Table I. Effect of Water on the Potential of the SCSE at 25.0° C.

Added water, grams/100 grams solvent[a]	0.258	0.387	0.644	1.16	1.81	2.58	3.35	4.25	5.16
Potential, mv.[b]	+1.1	+1.6	+1.7	+2.1	+2.3	+2.8	+3.1	+3.3	+3.6

[a] Distilled ethylenediamine. [b] ±0.5 mv. With respect to a similar half-cell with no added water.

~ 11 mv. negative to a fresh half-cell at the same temperature, and remained thus until observations were terminated about 1 week later. This effect has been confirmed by Bruckenstein (*1*), who noted that the spurious potential difference decreased on prolonged aging. Bruckenstein found that the difference was only 5.5 mv. after 27 days, and that a half-cell aged for 51 days at room temperature agreed with a fresh half-cell to within 0.5 mv.

The potentials of two fresh half-cells at 25.0° C., 450 ± 2 mv. negative with respect to the saturated (aqueous) calomel electrode at the same temperature, remained essentially constant for ~ 5 hours and then slowly fell numerically. Readings were −440, −425, −415, and −395 mv. (all ± 2 mv.) after 1, 2, 3, and 5 days, respectively, but remained close to −395 mv. during the next few days. The cell contents were not disturbed, apart from renewing the mercury surfaces in the EDA half-cells before readings were taken. These experiments were made only to obtain an approximate relationship between the potential of the SCSE and that of a common aqueous reference electrode. The pronounced drift may be due to inconstancy of the junction potential between the EDA and water systems.

Addition of water to a fresh half-cell caused its potential to become positive to that of an unadulterated half-cell. The results in Table I, taken 24 hours after each addition of water, were obtained in a single run. The surfaces of all six mercury pools were renewed before a reading was taken.

The potential of a fresh half-cell remained essentially constant during the passage of 6 liters of carbon dioxide over the surface of the solution.

DISCUSSION

Although the saturated corrosive sublimate electrode system of Bruckenstein and Mukherjee (*3*) has satisfactory short-term reproducibility, the potential should be checked at intervals if operations are extended. The temperature coefficient, −1.3 mv. per ° C. at room temperature, is about double that of the saturated (aqueous) calomel electrode. The potential of the SCSE shifts in the positive direction as water is introduced, but the shift is less than 3 mv. for not more than 2.5% of water.

ACKNOWLEDGMENT

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Identification of Some Cyclic Sulfides in a Wasson, Texas, Crude Oil Distillate Boiling from 111° to 150° C.

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Knowledge of the sulfide sulfur content of petroleum is both of theoretical interest and of practical value to the petroleum industry. This paper discusses a procedure for the isolation and identification of cyclic sulfides in petroleum and reports the identification of 17 cyclic sulfides in a 111° to 150° C. boiling-range distillate. This procedure should have general application in the characterization of petroleum distillates.

THE IDENTIFICATION of sulfur compounds in petroleum has special significance for petroleum scientists. Information about these sulfur-containing constituents is valuable, both as an addition to fundamental knowledge and as an aid in processing applications.

Historically, cyclic sulfides first were found in petroleum by Mabery (*6*) in 1900. In 1925, Thierry (*8*) corroborated the presence of cyclic sulfides in a Persian crude oil, and since then other investigators (*1, 2, 7*) also have found them in various crude oils. Previous studies by the author and coworkers report the identification of 22 chain sulfides (*9*) and 35 thiols (*3*) in a 111° to 150° C. boiling-range distillate of Wasson, Tex., crude oil. This paper presents a systematic procedure for the isolation and identification

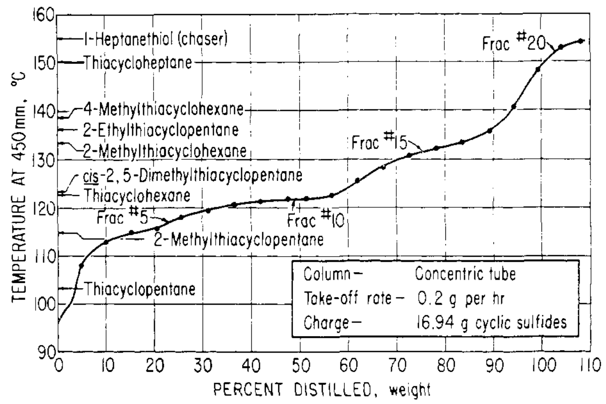


Figure 1. Distillation curve of cyclic sulfide concentrate from 111° to 150° C. Wasson distillate

of cyclic sulfides in this same boiling-range distillate. It describes the preparation of a cyclic sulfide concentrate, identification of sulfides in general, and identification of specific sulfides.

EXPERIMENTAL PROCEDURES

Preparation of Cyclic Sulfide Concentrates. To facilitate the identification of individual cyclic sulfides present in the distillate, the sulfides were first concentrated by both chemical and physical means. The procedures used in the concentration process included distillation, adsorption, chemical extraction, and gas-liquid chromatography (GLC). The actual steps involved in the processing of 159,000 grams of Wasson crude oil to produce 17 grams of a cyclic sulfide concentrate boiling from 111° to 150° C. were outlined in Figures 1, 2, and 3 of a recently published article (*9*) pertaining to the identification of chain sulfides.

After preparation of sulfur compound concentrates, a 16.94-gram sample of the predominantly cyclic sulfide concentrate was fractionated at reduced pressure in an all-glass concentric tube column (*5*). The distillation curve, based on this fractionation, is shown in Figure 1. The boiling points of some of the sulfides identified [corrected to 450 mm. of Hg using a Cox (*4*) chart] also are indicated in Figure 1. Shown in Figure 2 are gas-liquid chromatograms of distillation fractions, 1, 6, 14. These chromatograms were obtained using a ¼-inch by 40-foot column packed with 30–42 mesh firebrick which was coated with 30 to 100 weight-ratio of Dow-Corning silicone 550 oil. The order of sulfide emergence from this relatively nonpolar column depends principally on boiling point of the compounds involved. Figure 2 presents chromatograms of only three fractions from the distillation. However, during the course of this investigation, chromatograms were obtained on all 21 of the fractions, and the material associated with each peak was isolated and characterized. Also indicated in Figure 2 are retention times of the cyclic sulfides identified.

General Identification of Cyclic Sulfides. The general procedure for the identification of the sulfides in the 111° to 150° C. concentrate was as follows. The materials emerging under individual peaks of the chromatograms were trapped and desulfurized (*10*). The hydrocarbons produced by desulfurization were identified by GLC retention time secured with a 185-foot-long, 0.01-inch-I.D. stainless-steel capillary column coated with squalane. From this information, the search for the sulfide precursors of the hydrocarbons was narrowed to a few possibilities and occasionally

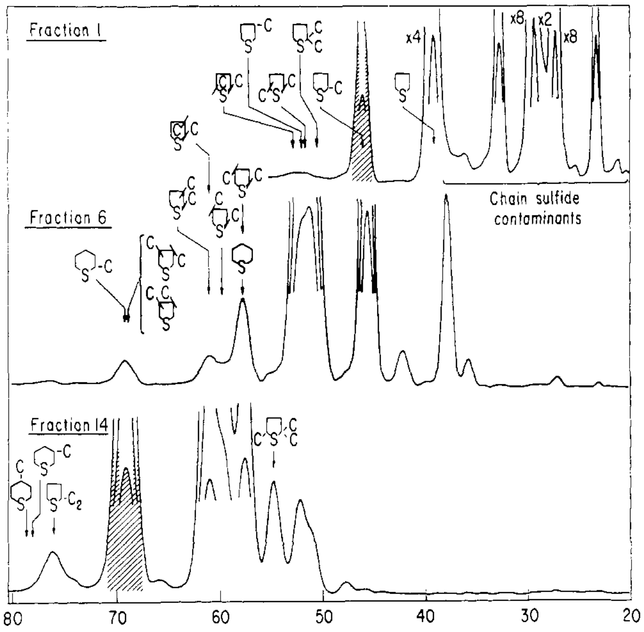


Figure 2. Gas-liquid chromatograms of distillation fractions 1, 6, and 14

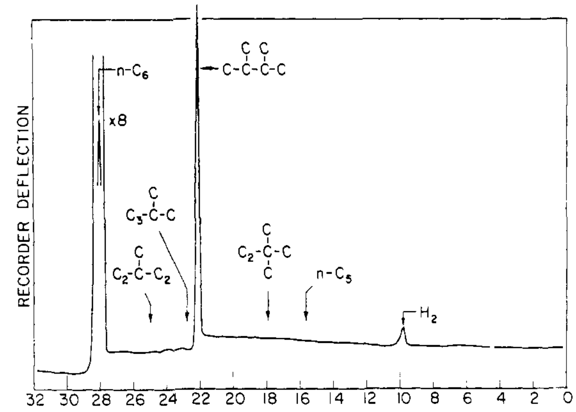
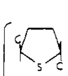
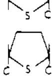
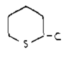
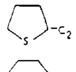
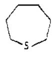
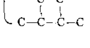
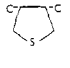


Figure 3. Gas-liquid chromatograms of the products of desulfurization of trapped material from fraction 14 of Figure 2

Table I. GLC-Desulfurization Data from Fraction 14 of Figure 2

(Indicating the presence of 2-methylthiacyclohexane and 3,4-dimethylthiacyclopentane in Wasson crude oil)

		Possible Cyclic Sulfide Precursors	
Time Interval of Trapping, Min.	Products of Desulfurization	Formula	Retention time, min.
67.4 to 70.4	n-C_6		50.2
			51.3
			68.3^a
			76.0
			113.5
	 $\mathrm{C{-}\overset{C}{\overset{\vert}{C}}{-}\overset{C}{\overset{\vert}{C}}{-}C}$		67.9^b

^{a}Only possible precursor of *n*-hexane with a retention time in agreement with interval of trap. ^{b}Only possible precursor of 2,3-dimethylbutane.

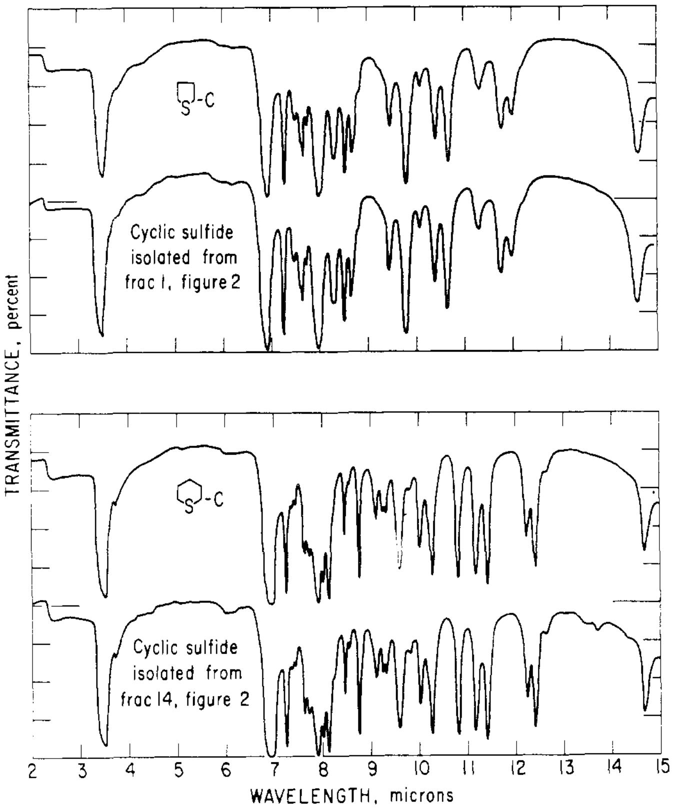
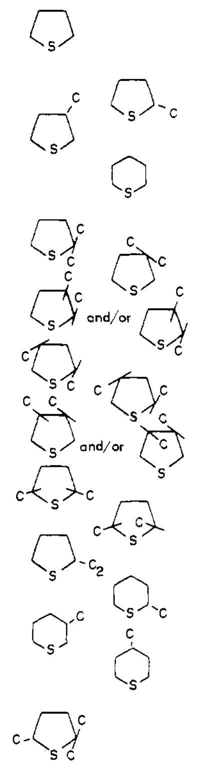


Figure 4. Comparison of infrared spectra of 2-methylthiacyclopentane and 2-methylthiacyclohexane with spectra of cyclic sulfides isolated from Wasson crude oil

Table II. Cyclic Sulfides Identified in Wasson, Tex., 111° to 150° C. Distillate by Bureau of Mines-API Research Project 48

Name	Structural Formula
C_4H_8S	
Thiacyclopentane	
$C_5H_{10}S$	
2-Methylthiacyclopentane	
3-Methylthiacyclopentane	
Thiacyclohexane	
$C_6H_{12}S$	
2,2-Dimethylthiacyclopentane	
3,3-Dimethylthiacyclopentane	
cis-and/or *trans*-2,3-Dimethylthiacyclopentane	
cis-2,4-Dimethylthiacyclopentane	
trans-2,4-Dimethylthiacyclopentane	
cis-and/or *trans*-3,4-Dimethylthiacyclopentane	
cis-2,5-Dimethylthiacyclopentane	
trans-2,5-Dimethylthiacyclopentane	
2-Ethylthiacyclopentane	
2-Methylthiacyclohexane	
3-Methylthiacyclohexane	
4-Methylthiacyclohexane	
$C_7H_{14}S$	
2,2,5-Trimethylthiacyclopentane	

to only one. If pure samples of the suspected sulfides were available or could be prepared readily, the retention times of these were determined to ascertain which coincided with that of the peak being investigated. Usually these data pointed unambiguously to the presence of an individual sulfur compound. For confirmation of identification, and where sample size and concentration permitted, the material emerging under the particular peak was retrapped, and the infrared spectrum of the trapped material was obtained using a microcell. These spectra were compared with those of reference sulfides. Two specific examples of the techniques used are discussed. However, the procedure is a general one and applies to all identifications reported in Table II.

Specific Identification of Cyclic Sulfides. The methods of identification are discussed in detail using as illustrations the two shaded peaks of fractions 1 and 14 shown in Figure 2. The materials emerging during the time interval encompassed by these two peaks were trapped and desulfurized, and the products of desulfurization were analyzed by GLC. The chromatogram of the products of desulfurization of the trapped material from fraction 14 is shown in Figure 3. This desulfurization produced predominantly *n*-hexane with some 2,3-dimethylbutane. Table I clearly indicates that of the five possible cyclic sulfide precursors of the hydrocarbon *n*-hexane, only 2-methylthiacyclohexane, having a retention time of 68.3 minutes, can be considered as present in the trapped area, 67.4 to 70.4 minutes, of fraction 14. These data tentatively identify 2-methylthiacyclohexane in Wasson crude oil.

Similarly, as shown in Table I, 3,4-dimethylthiacyclopentane is the only cyclic sulfide (cyclic sulfides with less than four carbon atoms in the ring have not been found in crude oil and are believed not to be present) that can produce 2,3-dimethylbutane on desulfurization. This cyclic sulfide is a likely constituent of the trapped material because its retention time is compatible also with that of the trapped fraction. These data indicate the tentative identification of the 3,4-dimethylthiacyclopentane.

The chromatogram of the products of desulfurization of the material associated with the shaded peak of fraction 1 (retention time, 45.0 to 47.0 min.) is not reproduced here. However, the hydrocarbon was identified as entirely *n*-pentane. The only cyclic sulfides that can produce *n*-pentane upon desulfurization are thiacyclohexane (retention time, 57.8 min.) and 2-methylthiacyclopentane (retention time, 45.9 min.). These data indicate, unmistakably, the presence of 2-methylthiacyclopentane in the material isolated from fraction 1.

Infrared spectroscopy provides additional evidence of the presence of 2-methylthiacyclohexane in fraction 14 and of 2-methylthiacyclopentane in fraction 1. Figure 4 reproduces infrared spectra of the reference compounds and of the sulfides isolated from the crude oil. The similarity of the spectra dispels any doubt of the identity of both sulfides in Wasson crude oil. The small amount of 3,4-dimethylthiacyclopentane mixed with the 2-methylthiacyclohexane producing the peak at 67.4 to 70.4 minutes in fraction 14 is only slightly evident, as indicated by two small bands between 13 and 14 μ, in the infrared spectrum. The sensitivity and utility of microdesulfurization and infrared techniques in structure characterization are evident in this study.

The procedures described above, which outlined steps in the identification of two cyclic sulfides, were applied to the individual peaks of each fraction of the cyclic sulfide concentrate.

Table II lists the cyclic sulfides identified in this study. In three instances, because of the lack of reference compounds or the nature of the data, it was impossible to distinguish unequivocally between cis- and trans-isomers. In these instances, the compounds are listed in Table II on an and/or basis, and each pair is reported as a single compound identification.

CONCLUSIONS

Seventeen cyclic sulfides were identified in a 111° to 150° C. fraction of Wasson, Tex., crude oil. This brings to 21 the total number of this class of sulfur compounds found in Wasson crude oil by the research staff of the Bureau of Mines-API Research Project 48.

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Hot Surface Ignition Temperatures of Hydrocarbon Fuel Vapor-Air Mixtures

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Autoignition temperatures (AIT's) and "wire" ignition temperatures of various hydrocarbon combustibles were determined as a function of heat source dimensions using stagnant or near-stagnant combustible vapor-air mixtures. The combustibles included *n*-hexane, *n*-octane, *n*-decane, JP-6 jet fuel, and an adipate ester aircraft engine oil (MIL-L-7808). Generally, the ignition temperatures obtained with heated Pyrex vessels and Nichrome wires or rods and tubes varied little with fuel-air ratio except at low ratios where they tended to increase. Consistent with thermal ignition theory, the ignition temperatures increased with decreasing heat source dimensions, but they correlated over a greater range of source dimensions when the surface area of the heat source rather than the radius was used. The best correlation was obtained with high AIT combustibles.

MINIMUM ignition temperatures of combustible mixtures are often determined for safety purposes under heating conditions where the energy source for ignition is a heated surface. In this connection, minimum autoignition temperatures (AIT's) are particularly useful and have been determined for many combustible materials (*1, 6, 17*). They are ordinarily determined under quiescent conditions in heated vessels sufficiently large to minimize wall quenching; under such conditions, the fuel contact times or ignition delays tend to be maximum, and the rate of heat input is not important. However, AIT values increase as the size of the vessel and the fuel contact time are decreased (*11, 14*). With a sufficiently small heat source, such as a fine heated wire, the heat input rate becomes an important factor. Generally, the ignition temperatures of combustible mixtures determined with heated wires or rods also increase with decreasing contact times and heat source dimensions (*5, 9, 10*). Surprisingly, little quantitative information is available for most combustibles on the correlation of these "hot surface" ignition temperatures over a wide range of heat source dimensions. The works of Silver (*16*) and Paterson (*12*) are noteworthy in this respect, but the relationships they obtained were primarily applicable to small platinum and quartz spheres.

The present work was initiated to define the hot surface ignition temperatures of various hydrocarbon fuel vapor-air mixtures and to obtain relationships which may be used to predict the ignition of the combustible mixtures when in contact with heated surfaces of various dimensions. The heat sources consisted of heated cylindrical and spherical Pyrex (No. 7740) vessels and Nichrome wires and rods or tubes. Since minimum ignition temperatures were of primary interest, stagnant and near stagnant flow conditions were employed. According to thermal ignition theory (*4, 15*), the temperature at which ignition occurs should vary inversely as a logarithmic function of the heat source size. Thus, autoignition and wire ignition temperatures, such as those determined here, should agree when the heat sources are of equivalent size; admittedly, the mode of heat transfer and the reaction kinetics can be limiting factors. In the present work, the ignition temperatures appeared to correlate over a greater range of heat source dimensions when the surface area of the heat source rather than the radius was used. The combustibles included *n*-hexane, *n*-octane,