	880	1 181	3 99	221	3 75	2 92	162	
~		550	1,101	5.00			- .0 -	2.02	
ti	D (1	1010				a =1		0.00	
	Residue	1040	1.285	3.55	3.14	3.55	2.53	2.23	
	~	• • • •							

Corrected for residual current of unoxidized sample (background current).

^b Crude estimate.

ſ	able XI. Summary of Results by Sulfur Compound Type							
	Weight Per Cent Sulfur							
	Aliphatic		Diarvl	Total				
Sample	sulfide∝	Thiophene	sulfide	Sum	Found ^b			
2								
Fraction 2	3.05	3.33	0.17	6.55	$\frac{7}{10}, \frac{67}{10}$			
3	2.71	$\frac{3.47}{2}$	0.24	6.42	7.10			
⁴	2.15	2.72	0.27	5.14	5.59			
Residue	1.25	1.89	0.29	3.41	3.33			
3								
Fraction 1	1.71	3.35	0.21	5.27	5.43			
2	1.87	3.80	0.27	5.94	6.45			
3	1.65	3.59	0.38	5.62	6.04			
4	1.43	2.82	0.35	4.60	5.23			
$\mathbf{Residue}$	0.93	2.40	0.41	3.74	3.48			
4								
Fraction 2	1 16	2 20	3 20	6 57	5 34			
3	1 36	1 96	2 37	5 69	5 79			
4	1 49	$2^{1}20$	1 93	5 62	5 43			
Residue	1.02	1.97	1.42	4.41	7.07			
D Exaction 2	1.09	2 60	9 51	7 19	6 02			
Fraction 2	1.02	2.00	3.01	6.00	0.92			
Bosiduo	1.40	2.00	1.92	5.20	5 54			
nesique	1.21	2.92	1.02	0.01	0.04			
6								
Residue	0.88	2.53	2 , 23	5.64	5.58			
^a Determine ^b Determine	ed by D. Taylor, ed by Gulf Resear	Mellon Institute rch and Develop	e, by iodine cor ment Co.	nplex method.				

latter stages of elution) are reproduced in Figure 9. Polarograms of the unoxidized samples are also included. The pronounced increase in what has been tentatively designated as diaryl sulfide sulfur (the second wave) as the aromaticity of the sample increases is noteworthy.

There is a remarkable parallelism between the total sulfur content as determined directly and the sum of the percentages of sulfur of each type (Table \overline{XI}). The only gross discrepancies appear in the cases of sample 4, fraction 2, and sample 4, residue. These data suggest that there may be only three main classes of sulfur compounds in crude petroleum. Thiols and disulfides, therefore, are probably not major sulfur types in crude oil, but are produced through thermal degradation during refining. Application of this method to most refinery distillates probably would require the preliminary removal of hydrogen sulfide, elemental sulfur, thiols, disulfides, and polysulfides by standard procedures.

It is possible that extensive alkyl substitution of dibenzothiophene may shift the half-wave potentials for the corresponding sulfones to more negative values. If this is the case, the sulfur compounds which are tentatively considered as diaryl sulfides may be dibenzothiophene derivatives or a mixture of both. Chemically, diaryl sulfides and dibenzothiophenes are very similar. If the second wave is indeed caused entirely by the dioxides of dibenzothiophenes, the weight per cent sulfur, as reported in this paper, should be divided by 2, as it was assumed that 4, not 2, electrons are transferred in the electrode reaction.

Because no good independent analytical methods are available for comparison, the ultimate accuracy of this procedure cannot be determined. However, the surprisingly good agreement between the total determined sulfur and the sum of the percentages of sulfur by compound type attests to the potentialities of the method, Even though interpretation of the polarograms is open to question, it is hoped that the study reported herein may serve as a basis or inspiration for a more exact procedure.

ACKNOWLEDGMENT

The authors wish to thank the Multiple Fellowship on Petroleum sustained at Mellon Institute by the Gulf Research and Development Co., which supported this work, for permission to publish this material. They also wish to thank R. T. Wendland who supplied the molecular distillates and Dorothy Taylor who analyzed the samples by the spectrophotometric iodine complex method.

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RECEIVED for review June 10, 1957. Accepted January 18, 1958. Group Ses-sion on Analytical Research, 22nd Mid-Year Meeting, Division of Refining, Division of Refining, American Petroleum Institute, adelphia, Pa., May 1957. Phil-

Spectroscopic Detection of Silicon in Organic Silicon Compounds

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► A qualitative spectroscopic test for silicon in organosilicon compounds has been developed. The method employs the Spectranal for detection of emission lines at 6347 and 6371 A. and has proved satisfactory for a wide range of organosilicon compounds.

 ${f R}$ ESEARCH efforts necessitated the development of a simple qualitative test for silicon in organosilicon compounds, a more rapid test than existing chemical methods. The spectroscopic procedure described proved satisfactory for a wide range of organic

materials incorporating silicon. The method involves decomposition of the insoluble organosilicon compound in an aqueous acid solution by a spark discharge between platinum electrodes. The Todd Spectranal was employed successfully, although the manufac-