# Identification of Thiols in a Wasson, Texas, Crude Oil Distillate Boiling from 111° to 150° C.

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**Characterization of the naturally occurring sulfur compounds in petroleum is of both theoretical and practical interest to petroleum chemists and geologists. This paper describes a systematic procedure for the concentration and identification of 35 individual thiols present in a Wasson, Texas, crude oil distillate boiling from 111° to 150° C. The procedures applied included distillation, alumina adsorption, chemical extraction, gas-liquid chromatography, microdesulfurization, and infrared spectroscopy. Many $C_5$ and $C_6$ thiols, not commercially available, were synthesized, and GLC retention times and infrared spectra of some of these are presented. The procedures described represent a systematic method of sulfur compound analysis that should have general application in petroleum studies.**

IDENTIFICATION through 1954 of 43 sulfur compounds in a Wasson, Texas, crude oil was reported by Thompson and coworkers (*15*). A related paper, (*5*), described the separation and identification of some sulfur compounds in a Wasson crude oil distillate boiling to 100° C. Since that date, the introduction of gas-liquid chromatographic (GLC) techniques has materially advanced the identification of sulfur compounds in petroleum. Additionally, the development of a microdesulfurization method (*14, 16*) has complemented the GLC technique, by providing a basis for identifications not possible otherwise. Recently, Thompson and coworkers (*13*), working with a 111° to 150° C. distillate from Wasson crude oil identified 22 chain sulfides of which six were reported earlier (*15*). The present paper records the continuation of the investigation of the 111° to 150° C. distillate with respect to the thiols, of which 35 were identified. Fourteen of these were reported in previous publications (*2, 5, 15*). Some of the thiols listed by the authors as present in Wasson, Texas, crude oil also have been reported in other crude oils (*1, 3, 4, 6, 7, 9, 10, 11*). Future work will deal with the cyclic sulfides present in the 111° to 150° C. distillate.

## EXPERIMENTAL PROCEDURES

**Preparation of Sulfur Compound Concentrate.** Both physical and chemical means were used in securing a suitable sulfur compound concentrate from the distillate for the identification of individual sulfur compounds. The procedures used in processing 159 kg. of Wasson crude oil to produce a thiol concentrate (22.5 grams) and an aromatic, neutral-sulfur compound concentrate (445.2 grams) have been described previously (*8, 13*). Both concentrates were investigated; however, the results from the thiol-free, neutral-sulfur compound concentrate, in which chain (*13*) and cyclic sulfides were identified, will not be discussed in this article. The thiol concentrate was vacuum fractionated, at a pressure of 450 mm. of Hg, in an all-glass concentric-tube column (rated at about 150 plates efficiency at atmospheric pressure). 1-Heptanethiol, not present in this boiling range of Wasson crude oil, was added as a "chaser." The distillation curve, based on this fractionation, is shown in Figure 1. The boiling temperatures of the thiols on this chart are included to give some comprehension of their distribution in the fractions. These boiling points were calculated from normal boiling points at 760 mm. of Hg. Each of the 24 fractions represents about 0.0009 wt. % of the crude oil.

**General Identification of Thiols.** Table I lists the thiols in Wasson, Texas, crude oil found by API Project 48. Included are all aliphatic thiols through the hexanethiols and five of the 39 theoretically possible heptanethiols. Also identified were cyclopentanethiol, cyclohexanethiol, 1-methylcyclopentanethiol, *cis-* and/or *trans*-3-methylcyclopentanethiol, and both *cis-* and *trans*-2-methylcyclopentanethiol. Cyclopentylmethanethiol, the only other theoretically possible $C_6$ cycloalkanethiol, is too high boiling to be included in the 111° to 150° C. boiling-range distillate. This boiling-range distillate has but relatively small quantities of $C_7$ thiols present, and these are branched isomers as represented by the identified 2-methyl-2-hexanethiol. Other $C_7$ thiols (1-, 2-, 3-, and 4-heptanethiols) have been identified in a higher (150° to 220° C.) boiling-range distillate, and these identifications will be discussed in the future.

The thiols found in the 111° to 150° C. Wasson distillate were all identified by the same general procedures: GLC analyses of the distillate fractions (Perkin-Elmer Model 154-D gas chromatograph equipped with a thermistor detector was used in the thiol investigation—in all instances,

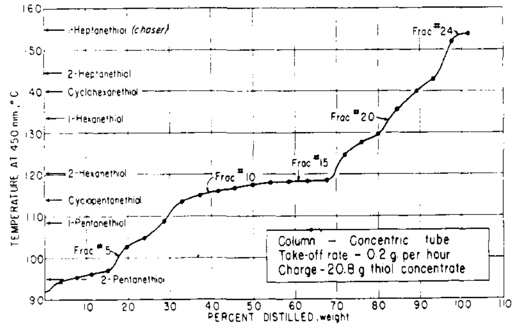


Figure 1. Fractionation of thiol concentrate from 111° to 150° C. Wasson distillate

Table I. Thiols Found in Petroleum by API Research Project 48

| | Reported in: | |
|---|---|---|
| Class Name | This paper | Ref. (*15*) |
| $CH_3SH$ | | |
| Methanethiol | | x |
| $C_2H_5SH$ | | |
| Ethanethiol | | x |
| $C_3H_7SH$ | | |
| 1-Propanethiol | | x |
| 2-Propanethiol | | x |
| $C_4H_9SH$ | | |
| 1-Butanethiol | x | x |
| 2-Butanethiol | x | x |
| 2-Methyl-1-propanethiol | x | x |
| 2-Methyl-2-propanethiol | | x |
| $C_5H_{11}SH$ | | |
| 1-Pentanethiol | x | |
| 2-Pentanethiol | x | x |
| 3-Pentanethiol | x | x |
| 2-Methyl-1-butanethiol | x | |
| 3-Methyl-1-butanethiol | x | |
| 2-Methyl-2-butanethiol | x | x |
| 3-Methyl-2-butanethiol | x | x |
| 2,2-Dimethyl-1-propanethiol | x | |
| $C_5H_9SH$ | | |
| Cyclopentanethiol | x | x |
| $C_6H_{13}SH$ | | |
| 1-Hexanethiol | x | |
| 2-Hexanethiol | x | x |
| 3-Hexanethiol | x | x |
| 2-Methyl-1-pentanethiol | x | |
| 3-Methyl-1-pentanethiol | x | |
| 4-Methyl-1-pentanethiol | x | |
| 2-Methyl-2-pentanethiol | x | |
| 3-Methyl-2-pentanethiol | x | |
| 4-Methyl-2-pentanethiol | x | x |
| 2-Methyl-3-pentanethiol | x | |
| 3-Methyl-3-pentanethiol | x | x |
| 2,2-Dimethyl-1-butanethiol | x | |
| 2,3-Dimethyl-2-butanethiol | x | |
| 2,3-Dimethyl-1-butanethiol | x | |
| 3,3-Dimethyl-2-butanethiol | x | |
| 3,3-Dimethyl-1-butanethiol | x | |
| 2-Ethyl-1-butanethiol | x | |
| $C_6H_{11}SH$ | | |
| Cyclohexanethiol | x | x |
| 1-Methylcyclopentanethiol | x | |
| *cis*-2-Methylcyclopentanethiol | x | x |
| *trans*-2-Methylcyclopentanethiol | x | |
| *cis*- and/or *trans*-3-Methylcyclopentanethiol | x | |
| $C_7H_{15}SH$ | | |
| 1-Heptanethiol | | [a] |
| 2-Heptanethiol | | [a] |
| 3-Heptanethiol | | [a] |
| 4-Heptanethiol | | [a] |
| 2-Methyl-2-hexanethiol | x | |

[a] Data not previously published but announced in API Research Project 48 Annual Report 7-1-63.

the GLC solid support, designated "F.B." on the appropriate figures, was 30-42 mesh "GC-22 Super-Support" supplied by Coast Eng. Labs.); desulfurization of selected trapped fractions from the GLC chromatograph and identification of the hydrocarbons produced; tentative identification of the sulfur compound precursor of the hydrocarbon desulfurization products by consideration of GLC retention times of both the trapped material and possible thiol precursors; confirmation of identification, if material was sufficient, by obtaining infrared spectrum (or other property) of the tentatively identified sulfur compound and comparing with that of a known standard.

IR spectra have consistently confirmed the tentative identifications afforded by combined GLC and desulfurization techniques. Occasionally desulfurization leads to an ambiguity because two sulfur compounds of nearly identical emergence times (inseparable in the GLC column) yield the same hydrocarbons on desulfurization (*16*, Figure 4). Seldom encountered is the ambiguous situation where two sulfur compounds of nearly the same retention times yield different hydrocarbons whose retention times are also nearly identical. Changing GLC column substrates usually circumvents these situations.

In the discussion that follows, typical examples are given to illustrate the general method of analyses outlined above. All identifications reported in this paper were accomplished in the same manner.

**Specific Identification of Thiols.** Figures 2 and 3 are gas-liquid chromatograms of fractions 1 and 18, obtained under column conditions stated below the figure title. On the bottom of both figures, arrows indicate the retention times of selected thiols. These are identified by letters keyed to the compound formula on the side of each chart. Also indicated on each chart are certain fractions ("traps"), numbered 1 to 11 on Figure 2, and 1 to 7 on Figure 3, that were studied in this investigation. The short vertical lines at the bottom of each chart denote the time intervals over which the material emerging from the column was collected in the numbered traps. Thus, for example, the shaded area in Figure 2, encompassing the time interval of 32.2 to 33.9 minutes, depicts the portion of fraction 1 collected in "trap 11." Attenuation ratios shown on the curve indicate that the amount of material collected in trap 11 is about one-hundredth that of trap 4 and is, in fact, a very minor part of fraction 1. The material collected in trap 11 was identified as essentially 100% 3-methyl-3-pentanethiol. Because of a slight time shift that occurs on the trailing edge of a large

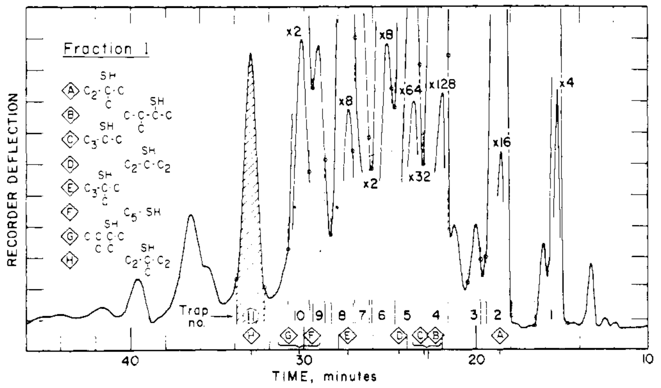


Figure 2. Gas-liquid chromatogram of fraction 1

| Column | Conditions |
|---|---|
| Dimensions: ¼-inch O.D. by 40-feet long | Temperature: 140° C. |
| Substrate: D.C. 550 silicone oil, 35 grams/100 grams 30-42 mesh F.B. | Gas flow rate: 60 ml./min. |
| | Charge: 20λ |

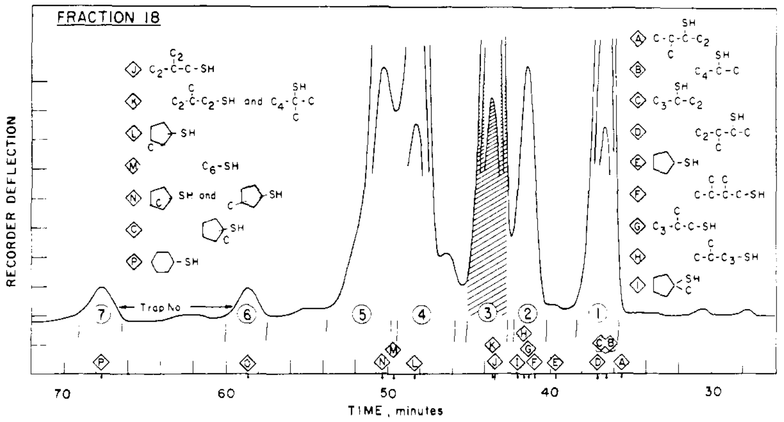


Figure 3. Gas-liquid chromatogram of fraction 18

*Column and conditions same as in Figure 2 except charge = 2.0λ*

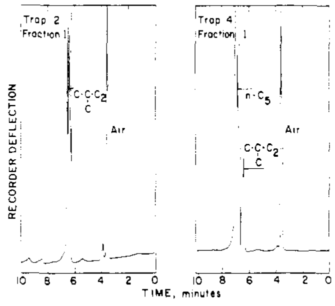


Figure 4. Gas-liquid chromatograms of desulfurization products of traps 2 and 4, fraction 1

peak, this trap avoided inclusion of 3,3-dimethyl-1-butanethiol, a trace component with a normal retention time of 33.8 minutes. Although all the materials forming "peaks," as shown in Figure 2, were trapped, examined, and identified, only traps 2 and 4 will be discussed here in detail.

The two panels of Figure 4 show gas-liquid chromatograms of the products of desulfurization of materials from traps 2 and 4, Figure 2. Trap 2 was collected over a time interval of 18.0 to 19.4 minutes, and the product of desulfurization of this trap, as indicated by retention time, was solely 2-methylbutane. Of the four possible thiol precursors of the hydrocarbon 2-methylbutane, shown in Table II in the order of their increasing GLC retention times, only 2-methyl-2-butanethiol (*tert*-amyl mercaptan), having a retention time of 18.6 minutes, can be considered as present in trap 2. The same reasoning can be applied to the data from trap 4. The material of this trap was collected during the time interval of 21.6 to 23.1 minutes. In this instance, two hydrocarbons were found in the products of desulfurization, as shown in Table II. The identity of these hydrocarbons and related GLC data permit the tentative identification of 2-pentanethiol and 3-methyl-2-butanethiol with the latter being present in only trace amounts.

Although the data of Table II permitted the tentative identification of 2-methyl-2-butanethiol in trap 2 and 2-pentanethiol and 3-methyl-2-butanethiol in trap 4, it was possible to obtain additional GLC data and confirmatory proof by infrared spectrometry. The 3-methyl-2-butanethiol was inseparable from 2-pentanethiol on the Dow-Corning 550 silicone oil substrate used to produce the chromatogram of fraction 1, shown in Figure 2. However, by rechromatographing a portion of the material of trap 4 on a ¼-inch O.D. × a 40-foot long di-2-ethylhexyltetraphenylphthalate column, 3-methyl-2-butanethiol was partially resolved as a minor peak just preceding the much larger 2-pentanethiol peak. Furthermore, sufficient sample, producing peaks 2 and 4, of Figure 2 was collected, rechromatographed for purification, and analyzed by infrared. Figure 5 shows these IR spectra compared with similar spectra of purified reference thiols. The similarity of these spectra is obvious and clearly proves that the material isolated from the Wasson crude oil fraction is indeed that determined from GLC retention time and desulfurization data.

In addition to the three thiol identifications discussed above, 12 other thiols were also found in fraction 1. Eight of these thiols are unlabeled with respect to the GLC peaks in Figure 2. Trap 1 consisted predominately of 2-butanethiol at 15.3 minutes with but a trace of 2-methyl-1-propanethiol represented by the minor peak at 16.1 minutes. The relatively small peak at 20.1 minutes, collected as trap 3, was identified as 2,2-dimethyl-1-propanethiol. 1-Butanethiol, identified in earlier work, was present in this sample in only trace quantities, which is indicated by the very small deflection between traps 2 and 3. Materials of traps 6, 7, and 9 were identified as 3-methyl-1-butanethiol at 25.5 minutes, 2-methyl-1-butanethiol at 26.8 minutes, and 4-methyl-2-pentanethiol at 29.4 minutes, respectively. The small deflection between traps 10 and 11 at 31.0 minutes was caused by a trace quantity of 3,3-dimethyl-2-butanethiol. The small peaks beyond 34 minutes were major peaks in the chromatograms of higher boiling fractions, for example, fraction 18 (Figure 3).

The procedure of gas-chromatographically separating each fraction into its individual components and applying desulfurization and infrared analysis for the identification of the isolated thiols was discussed with respect to traps 2 and 4 of fraction 1 (Figures 2, 4, 5, and Table II). The same procedural steps were followed throughout the investigation of each fraction of the thiol concentrate and provided the data essential for identifying the 35 thiols listed in Table I.

## DISCUSSION

The reported 35 thiol identifications were derived from a qualitative interpretation of the data obtained. However, some of these data are capable of quantitative interpretation and yield information on the relative abundance of certain thiol types in Wasson crude oil.

In the 111° to 150° C. thiol concentrate, the most predominant individual chain thiols present are the 2-alkanethiols. 2-Pentanethiol, for instance, constitutes 10% of the entire concentrate or 0.00189% of the original Wasson crude oil. Even assuming some azeotroping into the 100° to 111° C. boiling range, the concentration of 2-pentanethiol in the crude oil is considerably less than that found in earlier work for 2-butanethiol (5). 2-Hexanethiol is inseparable

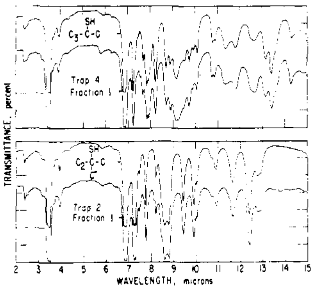
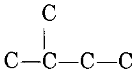
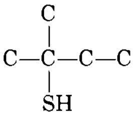
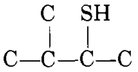
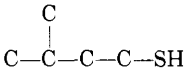
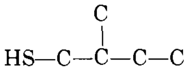
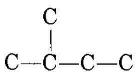
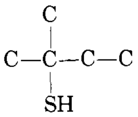
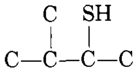
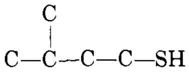
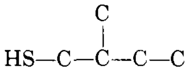
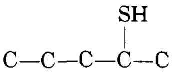
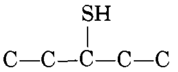


Figure 5. Comparison of spectra of 2-pentanethiol and 2-methyl-2-butanethiol with spectra of materials isolated from fraction 1

Table II. GLC and Desulfurization Data from Fraction 1 (Figures 2, 4)

(Pointing to the presence of 2-methyl-2-butanethiol, 3-methyl-2-butanethiol, and 2-pentanethiol in Wasson 111°–150° C. distillate)

| Trap Number and Time Interval of Trapping | Desulfurization Product of Trapped Material | Possible Thiol Precursors | |
|---|---|---|---|
| | | Formula | Retention time, min. |
| Trap 2<br>18.0-19.4 |  $C-\overset{C}{C}-C-C$ |  $C-\underset{SH}{\overset{C}{C}}-C-C$ | 18.6[a] |
| | |  $C-\overset{C}{C}-\overset{SH}{C}-C$ | 22.7 |
| | |  $C-\overset{C}{C}-C-C-SH$ | 25.5 |
| | |  $HS-C-\overset{C}{C}-C-C$ | 26.8 |
| Trap 4<br>21.6-23.1 |  $C-\overset{C}{C}-C-C$ |  $C-\underset{SH}{\overset{C}{C}}-C-C$ | 18.6 |
| | |  $C-\overset{C}{C}-\overset{SH}{C}-C$ | 22.7[a] |
| | |  $C-\overset{C}{C}-C-C-SH$ | 25.5 |
| | |  $HS-C-\overset{C}{C}-C-C$ | 26.8 |
| | C—C—C—C—C |  $C-C-C-\overset{SH}{C}-C$ | 23.0[a] |
| | |  $C-C-\overset{SH}{C}-C-C$ | 24.2 |
| | | C—C—C—C—C—SH | 30.3 |

[a] Only possible precursor with a retention time in agreement with time interval of trap.

from 3-hexanethiol and difficultly so from two or three other thiols; hence a quantitative figure cannot be assigned in this instance though it is presumed to approximate the concentration of 2-pentanethiol. Other abundant chain thiols in order of their decreasing concentration are: 3-alkanethiols (3-pentanethiol 0.00131%), 2-methyl-2-alkanethiols (2-methyl-2-pentanethiol 0.00128%), and 3-methyl-3-alkanethiols (3-methyl-3-pentanethiol 0.00101%).

1-Alkanethiols, as represented by 1-pentanethiol and 1-hexanethiol, are relatively minor constituents of the entire thiol concentrate. This is in agreement with data from lower boiling Wasson distillates (*12*). The concentration of 1-pentanethiol is conservatively estimated to be 0.0002%, and 1-hexanethiol approximately one-half that amount.

The highly substituted thiols such as 2,2-dimethyl-1-propanethiol, 2,2-dimethyl-1-butanethiol, 3,3-dimethyl-1-butanethiol, and 3,3-dimethyl-2-butanethiol are present in but trace quantities (<0.00001%). The 2-methyl-1-, 3-methyl-1-, and 4-methyl-1-alkanethiols are up another step in the concentration scale (approximately 0.00004 to 0.0001%), and the 2,3-dimethyl-2-alkanethiols are still more abundant (2,3 - dimethyl - 2 - butanethiol approximately 0.0003%). The boiling range limitation does not permit conclusions as to relative concentrations for these highly substituted $C_7$ thiols because, although some are present, their inclusion is incomplete.

Some $C_7$ chain thiols as well as some $C_6$ cyclic thiols, particularly cyclohexanethiol, have boiling points above 150° C. and are only partially included in this thiol concentrate. Cyclohexanethiol is known to be present in the boiling range above 150°, but it also constitutes 10% of the 111° to 150° C. thiol concentrate from Wasson distillate or 0.00188% of the original crude oil. This percentage is roughly one order of magnitude greater than the concentration of cyclopentanethiol. All methyl substituted cyclopentanethiols, as a group, represent only about half the cyclohexanethiol concentration.

## CONCLUSIONS

Using the combined techniques of distillation, alumina adsorption, chemical extraction, gas-liquid chromatography, microdesulfurization, and infrared spectroscopy, 35 individual thiols were identified in a Wasson 111° to

150° C. distillate, bringing to 44 the total number of this class of sulfur compounds found in Wasson, Texas, crude oil. From this study, some observations relative to the abundance of certain thiol types are presented. The perfected separation and identification techniques discussed should materially aid other researchers interested in similar studies.

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# Melting Point and Vapor Pressures of 3-Hexyne

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**The equilibrium vapor pressure of 3-hexyne was measured in the temperature range of −20° C. to 25° C. using a modified isotensioscope and a mercury manometer. From the slope of the Clausius-Clapeyron plot of the data, the heat of vaporization was calculated to be 7560 cal. per mole, and an equation was written to fit the data. The melting point of purified and degassed 3-hexyne was obtained with the use of a calibrated platinum resistance thermometer. The measured value of −102.5 ± 0.2° C. for the melting point falls within the wide range of scant literature values.**

LITTLE INFORMATION on the physical constants of 3-hexyne is available. The most recent chemical handbooks (*4, 5*) listed no melting point, boiling point, or vapor pressure data. An extensive search of the literature yielded reliable boiling point data (*1—3*) but the melting points found ranged from −101 to −105.53° C. (*1, 3*). No vapor pressure data could be found. In view of the discrepancy in the reported melting points and for want of vapor pressure data, the authors deviated slightly in this study of the radiation chemistry of 3-hexyne to look into its physical chemistry. No special effort was made to determine accurately the boiling point since good agreement was found in the literature.

## EXPERIMENTAL

**Purification.** The 3-hexyne was obtained from Farchan Research Laboratories and purified by distillation through a 5-foot, 5-mm. I.D., monel wire column at a 10 to 1 reflux ratio. The purification was monitored by gas-liquid chromatography. Analysis of the chromatogram of the middle third cut showed an impurity level of 0.05%.

**Boiling Point.** At total reflux, the middle third cut had a boiling point of 80.0–80.5° C. at 747 torr. Using the heat of vaporization obtained from the authors' vapor pressure data, the corrected boiling point for 760 torr was 81.2° C. This is in excellent agreement with the following literature