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

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A systematic procedure is described for the concentration and identification of sulfur compounds in a petroleum distillate. The application of this procedure to a Wasson crude oil distillate having a boiling range of 111° to 150° C. resulted in the identification of 35 thiols, 22 chain sulfides, and 10 cyclic sulfides. The identification of the chain-sulfide groups is discussed. The procedures described are considered applicable to any petroleum distillate for determining the nature and concentration of the sulfur constituents that are present.

COLEMAN AND COWORKERS (1), reporting in part the work of API Research Project 48A, described the separation and identification of sulfur compounds in a Wasson crude oil distillate boiling to 100° C. An earlier publication (5) discussed in some detail the equipment and methods of separation and identification used by Project 48A. The procedures used in the concentration and the identification of chain sulfides in a Wasson crude oil distillate boiling between 111° and 150° C. are described in the current paper. These procedures included distillation, adsorption, chemical extraction, gas-liquid chromatography, desulfurization, and spectral analyses. The identification of 35 thiols and 10 cyclic sulfides also found in this distillate will be discussed in subsequent reports.

EXPERIMENTAL PROCEDURES

Preparation of Sulfur Compound Concentrates. To accomplish the identification of individual sulfur compounds, it was necessary to concentrate the compounds by both physical and chemical means without subjecting the sample to conditions conducive to thermal decomposition or chemical change. As shown in Figure 1, a 159 kg. sample of Wasson crude oil was subjected to isothermal distillation at 100° C. in an all-gas, falling-film, flash still (5). The distillate containing all material in the crude oil boiling below 150° C. was fractionated under vacuum to yield two distillates. A part of the 111° to 150° C. distillate was concentrated further by alumina adsorption and chemically extracted (Figure 2) to produce a thiol concentrate and a sulfide concentrate.

Zinc Chloride Extraction of Cyclic Sulfides. In searching for methods of separating the chain and cyclic sulfides in the sulfide concentrate, it was found that concentrated solutions of zinc chloride were effective in extracting thiacyclopentane (the only cyclic sulfide available at the time) from mixtures containing 5-thianonane (n-butyl sulfide) and 2,2,4,4-tetramethyl-3-thiapentane (tert-butyl sulfide), respectively. However, when the "combined sulfide concentrate" (Figure 2) was treated with a solution containing 100 grams of $ZnCl_2$ in 50 ml. H_2O, the amount extracted was quite small. Treatment with a stronger solution, 100 grams of $ZnCl_2$ in 23 ml. H_2O, caused the mixture to separate into three layers, with the middle layer consisting of a viscous zinc chloride complex containing both sulfides and aromatics. Because of this complication it was necessary to rely on the weaker solution with which a series of 38 extracts and a residue were prepared. Extracts of similar density were combined into three composite extracts for mass spectrometer analyses (Table I) and subsequently were combined into

a single cyclic sulfide concentrate (Figure 3). However, this paper is concerned primarily with the composition of the residue that consists predominantly of chain sulfides.

The above procedure involved much handling of small fractions, and the material losses were high. Consequently, no quantitative estimate of the amount of any individual
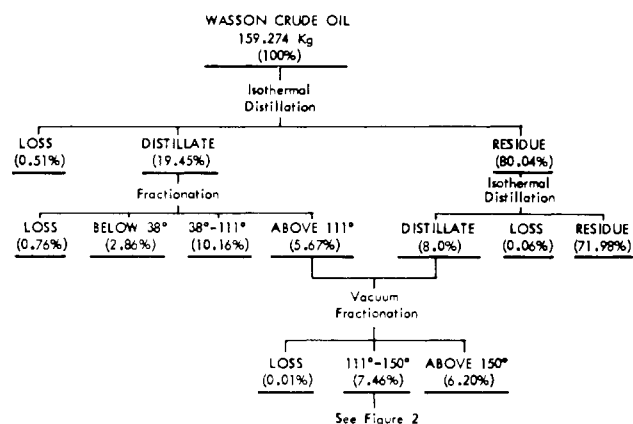

Figure 1. Treatment of Wasson Crude Oil to obtain distillate boiling from 111° to 150° C.
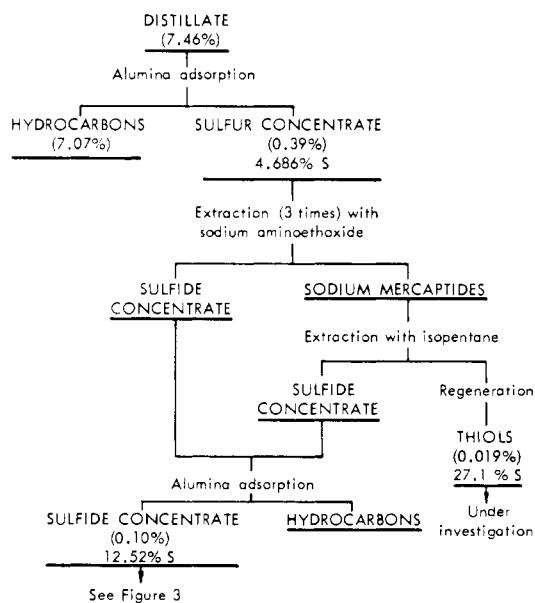

Figure 2. Treatment of 111° to 150° C. boiling-range distillate to obtain sulfide concentrate

sulfur compound isolated is warranted. Supporting evidence, discussed later in this report, indicates that no structural changes occurred in any of the compounds identified in the concentrate and that the zinc chloride extracts and residues contained only sulfur compounds originally present in the crude oil.

The results of mass spectrometer analyses of the three composite extracts and of the residue from the extractions are shown in Table I.

The data were obtained by the parent peak approach using average sensitivities for available reference chain and cyclic sulfides. There was no evidence of peaks associated with classes of compounds other than the chain and cyclic sulfide series for the molecular weights given. The salient fact is that although complete separation between cyclic and chain sulfides was not achieved, reasonably effective concentration was accomplished; this is evidenced by a ratio of cyclics to chain sulfides of 86-to-14 in the cyclic-sulfide concentrate and of 30-to-70 in the chain-sulfide concentrate (residue).

Fractionation. A sample of 2.717 grams of the predominantly chain-sulfide concentrate was fractionated at a pressure of 450 mm. of Hg in an all-glass, concentric-tube column (3), with 1-heptanethiol added as a "chaser." The fractionation curve is plotted in Figure 4. Fraction 6 (not represented completely in Figure 4) consisted almost entirely of the "chaser," 1-heptanethiol. The temperature-volume fluctuation appearing at the end of fraction 3 was caused by momentary irregular boiling of the small charge in the column pot. The boiling points of some of the sulfides identified (corrected to 450 mm. Hg using a Cox (2) chart) are also indicated in Figure 4. Figure 5 shows gas-liquid chromatograms of fractions, 1,3-6. These chromatograms were obtained using a ¼-inch by 40-foot column containing Dow Corning silicone 550 oil on 30-42 mesh firebrick support in the weight-ratio of 30 to 100. The order of compound emergence from this relatively nonpolar column depends primarily on boiling point.

The chromatogram of fraction 6 in Figure 5 indicates, as expected from the boiling point plot of Figure 4, that this fraction consists almost entirely of 1-heptanethiol, the "chaser" used in the fractionation. This fraction and fraction 5 were not examined further. Fraction 2 was consumed in some preliminary work and was not available for the survey illustrated by Figure 5, but comparison of chromatograms of fractions 1, 2, and 3 from runs on another column indicated that fraction 2 was a true transition fraction with no compounds present that were not present in fractions 1 or 3. Only fractions 1 and 3 were examined exhaustively in the work reported here. The emergence times of the sulfides identified in these fractions are shown by arrows in Figure 5.

IDENTIFICATION OF CHAIN SULFIDES—GENERAL

Table II lists 39 chain sulfides found to date in crude oil in the work of API Research Project 48 and indicates those found in the 111° to 150° C. Wasson distillate considered in this paper. The following tabulation shows the number of chain sulfides of C_1 to C_7 carbon number found in the crude oil as compared to the number theoretically possible:

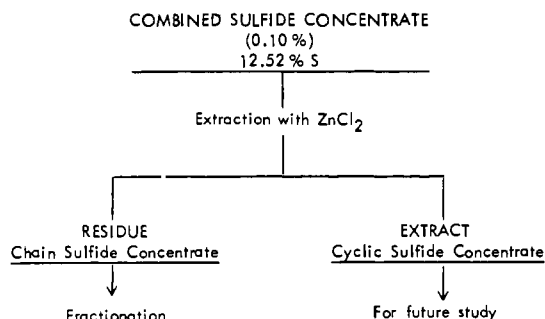| Carbon Atoms in Molecule	Number of Possible Isomers	Number Identified in Wasson Crude Oil
C_2	1	1
C_3	1	1
C_4	3	3
C_5	6	5
C_6	15	12
C_7	33	8
	59	30

Figure 3. Separation of chain and cyclic sulfides by $ZnCl_2$ extraction
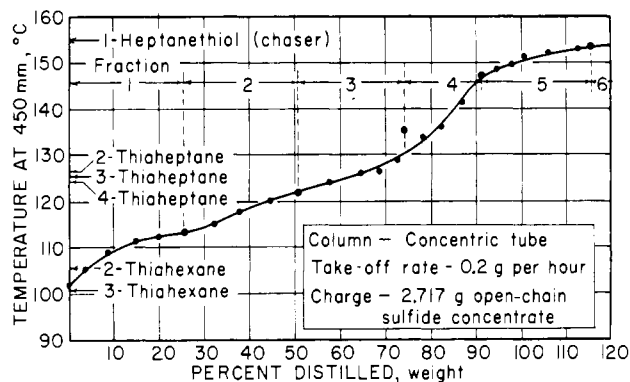
Figure 4. Fractionation of chain sulfide concentrate from 111° to 150° C. Wasson distillate
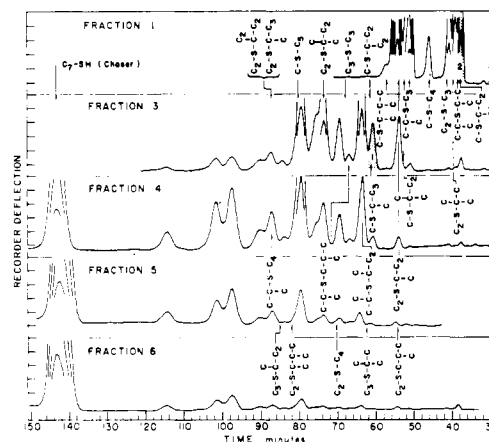
Figure 5. Gas-liquid chromatograms of distillations fractions, 1, 3-6

Table I. Mass Spectrometer Analysis of Residue and Extracts from $ZnCl_2$ Extraction of Sulfide Concentrate

	Per cent Component in:				
	Extracts				
Components	1-8	9-14	15-38	Average	Residue
C_4 Cyclic Sulfides	4.5	2.2	0	2.4	0
C_5 Cyclic Sulfides	24.5	8.1	0	12.2	0
C_6 Cyclic Sulfides	59.0	75.1	76.3	68.8	17.2
C_7 Cyclic Sulfides	1.7	2.2	4.5	2.8	12.6
Total cyclic sulfides	89.7	87.6	80.8	86.2	29.8
Total chain sulfides	10.3	12.4	19.2	13.8	70.2

These identifications were accomplished by the micro-desulfurization techniques developed in this laboratory (6) and by comparison of GLC emergence times and infrared spectra of pure sulfides with those of materials isolated from the Wasson crude oil.

The procedure followed 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 of fractions 1, 3, and 4 were trapped and desulfurized (6). The hydrocarbons produced by desulfurization were identified by GLC emergence time. From this information the search for the sulfide precursor of the hydrocarbons was narrowed to two or three possibilities and occasionally to only one. If pure samples of the suspected sulfides were available or could be prepared readily, the emergence times of these were determined to ascertain which fell under the peak of the fraction chromatogram. Usually these data pointed unambiguously to the presence of an individual sulfur compound. For confirmation of identification, the material emering under the particular peak again was trapped, and the infrared spectrum of the trapped material was obtained in a spectrophotometer using a microcell. These spectra were compared with those of pure sulfides. Occasionally mass spectra were also used as additional proof of identity. Two specific examples of the techniques used will be discussed.

Figure 6. Comparison of gas-liquid chromatograms of desulfurized materials from Wasson crude oil and of reference hydrocarbons

However, the procedure waś a general one and applies to all identificatíons reported in Table II.

Identification of Chain Sulfides—Specific. Two shaded peaks are shown in Figure 5, fractions 1 and 3: Trap 2 of fraction 1 at 36.2 to 38.2 minutes emergence time and trap 1 of fraction 3 at 58.4 to 61.7 minutes emergence time. The materials emerging during the time interval encompassed by these two peaks were desulfurized, and the products of desulfurization were analyzed by GLC. The chromatograms of the products of desulfurization of the two samples are shown in the top and bottom panels, respectively, of Figure 6. The center panel shows a chromatogram of a mixture of hydrocarbons from methane through n-pentane for reference purposes. Obviously, desulfurization of the material of trap 2, fraction 1, gave essentially pure propane, which might have originated from any one or any combination of three chain sulfides: 4-Thiaheptane, C_3—S—C_3; 2-methyl-3-thiahexane, C—C(C)—S—C_3; or 2,4-dimethyl-3-thiapentane, C—C(C)—S—C(C)—C. The emergence times of these three sulfides (see Figure 5) are 67.6, 51.0, and 37.8 minutes, respectively, and hence the material emerging under the shaded peak of fraction 1 (emergence time, 36.2 to 38.2 minutes) could be only 2,4-dimethyl-3-thiapentane. The small amounts of methane and n-butane and smaller quantities of ethane and isobutane undoubtedly originated from the presence of 3-methyl-2-thiapentane, C—S—C(C)—C_2, and from 4,4-dimethyl-3-thiapentane, C_2—S—C(C)₂—C; compounds whose emergence times (37.2 and 39.2 minutes, respectively) place them as very likely contaminants in material collected in trap 2. Later work has shown that these contaminants could be eliminated by trapping and rechromatographing on a highly polar column such as Reoplex 400, in which the retention time of such compounds as 2,4-dimethyl-3-thiapentane would be expected to be materially lowered below that of the other two compounds (4). Desulfurization of the material producing trap 1 of fraction 3 (bottom panel, Figure 6) gave methane and n-pentane in equal quantities. The chain sulfides producing these two materials could be any one of, or combination of, the following three sulfides: 2 - thiaheptane, C — S — C_5; 3 - methyl -2-thiahexane, C—S—C(C)-C_3; or 3-ethyl-2-thiapentane, C—S—C(C_2)—C_2. The emergence times of these three compounds are 80.0, 61.1, and 61.7 minutes, respectively. The retention time of the 2-thiaheptane at 80.0 minutes eliminates this compound from further consideration. However, both of the other sulfides would fall in the trapped area, 58 to 62 minutes, and both would produce methane and n-pentane upon desulfurization. From desulfurization and GLC data alone, it was necessary to place the identification of these two compounds on an "and/or" basis. However, infrared spectra of the trap material permitted the firm identification of both compounds, with 3-methyl-2-thiahexane found in much greater concentration than 3-ethyl-2-thiapentane.

Confirmatory proof of identification of 2,4-dimethyl-3-thiapentane in trap 2, fraction 1 of Figure 5, and of 3-ethyl-2-thiapentane and 3-methyl-2-thiahexane in trap 1, fraction 3, was obtained by infrared spectroscopy. Figure 7 portrays infrared spectra of a pure sample of 2,4-dimethyl-3-thiapentane and of the material from trap 2, fraction 1. Obviously, the two samples are essentially identical. Similarly, spectra are shown in Figure 8 of samples of 3-ethyl-2-thiapentane and 3-methyl-2-thiahexane and of the material from trap 1, fraction 3 of Figure 5. Here, too, the similarity of the spectra dispels any doubt of the identity of both sulfides in Wasson crude oil.

The procedure described above, detailing steps in the identification of two chain sulfides, was applied to other pertinent peaks in the chromatograms of fractions 1, 3, and 4 of Figure 5, leading to the identification of the additional sulfides listed in Table II. In two instances the data were insufficient to distinguish unequivocally between two
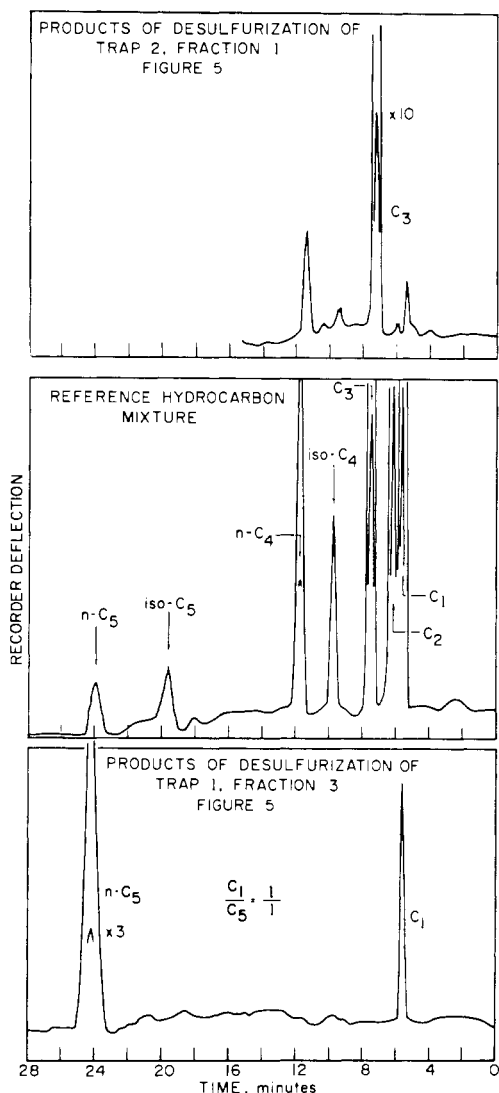
compounds. In these instances the compounds are shown in Table II on an "and/or" category, and each pair is reported as a single compound.

Zinc Chloride Extraction of Synthetic Blend. That of ZnCl₂ extraction method is effective in removing cyclic sulfides from sulfide mixtures without detectable decomposition in either the extract or residue is illustrated in Figure 9.

A two-ml. blend of 8 sulfides (5 chain, 2 cyclic, and 1 alkyl-cycloalkyl) diluted with 25 ml. pentane was extracted four times with 10 ml. of solution containing 100 grams of ZnCl₂ in 37 ml. H₂O. The material extracted was recovered from the ZnCl₂ solution after dilution with water by extraction with butane. The gas-liquid chromatogram of the 8-component blend is shown in the top panel of Figure 9,

Table II. Chain Sulfides found in Petroleum—API Research Project 48

Name	Structural Formula	Reported in: This Paper	Reported in: Reference (5)
C₂H₆S			
2-Thiapropane	C—S—C		X
C₃H₈S			
2-Thiabutane	C—S—C₂		X
C₄H₁₀S			
2-Thiapentane	C—S—C₃		X
3-Thiapentane	C₂—S—C₂		X
3-Methyl-2-thiabutane	C—S—C—C with C branch		X
C₅H₁₂S			
2-Thiahexane	C—S—C₄	X	X
3-Thiahexane	C₂—S—C₃	X	X
3-Methyl-2-thiapentane	C—S—C—C₂ with C branch	X	
2-Methyl-3-thiapentane	C—C—S—C₂ with C branch		X
3,3-Dimethyl-2-thiabutane	C—S—C—C with C branch		X
C₆H₁₄S			
2-Thiaheptane	C—S—C₅	X	
3-Thiaheptane	C₂—S—C₄	X	X
4-Thiaheptane	C₃—S—C₃	X	
3-Methyl-2-thiahexane	C—S—C—C₃ with C branch	X	
2-Methyl-3-thiahexane	C—C—S—C₃ with C branch	X	X
4-Methyl-3-thiahexane	C₂—S—C—C₂ with C branch	X	X
5-Methyl-3-thiahexane	C₂—S—C—C—C with C branch	X	
3,3-Dimethyl-2-thiapentane	C—S—C—C₂ with C branches	X	ᵃ
3,4-Dimethyl-2-thiapentane	C—S—C—C—C with C, C branches	X	
3-Ethyl-2-thiaphentane	C—S—C—C₂ with C₂ branch	X	
2,2-Dimethyl-3-thiapentane	C—C—S—C₂ with C, C branches	X	X
2,4-Dimethyl-3-thiapentane	C—C—S—C—C with C, C branches	X	X

and chromatograms of the residue and extract (at the end of the fourth extraction) are shown in the center and bottom panels, respectively. The charges of sample to the chromatograph to produce the chromatograms of the blend and of the residue were approximately aliquot quantities; hence, features of these two chromatograms are comparable quantiatively. This is evidenced by the approximately equal-area peaks for the 3-ethyl-2-thiapentane and for the 2-methyl-3-thiaheptane in both the chromatograms of the original blend and of the residue from its extraction by ZnCl₂. Neither of these compounds were extracted by ZnCl₂. However, the charge of sample to produce the chromatogram of the extract was approximately 10 times greater than the aliquot required to make this chromato-

Table II. Chain Sulfides found in Petroleum—API Research Project 48 (*Continued*)

Name	Structural Formula	Reported in: This Paper	Reported in: Reference (5)
$C_7H_{16}S$			
2-Methyl-3-thiaheptane[b]	C—C—S—C₄ (with C above second C)	X	[c]
4-Methyl-3-thiaheptane	C₂—S—C—C₃ (with C above center C)	X	[c]
2-Methyl-4-thiaheptane	C—C—C—S—C₃ (with C above second C)		[c]
3-Methyl-4-thiaheptane[b]	C₂—C—S—C₃ (with C above center C)	X	[c]
2,2-Dimethyl-3-thiahexane	C—C—S—C₃ (with C above and C below second C)	X	
2,4-Dimethyl-3-thiahexane	C—C—S—C—C₂ (with C above first C and C above third C)	X	[a]
2,5-Dimethyl-3-thiahexane	C—C—S—C—C—C (with C above first C and C above fourth C)	X	
4,4-Dimethyl-3-thiahexane	C₂—S—C—C₂ (with C above and C below center C)	X	
4,5-Dimethyl-3-thiahexane	C₂—S—C—C—C (with C above center C, and C above and C₂ below fourth C)	X	[c]
4-Ethyl-3-thiahexane[d]	C₂—S—C—C₂ (with C₂ below center C)	X	
$C_8H_{18}S$			
3,5-Dimethyl-4-thiaheptane	C₂—C—S—C—C₂ (with C above both center carbons)		[c]
2,4-Dimethyl-3-thiaheptane	C—C—S—C—C₃ (with C above first C and C above third C)		[c]
2-Methyl-4-ethyl-3-thiahexane	C—C—S—C—C₂ (with C above first C and C₂ below third C)		[c]
4-Ethyl-3-thiaheptane	C₂—S—C—C₃ (with C₂ below center C)		[c]
5-Methyl-4-thiaoctane	C₃—S—C—C₃ (with C above center C)		[c]
3-Ethyl-4-thiaheptane	C₂—C—S—C₃ (with C₂ below second C)		[c]
4-Methyl-3-thiaoctane	C₂—S—C—C₄ (with C above center C)		[c]
3-Methyl-4-thiaoctane	C₂—C—S—C₄ (with C above second C)		[c]
2-Methyl-3-thiaoctane	C—C—S—C₅ (with C above second C)		[c]

[a] Not previously published but announced in API Research Project 48 Annual Report 7/1/60. [b] Compound tentatively identified on "and/or" basis. [c] Not previously published but announced in API Research Project 48 Annual Report 7/1/62. [d] Tentatively identified on "and/or" basis with 4-methyl-3-thiaheptane in this work. 4-Methyl-3-thiaheptane identified in previous work—see column 4.
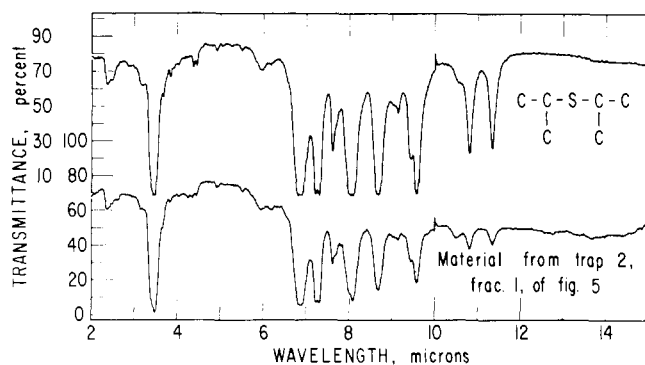
Figure 7. Comparison of infrared spectra of 2,4-dimethyl-3-thiapentane and sulfide isolated from Wasson crude oil
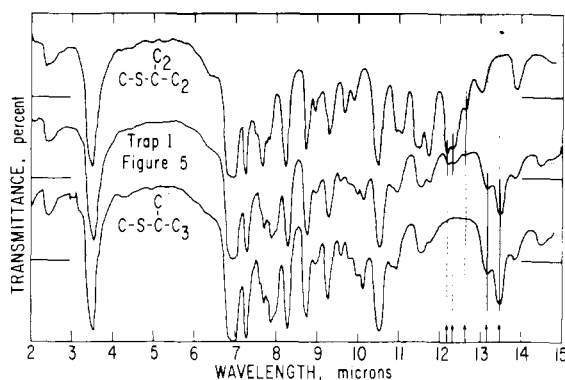

Figure 8. Comparison of infrared spectra of 3-ethyl-2-thiapentane and 3-methyl-2-thiahexane with spectrum of sulfides isolated from Wasson crude oil
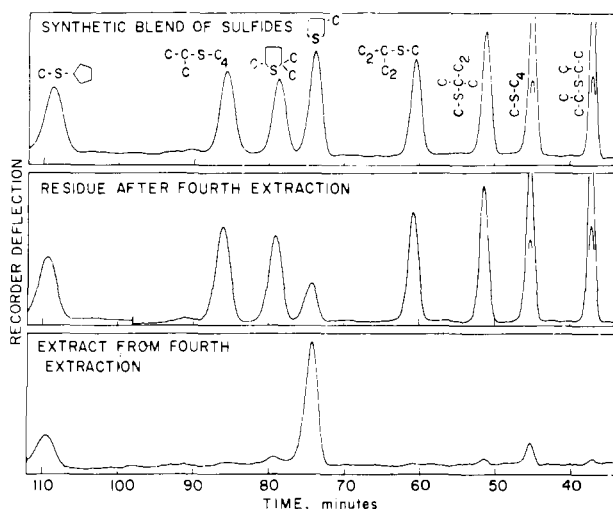

Figure 9. Gas-liquid chromatograms of synthetic blend, zinc chloride extract, and residue

Table III. Peak Areas and Relative Peak Areas of Chromatograms of Original Blend and of Residue after Four Extractions with ZnCl₂

	Peak Areas		Relative Peak Areas[a]		
Component	Original Blend	Residue	Original Blend	Residue	Percent Extracted
C–C–S–C–C (with C, C branches)	35	40	1.1	1.1	–
C–S–C₄	39	39	1.2	1.1	8
C–S–C–C₂ (with C branch)	34	38	1.1	1.1	–
C–S–C–C₂ (with C₂ branch)	32	35	1.0	1.0	–
(thiacyclopentane with C)	40	15	1.3	.4	70
(thiacyclobutane C, C)	31	35	1.0	1.0	–
C–C–S–C₄ (with C branch)	37	43	1.2	1.2	–
C–S–(cyclopentane)	37	35	1.2	1.0	17

[a] Relative to peak of the fourth component, 3-ethyl-2-thiapentane.

of this table, are calculated from "relative peak areas," which tends to compensate for inaccurate aliquot chromatograph charges. The figures in this table show that about 70 per cent of the 3-methylthiacyclopentane (component 5), 17 per cent of the cyclopentyl-1-thiaethane (component 8), and 8 per cent of the 2-thiahexane (component 2) originally present in the blend were removed in the four extractions. Lesser quantities of some of the other sulfides were also extracted, but the amounts do not fall within the range of accuracy of the data in the table. No evidence of extraneous peaks was apparent in the chromatograms of the residues or extracts, indicating that there was no decomposition or fragmentation of the sulfur compounds treated.

While tending to accomplish the desired objective of separating cyclic sulfides from chain sulfides, ZnCl₂ extraction, as employed here, is far from an ideal procedure for this purpose and suffers from faults common to other similar procedures. The method is not completely selective, in that some types of chain sulfides are partially extracted; it is not quantitative, in that the amount of sulfides extracted appears to depend on concentration of the material to be extracted and upon structure. Despite these limitations, multiple extractions of sulfide mixtures result in a considerable degree of segregation of cyclic sulfides in the extract and of chain sulfides in the residue.

A favorable feature of the extraction is that there does not appear to be any chemical change in the sulfur compounds induced by contact with ZnCl₂.

CONCLUSIONS

Using the techniques described in this paper, 22 chain sulfides were identified in a Wasson 111° to 150° C. distillate, bringing to 39 the total number of this class of sulfur compounds found in Wasson, Texas, crude oil under API Research Project 48.

Positive statements based on the limited quantitative data at hand are, perhaps, unwarranted, but it would appear that in any specific series of sulfides (for example, C—S—Cₙ), the amount of each present in Wasson, Texas, crude oil diminishes with increase in carbon-chain length.

gram (bottom panel of Figure 9) quantitatively comparable to the chromatograms of the original blend and of the residue. Thus, the chromatogram exaggerates the amount of 3-methylthiacyclopentane extracted. It also reveals the presence of small amounts of other sulfides extracted, for example, 2-thiahexane (peak at 45.1 minutes), and it indicates that the alkyl-cycloalkyl sulfide (cyclopentyl-1-thiaethane) is extracted but not as rapidly as the 3-methylthiacyclopentane. The extraction depends on the preferential formation of a ZnCl₂ complex with cyclic sulfides. Cyclic sulfides with the sulfur atom highly hindered, such as 2,2,5-trimethylthiacyclopentane, however, are affected but little by the reagent. The above observations are more obvious upon inspection of Table III in which peak areas and relative peak areas are recorded. "Percent Extracted" data, recorded in the last column

ACKNOWLEDGMENT

LITERATURE CITED

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(2) Cox, Edwin, R., *Ind. Eng. Chem.* **15**, 592 (1923).
(3) Donnell, C.K., Kennedy, R.M., *Proc. Am. Petrol. Inst. Sect. III* **26**, 23 (1946).
(4) Thompson, C.J., Coleman, H.J., Hopkins, R.L., Rall, H.T., *U. S. Bur. Mines Rept. of Invest.* **6252**, 11 pp. (1963).
(5) Thompson, C.J., Coleman, H.J., Rall, H.T., Smith, H.M., *Anal. Chem.* **27**, 175 (1955).
(6) Thompson, C.J., Coleman, H.J., Ward, C.C., Rall, H.T., *Ibid.* **32**, 424 (1960).

CORRECTIONS

In the article "Measurement of Dynamic Surface Tension in Bubbling Systems" by John B. Roll and John E. Myers [J. CHEM. ENG. DATA **9**, 257 (1964)] the captions for figures 3 and 4 should be reversed.

In the article "Interaction in Nonelectrolyte Solutions, Solubility of Naphthalene in Some Mixed Solvents Containing Benzene" by E.L. Heric and C.D. Posey [J. CHEM. ENG DATA **9**, 35 (1964)] a number of corrections should be made.

Equation 12 is: $RT\ln\gamma_2 = x_1^2 W_{12} + x_3^2 W_{23} + x_1 x_3 (W_{12} + W_{23} - W_{13})$

Equation 13 is: $RT\ln\gamma_2 = V_2^2 [\phi_1^2 W_{12}' + \phi_3^2 W_{23}'$

$$+ \phi_1 \phi_3 (W_{12}' + W_{23}' - W_{13}')]$$

Equation 16 is: $|W_{02}'|^{1/2} = \dfrac{\phi_1 |W_{12}'|^{1/2} \pm \phi_3 |W_{23}'|^{1/2}}{\phi_1 + \phi_3}$

The main column heading appearing on page 41 should read W', Cal. Ml.$^{-1}$ and the heading for column 11 should read $(\delta_{Benzene} - \delta_{second\ solvent})^{2,b}$.

In the article "Identification of Nitrogen Bases in Heavy Gas Oil; Chromatographic Methods of Separation" by D.M. Jewell and G.K. Hartung [J. CHEM. ENG. DATA **9**, 297 (1964)] the present address of G.K. Hartung is Munich 25, Germany, Marbachstrasse 12.

On p. 302 the lines 25–31 "absorbs at 251 mμ which would cause the disagreement in the λ minima values between the two curves illustrated.

"In order to ascertain the presence of the 1,10-phenanthroline isomer in fraction 2SF, the well known reaction of ferrous ions with these types of nitrogen bases was employed: the ferrous ions form stable, water soluble, red complexes with compounds having an α,α'-phenanthroline..." should immediately precede ."...type of linkage (8, 13, 14)" at the top of p. 302.

Two corrections should be made in the article "Thermodynamic Properties of HF" by R.M. Yabroff, J.C. Smith, and E.H. Lightcap [J. CHEM. ENG. DATA **9**, 178 (1964)]. The first conversion factor listed in the nomenclature should read C = specific heat, P.c.u./lb.-° C. or cal./g.-° C. On page 180, below Equation 8, the definition for C^* is

$$C_v + V \frac{\Delta P}{\Delta T}$$