SULFUR COMPOUNDS IN CRUDE OIL

By H. T. Rall, C. J. Thompson, H. J. Coleman, and R. L. Hopkins

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SULFUR COMPOUNDS IN CRUDE OIL

by

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ABSTRACT

This report summarizes a systematic 20-year study of the organic sulfur compounds in Wasson, Texas, crude oil and, to a lesser extent, of three other crude oils, that has culminated in some 200 individual sulfur-compound identifications. The development and application of special separation and identification techniques generally suitable for the characterization of sulfur compounds in any crude oil are discussed. This report reviews early sulfur literature covering petroleum sulfur compound identifications completed before this study was begun, and cites 58 papers resulting from this work. The sulfur compounds in petroleum, both as to type and quantity, have long been of concern to the petroleum industry, and such compositional data are not only of theoretical interest, but also of practical value.

INTRODUCTION

In 1947, having recognized the deleterious effects of sulfur compounds in petroleum and the dearth of knowledge of the character and properties of these compounds, the Executive Committee of the American Petroleum Institute's Advisory Committee on Fundamental Research on Composition and Properties of Petroleum, in cooperation with the Bureau of Mines, concluded that the establishment of a research project to study the occurrence and nature of sulfur compounds in petroleum was justified and timely (24).[4] This project was inaugurated in July 1948 as API Research Project 48. It was organized in two sections, RP 48A and RP 48B, under the directorship of Harold M. Smith of the Bartlesville Research Center and F. G. Bordwell of Northwestern University, respectively. RP 48A was divided into three phases: (1) The production and purification of sulfur compounds and the determination of their properties, conducted at the Laramie Research Center of the Bureau of Mines under Project Associate Director John S. Ball; (2) the measurement of thermodynamic properties of sulfur compounds, conducted at the Bartlesville Research Center under Project Associate Director Hugh M. Huffman; and (3) the identification of sulfur compounds in petroleum at the Bartlesville Research Center under Project Director Harold M. Smith.[5] The function of RP 48B, under Dr. Bordwell, was the development of methods of synthesis and studies of the reactions of sulfur compounds. RP 48B was terminated on June 30, 1963; RP 48A was continued until June 30, 1966.

This report is concerned only with the work of the Separation and Identification Section of RP 48A. The specific assignment or mandate of this section of the project was as follows: (1) To identify sulfur compounds in crude oils as they exist in the

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[1] Former project leader. Retired February 7, 1969.
[2] Project leader.
[3] Research chemist.
[4] Italic numbers in parentheses refer to items in the list of references at the end of this report.
[5] Upon the resignation of H. M. Smith to become Regional Director of the Bureau of Mines in July 1954, H. T. Rall became Codirector of RP 48 with jurisdiction over the Separation and Identification Section.

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geologic structure, (2) to develop separation methods applicable to sulfur compounds in crude oil fractions, and (3) to develop identification methods applicable to sulfur compounds isolated from crude oil or its fractions.

During the life of the project, 176 individual sulfur compounds were identified in four crude oils. These compounds were representative of 13 classes of sulfur compounds ranging from the simple thiols (mercaptans) to the more complex dibenzothiophenes. The presence of alkyl cycloalkyl sulfides, alkyl aryl sulfides, and thiaindans in Wasson petroleum, classes previously unreported in any crude oil, was established. Evidence was obtained that multiring thiophenes and sulfides were the major sulfur-compound components of high-boiling petroleum fractions.

In addition to the compounds identified, several controversial questions relative to sulfur compounds in crude oils were answered. For example, elemental sulfur was thought by many to be absent in crude oils or (when reported present) to have been formed during sample treatment. This concept was shown to be erroneous. Thiophenes, when identified, were thought to have been formed by decomposition of other, less stable, sulfur compounds under exposure to temperature. The project established the presence of thiophenes in crude oil by isolating them under very mild thermal conditions.

In addition to this new information, the project developed analytical procedures in the course of its investigations and used them to further its aims. Among these were several extractive methods for removing specific classes of sulfur compounds. A desulfurization method applicable to submicroliter-size samples, that rapidly and quantitatively removes the sulfur atom from sulfur compounds, was developed and found to be extremely effective in identification studies.

The methods evolved and the scientific data developed were made available to industry and to the scientific community through Bureau publications and journal articles.

This bulletin summarizes a systematic 20-year study of the organic sulfur compounds of Wasson, Texas, crude oil and, to a lesser extent, of three other crude oils. The special separation and identification techniques developed and applied and the individual sulfur compound identifications achieved are described. This bulletin, written for the student as well as the petroleum chemist, discusses sulfur in many natural products and cites early sulfur literature covering petroleum sulfur identifications completed before this project was begun. Information has been provided on some qualitative and quantitative trends, on the most prevalent structures, and on similarities and differences in the sulfur content of various crudes.

ACKNOWLEDGMENTS

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6 Deceased.

SULFUR IN NATURE

Sulfur [7] is one of the most plentiful elements in nature, ranking thirteenth in abundance in the earth's crust (3). It appears (1) in the elemental state, (2) combined with other elements as minerals, and (3) as a vital constituent in plant and animal tissue. Petroleum and petroleum science is directly concerned with all three modes.

THE MINERAL SULFUR

Sulfur was one of the two nonmetallic elements known to ancient civilizations, the other being carbon. As "brimstone," sulfur is mentioned in the Bible, and Homer (about 900 B.C.) tells of its fumigating properties when burned to SO_2.[8] Sulfur and "sulfurous fumes" are products of volcanic activity, and undoubtedly such sulfur was the source of supply of the element for ancient people as it is to a proportionately lesser extent today (10, 135, 158, 163). The origin of most of the Japanese deposits of elemental sulfur (400) is due to volcanism. For example, in recent times (1936) an eruption of Siretoko-losen on the Siretoka Peninsula, Hokkaido, Japan, discharged 150,000 cubic meters of elemental sulfur, according to Watanabe (239, p. 329; 449). Iwo Jima (Sulfur Island) [9] of World War II prominence, with its extinct volcano Suribachi, contains many extinct and active solfataras or fumaroles, the largest of which was mined for sulfur by the Japanese before World War II (239, pp. 259–265). The cone of Suribachi contains an active solfatara.

But the world's largest sulfur deposits are sedimentary and bear no relation to volcanism. The origin of the sulfur in the Sicilian sulfur beds has been discussed by W. F. Hunt (199), who suggested a biogenic reduction of sulfate in lagoon beds to produce H_2S:

$$CaSO_4 + 2C + 2H_2O \rightarrow 2CO_2 + Ca(OH)_2$$
$$+ Ca(SH)_2 \rightarrow CaCO_3 + 2H_2S$$

in which the carbon is furnished by the microorganism. The hydrogen sulfide, diffusing to the surface of the lagoon, would be oxidized to sulfur and water and the sulfur precipitated. The possibility that other bacteria also aid in this reaction is not excluded. The postulation of a biogenic reduction of sulfates was not original with Hunt, but was suggested by Plauchud (322) in 1877, Etard and Oliver (118) in 1882, and Beyerinck (33) in 1895, who investigated the action of algae and bacteria on the sulfates in water solution.

Enormous deposits of sulfur also occur over so-called salt domes.[10] The origin of this sulfur likewise is thought to be biogenic wherein the calcium sulfate (anhydrite and gypsum) present in the caprock of the dome is reduced by microbial action to hydrogen sulfide which subsequently is oxidized to elemental sulfur (121).

Sulfur also is present abundantly in nature combined with other elements as, for example, iron (FeS_2, pyrite, the most common sulfide); copper (Cu_2S, chalcocite); lead (PbS, galena); zinc (ZnS, sphalerite); and others. In addition it occurs extensively as metal sulfates, such as, gypsum ($CaSO_4 \cdot 2H_2O$, the most common sulfate), barite ($BaSO_4$), epsomite ($MgSO_4 \cdot 7H_2O$), mirabilite (Glauber's salt, $Na_2SO_4 \cdot 10H_2O$), and others.

The waters of the earth's surface, springs, rivers, lakes, and oceans, carry large amounts of sulfur in solution in the form of salts, principally as sulfates. Because of climatic conditions and other factors, these waters are never uniform in composition but vary greatly with time and with their geographical location and environment. This variation is not so pronounced in oceanic waters which are fairly uniform in the composition of their salt content but which vary considerably in their concentration in the water. This circumstance is well illustrated in the 24 sea water investigations listed by Clarke (67) in which the results of analyses of more than 275 ocean water samples, collected at miscellaneous points on the earth, are discussed. For example, in these samples the average sulfate (SO_4) concentration is 7.74 ± 0.12 percent of their total salt content, but the concentration of total salt in the samples ranges from 0.7 to 6 percent, averaging about 3.5 percent. An average value for the weight-percent of sulfur (as elemental sulfur) in sea water is given by Goldschmidt (145) as 0.088 weight-percent, which is in reasonable agreement with data reported by Clarke. This percentage of sulfur ranks the element in sixth

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[7] According to Raghu Vira's English-Indian Dictionary of Scientific terms (1950), the word "sulfur" (or sulphur) is derived from the Sanskrit *shulbari*, meaning "enemy (*ari*) of copper" (*shulba*) (314).

[8] "Bring me purifying brimestone, dame, and bring fire, for me to smoke the place through . . . Whereupon Odysseus carefully purged the hall, the private rooms, and the court with fire and brimestone. . . ." (365).

[9] The island was visited in 1783 by the British ship *Resolution* in command of Mr. Gare who had succeeded Capt. Cook after his death in Hawaii. Gare gave the island its name because of the "sulphuric" vapors which were seen rising from it (181).

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[10] Boling Dome of Wharton County, Tex., the largest in that State, has produced more than 53 million long tons of elemental sulfur since production started, 1929 through 1960 (301).

place of abundance in sea water, being exceeded in weight-percent only by oxygen, 85.89; hydrogen, 10.82; chlorine, 1.90; sodium, 1.06; and magnesium, 0.13. The value 0.088 weight-percent seems very small, but a simple arithmetic calculation indicates that if this sulfur were actually released as elemental sulfur and distributed evenly on the earth's surface, land and water, it would cover it to a depth of 7½ feet.

Depending upon regional rainfall and the nature of the soil traversed, surface or shallow subsurface streams (rivers, springs, etc.) can be comparatively free of dissolved salts or contain considerable quantities (67). The sulfate percentage of the total solids contained in the waters also varies widely. These waters have little relation to the question of sulfur in petroleum except in those instances where they are able to penetrate to the depths of petroleum-producing horizons and merge with the oilfield brines. These brines act as confining fluids for the accumulation of petroleum displaced from original source beds to geologic traps or reservoirs (436, 451). The forces producing this transfer or migration are not understood, but are thought to reside in one or more of the following agencies: compaction (18), buoyancy, solubility of oil (21, 34, 315) in water, or hydraulic pressure. The origin of the brines is not known with certainty (287) nor the manner in which dissolved salts became concentrated in some of them. The generally held view is that sea water was retained in the sediment of the source bed in which petroleum was formed or to which it was displaced after its burial. These waters, where undiluted or unconcentrated, in effect, are "fossil" (relict) sea waters. Dilution of these waters can be explained by ingress of surface water, but their concentration is less easily explained. Concentra-

tion by evaporation (287) has been proposed, but a mechanism whereby certain confining geologic strata act as semipermeable membranes (50, 97), to permit passage of water but retard the passage of salt, is receiving study and support.

Table 1 records an analysis of sea water and of five selected brines (332) from various oilfields of Kansas. The water sample in this table from Russell field resembles sea water fairly closely. This is true also of the sample from Goodrich field except that its sulfate content is materially lower. The remaining three samples illustrate waters containing a high sulfate content, Toulon field; one containing no sulfate, Snider field; and one of very high total solids (257,000 ppm or 7 times sea water) but a small sulfate content, Hugoton field. Since the extreme variation of sulfate concentration displayed in this series of water samples from petroleum-producing formations may have important significance to the sulfur content of the crude oils produced from these formations, a brief review is warranted.

The variation in sulfate concentration in oilfield brines was observed by Eichler (116) in Caucasian oilfields as early as 1874. Hofer (1909) commented upon the phenomenon in Das Erdol (175) and reported the analysis of 27 sulfate-free waters. Hofer proposed the equation:

$$CaSO_4 + CH_4 \rightarrow CaCO_3 + H_2S + H_2O$$

to account for the loss of sulfate, the increase of carbonate, and the appearance of hydrogen sulfide in the formation waters. Marino and Danesi (274) indicated that this reaction does occur at high temperatures ($>550°$ C), but other investigators (28) reported that it will not occur at temperatures encountered in oilfield formations. R. W. Pakc

Table 1.—Analysis of sea water and of five selected Kansas oil field brines

Field Depth, feet Date	Seawater [1]		Russell [4] 3,303–3,307 9–16–49		Goodrich 3,336–3,338 9–8–50		Toulon 3,560 3–14–17		Snider 3,376–3,397 5–11–49		Hugoton 2,576–2,680 12–7–51	
	Parts per million [2]	Percent [3]	Parts per million	Percent	Parts per million	Percent	Parts per million	Percent	Parts per million	Percent	Parts per million	Percent
Calcium	421	1.20	1,690	5.01	1,080	3.34	640	1.33	3,580	6.43	17,800	6.13
Magnesium	1,309	3.73	402	1.19	468	1.45	935	1.95	1,420	2.55	5,780	2.25
Sodium+potassium	11,139	31.70	10,400	30.85	10,700	33.12	16,000	33.34	15,800	28.38	72,700	28.30
Carbonate	73	.21	0		0		0		0		0	
Acid carbonate	....		404	1.20	546	1.69	1,420	2.96	170	.31	55	.02
Sulfate	2,703	7.69	3,010	8.93	112	.35	4,790	9.98	0	.00	570	.22
Chloride	19,430	55.29	17,800	52.81	19,400	60.05	24,200	50.43	34,700	62.33	160,000	62.28
Total solids	35,140	100	33,706	100	32,306	100	47,985	100	55,670	100	256,905	100

[1] Analysis from Challenger Expedition Report, 1884 (67). Average of 77 samples.
[2] Column 3×3.514×10⁴, see footnote 3.
[3] Salinity, 3.301 to 3.737. Average = 3.514.
[4] Analyses of oilfield brines from reference 333.

(313), studying the geology of the Sunset-Midway, California, oilfield, observed the loss of sulfate in the waters of that field in the vicinity of the oil zones. Indeed, this phenomenon was so marked that its observance was recommended to drillers as an indication that the drill was approaching the oil-bearing strata. Pack also commented upon a reaction between sulfate and the oil in the formation to produce "tarry oil and tar" and mentioned the concept that sulfate could not exist in the vicinity of oil because of this reaction. Rogers (345) reviewed some of the background of the bacterial conversion of sulfate to hydrogen sulfide known at that time (1919), but discounted this hypothesis in favor of the reaction of the sulfate with oil; a concept now known to be erroneous. The bacterial conversion of sulfate to hydrogen sulfide will be brought up again in a later section of this report.

Some sulfur always has been present in the atmosphere of the earth as hydrogen sulfide and sulfur dioxide, which are components of the exhalations of volcanoes. In addition, hydrogen sulfide is a product of the decay or putrefaction of dead plant and animal tissue. Both gases, particularly sulfur dioxide, are products of coal combustion, a factor of rising importance since the beginning of world industrialization. Thus, a report written in 1887 (448) estimated that at Rothamsted Experimental Station, Harpenden, England, 17.26 pounds of SO_3 was deposited annually by rainfall upon each acre of land. Air pollution by sulfur has steadily increased, and the addition of petroleum to the world's energy sources and the enormous increase in the world's fuel consumption have produced the current serious concern for the future purity of the atmosphere. Thus it has been estimated (346) that in the United States in 1963, 23,370,000 tons of sulfur dioxide were released to the atmosphere, of which 4,827,000 tons (20.7 percent) came from the combustion of petroleum products and 1,583,000 tons (6.8 percent) from refinery operations. An atmospheric phenomenon of lesser importance but of some scientific interest was the recent discovery (1961) by Junge and others (216) of the existence of an aerosol layer surrounding the earth, of which sulfur, probably as ammonium sulfate, constitutes 85 percent. The origin of the sulfate is thought to arise in the action of ozone or ultraviolet radiation on hydrogen sulfide or sulfur dioxide originating on the surface of the earth.

Sulfur is found in meteorites in elemental form (219, 294, 348); in minerals, such as iron sulfide

Table 2.—Relative abundance of elements and their rank

Element	In earth's crust		In cosmos [1]		In human body	
	Weight-percent [2]	Rank	Abundance [3]	Rank	Weight-percent [4]	Rank [5]
Oxygen	46.6	1	25,000	3	63.03	1
Silicon	27.7	2	1,000	6	....	......
Aluminum	8.13	3	94.8	11	....	......
Iron	5.00	4	85.0	12	.01	13
Calcium	3.63	5	49.0	13	2.46	5
Sodium	2.83	6	43.8	14	.10	11
Potassium	2.59	7	3.16	19	.12	10
Magnesium	2.09	8	912.	7	.07	12
Titanium	.44	9	1.68	22	....	......
Phosphorus	.118	10	10.0	16	1.13	6
Manganese	.100	11	6.85	18	....	......
Fluorine	.070	12	1.6	23	.14	8
Sulfur	.0520	13	375	9	.14	9
Strontium	.0450	14	....	....	....	......
Carbon	.0320	15	9,300	4	20.20	2
Nitrogen	.05	....	2,400	5	2.46	4
Argon	....	....	150	10	....	......
Neon	....	....	800	8	....	......
Helium	....	....	3,800,000	2	....	......
Hydrogen	....	....	25,000,000	1	9.87	3

[1] Silicon = 1000.
[2] From data of Ahrens and Taylor (3).
[3] Cameron (59).
[4] From Lotka (251).
[5] Chlorine ranks next below carbon in earth's crust and is not included in this table. This element ranks 7 in abundance in the human body.

(troilite) and calcium sulfide (oldhamite) (*438, 450*); and in more volatile chemical combinations, such as CS_2 and SO_2 (*399*). The spectrum of sulfur has been found in stars and nebulae (*282*), and it is of little wonder that Cameron (*59*) estimated sulfur to rank ninth in his table of cosmic abundance.

The crust of the earth, obviously, is of more significance to the life upon it than is the cosmos. Table 2, columns 2 and 3, gives the relative abundance and the order of abundance of the elements in the earth's crust. These data are estimates, excluding the atmosphere and hydrosphere, two important reservoirs of nitrogen, oxygen, and hydrogen. Columns 4 and 5 give comparative data for the cosmos. The element sulfur ranks high in both categories. Columns 6 and 7 give the weight-percent of these elements in the human body and the order of their abundance there. The 12 elements listed in column 6, with a few additional ones,[11] have been found vital to animal life. No organism lives independent of geochemical processes, which is probably why elements prominent in nature (carbon, hydrogen, oxygen, nitrogen, and sulfur) play such a significant role in organic or biological chemistry.

SULFUR IN BIOLOGY

Although the element sulfur is vital to life, its quantity in living matter usually is small. For example, the bulk of the human body is composed of oxygen, carbon, and hydrogen and contains only 0.14 percent sulfur. However, despite this small percentage, the element ranks ninth in abundance in the body. The first reported analysis for sulfur in any biological material is that of Cadet (*56*), who analyzed the ash of kelp in 1767 and reported finding potassium sulfate. Since then much work has been done on sulfur in biological materials, and the literature on the subject is extensive. Table 3 presents a few select sulfur-containing compounds identified in biological materials. Such compounds are numerous and those listed in the table are representative only. The compounds selected for this table were chosen for their historical or biological importance or to indicate structural similarities and ramifications. Many of the compounds identified in plant juices do not exist as such in the plant, but are produced by enzymic reaction upon injury to the plant tissues. Thus alliine, the first natural sulfide isolated in plants, is present in the cells of garlic. It is converted to allicine,

$$C{=}C{-}C{-}SO{-}S{-}C{-}C{=}C$$
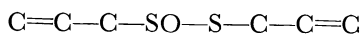
a principal component of the "oil of garlic," by an enzyme also present in the garlic cell but contacting the precursor alliine only upon rupture of the cell walls. Other such instances are known, and many are suspected. The function of the sulfur-containing compounds in the life of the organism in which they are found is understood in many instances. Thus the amino acid methionine acts in a vital capacity as a reservoir for methyl groups (*111*) in the metabolism of microorganisms, plants, and animals. Since it is not synthesized in the human, it must be taken in the diet. Thiamine was the first vitamin (i.e., B_1) to be identified and isolated and is essential in the diet for the prevention of beri-beri. Insulin, a vital hormone and the first protein whose structure was established (not included in table 3), contains two chains of amino acids joined at two points by a disulfide linkage with a third disulfide bridge in one of the chains.

The 0.14 percent sulfur reported in the body of man (table 2) is probably typical of *Vertebrata Mammalia*, whereas the amount in muscles of fish averages slightly higher or about 0.15 to 0.20 percent. Snails, clams, oysters, etc., (Mollusca), contain about 0.4 percent sulfur which, for the most part, is included in the muscular tissue of the animal, much of it as taurine. The leaves of land plants are in a slightly higher bracket of sulfur content, ranging from about 0.1 to 0.4 percent organic sulfur. But the highest percentages of sulfur in any organisms are found in the marine plants and in bacteria. Thus Hoagland (*174*) reports 13 percent sulfur in the brown marine alga *Macrocystis pyrifera*. Even higher percentages (i.e., 25 percent) are found in bacteria where granules of elemental sulfur are observed in the tissues of the bacterium *Beggiatoa alba* and others (*70, 437, 459*). It is at this point that the science of petroleum merges with that of biology, for it now is accepted generally that the remains of these rapidly multiplying plants [12] settling in the sediments of the geologic past became the source of the present petroleum deposits probably through some mechanism involving burial and anaerobic bacterial decay. This belief is supported, in part at least, by the finding of fossil algae in Precambrian rocks 3 billion years old (*208, 279, 359, 447*) as well as in the geologically younger Mesozoic and Tertiary beds, 180 million to 1 million years old (*207*).

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[11] Chlorine, zinc, copper, cobalt, and iodine.

[12] Consider, for example, that among the bacteria, generation times of 15 to 30 minutes are common. These times have been measured under ideal environments, and if such an environment could exist for 35 hours, one bacterium dividing once every 30 minutes could produce 1,000 cubic meters of material. Of course, generation on such a scale is self-annihilating through food depletion and self-destruction from accumulation of waste products. The calculations, however, readily suggest the potential capacity of these organisms to produce the organic matter from which petroleum may be derived.

Table 3.—Structure of some organic sulfur compounds occurring naturally in microorganisms, plants, and animals

Name	Structural formula [1]	Found in —	Reference
Cysteine	$\overset{\displaystyle NH_2}{HS-C-\underset{\;}{C}---C-O_2H}$	Protein keratin; wool; feathers: etc.; algae	Numerous, 117, 291
Taurine	$HO-\underset{\displaystyle O}{\overset{\displaystyle O}{S}}-C-\overset{\displaystyle NH_2}{C}$	Bile of mammals	Numerous
	$\underset{\displaystyle C}{\overset{\displaystyle C}{}}{\diagdown}{\diagup}\overset{\displaystyle Cl}{}\;S-C-C-C-O_2H$	Red marine algae	63, 55
Felinine	$HO-C-C-\overset{\displaystyle C}{\underset{\displaystyle C}{C}}-S-C-\overset{\displaystyle NH_2}{C}---C-O_2H$	Cat urine	454
Methionine	$C-S-C-C-\overset{\displaystyle NH_2}{C}---C-O_2H$	Protein casein; egg albumin; wool	293
	$\underset{\displaystyle C}{\overset{\displaystyle C}{}}{\diagdown}{\diagup}\;S-C-C-\overset{\displaystyle NH_2}{C}---C-O_2H$	Cabbages	263
Glutathione	$HO_2-C-\overset{\displaystyle NH_2}{C}---C-C-\overset{\displaystyle O}{C}-N-\overset{\displaystyle SH}{\underset{\;}{C}}-\underset{\displaystyle O}{C}-N-C-C-O_2H\;(H)$	Yeast; red blood cells	184
Lanthionine	$HO_2-C-\overset{\displaystyle NH_2}{C}---C-S-C-\overset{\displaystyle NH_2}{C}---C-O_2H$	Wool; feathers; hair	194
Cystine	$HO_2-C-\overset{\displaystyle NH_2}{C}---C-S-S-C-\overset{\displaystyle NH_2}{C}---C-O_2H$	Protein keratin	Numerous
Djenkolic acid	$HO_2-C-\overset{\displaystyle NH_2}{C}---C-S-C-S-C-\overset{\displaystyle NH_2}{C}---C-O_2H$	Djenkol bean	440
	$C-\overset{\displaystyle C-O_2H}{C}---C-S-C-\overset{\displaystyle NH_2}{C}---C-O_2H$	Onion	442
Isoralthine	$C-\overset{\displaystyle C}{\underset{\displaystyle C-O_2H}{C}}---S-C-\overset{\displaystyle NH_2}{C}---C-O_2H$	Urine of arteriosclerosis patients	311
	$C-\overset{\displaystyle C-O_2H}{\underset{\displaystyle C}{C}}---S-C-\overset{\displaystyle NH_2}{C}---C-O_2H$	Urine of arteriosclerosis patients and cats	289
	$C-\overset{\displaystyle O}{S}-C-\overset{\displaystyle NH_2}{C}---C-O_2H$	Cabbage and other crucifers	291, 402
	$C-C=C-\overset{\displaystyle O}{S}-C-\overset{\displaystyle NH_2}{C}---C-O_2H$	Onion	444
Alline	$C=C-C-\overset{\displaystyle O}{S}-C-\overset{\displaystyle NH_2}{C}---C-O_2H$	Garlic	394
Sulforaphen	$C-\overset{\displaystyle O}{S}-C=C-C-C-N=C=S$	Seeds of radish	355

Table 3.—Structure of some organic sulfur compounds occurring naturally in microorganisms, plants, and animals—Continued

Name	Structural formula [1]	Found in —	Reference
Cheirolin	(structure)	Yellow wall flower (mustard)	357
Erysolin	(structure)	Orange wall flower (hedge mustard)	358
Terthienyl	(structure)	Marigold	468
Junipal	(structure)	Wood rotting fungi	44
	(structure)	Tansy root	152
	(structure)	Coreopsis Grandiflora	387
	(structure)	Mayweed	388
Biotin	(structure)	Yeast	110, 236
	(structure)	Rutabaga root; cabbage; turnip; etc.	17
Cycloalliin	(structure)	Onion	443
Thiamine	(structure)	Yeast	136, 458
Lucifern	(structure)	Firefly "lantern"	45
Penicillin G	(structure)	Mold penicillium	125

[1] In these formulas hydrogen atoms where combined to carbon atoms are omitted.

The combination —C—O₂H indicates the acid group —C $\begin{smallmatrix} O \\ \parallel \\ \diagdown OH \end{smallmatrix}$

ORIGIN OF SULFUR IN PETROLEUM

It is obvious that the biological remains that settled to lake and ocean beds and eventually produced petroleum certainly, while living, contained some sulfur and contained it, therefore, when deposited. It would seem axiomatic that the geochemical processes, by whatever mechanisms they acted to produce the multitude of hydrocarbons [13] constituting petroleum from the carbon and hydrogen of this biological debris, would, at the same time, include the element sulfur (also present in the debris) as a constituent of some of the chemical structures engendered.

This logic should apply as well to other hetero atoms (nitrogen, oxygen, etc.), also present in the biological debris at the time of deposition. The quantity of these elements in petroleum ranges from essentially none to less than 1 percent (rarely more than 0.2 percent) for nitrogen (23, 26, 371) and probably around 1.0 percent for oxygen.[14] Thus the nitrogen and oxygen content of the organic debris from which petroleum eventually was formed was probably sufficient to account for the quantity of these elements in crude oils. However, for sulfur it would appear that percentages of sulfur such as 13.95 in a Rozel Point, Utah, seep (112), 9.6 in an Etzel, Germany, crude oil (301, 337), and 7.47 in an Oxnard, California, crude oil (375) would require a source of sulfur other than that contained in the organic matter from which the petroleum hydrocarbons were derived. Admittedly, the three crude oils cited are of maximum sulfur content and exceptional in this regard. However, crude oils of 5 to 1 percent sulfur content (259) are more common, and the mean sulfur content of all U.S. production in 1966 was 0.67 percent. In addition, natural gases are known which contain large percentages of hydrogen sulfide. Examples are those of Panther River field, Alberta, Canada, 86 percent hydrogen sulfide (197); several Wyoming fields producing gases containing 30 to 63 percent hydrogen sulfide (36); and some Persian oilfields, about 12 percent hydrogen sulfide (57).

Because it is questionable that the source of sulfur, in quantities previously discussed, lies only in the natural sulfur content of the tissues of the plant-animal remains deposited in ancient geologic beds, another origin must be sought. The biogenic reduction of sulfate has been mentioned in connection with the presence of sulfur over salt domes, and today, petroleum scientists, generally, believe that this mechanism also accounts for the major part of the sulfur in petroleum and natural gases. Starkey (392), among many other investigators, has discussed the action of the microorganism *Desulforibrio desulfuricans* on sulfates and proposed the general equation,

$$4H_2 + CaSO_4 \rightarrow H_2S + Ca(OH)_2 + 2H_2O,$$
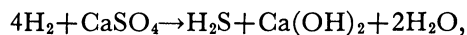
to account for the formation of hydrogen sulfide. The source of the hydrogen in this equation could be petroleum or similar organic material. Elemental sulfur would be produced in a nonbiogenic process by the reaction of hydrogen sulfide (213) with sulfates:

$$SO_4^{--} + 3H_2S \rightarrow 4S + 2H_2O + 2OH^-.$$
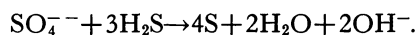
The hydrogen sulfide also might react with components of the petroleum, or of the formation (to yield inorganic sulfides), or remain in the gas cap of the reservoir. Elemental sulfur, where produced, could be precipitated in the formation (389) and, eventually, be dissolved by the crude oil. Here, under geological conditions of temperature, pressure, and time, reaction of the elemental sulfur with hydrocarbons of the crude oil could occur to produce organic sulfur compounds and hydrogen sulfide (373). This mechanism would account not only for the sulfur and sulfur compounds in crude oils, but also for the absence, or partial absence, of sulfates (28, 344) reported in many oilfield brines.

It is of significance that the biogenic reaction yielding hydrogen sulfide (and hence elemental sulfur), postulated to occur in deeply buried geological strata, has been observed in surface lakes [15]

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[13] Many hydrocarbons exist as such in plant and animal tissues (66); for example, heptacosane and other alkanes in the pollen of various plants (304). These saturated hydrocarbons (alkanes) are thought to be stable, even at 100° C, for times longer than the accepted age of the earth (4.5×10⁹ years) (255). Fragmentation of larger natural molecules is another suspected source of petroleum constituents. Thus phytane, $C_{20}H_{42}$, found in Precambrian formations (114), is thought to originate from the phytol chain of chlorophyll, an essential agent of photosynthesis in all green plant life.

[14] A value for an average oxygen content of crude oil is difficult to find in the literature. ZoBell (469) gives 0.5 percent.

[15] Butlin and Postgate studied (53) the small Libyan lake, Ain-ez-Zauia, and found it heavily infected with D. *desulphuricans*, with a red, gelatinous, carpetlike growth flourishing in the edgewaters of the lake, consisting mainly of photosynthetic sulfide-oxidizing bacteria. A 6-inch deposit of finely divided sulfur accumulated annually in the bottom of the lake. This production, with that of two other nearby lakes, was exploited by the local Arabs and said to have yielded 100 to 200 tons of crude (50 percent) sulfur per year.

G. A. Sokolova and G. I. Karavaiko (385) reported the similar instance of Sulfur Lake of the Kubibyshev Region in Russia, which was exploited for sulfur for the production of gunpowder in the days of Peter the Great. The bacteriological reactions proceeding in this lake were first studied by M. V. Ivanov (201).

where deposits of elemental sulfur are found which were produced by the same or similar biological reactions. The criticisms that it is difficult to prove that microorganisms can and do exist in deeply buried geological strata (142) were refuted to the satisfaction of many observers (29, 237) by the culturing and identifying of such bacteria from water samples removed from the strata under conditions thought to eliminate biological contamination.[16]

And, finally, it is worthy to note that several efforts of semi-industrial magnitude are being made (54, 209, 235, 350) to utilize, commercially, the bacterial reduction of sulfates to hydrogen sulfide with subsequent conversion of the hydrogen sulfide to elemental sulfur by known, industrially feasible, processes.

Until about 20 years ago it was generally believed that olefins, because of their chemical activity, were absent from petroleum. However, in 1945 Bureau of Mines chemists observed evidence of these compounds in distillates from a Bradford, Pennsylvania, crude oil.[17] In 1949 Fred and Putscher (132) reported finding an infrared absorption band in the spectra of lubricating oil fractions in several Pennsylvania Grade crude oils characteristic of *trans*- olefins. These crude oils, typified by Bradford crude oil, were from the same general geographical area, western Pennsylvania, southwestern New York, eastern Ohio, and the State of West Virginia, and are characteristically highly paraffinic and low in sulfur content. Fred and Putscher were unsuccessful in finding these absorption bands in spectra of similar lubricating distillate fractions from crude oils from several other fields, widely separated geographically. Their observations on Bradford crude oil were substantiated and extended to gasoline-range fractions by other investigators (153, 331). Now it is known that hydrogen sulfide will react with olefins (176, 206, 299) as typified in the following equation:

$$\underset{\text{Propylene}}{C\text{—}C\text{=}C} + HS\text{—}H \rightarrow \underset{\underset{SH}{|}}{\underset{\text{2-Propanethiol}}{C\text{—}C\text{—}C}}$$

Thus it may be postulated that the absence of olefins in crude oil is due to a series of natural circumstances—the occurrence of combined inorganic sulfur in geologic formations and its ready release

and conversion to hydrogen sulfide and to elemental sulfur by the chemical and biological processes discussed in the previous paragraphs. That is, any olefin laid down in the original debris from which petroleum derived, or formed from it after burial, would be short-lived, geologically, in the presence of the almost inevitable hydrogen sulfide. Thiols, also, are reactive with olefins as illustrated by the following equation:

2-Propanethiol   Propylene   2,4-Dimethyl-3-thiapentane

$$\underset{\underset{C}{|}}{C\text{—}C\text{—}SH} + \underset{\underset{C}{|}}{C\text{=}C} \rightarrow \underset{\underset{C}{|}}{C\text{—}C}\text{—}S\text{—}\underset{\underset{C}{|}}{C\text{—}C}$$
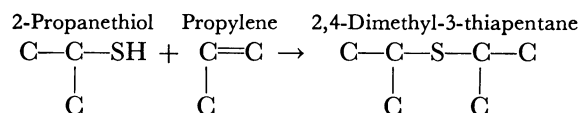
This class of sulfur compounds, therefore, on the basis of the above postulate, also ought to be absent, or in low concentration, in petroleums found to contain olefins. It would be of interest to know the relationships between the olefin structures in Pennsylvania Grade (or similar) crude oils and the sulfur types present. Information might be gained on several questions through such research. For example, Haak and Van Nes (153) report some of the olefins in Pennsylvania crude oil have their unsaturated bonds in the side chains of cyclic, nonaromatic compounds. Possibly these compounds are the precursors of the alkyl cycloalkyl sulfides, ⌬—S—C$_n$, found (418) in very small concentration in Wasson, Texas, crude oil.
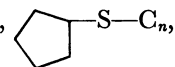
QUANTITY AND DISTRIBUTION

Because of the circumstances by which sulfur is, and may be, incorporated into petroleum, it is doubtful whether any crude oil exists, or can exist, that does not contain some sulfur. For the same reasons, it seems logical that the amounts of sulfur in crude oils should differ widely—as they do—depending upon the geologic history of the petroleum. Table 4 lists a selection of crude oils [18] varying in sulfur content from 0.05 to 13.95 percent. The low value of sulfur, 0.05 percent, given in table 4 is not unusual, and numerous domestic and foreign fields produce oils of comparable, and somewhat lower, sulfur content. The high value of sulfur, 13.95 percent (Rozel Point, Utah), is that of a crude-oil seep on the northeast shoreline of Great Salt Lake, and is exceptional. This is the highest recorded sulfur

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[16] It is interesting and astounding to note that viable bacteria have been reported isolated from samples taken from Permian salt beds (15, 339), 200 million years old, and from coal seams (245) of similar or older age. These microorganisms supposedly were trapped and buried at the time the geological beds were laid down.

[17] See acknowledgment on page 910 and reference 16 in the list of references on page 911 of a paper by Fred and Putscher (132).

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[18] Reference 259 tabulates major crude oil producing fields of the United States and of the free world, giving production records for 1966 and the sulfur content of the crude oils. Data on 1,060 U.S. crude oils and 201 foreign are included in this compilation.

Table 4.—Properties, origin, and production data of certain crude oils selected to illustrate wide range of sulfur content

Properties [1]			Source—Geographical and geological			Average depth feet [1]	Production 1966 [2]		Sulfur per thousand barrels, tons
Sulfur, percent	Specific gravity (60/60° F)	Residuum, percent	Field	State	Age and formation		Thousand barrels	Rank	
13.95	1.041		Rozel Point	Utah [3]	Formation unknown	Seep	......	..	25.42
7.47	1.021	65.1	Oxnard	California [4]	Upper Miocene, fractured lava	2,810	......	..	13.35
5.63	1.008	72.5	Zaca Creek	...do...	Miocene, Monterey Chert	4,420	......	..	9.94
5.06	.959	63.8	Santa Maria Valley	...do...	Miocene, Monterey shale	......	1,550	..	8.50
3.98	.933	51.6	Yellow Creek	Mississippi	Upper Cretaceous, Stanley sand	5,180	......	..	6.50
3.28	.929	45.2	Oregon Basin	Wyoming	Permian, Embar	3,570	8,712	..	5.33
2.79	.921	50.4	Yates	Texas	Permian, Grayburg-San Andres	1,750	6,273	..	4.50
2.41	.899	44.0	Hawkins	...do...	Upper Cretaceous, Woodbine	4,685	10,788	34	3.79
2.36	.935	47.9	Smackover	Arkansas	Upper Cretaceous, Blossom Sand	2,590	3,213	..	3.86
1.90	.867	27.0	Wasson	Texas	Permian, San Andres	5,285	13,170	29	2.88
1.63	.814	18.3	West Branch	Michigan	Devonian, Detroit River	3,592	......	..	2.32
1.38	.913	41.2	Wilmington	California	Miocene, Terminal Zone (Upper)	3,370	47,116	1	2.21
.88	.932	38.8	Midway-Sunset	...do...	Lower Pliocene, Etchegoin sand	1,850	25,992	6	1.44
.73	.849	24.1	Rangely	Colorado	Pennsylvanian, Weber sandstone	5,790	16,182	20	1.09
.58	.852	32.4	Deep River	Michigan	Devonian, Dundee	2,845	......	..	.87
.52	.835	24.1	Goldsmith	Texas	Permian, Upper Clearfork	5,670	13,608	23	.76
.32	.828	21.0	Hall-Gurney	Kansas	Pennsylvanian, Kansas City	3,157	3,290	..	.46
.26	.839	20.9	Timbalier Bay	Louisiana	Upper Miocene	10,900	23,775	8	.38
.21	.846	25.7	Burbank	Oklahoma	Pennsylvanian, Burbank sand	......	10,655	24	.31
.16	.878	31.4	Swanson River	Alaska	Tertiary, Hemlock Zone	Below 11,000	10,406	38	.24
.12	.820	19.5	Lance Creek	Wyoming	Pennsylvanian, 1st Converse	4,439	521	..	.17
.05	.817	17.6	Aneth	Utah	Pennsylvanian, Paradox limestone	5,850	10,280	40	.07

[1] Data apply to sample or samples available to authors.
[2] See reference 11.
[3] Seep, see reference 112.

[4] Heated with hot water under pressure—oil produced at about 250° F. See reference 220.

content of any crude oil. The second sample, that contained 7.47 percent sulfur, is from a well in the Oxnard field, California. Initial crude oil production (October 1944) was about 380 bbls per day (58). This sulfur content is also unusual.[19] The frequency of occurrence of crude oils containing less than 5 percent sulfur increases rapidly as the sulfur content drops and the average sulfur content of U.S. production in recent years (1966–67) is around 0.6 to 0.7 percent (259).

The third and fourth columns of table 4 give the specific gravity, 60/60° F, and percent residuum of the crude oils listed (routine analysis, see table 9). Note that, in a very general way, the sulfur content of the crude oils correlates with these two properties. This apparent interrelationship between sulfur content and specific gravity was observed by many early petroleum investigators (377) and others (149, 198, 261), but it is doubtful that the relationship is a direct one; that is, that the sulfur content, in itself, can have a prime influence on the magnitude of either property, gravity or carbon residue. The reverse is probably true also. Other factors related to the geologic history of the petroleum undoubtedly enter this situation.

The average depth given for each sample (column 7, table 4) is that of the sample available to

this laboratory and included in this table. Here, too, a general trend has been observed; that is, oils from the deeper formations have the lower sulfur content (27, 46, 180) and lower specific gravity. However, many instances counter to this observation are known. Figure 1 illustrates examples of this relationship in the case of sulfur in crude oils from several selected West Texas fields (257). This graph considers only two variables: depth of producing formation below surface of the earth and the percentage of sulfur in the sample. Obviously other factors than these must be considered (154) if a relationship, based on less dispersed data, is to be derived (see discussion of figs. 4 and 5, pp. 12–13).

The sulfur content of a crude oil expressed in weight-percent gives little conception of the quantity of sulfur involved from the standpoint of commercial exploitation or air pollution. The last column of table 4 records, for each crude oil listed, the amount of sulfur, expressed in tons, contained in 1,000 barrels of crude oil. Figure 2 is a chart from which this quantity can be estimated when the specific gravity and weight-percent sulfur of a crude oil (or distillate) are known. By way of example, the chart indicates that in a crude oil of 0.9 specific gravity, a sulfur content of 1.25 percent is equivalent to 2 tons of elemental sulfur per thousand barrels of crude oil. Viewed practically, this quantity of elemental sulfur is convertible (if no

[19] See page 9 for reference to a high-sulfur, German crude oil containing 9.6 percent sulfur, another exceptional occurrence.

Figure 1.—Relationship between depth of burial of several selected crude oils and their sulfur content.

tion of sulfur within crude oils was that of Mabery and Smith (267) who stated in 1891 that in a Lima, Ohio, crude oil, the sulfur compounds become propressively more concentrated as the boiling range of the fractions distilled increases. This result has been found to be true generally by other investigators (288, 404). Figure 3 shows data from distillations made at the Bartlesville Energy Research Center [20] of four crude oils containing substantial sulfur. In this graph, the sulfur content of the fractions removed is plotted as a function of the percent crude oil distilled. Obviously, the curves derived verify the views expressed by Mabery and Smith. The initial cut in two of these distillations (Huntington Beach and Maljamar) have slightly higher sulfur content than the next several succeeding cuts, which may be due to hydrogen sulfide or low-boiling mercaptans dissolved or condensed in these fractions. These four distillations were made by the Bureau of Mines routine method described in this report. Limited fractionation is achieved with this procedure.

A singular exception to the above observations is present in at least two crude oils of eastern Michigan and probably exists in other crude oils of that area. These are the oils from the Deep River and West Branch fields, about 11 miles apart, in adjoining Arenac and Agemaw Counties, respectively. In both fields oil is produced from the Dundee formation which is comparatively low in sulfur, 0.6 to 0.7 percent. In both fields, the Detroit River Formation, underlying the Dundee, is productive from at least two horizons. These are the Detroit River "sour zone" (168) and below it, separated by more than 150 feet of anhydrite, the Richfield. Crude oil from the Richfield is comparable in sulfur content (and distillation characteristics) to that from the Dundee, but the crude oil from the "sour zone" contains not only much hydrogen sulfide in solution

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[20] The authors are indebted to C. M. McKinney of the Bureau of Mines for these data.

losses occur) to 6 tons of useful sulfuric acid for commerce or 5.6 tons of obnoxious sulfur trioxide if released to the atmosphere as a pollutant. The above discussion illustrates the potential magnitude of sulfur in crude oils if economic methods for its recovery were available and employed.

One of the earliest observations of the distribu-
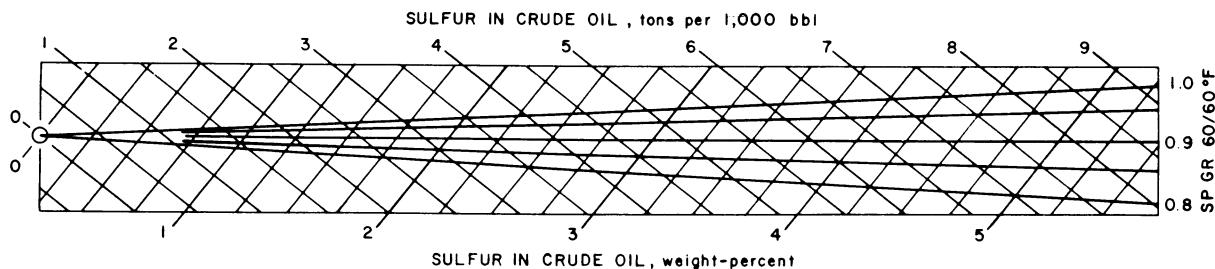
Figure 2.—Relationship between specific gravity at 60°/60° F, percent sulfur, and sulfur content in tons of sulfur per thousand barrels of crude oil.
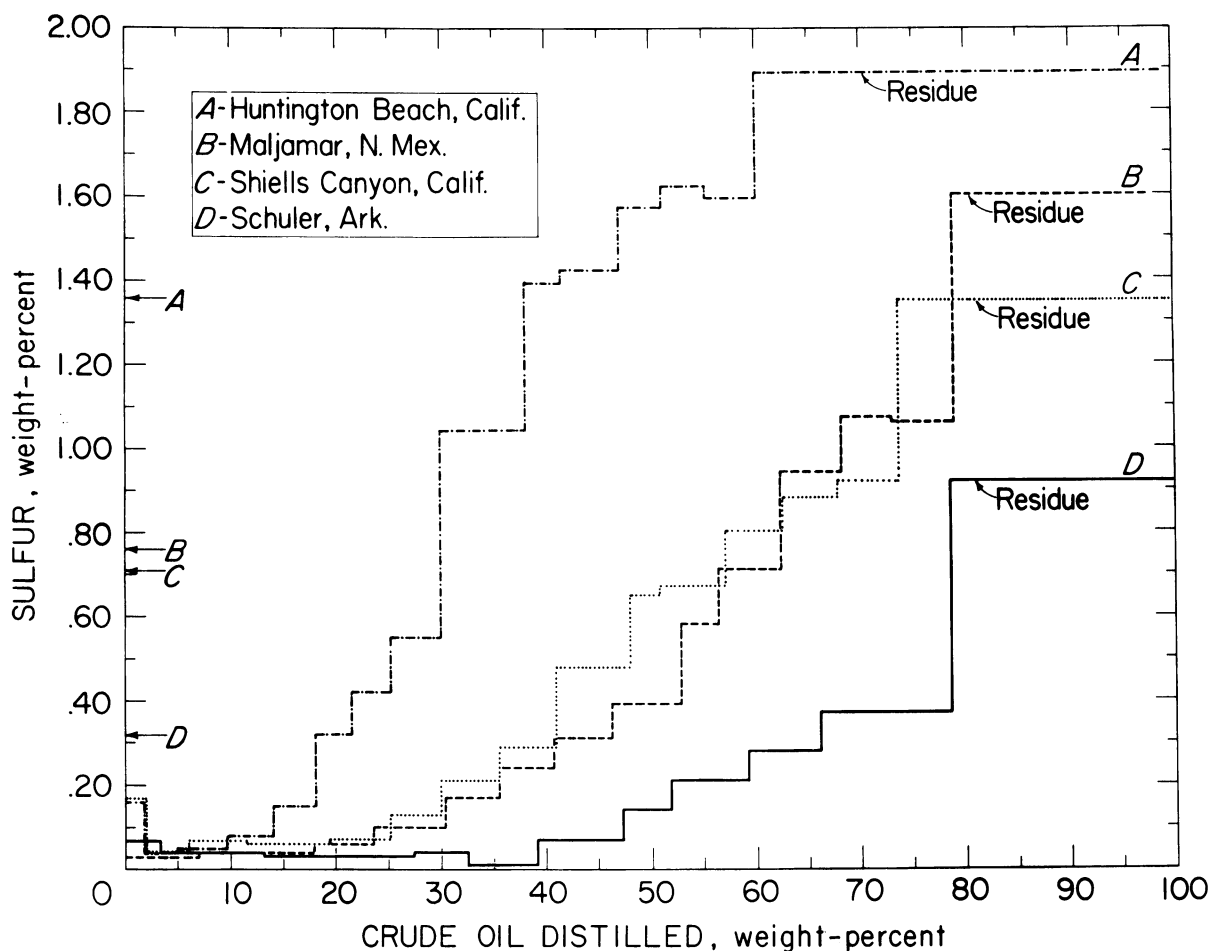
Figure 3.—Relationship between percent sulfur and percent distilled in four crude oils.

(estimated at about 0.3 percent), but its sulfur content, other than hydrogen sulfide, is also quite high (estimated at about 2.1 percent). Figure 4 shows data equivalent to that of figure 3 for the Deep River field crude oils. Here the sulfur pattern for the Dundee and Richfield follows the general form illustrated in figure 3; that is, the sulfur content, low in the low-boiling ranges of the crude oils, increases steadily as the boiling range of the distillates increases. The sulfur distribution of the oil from the "sour zone," on the other hand, is quite different. Of the 2.1 percent total sulfur (in excess of H_2S) in this crude oil, about 1.65 percent, the area under ordinate, $S = 1.65$ percent, or approximately 75 percent of the total sulfur, is distributed equally throughout the distillation range of the crude oil. Of the remaining 0.45 percent, one-fourth (0.11 percent) is distributed in fractions 1 through 4 in proportion to the heights of the curve above the 1.65 percent sulfur ordinate and three-fourths (0.34

percent) in fractions 8 through residue, also distributed as indicated by the curve above 1.65 percent S.

Figure 5 shows similar data for crude oils from the Dundee and Detroit river "sour zone" of the West Branch field. Obviously the circumstances here are similar to those indicated in figure 4, indicating that the situation in the Deep River field is not an isolated occurrence.

The situation discussed above also illustrates one of the exceptions to the general rule: the deeper the oil, the less sulfur. It is interesting to speculate why the Detroit River "sour zone" exists between two horizons producing relatively low sulfur crude oils. Bacterial reduction of sulfates is a logical assumption, but this problem has not been investigated.

EFFECTS OF SULFUR IN PETROLEUM

The interest of petroleum technologists and chemists in the sulfur compounds in petroleum
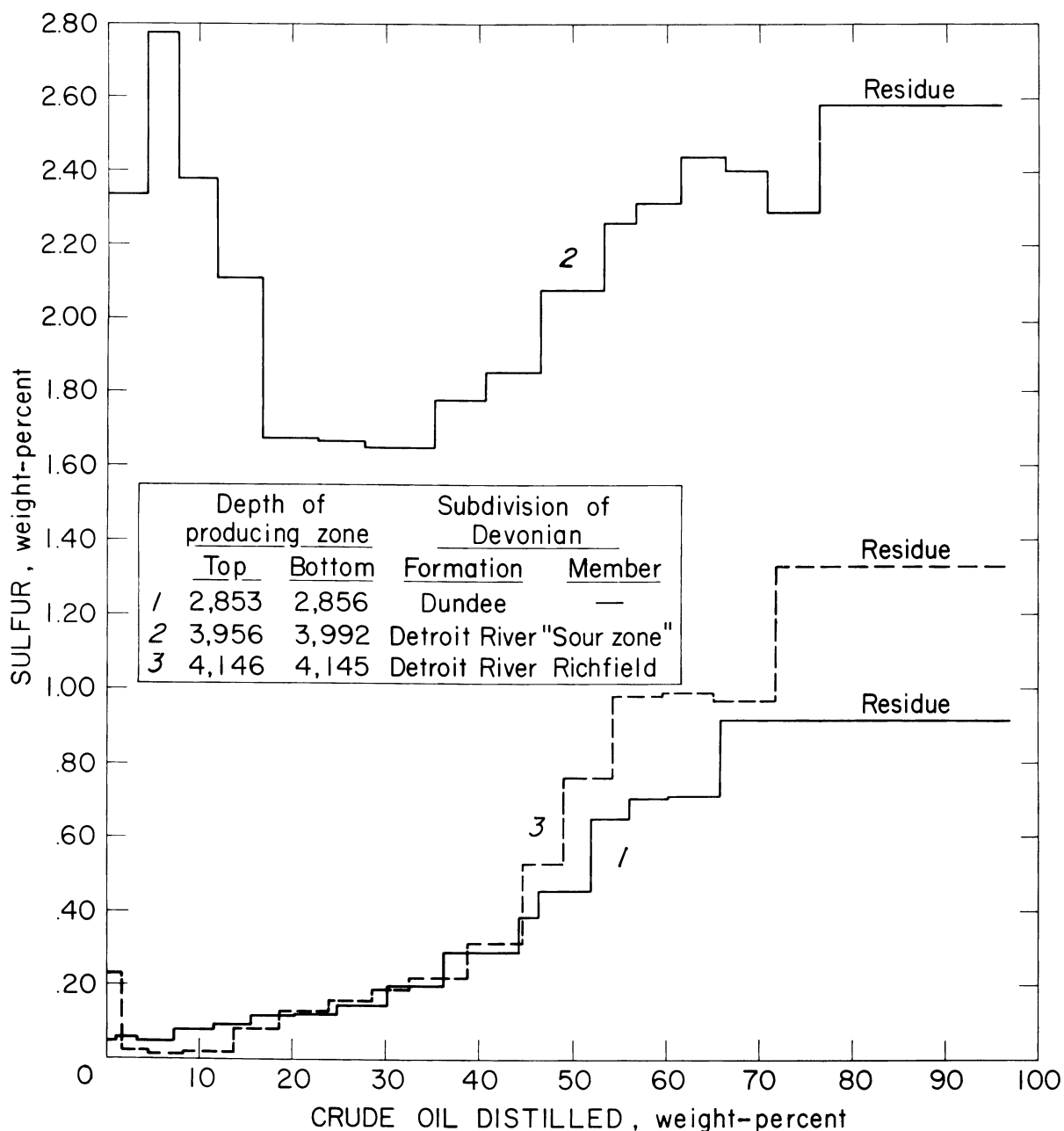
Figure 4.—Sulfur content of fractions from routine distillations
of three Deep River, Michigan, crude oils.

Depth of producing zone		Subdivision of Devonian	
Top	Bottom	Formation	Member
1 2,853	2,856	Dundee	—
2 3,956	3,992	Detroit River	"Sour zone"
3 4,146	4,145	Detroit River	Richfield

originates in the practical problems and theoretical questions engendered by the presence of these compounds in crude oils. From a practical point of view, this interest stems principally from the deleterious effects of sulfur compounds (300) on the metals used in processing crude oils and on the undesirable characteristics which sulfur compounds impart to the products derived from the crude oil. From the academic or theoretical point of view, the interest in sulfur in petroleum arises because of the possible bearing which sulfur and its compounds have upon the origin and composition and the geochemical and geological history of petroleum.

The corrosion of metals used to produce and re-
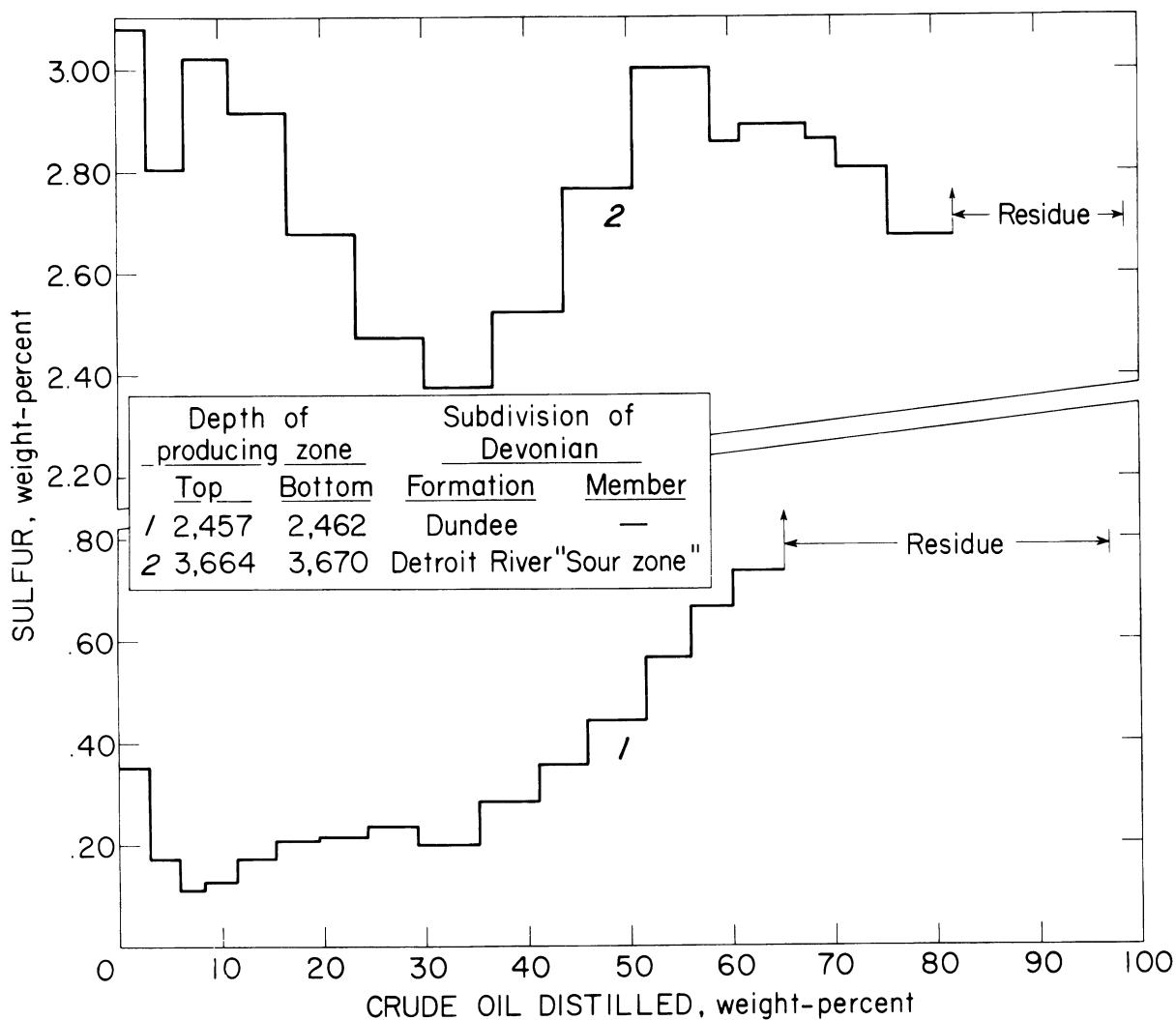
Figure 5.—Sulfur content of fractions from routine distillation of two West Branch, Michigan, crude oils.

fine crude oils is one of the most costly consequences of sulfur in petroleum. It has been estimated, for example (*320*), that in 1952 corrosion cost American refiners alone $220 million, or an average of 9 cents per barrel of crude oil processed. Corrosion, however, is not the only ill effect of sulfur in petroleum. In table 5 are listed some adverse effects, in addition to corrosion, resulting from sulfur and sulfur compounds in crude oil and its products. Since the ill effects of sulfur and its compounds in petroleum products are widely discussed in the literature, the references cited in table 5 are only representative.

It is fair to observe, however, that not all the effects of sulfur in petroleum products are deleterious. Thus, for example, while sulfur compounds are detrimental to the octane rating of gasoline in the internal combustion engine and antagonistic to the additive tetraethyllead in such fuels, they improve the cetane number of diesel fuels (*305*). Table 6 includes several applications in which sulfur or its compounds lead to improvement in the action of the petroleum base in which they are naturally or deliberately incorporated. Since this subject is also covered extensively in the literature, the references cited in table 6 are only illustrative.

Although sulfur's role in nature is vital and its applications in arts and technology are useful and

Table 5.—Detrimental effects resulting wholly or partly from sulfur in petroleum or in its products

Effect	Illustrative references
Corrosion in producing, processing, and utilizing...................	366
Reformer and cracking catalyst poisoning.......................	170, 280
Gum formation and decline of storage stability.......................	290, 435
Reduction in octane number of motor fuels and of antiknock efficiency of tetraethyllead..................	43, 126, 249, 360
Increased engine wear..............	69, 126
Increased deposits in combustion engines.........................	69
Reduced lubricating-oil life..........	441
Deterioration of color and odor......	115, 290
Atmospheric contamination.........	346

Table 6.—Beneficial actions resulting wholly or partly from sulfur in petroleum products

Action	Illustrative references
Antioxidant...........................	96, 227
Additive for high-pressure lubricants.....	7, 361
Thermal stability improver for fuel oils...	435
Diesel fuel ignition-quality improver.....	305
Cutting oil improver...................	7, 51, 148
Ore flotation-oil improver..............	268, 361, 391
Bearing corrosion inhibitor.............	123, 414
Asphalt improver......................	20, 109
Detergent.............................	150

many, paradoxically, the producers and refiners of petroleum encounter only its evil and obnoxious effects. The costly consequences of corrosion have been mentioned. Disastrous fires result when iron sulfide in corrosion-weakened equipment ignites spontaneously when such equipment ruptures. Deaths and accidents ensue directly from the very toxic effects of hydrogen sulfide produced from some oil wells and by crude oil refining. The costs of products derived from processing crude oils are increased and the quantity and quality of these products decreased by the presence of sulfur in the crude oil. Customer satisfaction (and hence demand) for these products often is influenced adversely by the ill effects of their use. These effects range from the liberation to the atmosphere of offensive combustion products to the malfunction, deterioration, and destruction of equipment. Color, sediments, odor, and other offensive characteristics of commercial petroleum products, often traceable to sulfur compounds, also influence customer demand in the domestic and foreign market.

To solve systematically the problem of removing the sulfur compounds from petroleum or its products, or to render these compounds harmless and acceptable, a knowledge of the type, structure, and chemical nature of the compounds present is desirable. It is a fortuitous circumstance that for modern refining processes, the structural character of the individual sulfur compounds need not be known for satisfactory removal. However, for a better understanding of the reactions involved and the mechanisms of these processes, and for efficient use of available materials and conditions, such data are essential.[21] It was the prime aim of the Separation and Identification Section of the Bureau of Mines–API Research Project 48 to eliminate partially this information void in petroleum science; that is, to identify, and to develop means for identifying, sulfur compounds in crude oils and estimate, where possible, their quantity in the crude oil.

PREVIOUS KNOWLEDGE
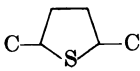
When API Research Project 48 was initiated, only 25 sulfur compounds had been identified in petroleum (see table 7), and many of those identifications rested on ambiguous or insecure data.

One of the earliest [22] investigators of sulfur compounds in petroleum was Prof. Charles F. Mabery of the Case School of Applied Science, Cleveland, Ohio. In 1891, while investigating the composition of a Lima, Ohio, crude oil, he claimed the identification of 10 alkyl sulfides (267). In 1900 (265) and 1906 (266), Mabery reported finding, in the same crude oil, 10 cyclic sulfides, of the formula $C_nH_{2n}S$, of 6 to 18 carbon atoms. These cyclic structures he termed "thiophanes." His analytical techniques did not enable him to distinguish whether these new structures were simple ring methylene sulfides or methylene sulfides of low carbon number with

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[21] The observation of British petroleum scientist Perkin made more than 50 years ago (377) was essentially as valid in 1948 as in 1917, and much truth lies in his 1917 appraisal of the sulfur-in-petroleum situation. "To the refiner, the chemical nature of the sulphur-compound is a matter of indifference, provided he can remove it. On the other hand, if more were known as to the chemical structure of the sulphur compounds, the chemist might be able to assist the refiner much more than at present. It is therefore a matter of great importance that further extended research into the composition of the sulphur compounds in petroleum oils should be undertaken. This is much more important at the present than in the past, because, owing to the exhaustion of some oil supplies, and the much greater demand for oil fuels, many new sources of oil are being exploited, a number of which are very rich in sulphur."

[22] Hager reported in 1867 (155) the finding of carbon disulfide in an American petroleum fraction boiling between 50° and 80°C (122° and 176° F) however, this finding was never substantiated, and it is doubtful whether CS_2 is present naturally in any crude oil.

Table 7.—Sulfur compounds reported identified in crude oil before 1948

Name	Formula [1]	Boiling point		Identification reported in reference—
		° C	Reference [2]	
Ethanethiol	C_2SH	35.000	312	42
2-Thiapropane	C—S—C	37.28	455	267
2-Propanethiol	C—C(C)—SH	52.558	312	42
2-Thiabutane	$C—S—C_2$	66.655	312	410
Thiophene	(thiophene ring)	84.10	455	64
2-Butanethiol	$C—C(SH)—C_2$	84.981	312	297
2-Methyl-1-propanethiol	C—C(C)—C—SH	88.493	312	42
3-Thiapentane	$C_2—S—C_2$	92.100	312	267
2-Thiapentane	$C—S—C_3$	95.54	455	410
3-Methyl-1-butanethiol	$C—C(C)—C_2—SH$	118.341	312	42, 297
3-Thiahexane	$C_2—S—C_3$	118.50	455	267
Thiacyclopentane	(ring)	121.114	312	133, 326, 408, 410
1-Pentanethiol	$C_5—SH$	126.638	312	297
2-Methylthiacyclopentane	(ring—C)	132.471	312	133, 326, 408
3-Methylthiacyclopentane	(ring—C)	138.330	312	134, 326
Thiacyclohexane	(ring)	141.75	455	133, 408, 410
2,5-Dimethylthiacyclopentane [2]	C—(ring)—C	(c) 138.67 (t) 142.28	455	408
4-Thiaheptane	$C_3—S—C_3$	142.83	455	267, 298
1-Hexanethiol	$C_6—SH$	152.660	312	297
3-Thiaoctane	$C_2—S—C_5$	170		267
2,6-Dimethyl-4-thiaheptane	C—C(C)—C—S—C—C(C)—C	[4] 168.5	19	267
5-Thianonane	$C_4—S—C_4$	188.91	455	267
5-Thiadecane	$C_4—S—C_5$			267
6-Thiaundecane	$C_5—S—C_5$	[5] 227.3	19	267
7-Thiatridecane	$C_6—S—C_6$			267

[1] The exact structure of some of the higher molecular weight thiaalkanes is not known with certainty.
[2] Reference to boiling point data.
[3] Configuration (cis- or trans-) not known.
[4] 749 mm Hg.
[5] 751 mm Hg.

numerous or long side chains, thus:
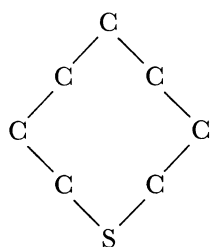
Heptamethylene
sulfide
(Thiacyclooctane)
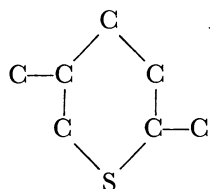
Dimethylpentamethylene
sulfide
(2,5-Dimethylthiacyclo-
hexane)
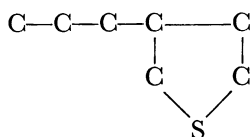
Propyltetramethylene
sulfide
(3-n-Propylthiacyclopentane)

He considered penta-, hexa-, and heptamethylene ring sulfides as probable petroleum components. No investigator, however, has yet isolated a seven-membered or higher cyclic sulfide from petroleum, but numerous five- and six-membered cyclic sulfides have been reported. To Mabery, thus, must go the honor of being the first to recognize, at an early date in petroleum science, the presence of this important class of compounds in crude oil. Proof of the precise structure of some of the higher molecular weight alkyl sulfides, claimed by Mabery and assumed to be symmetrical (see table 7), rests on insufficient data. However, for many, and probably all of these identifications, there is little reason to doubt that the class of compounds reported actually does exist in petroleum.

Charitschkoff, in 1899 (64), using the reaction between isatin and thiophene to produce the blue-colored addition product, identified thiophene in a distillate from Grosny crude oil.

In 1925 Birch and Norris (42) isolated four thiols from a Persian crude oil, and Thierry (410) identified 2-thiabutane and 2-thiapentane in addition to thiacyclopentane and thiacyclohexane, also in a Persian crude oil. In 1934 Teutsch (408) added 2-methylthiacyclopentane and 2,5-dimethylthiacyclopentane (cis/trans configuration not given) to the list of sulfur compounds found in petroleum and verified the presence of several others already reported. Polly and others (326) extended the list with 3-methylthiacyclopentane in 1942 and duplicated two known identifications.

Some of the identifications previously described (see references 133, 134, 267, and 410 of table 7) were made from sulfur-compound concentrates recovered from sludges obtained by treating petroleum fractions with concentrated sulfuric acid. Some sulfur types are thought to be stable in this drastic treatment, but at least one is not. Thus thiols, as a class, are converted to disulfides (463).

$$2RSH + \begin{matrix}HO\\ \\HO\end{matrix}\ S\ \begin{matrix}O\\ \\O\end{matrix} \rightarrow \begin{matrix}RS\\ \\RS\end{matrix}\ S\ \begin{matrix}O\\ \\O\end{matrix} + 2H_2O \rightarrow$$

$$\begin{matrix}RS\\ | \\RS\end{matrix} + SO_2 + 2H_2O$$
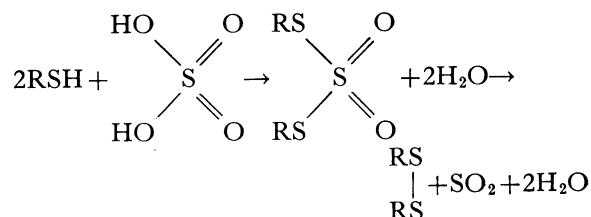
According to tests made with pure sulfides, disulfides, and thiophenes (461, 462), these types dissolve readily in concentrated sulfuric acid but react slowly with this reagent to form sulfoxides and sulfones which are soluble in the acid (218). Obviously of immediate concern here is that if existing structures are destroyed (or partly so) by the separating reagent, they would escape detection or be found in less proportion than originally present in the sample. On the other hand, if the treatment created new types from existing structures, these would be identified as bodies indigenous to the crude oil and possibly not be recognized as the artifacts they would actually be.[23] All of the compounds listed in table 7, except the last five alkyl thiols which were not specifically sought, were identified in one or another of three crude oils by Research Project 48 using thermally mild separation conditions.

In considering the sulfur compounds identified in crude oils before 1948, it is of interest that some reputable investigators in the era before 1948 preferred to believe that these compounds originated by thermal breakdown of high molecular weight compounds or from the reaction of sulfur or hydrogen sulfide with the hydrocarbon constituents of the petroleum (445). This skepticism, which, however, was not universal (48), was noted by S. S. Nametkin in his book Chemistry of Petroleum, as quoted by Postovsky, Bednyaghina, and Mikhailova (327):

There is no doubt that a large number of the simplest sulfur compounds detected in petroleum distillates are not present in the original oil itself at all, but on the contrary, only form during its distillation.

---

[23] Correctly or not, Sachanen (354) is quite emphatic on this point; "The sulfur compounds recovered from strong sulfuric acid, particularly in cases in which the action was prolonged and uncontrolled with respect to temperature, cannot be considered as virgin sulfur compounds present in the product treated, at least a part of which were transformed into new compounds by the uncontrolled action of the sulfuric acid."

Interpreted literally, this statement is still partly correct in that low molecular weight sulfur compounds are formed by thermal decomposition of the high molecular weight compounds; however, in the light of today's knowledge, it cannot be maintained that none of the "simplest sulfur compounds" are natural to crude oil and are formed only during its distillation.

The doubt of the presence of low molecular weight sulfur compounds in petroleum extended especially to certain types of sulfur compounds; for example, to thiophenes and to elemental sulfur (151). Speaking of thiophenes, Postovsky and others (327) remarked:

> On the basis of the experimental data given in the table, one may draw the conclusion that the simplest thiophene compounds are not present in the original samples of petroleums investigated, but are formed during distillation.

These authors were not alone in this opinion; an article in 1922 (109) stated:

> . . . thiophenes are rarely found in petroleum and then only in traces.

Oddly enough, the Russian chemist Charitschkoff in 1899 had reported the parent thiophene present in a Grosny crude oil (64) in the concentration of 1 part per 10 million. Despite what appears to be good evidence, this identification went unnoticed or unbelieved.

Much of the same skepticism was accorded elemental sulfur. In 1936 Comay (83) reported:

> Free or elementary sulfur is present in nearly all cracked and straight-run gasolines, but its presence in crude oils has not been established generally.

While as late as 1942, Gruse and Stevens (151) wrote:

> There does not seem to be any clear-cut evidence of the presence of uncombined sulfur in untreated crude oil.

Elemental sulfur, however, had been observed in commercial equipment used in handling Beaumont, Texas, crude oil as long ago as 1902 (340, 409). In the laboratory, Mabery (264) and others (42, 316) had observed it in the side arm of distilling flasks, a phenomenon the staff of the Separation and Identification Section has since verified (80). The early observations of elemental sulfur in crude oil usually were attributed to chemical reaction involving sulfur compounds or to the oxidation of hydrogen sulfide.

A final observation can be made emphasizing the great dearth of knowledge of sulfur compounds in petroleum and specifically, in this instance, of the chemical nature of sulfur compounds in the high-boiling portions of crude oil. As late as 1938, an eminent authority in petroleum science stated (338, p. 1034):

> It is well known that the sulfur compounds in petroleum are predominantly aliphatic. . . .

This was the conclusion to which the then-current knowledge pointed. Today, however, it is known that the aliphatic sulfur compounds are predominant only in the very low-boiling range of crude oil and that in the high ranges multiring thiophenes and cyclic sulfides are the predominant structures.

WORK OF BUREAU OF MINES-AMERICAN PETROLEUM INSTITUTE RESEARCH PROJECT 48

SELECTION OF CRUDE OILS FOR SURVEY

To provide information to aid in selecting a crude oil (or oils) for more intensive investigation, high-sulfur crude oils of differing geological origin were chosen for preliminary study. The crude oils selected for inclusion in this initial survey are listed in table 8. Group I in this table included seven U.S. crude oils chosen on the basis of (1) their high sulfur content, (2) their representation of major or important U.S. production in 1947, and (3) their geographical or geological origin. To these seven crude oils was added a crude oil from Kirkuk, Iraq (No. 9), and one from Agha Jari, Iran (No. 13), representing high-sulfur, high-production crude oils from the Middle East. A secondary selection, group II of table 8, was added to this list of crude oils to be surveyed. Because these additional samples exemplified variations in crude oil properties and origins, they were thought worthy of scrutiny.

Routine Inspection of Crude Oils

Upon receipt of these crude oils in the laboratory, they were subjected to the Bureau of Mines routine method for the analysis of crude oils (375, 376). Data from two of these analyses (Wasson, Texas, and Wilmington, California, crude oils) are summarized in table 9, and distillational characteristics of two (Oregon Basin, Wyoming, and Wasson, Texas), as determined by these analyses, are shown in figure 6. The curves presented in figure 6 are typical of the "heavier" and "lighter" of the series of 15 crude oils. Similar data for the other crude oils of the series fall within the area bounded by the two curves shown or only slightly to either side. From some of the data provided in these analyses (density, specific dispersion, and refractivity intercept), it is possible to estimate (374) a type composition; that is, the naphthene, paraffin, and aromatic content of the naphtha portion (up to 200° C boiling point) of these crude oils. The results of these calculations are

Table 8.—Crude oils selected for study

Group and identification number	Field	State or country	Sulfur, weight-percent	1948 Production [1] Million barrels	1948 Production [1] Rank (U.S.A.)
Group I:[2]					
2	Heidelberg	Mississippi	3.75	5.230	
3	Oregon Basin	Wyoming	3.25	3.756	
5	Hawkins	Texas	2.41	17.621	14
9	Kirkuk	Iraq	1.93	[3] 374.000	
10	Wasson	Texas	1.85	28.884	3
12	Wilmington	California	1.38	48.583	2
13	Agha Jari	Iran	1.36	[3] 125.500	
16	Rangely	Colorado	.76	13.412	19
17	Deep River	Michigan	.58	2.885	
Group II:[4]					
1	Santa Maria Valley	California	4.99	7.407	
4	Yates	Texas	2.79	18.103	12
6	Goldsmith	.do	2.17	11.128	26
7	Slaughter	.do	2.01	19.184	10
8	Elk Basin	Wyoming	1.95	5.769	
11	Schuler	Arkansas	1.55	3.751	
14	Velma	Oklahoma	1.36	12.486	22
15	Midway-Sunset	California	.88	15.167	17

[1] Reference 310.
[2] Initial selection.
[3] Reference 309.
[4] Additional selection.

Table 9.—Routine analysis of two selected crude oils

TABLE 9. - Routine analyses of two selected crude oils

CRUDE PETROLEUM ANALYSIS

IDENTIFICATION

Bureau of Mines Bartlesville Laboratory
Sample 48093[1]

Wasson field[2]
Limestone
4,950–5,150 feet

Texas
Yoakum County
Sec. 895–Blk. D
Gibson Survey

GENERAL CHARACTERISTICS

Gravity, specific, 0.861	Gravity, °API, 32.8	Pour point, °F., below 5
Sulfur, percent, 1.85		Color, brownish black.
Viscosity, Saybolt Universal at 100° F., 44 sec.		Nitrogen, percent,

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, _____ mm. Hg
First drop, _____ °F.

Fraction No.	Cut temp. °F.	Percent	Sum. percent	Sp. gr. 60/60°F.	°API 60°F.	C.I.	Refractive index, n_D at 20°C.	Specific dispersion	S.U. visc. 100°F.	Cloud test, °F.
1	122	2.2	2.2	0.643	88.6	-				
2	167	2.3	4.5	.680	76.6	12	1.38183	131.9		
3	212	5.3	9.8	.725	63.7	24	1.40414	138.4		
4	257	6.9	16.7	.755	55.9	29	1.42024	145.0		
5	302	5.8	22.5	.774	51.3	30	1.43166	150.4		
6	347	5.6	28.1	.787	48.3	30	1.43867	149.4		
7	392	5.2	33.3	.800	45.4	30	1.44475	146.1		
8	437	4.2	37.5	.813	42.6	30	1.45138	147.1		
9	482	4.8	42.3	.827	39.6	31	1.45972	151.5		
10	527	6.5	48.8	.846	35.8	36	1.47061	160.8		

STAGE 2—Distillation continued at 40 mm. Hg

Fraction No.	Cut temp. °F.	Percent	Sum. percent	Sp. gr. 60/60°F.	°API 60°F.	C.I.	Refractive index, n_D at 20°C.	Specific dispersion	S.U. visc. 100°F.	Cloud test, °F.
11	392	2.7	51.5	0.865	32.1	41			41	25
12	437	7.3	58.8	.877	29.9	43			47	40
13	482	4.3	63.1	.894	26.8	47			66	60
14	527	4.7	67.8	.903	25.2	49			91	75
15	572	4.2	72.0	.912	23.7	50			155	90
Residuum		27.5	99.5	0.986	12.0		too dark			

Carbon residue, Conradson: Residuum, 12.0 percent; crude, 3.8 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	°API	Viscosity
Light gasoline	9.8	0.696	71.8	
Total gasoline and naphtha	33.3	.733	56.4	
Kerosine distillate	4.2	.813	42.6	
Gas oil	18.7	.851	34.8	
Nonviscous lubricating distillate	9.9	.880-.904	29.3-25.0	50-100
Medium lubricating distillate	5.9	.904-.916	25.0-23.0	100-200
Viscous lubricating distillate	-			Above 200
Residuum	27.5	.986	12.0	
Distillation loss	0.5			

1/ Sample taken: 10-7-48.
2/ See Schneider, W. T. (1957), (Ref. 356), for history, maps, and geology of field.

CRUDE PETROLEUM ANALYSIS

IDENTIFICATION

Bureau of Mines Bartlesville Laboratory
Sample 49005[1]

Wilmington field[2]
Terminal Zone (Upper) Miocene
3,143–3,593 feet

California
Los Angeles County
SE NE Sec. 4,
T5S, R13W

GENERAL CHARACTERISTICS

Gravity, specific, 0.913	Gravity, °API, 23.5	Pour point, °F., below 5
Sulfur, percent, 1.38		Color, brownish black
Viscosity, Saybolt Universal at 100° F., 160 sec; 130° F., 97 sec		Nitrogen, percent,

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 752 mm. Hg
First drop, 81 °F.

Fraction No.	Cut temp. °F.	Percent	Sum. percent	Sp. gr. 60/60°F.	°API 60°F.	C.I.	Refractive index, n_D at 20°C.	Specific dispersion	S.U. visc. 100°F.	Cloud test, °F.
1	122	1.3	(1.3)	0.668	80.3	-	1.37380	123.5		Below 5
2	167	1.0	2.3	.732	61.8	27	1.40497	125.7		do.
3	212	3.4	5.7	.756	55.7	29	1.41720	128.2		do.
4	257	2.7	8.4	.776	50.9	31	1.42807	133.0		do.
5	302	3.6	12.0	.799	45.6	35	1.44035	136.7		do.
6	347	3.0	15.0	.818	41.5	38	1.45101	141.2		
7	392	2.9	17.9	.835	38.0	41	1.46023	144.3		
8	437	3.9	21.8	.849	35.2	42	1.46883	151.6		
9	482	4.7	26.5	.866	31.9	45	1.47912	161.0		
10	527	6.0	32.5							

STAGE 2—Distillation continued at 40 mm. Hg

Fraction No.	Cut temp. °F.	Percent	Sum. percent	Sp. gr. 60/60°F.	°API 60°F.	C.I.	Refractive index, n_D at 20°C.	Specific dispersion	S.U. visc. 100°F.	Cloud test, °F.
11	392	1.9	34.4	0.884	28.6	50			43	Below 5
12	437	5.8	40.2	.895	26.6	51			50	do.
13	482	5.1	45.3	.916	23.0	58			72	do.
14	527	5.0	50.3	.930	20.7	61			140	do.
15	572	6.5	56.8	.944	18.4	65			Over 400	do.
Residuum		41.2	98.0	1.010	8.6					

Carbon residue, Conradson: Residuum, 16.0 percent; crude, 7.3 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	°API	Viscosity
Light gasoline	5.7	0.706	68.9	
Total gasoline and naphtha	17.9	.761	54.4	
Kerosine distillate				
Gas oil	19.4	.861	32.8	
Nonviscous lubricating distillate	7.6	.895-.922	26.6-22.0	50-100
Medium lubricating distillate	4.3	.922-.933	22.0-20.2	100-200
Viscous lubricating distillate	7.6	.933-.951	20.2-17.3	Above 200
Residuum	41.2	1.010	8.6	
Distillation loss	2.0			

1/ Sample taken: 11-3-48.
2/ See Crown, Walter J. (1941), (Ref. 89), and Murray-Aaron et al (1948), (Ref. 295), for history, maps, and geology of field.
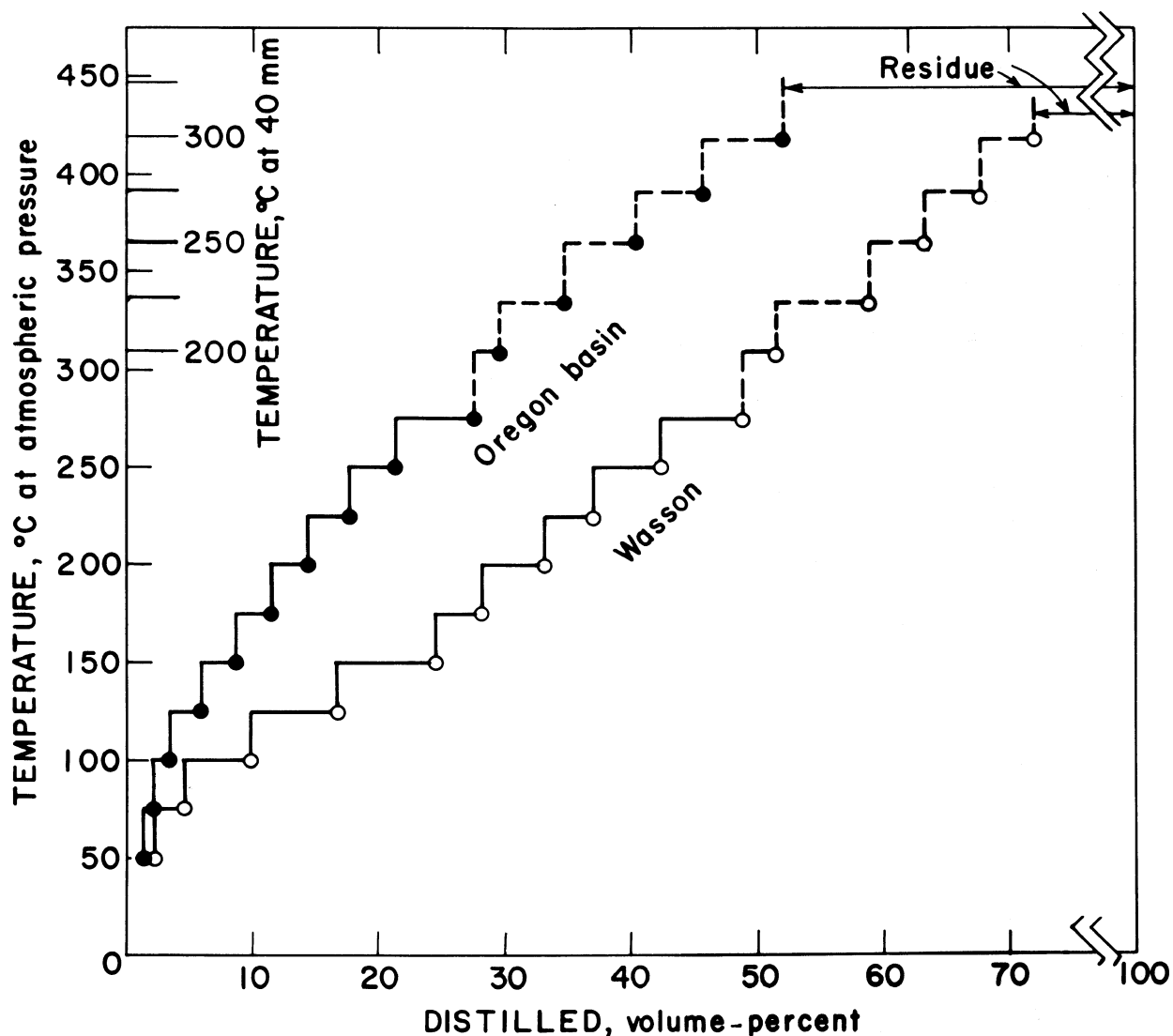
Figure 6.—Limiting distillation characteristics of crude oils chosen for preliminary study.

plotted in figure 7 and indicate the variation of type composition represented in the selection of crude oils. A comparison of the data of figure 7 and table 8 indicates no apparent relation between sulfur content of the crude oils and the type analysis. This is not unexpected as the "naphtha" of any crude oil contains only a minor part of its total sulfur content. The range in properties of the selected crude oils is illustrated also in figure 8 showing the correlation index (372, 374) of the routine fractions (table 9) plotted against volume mid-percent distilled. This index indicates the aromaticity of the sample whose index has been ascertained; that is, the farther the index of the sample departs from the zero correlation index axis, the more aromatic the character of

the sample. The left-hand panel of figure 8 indicates this relationship for fractions from three of the crude oils of table 8. The right-hand panel of figure 8 shows the relationship for four additional crude oils of table 8 compared with equivalent data from a Cotton Valley field, Louisiana, petroleum (372), a well-known highly paraffinic type of crude oil condensate. The end of fraction 7 is designated on these curves by an arrow and indicates the distillation range upon which the data of figure 7 are based. The order of the heights of these arrows on this chart, that is, their correlation index, is in reasonable agreement with the order, to the right, of the corresponding data point in figure 7. Both distances are, in fact, a rough measure of the naphthenic con-
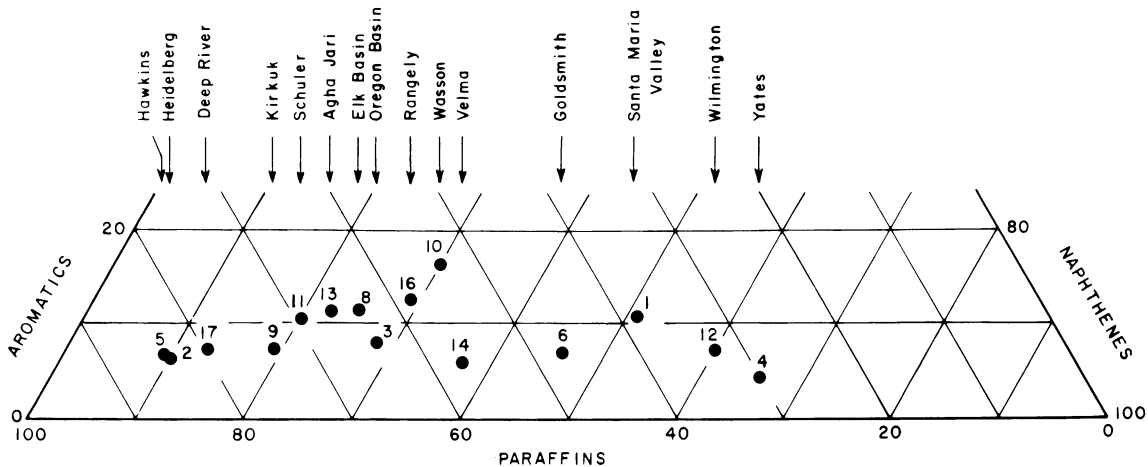
Figure 7.—Type composition of 0° to 200° C fraction of selected crude oils.
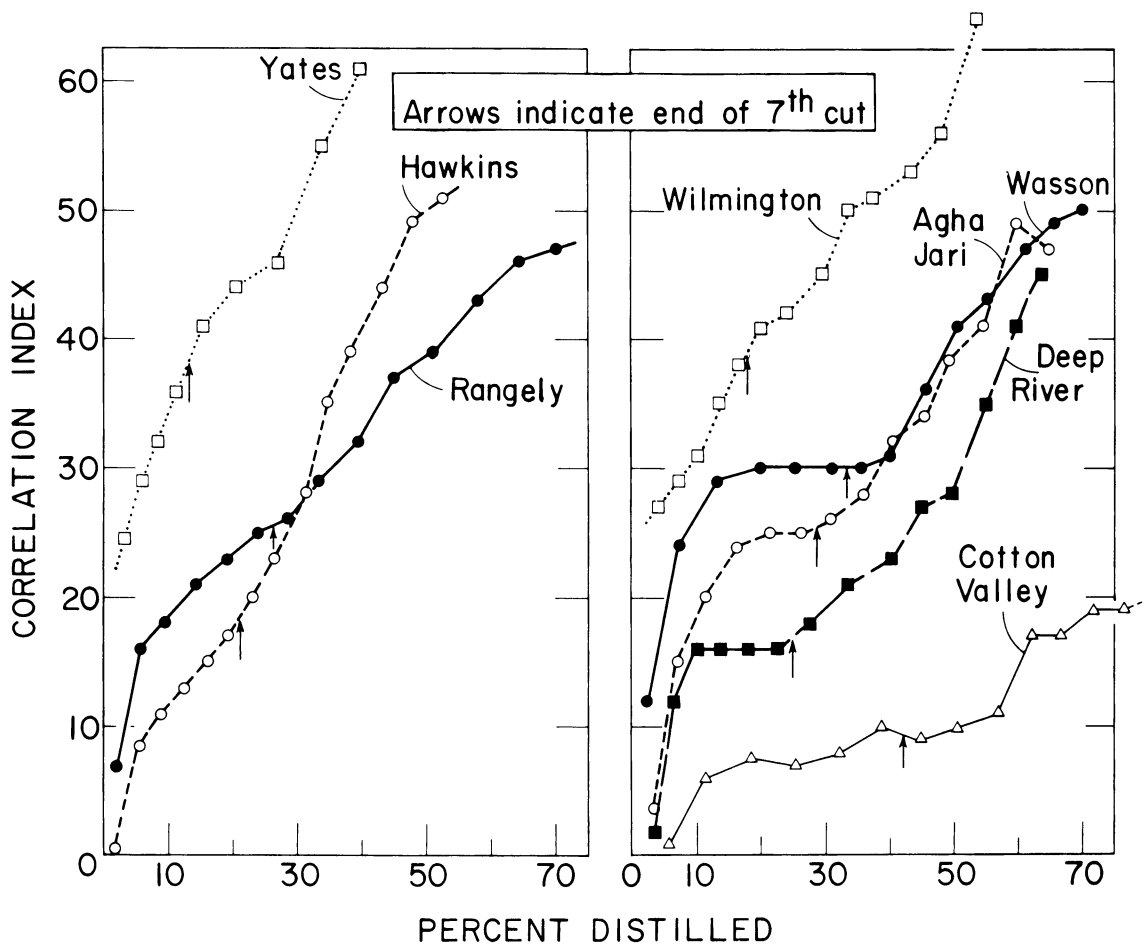
Figure 8.—Relationships between correlation index of routine distillation fractions and their mid-sum-percent distilled.

tent of this portion (below 200° C) of the crude oil. Note that Hawkins crude oil appears to be more paraffinic below 30 percent distilled than is Rangely crude oil and is more aromatic than Rangely above that point. Other such instances can be observed upon examination of these data.

These routine data on the 17 crude oils selected for preliminary study indicated that the samples selected represented a wide latitude of high-sulfur-content crude oils (ranging from 0.6 to 5.0 percent) as well as a considerable diversity of hydrocarbon compositions. In 1948 most of the American crude oils in the selection represented large domestic crude oil production; Wilmington and Wasson fields, for example, ranked second and third, respectively, in the United States (table 8).

Sulfur Types Present in the Selected Crude Oils—Their Thermal Stability

To determine the types and quantity of sulfur compounds present in the selected crude oils and to enable intercomparison of these data, separation of these crude oils into uniform boiling ranges was considered essential. The all-glass still, illustrated in figure 9, was constructed. This still could be operated at atmospheric pressure or under reduced pressures as low as 1 mm Hg. To determine the effects of thermal decomposition on the components of the crude oils, specifically on the sulfur compounds, the samples were distilled under two conditions; that is, at atmospheric and with two additional fractions at 40 mm Hg. Light distillate and hydrogen sulfide were collected in the liquid-air-cooled trap installed in the vacuum line. The various distillate fractions were collected and separated in the lower liquid-air-cooled trap at preselected temperature intervals. When the distillations were completed, the hydrogen sulfide was allowed to evaporate by gradual warming to room temperature. The hydrogen sulfide, thus released, was precipitated as cadmium sulfide from a solution of cadmium chloride and determined iodometrically.

In the distillation at atmospheric pressure, the first cut was made at a vapor temperature (top of column) of 100° C (212° F), and thereafter at every 50° C (90° F) rise in vapor temperature until a vapor temperature of 250° C (482° F) was reached, at which point the distillation was halted. The pot then was cooled slightly, the pressure reduced to 40 mm Hg, and the distillation continued at that pressure to two additional cut points of 200° C (392° F) and 250° C (482° F). The distillation was terminated at this point. Throughout the

distillation, the distillation rate was maintained at 5 to 6 ml per minute.

Table 9 shows that the special distillation simulated the routine distillation in all points except that each cut of the special distillation was equivalent to two of the routine (three in the instance of the first three cuts).

The vacuum distillation was conducted at about 1 mm Hg, except for the first fraction which, because of its high vapor pressure, was distilled at about 30 mm Hg. Approximately the same quantity of crude oil was distilled in this distillation mode as in the atmospheric, and care was taken to obtain cuts of approximately corresponding volume in the vacuum distillation as in the atmospheric. It was assumed that these cuts would have the same boiling range as the corresponding cuts in the atmospheric distillation and, thus, the same physical and chemical properties except for changes induced by the temperature differences and by the duration of that exposure. Indeed, determining the nature of these effects was one major purpose for the series of experiments. The distillation rate was maintained the same as in the atmospheric distillation, 5 to 6 ml per minute, and pot and vapor temperatures were determined.

Table 10.—Comparison of properties of comparative fractions taken in atmospheric and vacuum distillations for two crude oils

Properties	Fraction 2	
	Atmospheric distillation	Vacuum distillation
Wasson crude oil:		
Volume, ml	762	793
Weight:		
Grams	592	619
Percent	20.2	21.1
Specific gravity, 60/60° F	0.777	0.780
Sulfur, percent	.385	.405
Vapor temperature, °C	150	64.4
Deep river crude oil:		
Volume, ml	622	632
Weight:		
Grams	468	480
Percent	14.1	14.4
Specific gravity, 60/60° F	0.754	0.759
Sulfur, percent	.105	.111
Vapor temperature, °C	150	62.2

In both modes of distillation, nitrogen was passed through pyrogallol to remove traces of oxygen and allowed to bubble slowly through the oil in the flask to facilitate boiling and aid in sweeping the distillate vapors from the flask. All receivers containing
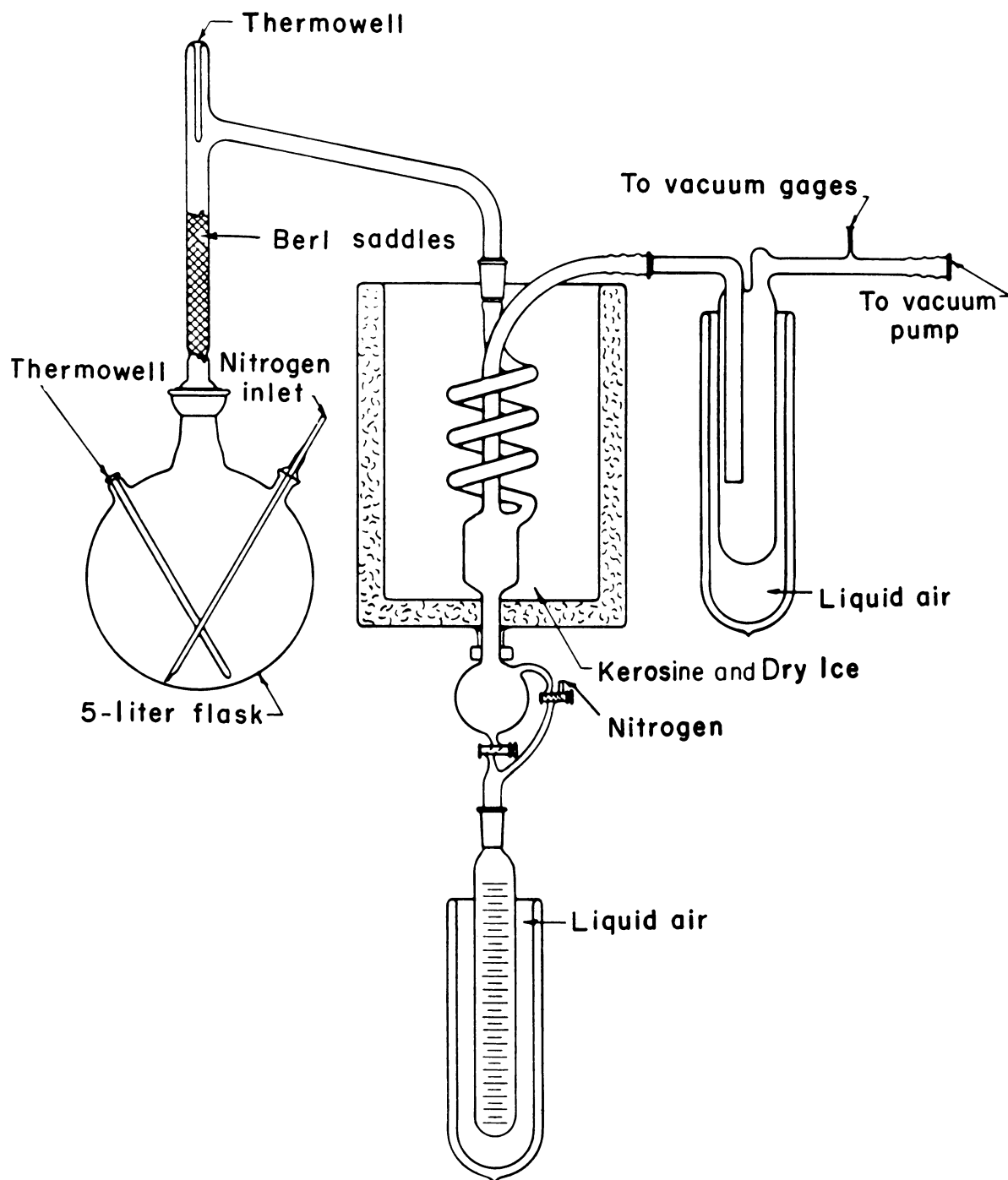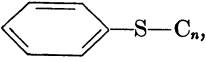
Figure 9.—All-glass still for operation at atmospheric or reduced pressure.

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fractions from the distillation were filled with nitrogen so as to exclude oxygen and prevent possible oxidation reactions, such as the conversion of thiols to disulfides. For the same reasons, and until analyses were completed, samples were stored in containers from which air was displaced with nitrogen.

That the two distillations, made under widely different conditions of temperature, produced fractions comparable in boiling range and properties is evident in the data of table 10. This table compares some properties of fraction 2 of Wasson, Texas, and Deep River, Michigan, crude oil samples taken in the two modes of distillation. A further substantiation of the similarity of the comparable cuts is shown in figure 10 reproducing ASTM D86 distillation curves for the same two fractions.

All distillate fractions through fraction 4 (cut temperature 250° C, or 482° F, at atmospheric pressure) were analyzed for sulfur types by the Ball (22) method. The types of sulfur compounds determined in this method and the procedure for determining them is outlined briefly in the following tabulation:

Figure 10.—Comparison of boiling range of atmospheric and vacuum distillates.

in this scheme of analysis, can and probably does include those higher molecular weight members or types which, because of their complex chemical

	Typical structures	Method of determination
Group:		
Hydrogen sulfide	H_2S	Titration with silver nitrate.
Mercaptan	C_n—SH	..........................Do.....................
Free sulfur	S	Removal with mercury and determination of difference in sulfur content.
Disulfides	C_m—S—S—C_n	Reduction with zinc and acetic acid followed by titration with silver nitrate.
Sulfides I	C_m—S—C_n, ⬡S, ⬠S	Extraction with mercurous nitrate and determination of difference in sulfur content.
Sulfides II	⬡—S—C_n, ⬠S	Extraction with mercuric nitrate and determination of difference in sulfur content.
Residual sulfur		Sulfur compounds remaining after complete procedure has been carried out.

As emphasized in the reference describing the above scheme of analysis (22), the method is applicable only to straight-run gasoline- and (with limitations) kerosine-range distillates. In higher boiling ranges the carbon-hydrogen content of the molecule and its configuration influence the chemical separation more than does the sulfur atom. Sulfur types that may be completely removed by certain reagents from low-boiling petroleum fractions may not be removed or only partly removed from higher boiling fractions. As a corollary, therefore, residual sulfur,[24]

structure, or other reasons, fail to follow the reaction patterns observed by lower molecular weight members. However, despite the limitations of the Ball method and for want of a better one, it was used in the analyses of the first four fractions from the distillations, not necessarily as an absolutely accurate portrayal of composition, but as a means of comparing fractions.

Typical data from the two modes of distillation and analyses of their fractions for the Wilmington, California, crude oil are recorded in table 11. Comparing the weight-percent distilled of equivalent atmospheric and vacuum fractions (table 11, row

[24] In general residual sulfur may be thought of as those sulfur compounds not reactive to the reagents employed in the group sulfur analysis.

Table 11.—Distillation data and sulfur type analysis of fractions on Wilmington, California, crude oil

Properties	Original crude oil		Fraction 1		Fraction 2		Fraction 3		Fraction 4		Fraction 5		Fraction 6		Residue		Loss	
	Atm.	Vac.	Atm.	Vac.	Atm.	Vac.	Atm.	Vac.	Atm.	Vac.	Atm.	Vac.	Atm.	Vac.	Atm.	Vac.	Atm.	Vac.
H_2S sulfur, weight-percent			0.000	0.000	0.002	0.000	0.011	0.000	0.037	0.000								
Free sulfur, do			.000	.000	Trace	.000	Trace	.000	Trace	.000								
RSH, do			.001	.001	.000	.002	.003	.001	.012	.000								
R—S—R, do					.057	.006	.086	.074	.005	.104								
R—S—R I, do					.010	.000	.100	.130	.027	.070								
R—S—R II, do					.010	.065	.180	.220	.485	.750								
Residual, do						.005			.370									
Total S: Analysis, do	1.39	1.39	.009	.009	.081	.078	.380	.425	.941	.924	1.510	1.280	1.403	1.405	1.840	1.989		
Total S: Cumulative, do			.001	.001	.081	.078	.380	.425	.936	.924								
Specific gravity, 60/60° F	.913	.913	.6998	.7014	.7823	.7882	.8450	.8511	.8677	.8822	.8554	.8998	.9089	.9081	.9910	.9815		
Volume, milliliters	4,396	4,435	282	292	542	543	517	516	411	410	84	83	365	366	2,183	2,197	12	23
Weight: Grams	4,015	4,051	197	205	424	432	437	439	357	362	73	75	332	332	2,163	2,156	32	50
Weight: Percent	100	100	4.9	5.1	10.6	10.7	10.9	10.8	8.9	8.9	1.8	1.9	8.3	8.2	53.9	53.2	0.7	1.2
Weight: Sum percent			4.9	5.1	15.5	15.8	26.4	26.6	35.3	35.5	37.1	37.4	45.4	45.6	99.3	98.8	100.0	100.0
Pot temperature:[1] ° C			192	75	289	97	352	168	382	209	268	218	313	263				
° F			377	168	553	207	665	335	720	409	514	425	595	506				
Vapor temperature:[1] ° C			100	31	150	44	200	100	250	125	200	132	250	171				
° F			212	88	302	111	392	212	482	257	392	269	482	340				
Sulfur balance, grams[2] (cumulative)	55.81	56.31	0.02	0.02	0.36	0.36	2.02	2.23	5.38	5.57	6.48	6.53	11.14	11.19	53.74	54.07	55.81	56.31

[1] Atmospheric-distillation: First four fractions at atmospheric pressure, next two at 40 mm. Vacuum distillation: First fraction at 31 mm pressure, others at 1 mm.

[2] 2.8 g sulfur as H_2S caught in liquid air cold trap in atmospheric distillation.

13) indicates that these quantities are closely similar, a result intended in the design of the experiments. In virtually each instance, however, the gravity of comparable fractions of the two distillation modes was higher for the vacuum than for the atmospheric. An exception to this order was apparent for fraction 6 of the Wilmington data (table 11) in which these data were reversed but essentially equivalent. The gravities of the distillation residues in the vacuum distillations were equally distributed between greater than, equal to, or smaller than the gravities of the residues from the atmospheric distillations. In many instances the data accumulated in this series of experiments were insufficient or of insufficient precision to explain all the questions raised, but it is evident that thermal decomposition occurred in the atmospheric distillation to produce lighter material than in the vacuum distillation.

The percentage of the total sulfur in the crude oil "naphtha," represented by each sulfur-compound group in the first four fractions is presented in table 12 for all the vacuum distillations and all available atmospheric distillations. Figure 11 shows the same information graphically for the naphthas from the vacuum distillations of the crude oils. During the vacuum distillations, essentially all of the crude oils liberated traces of hydrogen sulfide which were caught in the cold trap but only Yates crude oil showed measurable amounts of hydrogen sulfide. This crude oil contained an estimated 0.5 percent hydrogen sulfide in solution. Goldsmith and Yates and, to a lesser extent, Elk Basin and Slaughter crude oils, produced large quantities of hydrogen sulfide during distillation at atmospheric pressure. This phenomena undoubtedly resulted from elemental sulfur present in these crude oils, some of which reacted with the sample but much of which was distilled into the naphtha cut in the high vacuum distillations as indicated in figure 11. In fact, in distilling Goldsmith crude oil it was observed that a light-yellow solid collected in the neck of the condenser. This circumstance prompted a special and carefully conducted distillation of this crude oil, which will be discussed in a later section of this report.

The bottom section of figure 11 shows the total sulfur content of both the original crude oil and of the naphtha from the vacuum distillation, arranged in order of increasing total sulfur content of the naphtha.

The type-sulfur analyses, such as shown in figure 11, can be portrayed graphically under the percent-sulfur versus midpoint, sum-percent distilled curve, and examples of such portrayal are shown in figure 12 for the data from Wasson and Wilmington crude oils, both atmospheric and vacuum distillations. The areas in these charts representing the various sulfur groups are roughly proportional to percentages found by analysis and their boundaries are the best average based upon the limited data available.

Table 12.—Percent of sulfur in naphtha, based on total sulfur, present as constituent indicated for both atmospheric and vacuum distillates [1]

Field [2]	Sulfur in fraction, weight-percent		Residual		R-S-R II		R-S-R I		RSH		R-S-S-R		H₂S		Elemental S	
	Atm.	Vac.	Atm.	Vac.	Atm.	Vac.	Atm.	Vac.	Atm.	Vac.	Atm.	Vac.	Atm.	Vac.	Atm.	Vac.
Heidelberg	0.453	0.523	53.4	80.3	30.5	11.7	8.2	7.8	2.4	0.0	0.4	0.2	4.2	0.0	0.9	0.0
Hawkins	.322	.377	41.9	73.8	33.2	14.6	19.9	11.1	2.2	.3	.0	.3	2.8	.0	.0	.0
Rangely	.220	.271	61.8	72.0	31.4	20.3	4.1	7.7	1.8	.0	.4	.0	0.5	.0	.0	.0
Oregon Basin	.932	1.048	62.6	68.2	11.5	13.5	13.0	15.0	1.6	1.7	.6	1.3	7.0	.0	3.7	.3
Wilmington	.377	.387	40.3	66.7	41.4	19.9	13.3	12.7	1.3	.3	.3	.5	3.4	.0	.0	.0
Midway-Sunset	...	.385	..	66.5	..	26.0	..	7.3	..	.2	..	.0	..	.0	..	.0
Schuler	...	.313	..	66.4	..	22.7	..	9.3	..	.6	..	1.0	..	.0	..	.0
Agha Jari	.331	.353	57.7	65.7	10.9	9.6	13.6	12.8	9.1	8.5	.6	3.4	3.9	.0	4.2	.0
Santa Maria	...	2.014	..	58.2	..	35.5	..	6.1	..	..	..	.2	..	.0	..	.0
Elk Basin	...	.725	..	54.9	..	25.1	..	1.4	..	11.3	..	7.2	..	.0	..	.1
Wasson	.799	.857	10.6	52.6	6.5	13.0	56.2	11.6	18.0	15.3	3.1	7.4	5.1	.0	.5	.1
Slaughter	...	1.020	..	48.8	..	22.5	..	7.5	..	10.8	..	9.2	..	.0	..	1.2
Velma	...	.554	..	43.9	..	41.5	..	12.4	..	1.1	..	.7	..	.0	..	.4
Kirkuk	.320	.368	23.1	41.0	23.8	24.7	35.3	20.9	6.3	7.9	2.5	5.5	6.3	.0	2.7	.0
Deep River	.227	.231	19.4	28.6	.0	3.0	.4	.0	44.5	45.9	26.9	22.5	7.9	.0	.9	.0
Yates	...	1.297	..	20.5	..	20.1	..	9.2	..	7.5	..	6.9	..	1.2	..	34.6
Goldsmith	...	.729	..	17.3	..	11.6	..	9.6	..	10.6	..	8.4	..	.0	..	42.5

[1] Initial four fractions of distillation.
[2] Arranged in order of decreasing "Residual" component in vacuum distillation.
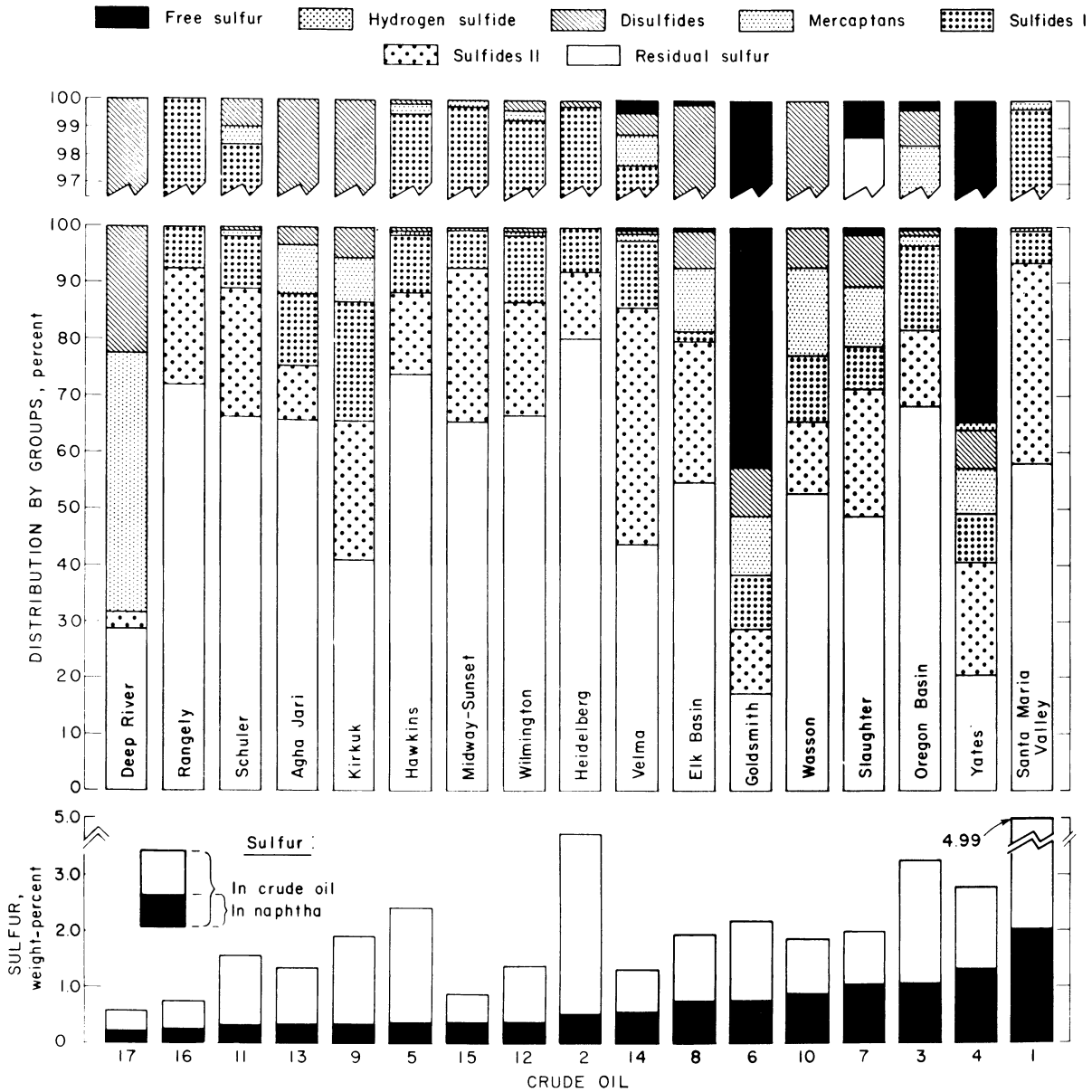
Figure 11.—Group sulfur analyses of naphthas from vacuum distillation and total sulfur analyses of crude oils and naphthas.

Inaccuracies in the analytical data, discussed previously, prevent elaborate interpretations, but several items appear significant, as follows:

1. Total sulfur in the four initial atmospheric cuts is somewhat lower than that in the corresponding vacuum cuts by a factor of about 0.9. This reduction is evident from a consideration of figure 13. This difference reflects more pronounced thermal decomposition in the atmospheric.

2. Up to a pot temperature of about 260° C

(500° F), the difference in the character of the sulfur content of the fractions does not appear to be pronounced. Above that temperature, definite changes take place, characterized principally by a decrease in residual sulfur in the atmospheric fractions. This also may be interpreted as decomposition of heavy sulfur compounds to a lower molecular weight.

3. Some of the residual sulfur appears to decompose during atmospheric distillation to more reactive sulfur types, principally to sulfides I and II, but
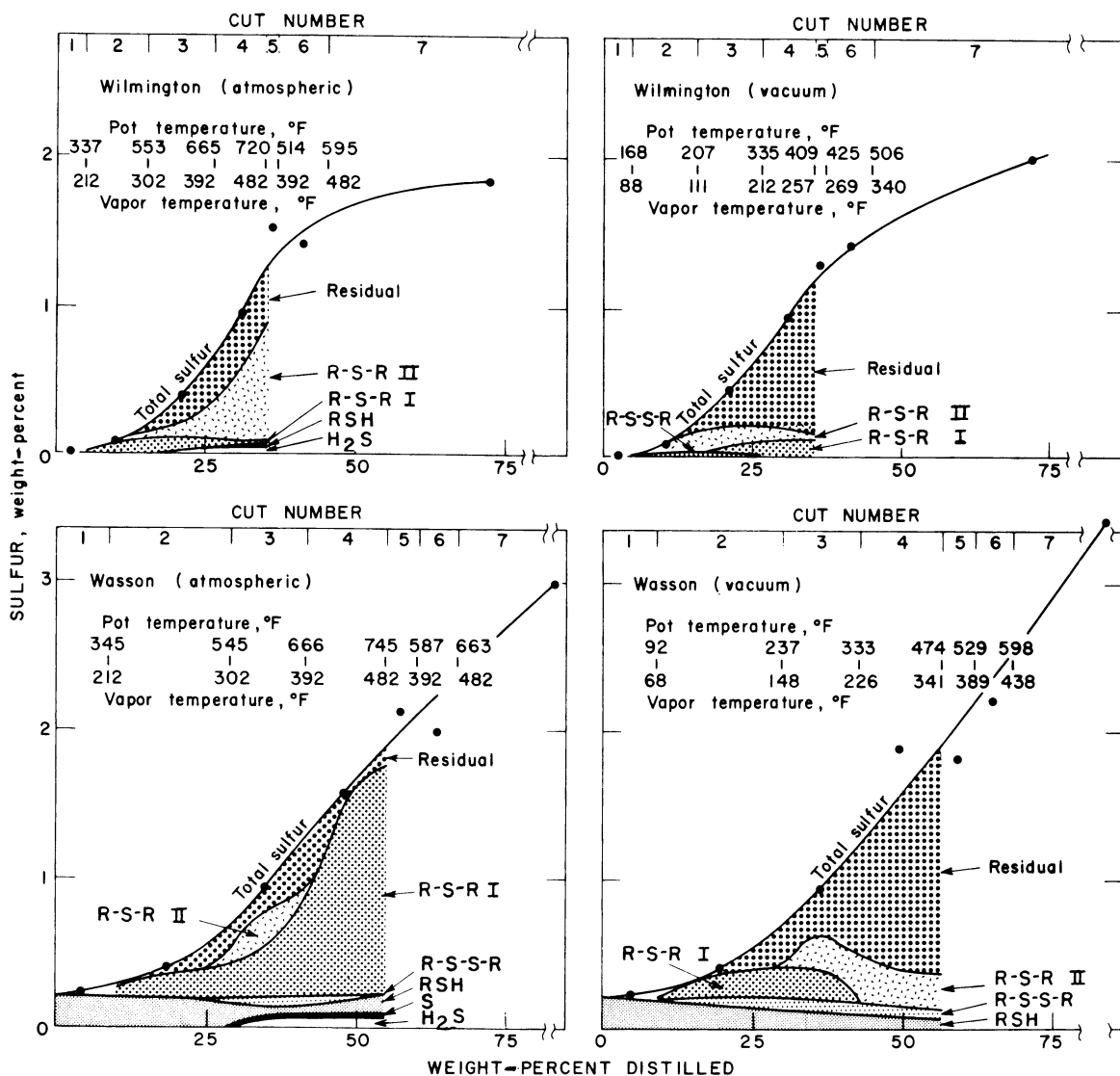
Figure 12.—Group sulfur analyses of distillates from two crude oils.

no preferential trend for either of these groups is evident. In Wasson and Kirkuk crude oils (Kirkuk data not shown), the conversion of residual sulfur favors sulfides I, whereas in Wilmington and Heidelburg crude oils (Heidelburg data not shown), the conversion favors sulfides II. Undoubtedly the character of the heavier compounds in the various crude oils, to a great extent, determines or guides the course or direction of decomposition. It is now known, although it was not so clear at the time of these experiments (156), that the naturally occurring sulfur compounds in Wasson and Wilmington crude oils are markedly different.

4. In the analyses of these crude oils the sulfur

compounds (other than residual) present in the vacuum naphtha can be segregated roughly into two categories: thiols plus disulfides [25] and sulfides I plus II. This division is illustrated graphically in figure 14. This bar graph, drawn for convenience to a large scale, is capable of precision not warranted by the data, and the areas indicated should be taken as comparative rather than precise. In this chart, Deep River crude oil stands out strikingly as a thiol-disulfide class. In further investigation of

[25] The inclusion of thiols and disulfides in a common group is appropriate as they are chemically readily interconvertible. The presence of disulfides in petroleum, when reported, has been viewed skeptically, partly because of this relationship.
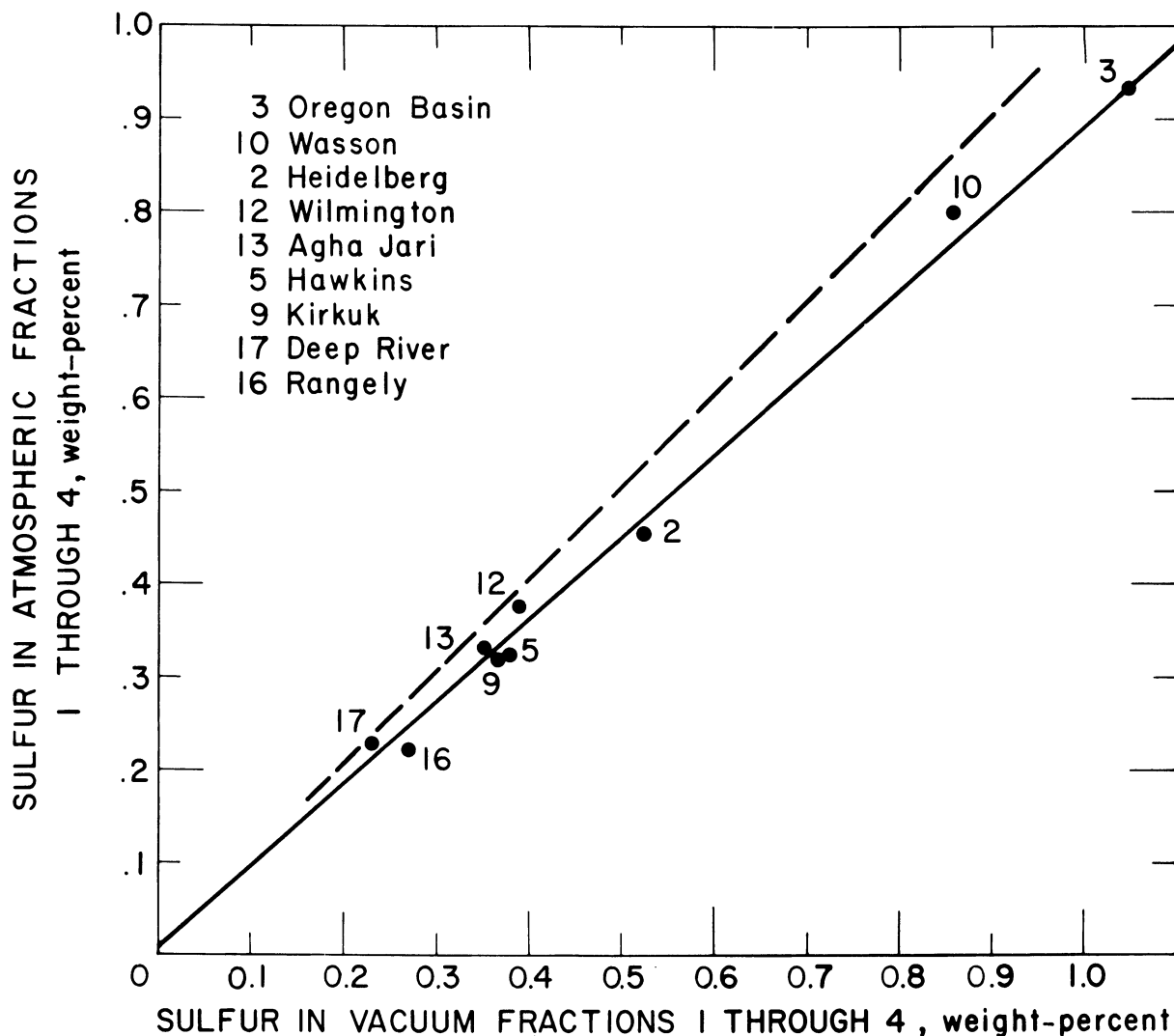
Figure 13.—Relationship of total sulfur in atmospheric and vacuum fractions.

this crude oil, made at a later date, it was shown that this crude oil did, indeed, contain disulfides, a sulfur-compound type thought to be nonexistent in straight run distillates. At the other extreme in the chart, to the right of Kirkuk, are crude oils containing very small quantities of thiols-disulfides and representing what could be termed sulfide-type crude oils. Between the sulfide-type (Rangely, etc.) and the thiol-disulfide type (Deep River) are the crude oils from Wasson, Texas, to Kirkuk, Iraq, inclusive, representing an intermediate type containing substantial amounts of thiol-disulfides, but predominantly sulfides I and II. Although these data from this small selection of crude oils suggest a separation of crude oils into the three sulfur-compound "types" mentioned, it is unknown, of course,

whether all crude oils would distribute into the same groups or grade gradually from one extreme to the other.

5. The data of figure 11 indicate that some of the crude oils listed in this table contain elemental sulfur. Outstanding among these in that respect are Goldsmith and Yates crude oils. However, Slaughter, Velma, and Oregon Basin and, to a lesser extent, Elk Basin and Wasson crude oils also contained some elemental sulfur. It should be emphasized that this information is based on the analyses of the four initial cuts (naphthas) from the vacuum distillation of the crude oils. During the atmospheric-pressure distillation of these crude oils, any elemental sulfur present can readily react with the hydrocarbons of the crude oil, but under reduced-
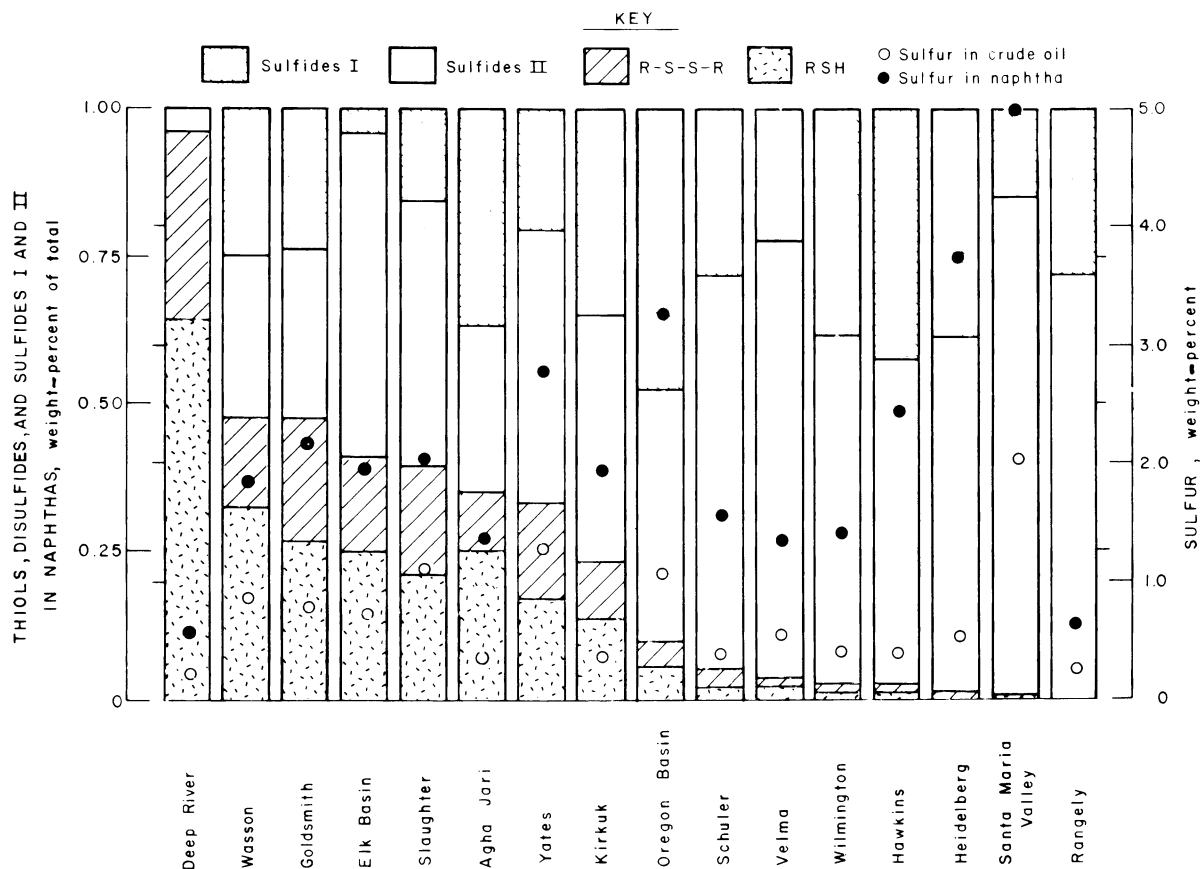
Figure 14.—Bar graph indicating relationship between thiol-disulfide and sulfides groups in "vacuum" naphtha from various crude oils.

pressure distillation, the sulfur can distill with the hydrocarbons when its vapor pressure, at pot temperature, approaches the distillation pressure. This circumstance accounts for the elemental sulfur found in some of the naphthas of figure 13. Where no elemental sulfur was detected in the naphthas from the vacuum distillations, presumably no elemental sulfur exists in the crude oil. Of the seven crude oils thus indicating an elemental sulfur content, four (Wasson, Slaughter, Yates, and Goldsmith) are from West Texas fields, and two (Oregon Basin and Elk Basin) from Park County, Wyo. Of these, Yates and Goldsmith contained, by far, the greatest quantity of elemental sulfur. When more elemental sulfur appeared in the naphthas from the atmospheric distillation than in the naphthas from the vacuum distillation, it was assumed that, for unexplainable reasons, conversion of hydrogen sulfide to elemental sulfur took place during atmospheric distillation or sample storage. This situation exists

for Heidelberg, Oregon Basin, Agha Jari, Wasson, Kirkuk, and Deep River oils.

In general it may be concluded that thermal decomposition is negligible up to about 125° C (257° F), but it increases at higher temperatures and can be detected by loss of sulfur presumably to hydrogen sulfide and to low-boiling thiols. In these reactions, structure modifications of sulfur compounds occur which result in the conversion of compounds that are unreactive to mercurous or mercuric nitrates in the group sulfur analyses (residual sulfur) to more reactive types and appear as sulfides I and II, probably with some liberation of hydrogen sulfide. In some crude oils (for example, Wasson) the compounds generated appear to be predominantly of the sulfides I type, reactive with mercurous nitrate. In other instances (for example, Wilmington) the conversion is predominantly to sulfides II. No obvious reason for this behavior is presently known, but the chemical character of the
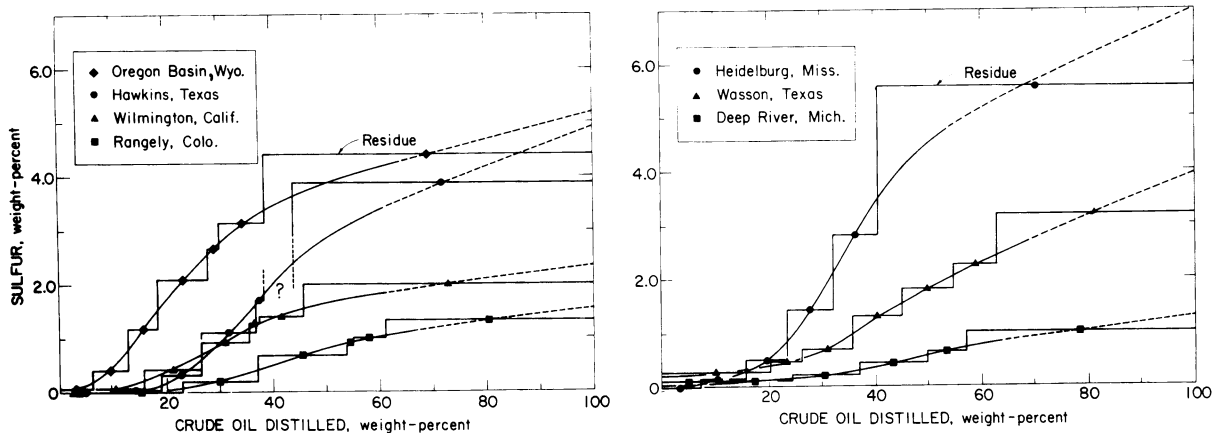
Figure 15.—Relationship between percent sulfur and percent distilled in seven crude oils.

heavier sulfur compounds is readily suspect. The nature of the compounds composing the residual sulfur is unknown, but they are thought to be largely benzothiophenes, dibenzothiophenes, and single and multiring sulfides whose boiling points are compatible with the boiling range of the fractions.

The general increase in the sulfur content of petroleum distillate fractions as their boiling point increases [26] has been previously discussed. Although exceptions to this observation have been cited, they are rare. The data from the vacuum distillations described in this section (data from one is recorded in table 11) also support the assumption that the sulfur content of crude oil fractions increases with boiling point. Figure 15 shows such data for seven of the crude oils listed in table 8. In each instance the general and orderly rise of sulfur with boiling point is indicated. The absence of analytical data on one fraction for the Hawkins oil is indicated by a question mark and a break in the line for sulfur concentration. From the average boiling point and gravity of the fractions taken in these distillations it is possible to estimate their molecular weight (286). It is assumed that molecular weights of the sulfur compounds in the fractions are essentially the same as for the hydrocarbons, and that they contain but one atom of sulfur, then the data of figure 15 may be replotted with percent sulfur compounds as the dependent variable in place of weight-percent sulfur (fig. 16). In figure 16 the entire area within the chart represents the total

mass of the crude oil sample, and the area under the curves represents the mass of the sulfur compounds in the crude oil. Thus, where the curve contacts the top of the chart (100 percent sulfur compound ordinate), all of the chart area to the right of that point and under the curve represents sulfur compounds. However, some hydrocarbons exist in the heavy fractions of petroleum, so this area cannot represent sulfur compounds only. The data prove, therefore, that the sulfur compounds in such crude oils as Oregon Basin, Hawkins, and Heidelburg must contain a large percentage of compounds containing two or more sulfur atoms. This does not mean, however, that crude oils such as Wilmington and Wasson, whose sulfur-compound versus crude-oil-distilled curve fail to intersect the 100-percent-sulfur-compound ordinate, cannot or do not contain some compounds of two or more sulfur atoms. It would appear that any crude oil containing more than 2 percent sulfur certainly must contain compounds of more than one sulfur atom.

SELECTION OF CRUDE OILS
FOR INTENSIVE STUDY

As a result of the experimentation described in the preceding section, Wasson, Texas, crude oil was chosen for intensive study of its sulfur components. Its reasonably high, 1.85 weight-percent, sulfur content offers somewhat less difficulty in concentrating and isolating its sulfur compounds than do crude oils that contain less sulfur. Production from the Wasson field in 1948 was high, and there was good promise that it would remain so for many years. The possibility, therefore, of relating chemical

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[26] This phenomenon results from the large number of compounds, both hydrocarbons and hetero compounds, present in the crude oil and from the inefficient fractionation obtained in "routine" distillation equipment. It is well known that distillation of petroleum or its fractions in precision fractionation equipment will produce a concentration by boiling point of hydrocarbons (146) as well as of sulfur compounds. However, even here, it is probably safe to say that the trend of sulfur content in the fractions is upward as the distillation progresses.
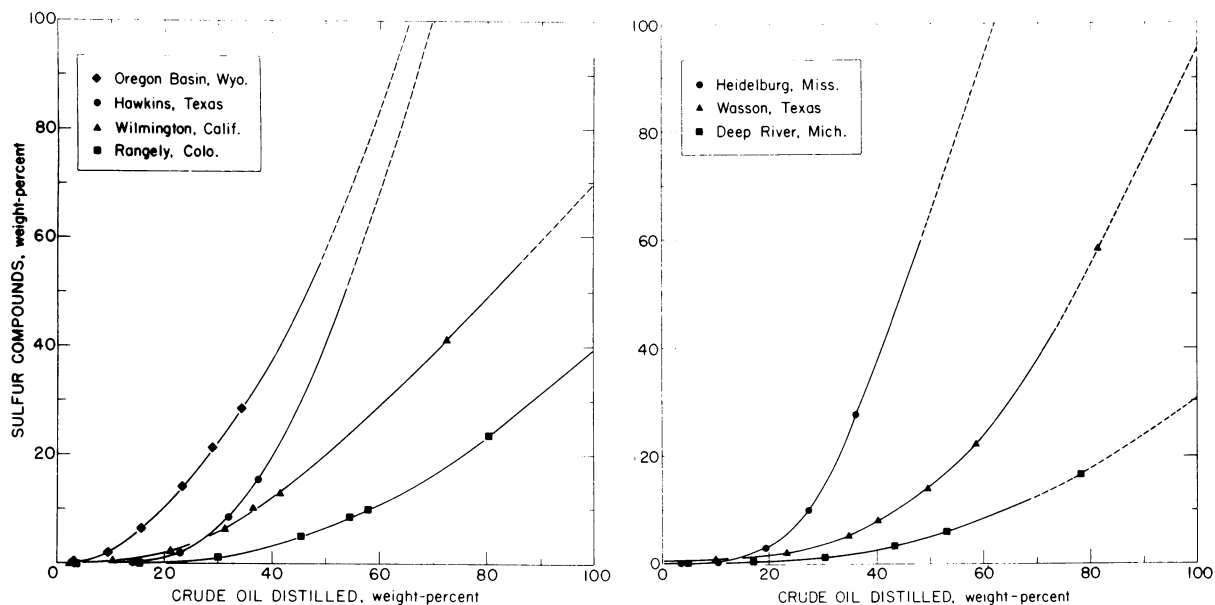
Figure 16.—Relationship between percent sulfur compounds and percent distilled in seven crude oils.

knowledge of this crude oil with commercial refining experience was favorable.

Because of its huge production (see table 8), Asiatic origin, and suspected similarity to Wasson, Texas, crude oil, casual attention to the light distillate of a crude oil from the Agha Jari, Iran, field was considered fitting and of scientific interest.

Preliminary routine inspection of Deep River, Michigan, crude oil indicated that it contained disulfides in higher concentration than any other known crude oil. Because of the general opinion that petroleum exists in nature in a reducing environment and that, therefore, disulfides cannot be present in crude oils, and because of a feeling of insecurity in the positive results obtained in chemical tests for these compounds, Deep River crude oil was selected for a restricted examination aimed specifically at the disulfide question.

When API Research Project 52, on the nitrogen constituents in petroleum, was begun early in 1954, Wilmington, California, crude oil was chosen for investigation of its nitrogen components. Many California crude oils are notorious for their nitrogen content; the Wilmington sample contained 0.65 percent. The sulfur content of Wilmington crude oil is 1.59 weight-percent. Because of the extensive work on its nitrogen components contemplated by Project 52, this crude oil [27] was selected by Pro-

ject 48 for a limited investigation of its sulfur components.

Table 13 lists a few properties of four crude oils and gives their geological origin where known. These four petroleums were selected for study to isolate and identify some of the sulfur compounds constituting their sulfur content. Principal attention was directed to the Wasson crude oil. For special problems, the other crude oils were studied; for example, the presence and concentration of elemental sulfur in certain West Texas crude oils were determined.

Experience gained in the preliminary work was utilized in the processing of the crude oils and fractions obtained from them. For example, it was concluded that distillates should be derived from crude oils at as low a temperature as possible, and never higher than 100° C. This procedure was followed to prevent the destruction of high molecular weight sulfur compounds by thermal decomposition with subsequent incorporation of the products into the lower boiling distillates. Furthermore, the crude oil and distillates would be treated wherever possible in all-glass containers, with Teflon [28] and stainless steel the only permissible extraneous materials to be used in apparatus construction.

Like reasoning was applied to sulfur concentrates and, wherever possible, to distillates. Thus,

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[27] Although quite similar to it, this sample is not the same sample designated as 12 in table 8, and whose routine analysis is shown in table 9.

[28] The mention of brand names is for identification only and does not imply endorsement by the Bureau of Mines.

Table 13.—Some properties of four crude oils selected for more detailed investigation

	Wasson [1]	Agha Jari	Deep River [2]	Wilmington [3]
Depth of formation.................feet......	4,890–5,140	4,500	2,853–2,856	....
Geologic system...............................	Permian	Tertiary	Devonian	....
Geologic formation...........................	San Andres	Lower Miocene-Oligocene	Dundee	....
Sulfur........................weight-percent	1.85	1.36	0.57	1.59
Nitrogen.................................do.......	....	....	.12	.65
Specific gravity, 60/60° F.....................	0.858	0.845	0.857	0.939
Gasoline and naphtha [4]..........volume-percent	33.7	28.5	25.0	11.4
Residuum..............................do.......	26.0	27.8	31.2	47.2
Bureau of Mines identification number...........	50070	48023	63279	PC–54–107
Date sample taken............................	1–?–50	3–3–48	9–11–63	4–30–54

[1] Not same sample as 48093, table 9.
[2] Not same sample as s iple 17, table 8, but same as sample 1, figure 4.
[3] Not same sample as 49005, table 9.
[4] Up to 200° C (392° F).

wherever doubt existed that temperature might affect the sulfur components of a distillate, an independent sample was subjected in similar apparatus to more severe temperature conditions to determine where thermal decomposition would begin. The evolution of traces of hydrogen sulfide indicated the beginning of deterioration.

Further Experiments in Thermal Stability

In the work described in the preceding section it was noted that in each atmospheric distillation of the crude oils, significant quantities of hydrogen sulfide appeared at near or below 260° C (500° F). This generation of hydrogen sulfide was investigated further. The general procedure was to heat the crude oil sample, under reflux conditions, at increasingly higher temperature levels and determine the amounts, if any, of hydrogen sulfide and low-boiling thiols liberated on each level before proceeding to the next higher temperature level. Temperature increases were to be effected by both the slow removal of distillate from the system and the cautious increase of heat to the stillpot. Temperature levels would begin at atmospheric and, after the first rise to 93° C (200° F), would continue at 38° C (100° F) steps to about 315° C (600° F). Liberated hydrogen sulfide and low-boiling thiols would be trapped in acid cadmium chloride solution and silver nitrate solution, respectively, and measured.

Apparatus

Apparatus for these experiments (fig. 17) consisted of a 2-liter, round-bottom flask equipped with a 29/42 standard-taper joint. To this joint is attached

a glass-bead-packed column about 15 cm long having a thermowell at the top for measuring vapor temperatures and a side arm connected to a vertical reflux condenser cooled to 10° C. At the bottom of the reflux condenser is a stopcock for control of withdrawal of reflux from the system. The flask has a sealed-in thermowell and a sidearm, which permits the introduction of a small stream of nitrogen below the flask contents to sweep uncondensable gases through the system. In later experiments, this opening was modified to remove samples from the flask. At the top of the condenser, a capillary line leads into an absorption train consisting of absorbers (sometimes three are necessary) filled with acidified cadmium sulfate solution for the collection of hydrogen sulfide, and two absorbers containing silver nitrate solution for retention of thiols. A Y-stopcock in the line from the top of the column permits use of a second train of absorbers while the solutions in the first are being analyzed and the flasks prepared for reuse.

Procedure

The apparatus is assembled as indicated in figure 17 and charged with about 1,000 grams of crude oil. A slow stream of inert gas is bubbled through the crude oil for about 30 minutes at room temperature to remove dissolved hydrogen sulfide. The flask is then heated, and all condensable vapors are returned to the flask. Materials not condensed under these conditions are swept into the collecting train. The temperature of the stillpot can be raised and maintained at any desired temperature level by removing some of the reflux. In the experiments reported here, the temperature levels used, as given below, were obtained by successive withdrawal of distillate and appropriate control of heat input.
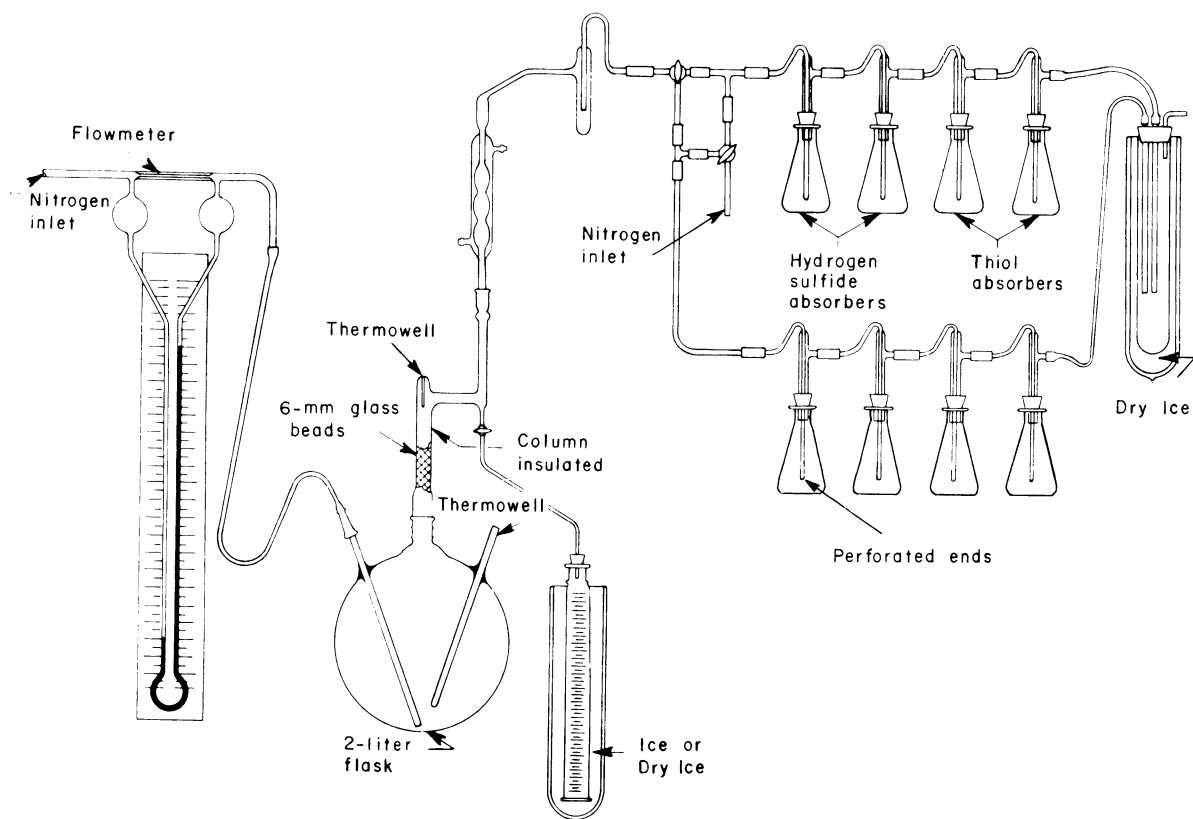
Figure 17.—Thermal stability apparatus.

Pot temperature		Time on plateau, minutes
° F	° C	
Room temperature		30
210	99	180
310	154	180
410	210	180
510	266	180
610	321	180

Analysis

Throughout each temperature plateau, the quantities of evolved hydrogen sulfide and volatile thiols are determined by analysis of the absorber solutions at the end of each 30-minute or shorter interval. As the reflux condenser is cooled with water at about 10° C, presumably the greater proportion of thiol trapped in the absorbers is methanethiol, and possibly some ethanethiol. However, at later stages of the heating, the odor of thiols of higher molecular weight could be detected in the absorbers. These were undoubtedly present in trace quantities. Thiols may also be present that do not react with the silver nitrate reagent, as used, and escape undetected.

Results

Figure 18 illustrates typical data obtained on Wilmington, Wasson, Slaughter, and Goldsmith crude oils. In these graphs, sulfur evolved (as H_2S and as thiols) is plotted in grams as a function of time. Thus, the areas under the curves are proportional to the amounts of hydrogen sulfide and thiol generated. The curves delineated by the data points in this figure are the pot-temperature versus time curves.

The hydrogen sulfide observed on the room temperature plateau (30 min), specifically in the Wasson and Goldsmith crude oil samples, is thought to be the gas in solution and a normal component of the crude oil. The thiols observed in the traps during the same interval are low-boiling members of the series, probably methane- and ethanethiol, the former in greater predominance. The reflux condenser, at 10° C (50° F), would probably condense higher boiling thiols and probably most of the ethanethiol. It is of interest that methanethiol and ethanethiol later were shown to be present in Wasson crude oil in high percentage.
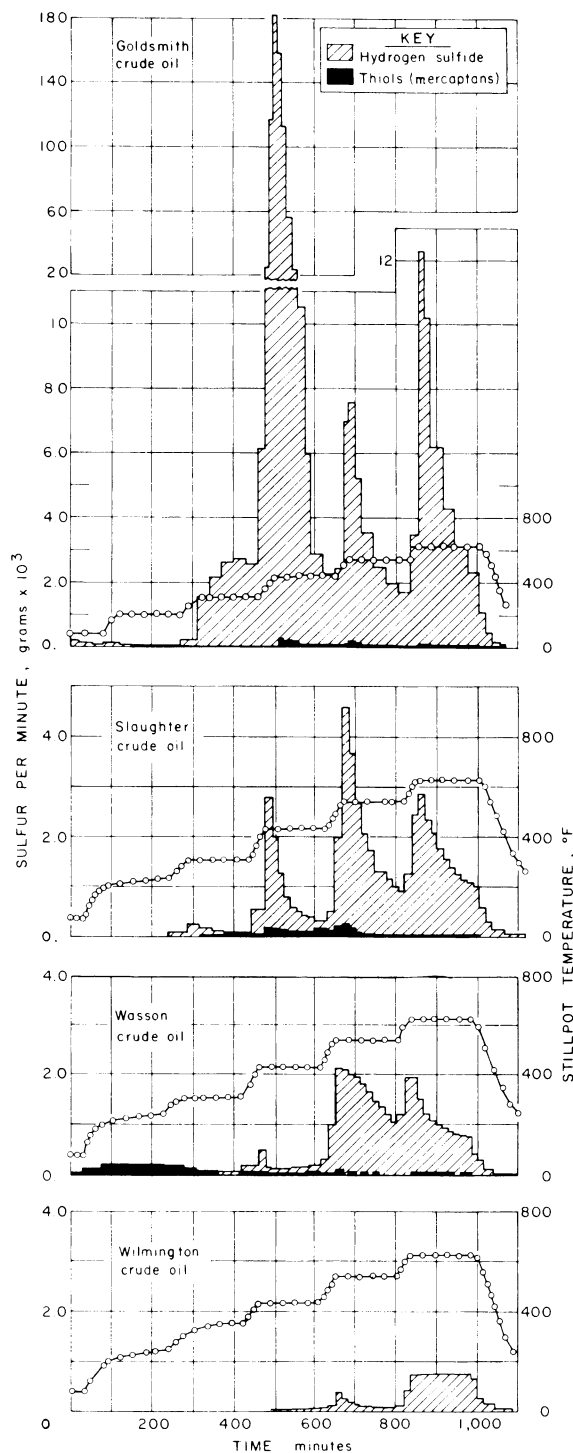
Figure 18.—Thermal stability tests of high-sulfur crude oils.

The pattern of hydrogen sulfide evolution was consistent in all crude oils tested. Upon heating the

crude oil, a temperature is reached where hydrogen sulfide is generated. On the succeeding temperature plateaus, the evolution of hydrogen sulfide reaches a maximum rather rapidly and then diminishes at a slower rate. Thiols, observed in far less quantity, develop a similar pattern.

These data have been interpreted as follows: Sulfur compounds which are thermally stable on one temperature plateau may be unstable at the next higher plateau and decompose with hydrogen sulfide as one product and low-boiling thiols in small amounts as another. This phenomenon is repeated on the next higher temperature plateau, where another group of sulfur compounds is thermally unstable. The duration of each temperature-time plateau was 3 hours, as previously indicated, and it is not known whether hydrogen sulfide evolution on any certain plateau would ever cease. The 210° C (410° F) plateau of Slaughter crude oil indicates that in some instances it might.

Each crude oil appears to have its own pattern of hydrogen sulfide generation because of the nature of the sulfur compounds it contains. Wilmington crude oil, for example, indicates little decomposition of its sulfur compounds until a temperature of 266° C (510° F) is reached.[29] Even at this temperature the quantity of hydrogen sulfide evolved is small and a temperature of 321° C (610° F) is attained before hydrogen sulfide evolution is reasonably brisk. This experience is in complete accord with circumstances as now known, for the sulfur in Wilmington crude oil consists principally of the thiophene-type compounds, the most thermally stable of sulfur compounds (*119, 272, 273, 352*). It would have been more informative had this experiment been carried on a few hours longer to determine for certain that the evolution of hydrogen sulfide was diminishing at the end of the experiment as a result of exhaustion of thermally unstable compounds or because of the drop in temperature caused by shutdown. The truncated pattern points to the first explanation above, although in no other crude oil did the maximum hydrogen sulfide generation last longer than 10 to 15 minutes.

Wasson crude oil indicated little generation of hydrogen sulfide on the 99° C (210° F) plateau, but considerable thiol. It is thought that thermal decomposition is not responsible for this production of thiol at this low temperature, but that it is more likely due to distillation of low-boiling thiols, principally methanethiol [b.p. 6° C (43° F)], naturally

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[29] A similar observation was made by Tarasov and Starostin (*405*), who in distilling various Russian crude oils to 300° C (572° F), noted that Malgobek crude oil lost 8 percent of its sulfur content by decomposition, whereas Ishimbaev crude oil lost 40 percent.

present in this crude oil. Later work indicated that Wasson crude oil did contain considerable methane- and ethanethiol. The main evolution of hydrogen sulfide began on the 265° C (510° F) plateau and developed normally. The small peak at about 450 minutes may have significance, as explained later.

The hydrogen sulfide evolution pattern for the Slaughter crude oil is typical—a medium evolution of hydrogen sulfide on the 154° C (310° F) plateau, increasing to a maximum peak at the beginning of the 265° C (510° F) plateau and a drop in evolution thereafter. Maximum production of thiols is on the 210° C (410° F) plateau. These circumstances hinted that the peak at the beginning of the 210° C plateau might be due, partly at least, to elemental sulfur reacting with the crude oil hydrocarbons. Figure 11 indicates that elemental sulfur was present in this crude oil. This explanation is substantiated by inspection of the hydrogen sulfide generation pattern for Goldsmith crude oil (fig. 18) which has an even greater elemental sulfur content than that of Slaughter (see table 11). Here the generation of hydrogen sulfide on the 210° C (410° F) plateau is quite extraordinary, requiring a 20× scale expansion (over preceding graphs) to maintain the pattern within the bounds of the chart. Table 14 records the

Table 14.—Sulfur balance in Goldsmith, Texas, crude oil stability test

	Sulfur		
	Weight-percent	Grams	Percent of charge
Sulfur in charge...........	2.20	18.86	100.0
Gas phase:			
Thiols................	....	.04	.2
Hydrogen sulfide.....	....	9.88	[1] 52.4
Liquid phase:			
Trap material........	....	....	......
Fractions 1, 2, and 3..	.104	.12	.6
Fraction 4.............	.323	.24	1.3
Fraction 5.............	.466	.42	2.2
Residue.............	1.40	7.47	39.6
Loss.....................	....	.69	3.7

[1] Released on 410° F plateau, 42 percent.

sulfur material balance obtained in the Goldsmith crude oil stability test. These data show that in this experiment, when 321° C (610° F) was reached, about 52 percent of the sulfur originally present in the crude oil was converted to hydrogen sulfide. Almost 80 percent of this quantity of hydrogen sulfide (or 42 percent of the sulfur in the charged crude oil) was liberated on the 210° C (410° F) plateau. In the reaction of sulfur with hydrocarbons,

usually about half of the sulfur is released as hydrogen sulfide and the remainder forms sulfur compounds by reaction with the hydrocarbons of the crude oil. Undoubtedly some of these compounds, together with some naturally present, undergo decomposition on the succeeding temperature plateaus. The extremely large hydrogen sulfide generation on the 210° C (410° F) temperature plateau points to a high elemental sulfur content in Goldsmith crude oil.

The above reasoning was substantiated by the data shown in figure 19. In this figure, the top chart is the hydrogen sulfide generation pattern for a Bradford, Pennsylvania, crude oil which contains very little sulfur, elemental or combined. To this crude oil was added 0.5 percent elemental sulfur, and its hydrogen sulfide generation pattern was redetermined. These data are shown plotted in the bottom panel of figure 19. Here again the extremely large evolution of hydrogen sulfide is evident on the 210° C (410° F) temperature plateau, duplicating, quite remarkably, the results obtained with Goldsmith crude. The initial hydrogen sulfide peak is now followed by two more on the succeeding temperature levels precisely as in the Goldsmith pattern but absent in the original Bradford crude oil pattern. This hydrogen sulfide, without doubt, is originating in the thermal breakdown of sulfur compounds formed by the reaction of elemental sulfur with the hydrocarbons of crude oil. Referring again to the Wasson panel of figure 18, the small peak at 500 minutes may be due to a breakdown of the small quantity of elemental sulfur in Wasson crude oil. The data of table 12 support this speculation.

At the beginning of this study it was suggested that crude oils must be handled under mild temperature conditions if isolation of sulfur compounds natural to crude oils is to be achieved because some higher boiling sulfur-containing constituents in crude oil may be thermally unstable and thus the source of some low-boiling sulfur compounds when crude oils are distilled. The validity of this suggestion is shown in figure 20. This figure shows the hydrogen sulfide-generation pattern for Santa Maria Valley, California, crude oil compared with that of a commercially deasphaltized sample of the same crude oil. The deasphaltizing operation removed material equal to 39 percent of the crude oil. The data shown in both panels of figure 20 were obtained on ad equal volume basis (1,000 ml), but were plotted on an equal weight basis (1,000 g). Thus, the shaden areas shown are comparable on this basis. In the bottom panel and superimposed on the data of the original crude oil, are the data of the top panel (deasphaltized crude oil) recalculated on the basis
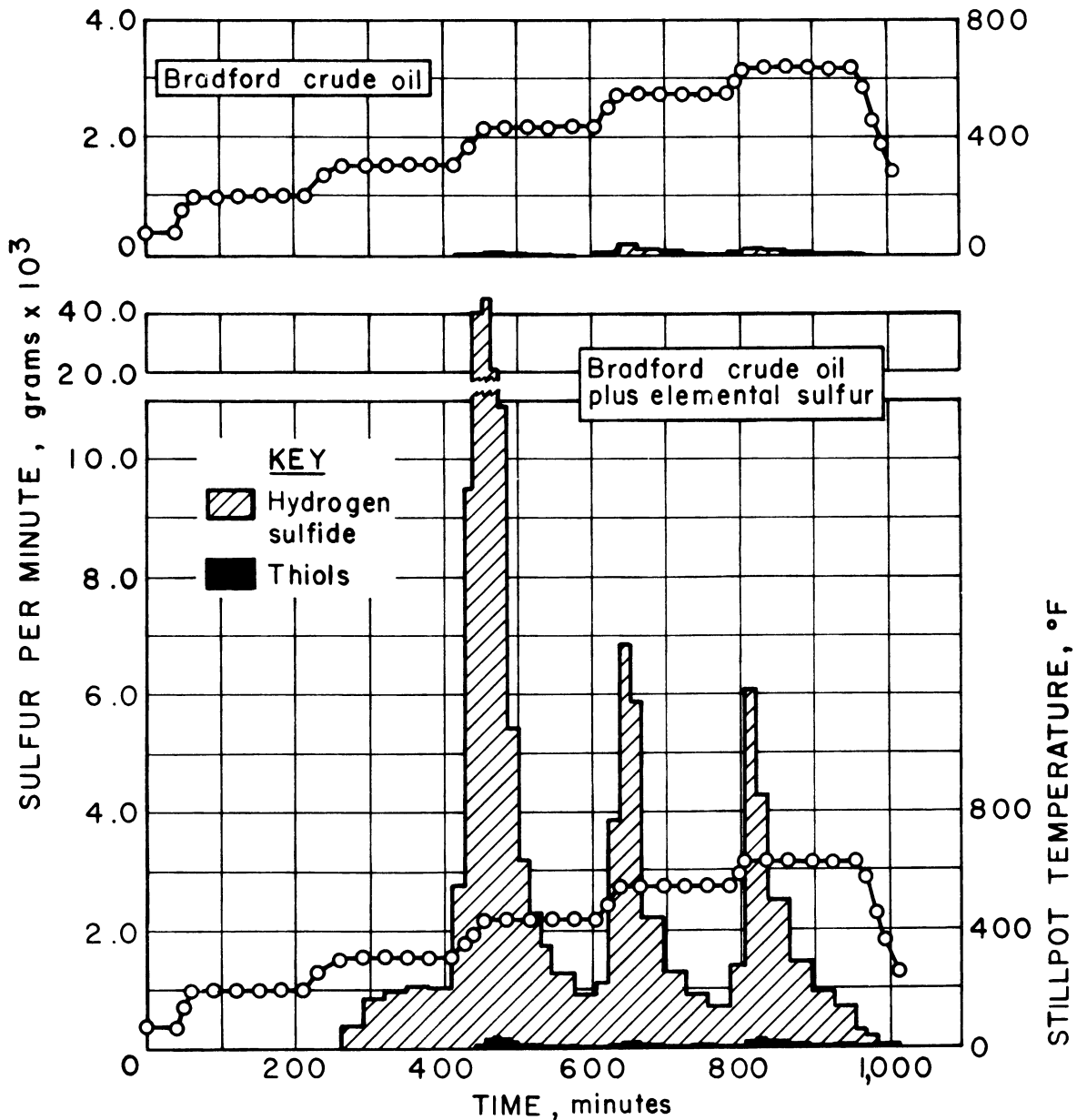
Figure 19.—Thermal stability tests of Bradford, Pennsylvania, crude oil
and Bradford crude oil with added elemental sulfur.

of 1,000 g of crude oil. These data indicate that concurrently with the removal of the 39 percent of the asphaltic and high-boiling material from the crude oil, labile sulfur compounds were also removed which had been the source of at least 75 percent of the hydrogen sulfide generated in the stability test of the untreated crude oil (323). A calculated sulfur balance shows that the asphaltic material (no sample available) should have had a sulfur content of about 7.5 percent. This figure compares with 5.0 percent for the crude oil and 3.41 percent for the deasphalted material. Table 15 records some of the data taken during the thermal stability tests on Santa Maria Valley crude oil and on deasphaltized Santa Maria Valley crude oil. These data indicate, as would be expected, that the residue in the deasphaltized sample was smaller than that in the original crude oil. Conversely,
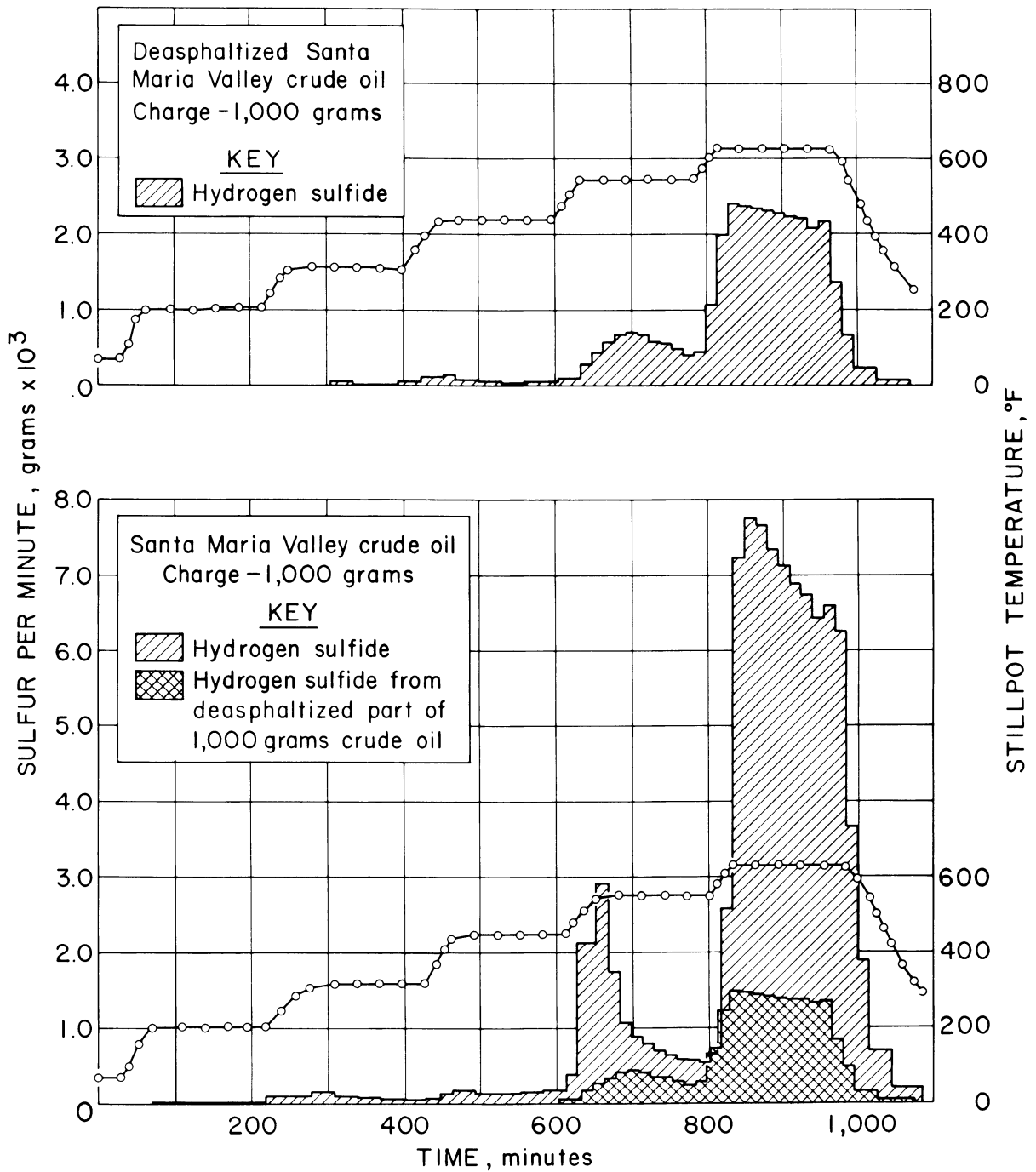
Figure 20.—Thermal stability tests of original and deasphaltized
Santa Maria Valley, California, crude oil.

distillate fractions 1 through 5 of the deasphaltized
sample are greater than their counterparts in the
original crude oil. The sulfur content of the com-
parable distillate fractions from the two experiments
were approximately the same. However, the sulfur

content of the residue from the deasphalted crude
oil is only 0.7 as large as that from the crude oil.
These results were also anticipated. The hydrogen
sulfide generated during the heating of the crude
oil was five times as much as that generated during

Table 15.—Data derived during thermal stability tests of Santa Maria Valley, California, crude oil and of the deasphaltized crude oil

Component	Original crude oil				Deasphaltized crude oil [1]					
	Weight-percent	Sulfur			Weight-percent		Weight-percent	Sulfur		
		Weight-percent	Grams [2]	Percent of total sulfur	Deasphaltized crude oil	Crude oil		Grams [2]		
								Deasphaltized crude oil	Crude	Percent of total sulfur
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Charge	100.00	4.98	49.77	100.00	100.00	61.00	3.414	34.14	20.83	100.00
Gas phase:										
Thiols	Trace	....	Trace				....	.01	.01	.03
Hydrogen sulfide	.14	....	1.46	2.93	.05	.03	....	.50	.31	1.48
Liquid phase:										
Trap material	.94	....			2.15	1.31				
Fractions 1, 2, and 3	4.72	.198	.09	.18	5.79	3.53	.178	.10	.06	.30
Fraction 4	2.63	.854	.23	.46	8.74	5.33	.860	.75	.46	2.20
Fraction 5	4.96	1.569	.78	1.57	9.05	5.52	1.783	1.61	.98	4.73
Residue	86.00	5.432	46.73	93.89	73.08	44.59	4.178	30.54	18.63	89.42
Loss	.61	....	.48	.97	1.13	.69	....	.63	.38	1.84

[1] Percent of crude oil, 61.
[2] On 1,000-gram charge.

the heating of a weight of the deasphaltized crude oil sample equivalent to that present in the crude oil. These data also point to the removal of the more labile sulfur compounds from the crude oil by the deasphaltizing operation. Columns 4 and 10 of table 15 show a sulfur material balance for both experiments, indicating that only half as much hydrogen sulfide, in terms of percentage, was generated by the sulfur compounds left in deasphaltized crude oil as by those in the original crude oil. The data also indicate that a greater percentage of the sulfur compounds in the deasphaltized sample were unstable or volatile, under the experimental conditions, than were those of the original crude oil, as indicated by comparison of the sulfur content of residues. These conclusions are more obvious in table 16 which compares the sulfur balance of column 4, table 15, with a sulfur balance of the deasphaltized crude oil (column 2, table 16) which includes the sulfur removed by the deasphaltizing.

The absence of an H_2S peak on the 200° F plateau indicated that elemental sulfur was not present in either sample, and this fact was verified by polarographic analysis, an analytical procedure to be discussed later.

The development of the polarographic method for the determination of elemental sulfur (113) provided a more direct method for observing the sulfur-hydrocarbon reaction. Figure 21 is the hydrogen-sulfide generation pattern for Fuhrman-Mascho, West Texas, crude oil. Here again is observed the extremely large production of hydrogen sulfide on the 210° C (410° F) plateau inter-

preted in previous examples as due to the reaction of elemental sulfur with the petroleum hydrocarbons. Samples withdrawn from the stillpot at intervals were analyzed polarographically for elemental sulfur to provide the data shown by the curve of figure 21. These data show that elemental

Table 16.—Sulfur material balance in thermal stability test of Santa Maria Valley crude oil and of the deasphaltized crude oil

Constituent	Portion of total sulfur (in crude oil) present in constituent indicated, weight-percent	
	Original crude oil (1)	Deasphaltized crude oil (2)
Removed by deasphaltizing	0.0	58.15
Recovered as H_2S	2.93	.62
Recovered as thiols		.02
In fractions 1, 2, and 3	.18	.12
In fraction 4	.46	.92
In fraction 5	1.57	1.97
In residue	93.90	37.44
Loss	.96	.76
Total	100.00	100.00

sulfur remains in solution in the crude oil at a constant level until 210° C (410° F) is reached. At this point, the concentration of elemental sulfur drops rapidly to zero. This effect is simultaneous with, and follows precisely, the increase and decay of hydrogen sulfide evolution. The absence of ele-
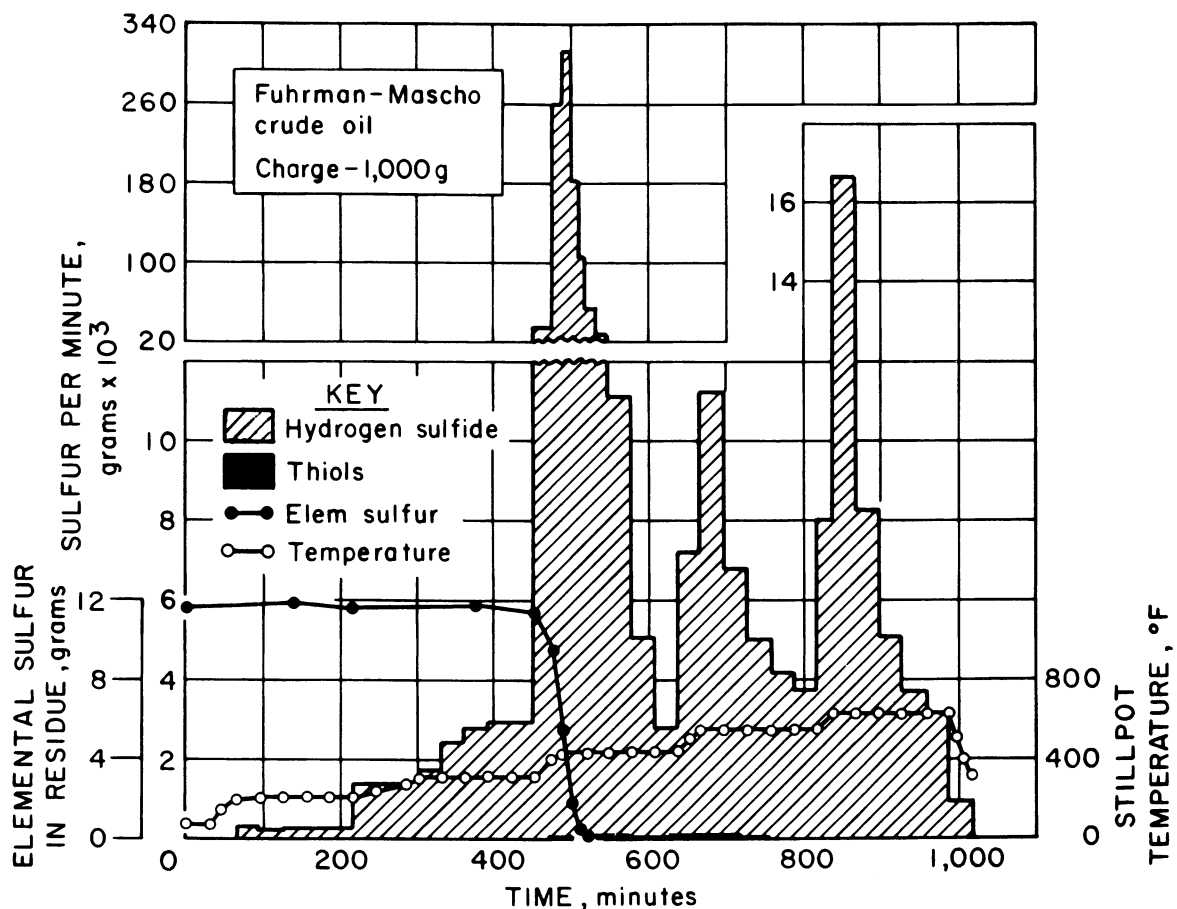
Figure 21.—Thermal stability test of Fuhrman-Mascho, Texas, crude oil indicating reaction of elemental sulfur.

mental sulfur in the crude oil charge after 500 minutes proves that any evolution of hydrogen sulfide or thiol, after that time, results from decomposition of sulfur compounds.

Figure 22 presents similar data for Yates, Texas, crude oil. In an earlier discussion of this crude oil the likelihood of it containing a large amount of dissolved hydrogen sulfide, as well as elemental sulfur, was mentioned (see fig. 11). This situation is now clearly indicated in figure 22. By polarographic analysis of pot samples, elemental sulfur, present in the crude oil, is shown to remain at its original concentration until the pot temperature arrives at 210° C (410° F), where reaction with hydrocarbons ensues, as noted in the Goldsmith crude oil. To a minor extent, the production of hydrogen sulfide on the 99° C (210° F) plateau was observed in other crude oils and could only have originated in hydrogen sulfide present in solution in the crude oil (323). The quantity of thiols developed in the Yates experi-

ment was too small (less than 0.01 g per min) to appear on the graph of figure 22.

In regard to the generation of hydrogen sulfide on the 99° C (210° F) plateau (and on succeeding plateaus), the question arises whether this phenomena could be traceable to tri- or polysulfides. This question stems from the knowledge that di-, tri-, tetra-, and pentasulfides, for example, have been synthesized from 3-thiapentane (and higher sulfides) and elemental sulfur (178). Disulfides are reported to react even more readily (179) with sulfur to form polysulfides. Thus, materials for the production of polysulfides in crude oils are readily available in some crude oils, if not all. Figure 23 shows a thermal stability test of Bradford crude oil (see fig. 19, top panel) to which had been added approximately 0.5 percent ditertiary butyl polysulfide. The sample of polysulfide was not pure and was known to be a mixture of di- to pentasulfide, with possibly some elemental sulfur. As in preceding experiments
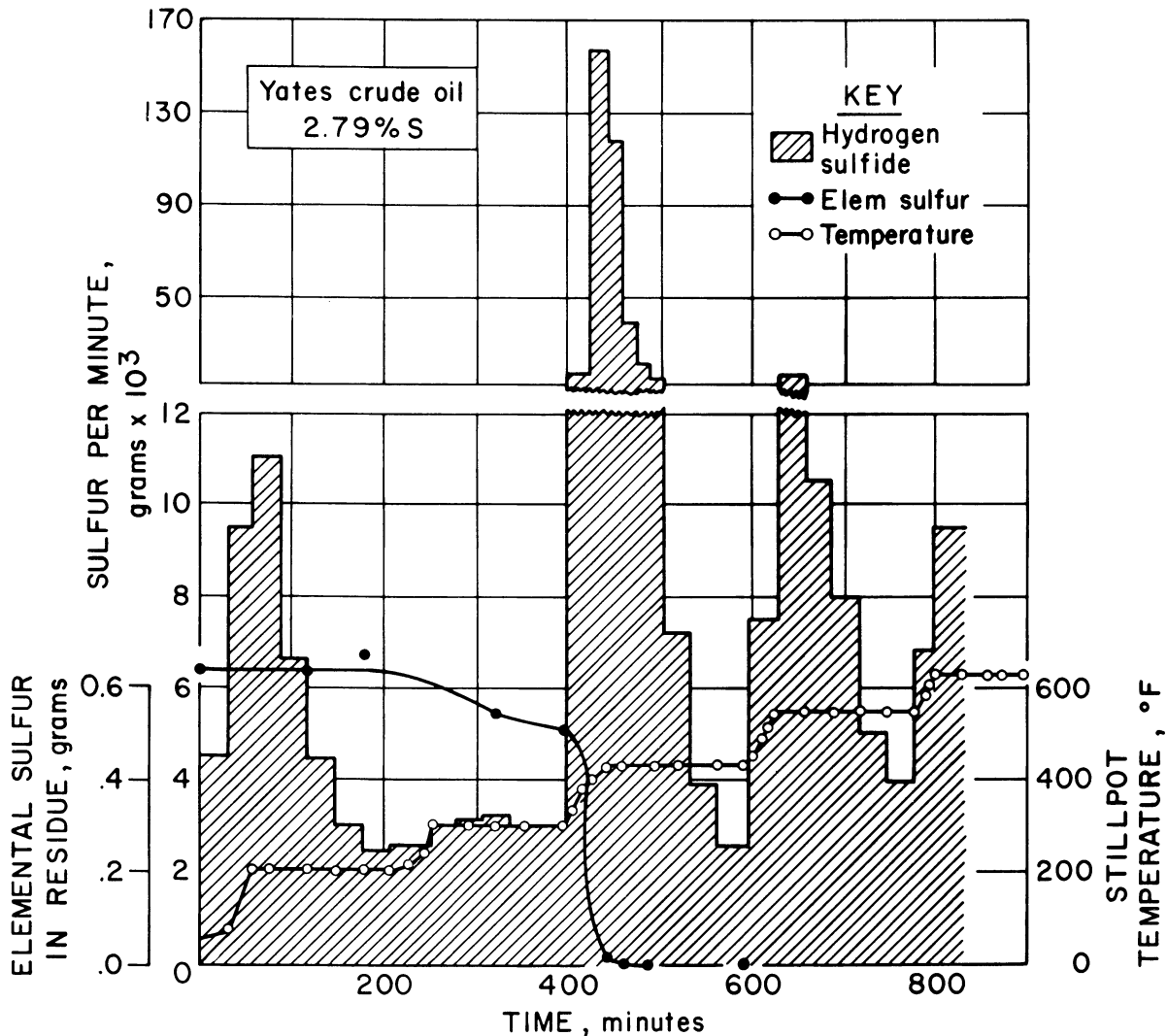
Figure 22.—Thermal stability test of Yates, Texas, crude oil.

samples were withdrawn from the pot periodically for the polarographic determination of polysulfides (222) and the amperometric determination of thiols. The data indicate (fig. 23) that the sample of ditertiary butyl polysulfide behaved similarly to elemental sulfur in that a large production of hydrogen sulfide occurred when the pot temperature reached 210° C (410° F). Simultaneously the polysulfide content of the charge, calculated as elemental sulfur, dropped to zero, and with a convenient production of thiol noted both in the traps (gas phase) and in the pot contents. The latter two developments definitely distinguish the reaction of crude oil containing polysulfides from that containing only elemental sulfur. This is evident from the comparable experiment (fig. 19, bottom panel) in which pure elemental sulfur was added to Bradford crude oil and found to cause no, or little, development of thiols, either in the gas stream or in the crude oil charge. The generation of thiols in this experiment is in agreement with Farmer and Shipley's observation (120) that thiols, monosulfides, and hydrogen sulfides result from the thermal decomposition of polysulfides above 140° C. The data of figure 23 do not indicate when the polysulfide began to decompose to elemental sulfur or even whether they did. The generation of hydrogen sulfide began slowly at 154° C (310° F) and became rapid at 210° C (410° F). Presumably this decomposition reaction began when or somewhat before the 154° C (310° F) plateau was reached.

Work similar to that previously described has
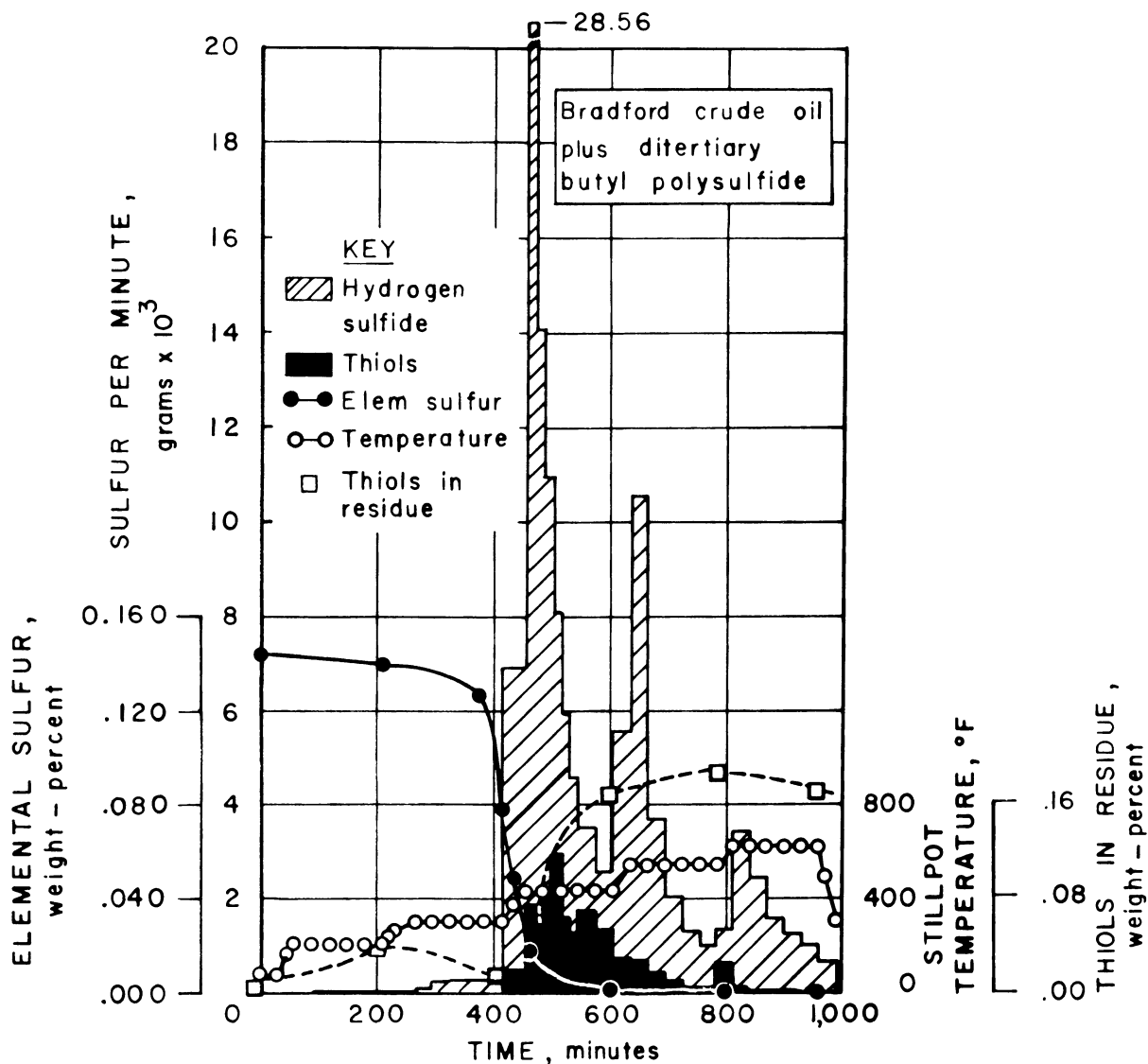
Figure 23.—Thermal stability test of Bradford, Pennsylvania, crude oil
with added (0.5 percent) di-*tert*-butyl polysulfide.

been repeated by several Russian observers on Russian crude oils and similar results obtained (*5, 202, 307, 370*).

Practical Considerations

The thermal stability of sulfur compounds has been examined by numerous investigators. Faragher, Morrell, and Comay (*119*) passed pure compounds and pure compounds in naphtha solution through a tube heated to 496° C (925° F). At this temperature, selected mercaptans decomposed to a tarry residue plus hydrogen sulfide and elemental sulfur; sulfides decomposed to mercaptans, hydrogen sulfide, and thiophene derivatives; and disulfides to alkylsulfides, mercaptans, hydrogen sulfide, elemental sulfur, and thiophene. Thiophene did not decompose at 496° C (925° F). These findings, in general, are still valid; that is, mercaptans are the least stable sulfur compounds found in petroleum, followed by sulfides and thiophenes. Malisoff and Marks (*272, 273*) checked the stability of selected sulfur compounds at 300°, 425°, and 475° C (572°, 798°, and 888° F), and found that mercaptans break down to olefins and hydrogen sulfide at 425° C (798° F) (about 10 percent decomposed). Higher molecular weight homologs are

probably less stable than lower, and branched chain isomers are less stable than are straight chain. Benzyl mercaptan is considerably less stable than are lower aliphatic mercaptans. n-Butyl sulfide, stable at 400° C (752° F), indicated slight decomposition at 450° C (842° F), and moderate decomposition at 500° C (932° F). Products of decomposition were hydrogen sulfide, mercaptans, and, in the presence of large amounts of hydrogen sulfide, free sulfur and thiophenes. Rudenko and Gromova (352) in general confirmed the order of group stability mentioned above and found thiophene stable at 500° C (932° F), while the 2,5-dimethyl derivative decomposed slightly at 475° C (888° F).

This brief review does not cover the literature on the thermal stability of sulfur compounds found in petroleum. It is intended to suggest that wide variation exists in regard to thermal stability among sulfur-compound types and among members within types. These facts lend more credence and understanding to the hydrogen sulfide generation pattern in the thermal stability experiments discussed in this section. Mercaptans, having the lowest stability to heat, probably predominate as contributors to the hydrogen sulfide peaks in the early temperature rise. Two products in addition to tars are indicated as fragments of mercaptan decomposition, hydrogen sulfide, and sulfur. Above 190° to 205° C (375° to 400° F), the secondary reaction of elemental sulfur with crude oil would occur to produce additional hydrogen sulfide and higher molecular weight sulfur compounds. Between the hydrogen sulfide peaks, exhaustion of the sulfur compounds unstable in that temperature region occurs. These cycles will occur as long as the temperature is increased and thermally unstable compounds are present in the crude oil.

Obviously, a very practical effect of elemental sulfur in crude oils is the release of a large amount of hydrogen sulfide in any industrial process in which such a crude oil is heated to about 154° to 175° C (310° to 347° F). It can be estimated that in this reaction half of the elemental sulfur will be converted to hydrogen sulfide and the remainder to sulfur compounds. The sulfur compounds are generated at the expense of hydrocarbons. Olefins, no doubt, are also formed at this time. If heating is continued, some of the less stable, newly generated, as well as naturally present sulfur compounds undergo further reaction and decompose to yield more hydrogen sulfide. The consequence is that any refiner processing crude oils containing elemental sulfur must be prepared to handle (corrosion problems, etc.) and dispose of hydrogen sulfide in greater

quantities than encountered in crude oils containing no or small amounts of elemental sulfur. An example has been given by Newton and Leach (303) who describe the distillation of 850 barrels of a Crane County, Tex., crude oil. Among other data, the authors give a time-yield record of hydrogen sulfide generated in this operation. These data are reproduced (in part) in figure 24 showing the hydrogen
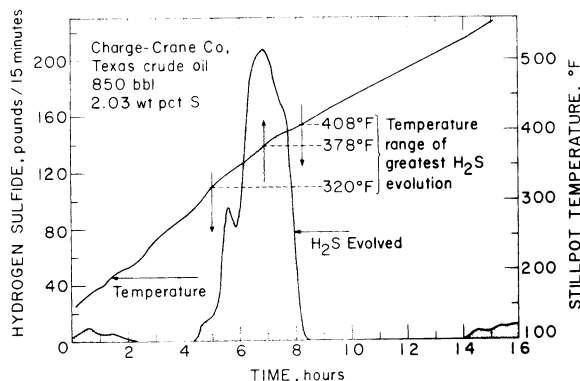
Figure 24.—Graph showing generation of hydrogen sulfide in the commercial processing of 850 barrels of Crane County, Tex., crude oil.

(From Oil and Gas Journal, Mar. 7, 1929.)

sulfide produced for 15-minute intervals during the heating of the 850 barrels of this West Texas crude oil. The similarity of this curve, obtained in industry, with those obtained in the laboratory (for example, fig. 18) is apparent. The maximum production of hydrogen sulfide occurred at about 192° C (378° F) and dropped to essentially zero at 208° C (408° F) to begin again at a higher temperature. The hydrogen sulfide released under the 192° C (378° F) peak (320° to 408° F) was equivalent, in elemental sulfur, to 0.8 tons, or about one-third of the total sulfur in the original 850 barrels of crude oil.

It would appear that the thermal stability patterns, such as those in figures 18 through 23, but produced in a more simplified apparatus and procedure, could be obtained routinely to determine thermal characteristics of crude oils, which might be useful to the refiner. In fact, such an application was suggested by Aivazov (4) who proposed a hydrogen sulfide number (milligrams of hydrogen sulfide and mercaptans evolved from 100 g crude oil at 300° C for 1 hour) as a method for sorting crude oils according to their capacity to produce hydrogen sulfide on heating. This information would be used as a basis for blending crude oils from various

sources to equalize the deleterious sulfur content of charging stocks to stills. This empirical test could be substituted for the analytical determination in the crude oil of hydrogen sulfide, elemental sulfur, and mercaptans.

ELEMENTAL SULFUR IN CRUDE OIL

When the initial routine vacuum and atmospheric distillations of the selected crude oils, listed in table 12, were made, it was suspected that the elemental sulfur, reported present in some fractions (see table 12 and fig. 11), was observed because of some analytical error, reagent failure, or unexplained chemical reaction. Other investigators had noticed crystals of elemental sulfur in crude oil shipments (*340, 409*), and some had reported observing the appearance of elemental sulfur in cool sections of crude oil distillation systems (*64, 264, 316*). These reported instances of elemental sulfur in crude oil were dismissed as having been due to oxidation of hydrogen sulfide or to some other unknown chemical reaction. However, when Yates and Goldsmith, Texas, crude oils were distilled, solid yellow material appeared in cool lines and other parts of the equipment and verified similar observations reported in the literature. In addition analyses of some of the distillates obtained indicated the presence of quite large percentages of elemental sulfur. These incidents were too important and significant to reject as accidental, and hence were investigated further.

Isolation and Identification of Elemental Sulfur

To verify whether elemental sulfur, if present in crude oil, could be distilled from the crude oil without reaction, a special distillation of Goldsmith crude oil was made. This distillation was conducted in an apparatus shown in figure 25. The distillation section of this apparatus was equivalent to the original (see fig. 9) in all essential dimensions. In this apparatus, all joints but two were sealed to minimize leakage and thus to avoid air contact with the heated crude oil or its vapors. A small tapered joint at the top of the column permitted alternate introduction of the crude oil and positioning of a thermowell as shown. The system was checked thoroughly for leaks before use and during its operation. No inert gas was allowed to enter into the crude oil during its distillation as was done in the previous work.

The oil was admitted to the evacuated system dropwise, at the center of the packing, as indicated in the insert of figure 25. This procedure removed from the crude oil all air and much of the light
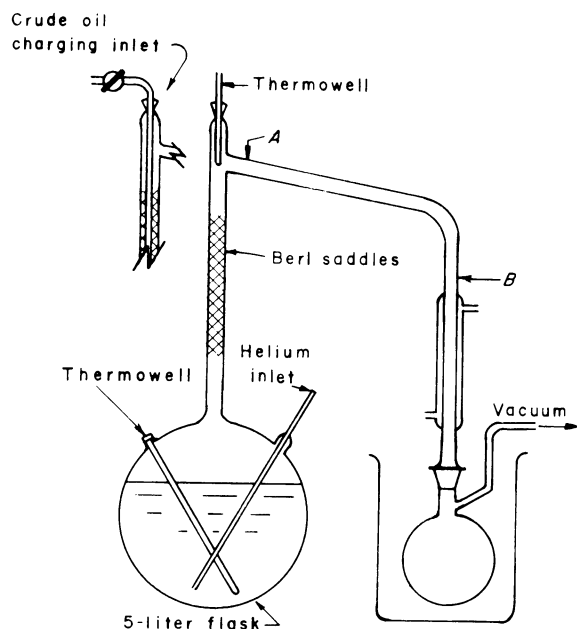
Figure 25.—Distillation apparatus used in isolating elemental sulfur from Goldsmith, Texas, crude oil.

gasoline. The distillate collector was emptied twice, once after the charging operation and replacement of the thermowell at the top of the column, and again when the pot temperature had reached 65° C (150° F). In each instance, helium was admitted to bring the system to atmospheric pressure in order to remove the collected distillate. From this pot temperature of 65° C (150° F) until the end of the distillation the pressure was maintained at less than 0.2 mm Hg. Free sulfur appeared at the top of the condenser at an overhead temperature of about 102° C (215° F). The distillation was continued with sulfur collecting in the vapor line and top of condenser. To recover the sulfur, the distillation line was cut at *A* and *B* (fig. 25), and the elemental sulfur was removed from the side-arm, condenser, and flask. It was washed with hexane to remove petroleum hydrocarbons and recrystallized from benzene and alcohol.

There was little doubt that these crystals were elemental sulfur, but photomicrographs of them were taken and one such photograph is reproduced in figure 26 *B* in comparison with that of a commercial sample of elemental sulfur crystallized in a like manner, figure 26 *A*. Visually, the crystals under the microscope and in the photographs are identical. A mass spectrum of the elemental sulfur isolated from Goldsmith was also taken and com-
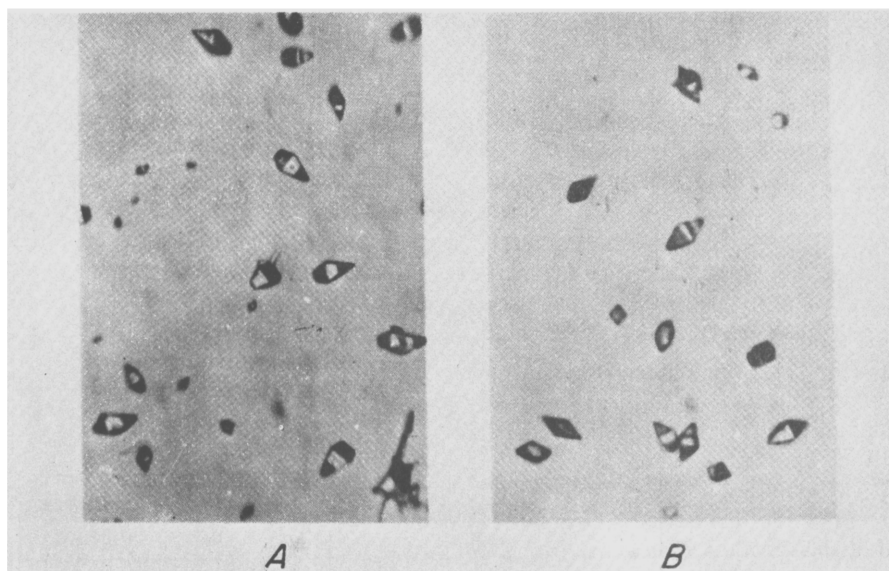
Figure 26.—Photomicrographs of elemental sulfur crystals from a commercial source (A), and isolated from Goldsmith, Texas, crude oil (B).

pared with a spectrum of a sample of commercial sulfur. These spectra, reproduced in figure 27, further confirm the identification.

These data establish, beyond doubt, that the material recovered from Goldsmith crude oil was truly elemental sulfur. Nor is there any doubt that it was present naturally in the sample of crude oil. In atmospheric distillations of crude oil, elemental sulfur usually remains undetected because of its disappearance via its chemical reaction with the hydrocarbons of the crude oil. In the distillation described above, the boiling point of sulfur, 182° C (360° F) at 1 mm Hg (453), was reached before its rapid reaction with hydrocarbons began (incipient probably at 100° C (212° F) and very brisk at about 200° C (392° F). Because of the exceptionally high concentration of elemental sulfur in some crude oils (specifically in Yates and Goldsmith crude oils) and its limited solubility in low-boiling petroleum hydrocarbons, its recovery, by distillation, from such crude oils is more readily achievable than from crude oils of lower elemental sulfur content.

Polarographic Determination of Elemental Sulfur in Crude Oils [30]

Elemental sulfur was determined in some of the crude oils listed in table 8 and in the Bradford crude oil. The samples had been collected in the

field, shipped to the laboratory in metal containers, transferred to glass bottles, and stored at 4° C (39° F) for about 2 years. The data, shown in table 17, are believed to be reliable. These samples had been carefully preserved, but as work progressed, it became more and more obvious that a change in elemental sulfur content between time of collection and time of analysis was a definite possibility. Plans were made, therefore, to collect fresh samples as directly from the wellhead as possible.

Preparation of Samples

One-pint polyethylene collapsible bottles were procured, and each was fitted with a metal ferrule around the polyethylene screw caps, so that considerable pressure could be applied to prevent leakage. Field sampling instructions for these bottles required that they be filled to overflowing with the crude oil samples by means of a tube extending to the bottom of the bottle. The full bottle was immediately collapsed to about three-fourths its volume, and during this procedure the cap was screwed tight. This procedure precluded any air space, but thermal expansion of the oil during transportation was amply provided by the flexible walls of the collapsed bottle. When received in the laboratory, the samples were promptly stored in a cold room. All containers and their contents were in apparently excellent condition when the samples for polarographic analysis were taken.

[30] Work done by B. H. Eccleston and Marilyn Morrison, Bureau of Mines Bartlesville Petroleum Research Center (113).
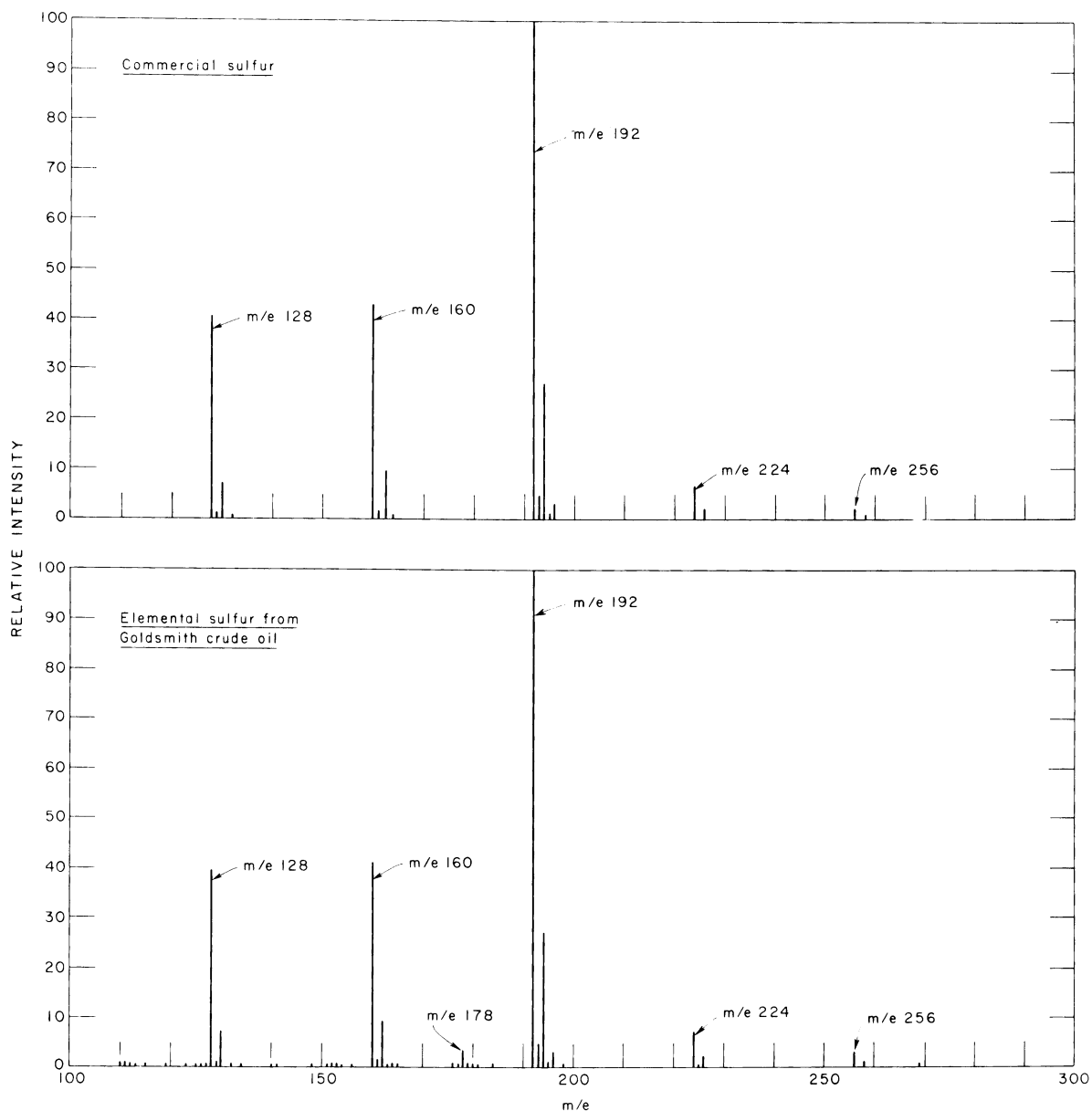
Figure 27.—Mass spectral comparison of commercial sulfur and of
elemental sulfur isolated from Goldsmith crude oil.

Before samples were removed from the bottle for analysis, the bottles were kneaded to mix the sample thoroughly, should any segregation have taken place. The bottle was then gripped in a three-fingered laboratory clamp to prevent its resuming its original volume and thus drawing in air upon the sample. The cap could then be removed and a sample quickly withdrawn from the neck for analysis. After this operation, the bottle was collapsed further, causing the crude oil within to overflow, and the cap then retightened. Table 18 gives the origin of all the samples involved in this program.

When this work was undertaken, no satisfactory analytical method was available for determining small quantities of elemental sulfur in crude oils. Gerber and Shusharina (138–139) in Russia had reported the analysis of gasolines for hydrogen sulfide, mercaptans, elemental sulfur, and disul-

fides by a polarographic method, and in the United States, Hall (157) had applied the polarographic method to determine elemental sulfur in petroleum fractions. This procedure was investigated as a means of determining elemental sulfur in crude oils.

Table 17.—Preliminary determination of elemental sulfur in various crude oils

Crude oil		Sulfur, weight-percent	
Field	State	Total [1]	Elemental [2]
Yates...........	Texas..........	2.79	0.67
Goldsmith......	.......do.......	2.17	1.0
Elk Basin.......	Wyoming......	1.95	.01
Bradford........	Pennsylvania...	<.14	.001
Oregon Basin...	Wyoming......	3.25	<.001
Hawkins........	Texas..........	2.41	<.001
Slaughter.......	.......do.......	2.01	<.001
Wasson.........	.......do.......	1.85	<.001
Wilmington.....	California......	1.39	<.001
Rangely........	Colorado.......	.76	<.001

[1] By bomb.
[2] By polarograph.

In applying the polarographic method to crude oils, the low solubility of crude oil in supporting electrolytes is a severe handicap. Hall (157) used an electrolyte that consisted of 90 percent methanol, 9.5 percent pyridine, and 0.5 percent concentrated hydrochloric acid. This electrolyte is not a satisfactory solvent for crude oils, particularly when their elemental sulfur content is low and it is desirable to have about 10 percent crude oil sample in the electrolyte. Substituting 60 percent of the methanol in the above formulation with benzene gave a better solvent for crude oil and a satisfactory electrolyte: 63.0 percent benzene, 27.0 percent methanol, 9.5 percent pyridine, and 0.5 percent concentrated hydrochloric acid.

Apparatus and Reagents

The following equipment and reagents were used in the polarographic analysis of elemental sulfur.

Sargent Model XXI recording polarograph, H-type electrolysis cell, and mercury pool cell.

Constant temperature bath held at 25° C (77° F). Capillary having the following characteristics: Mercury drop time in distilled water, 3.97 seconds; flow, 2.72 mg Hg per second at a mercury column height of 44.9 cm.

Reagents:
    Pyridine, Mallinckrodt analytical reagent.
    Methanol, absolute.
    Sulfur, U.S.P.

The mercury pool cell was used in initial work with fair results, but was found to develop a blackening of the metal surface. A cell was designed (after Lingane and Laitinen (244)) that reduced the possibility of sulfur reacting with mercury. The construction of this cell is shown in figure 28. It is
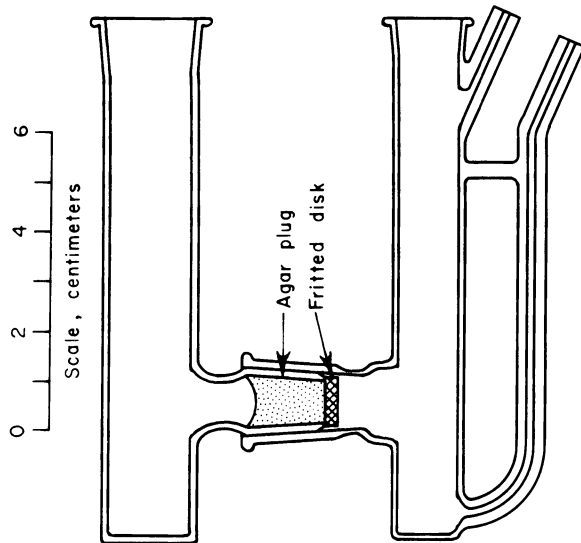
Figure 28.—Modified H-type polarograph cell.

Table 18.—Origin of Texas crude-oil samples

Field	County	Formation	Production method	Sample taken from:
Spraberry Deep........	Dawson.....	Spraberry, Permian............	Flowing.....	Separator, about 45 psi.
Diamond "M" area....	Scurry.....	Pennsylvania Reef.............	.....do.....	Separator, 60 psi.
Dune.................	Crane......	Grayburg-San Andres, Permian..	Pump......	Wellhead.
Sand Hill (Tubb)......	.....do.....	Clearfolk, Permian............	Flowing.....	Separator, "under pressure."
Means...............	Andrews....	Grayburg-San Andres, Permian..	Pump......	Gun barrel.
Sand Hills (McKnight).	Crane......	San Andres, Permian...........	Flowing.....	Separator, "under pressure."
McElroy.............	Upton......	Grayburg, Permian............	Gas lift.....	Separator, 15 psi.
Goldsmith............	Ector.......	San Andres, Permian...........	....do.....	Separator, about 30 psi.
Fuhrman Mascho......	Andrews....	Grayburg-San Andres, Permian..	....do.....	Separator.

the conventional H-type cell equipped with a tapered joint in the line connecting the legs in the H. This joint has a fritted disk sealed in the end of the inner member. The usual agar plug is located in this member. This construction has two advantages: (1) It enables the sample-containing arm to be removed, emptied, and cleaned without disturbing the calomel half-cell, and (2) it allows the fritted disk to be cleaned and dried by means of a stream of water from a wash bottle and blotting paper. The joint must be lubricated to prevent water (from the bath) diffusing through it into the cell. The calomel half-cell is the conventional saturated calomel electrode, excepting that 0.1 N lithium chloride is used as the electrolyte in the preparation of the agar plug.

Procedure

The required amount of crude oil is transferred to a tared bottle as rapidly as possible by means of a pipet. The crude oil is then weighed and the electrolyte, which previously has been swept with helium for 10 minutes, is added from a gas-washing bottle. The crude oil plus electrolyte is again weighed, and 5 ml introduced into the polarograph cell and bubbled for 4 minutes with helium. From a container of alcohol in which it has been stored, the capillary dropping electrode is removed, wiped carefully, and placed in the cell. The bubbling is continued for 1 minute, then stopped, and the polarogram is obtained using a span of 0.6 volt with no damping. After the polarogram is complete, the capillary is removed, washed with a stream of alcohol, and replaced in the alcohol container. The cell is removed from the constant-temperature bath, the sample-containing side of the H-cell is rotated to discard the sample into a beaker, removed, cleaned with solvent, and dried. The fritted disk of the calomel half-cell is then washed with benzene, followed by alcohol from suitable wash bottles, and dried with filter paper. The joint is lubricated, the sample container replaced, and the cell inserted in the constant-temperature bath for the next determination.

Several points in the procedure require careful attention because the elemental sulfur content of samples containing hydrogen sulfide increases upon exposure to air. Any handling of the crude oil, therefore, or of the dilution after the addition of the crude oil must be done so as to reduce the time of contact with air to a minimum. Dissolved oxygen in the supporting electrolyte is also difficult to remove completely, and if present, interferes with the sulfur polarogram.

Calibration

Calibration curves of diffusion current versus weight-percent elemental sulfur were determined for the work with both the mercury-pool cell and the H-type calomel cell. Elemental sulfur was dissolved in the electrolyte, and portions of this stock solution were diluted with electrolyte following the procedure used for the crude oil samples. Figure 29 gives the data obtained using the H-cell with the calomel electrode.

From these data:

$$I_d = 3,770 \text{ percent sulfur}$$

and this equation was considered valid between $I_d = 1.25$ and $I_d = 12$.

The calibration of the mercury-pool cell gave:

$$I_d = 3,590 \text{ percent sulfur}.$$

Results

The results of the polarographic analyses of the West Texas crude oils are shown in table 19. A typical polarogram from which these data were derived is shown in figure 30. Three curves are shown in this figure, the "residual" current curve of the supporting electrolyte, that of a 2.58-percent solution of Dune crude oil (see table 18), and of a solution of 0.0009-percent elemental sulfur in the Dune crude oil-electrolyte mixture. The curves for the two latter mixtures are identical in the anodic portion and of similar shape and half-wave potential in the cathodic portion. This similarity indicates that the wave for the crude oil is a true sulfur wave.

The data of table 19 were taken on the first sample of crude oil-solvent mixture after the dilution was made. A second analysis of the same dilution, not shown in the table, generally indicated
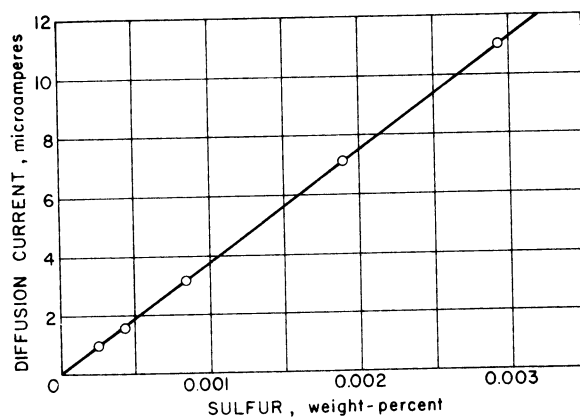
Figure 29.—Calibration curve for use with calomel cell.

Table 19.—Analysis of second group of crude oils

Crude oil		Half-wave potential	Sulfur, weight-percent		Deviation from average, percent
Field	Weight in electrolyte, grams		In electrolyte	In crude oil	
Spraberry	0.737	....	0.0000	0.000	....
	13.524	....	.0000	.000	....
Diamond M	7.253	....	.000	.000	....
Dune	4.146	−0.48	.00183	.0440	....
	3.940	.48	.00185	.0468	....
Average	....	....	....	.0454	3.1
Sand Hills (Tubb)	1.840	.47	.00152	.0829	....
	2.644	.49	.00215	.0815	....
Average	....	....	....	.0822	.9
Means	1.289	.48	.00213	.165	....
	1.153	.48	.00195	.169	....
Average	....	....	....	.167	1.2
Sand Hills (McKnight)	.468	.48	.00220	.471	....
	.482	.48	.00228	.472	....
Average	....	....	....	.472	.2
McElroy	.415	.48	.00217	.522	....
	.393	.47	.00201	.511	....
Average	....	....	....	.517	1.0
Goldsmith	.311	.48	.00218	.700	....
	.332	.48	.00234	.704	....
Average	....	....	....	.702	.3
Fuhrman-Mascho	.171	.48	.00226	1.32	....
	.198	.49	.00255	1.29	....
Average	....	....	....	1.31	1.1

a higher sulfur content than the first. This is thought to be caused by oxidation of hydrogen sulfide to elemental sulfur, which occurs much more rapidly in the supporting electrolyte than in the original crude oil. Occasionally the second sample removed from the crude oil-solvent mixture will indicate a decrease in elemental sulfur. This may be accounted for by the reaction of mercaptans with elemental sulfur, as discussed by Hall (157). Both phenomena point to a need for care in handling the original crude oil and for rapid analysis once the solution of crude oil in the supporting electrolyte is prepared.

Analyses made on the same crude oils but not reported here indicate that, in the method used for removing individual samples of crude oil from the polyethylene bottles, there is very little change in elemental sulfur content, even over a period of several days.

Analyses made at different crude-oil concentrations indicate that the half-wave potentials vary uniformly with the concentrations of sulfur in the electrolyte. The repeatability of the analysis is fairly good (±1 percent), as shown in the percentage-deviation column (table 19), but the accuracy is probably no better than ±5 percent.

Table 20 summarizes the data on the elemental sulfur concentration of the nine crude oils as determined polarographically upon receipt of the samples and on duplicates stored in the polyethylene bottles

for 4 months at 3° C (37° F). Only the Sand Hills (Tubb) sample changed significantly; the reason for this drop in sulfur content has not been determined. Table 20 also gives the total sulfur content for each oil, as determined by the ASTM D129–50 bomb procedure.

A possible interfering substance, diphenyl disulfide, yields a polarographic wave with a half-wave

Table 20.—Sulfur content of Texas crude-oil samples

Field	Sulfur, weight-percent		
	Total [1]	Elemental [2]	
		Upon receipt of sample	After 4 months storage
Spraberry Deep	0.24	0.000	......
Diamond M area	.24	.000	......
Dune	1.65	.045	0.043
Sand Hills (Tubb)	1.27	.082	.056
Means	2.48	.17	.17
Sand Hills (McKnight)	2.72	.47	.46
McElroy	2.42	.52	.51
Goldsmith	1.82	.70	.68
Fuhrman-Mascho	4.09	1.31	1.33

[1] Bomb method.
[2] Polarographic method
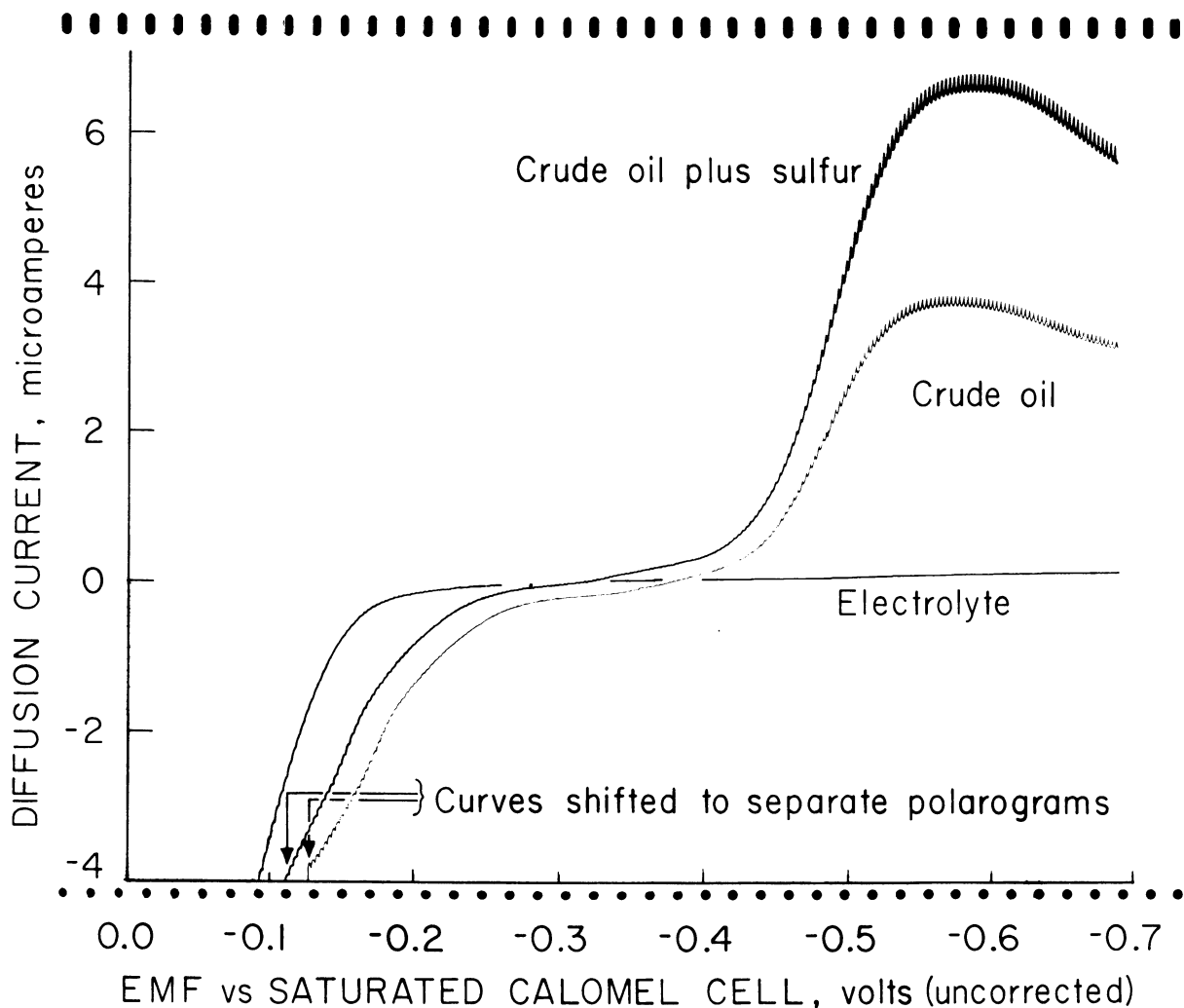
Figure 30.—Typical polarograms of elemental sulfur in Dune, Texas, crude oil.

potential sufficiently close to that of elemental sulfur to interfere if both compounds are present in the same sample. However, the concentration of the diphenyl disulfide would need to be about 100 times that of the elemental sulfur to yield a wave of comparable magnitude in the solvent electrolyte used. Evidence of the absence of the diphenyl disulfide in the crude oils was obtained by shaking a dilution of the sample with mercury to remove the elemental sulfur and then obtaining a polarogram on this treated sample. Of all the crude oils tested by this procedure, there was no significant wave remaining after mercury treatment except for Dune, Sand Hills (Tubb), and Sand Hills (McKnight), and in these cases, the waves obtained did not resemble the characteristic diphenyl disulfide wave.

Summary

The data presented confirm the presence of elemental sulfur in some West Texas crude oils. The samples were taken as near as conveniently possible (see table 18) to their source in the earth, but the possibility of change in elemental sulfur content between bottom hole and wellhead has not been eliminated. It was found necessary to use special sampling techniques to reduce the possibility of oxidation of hydrogen sulfide to elemental sulfur. The data also demonstrate that the polarographic method for elemental sulfur can be applied satisfactorily to crude oils. An application of this analysis to thermal stability studies is illustrated in figures 21 through 23 of the preceding section.

Because the sulfur content of crude oils is relatively low and the number of compounds large, the concentration in a crude oil of any individual sulfur compound is necessarily very small. It is axiomatic, therefore, that in any effort aimed at the identification of individual sulfur compounds in petroleum the development and application of separative and concentration procedures would be of first priority.[31] The procedures available for such concentration are both physical and chemical in nature.

SEPARATIVE PROCEDURES—PHYSICAL

Among the physical procedures are such operations as distillation, adsorption, and thermal diffusion, whereas procedures of chemical nature include such operations as precipitation, chemical combination, extraction, and adduction. In all applications of these procedures, care must be exercised to avoid experimental conditions that might change the structure of a compound, thus introducing the twofold liability—destruction of compounds naturally present in the crude oil and the addition of compounds to the crude oil normally foreign to it.

Distillation Techniques Used in Separation Studies

It is widely known that the extent of thermal decomposition of petroleum components in a heated zone is a function of both temperature and the time of exposure to that temperature. Furthermore, the effects of these conditions become more pronounced with increase in complexity of the component structure; that is, with the size and the architecture of the molecules. Thus, to obtain distillates from crude oils in unchanged form and uncontaminated by fragments produced by thermal decomposition, the crude oil must be heated to as low a temperature and for as short an interval as possible compatible with attaining the desired objective. Also, the apparatus should be constructed of inert material unlikely to effect catalytically induced changes in the crude oil. With these principles in mind, a continuous crude oil stripping column was designed and constructed.

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[31] The polarographic determination of elemental sulfur in crude oils, described in the previous section, is a lone contradiction of this need. Even here, however, concentration would be of some advantage.

Isothermal Distillation

The principal purpose of the isothermal still was to remove light distillates from the crude oil without decomposing sulfur compounds either in the distillates or (and more importantly) in the residue. The distillate sulfur compounds were thought to be reasonably stable and were found to be so. The more complex sulfur compounds in the residue were known to be less stable and thus less able to survive severe conditions.

A drawing of the apparatus is shown in figure 31. The main body of the still consists of a nominal 3-inch-diameter, flanged Pyrex glass pipe (48 inches long) closed at each end with a 25-cm-thick Pyrex glass disk. A hole ground in the top disk and a receptacle in the bottom one allow for the installation of Teflon bearings supporting a revolving glass cylinder or "drum," clearing the internal wall of the Pyrex pipe by approximately 3 mm. The cylinder was ground on its outside surface to aid in distributing the crude oil over its surface. Crude oil is injected at the top of the still through a ground glass joint, and is conducted to the inner area of the top of the steam-heated rotating drum and allowed to flow evenly down its outer wall. Inert gas sweeps countercurrently to the flowing crude oil and aids in carrying evaporated distillate from the still via the outlet at the top. The stripped residue flows from the still through the outlet in the bottom glass disk and is collected in a suitable container. Successive passes of the residue from the unit at increasing ratio of sweep gas to crude oil flow provided deeper cuts into the crude oil. Additional fractions were obtained by operating at pressures as low as 1 mm Hg. A sketch of the column and its accessory apparatus is shown in figure 32. Figure 33 shows distallation assays (ASTM D86 type) of typical successive fractions removed from crude oil with the stripping unit. Product from the column can be readily duplicated in properties, as indicated in figure 34. Here are plotted ASTM D86 distillation curves of two distillates and residues produced under identical operating conditions except that one run was of 20 minutes duration and the other of more than 8 hours. These runs were made in the initial model of the stripper. The improved model, shown in figure 31, is essentially identical to the first except that it was much revised in constructional detail to make its operation mechanically reliable, requiring less care and attention to control. That units of

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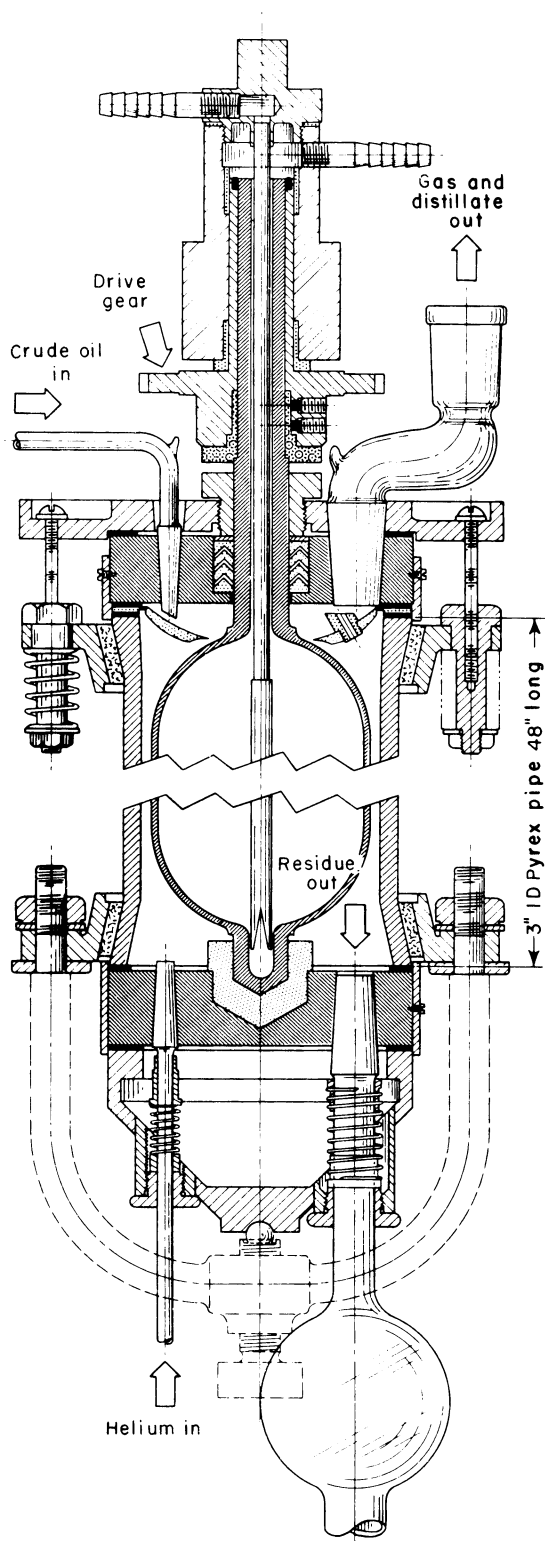
Figure 31.—Continuous isothermal stripping column.

(Reproduced by permission from reference 333.)

this nature operate in a systematic fashion is illustrated in figure 35, wherein is plotted the "yield plus loss," on one pass through the equipment, against the "gas-oil ratio;" that is, the ratio of sweep helium input to crude oil input. Material balance in the equipment is very good and the loss is essentially negligible after the first pass. Also plotted in figure 35 (top panel) is the end point, of the naphtha produced, against gas-oil ratio. Here, also, the data point to a smoothly functioning operation. These data are useful in predicting operating conditions necessary to produce products of desired characteristics. As can be noted, the crude oil, or the products from it, is in contact only with glass or Teflon and residues in the heated zone for only about 15 seconds.

Molecular Distillation

A final pass through the rotating-drum column at 4 to 5 mm Hg pressure and 150-ml/ml gas-oil ratio reduces the crude oil to such a degree that scarcely any additional distillate can be recovered by further processing in this equipment. The project, at this point, made use of molecular distillation equipment manufactured by the Consolidated Electrodynamics Corporation: a 14-inch, Model CMS-14, molecular still.[32] This commercial equipment is described in company literature, and one needs only to point out that the vital component is an electrically heated, slightly dished (conical) disk that rotates at high speed in a high vacuum. The material to be distilled is dropped on the disk at its center where centrifugal force drives it, in a thin film and at a rapid velocity, over the surface of the disk and off the rim into a collecting system. The vapors flashed from the residue during its sojourn on the heated disk are condensed and collected in another trap.

Figure 36 shows ASTM distillation curves of all the major distillates obtained from Wasson, Texas, crude oil by successive rerunning of the residues; first through the rotating-drum stripper and finally through the 14-inch centrifugal molecular still.[33] In both stills, fractionation is limited, but the low-boiling materials ("distillates," "naphthas") are effectively, if grossly, separated from the higher boiling without exposing either to a "cracking" environment.

Another type of molecular still used by the project for the production of high-boiling naphthas

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[32] Equipment made available through courtesy of Phillips Petroleum Co., Bartlesville, Okla.
[33] After two passes through the molecular still, the viscosity of the residue was too high for further processing, and it was deasphaltized with pentane at a 15-to-1, pentane-to-residue, ratio. The deasphaltized residue was again passed through the molecular still at a rotor temperature of 125° C (257° F) and system pressure of 0.003 mm, to produce the distillate represented by the final curve in figure 36.

Coolant

Coolant

Steam

Drum motor

Pump

Charge

Helium

Alternate vapor line

Dry Ice-cooled trap

Liquid air-cooled trap

Dry Ice-cooled absorber

Distillate receiver

Connection for evacuation (when required)
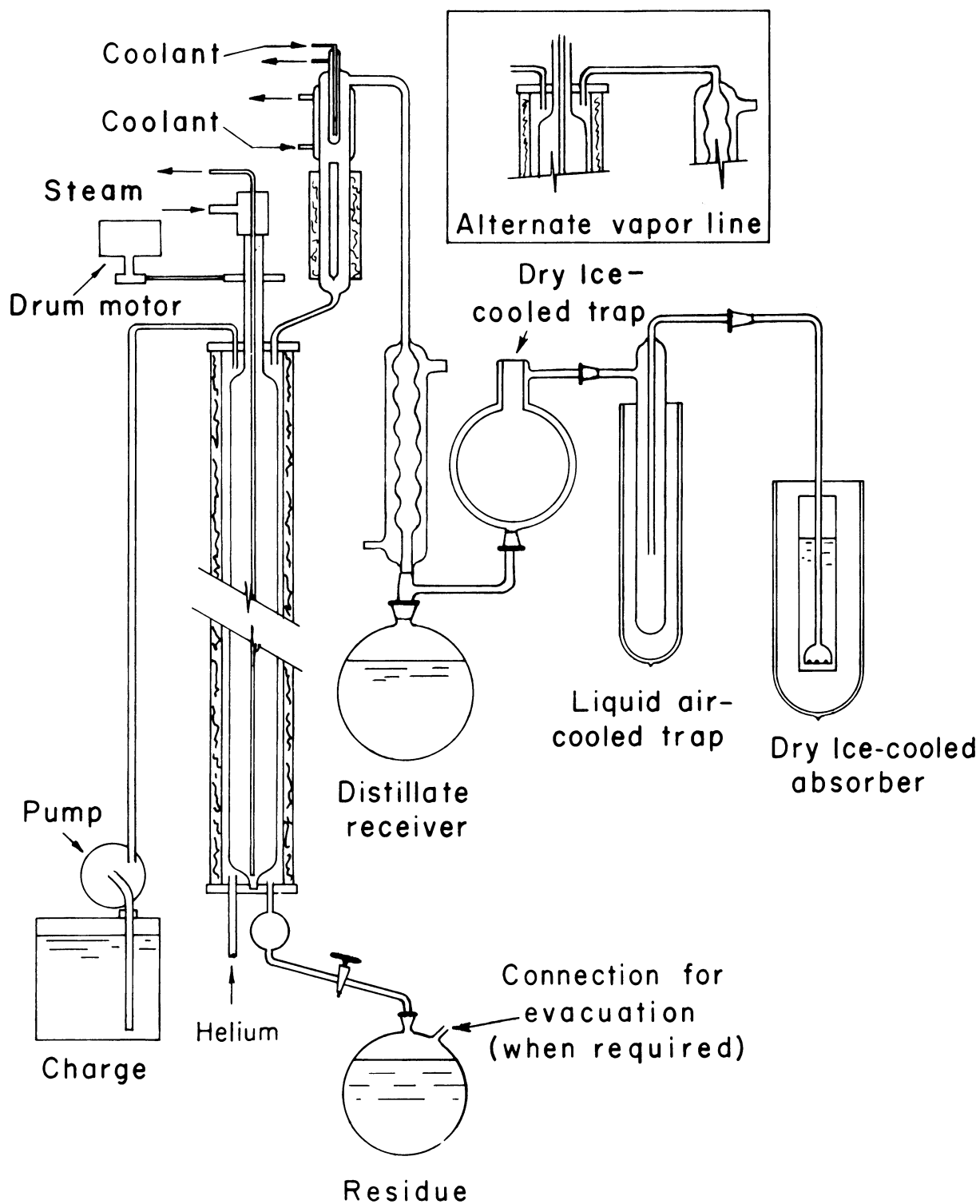
Residue

Figure 32.—Continuous isothermal still and auxiliary apparatus.
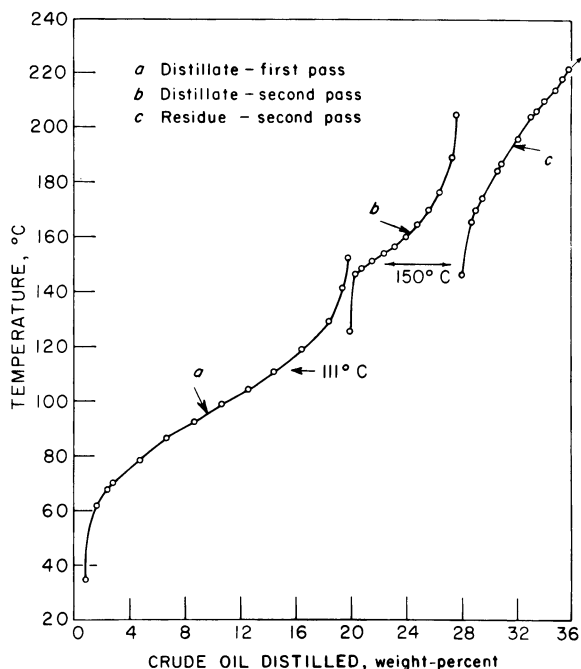
Figure 33.—Distillation analyses of products and residue from two-pass topping of Wasson, Texas, crude oil.

(Reproduced by permission from reference 333.)
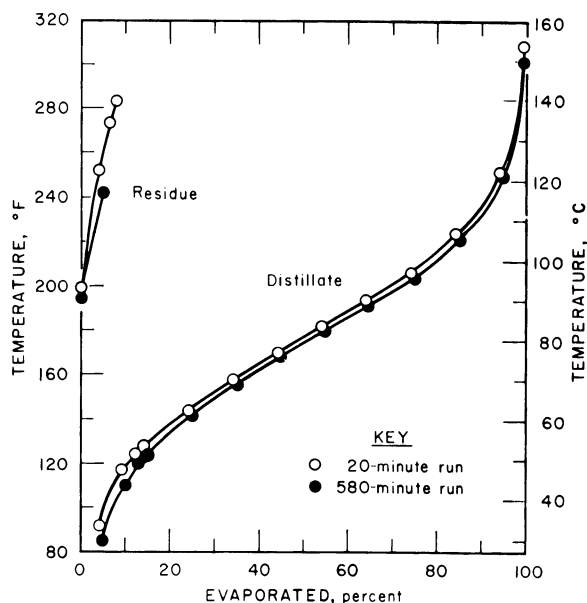
Figure 34.—ASTM D86 distillation data of products from duplicate runs of different duration from continuous isothermal still.
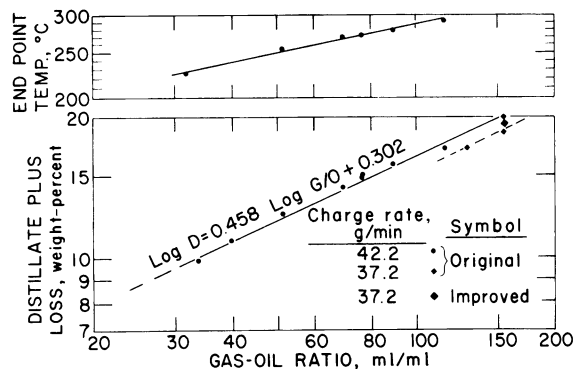
Figure 35.—Empirical relationships between distillate produced and gas-oil ratio (bottom) and between end point of distillate and gas-oil ratio (top) using Wasson crude oil.

(Reproduced with permission from reference 333.)

was the Consolidated brush still. This equipment is described in the literature (*318, 319, 456*) and in company brochures. A cross section of this still is shown in figure 37. The still's capacity is rated at 1,500 ml maximum, and is constructed wholly of glass and stainless steel. The brush, made of stainless steel "bristles" arranged in a spiral about the air-cooled shaft, is rotated about 400 rpm. The operation of the column is obvious from the sketch. The vapors arising from the pot are partly condensed on the spiral brush and thrown onto the column wall by centrifugal force. The ends of the wires brush the wall to provide turbulence in the reflux returning to the pot. Contact between liquid and vapor in the column is facilitated also by the motion of the wires of the brush. The condensing section contains a four-bladed paddle to propel vapors to the air-cooled walls to condense and collect in the annular gutter. The gutter connects with the distillate stopcock where the product can be collected in an appropriate receiver and removed. Column holdup is small—an obvious advantage. Being a "batch" still, residence time is high—an equally obvious disadvantage. Fractions checked for decomposition temperatures were found higher than stillpot temperatures and fractions did not indicate "cracking." No tests were made on the column, but the manufacturer's literature claims an efficiency of about nine theoretical plates.[34]

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[34] A more satisfactory molecular still was used in the terminal days of the project. This was the Arthur F. Smith, "Rota Film" still, a wiped-wall, falling-film type. Sample contact time, as in the "topping" still, is small and throughput can be quite high, 250 ml/hr or better for the 2-in still and as high as 2,500 ml/hr for the 4-in still.
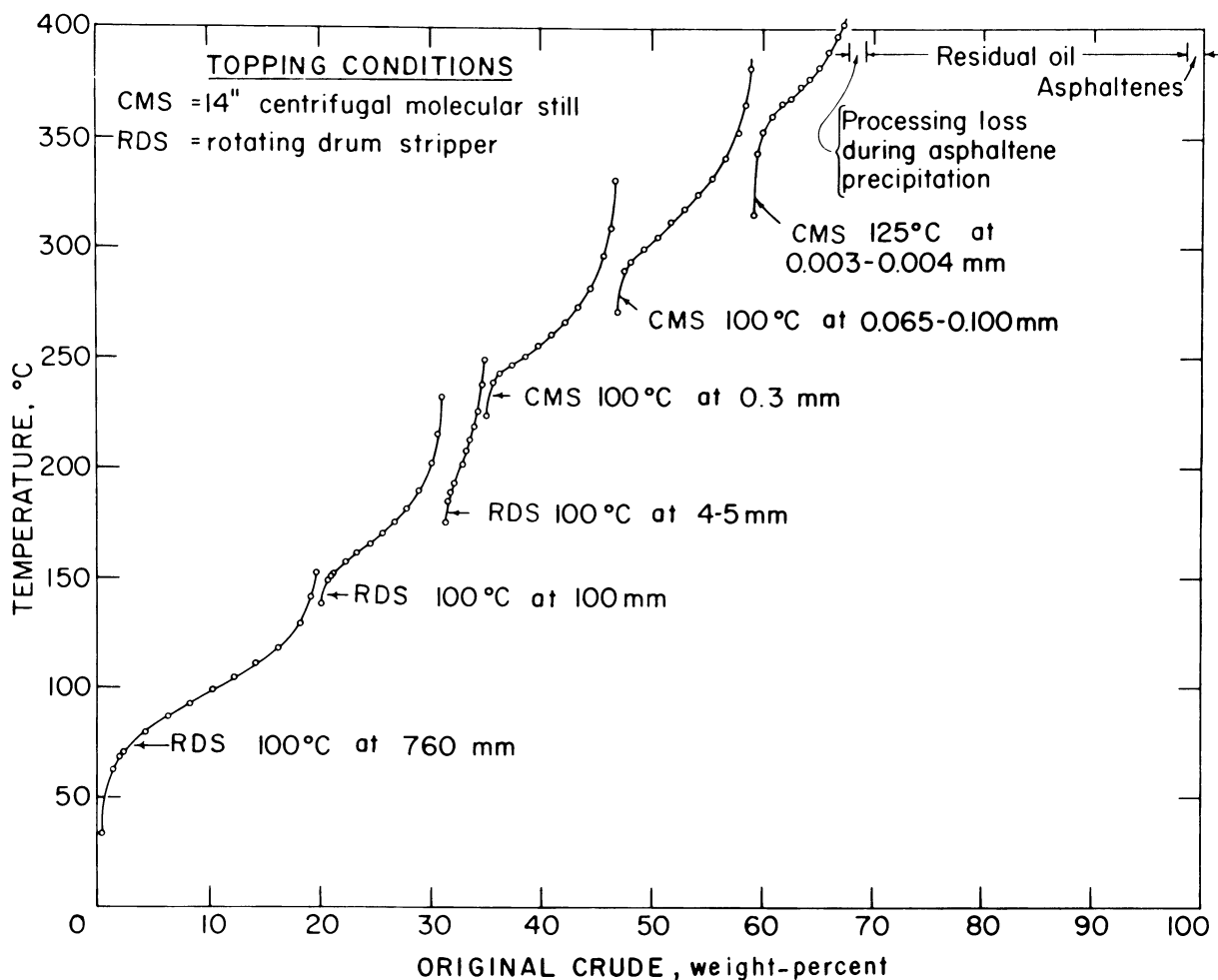
Figure 36.—ASTM D86 and D158 distillation curves of products from successive topping of Wasson crude oil.

(*Reproduced with permission from reference 333.*)

An illustration of the equipment's fractionating ability is shown in figure 38. The charge stock was a Wasson crude oil fraction, boiling approximately between 225° and 400° C. The heavy lines in this figure represent the variation of sulfur content and of distillation characteristics with volume-percent distilled for a preliminary five-cut distillation. The dotted brackets, enclosing dotted vertical lines, indicate the distillation range of cuts from a similarly conducted seven-cut distillation. In this instance, the fractions were to be preserved for additional work, and sample expenditure for ASTM distillations was deemed wasteful and unnecessary. The teven-cut distillation will be referred to in a later section.

Fractionation

To a great extent, gas-liquid chromatography has superseded fractionation as a separative procedure, particularly where only small quantities of sample are available or needed. Such a technique was not readily available early in the project when fractionating columns were used in this capacity.

Oldershaw Column.—This column is an all-glass, perforated-plate type developed by Oldershaw (*310*) and improved by Collins and Lantz (*82*). The column used by the project was essentially that of Collins and Lantz. The column proper contained 30 actual plates, about 28 mm in diameter, spaced 25 mm apart, and each perforated with eighty
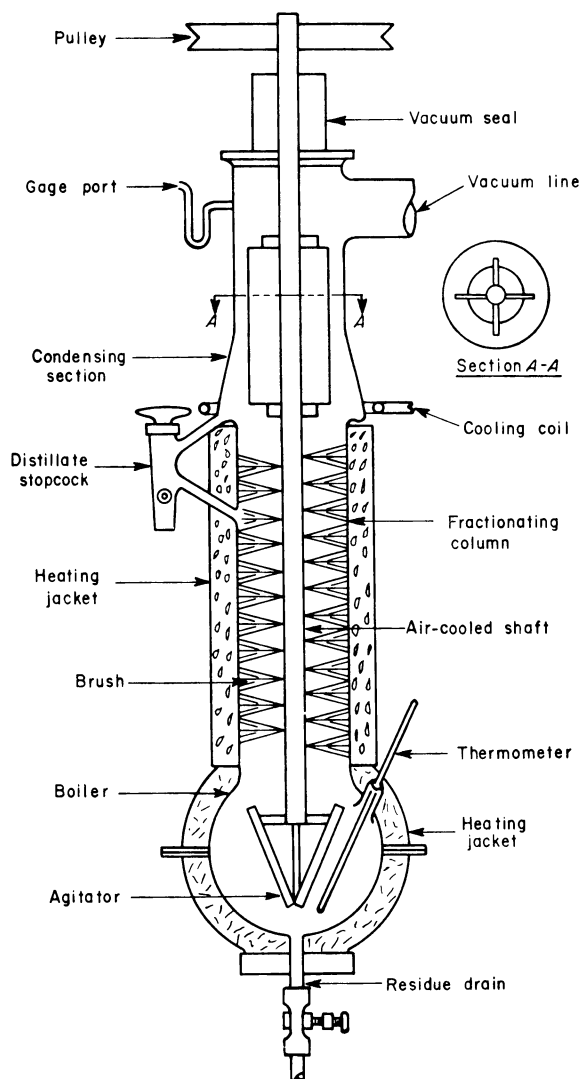
Figure 37.—Batch brush still.

0.9-mm holes. Each plate had a weir to maintain its liquid level constant and a drain to direct return distillate to the opposite side of the next lower plate. The column head contains a magnetically operated tilting funnel for diverting a desired ratio of the reflux to the outside of the column for collection. The developers of the column claimed a 15 to 20 theoretical plate efficiency for it, with a holdup of about 50 ml. The column could be operated under some reduction of pressure and served the project principally in dividing wide boiling range distillates into closer boiling range fractions for further processing.

Concentric-Tube Column.—The constructional features and performance characteristics of this column

have been described (*103, 364*). The fractionating capability of this column resides in an annular space of small width between two concentric tubes through which vapors from the stillpot ascend against a descending flow of reflux returning to the pot. In the column under consideration, the annular space is achieved between a 12.55-mm OD, precision-bore tube, 1,000 mm long, concentrically positioned within another tube of 14.05-mm ID, resulting in an annular space between them of 0.75-mm width. The reflux from a total condensing head is returned to the top of the column through a dripper, and by observing drop formation at this point, boilup rate can be regulated. The reflux return line has a connection to the column takeoff line. This connection contains a capillary, U-trap which is kept filled with reflux (and therefore closed) by a helium back pressure slightly greater than the column-head pressure. The back pressure is produced by a negligibly small but well regulated gas flow into the column head. Figure 39 illustrates the head section of the column, but the original paper (*103*) should be consulted for greater detail. Equalization of the slight differential pressure by a timer-operated valve allows the hydrostatic trap to empty and permit flow of reflux into the fraction collecting tubes.

Because of the very delicate nature of the takeoff mechanism, particularly when operating under reduced pressure, the changing of collecting receivers became a problem. The hydrostatic "leg," controlling the takeoff, is hardly greater than 1 cm of water, and any accidental change in pressure would tend to disrupt column equilibrium to which the column was sensitive. Various expedients were tried (including large bore stopcocks) to permit sample collection in a container which could be removed from the system without disturbing the 1 cm H_2O differential pressure. The problem was solved with the multitube device shown in figure 39 (*415*) in which distillate dripped into one of the radial tubes positioned below the takeoff tip. When sufficient sample had collected, the device was turned to the next receiver and the full tube sealed off with a torch. The collecting tube was kept cold with Dry Ice during distillate collection to prevent vaporization of the sample. No difficulty was experienced in dropping the distillate into the tube openings, although a more positive action could have been achieved, perhaps, with an auxiliary funnel device within the bulb of the collector and attached to the takeoff.

The column has an operating holdup of about 2 to 3 ml, and an efficiency of 100 to 150 theoretical plates, each characteristic dependent to some extent upon boilup rate. Control of boilup rate is essential,
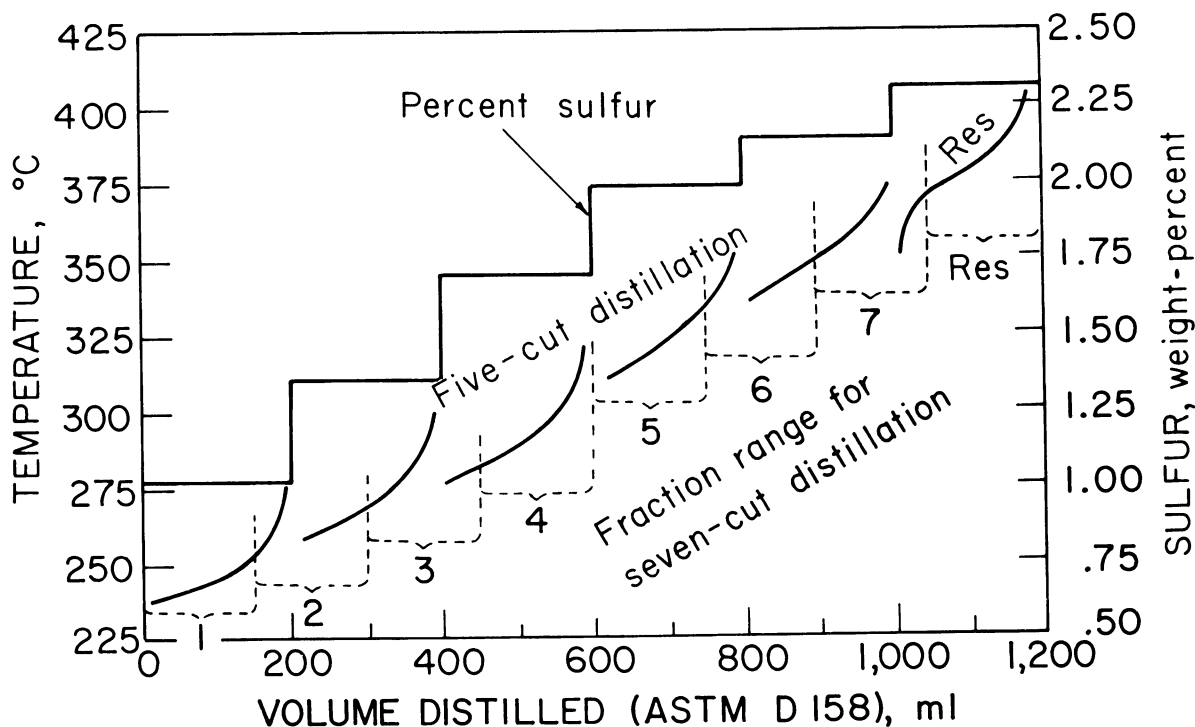
Figure 38.—ASTM distillation curves and percent sulfur of brush still fractions, Wasson 225° to 400° C distillate.

(Reproduced with permission from reference 333.)

and this problem gave some difficulty. However, the use of pumping-type stillpots reduced this problem to a negligible level. The column contains no metal parts, an advantage and almost a necessity in the fractionation of sulfur compounds.

Miniature "Hypercal" Column.—This column, manufactured by Podbielniak, Inc., was 8 mm in diameter and 30.5 cm (12 inches) in height. It was packed with "Heligrid" packing also of Podbielniak design. This column and packing are fully described in company brochures and in the technical literature.[35] Little further need be repeated here except to say that efficiency tests reported on the column and its packing indicate a low "HETP" (height equivalent to theoretical plates), low holdup, low pressure drop, and a fairly high throughput. Thus, for the 8-mm by 30-cm column, the efficiency (from reported data) should be about 50 to 20 theoretical plates corresponding to throughput of about 1.25 to 3.25 ml/min. A drawing of the column discussed will be found in Podbielniak and others (*325*), and a

sketch of its head and receivers in Coulson and Herington (*87*).

Liquid-Solid Chromatography

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

A major obstacle in separating and identifying any particular sulfur compound from a crude oil is the minute quantity usually present. Although the continually improving identification techniques of mass spectrometry, infrared spectroscopy, micro-hydrogenation, and so forth, require less and less sample, it is still necessary to obtain suitable sulfur compound concentrate fractions, and liquid-solid or adsorption chromatography has been of major importance in securing such fractions.

Historically, as early as 1900, Day (*92*) reported before the First International Petroleum Congress in Paris, the filtration of a light Pennsylvania crude

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[35] The literature on fractionation and fractionating columns, including those of Podbielniak, Inc., is quite extensive. Discussion relative and pertaining to "Heligrid" packing and to the minature "Hypercal" column may be found in references 49, 87, 143, 296, 324, 325, 349, which are cited only as typical.

Slight differential pressure
maintained between "A" and
"B", intermittently equalized
by valve for takeoff

Evacuated jacket

"Hairpin" condenser

Thermocouple well

Reflux return

Capillary hydrostatic
trap

Drip tip

Concentric
tube
column

Sample
collecting
tubes

Figure 39.—Head section of concentric-tube column illustrating construction details and method of fraction collection.

oil through a long glass tube filled with Fuller's earth to secure three distinctive subfractions. Early comprehensive book reviews on chromatography (60, 61, 240, 395, 466, 467) record the significant contributions of the Russian botanist, Tswett, in separating various pigments, and so forth, by filtration through columns of various adsorbents followed by development with various pure solvents. Cassidy (61) and Lederer (240) also reviewed adsorption chromatographic applications into the mid-1950's.

Admittedly, most of the early petroleum adsorption studies completed before the sulfur research by the Bureau was begun in 1948 were related to hydrocarbons (147, 269, 271) rather than sulfur compounds, and researchers relied primarily on silica gel as an adsorbent. There were early studies that

involved several types of adsorbents (124, 173, 241), and additional materials were subsequently investigated (65, 171, 382, 407) with the increased application of adsorption to a wide variety of samples (68, 100, 137, 200, 224, 270). The following adsorption techniques were considered: frontal analysis (61, 240) involving the continuous introduction of a given mixture; displacement development (101, 270) involving complete sample displacement from the adsorbent with a solvent possessing stronger adsorption than any of the sample components; and elution development (124, 200, 285, 407) involving elution with solvents of usually increasing adsorptive strengths (gradient elution).

Although some of the Bureau's early work in cooperation with the American Petroleum Institute Research Project 48 involved some adsorption work using displacement techniques for concentrating sulfur compounds in petroleum, the liquid-solid chromatographic technique that evolved for general usage employed solvent elution. H. H. Strain and others (396, 397, 398), in their several biennial chromatographic reviews in Analytical Chemistry, covered many of these developments. L. R. Snyder recently completed a rather comprehensive study of elution chromatography. His work dates back to the early 1960's (378, 383, 384) and continues to the present (380). A recent book on chromatography, edited by Erich Heftmann (169), includes not only several chapters on chromatographic theory and applications by H. H. Strain, J. C. Giddings, L. R. Snyder, and others, but also an extensive bibliography.

The purpose of this chapter on liquid-solid chromatography is to trace the Bureau's development and usage of adsorption as a separation tool for sulfur compounds in securing suitable sulfur compound concentrate fractions from various crude oil distillates of varied boiling ranges.

Silica Gel

Silica gel, as an adsorbent for various sulfur compounds, was investigated as early as 1926 (462) and 1927 (463). Several years later Mair (269) found, in developing a silica gel adsorption analysis for petroleum distillates, that sulfur compounds present in a distillate interfered with aromatic analyses and thus required the use of a small correction. Dinneen and others (100) later pointed out that the properties of an aromatic fraction obtained by silica gel adsorption of high-sulfur shale-oil naphthas are considerably modified by the presence of sulfur compounds. Experiments with silica gel using blends of different sulfur compounds in toluene showed that some sulfur compounds were

not completely separable from the toluene by adsorption.

Haresnape, Fidler, and Lowry (162) in their work on the separation of sulfur compounds by adsorption on silica gel, indicated the relative adsorptive strengths of various sulfur compound types and showed that some sulfur compounds were not completely separable from aromatic hydrocarbons. Preliminary experimental silica gel adsorption work by the Bureau on various petroleum distillates confirmed these findings. Results showed that, although most of the sulfur compounds in the distillate tend to concentrate at the trailing edge of the aromatic fraction, a significant quantity of sulfur compounds occurs throughout the entire fraction, so as to require inclusion of all the aromatics in the "sulfur concentrate." This circumstance is not desirable, because inclusion of substantial quantities of aromatics with the sulfur compounds seriously hampers separation and identification of the individual sulfur compounds in subsequent procedures. Attention therefore was turned to alumina as an adsorbent.

Alumina

Alumina as an adsorbent had been investigated to some extent for hydrocarbon separations of various kinds before the Bureau's research on sulfur compounds was begun in 1948. However, compared to silica gel, the study of alumina for hydrocarbon separations had not progressed very far with the then-common Alcoa grades F-1 and F-20. For concentration or separation of sulfur compounds, alumina as an adsorbent had received even less attention.

A new alumina adsorbent, designated grade H-41, of 80 to 200 mesh size from the Aluminum Company of America, which the Bureau of Mines was using for the analysis of jet fuels (258), was found to be highly selective for sulfur compounds. Measurement of the selective adsorption of this alumina, following activation at various temperature levels by Rao's liquid phase method (334) and employing a standard blend of 10 percent toluene in isooctane, established that 400° to 500° C (752° to 932° F) was a better activation temperature level than 200° to 300° C (392° to 572° F). Alumina gel activation in our laboratory is now standardized at 400° C for 16 hours. Investigation of possible oxidation affects by the gel on sulfur compounds involved a number of special tests with 2-propanethiol designed to determine the effect of time and temperature. Over long periods at room temperature, some slight oxidation of 2-propanethiol to its respective disulfide (2,5-dimethyl-3,4-dithiahexane)

did occur when in contact with activated H-41 alumina. One test that involved 7.3 grams of the branched chain thiol, 2-propanethiol, on a column of 360 grams of activated H-41 alumina for 50 hours at room temperature, showed as much as 7 percent conversion to the respective disulfide. As a result of such studies, the time factor seemed important, and the duration of all adsorption runs that involved concentration of sulfur compounds was kept to a minimum, usually less than a day. Also, the number of adsorption steps involving the concentration of thiols was kept to a minimum through the use of an effective chemical extraction procedure developed by the Bureau specifically for thiols as is discussed in earlier publications (192) and elsewhere in this report (pp. 74–79).

Some of the extensive experimentation with this relatively new H-41 alumina involved several trial separations of equal volume blends of benzene and thiophene, two compounds that are closely related in boiling point, molecular weight, and adsorptive strength. The adsorptive strengths of these two compounds were so close on both silica gel (162) and F-20 alumina (379) that for all practical purposes they were considered inseparable. However, figure 40 illustrates an experiment which shows the superior separating power of H-41 alumina. A mixture of 10 ml of benzene, 10 ml of thiophene, and 30 ml of pentane was charged to the column and eluted with 400 ml of additional pentane followed by displacement with ethanol. Only 0.5 percent of the thiophene had eluted when the elution of benzene was 85 percent complete. Although major improvements could have been effected by changes in dilution, elution, and gel-to-sample ratios, these data and other comparable data established the separability of these two classes of compounds.

Later experimentation with a blend of sec-butylbenzene and tert-butylthiophene (mixture of 2- and 3-substitution) involving a much greater gel-to-sample ratio (67 to 1 versus about 30 to 1) and a much larger height-to-diameter ratio (1,000 to 1) (12 mm by 12.2 m all-glass column) proved without doubt that thiophenes are chromatographically separable from benzenes with this highly selective alumina adsorbent. The chromatogram of figure 41 illustrates the relative adsorption of these two compound types, both by the refractive index plot and by the quantitative distribution data determined by mass spectrometry. This experiment involved minimal dilution with isooctane followed by complete desorption displacement with ethyl alcohol (ethanol). In this instance, 96 percent of the benzene eluted with but 0.05 percent of the thiophene.
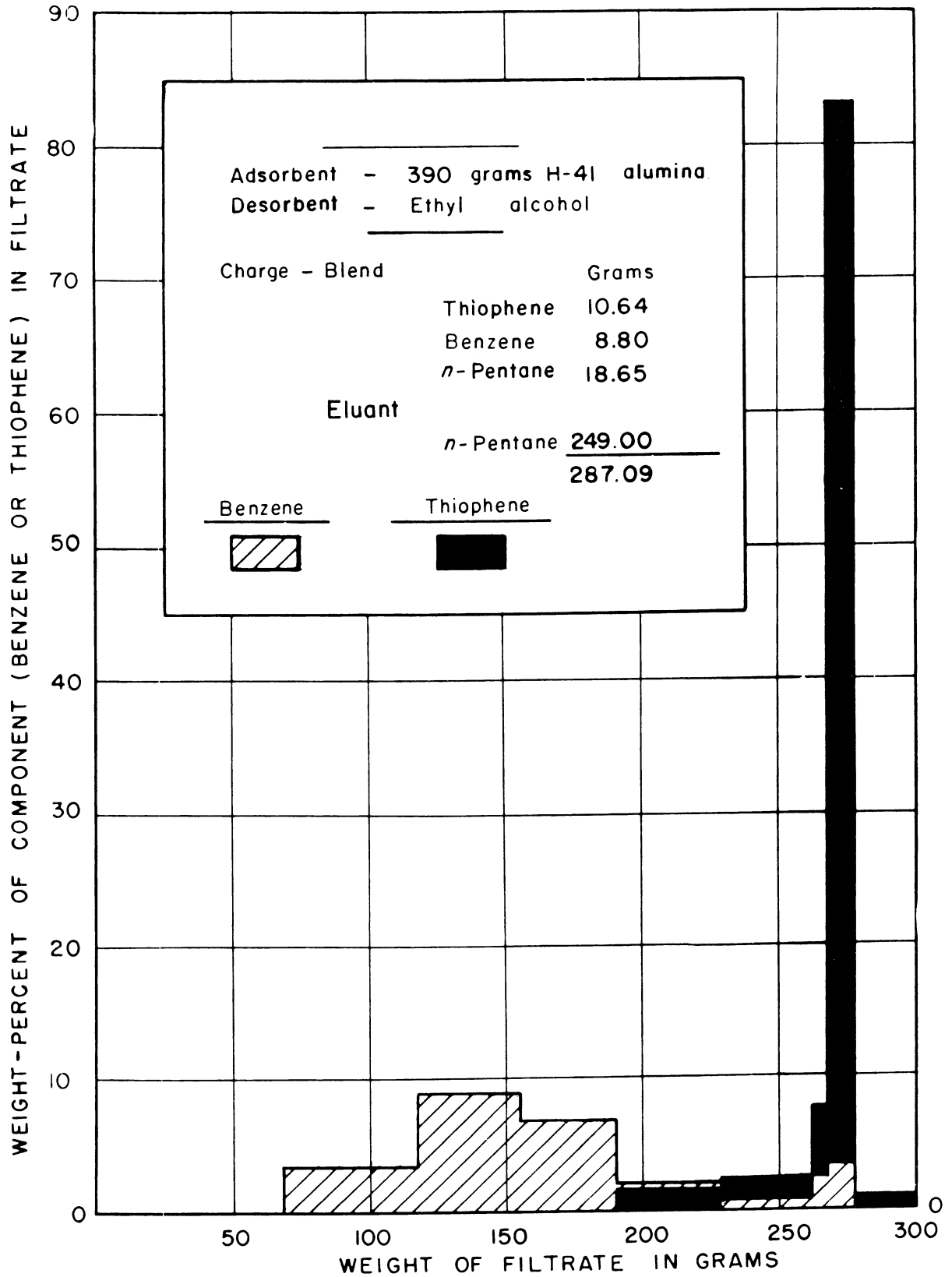
Figure 40.—Separation of benzene and thiophene by alumina adsorption.
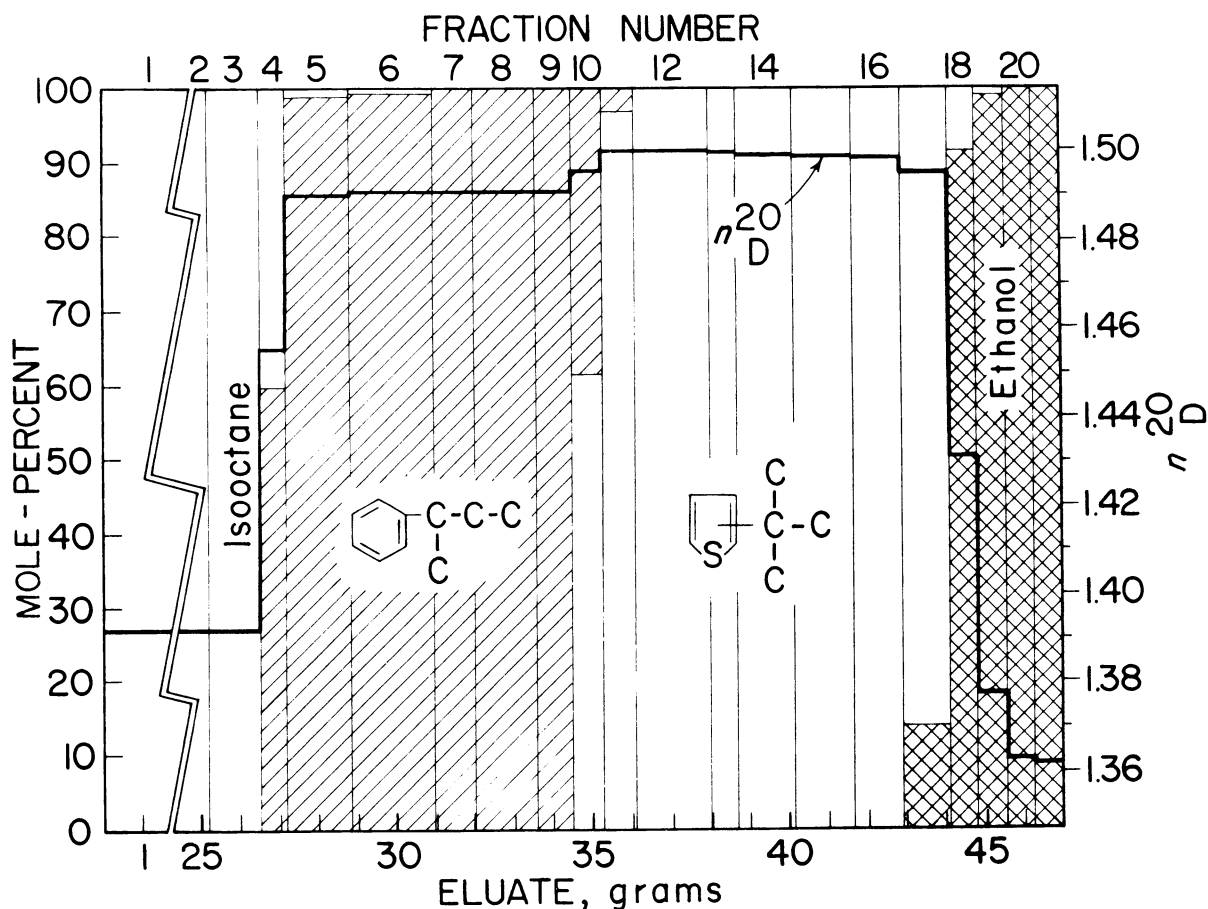
Figure 41.—Bar graph illustrating the separation of sec-butylbenzene and tert-butylthiophene obtainable in a 40-ft-long, 1,000-to-1, height-to-diameter ratio adsorption column.

In the early 1950's, chromatographic studies on the separation and identification of aromatic types in petroleum (65, 255) relied on prior separation with silica gel into two main subgroups; namely, paraffin and naphthene, in one fraction and aromatics in a second fraction, followed by rechromatographing the aromatic fractions on F–20 alumina with extensive elution. However, because of our exclusive emphasis on sulfur compounds, the relatively selective adsorption differences between aromatics and sulfur compounds could be advantageously employed to remove paraffins, naphthenes, and most of the aromatics with a single alumina adsorption step that involved suitable amounts of appropriate eluting solvents. The earliest work employed gel-to-sample ratios as low as 10-to-1, figures on the basis of grams adsorbent versus grams of aromatics and sulfur compounds,

but with increasing usage, this ratio gradually grew to a minimal 100-to-1. Recently partially deactivated gel has been used by some researchers to achieve some degree of linearity, but its use can reduce sample capacity to the extent that the 100-to-1 minimal gel-to-sample ratio should be increased by a factor of 10 to 100 (381).

For low-boiling distillates, the procedure generally followed after sample introduction was to elute with a hydrocarbon solvent, such as isopentane or n-pentane, until the refractive index of the eluate approached that of the eluting solvent when complete sample displacement began with the introduction of ethyl alcohol as a desorbent. Such adsorption runs always employed jacketed adsorption columns and ice water circulation through the outside jacket to reduce volatilization losses and to increase adsorption capacity and selectivity. If

too much aromatic contamination remained, the resulting sulfur concentrate fraction could be re-chromatographed repeatedly until little or no aromatics remained to contaminate the sulfur compound concentrate. Sulfur compounds contained in the leading edge of the desorbing alcohol front were removed by salt water wash and extraction with isopentane. Then these isopentane extracts were usable as part of the diluting material in the next liquid-solid chromatographic rerun through alumina. For the 38° to 100° C (100°–212° F) Wasson distillate, a total of four reruns were made, using adsorption columns having dimensions suitable for the sample requirements. The final product in this particular series of runs was a sulfur concentrate that weighed 37.6 grams, which is equivalent to 0.0349 percent of the original Wasson crude oil. Two early Bureau publications (71, 427) cover the initial alumina adsorption experimental work and describe some of the related sulfur compound identification techniques. The efficacy of H–41 alumina for concentrating sulfur compounds from petroleum fractions has been substantiated by other independent research (9, 205).

For the lower boiling distillates that contained only a few compound types, the liquid-solid chromatographic separations were comparatively straightforward and precise. In addition to the liquid-solid chromatography of the low-boiling 38° to 100° C (100° to 212° F) Wasson distillate mentioned above, alumina adsorption of low-boiling Agha Jari, Iran (87), and Wilmington, California (426, 430), distillates provided sufficient sulfur compound concentration to permit many individual identifications.

The selective adsorptivity of H–41 alumina was especially noted in the study of a Wilmington 111° to 150° C (232° to 302° F) distillate. Alumina adsorption proved quite effective in concentrating thiophenes (77) and cyclic sulfides (76) from this distillate as it did for the chain and cyclic thiols and sulfides (78) of a similar boiling-range Wasson distillate. The Wilmington 111° to 150° C (232° to 302° F) distillate represented an optimum limited molecular-weight-range fraction comprising 2.70 percent of the original crude oil and containing only 0.038 percent sulfur. Because of the low sulfur content, the initial adsorption step for 2.3 kg of this distillate could be handled in four small (750-ml) batch runs. The method used for each of these four individual adsorption runs included the following: (1) Dilution of the distillate with an equal volume of n-pentane; (2) introduction of the diluted sample to an adsorption column, 225 cm long, containing 1,500 ml of alumina; (3) elution

with n-pentane (2,500 ml) until the refractive index approached that of n-pentane; (4) introduction of ethyl alcohol to effect complete sample displacement; (5) collection of the sulfur and aromatic compound concentrate as one fraction and a sulfur-containing alcohol portion as another fraction; (6) recovery of sulfur compounds from the alcohol fraction by dilution with salt water and extraction with n-pentane and rechromatographing of the pentane extract; and (7) combining both sulfur compound concentrates for further testing.

This preliminary adsorption produced a volume concentration of 63 times (now 0.043 percent of the crude oil), and gas-liquid chromatographic (GLC) analyses combined with microdesulfurization established the presence of sulfur compounds. However, the high aromatic content of the resulting sulfur and aromatic compound concentrate interfered with GLC separation and identification of individual sulfur compounds. Therefore, further concentration by alumina adsorption was desirable. The second adsorption step included the following procedures: (1) Dilution of 28 grams of sulfur- and aromatic-compound concentrate from the preliminary adsorption step with 36 grams of isooctane; (2) introduction of the diluted sample to a 12-mm by 12.2-m (40-ft) column containing 1,350 ml of alumina (gel-to-sample ratio roughly 50-to-1); (3) addition of a small amount of fresh alumina at the top of the column as a "spacer" following complete sample entry into the alumina column; introduction of ethyl alcohol to effect complete sample displacement; and (4) collection of small (0.7 to 1.5 g) fractions eluting from the bottom of the adsorption column.

Factors influencing the fraction collection included (1) volume of fraction, (2) the observation of schlieren (an optical effect caused by a sharp change of refractive index and density of the eluate or effluent material over that already accumulated in the test tube), (3) visible boundary shadings of the liquid on alumina, and (4) noticeable odor changes of effluent, particularly for the later fractions containing sulfur compounds.

This final alumina adsorption run not only reduced the amount of extraneous aromatic compound contamination by a factor of five based on the overall weight of sulfur-containing fractions, but also produced some fractions completely free of aromatic compound contamination.

GLC analysis of the resulting adsorption fractions indicated major differences of adsorptive strength for aromatic hydrocarbons, alkylthiophenes, and alkyl-substituted cyclic sulfides on alumina. In addition to showing alkylthiophene separations

from alkylbenzenes and from cyclic sulfides, the data from this precision liquid-solid chromatographic separation showed some fine adsorptive differences between individual compounds within a class. Some general observations with respect to the aromatics include the following:

1. C₃-substituted benzenes, such as isopropyl- , *n*-propyl- , and the methyl, ethyl isomers occur only in the earlier fractions; 1,2,3-trimethylbenzene occurs in adsorption fractions 10 to 27.

2. Ethylbenzene reaches peak concentration in fraction 10, followed slightly later by *m*-xylene, and both, though decreasing in concentration, remain as minor contaminants in the analyses for alkylthiophenes present in fractions 26 to 28.

3. *p*-Xylene, present in the earliest fractions, rapidly decreases to extinction; *o*-xylene, representing the most strongly adsorbed C₂-substituted benzenes, appears in the middle fractions and continues to increase through fraction 26 to cause considerable contamination troubles in the alkylthiophene-containing fractions.

4. Toluene makes a very late appearance and reaches its maximum concentration in fraction 27.

5. Traces of benzene occur only in fractions 27, 28, and 29.

Adsorption data on this precision liquid-solid chromatographic run show that elution order is determined by steric effects around the sulfur atom, being influenced both by chain length and position of the substituents. Consequently, the following order of decreasing adsorptivity was observed: 3,4-dimethylthiophene > 3-ethylthiophene > 2,3-dimethylthiophene > 2,4-dimethylthiophene > 2-ethylthiophene > 2,5-dimethylthiophene > 2-isopropyl- and 2-*n*-propylthiophene.

Adsorption fraction 29, as shown in figure 93 (p. 152) of the Wilmington crude oil section, was a transition fraction between the more strongly adsorbed of the thiophenes and the more weakly adsorbed cyclic sulfides. Fractions 30, 31, and 32 were essentially pure cyclic sulfides, and the quantitative distributions of given cyclic sulfides in the various fractions were the result of definitive differences in adsorptive strength which is directly related to the degree of steric hindrance around the sulfur atom. Thus, 2,2,5,5-tetramethylthiacyclopentane appeared first, followed in order by 2,2,5-trimethylthiacyclopentane, 2,2-dimethylthiacyclopentane, *trans*- and *cis*-2,5-dimethylthiacyclopentanes, and 2- and 3-methylthiacyclopentanes. For cyclic sulfides, the appearance of *cis*- and *trans*-isomers at least doubles the problem of differentiation and quantification. The fine adsorptive differences of the various cyclic sulfides fitted together in a pattern consistent with the findings for the alkylthiophenes and allowed the observation that the *trans*-isomers are less strongly adsorbed than are the *cis*-isomers.

For distillates boiling much above 150° C (302° F), the separation of sulfur compounds from hydrocarbons by liquid-solid chromatography becomes more difficult and less satisfactory. The increased complexity is troublesome; but the use of graded elution by increasing concentrations of benzene in pentane followed by ether-pentane blends and finally desorption with methyl alcohol gave excellent separations on fractions boiling above 200° C (392° F) (*74*). Recovery of the chromatographic fractions from the large amount of solvents involved was aided greatly by the use of a continuous solvent stripper (*185*) previously developed by the Bureau of Mines for this purpose. Application of such a separation technique to an aromatic fraction from a Wasson, Texas, crude oil distillate boiling in the 200° to 250° C (392°–482° F) range, effectively concentrated all of the sulfur in the final 22 percent of the charge with some of the adsorption fractions having sulfur concentrations as high as 14 percent, which in this boiling range represents approximately 70 to 75 percent sulfur compounds calculated on the basis of one atom of sulfur per molecule.

A report published in 1961 (*74*) shows a chromatogram of a narrow-boiling, Wasson 220° to 225° C (428° to 437° F) distillate as obtained with an efficient adsorption column (12 mm ID by 12.2 m long). This chromatogram illustrates some overlapping of compound types as from paraffins and naphthenes to monoaromatics, monoaromatics to diaromatics, and finally diaromatics to polar compounds. The sulfur compound plot in the lower portion of the chromatogram, shown in reference 74, indicates increasing adsorptivities of sulfur types ranging from thiophenes to benzothiophenes to cyclic sulfides. In instances like these, repeated adsorption steps often were quite helpful in achieving better sulfur compound concentrations, particularly when aided by special chemical extractions of selected sulfur compound types as discussed elsewhere in this report.

Two recent publications (*106*, *221*) point out the effectiveness of oxidizing sulfur compounds to their respective sulfones or sulfoxides and then chromatographing. Because of the much stronger adsorptivities of such oxygenated sulfur compounds, compared with their parent compounds, liquid-solid chromatographic separations even on silica gel are easily attained even when dealing with high molecular weight sulfur compounds and the related

polycyclic aromatics that occur in the same high-boiling distillates. An attempt by the project to apply this technique to the separation of benzothiophenes from naphthalenes was unsuccessful because of simultaneous oxidation of the naphthalenes to naphthoquinones.

With current emphasis on the heavy ends of petroleum, it is interesting to note that liquid-solid chromatography was applied to crude oils and similar materials by the Bureau of Mines (427) and others (224) early in the life of API Research Project 48, and such adsorption work produced a fair degree of concentrated sulfur compound types (see 430, table 1).

Adsorption techniques were developed or extended throughout the project, by the use of improved graded elution, larger gel-to-sample ratios, special gels, and columns with larger length-to-diameter ratios, for sulfur compound concentrations and separations previously unobtainable. Even now chromatographic research continues at a seemingly fast pace with the advent of special pumps, fraction collectors and detectors (ultraviolet and infrared). The most recent modification coming out of the Bureau of Mines research laboratories is the use of dual gel loading (172) to improve on compound-type separations. Once fractions are separated by liquid-solid chromatography, a more recent chromatographic development, gel permeation chromatography (72), can be applied to secure even more finely detailed separations.

Gas-Liquid Chromatography

The first hint of gas-liquid chromatography as an analytical technique occurred in a 1941 paper by Martin and Synge (275) on liquid-liquid chromatography, wherein they expanded upon their investigation with liquid-liquid systems to suggest that volatile materials could be separated by the use of columns having a stationary liquid phase and a moving gas phase. This suggestion went comparatively unnoticed for more than 10 years until Martin, in collaboration with A. T. James (203), described the application of gas-liquid partition chromatography to the separation of volatile fatty acids. Admittedly, during these intervening 10 years some experimental work in gas chromatography, as in the case of Phillips (327), did develop, but this was meager and was related to gas-solid chromatography that involved both elution and displacement techniques from solid adsorbents like activated charcoal, etc. Certainly, the use of a relatively inert solid, coated with a liquid stationary phase, presented a much more applicable and reproducible technique that lent itself to rather precise theoretical treatments starting with James and Martin in 1952 (203) and continuing with many others, such as Van Deemter and coworkers (439), Jones (215), Giddings (140, 141), Keulemans and Kwantes (229), Littlewood (248), Purnell (330), Golay (144), and Klinkenberg (233, 234).

The various parameters affecting the efficiency of separations are discussed in an early GLC paper by Dimbat, Porter, and Stross (99). Application and extension of the GLC work of James and Martin is exemplified by the work of Ray (335). His early work included the use of various stationary liquid phases with which he obtained good separations of many different types of compounds, including hydrocarbons, alcohols, aldehydes, and ketones. Keulemans' book of 1957 (228) covered much of the extensive work of the Shell laboratories here and abroad and compiled much of the earliest published work in the field.

Admittedly the amount of published material related to GLC was miniscule in the early 1950's, but according to a graph drawn by Dal Nogare and Juvet in their book on gas-liquid chromatography (91), the number of publications per year began increasing to formidable proportions about 1956. Some 200 GLC publications appeared in 1956, followed by about 400 in 1958, and 1,200 in 1960. An excellent review of gas chromatography was published in 1959 by Hardy and Pollard (161) wherein they listed over 600 specific references. This was followed by the 1960 review by Dal Nogare (90), which listed 244 additional references dealing primarily with technique. Ten years later, in a similar review, Juvet and Cram (217) estimated that 2,430 articles and major addresses on GLC were published or presented in 1968, compared with more accurate figures of 2,045 in 1967; 2,175 in 1966; 2,060 in 1965; and 1,878 in 1964. Thus, gas chromatography continues to be one of the most active areas in analytical chemistry.

GLC literature concerning sulfur compounds, on the other hand, was practically nonexistent for several years as early researchers in the petroleum field looked primarily to the analysis of hydrocarbons. Indeed, some of the earliest GLC work at this Center dealt primarily with the separation and identification of hydrocarbons and oxygenated hydrocarbons in combustion products from automotive engines (196). However, with the equipment and experience readily available, staff personnel easily adapted the analytical technique to the separation and identification of sulfur compounds in a sulfur compound concentrate prepared from Agha Jari, Iran, crude oil as early as 1958 (87). This

was some 2 years after publication of the first GLC paper related to sulfur compounds. Sunner and others (401), in this initial GLC paper on sulfur-compound separations, described the separation and quantitative determination of low-boiling C_4 and C_5 thiols (mercaptans) on an ultramicro scale. Their 2.4-meter column, containing dioctylphthalate-coated carborundum, performed quite well with a nitrogen carrier gas in separating all of the C_4 thiols and all but one pair of C_5 thiols (2- and 3-pentanethiols) in their prepared synthetic blend.

Desty and Whyman (98), Amberg (8, 9) and others included sulfur compounds in their studies of GLC retention-time relationships for hydrocarbons; Ryce and Bryce (353), Spencer and others (390), Karchmer (223), Adams and Koppe (2), and Liberti and Cartoni (243) and others dealt primarily with sulfur-compound relationships. Liberti and Cartoni, in their 1957 paper, and Klaas (232), 4 years later, worked specifically with GLC of sulfur compounds and their detection by automatic coulometric titration of the individually separated compounds. Recent papers by Martin and Grant (276, 277) report the distribution of sulfur in a variety of petroleum samples by a combination of GLC and microcoulometric sulfur detection. A paper by Adams and others (1) summarized the state of the art with respect to microcoulometry.

Since the first applications of GLC in API Research Project 48 in 1957, the technique was used almost daily by the project staff, and its use contributed most significantly to the increasing number of sulfur compound identifications in the later years of the project.

The Bureau's earliest published work on the separation of sulfur compounds by GLC (81) recorded the use of a short (6-foot-long), ¼-inch-diameter (2 m by 6.5 mm) copper tube packed with 40- to 50-mesh acid-washed fire brick coated with 17 weight-percent Dow Corning 550 silicone oil. The column was used for analyzing low-boiling thiols and sulfides. This initial analytical work at 38° C (100° F) with a helium flow rate of 100 ml per minute provided the basis of separating and identifying 11 different compounds (six thiols and five chain sulfides), as discussed in more detail under Agha Jari, Iran, crude oil analysis. This column, with the same operating conditions, was also used in identifying 3-methylthiophene in a low-boiling distillate (38° to 111° C, 100° to 232° F) from a Wilmington, California, crude oil (430).

All of the early project GLC studies employed equipment designed and built in Bureau laboratories, including the constant-temperature air bath, an 8,000-ohm thermistor-equipped detector block,

and a sample input assembly. Later GLC work was carried out principally with a thermistor-equipped, Perkin-Elmer Model 154–D vapor fractometer in conjunction with other commercial units, including Research Specialties Model 60–1 chromatograph equipped with a hydrogen-flame ionization detector; Beckman Instruments Models GC–2 and GC–100 equipped with filament-type thermal-conductivity detectors; Barber-Colman Model 20 chromatograph equipped with an argon-ionization detector; Micro Tek Model 2500 chromatograph equipped with both a flame ionization detector and an electron-capture detector; and an F & M Model 810 chromatograph equipped with a flame ionization detector.

Increased emphasis on studying sulfur compounds in higher boiling petroleum distillates began first with the thiols in a Wasson distillate boiling from 111° to 150° C (232° to 302° F) because of the ready availability of an excellent thiol concentrate fraction obtained through the application of efficient chemical extraction techniques discussed later. Distillation of this thiol concentrate fraction with a highly efficient all-glass concentric tube distillation column (about 150 theoretical plates) into very limited boiling-range fractions proved to be especially advantageous for further separation and identification studies by GLC. The use of narrow-boiling distillation fractions permitted selection of a GLC column for maximum resolution without requiring the unrealistically long retention times necessary when an extract from the whole distillate was used.

GLC analytical studies on higher boiling thiols at higher column operating temperatures quickly established the unsuitability of copper for construction of columns. Although thiols react with copper under the conditions employed, they could be analyzed satisfactorily on columns constructed of stainless steel or aluminum. Such analytical probing also established the advantages of using longer columns and varied stationary phases of differing polarity. The use of columns as long as 40 feet provided excellent resolution on samples large enough for individually isolated components to be trapped and analyzed by mass spectrometry, infrared spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, or microdesulfurization. When a single column proved inadequate for resolving each thiol, a given unresolved peak was trapped and rechromatographed on a second and even a third column of different polarity. Figures 42 and 43 illustrate GLC separations that were instrumental in separating and identifying these thiols. Figure 42 is a chromatogram of a small
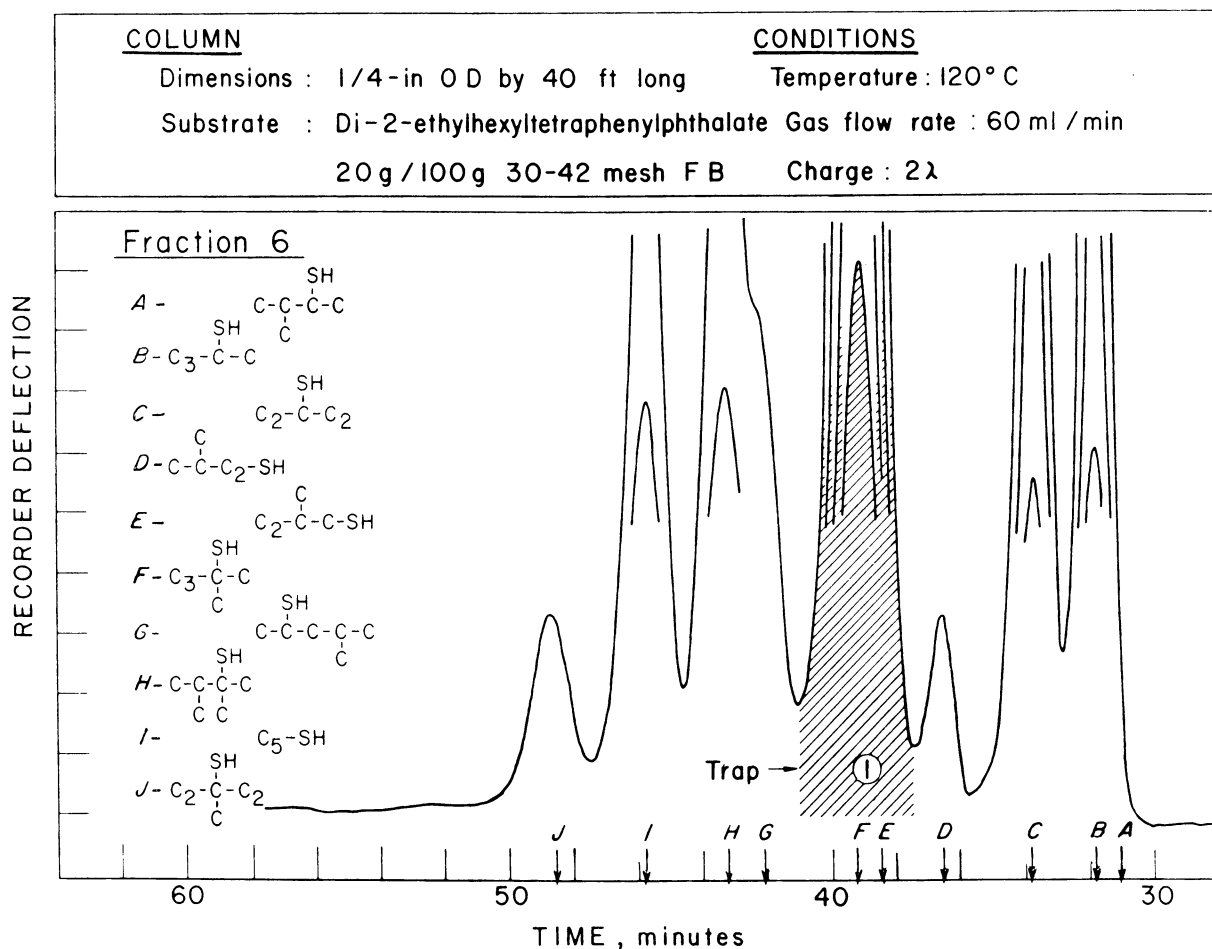
Figure 42.—Gas-liquid chromatogram of fraction 6.

(Reproduced by permission from reference 424.)

boiling subfraction of the overall 111° to 150° C (232° to 302° F) Wasson thiol concentrate as obtained on a 40-foot long di(2-ethylhexyl)tetraphenyl-o-phthalate column. Although the resolution appears satisfactory, the retention time data of the various components present indicate the shaded peak 1 coincides with the retention times of two thiols, 2-methyl-1-butanethiol and 2-methyl-2-pentanethiol. Trapping of the material emerging during the time interval of the shaded peak (from 37.5 to 41 minutes) and rechromatographing this trapped material on another column of different polarity (aluminum column packed with Reoplex 400-polypropylene glycol adipate on 30-42 mesh GC–22 super support, 20/100 wt ratio) produced the chromatogram of figure 43. This chromatogram shows that the two thiols were present in the original sample at a ratio of about 1 to 25.

The search for suitable stationary phases for GLC operation at elevated temperatures has been a matter of much study by numerous researchers (52, 246, 386, 406, 446). Much of this work was based on trial and error, and when a certain stationary phase was found to be especially good for a given separation, the researchers usually would write a short paper or communication (195, 328). Di(2-ethylhexyl)tetraphenyl-o-phthalate, synthesized in our laboratory, proved to be a thermally stable, low vapor pressure compound which, as a stationary phase, was especially useful in separating thiols. Rotzsche (351) reported special synthesis methods for obtaining stationary phases of desired polarity; other researchers (177, 278) developed and used specially synthesized porous polyaromatic or polyamide polymer beads without any liquid coating. Stationary phases chemically bonded to the
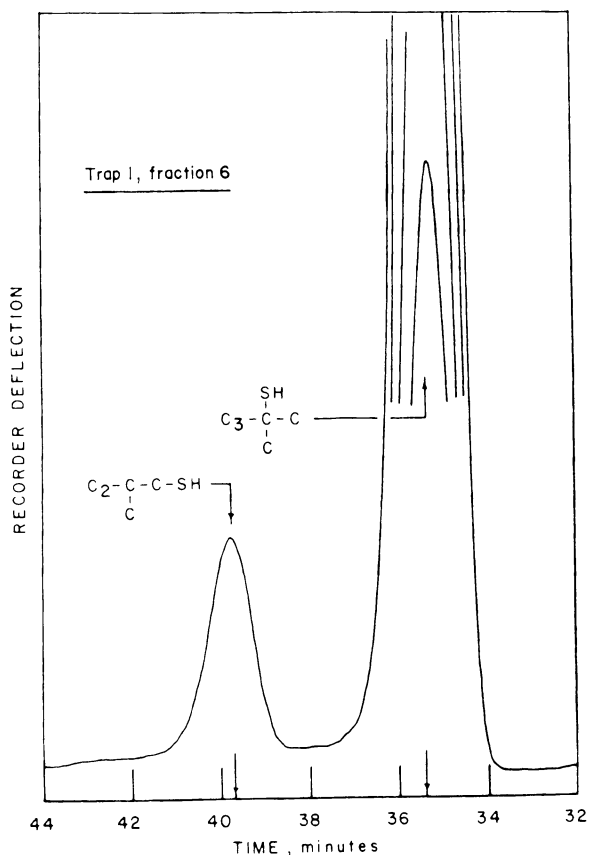
Figure 43.—Gas-liquid chromatogram of material of trap 1, fraction 6, in a reoplex 400 column.

(Reproduced by permission from reference 424.)

active hydroxyl sites of solid supports like silica gel constitute a more recent development (247).

The number of possible and proven stationary phases has increased to the point that the recent development of an evaluation tool by Rohrschneider (347) was essential to help present-day GLC researchers, as evidenced in the book by McReynolds (262) which compares most commonly used stationary phases.

Following the study of the sulfur compounds in the Wasson distillate boiling from 111° to 150° C (232° to 302° F), project interest turned to applying these separation and identification techniques to the Wilmington, California, crude oil. Liquid-solid chromatographic concentration steps were used to provide sulfur concentrate fractions for studying thiophenes and cyclic sulfides in the 111° to 150° C boiling range covered in the Wasson

studies. The initial GLC and microdesulfurization studies pointed to adsorption fraction 28 for alkyl-thiophene emphasis and adsorption fraction 31 for cyclic sulfide emphasis. This latter fraction, as well as fraction 30, was entirely cyclic sulfides.

GLC studies of alkylthiophenes, alkyl-substituted thiacyclopentanes, and thiacyclohexanes involved extensive experimentation with different stationary liquid phases to establish suitable and workable retention-time relationships. Figure 44 illustrates the GLC separation attained on the alkylthiophene concentrate fraction with four different stationary phases. The top chromatogram of this figure shows that polyepichlorohydrin separates only 2,3-di-methylthiophene as an individual component while leaving 2-ethyl- and 2,5-dimethylthiophene together as a single peak, 2-n-propyl- and 3,4-di-methylthiophene together as a single peak, and 3-ethyl- and 2,4-dimethylthiophene together as an unresolved shoulder on the leading edge of the large o-xylene peak. The second chromatogram shows that sucrose acetate isobutyrate (SAIB) satisfactorily resolves five individual thiophenes, including 2,4-dimethylthiophene, a compound unresolved by any of the other stationary phases. However, it failed to separate 3-ethylthiophene and 2,3-dimethylthiophene from o-xylene. The third chromatogram shows separations obtained with Reoplex 400. On this column the retention times of 2,4-dimethylthiophene and o-xylene are identical; however, use of both the SAIB column and the Reoplex-400 column separated all thiophenes in this Wilmington distillate. The fourth panel shows the chromatogram obtained with a DC 550 silicone oil column. This column produced only two distinct separations; namely, 3,4-dimeth-ylthiophene and 2-n-propylthiophene. 2-Ethyl- and 2,5-dimethylthiophene emerge as a mixture under one peak as do 2,4-dimethyl- and 3-ethylthiophene at a slightly later time. 2,3-Dimethylthiophene emerges from the GLC column at the retention time coinciding with o-xylene. Such binary mixtures may be trapped from the silicone column and rerun on a different column, such as the SAIB or Reoplex 400 column, for separation and identification of each individual compound.

The chromatograms of figure 44 indicate that no one of the four stationary liquids separates each thiophene as an individual peak. However, study of the chromatograms and the discussion of them indicate that a selected combination of two columns involving trapping from one column and rechromatographing the trapped material on another column of different polarity will resolve all peaks. The use of such a technique provided the
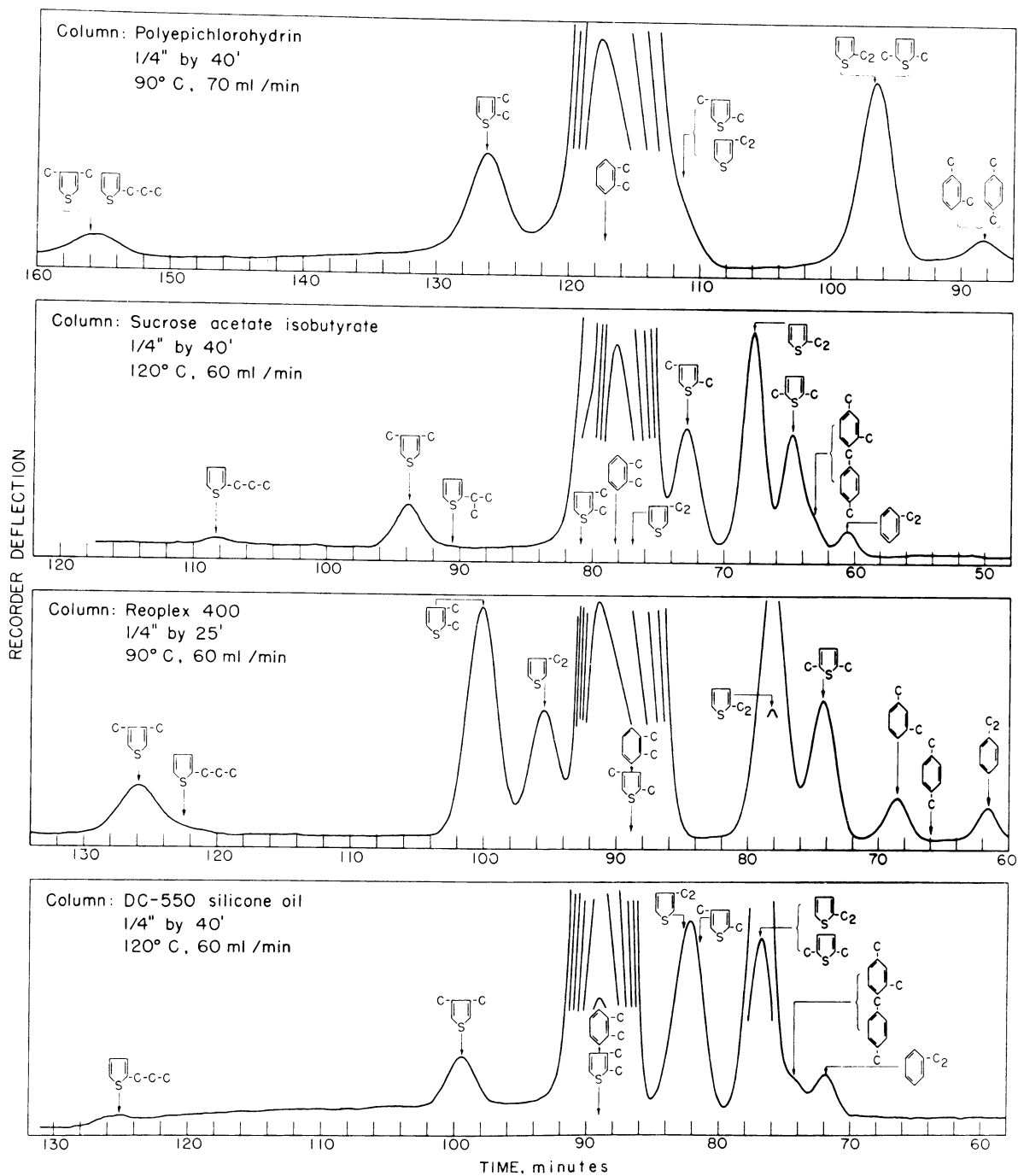
Figure 44.—Chromatograms showing resolution of thiophenes and aromatics in fraction 28 achieved with various GLC stationary liquids.

(*Reproduced by permission from reference 77.*)

necessary means to separate and identify each alkyl-thiophene both qualitatively and quantitatively.

GLC studies of cyclic sulfides were more compli-cated than the alkylthiophene studies previously described because of the increased number of isomers resulting from cis- and trans- configurations. Figure 45 shows the GLC separations attainable on the main cyclic sulfide concentrate fraction with three different stationary phases. The top chromato-gram of this figure shows several of the individual cyclic sulfides to be resolvable with the Reoplex 400 column. The middle chromatogram shows that di(2-ethylhexyl)tetraphenyl-o-phthalate as a sta-tionary phase is lacking except for the excellent resolution of 2-methylthiacyclopentane at 41 min-utes and of trans-2,4-dimethylthiacyclopentane at 50 minutes. However, the order of elution of cyclic sulfide isomers on this column compared with the Reoplex column was so widely different that, in many instances, material could be trapped from one column and rechromatographed on the other for good resolution of each individual component. The bottom chromatogram shows cyclic sulfide separations obtained with a polyphenylether, m-bis(m-phenoxyphenoxy)benzene. This particular column was especially useful in isolating 3-methyl-thiacyclopentane as a single peak—the only column to do so. This chromatogram also shows the separa-tion of cis- and trans-2,5-dimethylthiacyclopentane to be better than that obtainable with the other columns. Thus, by the use of all three stationary phases, and others such as DC 550 silicone oil, Arochlor–1260 (a chlorinated biphenyl), all indi-vidual cyclic sulfides were isolated individually for proof of structure by microdesulfurization, infrared spectroscopy, mass spectrometry, and in some instances, nuclear magnetic resonance spectrom-etry. Here again, as with the thiophene studies, no single GLC column could provide all the separa-tions necessary for isolating each individual compound.

GLC separations become more difficult with increasing boiling point of the sample because of factors such as limited availability of suitable low-volatile stationary phases; reduced detector sensi-tivity at higher temperatures if thermal conductivity detectors are used; increased problems in effecting complete sample introduction and recovery; and, of course, the greatly increased number of com-pound types and number of isomers and homologs within a given type or class.

In addition to the detailed sulfur compound studies of the 111° to 150° C (232° to 302° F) boiling range distillates, some studies employing GLC were made on selected higher boiling fractions as 170° to 180° C (338° to 356° F), 200° to 250° C (392° to 482° F), 225° to 275° C (436° to 526° F), and even a 300° to 325° C (572° to 617° F). The latter high boiling range distillate, following extensive liquid-solid chromatography, fractional crystallization, and GLC, yielded a fraction of pure dibenzothio-phene as identified by microdesulfurization, mass spectrometry, and infrared spectroscopy (416). Some early GLC work with the 200° to 250° C boiling range distillates and sulfur concentrate fractions therefrom provided much useful data, but some separations appeared impossible. For instance, in an early study of alkylbenzothiophenes (74), resolution by GLC of 2- and 3-methylbenzothio-phenes from associated 2- and 1-methylnaphtha-lenes was incomplete. However, a later study (187), using improved equipment, stationary phases, and techniques, resulted in good separation of these respective alkylnaphthalenes and benzothiophenes as denoted in figure 46. The complexity of this boiling range still dictated the use of specific chemical treatments for concentration of types of compounds and derivative formation for their identification. Derivative formation involved the use of Raney nickel desulfurization of benzothio-phenes and thiaindans to alkylbenzenes, and calcium hexamine reduction of benzothiophenes to alkyl substituted benzene thiols. Although the prepara-tion of these derivatives on a micro scale and their subsequent separation and identification by GLC mass spectrometry, infrared, and ultraviolet spectro-photometry required much experimentation, it resulted in more complete qualitative and quantita-tive data on benzothiophenes than on any other class of compounds in Wasson crude oil.

GLC has been a most versatile tool throughout the latter half of API Research Project 48 for separating and helping to identify individual sulfur compounds in crude oil fractions. GLC usage made possible the isolation and identification of many sulfur compounds which had not even been char-acterized chemically.

The development and application of special columns, involving extra long length and specially selective stationary liquid phases, combined with improved sample-trapping techniques and re-chromatographing difficulty separable pairs on columns of different polarity provided individual compound separations in most instances. Once separated and trapped from a given GLC column, these individual compounds could be qualitatively identified through the use of GLC retention time data, mass spectrometry, and infrared, ultraviolet, and NMR spectroscopy. In most instances, those GLC separated compounds, or even mixtures of
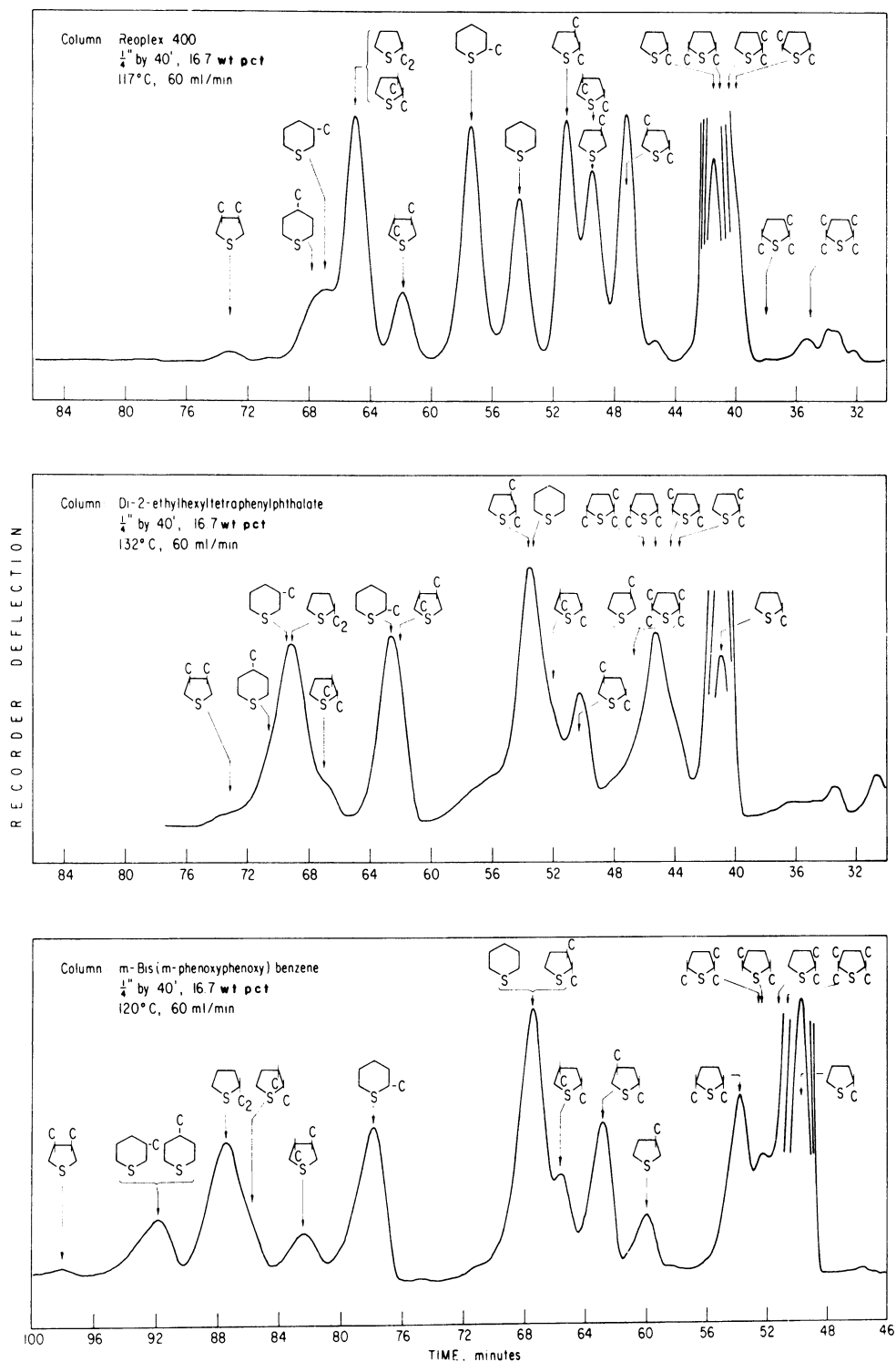
Figure 45.—Gas-liquid chromatograms showing resolution of cyclic sulfides
in fraction 31 achieved with various GLC stationary phases.

(*Reproduced by permission from reference 76.*)
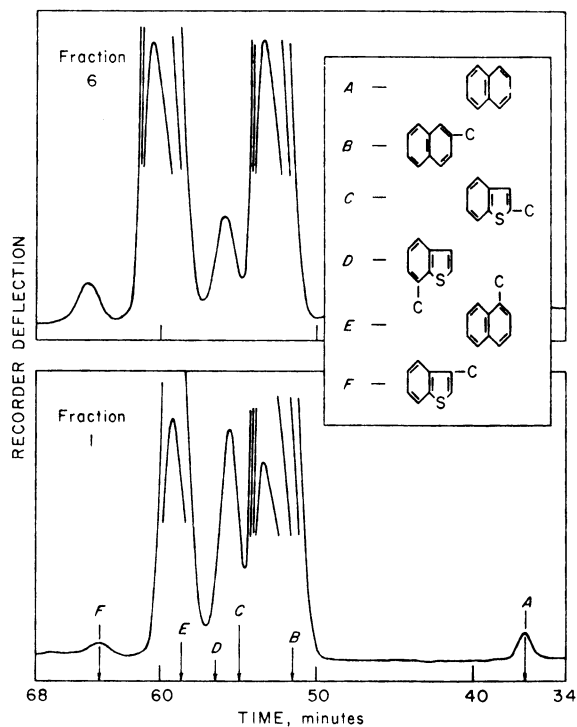
Figure 46.—Gas-liquid chromatograms of distillation fractions 1 and 6.

compounds, could be hydrogenated or treated chemically and rechromatographed for additional characterization including obtaining many useful quantitative relationships.

GLC as an analytical tool has been applied successfully to both simple and complex mixtures in the Bureau of Mines sulfur studies, and its applications continue to become even more effectual for studying the constituents of petroleum.

Thermal Diffusion

Liquid thermal diffusion was investigated in the search for new and improved methods for the separation of sulfur compounds from petroleum. This technique was first reported in 1856. From that date until about 1958, literature references to the process were scarce and dealt primarily with the application of gaseous thermal diffusion. In recent years liquid thermal diffusion has attracted increased attention. In 1951 Jones (210) developed a continuous process of liquid thermal diffusion for the separation of various petroleum stocks. Other

papers (211, 212) reported the study of tall oil in glass thermal-diffusion columns and research on the separation of organic liquid mixtures.

Although the exact mechanism of liquid thermal diffusion is not fully understood, the direction and magnitude of the concentration or separation are believed to depend to a great extent upon the relative shapes of the molecules present in the mixture. Compounds having identical molecular weights and boiling points can be separated. Many isomers may be efficiently separated. It has been observed that certain molecules, such as straight-chain molecules, will migrate to the hot wall and rise, while more compact ring structures will concentrate at the cold wall and settle.

For the separation of liquid hydrocarbon mixtures, Kramers and Broeder (238) proposed the following qualitative rules:

1. In general, for mixtures of substances with the same boiling point, the component with the smallest molecular volume will tend to move toward the cold wall.

2. In mixtures of substances with about equal molecular volumes and boiling points, the component with the smallest surface area of its molecules tends to move toward the cold wall.

3. In mixtures of molecules that have equal molecular volumes and equal surface areas, the higher boiling component tends to move toward the cold wall.

4. Of a homologous series, the component with the largest number of carbon atoms tends to move toward the cold wall.

Bibliographies of early work and discussions of theory are available in the literature, and only the papers of de Groot (93), Jones and Furry (214), Powers (329), and Stickle (393) need be cited here.

Except for two publications (427, 432) from this laboratory, the literature is essentially devoid of experimental data on the employment of thermal diffusion for the separation of sulfur compounds. This void can be explained, in part, by the unavailability of sulfur compounds in sufficient quantity and of good purity. Liquid thermal diffusion was investigated as a possible tool to augment other separation processes in the investigation of sulfur compounds in petroleum. This study has included mixtures of hydrocarbons, hydrocarbons and sulfur compounds, and various types of sulfur compounds.

Most of the separations reported in this investigation were accomplished in batch operation in 6-foot stainless steel columns of the concentric tube type. These columns have a 0.3-mm annulus and a 30-ml sample capacity. The outer tube is heated electrically with a resistance winding, and the inner

tube is cooled with tap water flowing from bottom to top. The column is equipped with withdrawal ports located at 7-inch intervals along the length of the column, to allow sample withdrawal in 10 fractions after separation has been accomplished. Special micro and semimicro columns were constructed and used for unique separations.

In an effort to improve the quantity of product and degree of separation achieved, continuous sampling devices (434) were designed and constructed. These devices permitted the slow continuous withdrawal of separated sample from the top and bottom of the column while a like quantity of charge was fed through the center port of the column. This technique, while not fully developed, was promising until the advent of gas-liquid chromatography with its superior resolution.

Figure 47 is a typical example of the type and degree of separation that may be achieved by liquid thermal diffusion. A 50-50 mixture of thiacyclohexane and ethylbenzene was separated into 10 fractions in which ethylbenzene was concentrated at the top (fraction 1) and thiacyclohexane at the bottom of the column (fraction 10). Cyclic sulfides and aromatics can be separated with excellent results, if thiacyclohexane and ethylbenzene can be considered representative of these two classes of compounds. A chain sulfide (4-thiaheptane) and ethylbenzene show very little tendency to separate by this process.
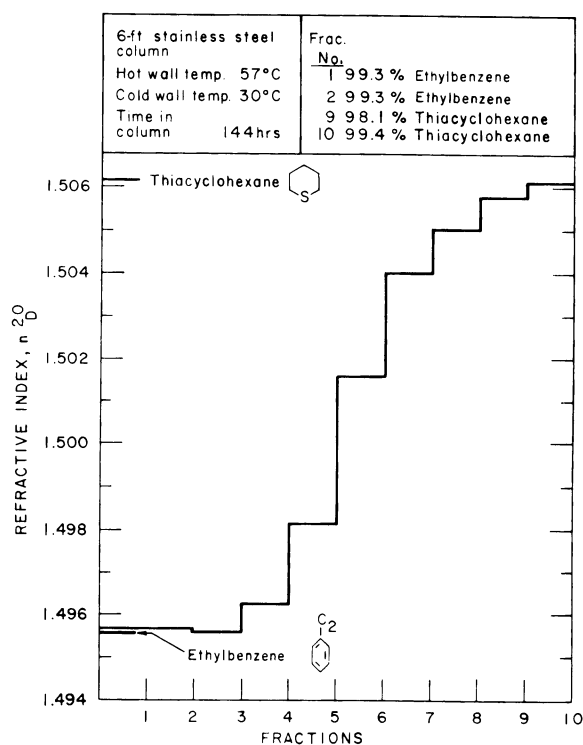
Figure 48 shows the degree, from excellent to none, of separations achieved with several binary mixtures. Accurate evaluation of the degree of separation obtained is difficult in many instances. The required sample size is such that the use of API standards is unrealistic. Impurities in commercial samples are concentrated to the top or bottom of the columns and complicate an accurate evaluation of the experiment. The use of "fair," "good," or "excellent" to describe the results of an experiment is none too precise, but serves as a guide to the degree of separation or concentration that can be expected with such materials.

A representative compound from each of the following classes of sulfur compounds or aromatics was subjected to thermal diffusion in a 50-50 mixture with a representative of each of the other classes: cyclic sulfides, alkyl cycloalkyl sulfides, chain sulfides, disulfides, thiophene, thiols, aromatic thiols, 1-ring aromatics, and naphthalenes. Qualitative results of this study are shown in figure 49.

Liquid thermal diffusion is an effective method for separating many classes of sulfur compounds. Continuous withdrawal of sample from the extreme ends of the column is somewhat superior to batch operation, in that a greater percentage of a given charge can be separated more conveniently.

Separations by thermal diffusion can be achieved in many instances on materials with identical boiling points and/or molecular weights. Thermal diffusion, while not replacing other conventional separation processes, should augment them.

SEPARATIVE PROCEDURES—CHEMICAL

Early in the course of API Research Project 48, it became apparent that, in order to identify individual sulfur compounds, it would become necessary first to extract each principal class of sulfur compound from a concentrate of the total sulfur compounds in a distillate.

Extraction and Separation of Thiols from Petroleum Distillates

Thiols lend themselves to extractive techniques by virtue of the acidic sulfhydryl hydrogen when

Figure 47.—Separation of ethylbenzene and thiacyclohexane by liquid thermal diffusion.

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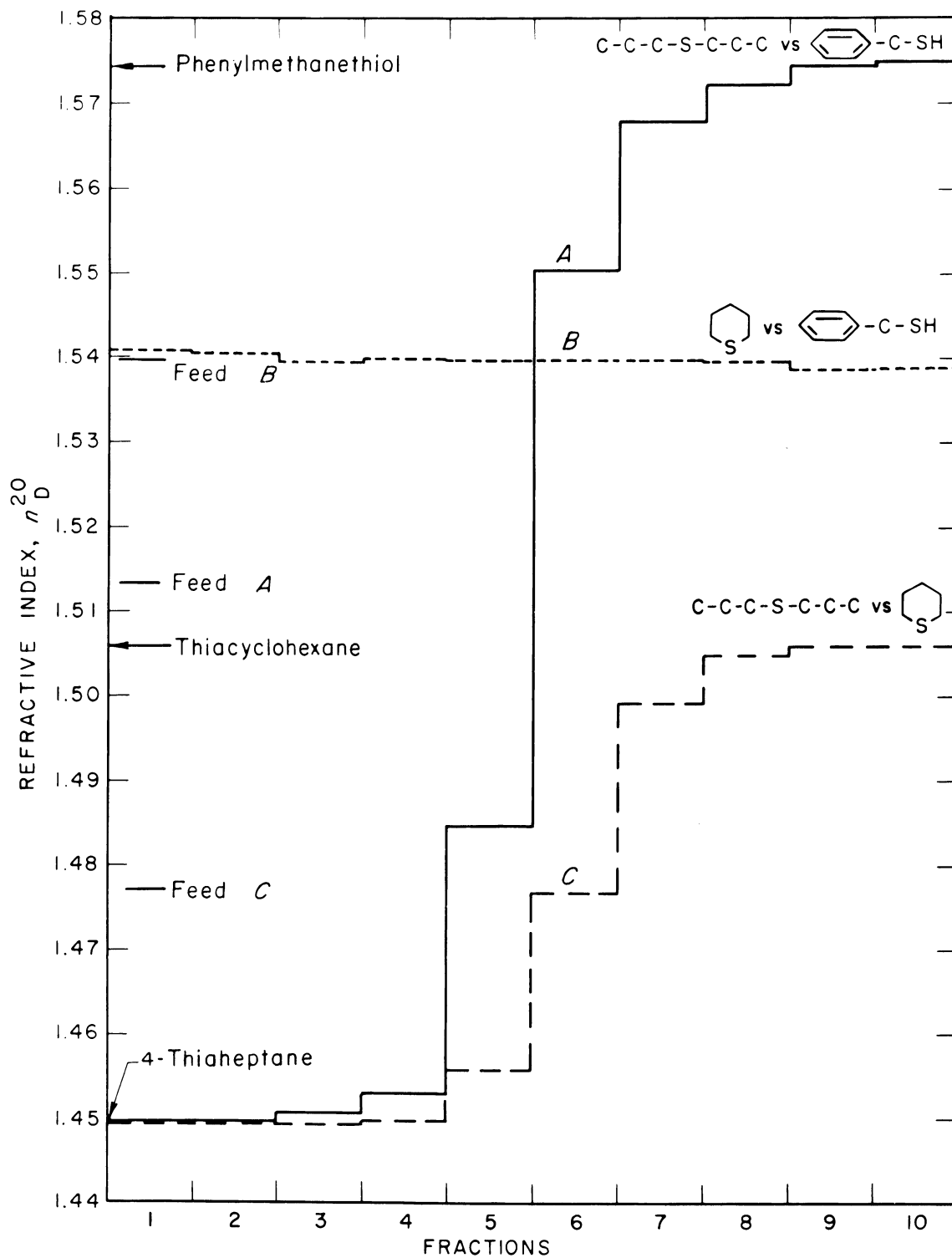
Figure 48.—Curves illustrating separations classified from "excellent" to "no separation."

KEY

Ex	— Excellent	P	— Poor
VG	— Very good	VP	— Very poor
G	— Good	N	— None
F	— Fair	NT	— Not tested

Figure 49.—Degree of separation achieved by liquid thermal diffusion.

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aqueous sodium or potassium hydroxide is used. Extraction efficiency falls rapidly as the molecular weight of the thiol increases. While aqueous alkali with added solutizer or aqueous-alcoholic alkali solutions improve the extractability of low molecular weight thiols, the higher molecular weight thiols are not removed with adequate efficiency, and a more effective reagent was sought for their extraction.

A reagent described by Moss, Elliott, and Hall (*292*) for the titration of phenols and other very weak acids was tested to determine its suitability as an extractant for thiols. The reagent consists of a solution of sodium aminoethoxide in anhydrous ethylenediamine. The strength of the reagent, as used in this work, was approximately 1 to 2 N in sodium aminoethoxide. While the extraction is sometimes applied to whole distillates, it is generally preferable to concentrate the thiols by adsorption and dilute the concentrate with pentane before extraction to minimize the extraction of aromatic hydrocarbons. It is necessary to back extract the extract layer several times with pentane to remove any dissolved aromatic hydrocarbons and sulfides before releasing the thiols. The thiols are released simply by diluting the extract layer with ice and water containing hydrochloric acid equivalent to the sodium aminoethoxide. The thiols are recovered by steam distillation into the trap shown in figure 50, or may be extracted with pentane.

This procedure was tested on various thiols rang-
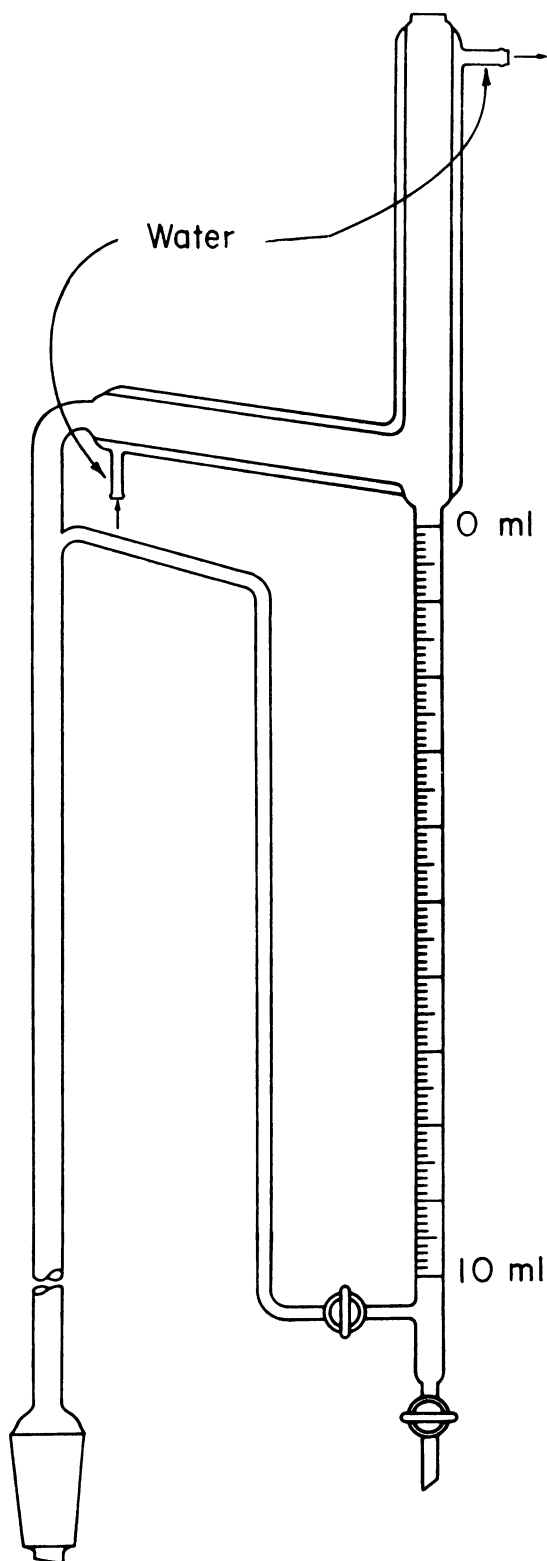
Figure 50.—Distillation trap.

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ing from C_8 to C_{16} including primary, secondary, and tertiary thiols. The results are summarized in table 21. Most of the compounds tested were commercial materials used without purification. In

Table 21.—Efficiency of thiol extraction

Thiol	Recovery, percent	Residue, percent
Cyclohexanethiol.................	95	5
1-Octanethiol....................	95	......
2-Octanethiol....................	98	......
tert-Octyl mercaptan [1]...........	90	2
1-Decanethiol....................	90	2
1-Dodecanethiol.................	85	3
tert-Dodecyl mercaptan [1]........	96	2
tert-Tetradecyl mercaptan [1]......	85	3
1-Hexadecanethiol...............	80	Solid
tert-Hexadecyl mercaptan [1].......	70	20
tert-Hexadecyl mercaptan [1].......	95	3

[1] Structure not known.

each test, 1 ml of thiol dissolved in 25 ml of isopentane was extracted twice using 50- and 10-ml portions of 1.1 N reagent for each test. The thiol was recovered by dilution, partial acidification, and steam distillation of the extract. Each residue was tested with silver nitrate for thiol and found negative in every instance. A similar test on a mixture of 1-octanethiol and 5-thianonane (n-butyl sulfide) to determine the separability of thiols and sulfides yielded 95-percent recovery of thiol which titrated 98 percent by silver nitrate titration. The theoretical amount of residue was recovered. Similarly, a mixture of 1-dodecanethiol and 7-thiatridecane yielded 87-percent thiol recovery of 99-percent purity.

Application to Distillates

All distillates boiling above 150° C (302° F) were extracted first with aqueous sodium hydroxide to remove phenols and aromatic thiols, if present. Examination of the aqueous extracts, however, failed to detect any aromatic thiols in these distillates. These extractions were conducted in an atmosphere of nitrogen.

A concentrate of sulfur compounds prepared from 8,973 g of a 111° to 150° C (232° to 302° F) Wasson crude oil distillate by adsorption on alumina was extracted twice with 125 ml and once with 100 ml of 1.9 N sodium aminoethoxide in ethylenediamine. The combined extracts were back extracted four times with 50 ml of isopentane to remove aromatic hydrocarbons and sulfides dissolved in the extract. The extract was diluted with 500 g of crushed ice and dilute hydrochloric acid

(78 ml concentrated HCl in 500 ml of water), and the thiols were distilled from the mixture into a trap similar to that shown in figure 50, to yield 22.5 g of thiols. A detailed treatment of the sample is outlined in figure 51.

Wasson crude oil distillates boiling from 150° to 220° C (302° to 428° F) and 200° to 250° C (392° to 482° F) were concentrated on silica gel and alumina and extracted similarly with sodium aminoethoxide following a preliminary extraction with 20 percent aqueous sodium hydroxide. The 150° to 220° C distillate yielded 6 g of extract which contained both thiols and phenols and was treated with lead acetate to separate thiols and phenols. The regenerated thiol fraction was treated with liquid ammonia to separate primary and secondary from tertiary and aromatic thiols. The fraction precipitated by ammonia was analyzed by mass spectrometry and consisted of cyclohexanethiol and homologs. The filtrate was very small and did not contain detectable amounts of aromatic thiols. The thiol content of Wasson crude oil diminishes rapidly with increase in boiling point becoming insignificant above about 200° C (392° F).

The sulfur-aromatic concentrate from 1,900 g of 200° to 250° C distillate was extracted twice with 20 percent sodium hydroxide and yielded 2.2 g of extract. Extraction with the sodium aminoethoxide reagent yielded an additional 5 g; however, mass spectrometric analysis detected only minor amounts of thiols (m/e 146, 160, 164), the remainder being phenols and napthalenes (occluded by solubility in the reagent).

One special study by Research Project 48 had as its objective the unequivocal identification of disulfides in Deep River, Michigan, crude oil. For this purpose, it was necessary to prepare a distillate free of thiols while excluding oxygen in each step of the handling from collection of the sample through the extraction of thiols. For the purpose of extracting thiols from this distillate, a 12-liter, three-neck flask was fitted with a vacuum stirrer, a dropping funnel with pressure-equalizing tube, and an adjustable polyethylene tube containing a stopcock for withdrawing the extract layer.

The system was evacuated and filled with purified-grade nitrogen several times. The sample (3,551 g) was then poured into the flask while blanketed with a stream of nitrogen. Half of the sodium aminoethoxide reagent, made by reacting 5 g of sodium with 50 ml of monoethanolamine and diluting to 200 ml with anhydrous ethylenediamine, was added from the dropping funnel and the mixture stirred for 15 minutes. Following stirring, stratification occurred, thus allowing the extract

Figure 51.—Treatment of 111° to 150° C boiling range Wasson distillate to obtain thiol concentrate.

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layer to be withdrawn into a nitrogen-filled flask. The other half of the reagent was added and the extraction repeated. A sample of the oil layer showed the absence of thiols by electrometric titration, so the sample was washed twice with ethanolamine to collect adhering extract from the walls of the flask.

The extract was concentrated by vacuum distillation of most of the amines and dissolved aromatics; however, some thiols also appeared in the distillate.

It was necessary to reconvert them to their sodium salts and extract the dissolved aromatics with pentane. The thiols plus phenols were then regenerated from the extract by dilution with water, acidification equivalent to the sodium present, and steam distillation. The yield was 12 g. The raffinate was water washed free of amines and used in the subsequent investigation.

The composition of the thiol-phenol extract was not studied in detail; however, an effort was made

to detect benzenethiol and toluenethiols with negative results.

Separation of Thiols

A method was developed for separating certain primary and secondary thiols from tertiary thiols by mercaptide formation in liquid ammonia. The method is based on the discovery that primary and secondary thiols in the C_6–C_{12} range, if not excessively branched, form insoluble ammonium mercaptides. Ammonium mercaptides are unstable and dissociate when allowed to warm to room temperature. Methyl ammonium mercaptide is exceptional in this respect in that it remains undissociated at room temperature. It is sparingly soluble in liquid ammonia, whereas ethyl ammonium mercaptide is highly soluble. Mercaptide formation may be used to separate methanethiol from hydrogen sulfide, as ammonium sulfide is very soluble in liquid ammonia.

The method found limited application because of the limited range over which it is applicable and the diminishing thiol content of the crude oil with increase in boiling point. However, the application of the method to a 150° to 220° C (302° to 428° F) thiol extract from Wasson crude oil is briefly described. The extract was dissolved in seven volumes of dimethyl ether and added to 80 volumes of liquid ammonia. After chilling to −78° C (−108° F), the sample was filtered and the cake compressed on the filter. Regeneration was accomplished by warming to room temperature and washing the filter with isopentane. After evaporation of the solvents, the precipitate yielded 53 percent of the charge and the filtrate 25 percent. The high loss is believed to have occurred during evaporation of the large amounts of solvents used. The filtrate consisted largely of phenols which were extracted with the thiols.

Extraction of Sulfides

Except in the lowest boiling range, the identification of individual sulfides in petroleum distillates requires that the sulfides be isolated as a class from the other components because of the complexity of these distillates. Various reagents for removing sulfides from petroleum distillates have been used but failed to meet the requirements of the project in one or more respects. In the method of Ball (22) for sulfur type analysis, mercurous nitrate and mercuric nitrate are used for removing type I and type II sulfides, respectively. The method does not provide for recovery of the sulfides, indeed extensive change in composition of the sample may occur. Mercuric chloride long has been known to yield insoluble precipitates with sulfides from which the sulfides may be recovered by treatment with dilute hydrochloric acid, hydrogen sulfide, or sodium sulfide. However, extensive decomposition may occur, particularly during regeneration with hydrochloric acid.

Challenger, Haslam, Bramhall, and Walkden (62) used mercuric acetate for extracting sulfides from shale oil. Birch and McAllan (41) used the acetate for fractional extraction of sulfides from the acid sludge of a Middle East crude oil. Mercuric acetate gives water-soluble complexes with the lower boiling sulfides, but the complexes become increasingly oil soluble with increase in molecular weight of the sulfide, so that the usefulness of the reagent is limited to the lower and middle boiling ranges. All mercury compounds have the disadvantage of causing cleavage of tertiary carbon-sulfur bonds.

Another method, suggested by Dr. Stanley Birch was tested. It is based on oxidation of the sulfides to sulfoxides with t-butyl hydroperoxide in glacial acetic acid, extraction of the sulfoxides with 80 percent sulfuric acid followed by reduction of the sulfoxides by titanium trichloride. The method yielded a sulfide extract of good quality, but losses were high, and the remainder of the sample appeared to be affected adversely.

The formation of sulfonium salts was considered as a means of extracting sulfides because they are insoluble in hydrocarbons and soluble in water. Methyl iodide is the best known reagent which forms sulfonium salts, but a literature study and laboratory tests proved it to be unsatisfactory because the reaction reaches equilibrium far short of completion, and methyl displaces higher alkyl groups:

$$R\text{---}S\text{---}R' + CH_3I \rightleftharpoons [R\underset{+}{\overset{\overset{\displaystyle CH_3}{|}}{\text{---}S\text{---}}}R']I^- \overset{CH_3I}{\rightleftharpoons}$$

$$[CH_3\underset{+}{\overset{\overset{\displaystyle CH_3}{|}}{\text{---}S\text{---}}}R']I^- \overset{CH_3I}{\rightleftharpoons} [(CH_3)_3S^+]I^-$$
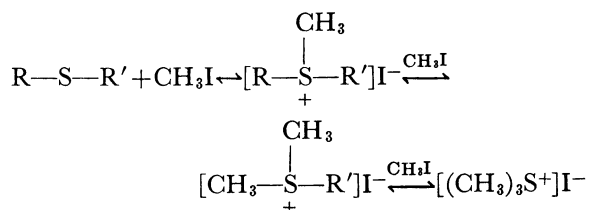
Methyl-p-toluenesulfonate is a strong alkylating agent which forms sulfonium salts readily without displacement of other alkyl groups, and one method of extracting sulfides developed by Project 48 is based on this reaction. The sulfides are regenerated from the sulfonium salt by heating with a tertiary amine. Alternately, the sulfides may be

regenerated from an aqueous solution of the sulfonium salts by heating with sodium sulfide. The formation and regeneration reactions are shown in the following sequence:

method, but it produces no volatile byproducts (dimethyl sulfide).

It was discovered upon applying the reaction of methyl-*p*-toluenesulfonate with petroleum distil-

The amine route, using triethanolamine, was generally used because the regenerated sulfides can be diluted with water and steam distilled from the reaction mixture. It is, however, more prone to the occlusion of hydrocarbons than is the sulfide

lates that aromatic hydrocarbons, particularly naphthalenes, are fairly soluble in the sulfonium salts but may be removed by repeated extraction of the sulfonium salts with pentane. Table 22 shows the results of the application of this method to a

Table 22.—Efficiencies of extracting various sulfides from ternary mixtures with methyl-*p*-toluenesulfonate

Sulfide	Formula	Yield of regenerated sulfide, percent	Contaminants in extract	
			Diethylbenzene, percent	Ethyl-naphthalene, percent
2-Methyl-3-thiaheptane......................	C—C—S—C₄	91	....	....
5-Thianonane.................................	C₄—S—C₄	94	<0.1	0.9
2,2,4,4-Tetramethyl-3-thiapentane [1].............	C—C—S—C—C	....	....	....
Thiacyclopentane............................		83	< .1	.3
Thiacyclohexane.............................		96	.2	.4
2-Methylthiacyclopentane.....................		80	.7	1.7
(1-Thiahexyl)cyclopentane....................		89	.4	1.3
4-Methyl-(1-thiaethyl)benzene.................		90	....	....

[1] Decomposed during heating period.

series of ternary mixtures each containing 40 percent of a sulfide, 30 percent diethylbenzene, and 30 percent ethylnaphthalene.

Application to Distillates

A 70-ml aromatic-sulfide concentrate from Wasson 150° to 220° C (302° to 428° F) boiling range was heated on a steam bath for 18 hours with 62 g of methyl-p-toluenesulfonate. A viscous liquid sulfonium salt layer gradually separated and at the end of the reaction was washed repeatedly with pentane by mixing on a mechanical shaker. The sulfides were regenerated by heating the sulfonium salts for 16 hours with 50 ml of triethanolamine, diluting with water and distilling by steam. The yield of sulfides was 20 ml (about 18.5 g). Half of this material was percolated through a column of alumina and separated into 36 fractions. For comparison, 10 ml of the aromatic-sulfide concentrate was percolated through a similar alumina column. Mass spectral type analyses of the fractions from both runs are shown in figure 52. It is seen that the separation procedure was very effective removing aromatics. Ultraviolet analysis confirmed this conclusion.

Fraction 15 from the alumina percolation of the sulfide extract was selected for more detailed study of composition by gas-liquid chromatography and catalytic microdesulfurization. Figure 53 shows a chromatogram of this fraction as obtained on a $\frac{1}{4}$-inch by 25-foot Reoplex-400 column with the area trapped for desulfurization shaded. At least five possible compounds would emerge under this peak, if present. Desulfurization of the trapped material yielded ethane, propane, n-butane, and n-pentane (fig. 54).

Consideration of the combinations of radicals with sulfur which would produce sulfides emerging between the 9.5 to 10 minute limits of the trapped area permits only four structures:

(I) C_2—S—C—C_3, (II) C_2—S—C—C_2,

             | |

             C   C

(III) C—C—S—C_4, and (IV) C_3—S—C—C_2.

               | |

               C   C
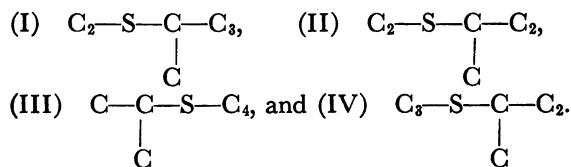
Of these structures, only I and II can yield ethane and n-pentane; similarly, only III and IV can yield propane and n-butane. Infrared spectra yield some additional information. Absorption bands at 12.75, 13.00, 15.00, and 13.40 microns charac-
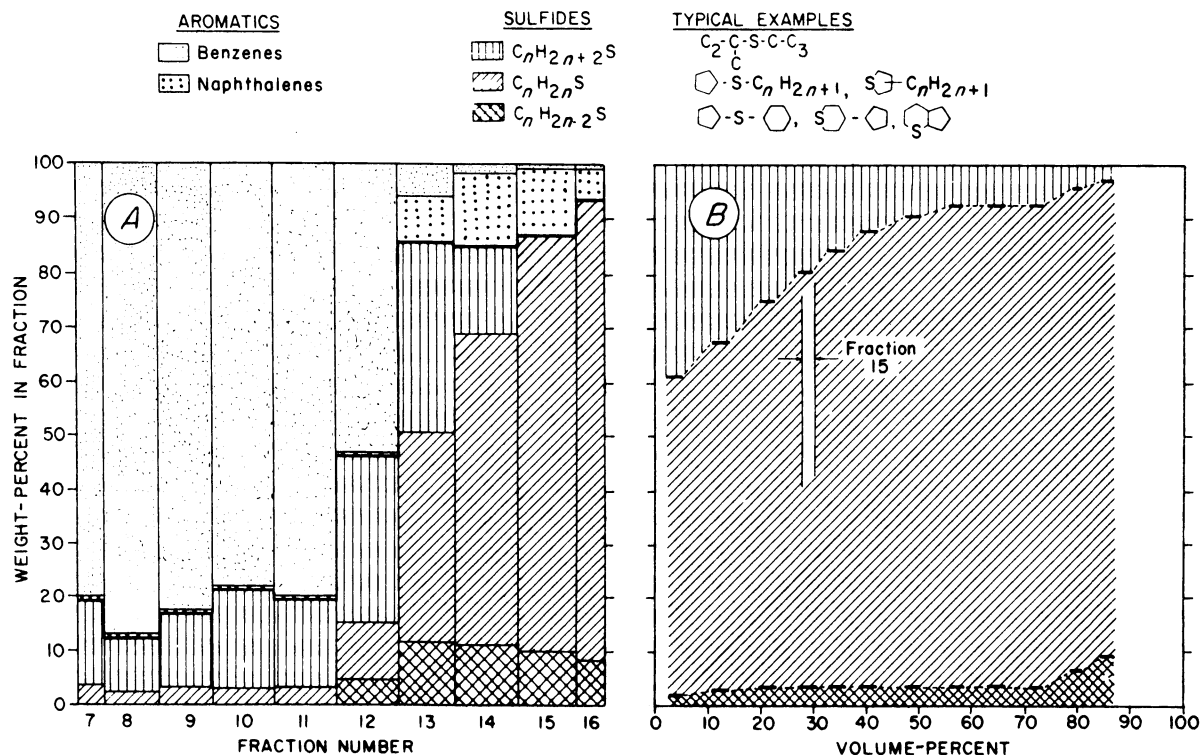
Figure 52.—Mass-spectrometer type analyses of fractions from alumina filtration.
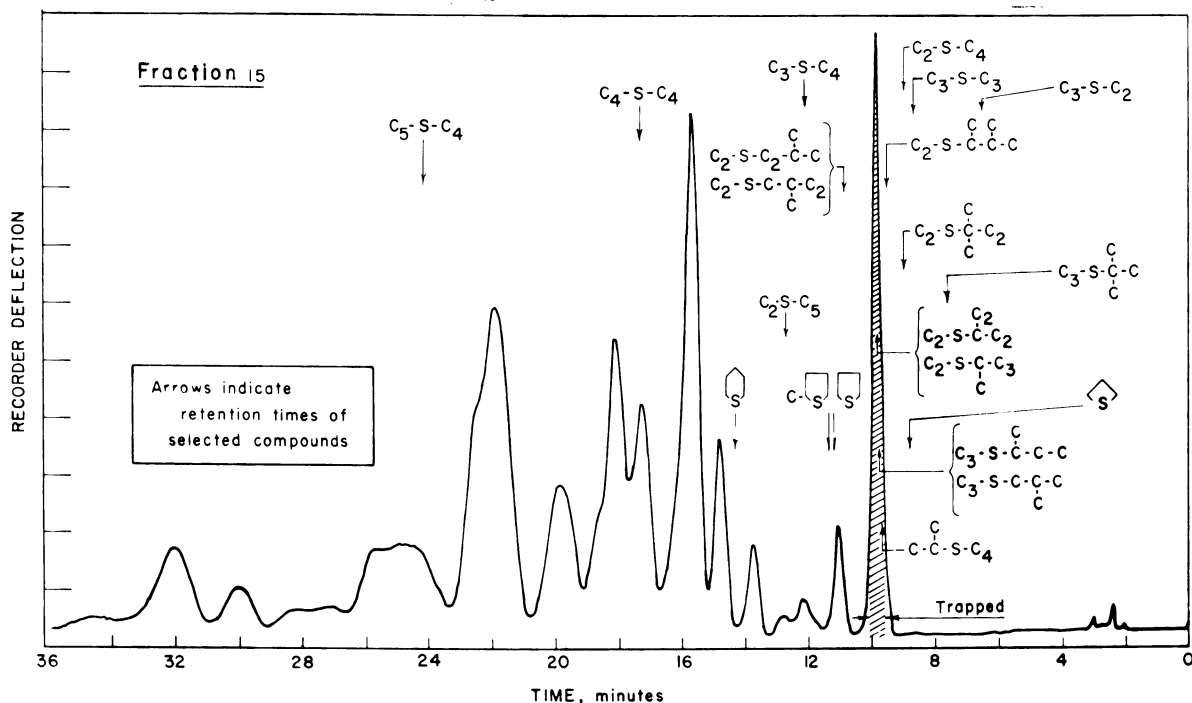
Figure 53.—Gas-liquid chromatogram of an alumina filtration fraction of a sulfide extract.

terized 4-methyl-3-thiaheptane I as positively present. Likewise, a doublet at 7.22 and 7.30 microns, characteristic of the isopropyl group, identified 2-methyl-3-thiaheptane III as the second major constituent. The other possible compounds II and IV, if present, are minor constituents.

Hydrogen Iodide Method

Hydrogen halides combine with sulfides at low temperature to form sulfonium halides which are insoluble in hydrocarbons. Since hydrogen iodide is somewhat more reactive than hydrogen chloride or hydrogen bromide in this respect, it was chosen for this work. Hydrogen iodide was generated from the elements in an apparatus (fig. 55) which consists of a reaction tube having a reservoir of iodine heated by a glass chimney and a reaction tube packed with 5 percent platinum on charcoal catalyst heated by a furnace to about 200° C (392° F). This generator is capable of producing hydrogen iodide up to almost 100 percent concentration without excess hydrogen or iodine. The hydrogen iodide is passed directly into the reactor either through the fritted disk or through a tube inserted from the top of the reactor.

The reaction vessel, shown in figure 56, contains a fritted disk in the bottom for filtration of the precipitated sulfide addition products. The

hydrogen iodide may be added to the sample solution through the disk, but generally is added through another tube introduced through the top of the reactor. n-Pentane is the solvent most commonly used, but n-butane is useful for the more
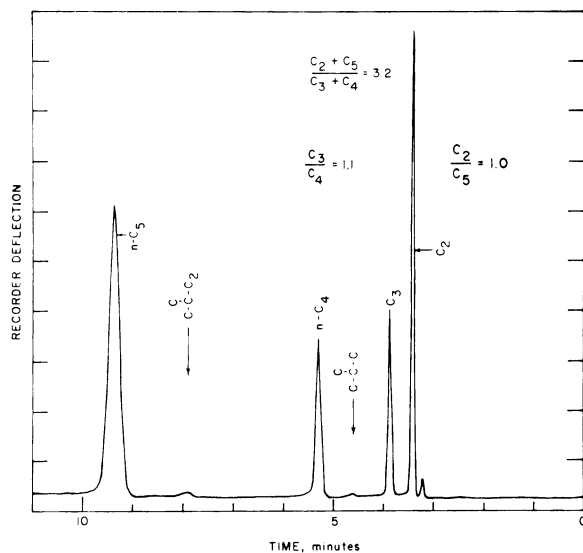
Figure 54.—Products of desulfurization of material producing shaded peak in figure 53.
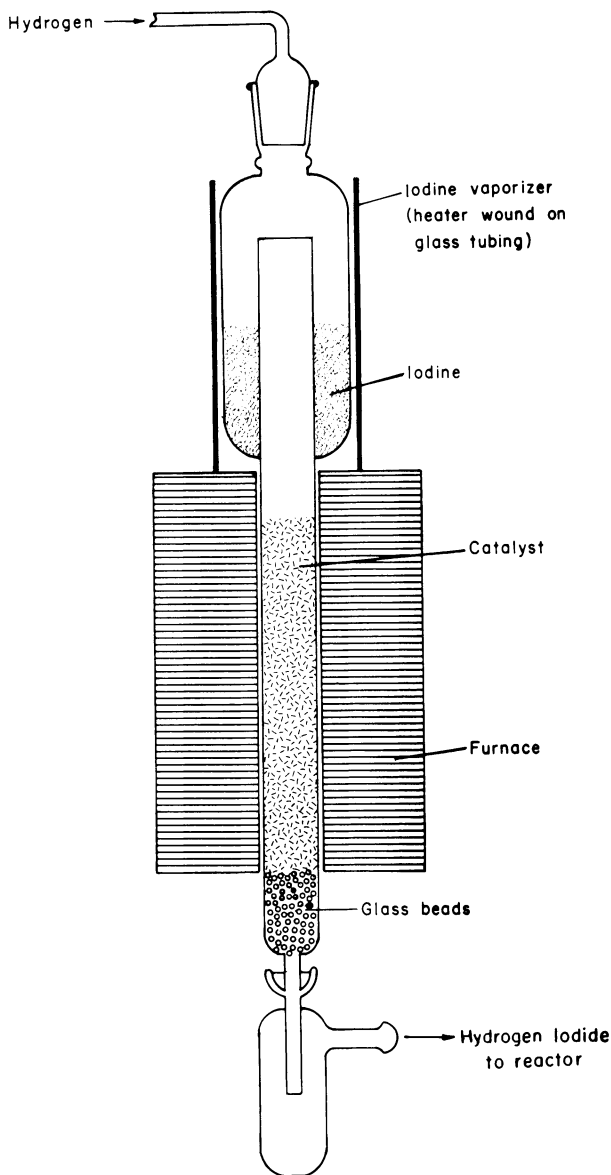
Figure 55.—Hydrogen iodide generator.

Figure 56.—Reaction vessel for extraction of sulfides with hydrogen iodide.

volatile samples. The concentration of sample in solvent is generally 1 to 5 percent.

The procedure generally used in this investigation is briefly described as follows: The solution of sample is cooled in a suitable container to −78° C (−108° F) and held at this temperature at least 1 hour. If material crystallizes, it is removed by filtration and the filtrate transferred to the reaction vessel. The reactor is immersed in a Dewar flask, packed with Dry Ice, and chilled to −78° C after which hydrogen iodide is passed in until the solution is nearly saturated. A precipitate forms

immediately but may require several hours to settle sufficiently for filtration or decantation. Precipitates from petroleum fractions are always amorphous, tacky semisolids, and it is generally preferable to allow complete settling and to decant rather than attempt filtration. After washing the precipitate with cold solvent containing hydrogen iodide, water is added quickly to the precipitate. The precipitate immediately dissociates to its components and the sulfide is removed from the vessel

by steam distillation. It is generally necessary to add some sodium thiosulfate to the reactor to remove small amounts of free iodine before distillation.

The yields of nonaromatic sulfides extracted by the foregoing procedure are nearly theoretical in the molecular-weight range covered in this report. Table 23 shows the yields for a series of sulfides

Table 23.—Extraction of sulfides by hydrogen iodide method

Name	Formula	Recovery, volume-percent
2-Methyl-3-thiaheptane	C—C(C)—S—C₄	100
2,4-Dimethyl-3-thiahexane	C—C(C)—S—C(C)—C₂	100
5-Thianonane	C₄—S—C₄	99
2,5-Dimethyl-4-thiaheptane	C₂—C(C)—S—C(C)—C₂	100
2,2,4,4-Tetramethyl-3-thiapentane	C—C(C)(C)—S—C(C)(C)—C	98
Thiacyclopentane	(ring with S)	102
Thiacyclohexane	(ring with S)	102
2,5-Dimethylthiacyclopentane [1]	C—(ring with S)—C	94
4-Methylthiacyclohexane [1]	C—(ring with S)	96
2-n-Propylthiacyclohexane	(ring with S)—C₃	96
(2,2-Dimethyl-1-thiapropyl)-cyclopentane	C—C(C)(C)—S—(ring)	100
2-Isobutylthiacyclohexane [1]	C—C(C)—C—(ring with S)	91
(1-Thiahexyl)cyclopentane	(ring)—S—C₅	98

[1] Unpurified preparation.

containing primary, secondary, and tertiary C—S bonds. Unlike other methods, the hydrogen iodide method extracts tertiary alkyl sulfides in excellent yield and without visible cleavage of the C—S bond. Conversely, the hydrogen iodide method is less effective than the methyl-p-toluenesulfonate method on sulfides containing one or more aromatic rings such as aryl alkyl sufides and thiaindans.

A 170° to 180° C (338° to 356° F) Wasson crude oil distillate was freed of thiols and the sulfides concentrated further by alumina adsoprtion. The sulfide concentrate, containing 13.6 percent sulfur, was treated in n-butane solution with hydrogen iodide at −78° C (−108° F). A sulfide extract constituting 62 percent of the concentrate and containing 20.3 percent sulfur resulted. Figure 57 shows gas chromatograms of the concentrate before extraction (middle panel), the sulfide extract (top panel), and the residue (bottom panel).

The residue consisted mostly of alkylbenzenes of which one (probably 1,4-dimethyl-2-ethylbenzene) predominates. A small amount of this aromatic hydrocarbon carried over into the sulfide extract and is indicated in the top panel. Limited studies of the composition of the sulfide extract conducted similarly to those just described resulted in the firm or tentative identification of six chain sulfides and one cyclic sulfide.

The hydrogen iodide method was applied to a series of adsorption fractions of a Wasson crude oil 200° to 250° C (392° to 482° F) distillate. Considerable difficulty was caused by the occlusion of naphthalenes and benzothiophenes in the precipitate, making necessary one or more retreatments of some fractions. (Present refinements in technique have overcome most of this difficulty.) The final extracts of the separate adsorption fractions were combined and distilled on a spinning band column into 23 fractions and a residue. Each fraction was given a mass spectrometer type analysis. The results are shown in table 24 and figure 58. Monocyclic sulfides are more abundant than other classes yet diminish as bicyclic sulfides increase. Chain sulfides show a gradually diminishing trend becoming a minor component in the residue.

Separation of Chain and Cyclic Sulfides by Zinc Chloride Extraction

In the early days of API Research Project 48, it was discovered that concentrated zinc chloride solutions are capable of extracting cyclic sulfides with a considerable degree of selectivity over chain sulfides. Experiments aimed at extracting the cyclic sulfides selectively from an aromatic hydrocarbon-sulfide concentrate of a Wasson crude oil 111° to 150° C (232° to 302° F) distillate were moderately successful, but handling losses were high.

Initially a solution containing 1.25 g of zinc chloride per ml of solution (1 g $ZnCl_2$ +0.5 ml H_2O) was used, but was too weak to be very effective. A stronger solution containing only half the amount of water caused the mixture to separate into three
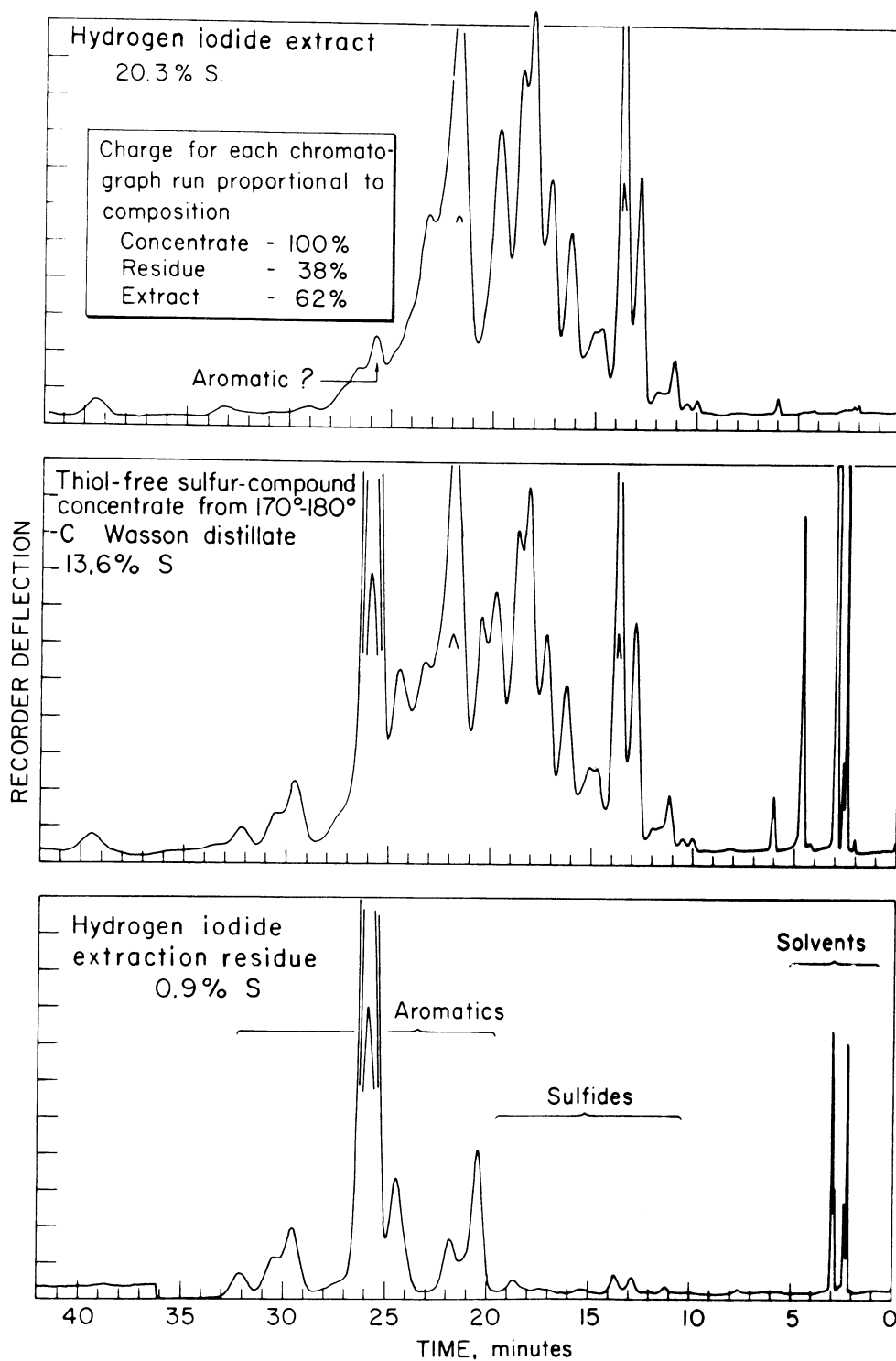
Figure 57.—Gas-liquid chromatograms showing separation of sulfides from sulfur compound concentrate by hydrogen iodide extraction.

KEY

Series-12, naphthalenes	Series +2, cycloalkyl sulfides
Series-6,-20, benzothiophenes, alkyl benzenes	Series-10,-24, cycloalkyl sulfides
Series-4,-18, thiaindans, thiatetralins and other sulfur compounds	Series-8,-22, chain sulfides (tetralin-indans)
Series 0,-14, biphenyl, alkyl thiophenes, thienothiophenes, tricycloalkyl sulfides	
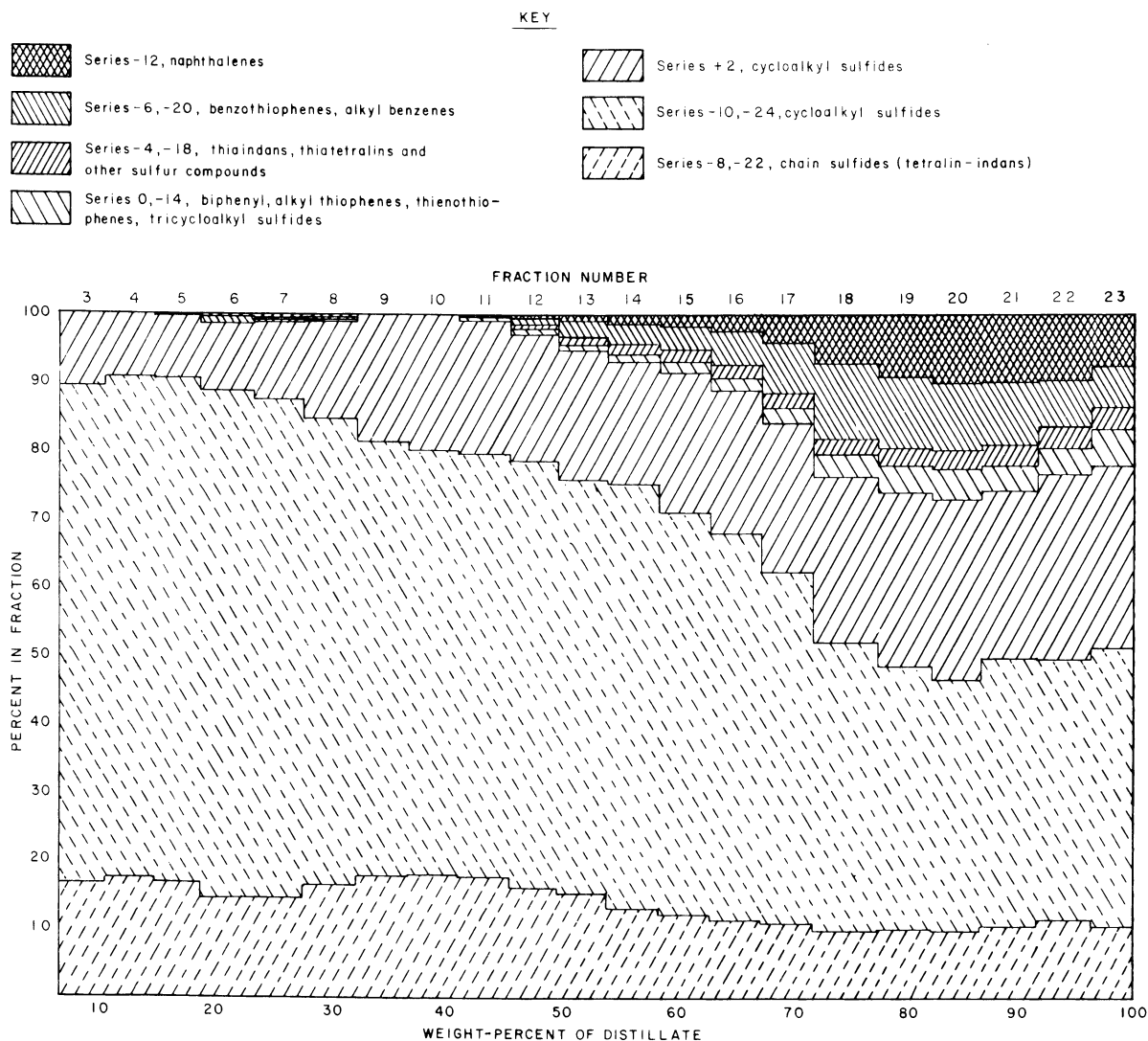
Figure 58.—Sulfur compound distribution in a sulfide extract from Wasson 200° to 250° C distillate.

layers. The bottom layer was zinc chloride solution containing sulfides. The middle layer appeared to contain zinc chloride complexes of both sulfides and aromatic hydrocarbons which were separated by a series of extractions with a zinc chloride solution of intermediate strength (3 g $ZnCl_2 + 1$ ml H_2O). The combined sulfide extract fractions then were fractionally extracted with zinc chloride, 1.25 g per ml, into 38 fractions.

The density of the fractions decreased steadily from 0.931 for fraction 1 to 0.888 for fraction 38. The cyclic and chain sulfide fractions were composited and distilled. The distillate fractions were used for identification studies.

Later in the project when GLC and a greater variety of reference compounds became available, some further evaluation of zinc chloride extraction was made using an eight-component blend of the following sulfides: 2,4-dimethyl-2-thiapentane (diisopropylsulfide), 2-thiaheptane (1-pentylmethylsulfide), 3,3-dimethyl-2-thiapentane (t-pentylmethylsulfide), 3-ethyl-2-thiapentane (3-pentylmethylsulfide), 3-methylthiacyclopentane, 2,2,5-trimethylthiacyclopentane, 2-methyl-3-thiaheptane (n-butylisopropylsulfide), and cyclopentyl-2-thiaethane (cyclopentylmethylsulfide).

A pentane solution of the blend was extracted four times with a 1.5 g per ml solution of zinc chlo-

Table 24.—Semiquantitative analysis by low ionization voltage mass spectrometry of distillation fractions from sulfide extract of Wasson 200° to 250° C material

Series	Compound or Class	Parent Peak	Fraction																				
			3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
+2, −12	Naphthalenes:																						
	C10	128				0.4	0.6	0.5			.3	.5	.8	1.2	1.6	2.4	4.0	7.1	8.5	9.3	9.1	7.8	5.0
	C11	142																	.5	.5	.6	1.1	1.9
	C12	156																					
	Total aromatics		0.0	0.0	0.0	0.4	0.6	0.5	0.0	0.0	0.3	0.5	0.8	1.2	1.6	2.4	4.0	7.1	9.0	9.8	9.7	8.9	6.9
+2, −12	Bicycloalkyl sulfides:																						
	C8S	142	5.2	2.9	1.4	0.7	0.8	1.0	0.9	0.7													
	C9S	156	4.8	5.3	5.4	6.0	6.4	7.5	7.6	6.5	5.7	4.3	3.6	2.5	2.2	1.5	1.2	0.8	.7	.7	.7	.6	.6
	C10S	170	.5	1.0	2.3	3.0	4.1	5.7	8.8	9.5	10.5	10.1	9.6	9.0	10.1	9.8	9.5	8.6	7.7	7.5	7.2	6.7	6.0
	C11S	184							1.2	2.9	3.2	4.0	5.7	6.2	7.9	9.2	10.5	13.3	15.7	16.4	15.4	16.5	15.4
	C12S	198													.2	.4	.5	1.5	1.9	2.3	2.9	3.9	5.1
0, −14	Thiadamantanes and/or other tricyclic sulfides:																						
	C10S	154			.2		.3	.2					.8				.4	.7	.9	1.1			
	Thiophenes and/or thienylthiophenes:																						
	C11S	168									.6	.4		.6	.8	.8	1.0	1.3	1.3	1.2	1.4	1.4	2.2
	C12S	182										.4	.8	.5	.5	.7	.8	1.2	1.3	1.8	1.7	1.9	2.3
	C13S	196																	.3	.4	.5	.5	2.9
−4, −18	Tetracycloalkyl sulfides and/or terthienyls:																						
	C9S	150										.9	1.9	2.7	3.4	4.9	7.4	10.9	10.4	9.9	8.0	5.3	3.3
	Thiaindans-thiatetralins, dialkyl disulfides:																						
	C10S	164				1.1	.3	.3				.7	.7		.5	.4	.4	.7	1.1	1.3	1.8	2.1	2.5
−6, −20	Benzothiophenes:																						
	C8S	134	12.9	9.8	6.2	3.7	2.9	1.9	1.0	.5													
	C9S	148	3.7	7.6	10.3	10.7	10.2	11.8	11.6	10.2	8.8	6.2	4.4	3.3	2.4	2.1	1.6	.8	.6	.8	.3	.2	.3
	C10S	162			.3	Tr.	1.4	2.6	5.2	7.2	8.8	9.4	8.7	8.5	8.5	7.5	6.8	5.6	5.5	5.0	4.9	4.9	4.2
	C11S	190										.5	1.2	1.3	1.3	1.8	2.6	3.4	4.0	4.1	4.8	5.3	5.0
−8, −22	Alkyl sulfides and/or indanothiophenes:																						
	C9S	160																					
	C10S	174																					
	C11S	188																					
	C12S	202																					
	C13S	216																					
−10, −24	Cycloalkyl sulfides and/or thienyl sulfides:																						
	C8S	144	19.1	6.4	2.4	.7	1.0	.6	.3		.3	.4	.4	.4	.3	.3	.2	.2	.2	.3	.3		.3
	C9S	158	46.3	54.7	51.6	48.1	35.7	23.6	11.9	7.9	4.8	2.7	1.9	.7	.7	.4	.2			1.3	1.8	2.8	
	C10S	172	7.5	12.3	19.6	25.6	34.8	41.4	45.4	44.7	42.6	38.7	34.2	34.3	28.8	27.8	22.0	11.3	8.6	6.4	4.6	3.5	2.7
	C11S	186			.3	Tr.	1.5	2.9	6.1	9.0	14.6	20.8	24.2	25.7	27.6	25.9	26.4	26.4	25.9	25.9	24.4	23.6	23.4
	C12S	200												1.2	1.6	2.3	2.8	4.5	6.1	7.0	7.8	9.4	11.8
	C13S	214																					
	Total sulfur		100.00	100.00	100.00	99.6	99.4	99.5	100.00	100.00	99.7	99.5	99.2	98.8	98.4	97.6	96.0	92.9	91.0	90.2	90.3	91.1	93.1
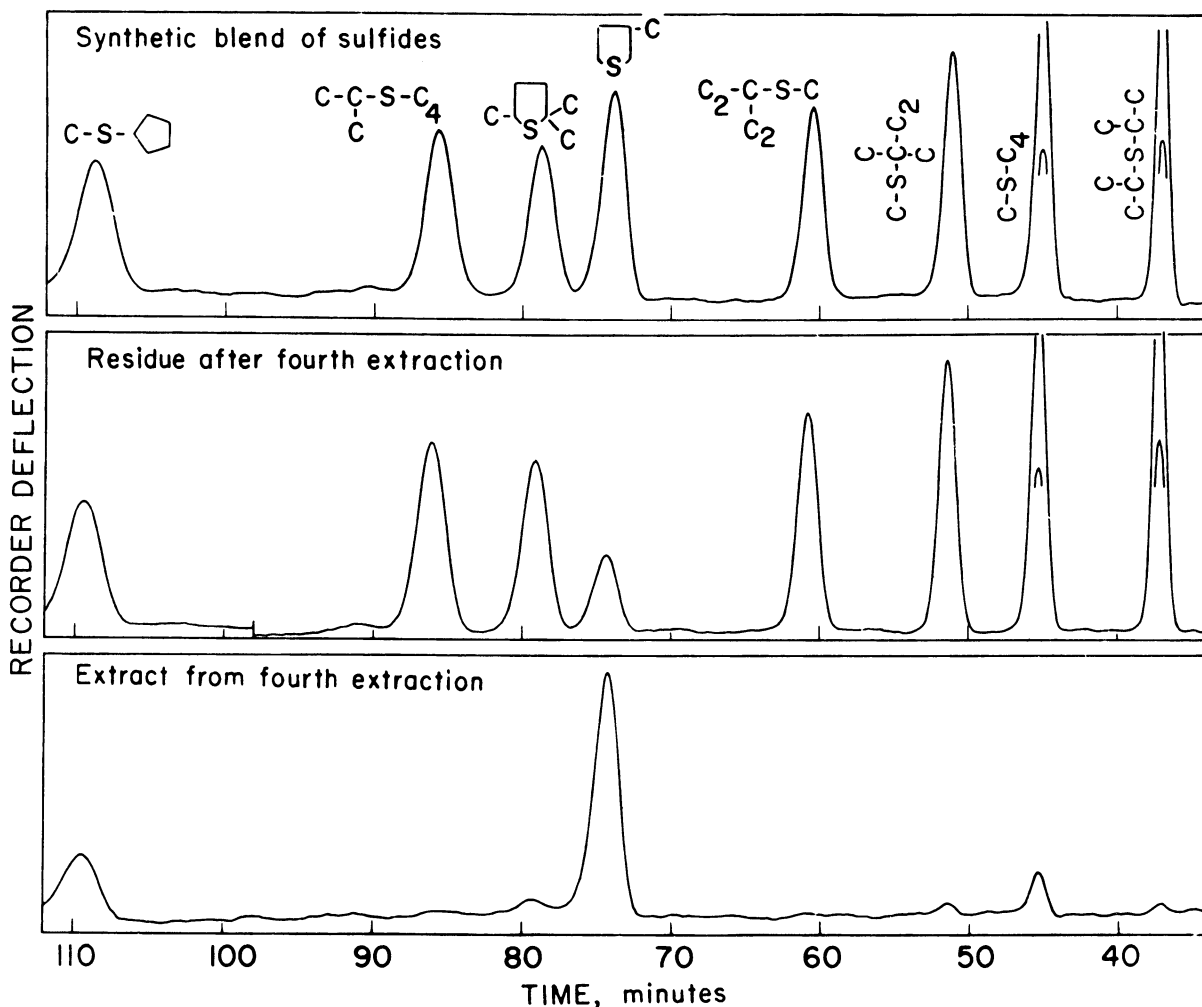
Figure 59.—Gas-liquid chromatograms of synthetic blend, zinc chloride extract, and residue.

ride, and the extract and residue fractions were analyzed by GLC. The results are shown in figure 59. It is evident that steric hindrance has a major effect on the extraction and that cyclic sulfides with no substitution adjacent to the sulfur are most readily extracted.

Adduction Methods

The formation of molecular adducts long has been used in the separation of complex mixtures such as coal tar and petroleum fractions, and the number of known complexing agents has increased greatly in the past quarter century. Several of these were investigated for possible usefulness in sulfur program, but only three, urea, thiourea, and 1,3,5-

trinitrobenzene, were applied to concentrates of sulfur compounds.

Urea complexes specifically with unbranched chain compounds; for example, 1-octanethiol forms a complex, whereas 2-octanethiol does not. In the C_6–C_{10} region, the urea complexes are unstable at room temperatures and dissociate readily on washing; however, the adduction may be carried out successfully at $-78°$ C ($-108°$ F).

The thiourea complexes even of low molecular weight compounds are much more stable than the urea complexes; but tests on binary mixtures resulted in much overlapping of each component into the adduct and nonadduct fractions. A multi-stage treating apparatus was devised and tested but did not improve the degree of separation.

Urea and thiourea adduction were applied to a

Wasson 111° to 150° C (232° to 302° F) thiol extract from which tertiary thiols were removed. Treatment with urea at −78° C did not yield any adduct which is consistent with the near absence of straight chain-1-substituted sulfur compounds in Wasson crude oil. Treatment with thiourea yielded 25.1 percent of the charge as adduct and 64.3 percent as nonadduct.

In contrast to urea and thiourea, 1,3,5-trinitrobenzene adduction was of importance to the progress of Project 48. In general trinitrobenzene forms stable adducts with condensed ring aromatic compounds in which the aromatic ring may be carbocyclic or heterocyclic. In view of this principle, the method should be applicable only to those distillates boiling above 200° C (392° F).

The principal application of trinitrobenzene adduction was the isolation of naphthalenes and benzothiophenes in a 200° to 250° C (392° to 482° F) Wasson distillate. Prior adsorption on silica gel and alumina produced a sulfide-aromatic-benzothiophene concentrate from which the nonaromatic sulfides were extracted with anhydrous hydrogen iodide. The sulfide-free concentrate was added to a solution of trinitrobenzene in methanol. Complexes of naphthalenes and benzothiophenes soon crystallized. Additional complex was obtained from the filtrate by distilling off the methanol under reduced pressure and adding pentane. The filtrate on chilling to −78° C (−108° F) yielded additional crystals which were very difficult to filter and wash without going back into solution or dissociating.

By changing the solvent to propane and maintaining the temperature at −78° C, a small additional yield of adduct was obtained which upon regeneration and mass spectral analysis was found to consist of biphenyl and one or more 2-sulfur molecules which by microdesulfurization proved to be 3-methylthieno-[2,3-b]thiophene and 2-methylthieno[3,2-b]thiophene.

The main adduct fraction was dissolved in benzene and chromatographed on alumina to recover the adductable material which consisted entirely of naphthalenes, benzothiophenes, and approximately 1 percent biphenyls. This concentrate was fractionally distilled into 10 fractions and a residue. An exhaustive qualitative and quantitative study of these fractions resulted in the identification of 22 benzothiophenes and a determination of their concentrations in Wasson crude oil. The nonadduct from the trinitrobenzene treatment consisted principally of alkylbenzenes and tetralins-indans; however, some sulfur compounds still remained. Investigation of this residue resulted in the identification of 18 thiaindans and 4 aryl alkyl sulfides, both of which classes were previously unidentified in petroleum.

Dibenzothiophene was isolated and identified by a similar series of adsorption and adduction steps from a Wasson 300° to 325° C (572° to 616° F) distillate. The presence of methyldibenzothiophenes was indicated by mass spectrum and desulfurization, but identification was not completed for lack of suitable reference compounds.

IDENTIFICATION PROCEDURES

DESULFURIZATION WITH RANEY NICKEL

There exists a very extensive literature on desulfurization with Raney nickel, and it is inevitable that such a widely used technique should be applied by API Research Project 48 to the identification of sulfur compounds. However, early in the life of the project, the catalytic microdesulfurization method was developed while application of the Raney nickel technique was still experimental. Because the catalytic method could handle much smaller samples in a much shorter time, no further use was made of the Raney nickel method until the study of benzothiophenes was undertaken.

The Raney nickel method found a field of usefulness here because of its ability to desulfurize without hydrogenating the benzene ring. This is a very useful property because the resulting alkylbenzenes are more easily identified than the corresponding cyclohexanes. For ultimate usefulness, it was necessary to adapt the method to a microscale, so that individual GLC peaks could be desulfurized and the resultant alkylbenzene identified. This result was accomplished successfully.

Preparation of Catalyst

Most methods of preparing nickel catalyst from the Raney alloy require adding the powdered alloy to a strong solution of sodium hydroxide. The reaction is violently exothermic and requires very careful addition of the alloy to avoid boiling over. In the technique developed by the project, sodium hydroxide solution (about 20 percent) is added a few drops at a time to a slurry of the alloy in water beginning with the addition of about 1 ml and waiting until the reaction has started and subsides before the next addition. Not only is the reaction more easily controlled, but also a large excess of sodium hydroxide is avoided, thus requiring less washing to reach neutrality. When washing is complete the water is replaced with methanol, the solvent in which most reactions are done.

Technique for Microdesulfurization

The desired peak is trapped from the GLC column by bubbling the carrier gas through chilled pentane. Alternately, the material may be trapped in a solid trapping device and the trapped material removed by washing with methanol. If trapped in pentane, the pentane is evaporated and the residue dissolved in methanol and transferred to a 15- by 125-mm test tube to which about 0.1 g of nickel catalyst in methanol has been added. The nickel and sample solution are thoroughly mixed, and the tube is stoppered and heated in a water bath at 60° C (140° F) for about 1 hour. The liquid layer is decanted from the nickel, and the nickel is stirred with about 0.5 ml of methanol, centrifuged, and decanted. The washing operation is repeated and an equal volume of pentane added to the combined solution and washings. Water equal in volume to the volume of methanol is added and the tube shaken vigorously and centrifuged. The pentane layer is withdrawn and nearly all of the pentane is allowed to evaporate. The product is then charged into the gas chromatograph.

Generally naphthalenes associated with a mixture being desulfurized by Raney nickel are partially hydrogenated to tetralins. Benzothiophenes are desulfurized under very mild conditions, and a benzothiophene-naphthalene mixture may be desulfurized under the mild conditions described with little tetralin formation, particularly if heating does not exceed 30 minutes.

HYDROGENOLYSIS

The work of the Bureau of Mines-API Research Project 48 on the identification of sulfur compounds in petroleum became increasingly more difficult with each increase in boiling point. With the exception of the lower boiling ranges, the extremely small number of reference compounds available, compared to the number of possible isomers, precluded most individual identifications, regardless of the degree of concentration and separation that was obtained. This unavailability of both reference spectra and compounds was serious in boiling range as low as 111° to 150° C (232° to 302° F) and almost hopeless above 175° C (347° F). To propose the synthesis of the desired but unavailable sulfur compounds was unrealistic in view of the magnitude of the work.

With the knowledge that reference samples and spectra were available for the pure hydrocarbons that would be produced upon desulfurization of most sulfur compounds, steps were taken to develop a suitable method of desulfurization.

90

While Raney nickel and other hydrogenation procedures are satisfactory for samples of reasonable size, a technique was needed for the desulfurization and identification of the resulting hydrocarbons on samples of less than 0.0002 ml.

In the preliminary work a small furnace containing a reaction tube packed with catalyst was constructed. Using this equipment, sulfur compounds were passed over the catalyst at an elevated temperature and in the presence of hydrogen. Optimum conditions of time, temperature, hydrogen-to-sample ratio, and catalysis were selected on the first experiments, and the desired hydrocarbons were produced. With this success, a somewhat larger and improved furnace, feed, and trapping system were designed and constructed.

Apparatus

The improved apparatus consisted of an aluminum reaction tube packed with catalyst, a furnace for heating the reaction tube to the desired temperature, a motor-driven syringe for charging quantities of pure compounds in the liquid state as large as 0.01 ml, and the necessary adapters, valves, and connectors for handling very small trapped samples from a GLC column. All these

items, including one of the special "traps" for collecting GLC fractions, are illustrated in figure 60. The reaction tube, 8 inches in length, has an outside diameter of approximately 0.5 inch and a 0.136-inch bore that is filled with a catalyst usually consisting of 0.5 percent palladium on activated alumina or 5 percent platinum on porous glass. The hydrocarbons produced in the reaction tube are collected either in a trap made of stainless steel tubing cooled with Dry Ice or in a ⅛-inch, U-tube cooled with liquid air, the choice depending upon the vapor pressure of the sample being collected and the method of its analysis.

To introduce previously trapped GLC samples into the reaction furnace, the syringe and its mechanical drive are removed from the front of the furnace to allow positioning of special stainless steel tubes employed in trapping materials from the GLC columns. These traps are equipped with a taper at the entrance end and a threaded adapter at the exit end to permit rapid installation of the trap between the catalyst bed and a three-way valve connected to the hydrogen source. By use of this valve, the hydrogen stream can be diverted through the trap. The trap then is warmed gradually, whereupon the contents are swept through the furnace.
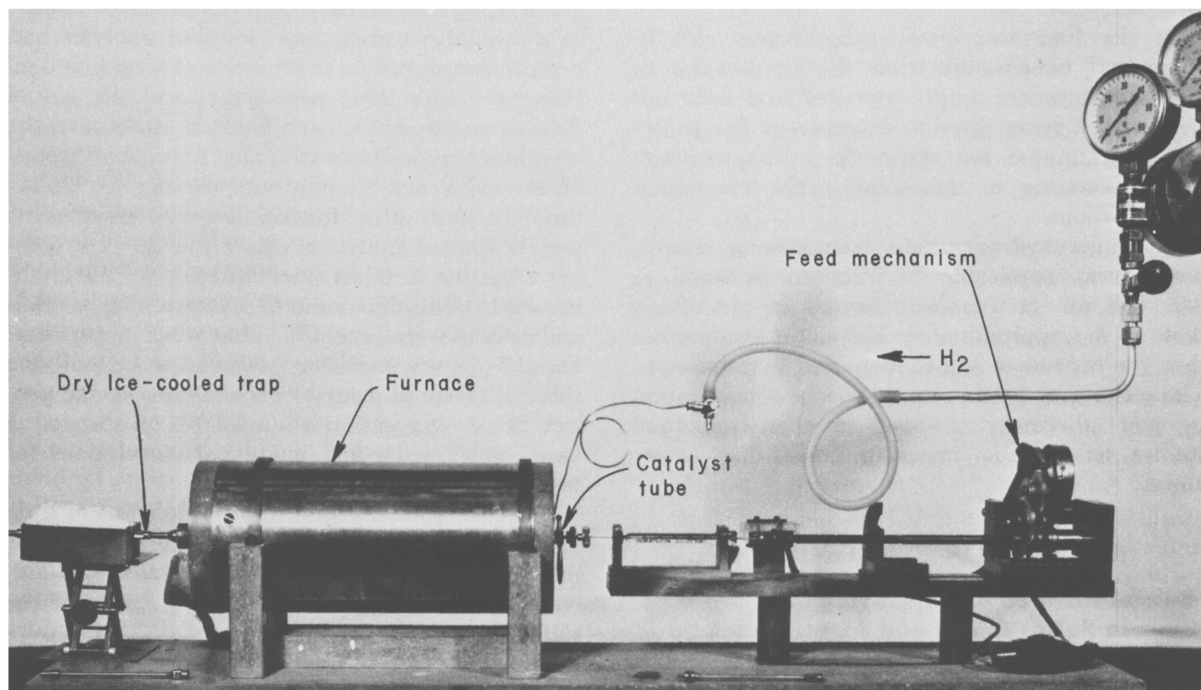
Figure 60.—Microhydrogenation apparatus.

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Experimental

In developing the hydrogenation technique, samples of pure compounds were passed over the heated catalyst in the presence of hydrogen using the motor-driven syringe, operating at a feed rate of about 1 microliter per minute. A hydrogen flow of about 40 ml per minute was used with furnace temperatures from 150° to 200° C (302° to 392° F). The produced hydrocarbons were collected and identified by GLC or mass spectrometry. Excellent results were achieved in removing the sulfur (428), oxygen (425), nitrogen (431) (with change of catalyst), or halogen (429) atoms from representative members of various classes of compounds containing such elements. With but few exceptions the expected hydrocarbon fragments were obtained without breaking carbon-to-carbon bonds or causing other side reactions.

Desulfurization of the materials causing selected "peaks" in the GLC fractionation of sulfur compound concentrates from crude oil fractions was equally successful. The procedure was identical to that used with the pure compounds, except that the sample was carried by the hydrogen stream from the trapping tube into the reactor. Subsequent refinements in the technique and application to solids and metal-containing samples were described (416, 417, 423).

In the literature cited, experimental details, data, and conclusions from the application of hydrogenolysis are amply provided and need not be repeated here. Specific examples of the utility of the technique are shown in subsequent sections pertaining to individual sulfur compound identifications.

The microhydrogenation technique is simple, direct, and applicable to fractions as small as 0.000005 ml. It was instrumental in identifying most of the approximately 175 sulfur compounds that the Bureau of Mines identified in petroleum. The technique should receive serious consideration by any laboratory involved in characterization studies on organic materials containing hetero atoms.

ABSORPTION SPECTROSCOPY

Role of Infrared and Ultraviolet Spectroscopy in Sulfur Compound Identification

During the course of API Research Project 48, the infrared and ultraviolet regions of the electromagnetic spectrum provided information necessary for the identification of individual sulfur compounds isolated from petroleum. The infrared region was particularly well suited for single compound identification because each sulfur compound produces its own unique spectrum or "fingerprint," as it is sometimes called, and provides a means for the positive identification of individual isomers without the necessity of auxiliary spectral techniques. The broad absorption bands produced in the ultraviolet region are not well defined and, consequently, of limited analytical value in single compound identification. On the other hand, related chemical classes provide the same general spectral patterns, making ultraviolet spectroscopy useful for compound type analysis.

The discussion in this section will be related to the development of infrared and ultraviolet spectroscopy as applied to the work of Project 48. Each spectral method will be treated as a separate entity with emphasis on the infrared technique which was frequently employed throughout the program. Infrared and ultraviolet correlations are established for the types of sulfur compounds investigated.

Development of Infrared Spectroscopy for Sulfur Compound Identification

At the outset of Project 48, infrared spectroscopy was not a routine method of analysis. Although commercial instruments were beginning to appear in a few laboratories, most infrared analyses had been accomplished on instruments of special design. However, with these prototypes, and the aid of Raman spectroscopy, early workers established the wavenumber positions of major functional groups for several classes of sulfur compounds (77). Unfortunately, most of the functional group assignments were of limited analytical value. The S—H stretching vibration in thiols (mercaptans), S—S stretching mode in disulfides and C—S stretching in thiols and sulfides were generally either weak in intensity, variable in wavenumber position, or beyond the spectral range of instruments available to the project. Some information was available on absorption band assignments and analytical correlations for cyclic sulfides and alkylthiophenes.

Since functional group information was of little value, it was established early in the work of the project that the principal role of infrared spectroscopy would be played in comparing spectra of the sulfur compounds isolated from crude oil fractions with the spectra of known references—a method that had been successfully used in identifying aliphatic hydrocarbons separated from petroleum.

Although feasible, the "comparison" analysis had some restrictions, especially in the early stages

of the project. A major restricting factor was the shortage of standard reference spectra. In 1948 when the project was begun, data on only a few reference sulfur compounds were available in the published literature. Realizing the need for additional reference compounds and physical-property data thereon, project directors began additional programs. Other research organizations, also aware of the importance of sulfur compounds in petroleum, provided spectral data; however, it was not until the middle 1950's that sulfur-compound references were in reasonable supply, and these were only for the simple isomers.

The first work reported by the project in which infrared played a part, was in the identification of seven alkyl thiols and five alkyl sulfides that were isolated from a Wasson crude oil distillate (71). In the late 1950's thiophene, 2-methylthiophene, and 3-methylthiophene were identified in a Wilmington, California, low-boiling crude oil distillate (426, 430) using infrared techniques.

All of the above identifications were made by using one of the first infrared instruments commercially available, a Perkin-Elmer Model 112 single beam spectrophotometer. In 1957 a Perkin-Elmer Model 21 double beam instrument was acquired and used for the remainder of the program.

In the late 1950's gas-liquid chromatography (GLC) was used to separate complex petroleum concentrates into fractions that contained simple mixtures, or frequently, just a single compound. This development was certainly welcomed by the spectroscopist; but it presented additional problems in that sample quantities collected at the GLC exit were usually insufficient for spectral analysis. The infrared instrument required a sample size of several hundred microliters, and the material collected at the GLC exit was usually less than 2 microliters. However, by repeatedly trapping the effluent in solvent, infrared spectroscopy could be used for identification. This technique was instrumental in the identification of benzo[b]thiophene and its 2- and 3-methyl homologs that were isolated from a 220° to 225° C (428° to 436° F) distillate (74).

As Project 48 moved into the analysis of higher boiling distillates, spectral identification became more difficult because of the increased number of isomers that were possible in each petroleum fraction. Even when fractions were separated into single components by GLC, it was often difficult to make a positive identification, as reference spectra were not available. Project workers devised a microhydrogenation apparatus that made possible the removal of the sulfur atom from a molecule over a palladium-alumina catalyst leaving only the hydro-

carbon skeleton. The availability of simple reference hydrocarbons made it relatively easy to establish the identity of the hydrocarbons produced by microhydrogenation. With this information, the configuration of the original sulfur compound (hydrocarbon precursor) could usually be determined. For positive identification, the suspect sulfur compounds were synthesized, so that their spectra could be compared with those of the compounds isolated from the petroleum concentrates. With the exception of the large sample sizes required for infrared analysis, this combination of analytical techniques worked extremely well and led to the identification of 2,2,5-trimethylthiacyclopentane and 2,2,5,5-tetramethylthiacyclopentane in a 111° to 150° C Wilmington crude oil distillate (422). In addition, 4-methyl-3-thiaheptane and 2-methyl-3-thiaheptane were found in a Wasson distillate boiling from 150° to 220° C (302° to 428° F) (186).

In 1962 a "miniature" infrared cell became available that permitted the analysis of samples as small as 1 microliter without the need for solvents. These ultramicro cavity cells were used in conjunction with a device designed to condense the beam emanating from the infrared instrument. The cells were equipped with a commercial trapping apparatus which permitted the collection of GLC effluents directly into the cavity cell. As this innovation was found to be time consuming and cumbersome in operation, project workers designed a stainless steel trapping needle that could be used for transferring the trapped effluent into the cavity cell via centrifugation (226). The total transfer required only 3 minutes, and successive GLC traps could be stored, at reduced temperatures in the cell, until infrared spectra could be recorded.

With the advent of ultramicro cavity cells, the GLC-infrared-microdesulfurization combination became truly compatible. These analytical procedures were used throughout the remainder of the program and aided in the identification of 22 chain sulfides (419), 35 thiols (79), 17 cyclic sulfides (420), 8 alkylthiophenes (77), 10 alkyl cycloalkyl sulfides (188), 18 thiaindans (421), 4 alkyl aryl sulfides (190), and 22 alkylbenzo[b]thiophenes (187).

Analytical Correlations and Functional Group Analyses of Sulfur Compounds Identified in Petroleum

Of particular interest to the program were spectra of substituted thiophenes, cyclic sulfides, alkyl cycloalkyl sulfides, and alkyl aryl sulfides. Time limitations prevented the thorough analysis of

alkylthiaindans, but the other compound types were studied in detail.

For this review the correlations established in Project 48 have been incorporated into the correlations proposed by others, so that the data presented will provide a comprehensive survey for the types of sulfur compounds identified in petroleum.

Thiols and Sulfides

The first series of compounds identified in Project 48 was alkyl thiols and alkyl sulfides. In alkyl thiols the S—H stretching vibration is located in the spectral range of 2600 and 2550 cm^{-1}. Generally, the band is weak in intensity, but it can afford decisive evidence for the occurrence of the thiol group if samples are analyzed in concentrated solutions or in cells of large pathlength. The S—H absorption changes only slightly in wave number position in going from pure liquid to dilute solutions, indicating a low degree of intermolecular hydrogen bonding (31).

The C—S stretching vibration in thiols and aliphatic sulfides is located in the spectral region between 700 and 600 cm^{-1}. This absorption falls in the area where many skeletal vibrations occur and is weak in intensity and variable in position. Sheppard (367) investigated the infrared and Raman spectra of a wide range of thiols, sulfides, and disulfides. He noted a progressive lowering of the C—S wavenumber in primary, secondary, and tertiary C—S compounds and suggested the following subdivision:

	Radical	Wavenumber range, cm^{-1}
	CH$_3$S—	706–685
Primary	RCH$_2$—S—	660–630
Secondary	RR'CH—S	630–600
Tertiary	RR'R''C—S	600–570

Menefee and coworkers (281) studied the spectra of 4 thiols, 29 sulfides, and 14 disulfides. They proposed correlations for distinguishing alkyl thia groups such as: —S—CH$_3$, —S—C$_2$H$_5$, —S—n-C$_3$H$_7$, —S—i-C$_3$H$_7$, and —S—n-C$_4$H$_9$.

Substituted Thiophenes

Alkylthiophenes were the third major class of sulfur compounds to be isolated from petroleum by Project 48. Infrared spectral data for this class were in short supply at the outset but became more prevalent as the investigation of substituted thiophenes progressed.

The first comprehensive study of substituted thiophene spectra was reported by Hartough (164) in 1952. His work was extended by Zack (465) in 1956, and by Richardson and coworkers (341) of

API Research Project 48, in 1961. Richardson correlated specific absorption bands for a series of 2-monoalkyl- and 2,5-dialkylthiophenes.

Table 25 is a compilation of the various alkylthiophene correlations established by earlier workers and by those derived from the spectra examined during the course of Project 48. Note that the correlations for all but the 2-monoalkyl- and 2,5-dialkylthiophenes were based on a limited number of spectra and may require revision as additional spectra become available.

When benzo[b]thiophene and 2-, and 3-methyl-benzo[b]thiophene were isolated from petroleum, reference spectra were available in the literature (12). However, insufficient data were available to establish analytical correlation for this class of sulfur compounds. In 1967 McDonald and Cook (256) compared the spectra of a series of benzo-thiophenes (thiaindenes) with known correlations between the spectra of substituted benzothiophenes and alkylbenzenes, which were based on the number of aromatic-free hydrogen atoms available to the benzene ring. In their investigation, they observed similarities between the two classes in the 2000 to 1666 cm^{-1} region that are the result of overtone and combination bands from the C—H out-of-plane fundamentals located below 1000 cm^{-1}. Correlations were also established in the 1250–909 cm^{-1} region where C—H in-plane deformation vibrations are prevalent, and in the 1000–650 cm^{-1} region where out-of-plane C—H bending vibrations occur.

Cyclic Sulfides

The primary reason for characterizing the spectra of cyclic sulfides was to develop analytical correlations that could be used in differentiating between alkylthiacyclopentanes and alkylthiacyclohexanes. In 1962 Yur'ev and coworkers (464) attempted to establish correlations that would characterize the two ring systems; however, their work was based on few reference spectra, and the correlations did not always hold when the spectra of additional isomers were examined. Their studies were concerned mainly with derivatives of thiacyclohexanes, but in Project 48, alkylthiacyclopentanes were explored in greater detail. By combining information from both studies, correlations were established for the individual ring systems.

The most definitive spectral region for ring differentiation was found between 700 and 655 cm^{-1}. The spectra of thiacyclopentane, 2-alkyl-, 3-alkyl-, and 2,2-dialkylthiacyclopentanes have a medium intensity band at 686±2 cm^{-1}. 2,3-Disubstituted varieties do not have the 686 cm^{-1}

Table 25.—Infrared absorption bands characteristic of alkylthiophenes

Wavenumber (frequency), cm^{-1}, and intensity [1]	Comments and assignment
3077W	In 2,5-dialkylthiophenes. C—H (ring) stretch.
1555WSH	In 2,5-dialkylthiophenes, 2,3- and 2,4-dimethylthiophene. Asymmetric C=C stretch.
1538–1515MSH	In 2-alkylthiophenes, 3-methyl- and 3-t-butylthiophene. Asymmetric C=C stretch.
1266–1235S	In 2-n-alkylthiophenes except 2-ethylthiophene, 3-methyl-, 3-t-butyl, and 2,3-dimethyl-thiophene. C—H in-plane bend.
1220–1205MS	Only in 2,4-dimethyl-, 2,3,4-trimethyl-, and 2,3,5-trimethylthiophene. C—H in-plane bend.
1176–1143MS	All alkylthiophenes including 2,3,4,5-tetramethylthiophene except 3,4-dimethyl- and 3-t-butylthiophene. Mixed mode [C—C, C—S, and C—R stretch (and C—H in-plane bend except for tetramethyl derivative)].
1109MS	In 3,4-dimethyl- and 2,3,4-trimethylthiophene. Asymmetric C—CH$_3$ stretch in 3,4-dimethyl-thiophene.
1080–1035M	Doublet in all 2-alkylthiophenes. Only higher component in 3-alkylthiophenes. Higher component splits in 2-isobutyl-, 2-isoamyl-, and 2(2-ethylbutyl)thiophene. Higher component C—H in-plane bend. Lower component mixture of C—H in-plane bend and C—C stretch.
1012S	In 2,5-dialkylthiophenes except 2,5-dimethylthiophene. Not assigned.
1000– 980M	In 3-alkyl-, 2,4-dialkyl-, and 2,3,4-trialkylthiophenes. CH$_3$ rock.
943M	In 2-ethyl-5-alkylthiophenes. Not assigned.

877– 820S	One or two bands in all alkylthiophenes except 2,5-dialkyl- and 2,3,4,5-tetraalkylthiophenes.
	  2-alkylthiophene. 847 and 816 cm^{-1}. Higher component, C—S stretch and ring angle bend. Lower component, C—H out-of-plane bend.
	  3-alkylthiophene. 858 and 830 cm^{-1}. Both components C—S stretch.
	  2,3-dialkylthiophene. 877 and 826 cm^{-1}. Higher component C—H out-of-plane bend. Lower component, C—S stretch.
	  2,4-dialkylthiophene. 851 and 826 cm^{-1}. Higher component, C—H out-of-plane bend. Lower component, C—S stretch.[2]
	  3,4-dialkylthiophene. 858 cm^{-1}. Symmetric. C—S stretch.
	  2,3,4-trialkylthiophene. 858 cm^{-1}. Not assigned.
	  2,3,5-trialkylthiophene. 826 cm^{-1}. Not assigned.
	The second strongest band in the 1000–650 cm^{-1} region appears in this 877–820 cm^{-1} region for all of these alkylthiophenes except 2,3,5-trialkylthiophenes, which have the strongest band at 826 cm^{-1}.

800– 690VS	In all alkylthiophenes except 2,3,5-trialkyl- and 2,3,4,5-tetraalkylthiophenes.
	  2-alkylthiophene. 699–690 cm^{-1}. C—H out-of-plane bend.
	  3-alkylthiophene. 760 cm^{-1}. C—H out-of-plane bend.
	  2,3-dialkylthiophene. 699–690 cm^{-1}. C—S stretch and ring angle bend.[2]
	  2,4-dialkylthiophene. 730–725 cm^{-1}. C—S stretch.[2]
	  2,5-dialkylthiophene. 796 cm^{-1}. C—H out-of-plane bend.
	  3,4-dialkylthiophene. 784 cm^{-1}. C—H out-of-plane bend.
	  2,3,4-trialkylthiophene. 784 cm^{-1} and 730–725 cm^{-1}. Not assigned.
	Strongest band in 1000–650 cm^{-1} region. For 2,3,4-trialkylthiophenes, this strongest band is at 730–725 cm^{-1}.

680S	In 3-alkylthiophenes. C—H out-of-plane bend.

[1] Letter symbols indicate observed absorption band intensity.
  W = Weak
  M = Medium
  MS = Medium to strong
  S = Strong
  VS = Very strong
  SH = Sharp
[2] Akiyama and Kakuiti (6) interchange assignments to C—H out-of-plane bend and C—S stretch (or C—S stretch and ring angle bend).

band in their spectra but have a strongly absorbing doublet between 705 and 677 cm^{-1}. Thiacyclopentanes with 2,5-dialkyl substitution do not have correlatable bands in this region. The only six-membered ring compound with an infrared band near 686 cm^{-1} was the parent compound—thiacyclohexane. In the spectra of alkyl-substituted thiacyclohexanes, the bands shift to lower wave numbers and are located at 680±2 cm^{-1} for 2-alkyl-substituted isomers; 667±2 cm^{-1} in 3-alkyl-, and 677±2 cm^{-1} in compounds with 2,3-disubstitution. 4-Methylthiacyclohexane was the only compound studied with four-position substitution, and only weak bands were observed in its spectrum in the vicinity of 680 to 677 cm^{-1}. Another region useful in elucidating the structure of six-membered rings was between 850 and 805 cm^{-1}. A doublet with medium to strong intensity was observed in the spectra of all alkylthiacyclohexanes studied except in that of 4-methylthiacyclohexane.

Other observed correlations can be useful in the structural evaluation of cyclic sulfide isomers. A strong absorption band between 952 and 935 cm^{-1}, in addition to a medium band at 1025±2 cm^{-1},

Table 26.—Infrared spectra correlations for alkylthiacyclic sulfides

Recurrent absorption bands observed in the spectra of alkylthiacyclopentanes		Recurrent absorption bands observed in the spectra of alkylthiacyclohexanes	
Wavenumber (frequency) cm⁻¹ and intensity [1]	Comments	Wavenumber (frequency) cm⁻¹ and intensity [1]	Comments
1025MS..........	A band in this region was found only in the spectra of 2-alkyl-, 2,2-di-alkyl-, and 2,3-dialkylthiacyclopentanes that have a methyl group in the 2-position. This correlation should be used in conjunction with a strong band located between 952 and 935 cm⁻¹.	850–805MS......	Doublet—in all alkylthiacyclohexanes except 4-methylthiacyclohexane.
		680M...........	Indicates 2-alkylthiacyclohexanes.
		677M...........	Indicates 2,3-disubstituted thiacyclohexanes.
952–935S........	Found only in the spectra of 2-alkyl-, 2,2-dialkyl, and 2,3-dialkylthiacyclopentanes.	667M...........	Indicates 3-alkylthiacyclohexanes.
810–790M.......	Doublet, indicates 2-ethyl substitution		
740–715M.......	Doublet, observed only in 3-methyl-thiacyclopentane.		
705–677MS......	Doublet, found only in 2,3-disubstituted isomers.		
686M...........	Observed only in 2-alkyl-, 3-alkyl-, and 2,2-dialkylthiacyclopentanes.		

[1] Code for observed absorption band intensity.
M = Medium
MS = Medium to strong
S = Strong

was noted in the spectra of thiacyclopentanes that have a methyl group in the 2-position. This correlation also applies to the 2,3-disubstituted isomers which have a methyl group in the 2-position, and to 2,2-disubstituted thiacyclopentanes that have at least one methyl group attached to the No. 2 carbon atom. Thiacyclopentanes with an ethyl group attached to the ring in the 2-position have a distinctive doublet in their spectra between 810 and 790 cm⁻¹. In the spectrum of 3-methylthiacyclopentane, an intense doublet was noted in the 740–715 cm⁻¹ region, but this correlation could not be confirmed because of lack of additional 3-substituted isomers.

For easy reference, these correlations are tabulated in table 26. Spectral correlations that apply to alkylthiacyclopentanes are listed separately from those observed in alkylthiacyclohexanes.

Alkyl Cycloalkyl Sulfides

Spectrophotometric identification of five- and six-membered ring systems was much easier for alkyl cycloalkyl sulfides than for cyclic sulfides, mostly because the spectra of alkyl cyclopentyl sulfides are analogous to the spectra of other substituted cyclopentanes and produce relatively few absorption bands in the infrared region between 5000 and 650 cm⁻¹. Conversely alkyl cyclohexyl

derivatives produce spectra with a greater abundance of recognizable absorption bands. This point is easily discernible in the typical spectra shown in figure 61. The alkyl cyclopentyl sulfides have weak, but distinctive, bands in the region from 970 to 890 cm⁻¹. Cyclohexyl sulfides have several prominent bands between 1050 and 740 cm⁻¹ and a strong absorption near 1200 cm⁻¹. A unique triplet can be observed between 1035 and 1000 cm⁻¹. In the spectrum of cyclopentyl cyclohexyl sulfide, shown in the bottom panel of figure 61, absorption bands are clearly defined for both the C₅ and C₆ ring systems.

In API Project 48 nine alkyl cyclopentyl and 11 alkyl cyclohexyl sulfides were synthesized and spectrally examined to augment the identification of alkyl cycloalkyl sulfides isolated from petroleum. For this review the correlatable information obtained was compared with correlations established for other substituted derivatives of cyclopentane and cyclohexane.

In 1964 Szymanski (403) published infrared spectral correlations for several isomeric cyclopentanes and cyclohexanes. His correlations included the spectrum of dicyclopentyl sulfide, but he made no mention of alkyl-substituted derivatives. In the correlations for the spectra of variously substituted cyclopentanes, six recurrent bands were
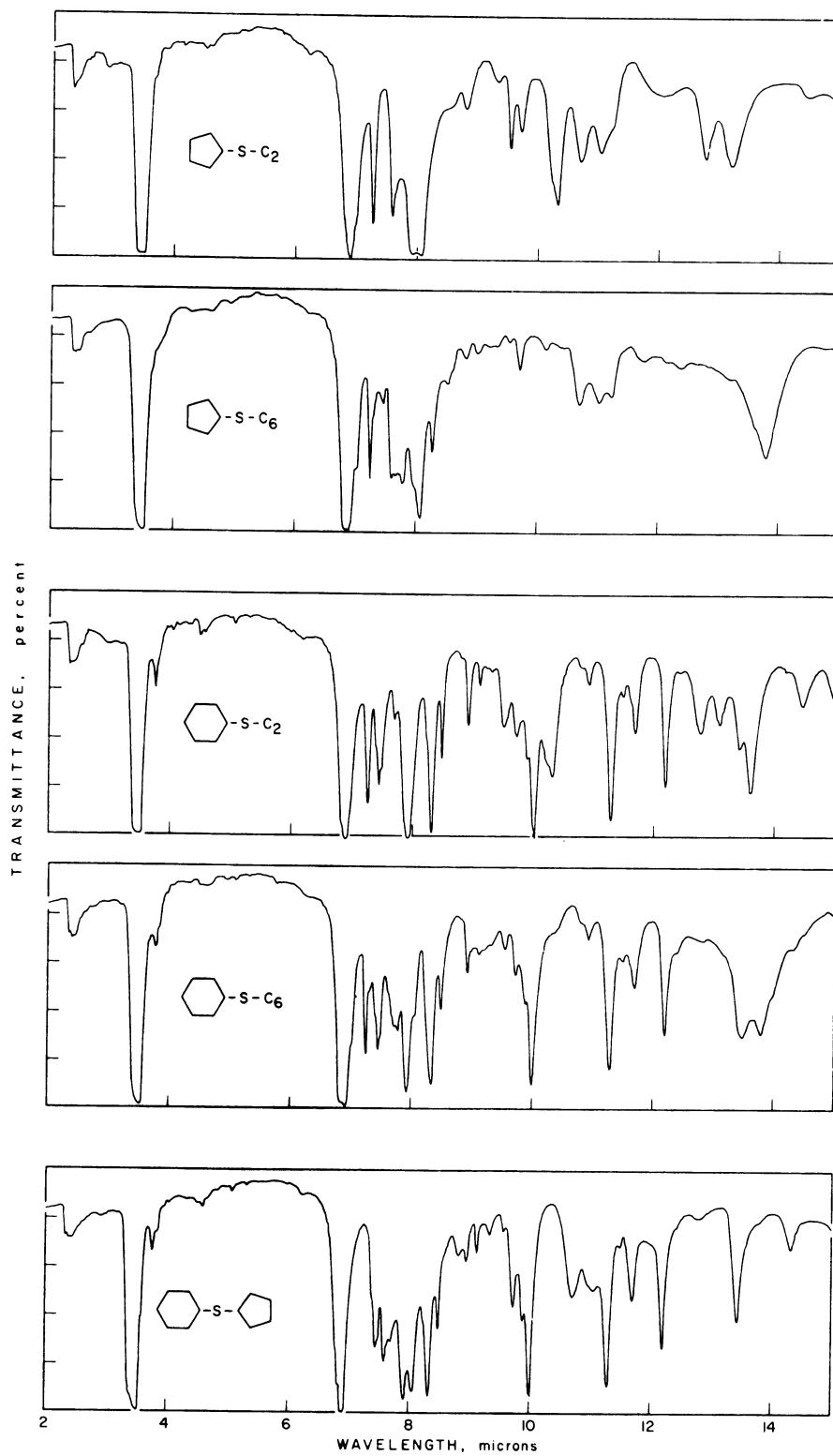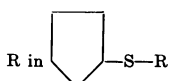
Figure 61.—Infrared absorption spectra of five alkyl cycloalkyl sulfides.

Table 27.—Comparison of absorption band wave number positions in alkylcyclopentyl sulfides with positions observed in other derivatives of cyclopentane

R in [cyclopentyl]—S—R	Recurrent wave numbers (403) in derivatives of cyclopentane, cm⁻¹					
	1205	1030	975	930	890	795
CH_3	....	1030W	962S	930S	¹890M	....
C_2H_5	....	1030W	970S	935M	¹895M	....
n-C_3H_7	....	1030W	....	935M	890MS	795M
i-C_3H_7	....	1028W	....	924M	882M	....
n-C_4H_9	1218S	1028W	965W	933M	895M	787M
i-C_4H_9	....	1030W	....	940M	¹890W	805M
t-C_4H_9	....	²1029–1025	....	930M	890M	....
n-C_5H_{11}	1212S	1028W	965W	930M	908M	....
n-C_6H_{13}	1205S	1029W	985W	935MW	890MW	....

W = Weak, M = Medium, MS = Medium to strong, S = Strong
¹ Shoulder.
² Doublet.

noted which Szymanski suggested as possible group frequencies and with the work of others, proposed vibrational assignments for these particular absorptions. The wave number positions for the six recurrent bands were located at 1205, 1030, 975, 930, 890, and 795 cm⁻¹. Corresponding bands were observed in the spectrum of dicyclopentyl sulfide except in the region near 975 cm⁻¹. The nine alkyl cyclopentyl sulfide spectra studied by Project 48 are summarized in table 27. Recurrent bands were noted only at 1030, 930, and 890 cm⁻¹; however, the 975 cm⁻¹ absorption was indicated in the spectra of five compounds. The only compounds that had spectra with the absorption at 1205 cm⁻¹ were n-butyl-, n-pentyl-, and n-hexylcyclopentyl sulfide, whereas the absorption at 795 cm⁻¹ was limited to n-propyl-, n-butyl-, and isobutylcyclopentyl sulfide.
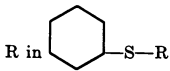
In the spectra of substituted cyclohexanes, Szymanski noted four spectral regions which contained distinctive absorption bands. These were near 1260 cm⁻¹ and between 1055–1005, 1005–950, and 890–840 cm⁻¹. In the spectra of the 11 compounds examined by Project 48 distinctive absorption bands were also observed at these wave numbers, but were not necessarily limited to these specific regions. In addition to the 1260 cm⁻¹ band, a strong band was noted at 1201 ± 1 cm⁻¹. A band of medium intensity was indicated at 1179 ± 1 cm⁻¹; and medium to strong bands at 819 ± 2 and 752 ± 2 cm⁻¹. In table 28 the wave number positions for prominent bands in the spectra of the 11 alkyl cyclohexyl sulfides are compared to those proposed for other substituted derivatives of cyclohexane. Wave number positions for the four additional recurrent bands are also indicated.

Alkyl Aryl Sulfides

Alkyl aryl sulfides follow the general correlations established for other substituted benzene derivatives

Table 28.—Comparison of absorption band wave number positions in alkyl cyclohexyl sulfides with positions observed in other derivatives of cyclohexane

R in [cyclohexyl]—S—R	Recurrent wave numbers (406) in derivatives of cyclohexane, cm⁻¹								Additional recurrent absorption bands observed in the spectra of alkyl cyclohexyl sulfides examined by API RP 48			
	1260	1055	– 1000	1005	– 950	890	– 840		1201	1179	819	742
CH_3	1263S	1030W	1012M	1002S	960S	886S	855M		1202S	1180M	820MS	744MS
C_2H_5	1261S	1030W	1010M	998S	967S	885S	855S		1202S	1179M	820MS	743M
n-C_3H_7	1260S	1028W	1011M	998S	......	883S	855M		1200S	1178M	818MS	740MS
i-C_3H_7	1262MS	1028W	1012M	998S	......	883S	855M		1202S	1178M	819MS	743MS
n-C_4H_9	1262S	1028W	1011M	999S	......	886S	855M		1200S	1178M	819MS	744MS
t-C_4H_9	1260S	1028W	1010M	997S	......	882S	855M		1202M	......	817MS	742MS
s-C_4H_9	1260S	1028W	1012M	997S	953MS	886S	855M		1200S	1180M	820MS	744MS
n-C_5H_{11}	1263S	1029W	1012M	1001S	......	886S	855M		1202S	1180M	819MS	743MS
i-C_5H_{11}	1260S	1028W	1012M	1000S	......	887S	855M		1201S	1180M	820MS	743MS
n-C_6H_{13}	1260S	1029W	1012M	1001S	......	886S	855M		1202S	1179M	819MS	743MS
Cyclo-C_5H_9	1262S	1030M	1014M	1002S	......	886S	855M		1201S	1180M	820MS	744MS

W = Weak, M = Medium, MS = Medium to strong, S = Strong

(31). Alkyl aryl sulfides can be readily identified by observing strong bands in the 900–730 cm⁻¹ region where out-of-plane deformation vibrations occur. Vibrations in this region are dependent on the number of free hydrogens available to the benzene nucleus and provide an immediate clue to the position of alkyl substituents.

Development of Ultraviolet Spectroscopy for Sulfur Compound Identification

In Project 48, the principal use of the near ultraviolet region of the electromagnetic spectrum was in the confirmation of certain aromatic sulfur compounds (74) isolated from petroleum fractions. As compared to the infrared region of the spectrum, the ultraviolet is somewhat limited for the analysis of individual compounds. First, only certain compound types absorb strongly in the region between 200 and 380 millimicrons (mμ) and secondly, absorption bands are generally broad and ill defined.

When radiant energy is absorbed by molecules in the near ultraviolet, changes in the electronic energy of the molecules result from transitions of the valence electrons. Such transitions consist of the excitation of an electron from a filled molecular orbital, usually a nonbonding p- or bonding π-orbital, to the next higher energy orbital—an antibonding π- or σ-orbital. As an example, a typical transition for a π-bonding orbital to a π-antibonding orbital is indicated as $\pi \rightarrow \pi^*$, where the asterisk denotes the antibonding orbital. Generally, the only compounds that absorb strongly in the near ultraviolet region are those that contain a covalently unsaturated linkage such as C=C, C=O, or NO₂. Thus, aromatic sulfur compounds usually have intense absorptions in the 200 to 380 mμ region. Saturated compounds contain only σ-bonds, and the energy required for the $\sigma \rightarrow \sigma^*$ transition is available only in the far ultraviolet region (10 to 200 mμ). Thus, saturated compounds containing only σ-bonds are transparent in the near ultraviolet. On the other hand, saturated compounds containing heteroatoms such as oxygen, nitrogen, sulfur, or the halogens, possess nonbonding (n- or p-electrons) in addition to σ-electrons. Energy requirements for the $n \rightarrow \sigma^*$ transition are less than those for the $\sigma \rightarrow \sigma^*$ transition, and this allows some unsaturated compounds to absorb in the near ultraviolet. However, depending on the solvent used for analysis, the region of absorption for such compounds is usually confined to the narrow wavelength range between 200 and 220 mμ.

Most of the ultraviolet spectra reported from Project 48 were recorded on a Beckman DU ultra-violet spectrophotometer. A Perkin-Elmer Model 350 instrument acquired during the latter stages of the project was used infrequently in this work.

Analytical Correlations for Sulfur Compounds Identified in Petroleum

Correlations applicable to the types of sulfur compounds isolated from petroleum are discussed in the following paragraphs. In all cases, the intensity of absorption is given in addition to the wavelength position. Intensities are indicated as the log of the molar absorptivity (ϵ), which is the product of the concentration; cell-path length; and molecular weight (liters per mole centimeter). The correlations are based primarily on the wavelength position of the most intense absorption band for each type of compound. This position is denoted as the wavelength maximum (λ max).

Aliphatic Sulfides and Cyclic Sulfides

Dialkyl sulfides have a low-intensity absorption band, which usually appears as an inflection, near 230 mμ (log $\epsilon = 2.14$). An additional band of stronger intensity can be observed at about 210 mμ with a log ϵ value equal to 3.00. With increased branching of the alkyl groups, this latter band shifts to slightly longer wavelengths and increases in intensity (122). The 210-mμ band is of little analytical value because many compounds absorb at this wavelength.

In alkylthiacyclopentanes and alkylthiacyclohexanes, maximum wavelength ranges from about 212 to 216 mμ, with log ϵ approximating 3.2.

Aliphatic Thiols

Aliphatic thiols display a weak absorption between 225 and 230 mμ and have a log ϵ of about 2.18. Unlike aliphatic sulfides, the structural configuration of the molecule has little influence in altering the wavelength position or band intensity (165).

Aromatic Thiols

In isooctane solvent the most intense absorption (λ max) for aromatic thiols is near 236 mμ with an average log ϵ of 3.90. However, when aromatic thiols are dissolved in aqueous sodium hydroxide, λ max shifts to about 265 mμ, and the intensity doubles. This shift in wavelength and intensity provides a sensitive method for determining benzenethiols in petroleum fractions (165).

Alkylthiophenes

Hartough (164) examined the ultraviolet spectra of thiophene and alkyl-substituted thiophenes in isooctane solution and found that the maximum

absorption for these sulfur compounds ranged from 231 to 238 mμ. Thiophene has a λ max at 231 mμ with log ϵ 3.85; however, this maximum shifts to longer wavelengths for the alkyl-substituted derivatives. Methyl substitution in the 2- or 3-position, ethyl substitution in the 2-position, and 2,3-dimethyl substitution cause a shift of 3 mμ to 234 and log ϵ values are 3.88, 3.72, 3.92, and 3.78, respectively. In 2,5-dimethylthiophene, the band shifts to 236 mμ (log $\epsilon = 3.88$), whereas 3,4-dimethylthiophene has a λ max at 238 (log $\epsilon = 3.76$)—a shift of 7 mμ.
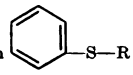
Benzothiophenes

In Project 48, spectra of benzothiophene and reference spectra of 14 substituted isomers (13) were examined to confirm the identity of this class of compounds in petroleum fractions. The wavelength maxima for these compounds were found to lie between 223 and 233 mμ, and log ϵ values were greater than 4.36.

Alkyl Aryl Sulfides

Fehnel and Carmack (122) studied the ultraviolet spectra of a series of alkyl aryl sulfides and noted two intense bands for the isomers examined. As shown in table 29, one region of absorption is

Table 29.—Ultraviolet absorption spectra of alkyl aryl sulfides [1]

R in [benzene]—S—R	λ max in the 254–270 mμ region	Log ϵ	λ max in the 210–218 mμ region	Log ϵ
CH$_3$	254	3.98	. . . . . .	. . . .
C$_2$H$_5$	256	3.90	210	3.94
i-C$_3$H$_7$	258	3.75	215	3.94
t-C$_4$H$_9$	266	3.19	218	4.08

[1] Data taken from reference 122.

located between 254 and 270 mμ and the other is between 210 and 218 mμ. They observed that the absorption maximum at the longer wavelengths increased when the α-hydrogen was replaced by alkyl groups.

LOW-RESOLUTION MASS SPECTROMETRY IN PETROLEUM ANALYSIS

The principle of mass spectrometry has been known and applied since the turn of the century. At first, instruments of the designs of Dempster (95) and Aston (16) were used, primarily for deter-

mining the relative abundances and exact masses of the isotopes of the known elements.

The demand for analysis of aviation fuels during World War II brought mass spectrometry to the fore as an analytical tool. The electronics industry answered the demand for analytical instruments with two mass production instruments: the CEC 21–103 (electrical scanning) in the United States and the Metropolitan-Vickers MS-2 (magnetic scanning) in Great Britain. With these instruments available, organic chemists soon realized their value in identifying and confirming identification of reaction intermediates and products.

The "boom" in gas-liquid chromatography (GLC) relieved some of the quantitative analysis load from the mass spectrometers, and use of GLC to separate many complex mixtures prior to spectral analysis was of significant value. These two factors enhanced the availability and the analytical power of the mass spectrometer. The rapid increase in the use of the mass spectrometer by chemists in their search for knowledge of the composition of higher boiling petroleum distillates and advances in the electronics industry have spurred improvement in these instruments as analytical and research tools.

Birch and others (38), investigating the problem of petroleum composition, saw the availability to chemical attack of the sulfur atom as a means of gaining insight into the structure of petroleum molecules. It was assumed that if a sulfur compound could be identified, one could then look for its hydrocarbon and possibly other heteroatom analogs to be present. This proved to be a correct assumption in several instances. The close association of analytical mass spectrometry to the petroleum industry led to an opposite approach: Identify the hydrocarbons and then look for the heteroatom analogs. Hood, Clerc, and O'Neal (182, 183) used mass spectrometry to study petroleum distillates and developed some structural models for petroleum molecules. This approach led to a much faster acquisition of knowledge of petroleum composition than had the chemical approach, although it must be said that a combination of the two has proved more fruitful than either approach alone. Bestougeff (32), using methods other than mass spectrometry, confirmed most of the model petroleum molecules suggested by mass spectrometry.

Instrumentation and Nature of the Data

The instrument used by the Bureau during Project 48 was a Consolidated Electrodynamics Corporation (CEC) model 21–102, modified to the
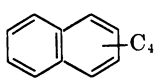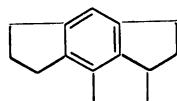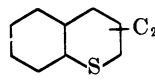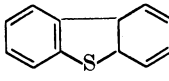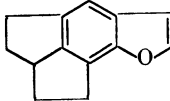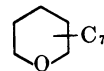
equivalent of a (CEC) 21–103, except that the two-stage magnet was rewound and retained. At the onset of its use in the project, the instrument was equipped with a standard stainless steel inlet system of about 3.2-liter volume maintained at room temperature and charged by a constant-volume capillary dipper through a mercury orifice. As the project progressed to higher boiling ranges, the inlet system was enclosed in a commercial oven heated to 135° C (275° F). A constant-volume stainless steel needle, and rubber-septum charging system was added. In addition a valve was installed which could reduce the inlet system volume from 3.2 to 0.2 liters, if desired. An all-glass (including valves), 3.2-liter volume inlet system heated to 300° C (572° F) and charged by needle and septum was installed, so that the two inlets had tandem molecular leaks to the analyzer assembly. Other instrumental changes were (1) replacement of the mercury-diffusion pump and fore pump used to evacuate the analyzer assembly with an ion pump; (2) addition of a (CEC) "Mascot" digitizer; (3) installation of a low-ionizing voltage circuit similar to that described by Lumpkin (252); and (4) installation of a "superhigh" sensitivity circuit to be used when the 0.2-liter volume of the 135° C (275° F) inlet was employed.

Four magnet settings were used: 0.5635 amp (2,400 gauss), 0.7969 amp (3,280 gauss), 1.1270 amp (4,540 gauss), and 1.400 amp (5,600 gauss). Varying the accelerating voltage from 3,240 to 440 volts produced spectra which covered the following overlapping mass to charge ratio (m/e) ranges: 12 to 100, 26 to 220, 48 to 308, and 69 to 550.

With the instrument just described, spectra were obtained on a wide variety of sulfur compounds prepared and purified by the project staff. Many of these spectra were published in the API Research Project 44 Certified and Uncertified Mass Spectra Catalogs. In addition, analytical data (qualitative, quantitative, and average molecular weights), were obtained and used in guiding separation and syntheses projects, analyzing prepared fractions, and in supporting conclusions from other independent experimentation. Samples analyzed came from synthesis, crude oil distillates, analytical distillations, liquid-solid chromatography, thermal diffusion, a variety of chemical treatments, and trapping from GLC columns.

In nature, homologous series of hydrocarbons and their sulfur and oxygen compound analogs have "even" molecular weights, and their formulas can be developed from the general formulas C_nH_{2n+z}, $C_nH_{2n+z}S$, and $C_nH_{2n+y}O$, respectively. In the first formula, as z decreases in steps of two mass units from $+2$ to 0 to -2, etc., compounds of increasing unsaturation (total rings and/or double bonds) are generated. When z numbers of two compound types differ by 14, 28, etc., mass units, they have different carbon-hydrogen ratios but are coincident in the same "even" nominal m/e series. Since seven, "even" nominal m/e series are discernible by mass spectrometry, between adjacent homologs, these series must be designated by groups of z numbers as follows: $(+2, -12, -26)$; $(0, -14, -28)$; $(-2, -16, -30)$; $(-4, -18, -32)$; $(-6, -20, -34)$; $(-8, -22, -36)$; and $(-10, -24, -38)$. Sulfur and oxygen compounds will be coincident in the same nominal m/e series as a hydrocarbon of given z number when $x=z-4$ and $y=z-2$, respectively. The following structures illustrate this point with a series of compounds having a nominal mass of 184:

	(I)	(II)	(III)
Empirical formula...........	$C_{13}H_{28}$	$C_{14}H_{16}$	$C_{14}H_{16}$
Structural formula..........	$n(C_6H_{13})-CH_2-n(C_6H_{13})$		
Nominal mass..............	184	184	184
Exact mass................	184.219089	184.125194	184.125194

	(IV)	(V)	(VI)	(VII)
Empirical formula...........	$C_{11}H_{20}S$	$C_{12}H_8S$	$C_{13}H_{12}O$	$C_{12}H_{24}O$
Structural formula..........				
Nominal mass..............	184	184	184	184
Exact mass................	184.128565	184.034670	184.088809	184.182705

In this report and in keeping with the format established for the project, a sulfur or oxygen compound is listed as in the same nominal m/e series as the hydrocarbon with which they are coincident. Hence, (I), (IV), and (VII) are in the +2 series, and (II), (III), (V), and (VI) are in the −12 series. Note that all are in the same "even" nominal m/e series: (+2, −12, −26).

A hydrocarbon-sulfur concentrate analysis is rendered somewhat simpler than would first appear by the fact that some physical separations, for example, liquid-solid chromatography, generally produce samples depleted of the more saturated hydrocarbon types (z= +2, 0, −2, and −4), and only aromatic hydrocarbons ($z \leqq -6$) and sulfur compounds are present.

Note that for a low-resolution instrument, such as the (CEC) 21–103, some ambiguity can result because the following species have coincident nominal masses: O_2 = 32, and SO_2 = S_2 = 64. For this reason, oxygen and oxysulfur compounds, present in low concentration in aromatic-sulfur concentrates, are difficult to detect and analyze. Supplementary data such as that from infrared analysis or high-resolution mass spectrometry, or both, are necessary. High-resolution mass spectrometry, for example, will distinguish between all of the structures above, except II and III which have the same exact mass.

Mononitrogen compounds are sometimes found in aromatic hydrocarbon-sulfur concentrates from petroleum. Nitrogen compounds have N (mass 14) in place of CH (mass 13), NH (mass 15) for CH_2 (mass 14), or NH_2 (mass 16) for CH_3 (mass 15) and hence fall in the "odd" nominal m/e series which makes their detection simpler than might be expected. Note, however, that the "even" nominal m/e series compounds previously discussed have intense "odd" nominal m/e fragment ions caused by loss of alkyl groups from their alkyl chains. These peaks appear primarily in the "odd" parent molecule minus one (p−1) series and to lesser extent in other "odd" nominal m/e series (p−3, p−5, . . . p−13) and can mask the nitrogen compounds. For this reason, the best way to analyze for nitrogen compounds with a low-resolution instrument is to concentrate them by physical or chemical means and employ low-voltage mass spectrometry (LVMS). Such analysis essentially eliminates the "odd" nominal m/e fragments from the spectrum while retaining the parent molecule ions of the nitrogen compounds.

For presentation, high-voltage (70 v) and low-voltage (7 to 15 v) analyses are generally reported as a percentage by nominal m/e series with com-

pound types and the fractions where they are found indicated (tables 30 and 31). If it is desirable to point out specific detail, the spectra can be presented graphically with "discrete" profiles (fig. 62) for both high- and low-voltage spectra. For low-voltage spectra, "continuous" profiles (fig. 63) are used which connect all of the peaks belonging to each of the seven "even" nominal m/e series.

Preparation and Treatment of Data

Before discussing the two methods of analysis used, it is necessary to discuss various corrections that must be applied to the raw data that comes from the instrument in order that it be uniformly representative of the sample components.

Because of the natural abundance of ^{13}C in hydrocarbons, isotope corrections must be made for the contribution of a given m/e peak to the m/e +1 and m/e +2 peaks. Contributions to the m/e +3 and higher peaks may be considered negligible for most petroleum derived samples. For hydrocarbons, contributions to m/e +1 amounts to 1.1 percent per carbon atom and for m/e +2, in the molecular-weight range of the usual project samples, 0.05 to 1.5 percent. For compounds containing sulfur, naturally occurring ^{34}S must be corrected on the m/e +2 peak. This correction, for a single sulfur atom, is about 3.3 to 6.1 percent in the molecular-weight range of samples studied by the project. Where hydrocarbons and sulfur compounds occur in mixtures, the concentration of each must be estimated and isotope corrections adjusted accordingly.

As previously stated, fragments from "even" nominal m/e series compounds fall predominantly in the p−1 series. Some fragments are produced to a lesser, but significant, extent in the (p−3, p−5, . . . p−13) series of a given compound. These series are coincident on the p−1 series of the other six "even" nominal m/e series. For this reason, corrections must be made for the contributions of each type to the p−1 series of the other types in a high-voltage analysis. These corrections are called the pattern coefficients of each type.

All compounds have different instrumental sensitivities because of differences in the ionization cross sections of their molecules. Sensitivities for high-voltage spectra are generally reported as divisions per microliter, micron, or microgram of the base peak (largest peak in the spectrum) or divisions of the total ion intensity (a summation of the heights of all peaks registered). Because constant volume charging is used most often and

Table 30.—Mass spectrometer analyses of fractions from alumina-gel percolation of Wasson crude oil 220° to 225° C boiling range distillate, mole-percent

Compound or class		Parent peak	Fraction																				
			8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27a
Naphthenes:																						
Cycloparaffins	C12	168	3.1	3.1																		
	C13	182	1.7	1.1																		
	C11	152	2.5	2.5																		
Dicycloparaffins	C12	166	23.2	21.9	1.4		0.6															
	C13	180	28.5	29.6	10.4	1.6																
	C14	194	1.6	1.1	11.4	2.2																
Tricycloparaffins	C11	150	1.8	1.8	1.0																	
	C12	164	1.8	1.8	.9	1.3		0.2														
	C13	178	7.5	7.7	4.1	.9																
	C14	192	7.0	7.3	3.5	.7																
Total naphthenes			78.5	77.7	33.4	6.0	0.6	0.2														
Alkylbenzenes	C11	148			29.6	48.1	0.3		0.3	1.0	2.6	13.0	33.5	16.7	1.3							
	C12	162			34.6	40.1	53.3	65.9	79.4	71.8	39.2	13.3	2.5									
	C13	176					38.5	24.7	6.8													
	C14	190																				
Tetralins-indans	C10	146		7.9		.2	1.7	3.1	.7	1.3	8.0	25.3	36.8	52.6	18.9	2.8						
	C11	160		13.4			1.2	3.3	6.7	13.3	42.0	46.0	25.7	7.7	.8							
	C12	174		.2					4.8	10.9	6.0	.6										
Naphthalenes	C10	128												.5		.4	0.2	2.4	0.3	0.5	0.8	1.5
	C11	142													25.6	77.6	86.6	82.4	72.7	59.1	41.8	14.5
	C12	156															.4	.8	1.4	.6	.2	
Total aromatics			20.7	21.5	64.2	88.3	94.9	97.0	98.7	98.3	97.8	98.2	98.5	77.5	46.6	80.8	87.2	84.3	74.4	60.2	42.8	16.0
Alkyl thiols }	C8	146	0.8	0.8	2.4		1.2	0.6	0.2					8.7	0.5	1.4			0.3	0.4	0.6	2.0
Alkyl sulfides } Fractions 8–14, 19–21, 24–27a	C9	160					.7	.2						2.7	5.7	6.1			7.8	6.0	3.4	1.4
Unknown B	C10	174					2.5	.8							18.0				8.7	14.7	10.6	8.2
	C11	188																				
Cyclic sulfides	C9	158								0.8	2.2			8.2	10.0	5.6	3.8	3.8	3.9	3.0	2.0	8.6
	C10	172								.9					17.5	6.1	5.0	6.2		.5	2.7	15.1
	C11	186															4.0	3.6				1.8
Unknown A }	C9	156												2.4				.9	.6	2.0	6.5	5.7
Bicyclic sulfides } Fractions 19–20, 23–27a	C10	170																	1.8	3.0	3.2	8.1
Thiophenes }	C11	184										1.8	1.5									
Unknown C } Fractions 13–17, 27a	C10	168																				25.3
Benzothiophenes	C11	182																1.2	2.5	10.2	27.7	
Disulfides	C9	148																			.5	7.6
	C8	150																				
Total sulfur compounds			0.8	0.8	2.4	5.6	4.4	2.8	1.3	1.7	2.2	1.8	1.5	22.5	53.4	19.2	12.8	15.7	25.6	39.8	57.2	84.0
Sum percent			100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.1	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Weight-percent sulfur (lamp)			0.017	0.212	0.48	0.57	0.41	0.24	0.14	0.12	0.24	0.20	0.30	4.67	7.88	3.45	2.28	2.66	3.57	5.66	8.92	12.32

Table 31.—Alumina gel fractions 1-8, (silica gel fraction No. 4—aromatic sulfur concentrate) from Brush still distillation cut No. 3 of Wasson 225° to 400° C distillate [1]

Series	Fraction								Reconstituted total, weight-percent [2]	Reconstituted average molecular weight
	1	2	3	4	5	6	7	8		
Weight-percent of total..	4.49	16.45	15.18	18.18	10.78	19.61	4.99	10.32	......	....
+2, −12 [3]	1.8	2.0	2.9	16.5	25.3	24.3	16.5	27.0	15.0	....
0, −14	3.0	1.5	1.1	12.7	21.4	23.8	52.7	24.6	15.0	....
−2, −16	3.9	0.9	0.5	2.9	2.8	4.3	4.8	15.4	3.9	....
−4, −18	1.3	0.6	0.3	2.2	2.9	5.8	8.4	17.7	4.3	....
−6, −20 [3]	37.6	38.7	23.4	32.4	40.3	33.3	13.5	6.6	29.7	....
−8, −22	35.9	38.3	41.5	13.3	3.8	3.6	2.0	2.3	18.1	....
−10, −24	16.5	18.0	30.3	20.0	3.5	4.7	2.1	6.4	14.0	....
Total............	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	....
Average molecular weight.........	228.1	209.5	202.9	203.5	188.3	188.9	198.2	195.6	......	200.0 [2]

Probable compound types [4]

Series	Hydrocarbon type	Fractions	Sulfur types	Fractions
+2, −12	Paraffins............................ Naphthalenes........................ Trinaphthenobenzenes................	[1-2] [4-7] [4-6]	Bicyclic sulfides..................... Dibenzothiophenes...................	[4-8] [6-8]
0, −14	Cycloparaffins....................... Diphenylalkanes..................... Biphenyls........................... Naphthenonaphthalenes..............	[1-2] [5-8] [6-8] [4-7]	Thiophenes........................ Tricyclic sulfides..................... Thienothiophenes.................... Phenylbenzothiophenes..............	[2-5] [4-6] [7-8] [7-8]
−2, −16	Dicycloparaffins..................... Phenyl-(indans-tetralins)............. Fluorenes........................... Acenaphthalenes....................	[1-2] [5-7] [5-7] [5-7]	Alkyl aryl sulfides.................... Tetracyclic sulfides................... Dithienyls........................... Naphthenothiophenes................	[6-8] [5-7] [7-8] [4-7]
−4, −18	Tricycloparaffins.................... Phenanthrenes-anthracenes...........	[1-3] [6-8]	Thia-(indans-tetralins)............... Dinaphthenothiophenes..............	[4-6] [5-7]
−6, −20	Alkylbenzenes...................... Phenylnaphthalenes.................	[1-4] [7-8]	Benzothiophenes..................... Thienobenzothiophenes..............	[4-7] [7-8]
−8, −22	Alkyl-(indans-tetralins).............. Pyrenes............................	[1-4] [7-8]	Alkane sulfides...................... Naphthenobenzothiophenes.......... Phenylthiophenes	[3-6] [6-8] [6-8]
−10, −24	Indenes............................. Dinaphthenobenzenes................	[1-5] [1-5]	Monocyclic sulfides................... Thienyl sulfides......................	[4-8] [6-8]

[1] Low-voltage mass spectrometer analysis at 10.75 v (nominal).
[2] Compare reconstituted (percent by series and average molecular weight) with corresponding values for unseparated sample.
[3] Note bimodal distributions, +2, −12 and −6, −20 series indicating compound type separation.
[4] Numbers in brackets indicate fractions containing given type.

frequently without the benefit of a pressure gage, the number of moles charged, of each compound, differs depending on molar volumes. The result is that different volume sensitivities are obtained for each compound. For LVMS spectra, divisions per microliter or microgram of the parent peak (molecular ion) are compared to a standard compound, arbitrarily assigned a value of 1.00, to develop sensitivities. Molar-volume and molecular-weight data can be used to convert these volume and weight sensitivities to molar sensitivities. The sensitivities used in LVMS, a different value for each type at each carbon number, imply that many data need to be acquired. For the analysis of a variety of complex mixtures, they must also be averaged in several different combinations.

Sensitivities and pattern coefficients can be determined in the following ways: (1) From the spectra of pure compounds or blends of them; (2) application of physical or chemical separations, or both,
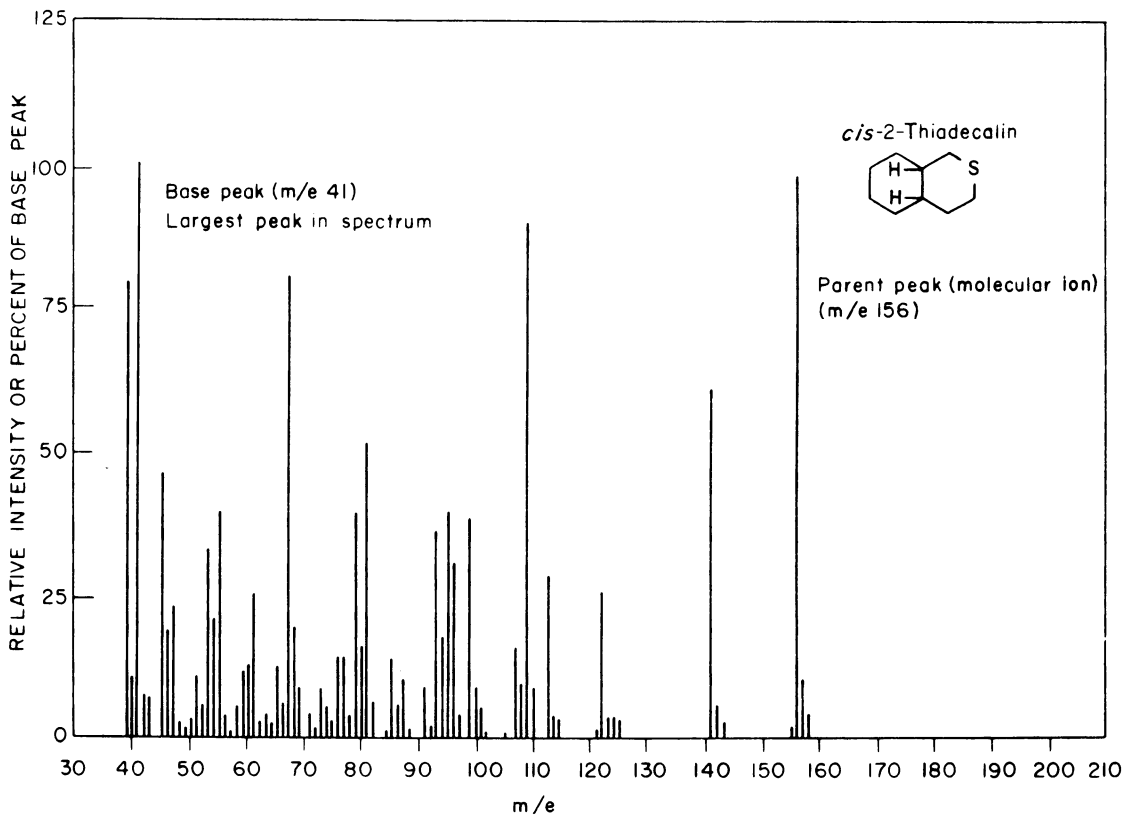
Figure 62.—High-voltage discrete profile of *cis*-2-thiadecalin.
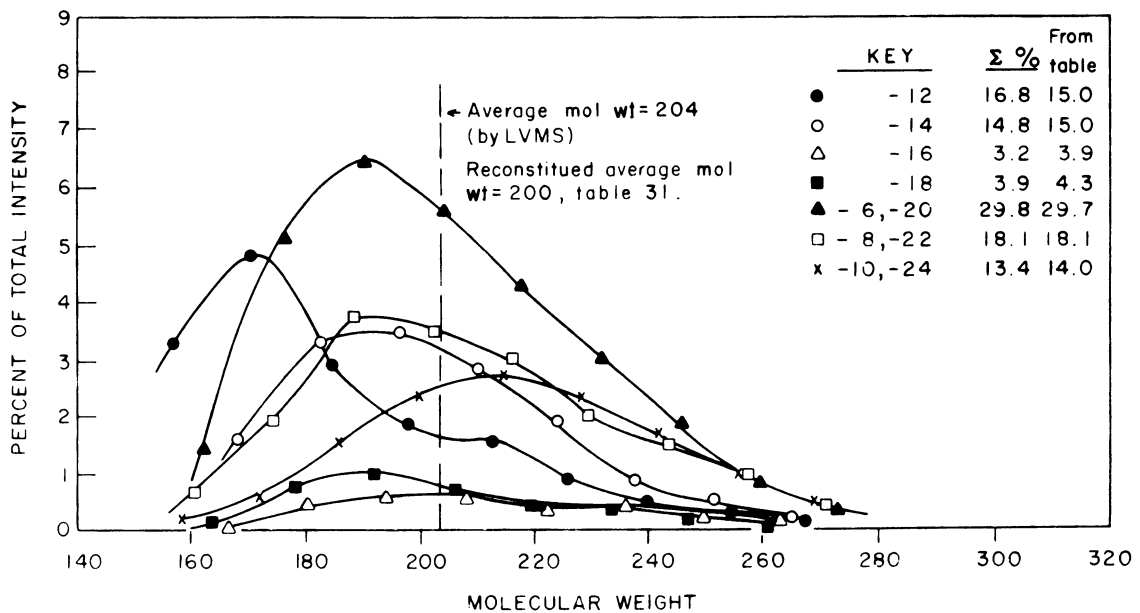

Figure 63.—Low-voltage mass spectra continuous profile of sulfur-aromatic concentrate from Wasson 225° to 400° C distillate.

to mixtures which maximize the concentration of a given type at the expense of the other types, and (3) for LVMS, molar sensitivities of compounds of known structure can be used to calculate the sensitivity of unavailable compounds on the basis of structural similarities and by use of the LVMS rules given below.

For LVMS, numerous literature references (*88, 225, 252, 253*) suggest application of the following rules will yield an abundance of useful sensitivity data from minimal experimental data.

1. Sensitivity increases as the number of condensed aromatic rings increases.

2. Sensitivity increases as the number of alkyl substitutions on an aromatic nucleus increases, but the percentage increase diminishes as the number of condensed aromatic rings increases.

3. Sensitivity is affected by the position of alkyl substitution; for example, for disubstituted benzenes the order of sensitivities is *ortho* < *meta* < *para;* for naphthalenes, β substitution results in a greater sensitivity increase than α substitution.

4. Where naphthene rings are condensed to aromatic rings, the increase in sensitivity is about that of a disubstituted benzene, and further substitution on the aromatic ring gives sensitivity increases similar to tri-, tetra-, and so on, substituted benzenes, while substitution on the naphthene ring alters the sensitivity only slightly.

5. Sensitivity for a single alkyl group increases through about one to four carbon atoms, depending upon the number of aromatic rings in the compound, and may then be considered to decrease to zero sensitivity at infinite mass.

Using these rules and molar sensitivities for a few compounds, sensitivities for the lower members of many homologous series can be computed. Then, by rule 5 above, the peak height per unit (volume, weight or mole) can be plotted versus the reciprocal molecular weight and the curve extrapolated to zero to obtain sensitivity values for the higher homologs. Once these sensitivities have been determined, average curves can be constructed (*225, 253*) which involve knowledge of the "history" of the sample to be analyzed. This reflects boiling range, m/e's at which each type appear in this range, physical and/or chemical treatments that have been employed in preparation of the sample, and physical property data.

Sensitivities for LVMS are subject to significant change in the ratio of one parent peak to another, for slight changes in the ionizing voltage, at voltages near the ionizing potential. In addition, for multi-component mixtures, adequate instrumental sensitivity is not realized. To eliminate these problems,

an ionizing voltage of 10.75 v (nominal) with 1.5- to 2.0-v repellers was chosen. The repeller voltages are essentially additive to the ionizing voltage, so that for 2.0-v repellers the 10.75-v nominal meter voltage corrects to about 12.75-v instrumental and to about 14.75-v absolute when calibrated against argon. This is well above the ionizing potential of the sulfur and aromatic compounds encountered by the project. Some fragment peaks and rearrangement peaks occur, but at this voltage, the ratios of these to their parent precursors are not affected significantly by failure to reproduce the ionizing voltage exactly, and they can be corrected for by calculation.

Methods of Analysis

In mass spectrometry two essentially unique methods for analyzing petroleum fractions have been developed: high-voltage (70-v) analysis (generally a fragment peak method) and a low-voltage (5- to 15-v) analysis (a parent-peak method.) Because they involve two different parameters, these methods can frequently be used as a check on one another.

Below C_7S, both high- and low-voltage methods could be used for qualitative and quantitative purposes because of the few isomers possible for each compound type at a given carbon number. All or most of these isomers were prepared in high purity to obtain sensitivities and pattern coefficients with which to calibrate the instrument. Individual thiols, sulfides, cyclic sulfides, and thiophenes were determined in this manner.

Above C_7S, with the number of isomers increasing exponentially, all isomers of a compound type are not available for reference. In this case, the use of a few selected compounds, as described earlier, gives the necessary sensitivity data and pattern coefficients for what have been called semiqualitative and semiquantitative analyses. This terminology is used because one of the following results is obtained in lieu of individual compound identification and concentration: (1) Total nominal m/e series, (2) nominal m/e series by individual carbon number, (3) total homologous type by series, or (4) homologous type by individual carbon number.

It should be pointed out that for fractions obtained from distillates by physical or chemical separations, several carbon numbers of each compound type are generally present. For this reason, certain factors may vary from fraction to fraction. The analyst must be continually aware of these

factors and be prepared to make corrections accordingly:

1. The relative concentrations of isomers may vary from fraction to fraction because of the separation being achieved. These give rise to continually varying sensitivities.

2. For a given homologous series or for a group of homologous series falling on the same nominal m/e's, the concentration of each compound type may be changing; for example, in an analytical distillation, the lower carbon number homologs are collected first while in a liquid-solid chromatography separation the higher carbon number homologs tend to elute first.

Changing concentrations can necessitate adjustment, from fraction to fraction, of both sensitivity and isotope corrections.

Because of the continual adjustment of sensitivity and isotope corrections, the analyst must be careful that he does not create artifactual qualitative detail or, by the same token, destroy some detail that actually exists.

For low-resolution mass spectrometry, useful supplemental data can often be obtained from high-resolution mass spectra, infrared spectra, ultraviolet spectra, nuclear magnetic resonance spectra, chemical treatment data, liquid-solid chromatography adsorption data, GLC relative retention times on a variety of columns, and total sulfur, total nitrogen, and total oxygen determinations. Consideration of data obtained from two or more of these sources will, almost without exception, be more prolific in yielding information to the analyst than data taken from any of these sources alone.

High Voltage.—For the high-voltage method, above C_7S, semiqualitative and semiquantitative data are generally obtained. Fragment peaks for each type to be analyzed are chosen. If more than one type is expected in each series, two groups of fragment peaks (one at m/e's representative of each type) are selected. Pattern coefficients and sensitivities are developed as described above. The mutual contribution of the peaks of each type to the selected peaks for the other types (pattern coefficients) give rise to an equation of n unknowns (n representing the total of all types considered). When this is done for each of the n types, a system of n equations in n unknowns is obtained. These equations are solved simultaneously by matrix algebra using values from the mixture spectrum to obtain the analysis. Types of samples and compounds analyzed by this method are given (table 32).

Advantages of the high-voltage method are as follows: (1) Two or more compound types coincident in the same nominal m/e series can be determined simultaneously. (2) The spectra, in many instances, need not be corrected for isotopes. This tedious process can be manipulated in construction of the matrix. (3) Sensitivity corrections

Table 32.—Types of compounds analyzed by high-voltage mass spectrometry

Sulfur compounds	Hydrocarbons
1. Alkane sulfides.	1. Alkylbenzenes.
2. Monocyclic sulfides (sulfur in or out of ring).	2. Tetralins-indans.
3. Dicyclic sulfides.	3. Dinaphthenobenzenes.
4. Tricyclic sulfides.	4. Naphthalenes.
5. Tetracyclic sulfides.	5. Acenaphthenes.
6. Alkanethiols.	6. Acenaphthylenes.
7. Cycloalkanethiols.	7. Biphenyls.
8. Disulfides.	8. Phenyl- (indans-tetralins).
9. Benzenethiol.	9. Diphenylalkanes.
10. Thia- (indans-tetralins).	10. Fluorenes.
11. Alkyl aryl sulfides.	11. Indenes.
12. Diphenyl disulfides.	12. Naphthenonaphthalenes.
13. Thiophenes.	13. Anthracenes-phenanthrenes.
14. Thiophenethiols.	14. Phenylnaphthalenes.
15. Thienyl sulfides.	15. Pyrenes.
16. Thienothiophenes.	16. Paraffins.
17. Dithienyls.	17. Naphthenes.
18. Naphthenothiophenes.	18. Dinaphthenes.
19. Benzothiophenes.	19. Trinaphthenes.
20. Dibenzothiophenes.	
21. Phenylthiophenes.	
22. Thienobenzothiophenes.	

Types of samples analyzed

Physical separations

1. Wide boiling range distillates (>50° C).
2. Narrow boiling range distillate (<50° C).
3. Analytical distillation fractions.
4. Thermal diffusion fractions.
5. Silica gel liquid-solid chromatography fractions.
6. Alumina gel liquid-solid chromatography fractions.
7. Gas-liquid chromatography (GLC) fractions containing sulfur compounds and hydrocarbons.

Chemical treatments

1. Hydrogen iodide sulfide extracts.
2. Oxidation process sulfide extracts.
3. Urea adducts for *n*-alkanesulfides and thiols.
4. Thiourea adducts for select branched chain and cyclic sulfides.
5. Zinc chloride for separation of chain and cyclic sulfides.
6. Trinitrobenzene adducts.
7. *p*-Toluenesulfonate extracts.
8. Raney nickel desulfurization products.
9. Sodium aminoethoxide in diethylamine thiol extract.

need be applied only once (in construction of the matrix). (4) The matrix can be inverted to simplify its use in handling many similar samples. Disadvantages are as follows: (1) The inflexibility of the matrix when applied to a wide variety of samples. (2) Several different matrices are necessary to handle the variety of samples obtained from petroleum, and matrix inversion without a computer is laborious. (3) The presence of abundant fragment peaks often obliterates some qualitative detail in the spectra.

Hastings, Johnson, and Lumpkin (*167*), Dudenbostel and Klaas (*107*), and Andre, Hood, Longman, and O'Neal (*14*) have reported high-voltage methods for analyzing 12, 19, and 31 compound types, respectively (including several sulfur types). References to investigations and/or correlations of spectra with structure for a variety of sulfur com-

pounds are given in table 33. Several reference books (35, 159, 260, 336, and 369) are also available that contain information of interest on interpretation of mass spectra of organic sulfur compounds. In the method of Andre and coworkers (14) the single fragment peak, chosen as best for representing each type, corresponds, in general, to the p−1 series fragment peak for a trisubstituted species.

Table 33.—Investigations and/or correlations with structure for mass spectra of organic sulfur compounds

	References
Compound type:	
Alkylthiols	84, 242
Alkyl sulfides	84, 242
Thiacycloalkanes	84
Alkyl-cycloalkyl sulfides	84, 104
Bicyclic sulfides	84, 104
Disulfides	84
Alkyl aryl sulfides	84, 336
Arylthiols	84, 336
Diaryl sulfides	336
Diaryl sulfoxides	336
Diaryl sulfones	283, 336
Alkyl aryl sulfones	336
Thiaindans-thiatetralins	85
Thiophenes	127, 128, 129, 160, 231
Benzothiophenes	84, 85, 343
Dibenzothiophenes	85
Benzodithiophenes	85
Thienylsulfides	131
Benzothienyl sulfides	130
Phenylthiophenes	204, 284
Thienothiophenes	193

Low Voltage.—The low-voltage mass spectrometer (LVMS) method is dependent on parent peaks (molecular ions) being produced while the fragment peaks are essentially eliminated. Each peak in the spectrum is measured and predetermined sensitivity and isotope corrections applied. The corrected peaks are then summed and the results normalized to give a homologous type by individual carbon number or total homologous type by series analysis.

Advantages of the method are as follows: (1) Fragment peaks, essentially eliminated, do not obliterate the qualitative detail in the spectrum; (2) sensitivities, once obtained, can be adapted in a variety of combinations making the method quite flexible in handling fractions highly different in nature, and (3) the laborious multicomponent matrix inversions are avoided. Disadvantages are (1) each peak in the spectra requires unique sensitivity and isotope corrections determined by the nature of the sample; (2) rearrangement peaks, which fall on even m/e series, must be corrected for in the analysis; (3) detection of two or more types in the same m/e series is often difficult.

Sometimes this will be possible as a result of bi- or polymodal distributions in the "continuous" profile (fig. 63). Examples of compound types and samples that have been analyzed are given (table 32).

For the boiling ranges investigated by the project in its latter stages, 200° to 400° C (392° to 752° F), the averaging of LVMS sensitivity data for distillates (and liquid-solid chromatography fractions from them) led to the adoption of a set of sensitivity data for general routine use. The data obtained on complex mixtures in which the presence or absence of certain compound types cannot be established are subject to greater error than those from which qualitative aspects can be determined. So, while some semiquantitative accuracy is lost using this general sensitivity data, the ability of such an analysis to guide further separations is not lost. The sensitivities determined for general use considered, in most instances, a di- to trisubstituted species average sensitivity. This agreed well with the findings of Andre and others (14) for their high-voltage method which covers analysis of material through a slightly higher boiling range. Examples of applications of these sensitivity data follow.

Table 31 and figure 63 represent data from a major study on a Wasson, Texas, 225° to 400° C (436° to 752° F) distillate fractionated into eight fractions with a Brush still. Brush still fraction 3 was passed through silica gel to obtain an aromatic-sulfur compound concentrate (fig. 63). This concentrate was then passed through alumina gel and eight fractions were collected (table 31). LVMS showed the silica gel aromatic-sulfur compound concentrate (fig. 63) had a molecular-weight range of 156 to 274, an average molecular weight of 204, and a total nominal m/e series analysis as given in the figure. Other data obtained showed the concentrate contained 4.17 percent sulfur and represented 3.919 percent of the crude oil. Also shown in figure 63 is the total nominal m/e series analysis compared with that obtained by reconstituting the results of the analyses of the eight fractions obtained by alumina gel separation of this sample (discussed below).

The alumina gel fractions from the silica gel, aromatic-sulfur compound concentrate (discussed in the preceding paragraph) were analyzed by LVMS. The total nominal m/e series type analyses, weight-percent data, average molecular weights, and probable compound types and the fractions in which they are expected are recorded in table 31. The silica gel aromatic-sulfur concentrate contained small amounts of saturates (+2, 0, and −2 series of alumina gel fractions 1 through 3). The bulk of fractions 1 through 3 were monoaromatics (−6,

**Table 34.—Analyses of sulfides from Wasson crude oil (150° to 220° C)
distillate and Wilmington crude oil (>150° C) distillate**

	Series							Total
	+2	0	−2	−4	−6	−8	−10	
Wasson sulfide extract:								
Percent...................	6.7	3.8	.....	5.5	5.2	22.8	56.0	100
Molecular weight range.......	128–268	154–266	.....	122–262	148–260	118–244	116–256	.....
Bulk molecular weight range..	142–198	168–210	.....	150–206	162–290	132–188	130–200	.....
Wilmington sulfide extract:								
Percent...................	17.7	8.1	4.8	4.6	5.8	5.2	53.8	100
Molecular weight range.......	128–202	126–210	124–194	122–164	120–176	118–188	116–214	.....

−8, −10 series) with the higher molecular weight homologs eluting first (average molecular weight drops across these fractions). The inflection in the −6 series (fractions 2 through 4) indicates the depletion of the alkylbenzenes and the beginning of elution of benzothiophenes. The sharp increase in percentage in fraction 4 of the −12 and −14 series also indicates diaromatics beginning to elute (naphthalenes and naphtheno naphthalenes, respectively). The inflection in the −2 series (fractions 6 through 8) indicates depletion of the diaromatics (naphthalenes) and the start of elution of the triaromatic dibenzothiophenes, which were azeotroped in the distillation, and the presence of some bicyclic sulfides which also elute in this region. The sharp increase in percentage in fraction 8 (−16 and −18 series) also indicates triaromatics eluting (acenaphthylenes and anthracenes-phenanthrenes, respectively). The slight increases in percentage in fraction 8 (−8 and −10 series) are due in part to chain and monocyclic sulfides and may be indicative of small amounts of polynuclear aromatics. A more detailed discussion of the analyses of corresponding fractions from a similar treatment of Brush still fraction 1 is given in the literature (433).

Examples of analyses of sulfide concentrates removed from similar boiling-range distillates of two different crudes by two different extraction procedures are discussed below. These data are presented to show how LVMS can be applied to compound type concentrates which, although still complex, are much simpler than the aromatic-sulfur compound concentrates or whole crudes from which they are extracted. Again the general sensitivity data were used.

Sulfides were extracted from a Wasson, Texas, crude oil 150° to 220° C (302° to 428° F) distillate by an oxidation process employing t-butylhydroperoxide to produce the sulfoxides which were extracted with H_2SO_4 and reduced back to the original sulfides by $TiCl_3$. The results of the analy-

sis are shown in table 34. This sulfide extract contained in excess of 80 percent sulfides of the chain, monocyclic, bicyclic, and tricyclic sulfides classes (−8, −10, +2, and 0 series, respectively). In addition, other compounds containing sulfide sulfur [thiaindans-thiatetralins (−4 series) and naphtheno thiaindans-thiatetralins (−6 series)] were present. The total sulfide sulfur compounds of all classes were therefore in excess of 85 percent. Fragment peaks in the −7 and −9 series of the spectrum indicated small amounts of some monoaromatics (alkylbenzenes and alkylindans-tetralins) which had been carried over in the extraction.

Sulfides were extracted from a Wilmington, California, crude oil distillate boiling above 150° C (302° F) by hydrogen iodide treatment (186). The results of the LVMS analysis are recorded in table 34. This sulfide extract contained in excess of 80 percent sulfides of the monocyclic, bicyclic, tricyclic, and tetracyclic sulfides classes (−10, +2, 0, and −2 series, respectively). In addition, other sulfide sulfur compounds [thiaindans-tetralins (−4 series), naphthenothiaindans-tetralins (−6 series), and possibly dinaphthenothiaindans-tetralins (−8 series)] were present. The total sulfide sulfur compounds of all classes were therefore in excess of 85 percent. Fragment peaks in the −7 and −9 series of the spectrum indicated small amounts of monoaromatics (alkylbenzenes and alkylindans-tetralins) which had been carried over in the extraction. An exhaustive study of this and lower boiling Wilmington distillates revealed the crude contained no chain sulfides, so the 5.2 percent (−8 series) must be all monoaromatics and/or dinaphthenothiaindans-thiatetralins.

In conclusion, whether confirming results of research or guiding research, all available data from all other previously described sources must be considered, compiled, and weighed together to obtain the most thorough mass spectral interpretation possible.

The program of the Separation and Identification Section as originally organized did not provide for the synthesis of sulfur compounds by the section, as it was anticipated that the need for experimental reference compounds could be met by commercial sources, by compounds provided by API Research Project 48B, and through donations from other laboratories. However, early in the program, it became apparent that many more compounds than could be provided by these sources would be required; consequently, a synthesis program was begun which became a significant part of the efforts of the Separation and Identification Section.

All of the preparations made in the early part of the project were done on a scale sufficiently large for purification by fractional distillation. However, after the acquisition of GLC equipment it was found that the scale of the preparations could be reduced greatly and still provide sufficient purified material. The production rate for compounds which could be prepared routinely, particularly chain sulfides, increased substantially. Many compounds required the preparation of several intermediates together with much experimentation. In general, these preparations were not scaled down except on steps that required the testing of alternate procedures.

The Separation and Identification Section required the preparation not only of sulfur compounds of the types found in petroleum, but also of many of the hydrocarbons derived from them by desulfurization. These compounds are listed by class in the appendix. Portions of this work dealing with synthesis of thiolacetic acid (*191*), alkyl cycloalkyl sulfides (*188*), and cyclic sulfides (*189*) have been published and are not reviewed in detail. Similarly, routine syntheses by purely conventional methods are not covered in detail. The following discussion is limited to methods and techniques developed by the project or to those that may be less well known to the reader.

THIOLS

Thiols listed in appendix D were synthesized by seven methods, two of which were original with the project:

1. Alkylation of NaSH or thiourea with an alkyl bromide.
2. Addition of thiolacetic acid to an olefin

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followed by alkaline hydrolysis of the resulting thiolacetate.
3. Alkylation of an alkyl *p*-toluene sulfonate with NaSH or thiourea.
4. Reaction of a diazonium salt with

$$K-S-\overset{\overset{\displaystyle S}{\|}}{C}-OC_2H_5.$$
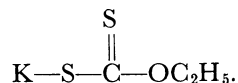
5. Reaction of a Grignard reagent with an alkyl polysulfide.
6. Reaction of a tertiary alcohol with liquid H_2S acidified with H_2SO_4 at $-78°$ C.
7. Reaction of pinacolone with H_2S and zinc dust in glacial acetic acid acidified with anhydrous HCl.

By far the most useful method of synthesizing thiols was the addition of thiolacetic acid to olefins (*47, 188, 189, 191*). The yields generally were excellent, and a product of high purity was obtained as the thiolacetic acid adds exclusively anti-Markownikoff. Substituted cyclic olefins yield a mixture of *cis* and *trans* isomers which are generally difficult or impossible to separate. Many olefins and alcohol precursors were synthesized as intermediates for preparing thiols. Also large amounts of thiolacetic acid were required, and as the reagent is rather expensive, a new procedure was developed for producing it on a large scale in a continuous reactor (*191*). The method involves passing acetic anhydride and hydrogen sulfide concurrently through a column of Amberlite IR4B ion-exchange resin with continuous separation of the product from the column effluent.

Method 4, which uses *p*-toluene sulfonates as the alkylating agent, is especially useful for preparing thiols of the neopentyl type. The sulfonates may be prepared from the alcohols without rearrangement and are much more reactive than the bromides. 2,2-Dimethyl-1-butanethiol was prepared by this method.

Only one thiol, 2,5-dimethylbenzenethiol, was prepared by method 5 in which 2,5-dimethylphenylmagnesium bromide was reacted with *t*-amylpolysulfide. The polysulfide is preferable to elemental sulfur in this reaction as the reactive sulfur reacts more as a monomer than as the S_8 molecule, resulting in higher yields.

The synthesis of tertiary alkanethiols is much more difficult than that of primary or secondary

thiols. The tertiary thiols can be made commercially by catalyzed addition of hydrogen sulfide to branched chain olefins under pressure. The addition, in contrast to the thiolacetic acid addition, is Markownikoff. 2-Methyl-2-pentanethiol was obtained, but in low yield, by adding liquid H_2S to 2-methyl-1-pentene at $-78°$ C ($-108°$ F) and with sulfuric acid added as a catalyst. 3-Methyl-3-hexanethiol was obtained in excellent yield by treating a solution of 3-methyl-3-hexanol in liquid H_2S at $-78°$ C with concentrated sulfuric acid. The method failed with 1-methyl-1-cyclohexanol, probably because the high melting point of the alcohol prevented it from dissolving in the acidified H_2S. It is believed that the reaction of a tertiary alcohol with H_2S in the presence of H_2SO_4 at $-78°$ C should be a generally useful method of preparing tertiary alkanethiols. The reaction is as follows:

$$\underset{\underset{R''}{|}}{\overset{\overset{R'}{|}}{R-C-OH}}\xrightarrow{H+}R-\overset{\overset{R'}{|}}{C}+\xrightarrow{HS^-}\underset{\underset{R''}{|}}{\overset{\overset{R'}{|}}{R-C-SH}}$$
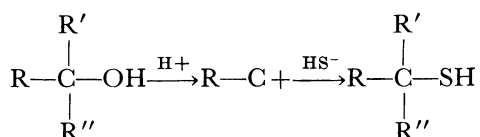
During the investigation of the thiol extract from the 111° to 150° C (232° to 302° F) fraction of Wasson crude oil, a need arose for 3,3-dimethyl-2-butanethiol as a reference compound. None of the foregoing methods was suitable for this synthesis. Two new methods starting with pinacolone were tried with success. In the first method, pinacolone was condensed with thiolacetic acid in the presence of zinc chloride at room temperature. A cherry-red layer separated and was isolated and washed repeatedly with pentane to remove unreacted starting materials. The layer was dissolved in ether and washed with water and distilled at reduced pressure. A cherry-red distillate was obtained in moderate yield. A portion of the red distillate was reduced by lithium aluminum hydride in ether solution to yield ethanethiol and 3,3-dimethyl-2-butanethiol of excellent purity. The reactions are believed to be as follows:

$$\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C-C}}\overset{\overset{O}{\|}}{C}-C+2CH_3COSH\xrightarrow{ZnCl_2}$$

$$\underset{\underset{C}{|}\ \underset{S-Ac}{|}}{\overset{\overset{C}{|}\ \overset{S-Ac}{|}}{C-C-C-C}}\xrightarrow{LiAlH_4}\underset{\underset{C}{|}}{\overset{\overset{C}{|}\ \overset{SH}{|}}{C-C-C-C}}+2C-C-SH$$

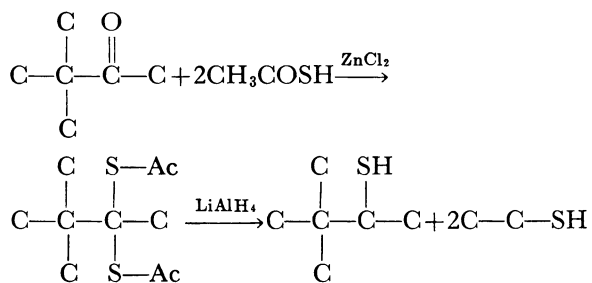In the second method, a solution of pinacolone and zinc chloride in glacial acetic acid was stirred with zinc dust as hydrogen sulfide was passed into the solution. Little reaction took place until a small amount of hydrogen chloride was passed in. The reaction flask was cooled in an ice bath and the reaction maintained for about 4 hours while several small increments of hydrogen chloride were added. The mixture was diluted with water, and the product was extracted with pentane and distilled, boiling at 126° C (259° F). The yield was 33 percent. The structure was proved by GLC, desulfurization, and mass, infrared, and NMR spectroscopy.

ALKYL AND CYCLOALKYL SULFIDES

Most of the chain sulfides were made by alkaline alkylation of a thiol (or Na_2S in two preparations) with the appropriate alkyl bromide. Primary, secondary, and tertiary thiols are readily alkylated if the bromide is primary, less readily if secondary. Tertiary halides and cyclohexyl halides are very unreactive, although two sulfides, 2,2,4,5-tetramethyl-3-thiaheptane and 2,2,4-trimethyl-4-ethyl-3-thiahexane, were obtained in very low yield using a tertiary chloride.

When alkylating a thiol with a tertiary alkyl group, the method of Fehnel and Carmack (122) generally gives excellent yields. In this reaction, a thiol is alkylated with a tertiary alcohol in 80 percent sulfuric acid at 5° to 15° C (41° to 59° F). 2,2,4,4-Tetramethyl-3-thiapentane (t-butyl sulfide), 3-ethyl-3-methyl-2-thiapentane, 3,3-dimethyl-2-thiahexane, cyclohexyl t-butyl sulfide, and dicyclohexyl sulfide were made by this procedure.

4,4-Dimethyl-2-thiapentane (neopentyl methyl sulfide) was made by a special procedure. Chloromethyl methyl sulfide (1-chloro-2-thiapropane) was added to t-butyl magnesium chloride in ether solution. A vigorous reaction occurred immediately. The structure of the sulfide (b.p. 125° C) was proved by desulfurization to neopentane and methane and by mass spectrometry.

CYCLIC SULFIDES

The synthesis of cyclic sulfides in general is more difficult than synthesis of thiols and chain sulfides. Several steps are commonly necessary, each requiring the synthesis of an intermediate. The synthetic work of the Separation and Identification Section was concerned only with 5- and 6-membered ring cyclic sulfides and to a minor extent with bicyclic and tricyclic sulfides.

In the summer of 1954 an extensive program for synthesizing a series of alkyl cycloalkyl sulfides and a series of 2-alkyl thiacyclohexanes was begun. The results of this work were published (188). Only some general observations about it are made here. The starting material for these syntheses was dihydropyran which yields 2-alkyltetrahydropyrans when hydrochlorinated and coupled with alkyl Grignard reagents. Two methods of replacing oxygen with sulfur were used. In the first method, the tetrahydropyran was converted into the 1,5-dibromoalkane by heating with hydrobromic acid and additional hydrogen bromide. Reaction of the dibromoalkane with sodium sulfide in methanol produced the cyclic sulfide. If the alkyl group is attached to the ring in a secondary position, the reaction with hydrogen bromide leads to serious decomposition, and the dibromoalkane cannot be distilled without further decomposition.

In the second method, the tetrahydropyran was converted directly to cyclic sulfide by vapor phase reaction at about 260° C (500° F) with hydrogen sulfide over a specially prepared chromia-alumina catalyst. Both methods led to extensive isomerization between the 5- and 6-membered rings:
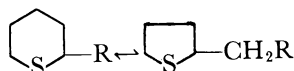
The isomer ratios from the two methods were reversed with the dibromide method favoring the 6-membered ring and the catalytic method the 5-membered ring. The structure of each isomer was determined by separation and trapping by GLC, desulfurization, and infrared and NMR spectroscopy.

Another method used for preparing cyclic sulfides is by heating a 1,4- or 1,5-diol with phosphorus pentasulfide. The method is especially useful when one or both OH groups are tertiary, a circumstance unfavorable to other methods. 2,2-Dimethylthiacyclopentane, 2,2,5-trimethylthiacyclopentane, and 2,2,5,5-tetramethylthiacyclopentane were prepared by this method. An attempt to prepare 3,3-dimethylthiacyclohexane by heating 2,2-dimethyl-1,5-pentanediol (by lithium aluminum hydride reduction of 2,2-dimethylglutaric acid dimethyl ester) with P_2S_5 produced instead 2-ethyl-3-methylthiacyclopentane because of rearrangement of the neopentyl group. Similarly, 2,2,4-trimethyl-1,3-pentanediol when heated with P_2S_5 produced 2,2,5,5-tetramethylthiacyclopentane as the most abundant sulfide, also 2,2,4,4-tetramethylthiacyclopentane, 2,2,3,4-tetramethylthiacyclopentane, and other unidentified sulfides.

Another useful method of preparing cyclic sulfides is the addition of thiolacetic acid to an unsaturated alcohol having a suitably positioned double bond followed by ring closure. In this manner, 2-ethyl-2-methylthiacyclopentane was prepared by the addition of thiolacetic acid to 3-methyl-5-hexene-3-ol. The resulting thiol-alcohol was condensed by cold 80 percent sulfuric acid to give an 80 percent yield of the sulfide.

Likewise the addition of thiolacetic acid to endomethylenetetrahydrobenzyl alcohol (from Diels-Alder addition of allyl alcohol to cyclopentadiene) gave a product which when passed over the special chromia-alumina catalyst gave a product which partially crystallized into camphorlike crystals. Probably two isomers,
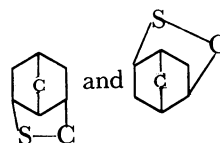
were present, but the structures of the liquid and solid fractions were not established.

Perhaps the most versatile method for preparing thiacyclopentanes is by the Dieckmann condensation of suitable substituted thiaalkane-1,3-dioic esters (460). If both α-methylene positions are unsubstituted, ring closure can take place in two directions,
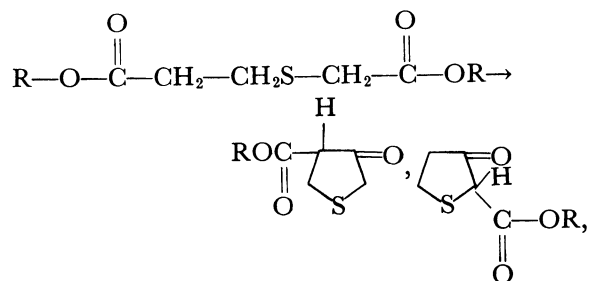
the predominant product depending upon reaction conditions.

Theoretically, the active hydrogen, geminal with the carboxyl group, should be available for substitution; however, all attempts to alkylate this position failed. The thiacyclopentanone carboxylates were therefore hydrolyzed and decarboxylated to the corresponding thiacyclopentanones. Monosubstitution in the 3-position was accomplished by reaction with a Grignard reagent to give a 3-alkylthiacyclopentanol-3. The hydroxyl group was replaced by chlorine by treatment with concentrated hydrochloric acid, and the chloride was reduced by sodium in liquid ammonia. 3-Ethyl-

3-methyl-, 2-ethyl-3-methyl-, and 2,3-dimethyl-thiacyclopentanes were made in this manner.

3,3-Disubstituted thiacyclopentanes may be prepared by reacting the 3-alkyl-3-chloro-thiacyclopentane with a Grignard reagent:
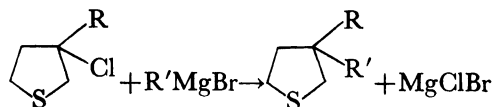
This reaction was used to prepare 2,3,3-trimethyl-, 2,3-dimethyl-3-ethyl-, and 3,3-dimethylthiacyclopentanes.

3,4-Dimethylthiacyclopentane was made by reducing 2,3-dimethylsuccinic ester to 3,4-dimethylbutane-1,4-diol and reacting with H_2S over chromia-alumina catalyst.

The thiaalkanedioic esters may be made by coupling a chloro or bromo acid with a mercapto acid and esterifying. It seems generally preferable to couple the esters of the two acids, particularly if the starting esters are available commercially. Hydrolysis of the ester is avoided by adding methanolic sodium hydroxide to the reaction flask containing a methanol solution of the two esters, avoiding an excess of sodium hydroxide.

AROMATIC SULFIDES

A series of alkyl aryl sulfides was needed to help establish the presence and identity of this class of compounds in Wasson crude oil. All but one of those listed in the appendix were prepared by alkaline alkylation of the appropriate aromatic thiol with an alkyl bromide. Phenyl t-butyl sulfide was made from benzenethiol and t-butyl alcohol by the Fehnel and Carmack method (122).

1-Thiaindan was prepared in low yield by coupling benzenethiol with ethylene chlorohydrin and heating with polyphosphoric acid at 120° C. An attempt to prepare 2-methyl-1-thiaindan by the same procedure failed during the last step.

1,2,3,4,4a,4b-Hexahydrodibenzothiophene was prepared by addition of benzene-sulfenyl chloride to cyclohexene and treatment of the 2-chlorocyclohexyl phenylsulfide with aluminum chloride:
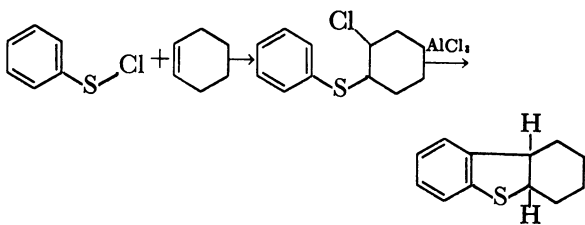
The reaction was very slow and after refluxing for 3 hours in carbon disulfide was allowed to stand for several days. The product was water washed and extracted with pentane. Upon chilling, a white solid, which proved to be diphenyl disulfide, separated. The main oil portion was chromatographed on alumina and fractionally distilled. Mass spectral analysis of the product showed it to be hexahydrodibenzothiophene, and GLC showed two principal products, probably the cis and trans forms.

THIOPHENES AND BENZOTHIOPHENES

Only a small amount of work was done on the synthesis of thiophenes. 3-Methylthiophene was made by passing isoprene through a column that contained molten sulfur at about 400° C (752° F). The product was purified by distillation and chromatography on alumina. The yield was approximately 30 percent.

2,3-Dimethylthiophene (containing 2,4-dimethylthiophene, separable by GLC) was prepared from 3-methylthiophene-2-aldehyde (230, 368) by Wolff-Kishner reduction. 2-Ethyl-5-methylthiophene was prepared by acetylation of 2-methylthiophene followed by Wolff-Kishner reduction of the 2-acetyl-5-methylthiophene.

1,2,3,4,6,7,8,9-Octahydrodibenzothiophene was prepared by the method of Cooper (86) which consists of refluxing cyclohexanone with sulfur for 24 hours. The product was distilled at reduced pressure, the residue extracted with pentane, and the recovered cyclohexanone returned to the reaction. The process was repeated several times. The product was distilled at 1 mm, washed with sodium hydroxide solution, treated with maleic anhydride, and redistilled. The product, still not homogeneous, was chromatographed on alumina and recrystallized.

A mixture of 2- and 3-cyclohexylthiophenes was prepared by passing cyclohexene and thiophene over alumina at 250° C (482° F).

By far the most useful method of preparing benzothiophenes in this program was a modification of the method of Werner (452). The yields were generally excellent, and the product was of good quality. The method involves heating an aryl β-ketosulfide, derived by coupling an α-chloroketone with an aromatic thiol, with polyphosphoric acid at 120° C (248° F). Benzothiophenes prepared by this method were 3-methyl-, 2,3-dimethyl-, 3-ethyl-, 3,5-dimethyl-, 3,7-dimethylbenzothiophene, 1,2,3,4-tetrahydrobenzothiophene and cyclopentabenz[b]thiophene. A related method which uses a chlorodiethylacetal instead of a

chloroketone, was used for benzothiophenes unsubstituted on the thiophene ring: 4-methyl- and 6-methyl- (mixture), 5-methyl-, 7-methyl-, 5-ethyl-, and a mixture of 2,4-dimethyl- and 2,6-dimethylbenzothiophenes. The yields were usually low with the formation of much tar.

2-Methylbenzothiophene was obtained in apparently good yield and purity in a small test run by an experimental reductive cyclization procedure in which α-phenyl-mercaptopropionic methyl ester was heated with a mixture of polyphosphoric acid and phosphorous acid to about 120° C. However, many attempts to duplicate the results produced only minor amounts of the desired product. Sufficient 2,4- and 2,6-dimethylbenzothiophene mixture to serve as reference material was obtained by this procedure.

AROMATIC HYDROCARBONS

The key step in the identification of benzothiophenes and thiaindans is desulfurization by Raney nickel to alkylbenzenes. Few C_{10} and C_{11} alkylbenzenes are available commercially, so it became necessary to synthesize those most needed for reference. The compounds synthesized are listed in the appendix with an identification number. The methods used are discussed briefly and the identification numbers given for the compounds synthesized by that method.

1. Acylation of an aromatic hydrocarbon was followed by reduction of the phenone by (a) the Wolff-Kishner reduction, 5, or (b) by passing the ketone over copper chromite catalyst with hydrogen at 200° to 250° C (392° to 482° F). Hydrocarbons produced by this method were 6, 22, 23, 25, 28, 29, and 30. The yields by the copper chromite method are somewhat lower than those by the Wolff-Kishner method as some of the phenone dimerizes and undergoes cyclization to give 9,10-dihydrophenanthrenes and other products.

2. (a) Addition of an aryl Grignard reagent to an aliphatic aldehyde or ketone or (b) addition of an alkyl Grignard to an aromatic aldehyde or ketone gives an aromatic alcohol which when passed with hydrogen over copper chromite at 200° to 250° C gives the alkylbenzene in good yield. Copper chromite has the property of hydrogenating the olefinic double bonds produced by dehydration of the alcohol without hydrogenating the aromatic ring. Hydrocarbons produced by this method were (a) 7, 9, 10, 11, 13, 16, 24, 26, 27, 36, and (b) 10, 17, 18, and 19 (see appendix). Some hydrocarbons, for example, 10, were prepared by two methods.

3. Aryl Grignard reagents when coupled with allylic chlorides yield aromatic olefins which are readily hydrogenated over copper chromite catalyst as in methods 1 and 2 to give alkylbenzenes. This method was employed for hydrocarbons 1, 3, 4, 21, 33, 34, and 35.

4. Friedel-Crafts alkylation is less specific than the preceding methods, as few hydrocarbons can be produced free from isomers. However, this reaction found considerable usefulness since it required only one step and yields were generally good. Usually the isomers can be separated by GLC, so that many times two useful products are produced. Hydrocarbons 2, 6, 8, 12, 14, 15, 18, 31, 32, 37, and 38 (see appendix) were made by this method.

1,3-Dimethyl-5-propylbenzene (compound 20) was synthesized by Raney nickel desulfurization of 2,5,7-trimethylbenzo[b]thiophene. Only a few milligrams of this compound were prepared for reference infrared spectrum.

WASSON, TEXAS, CRUDE OIL

The sulfur-containing constituents of petroleum have been of interest and concern to the petroleum industry almost since its beginning. However, it was not until the inception of this project that a systematic study was undertaken to isolate and identify the sulfur compounds present in the distillate fractions of several crude oils. Of the four crude oils investigated, the Wasson, Texas, crude was studied in greater detail than the other three, and this is evident in the greater number of sulfur compounds found in this oil. Some quantitative data were developed, and these are reported in both text and tables. The quantitative data are too few and fall far short of the desires of the authors. This results, in part from the pioneering nature of this study, the necessary gradual development of equipment and techniques, the limited availability of reference samples, the lack of GLC in the early years of this study, and little or no opportunity to repeat past work after better techniques and equipment were developed and refined.

Preceding sections of this report include adequate descriptions of the equipment and techniques developed and employed in the isolation and identification of individual sulfur compounds. At this point, specific examples and proof of identification are given for many of the 156 sulfur compounds identified in the various fractions of Wasson crude oil.

It should be pointed out that some of the methods used would not necessarily be the methods of choice today. However, in many instances (some 20 years ago), they were the best or only methods available, and their use is reported to provide an accurate description of the research.

0° to 100° C Boiling Range

The first petroleum fraction investigated was a Wasson distillate boiling from 0° to 100° C (32° to 212° F). This distillate was isothermally distilled from the crude oil using the isothermal still previously described. The problem then was to concentrate, without appreciable loss, the sulfur compounds (approximately 40 grams) from 9,000 grams of distillate, to identify these sulfur compounds, and to estimate the concentration in which each was present. Theoretically, 21 compounds of carbon, hydrogen, and sulfur exist which boil

below 100° C (212° F), in addition to hydrogen sulfide and carbon disulfide. However, thiacyclopropane (*94*), its methyl and dimethyl derivatives, and thiacyclobutane (*362*) are very unstable and not likely to be present in petroleum. While carbon disulfide (*155, 338*) has been reported present in straight-run petroleum distillates, its identification is generally discounted.

The several processing steps, see figure 64, used in this study were isothermal distillation, fractionation, concentration of sulfur compounds by adsorption on alumina, and semimicrofractionation of the concentrate. Identification and quantitative estimation of the individual compounds were based on infrared spectra of the individual distillation cuts. Figure 65 shows a distillation curve resulting from the semimicro distillation of 37.6 grams of the sulfur compound concentrate at a takeoff rate of less than 0.7 g/hr in a semimicro Heligrid packed column.

Because of the high volatility of methanethiol, ethanethiol, and 2-thiapropane, these three compounds were determined independently. This was

Table 35.—Sulfur compounds identified in Wasson crude oil distillate boiling below 100° C and estimated weight-percent present

Name	Boiling point, °C	Weight-percent in Wasson crude oil [1]	Literature references to compounds found in petroleum
Methanethiol (methyl mercaptan)	5.96	0.00240	457
Ethanethiol (ethyl mercaptan)	34.0	.00530	43
2-Thiapropane (methyl sulfide)	37.31	.00088	267
2-Propanethiol (isopropyl mercaptan)	52.56	.00199	43
2-Methyl-2-propanethiol (*tert*-butyl mercaptan)	64.22	.00055	([2])
2-Thiabutane (methyl ethyl sulfide)	66.65	.00222	267, 410
1-Propanethiol (*n*-propyl mercaptan)	67.5	.00041	([2])
3-Methyl-2-thiabutane (methyl isopropyl sulfide)	84.81	.00064	([2])
2-Butanethiol (*sec*-butyl mercaptan)	85.15	.00386	43, 297
2-Methyl-1-propanethiol (isobutyl mercaptan)	88.72	.00003	43
3-Thiapentane (ethyl sulfide)	92.10	.00075	267
2-Thiapentane (methyl *n*-propyl sulfide)	95.52	.00030	410
1-Butanethiol (*n*-butyl mercaptan)	98.4	Trace	([2])
3,3-Dimethyl-2-thiabutane (methyl *tert*-butyl sulfide)	99.0	Not determined	([2])
2-Methyl-2-butanethiol (*tert*-amyl mercaptan)	99.0	0.00126	([2])

[1] Minimum values.
[2] Not previously reported in literature.
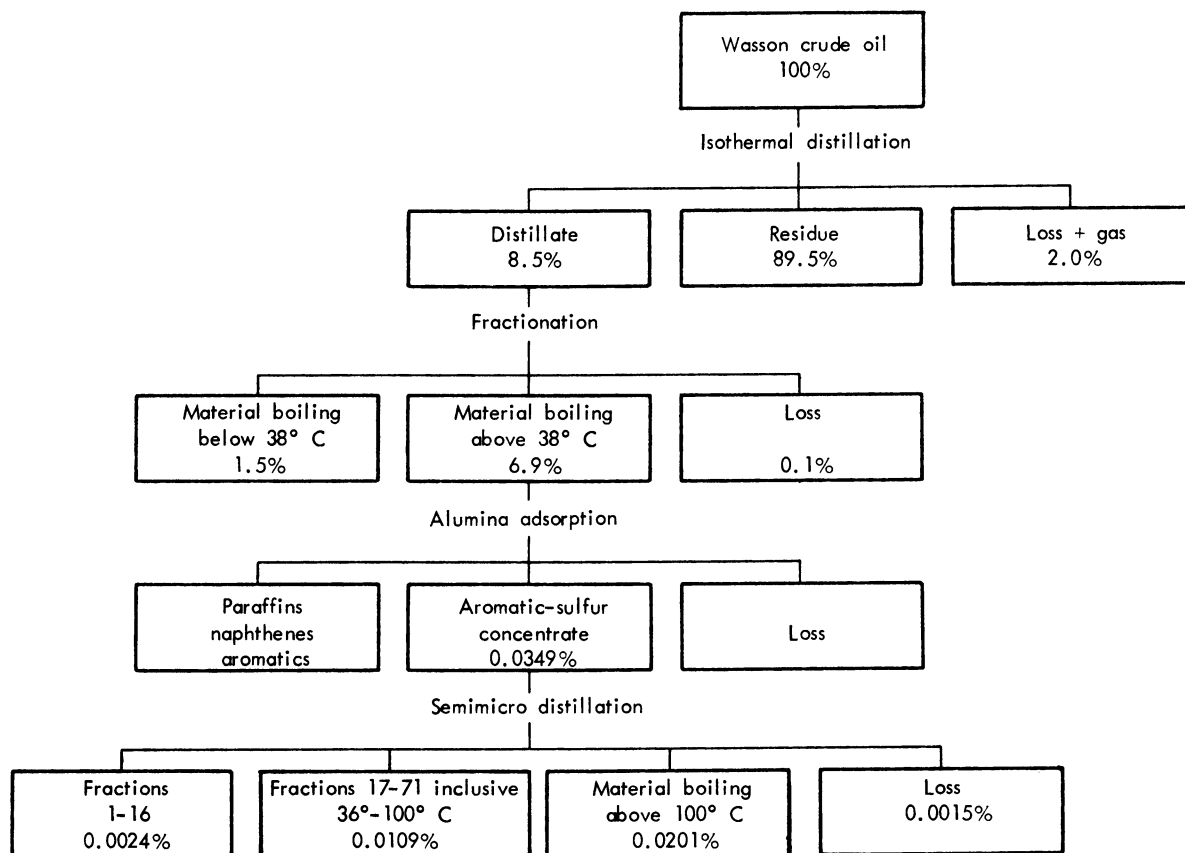
Figure 64.—Outline of sample treatment.

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accomplished by distilling about 3 liters of crude oil in a high-temperature Heligrid packed column and taking fractions at 9° and 28° C (48° and 82° F). The fractions were collected in special aluminum liquid petroleum gas "bombs" and analyzed for thiols by amperometric titration and for sulfides by the ultraviolet absorption of the iodine complex, as described by Hastings (*166*). The only sulfur compound in fraction 1 was methanethiol, 0.0024 percent of the crude oil. The second fraction contained ethanethiol, 0.0053 percent, and 2-thiapropane, 0.00088 percent. Ethanethiol and 2-thiapropane distill as azeotropes (with *n*-pentane) boiling at about 26° to 27° C (79° to 81° F), instead of at the normal boiling points of the compounds, 35.0° and 37.3°, respectively.

Table 35 lists all the compounds identified in the fraction of Wasson crude oil boiling below 100° C, and gives an estimate of their concentration in the crude oil. These compounds were identified by a comparison of the infrared spectrum of each distillation fraction with the spectrum of the individual reference thiols and sulfides. These spectra and other details of the study were reported in detail by Coleman and coworkers (*77*). Several of the compounds found had not been identified previously in crude oil. All of the theoretically possible compounds of carbon, hydrogen, and sulfur except thiacyclopropane, 2-methylthiacyclopropane, 2,2-dimethylthiacyclopropane, *trans*-2,3-dimethylthiacyclopropane, thiacyclobutane, and thiophene were found. The three- and four-membered cyclic sulfides are unstable and were not expected. In this investigation, no evidence of thiophene absorption bands was present in the infrared spectra of appropriate boiling-range cuts. Negative results were also obtained with the isatin reagent when applied to selected fractions from the adsorption column, including those eluted before the sulfur concentrate; however, this test can be expected to fail in the presence of large amounts of thiols. While
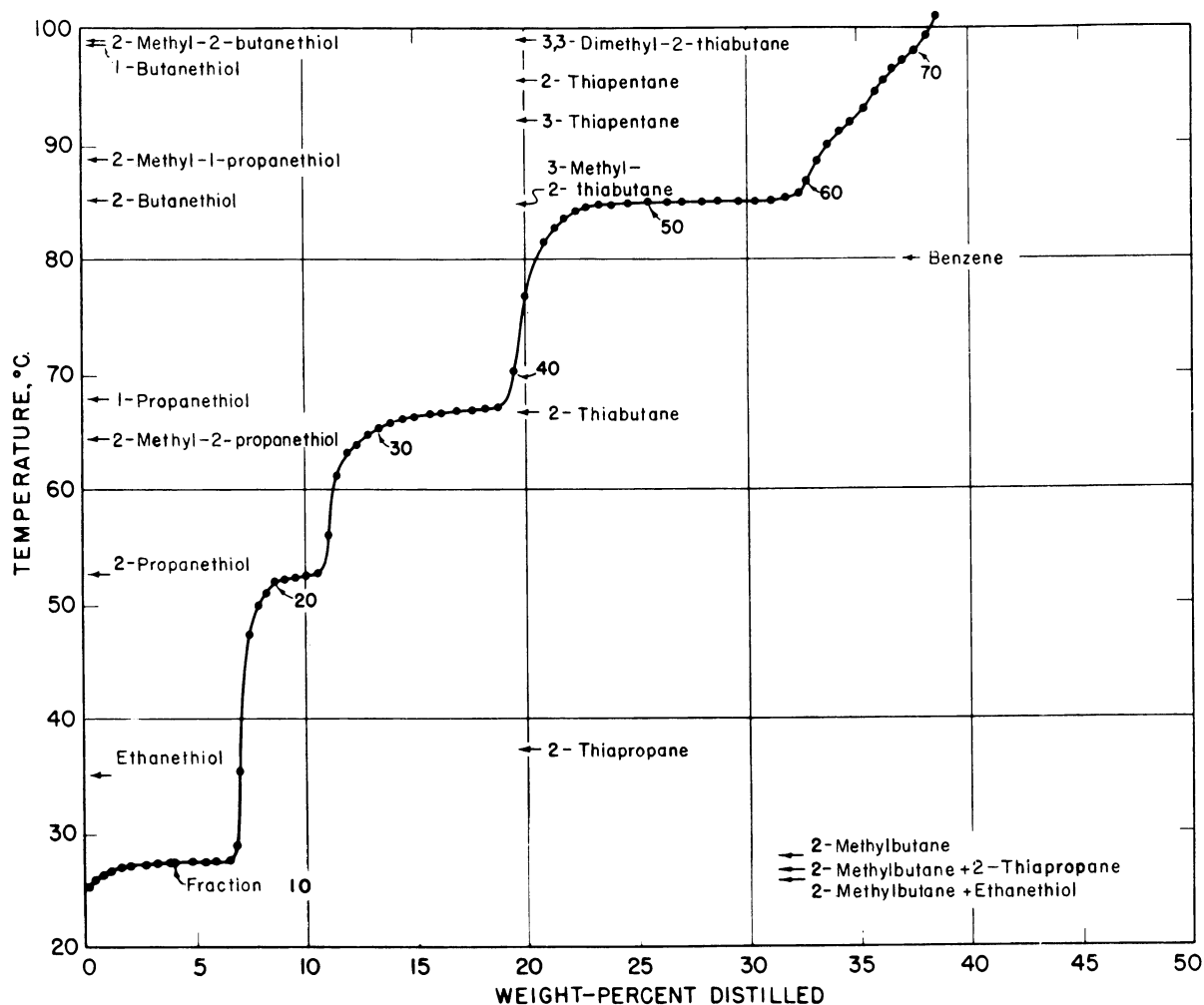
Figure 65.—Fractionation of sulfur concentrate from Wasson distillate.

there was no evidence for thiophene, traces of this material could have been lost in the adsorption step.

111° to 150° C Boiling Range

During the investigation of the sulfur-containing constituents in the 111° to 150° C (232° to 302° F) boiling range, new and improved analytical methods, such as gas-liquid chromatography and microdesulfurization became available, and thus provided means for identifications not previously possible.

The systematic procedural steps involved in this investigation, shown in figure 66, included isothermal distillation to produce a wide-boiling cut, followed by fractionation at reduced pressure to prepare a distillate boiling from 111° to 150° C (232° to 302° F). This distillate comprised 7.46 percent of the original crude oil and provided a limited molecular-weight spread, which was desirable for subsequent chromatographic separations on alumina. The initial sulfur concentrating step with liquid-solid chromatography involved percolating fifteen 750-ml aliquot portions of the 111° to 150° C distillate through a 225-cm-long adsorption column packed with Alcoa H–41 alumina (gel-to-sample ratio of approximately 2 to 1). Elution with 1,500 ml of isooctane preferentially removed a large amount of the aromatics from the fraction. The resulting aromatic and sulfur compound concentrate (4.686 percent sulfur, 0.39 per-
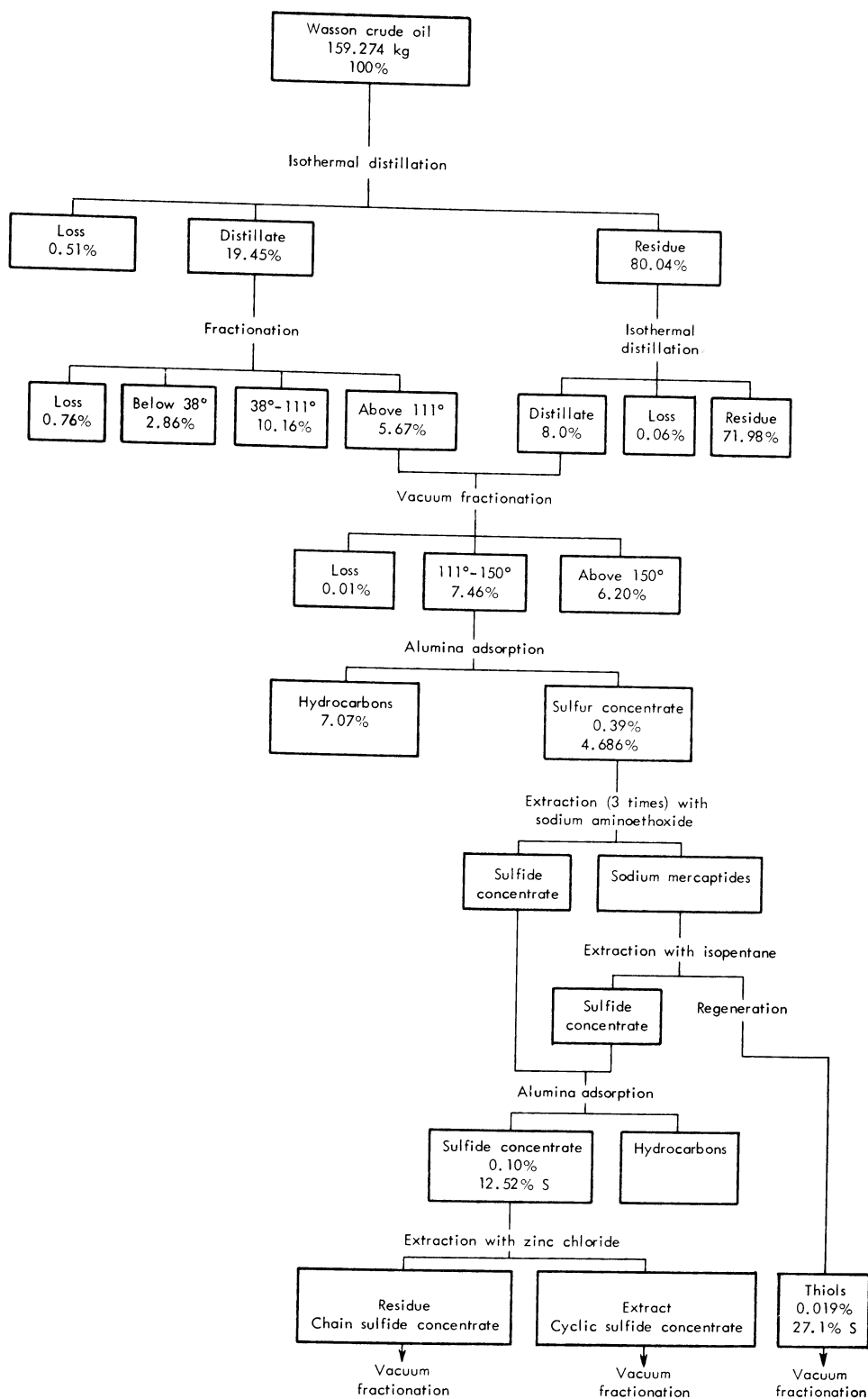
Figure 66.—Processing of Wasson crude oil to produce sulfur compound concentrates.
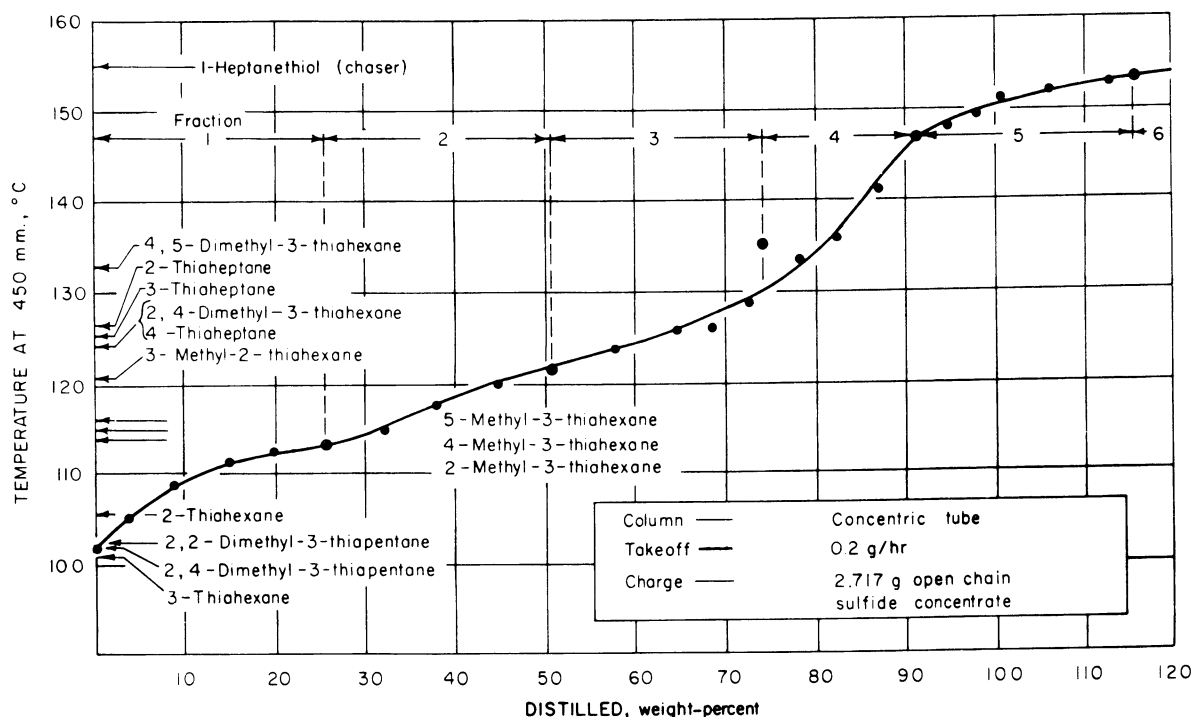
Figure 67.—Distillation curve of chain sulfide concentrate from 111° to 150° C Wasson distillate.

cent of the crude oil), constituted a suitable sample for applying chemical extraction of thiols as the next concentration step.

The extraction method used at this stage consisted of reacting the sample with sodium aminoethoxide ($H_2NC_2H_4ONa$) dissolved in anhydrous ethylenediamine ($H_2NC_2H_4NH_2$), regenerating the thiols by acid hydrolysis of the sodium mercaptides, and finally recovering the thiols by steam distillation.

Following extraction of the thiols from the aromatic and sulfur compound concentrate, an additional alumina adsorption step was employed to increase the sulfide concentration for chemical extraction. The resulting sulfide concentrate fraction represented 0.10 percent of the original crude oil and contained 12.52 percent sulfur which, based on the average molecular weight of the fraction, represented approximately 45 percent sulfides. The zinc chloride extraction, used for a general separation between chain and cyclic sulfides, has been described (419). The procedure entailed many qualitative tests on the small fractions, so that the material losses precluded the securing of good quantitative data. However, this chemical extraction did achieve a reasonably effective separation of sulfide types as evidenced by a 6.1-to-1 ratio of cyclics-to-chain sulfides in the cyclic-sulfide con-

centrate and a 1-to-2.3 ratio in the chain-sulfide concentrate.

Each individual concentrate (chain sulfides, cyclic sulfides, and thiols) was fractionated in a commercial all-glass concentric-tube column similar to that described by Donnell and Kennedy (103). The conditions of column operation included reduced pressure at 450 mm Hg to reduce the possibility of thermal degradation. The product takeoff rate was 0.2 gram per hour to insure optimum fractionation. The resulting distillation curve for the chain sulfides is shown in figure 67; for the cyclic sulfides in figure 68; and for the thiols in figure 69. Boiling points for some of the identified compounds are indicated in each of the distillation charts. These boiling points have been corrected to 450 mm Hg. Some of the identified sulfur compounds listed in table 36 admittedly have boiling points either below 111° or above 150° C. The presence of the low-boiling compounds is the result of minor distillation carryover, and the presence of compounds boiling above 150° C is, primarily, the result of azeotropic effects.

Following vacuum fractionation of each concentrate, GLC analyses of all distillation fractions with a Perkin-Elmer Model 154–D vapor fractometer employing a thermistor-type thermal conduc-
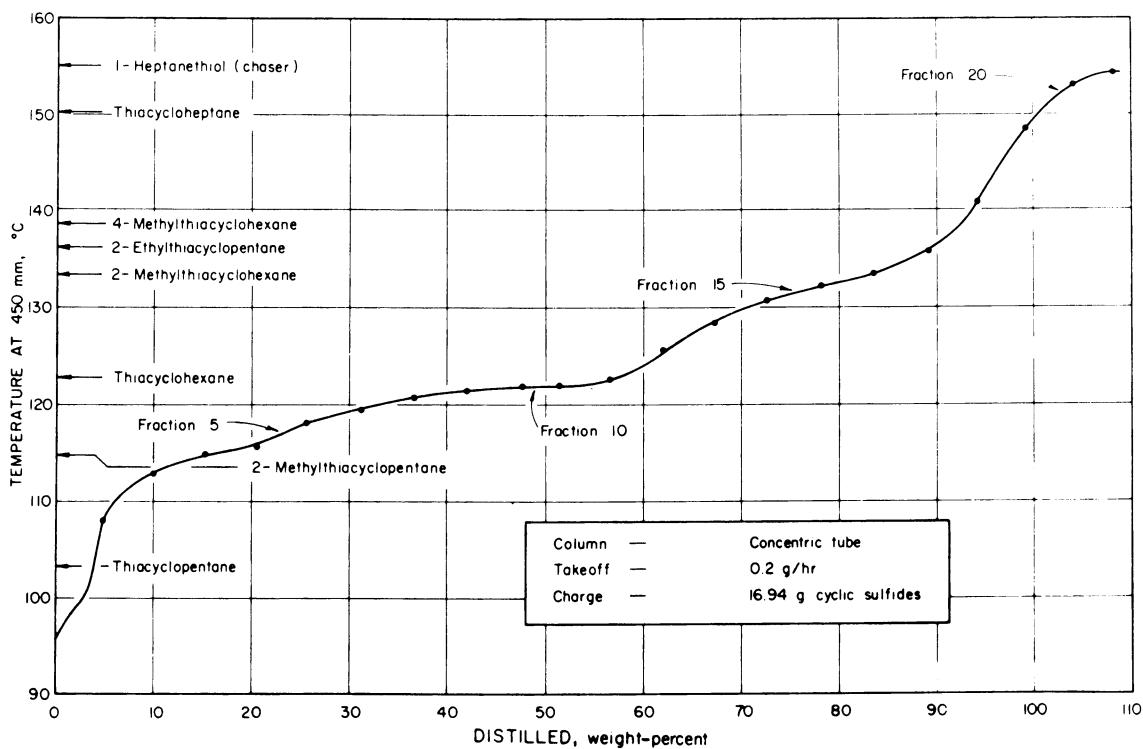
Figure 68.—Distillation curve of cyclic sulfide concentrate from 111° to 150° C Wasson distillate.
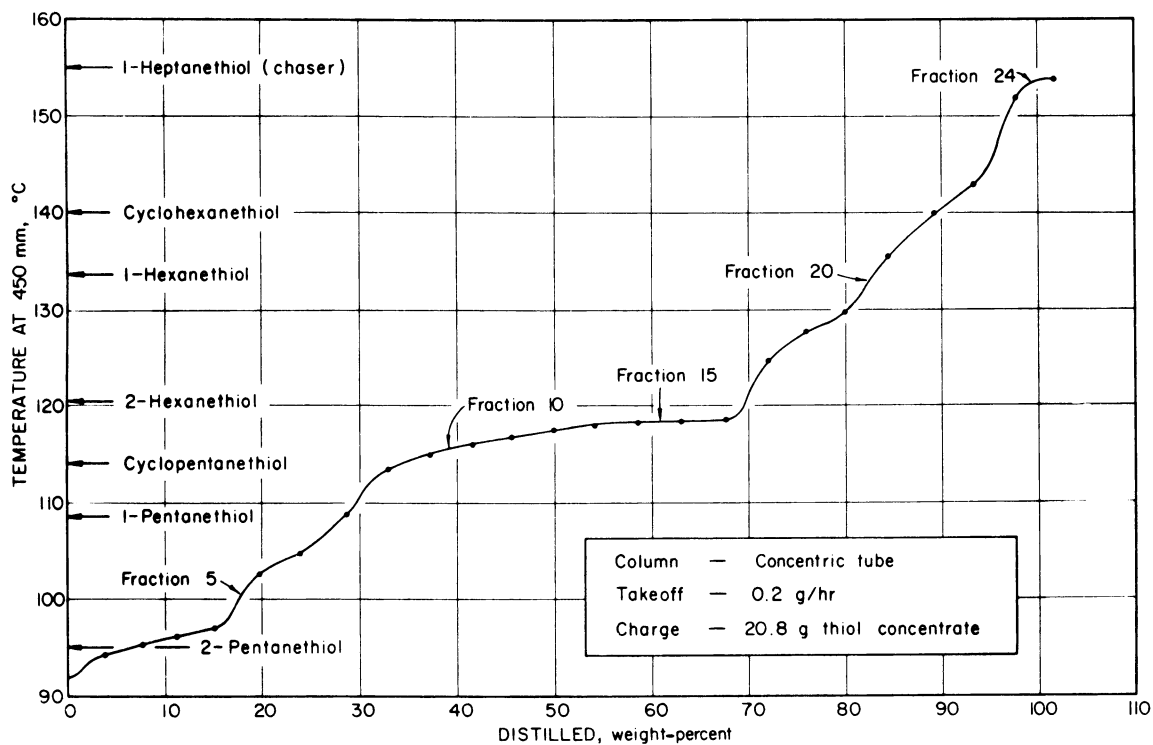
Figure 69.—Distillation curve of thiol concentrate from 111° to 150° C Wasson distillate.

Table 36.—Sulfur compounds identified in a Wasson, Texas, crude oil distillate boiling from 111° to 150° C

Cyclic sulfides	Thiols	Chain sulfides

C₄H₈S:
  Thiacyclopentane
	C₄H₉SH:
	  1-Butanethiol
	  2-Butanethiol
	  2-Methyl-1-propanethiol	

C₅H₁₀S:
  2-Methylthiacyclopentane
  3-Methylthiacyclopentane
  Thiacyclohexane
	C₅H₁₁SH:
	  1-Pentanethiol
	  2-Pentanethiol
	  3-Pentanethiol
	  2-Methyl-1-butanethiol
	  3-Methyl-1-butanethiol
	  2-Methyl-2-butanethiol
	  3-Methyl-2-butanethiol
	  2,2-Dimethyl-1-propanethiol
	
	C₅H₉SH:
	  Cyclopentanethiol
		C₅H₁₂S:
		  2-Thiahexane.
		  3-Thiahexane.
		  3-Methyl-2-thiapentane.

C₆H₁₂S:
  2,2-Dimethylthiacyclopentane
  3,3-Dimethylthiacyclopentane
  cis- and/or trans-2,3-Dimethylthia-
    cyclopentane
  cis-2,4-Dimethylthiacyclopentane
  trans-2,4-Dimethylthiacyclopentane
  cis- and/or trans-3,4-dimethyl-
    thiacyclopentane
  cis-2,5-Dimethylthiacyclopentane
  trans-2,5-Dimethylthiacyclo-
    pentane
  2-Ethylthiacyclopentane
  2-Methylthiacyclohexane
  3-Methylthiacyclohexane
  4-Methylthiacyclohexane
	C₆H₁₃SH:
	  1-Hexanethiol
	  2-Hexanethiol
	  3-Hexanethiol
	  2-Methyl-1-pentanethiol
	  3-Methyl-1-pentanethiol
	  4-Methyl-1-pentanethiol
	  2-Methyl-2-pentanethiol
	  3-Methyl-2-pentanethiol
	  4-Methyl-2-pentanethiol
	  2-Methyl-3-pentanethiol
	  3-Methyl-3-pentanethiol
	  2,2-Dimethyl-1-butanethiol
	  2,3-Dimethyl-1-butanethiol
	  2,3-Dimethyl-2-butanethiol
	  3,3-Dimethyl-1-butanethiol
	  3,3-Dimethyl-2-butanethiol
	  2-Ethyl-1-butanethiol
	
	C₆H₁₁SH:
	  Cyclohexanethiol
	  1-Methylcyclopentanethiol
	  cis-2-Methylcyclopentanethiol
	  trans-2-Methylcyclopentanethiol
	  cis- and/or trans-3-methylcyclo-
	    pentanethiol
		C₆H₁₄S:
		  2-Thiaheptane.
		  3-Thiaheptane.
		  4-Thiaheptane.
		  3-Methyl-2-thiahexane.
		  2-Methyl-3-thiahexane.
		  4-Methyl-3-thiahexane.
		  5-Methyl-3-thiahexane.
		  3,3-Dimethyl-2-thiapentane.
		  3,4-Dimethyl-2-thiapentane.
		  3-Ethyl-2-thiapentane.
		  2,2-Dimethyl-3-thiapentane.
		  2,4-Dimethyl-3-thiapentane.

C₇H₁₄S:
  2,2,5-Trimethylthiacyclopentane
	C₇H₁₅SH:
	  2-Methyl-2-hexanethiol
	  3-Methyl-3-hexanethiol
		C₇H₁₆S:
		  2-Methyl-4-thiaheptane.
		  2-Methyl-3-thiaheptane and/or
		    3-methyl-4-thiaheptane.
		  4-Methyl-3-thiaheptane and/or
		    4-ethyl-3-thiahexane.
		  2,2-Dimethyl-3-thiahexane.
		  2,4-Dimethyl-3-thiahexane.
		  2,5-Dimethyl-3-thiahexane.
		  4,4-Dimethyl-3-thiahexane.
		  4,5-Dimethyl-3-thiahexane.

C₈H₁₆S:
  2,2,5,5-Tetramethylthiacyclo-
    pentane		

Figure 70.—Gas-liquid chromatograms of chain sulfide distillation fractions 1, 3, 4, 5 and 6.

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tivity detector provided the basis for further study. Typical gas-liquid chromatograms shown in figures 70, 71, and 72 are of selected chain sulfide distillation fractions, cyclic sulfide distillation fractions, and thiol distillation fractions, respectively. Each figure includes retention time markers for the identified compounds. Some individual peaks of the chromatograms represent a single compound; where an individual peak (figs. 70–71) represents more than one compound, trapping and rechromatographing the complex mixtures on other GLC columns of differing polarity often achieved a complete separation of each individual component. Analyzing these isolated GLC subfractions by means of the micro-desulfurization technique (*428*) provided key information relative to sulfur compound structures present. This technique involved desulfurizing the trapped material, identifying the hydrocarbon products of desulfurization by GLC-retention-time data, and, from this information, determining the possible sulfur compound precursor. Combining such information with pertinent GLC-retention-time data usually pointed with high probability to the identity of certain individual sulfur compounds.

Final proof of identification was achieved by trapping the material emerging from the GLC column during the time interval of a given peak, obtaining its infrared spectrum, with a Perkin-Elmer Model 21 spectrophotometer with a cavity cell of 0.05-mm path length and a 4X beam condenser, and comparing the infrared spectrum of the isolated material with that of a reference compound. In some instances, mass spectrometry provided additional proof of identity.

Identification of Chain Sulfides

Five distillation fractions of the chain sulfide concentrate (fig. 66) were selected for a detailed study by gas chromatography and other analytical methods. Figure 70 shows chromatograms of these fractions, which were obtained with a $\frac{1}{4}$-inch OD by 40-foot-long aluminum column operating at 120° C (248° F) and with a helium flow rate of 60 ml per min and packed with 30- to 42-mesh GC-22 "Super-Support" coated with 23 percent DC–550 silicone oil. In some instances the use of different GLC columns, particularly those with more polar stationary phases, such as Reoplex 400 (polypropy-

Figure 71.—Gas-liquid chromatograms of cyclic sulfide distillation fractions 1, 6, and 14.

lene glycol adipate) and Zonyl–E (fluoroalcohol pyromelitate ester), provided key separations.

The chain sulfides comprising a given fraction presented a complicated identification problem, but the combination of GLC retention-time data and microdesulfurization data, with but few exceptions, permitted the identification of individual compounds. The desulfurization of each chain sulfide produced two hydrocarbon fragments; however, the pairing of two fragments with sulfur to effect the appropriate sulfide usually is quite evident.

For example the material producing the peak of figure 73 emerging between 36.6 and 38.4 minutes, produced predominantly propane upon desulfurization. In this instance only three chain sulfides could produce propane exclusively upon desulfurization: 2,4-dimethyl-3-thiapentane (diisopropyl sulfide), 2-methyl-3-thiahexane (isopropyl n-propyl sulfide), and 4-thiaheptane (di-n-propyl sulfide). As the retention time of the lowest boiling of the three

propyl sulfide isomers, namely 2,4-dimethyl-3-thiapentane (diisopropyl sulfide), corresponds exactly with that of the trapped peak, and that of the next higher boiling isomer, 2-methyl-3-thiahexane (isopropyl n-propyl sulfide) emerges almost 15 minutes later, a tentative identification was possible. In this instance, adequate sample was available for an infrared analysis, and the infrared spectral comparison of the trapped sample with a reference sample of 2,4-dimethyl-3-thiapentane confirmed the initial identification determined solely with GLC and microdesulfurization. The combination of these techniques proved to be effective even when more than one compound eluted as a single GLC peak.

The retention time of the shaded peak A of figure 73 corresponded exactly with that of 4-methyl-3-thiahexane but the GLC column used to obtain this chromatogram did not separate 5-methyl-3-thiahexane (ethyl isobutyl sulfide) from 4-methyl-3-thiahexane (ethyl sec-butyl sulfide). Also, the nearness of the retention times of 3,3-

Figure 72.—Gas-liquid chromatograms of thiol distillation fractions 1, 10, and 18.

dimethyl-2-thiapentane (methyl *t*-amyl sulfide) and 2-methyl-3-thiahexane (isopropyl *n*-propyl sulfide) constituted additional difficulty in trapping a sample containing only one compound.

Desulfurization of the material emerging from the GLC column during the time interval, denoted by the shading of peak *A* in figure 73, produced a number of hydrocarbons as identified in the GLC analysis shown in figure 74. With this chromatogram indicating methane, ethane, propane, isobutane, *n*-butane, and isopentane as products of desulfurization of trap *A*, the pairing of alkyl groups with a sulfur atom to form the appropriate precursors was accomplished by considering quantitative relationships of the individual hydrocarbons produced. With the aid of known retention-time data of alkyl sulfides, the assignment of alkyl groups derived from each hydrocarbon (for example, isobutyl or *t*-butyl from isobutane) was possible. Thus, propane as a product of desulfurization points to either an isopropyl or *n*-propyl radical, and the retention time considerations mentioned

above permit selection of the correct radical. The presence of *n*-butane indicates either *sec*-butyl or *n*-butyl substitution in a chain sulfide. Retention time of the sulfide "peak" (which implied a C_6 sulfide) and the relative quantitative data, indicated in figure 74, point to the fact that ethane and butane pair to form one sulfide. The retention time of 4-methyl-3-thiahexane (ethyl *sec*-butyl sulfide) corresponds exactly with that of the trapped material, and the retention time of the only other possible ethane-*n*-butane precursor, 3-thiaheptane (ethyl-*n*-butyl sulfide) is 16 minutes longer. Therefore, 4-methyl-3-thiahexane is identified as the major constituent (96.7 percent) of trap *A*. On the basis of retention time considerations for a number of chain sulfides it may be assumed that the isobutane found in the desulfurized product was paired with the ethane to form the sulfide from which these hydrocarbons had originated. This assumption is sound as other possible combinations of the butyl radical with the other available alkyl radicals, methyl and propyl, would yield sulfides
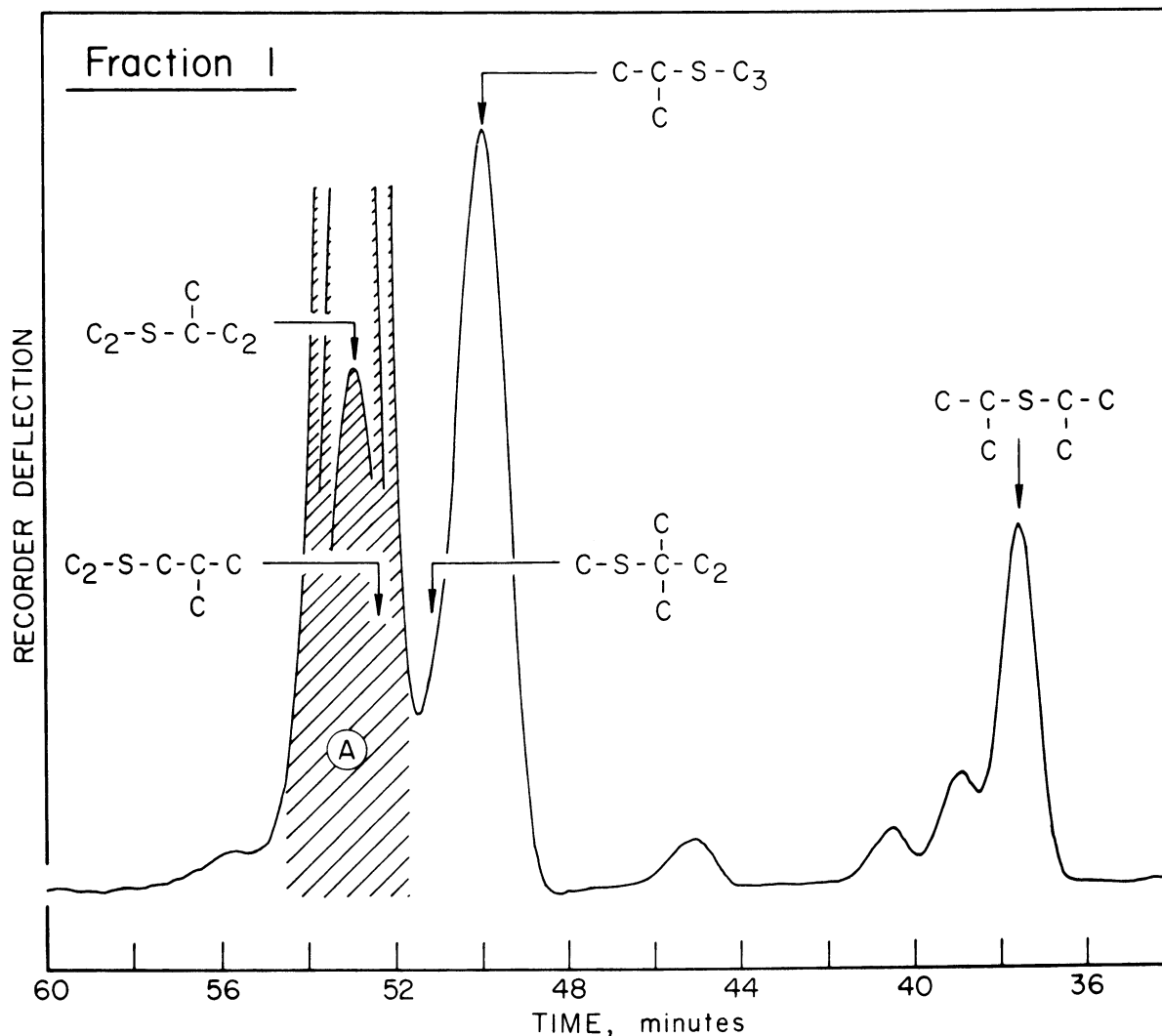
Figure 73.—Gas-liquid chromatogram of chain sulfide distillation fraction 1, figure 70.

of too short or too long retention times to fall within collection limits of trap A. Thus the identified chain sulfide constituent is 5-methyl-3-thiahexane (ethyl isobutyl sulfide). Continuing with the same reasoning, the t-amyl radical requires a methyl radical with which to form the sulfide because ethyl t-amyl sulfide emerges 21 minutes too late to fall in peak A. The application of such considerations identifies the chain sulfide precursor as 3,3-dimethyl-2-thiapentane (methyl t-amyl sulfide). In this instance, the presence of 1.5 percent of this compound in trap A is the result of carryover during the trapping procedure. Where contamination exists, rechromatographing the trapped material in the same column, or possibly in another column of differing polarity, produces a purified product. The propane fragment, on the basis of quantitative data, represented substitution on both sides of the sulfur atom, and retention time considerations then pointed unmistakably to 2-methyl-3-thiahexane (isopropyl n-propyl sulfide). The presence of 0.7 percent of this sulfide in trap A was the result of carryover and does not represent its concentration in the entire fraction.

The concentration of 4-methyl-3-thiahexane, the major component of peak A, was adequate for retrapping and obtaining an infrared spectrum of the product. Beginning the sample collection for infrared analysis at a slightly later time than that used for the microdesulfurization sample eliminated the carryover of the two compounds contained in the preceding peak, and also reduced the con-
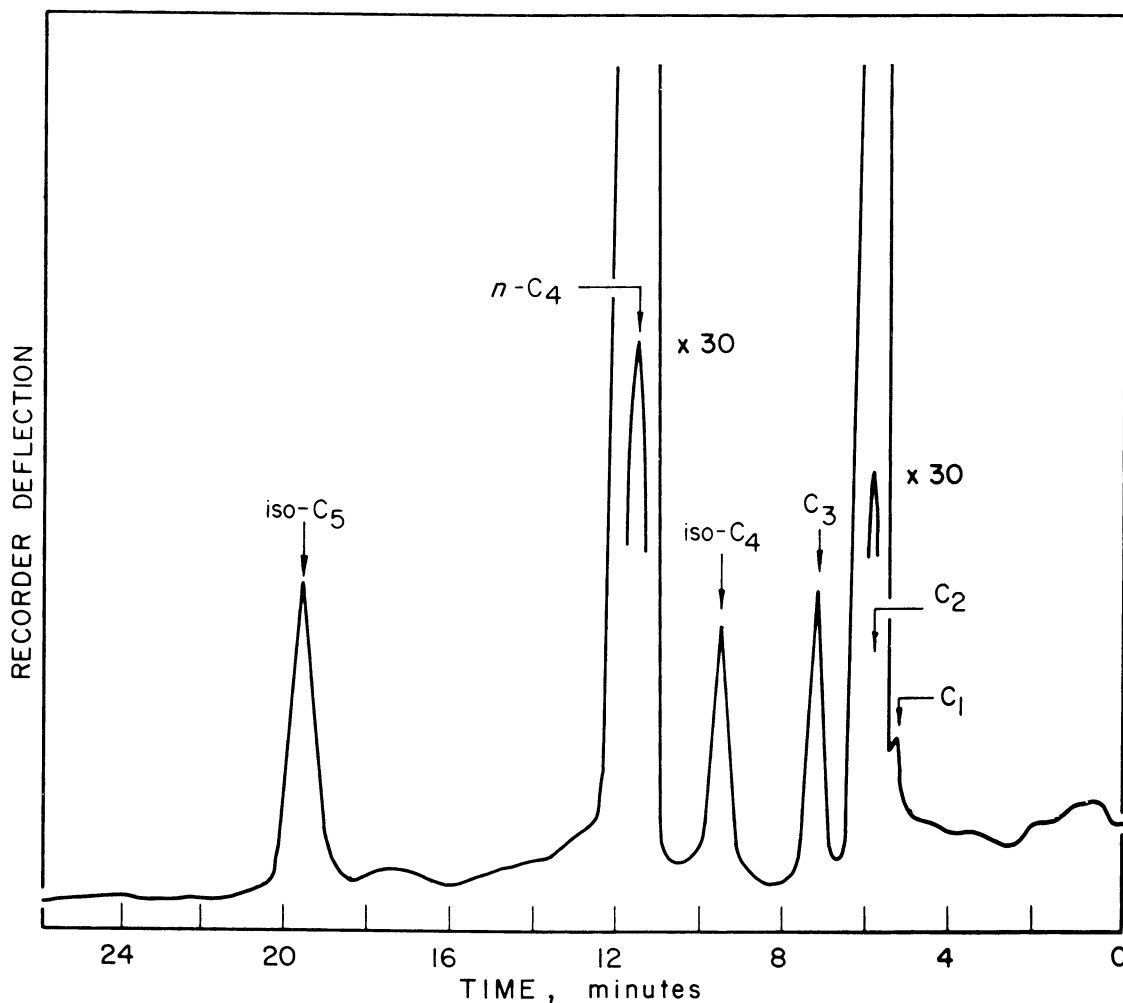
Figure 74.—Gas-liquid chromatogram of desulfurization products of trap A, figure 73.

centration of the 5-methyl-3-thiahexane emerging in the front portion of peak *A*. Figure 75 shows a comparison of the infrared spectrum of the material isolated from the crude oil fraction with the spectrum of a purified reference sample of 4-methyl-3-thiahexane (top spectrum). The excellent agreement of the two spectra provides positive proof of identification of this compound in the 111° to 150° C (232° to 302° F) boiling range distillate of Wasson crude oil.

Application of such procedures to other pertinent peaks in the chromatograms of the chain sulfide fraction resulted in the identification of 23 chain sulfides.

Identification of Cyclic Sulfides

The procedures employed for identifying individual cyclic sulfides in each of the 21 cyclic sulfide distillation fractions shown in figure 68 are similar to those discussed in the chain sulfide section. A comparison of the sample quantities distilled for both the chain sulfides (fig. 67) and cyclic sulfides (fig. 68) indicates that the cyclic sulfides are more abundant in this distillate. Admittedly the chemical separation of the two sulfide types did not achieve a clean-cut separation as mentioned earlier in the text. This is evidenced by chain sulfide contaminants in fraction 1 of figure 71 and small amounts of some methyl-substituted cyclic sulfides such as 2,2,5,5-tetramethyl-, 2,2,5-trimethyl-, and 2,5-dimethylthiacyclopentanes in the chain sulfide concentrate.

The chromatograms of figure 71 show the relationship of one distillation fraction to another for three selected fractions, as well as the relationship of the various cyclic sulfide retention times within
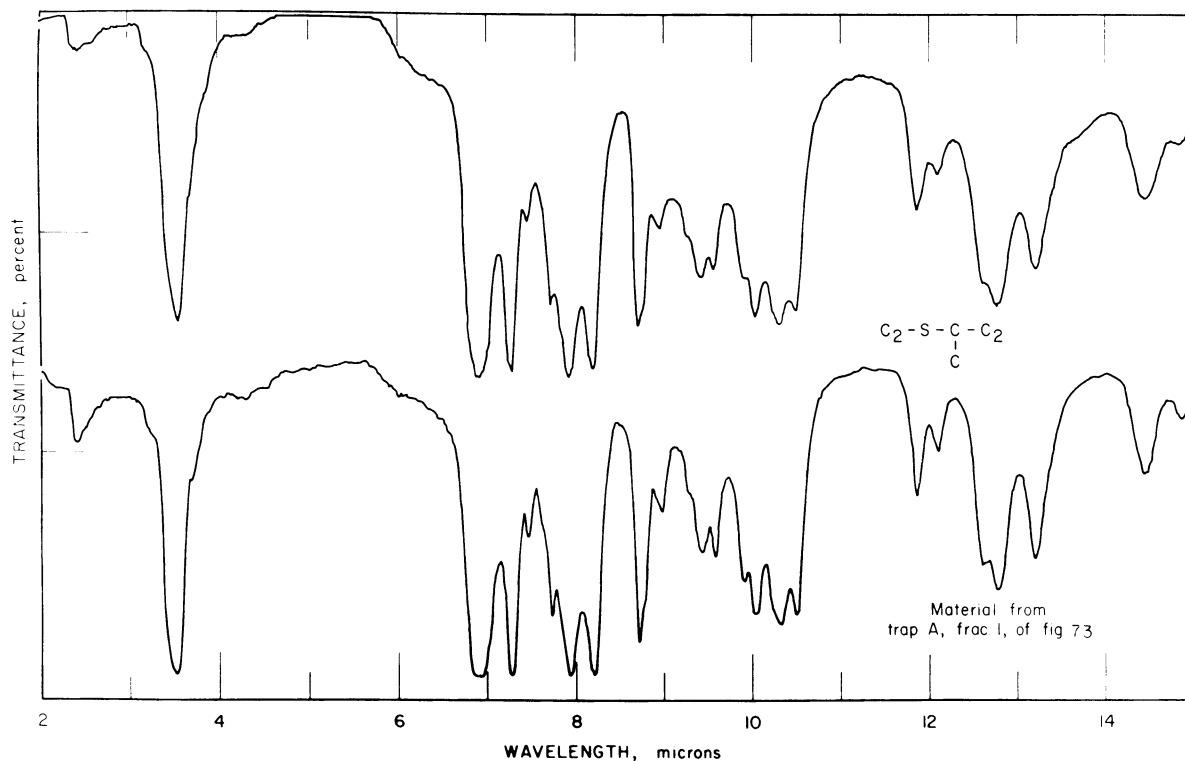
Figure 75.—Comparison of infrared spectrum of 4-methyl-3-thiahexane
with sulfide isolated from Wasson crude oil.

each fraction. These chromatograms were obtained with the same silicone oil column used for the chain sulfide analysis but at a higher temperature. Examination of figure 71, with respect to the retention times of the various cyclic sulfides, indicates only a few instances of a GLC peak representing but one compound. Two such examples are cited: the 2-methylthiacyclopentane peak of fractions 1 and 6 at 46 minutes retention time, and the 2,2,5-trimethylthiacyclopentane peak B of fraction 14 at 55 minutes retention time. Although peak B is not as isolated as desired, trapping and rechromatographing on the same column adequately removed any impurities caused by carryover from compounds emerging slightly earlier, and provided a sample suitable for infrared analysis. Figure 76 reproduces infrared spectra of the reference compound (top spectrum) and of the sulfide isolated from the crude oil (bottom spectrum). The similarity of the spectra proves the presence of 2,2,5-trimethylthiacyclopentane in fraction 14. Microdesulfurization of the isolated sulfide produced 2 methylhexane which provides further proof of the presence of the cyclic sulfide, 2,2,5-trimethyl-

thiacyclopentane. An earlier paper (*420*) presents infrared spectra for two additional cyclic sulfides (2-methylthiacyclopentane and 2-methylthiacyclohexane) identified in this study.

The chromatograms of figure 71 show changing concentrations for various cyclic sulfides from one fraction to another, and these changes continued through the higher boiling distillation fractions not shown in this figure. With so many of the GLC peaks in the chromatograms of figure 71 containing more than one component, resolution of each individual cyclic sulfide entailed extensive use of different GLC columns. Sometimes this involved trapping the components of a certain peak from one column and rechromatographing the trapped material on a column of differing polarity. In some instances, the material from the second trapping required another chromatographing step to effect ultimate resolution or purification. Several of the more successful GLC stationary phases used for some of the difficult cyclic sulfide separations were *m*-bis(*m*-phenoxyphenoxy)benzene, Reoplex 400, di-2-ethylhexyltetraphenylphthalate, and Aroclor–1260 (a chlorinated biphenyl). The latter sub-
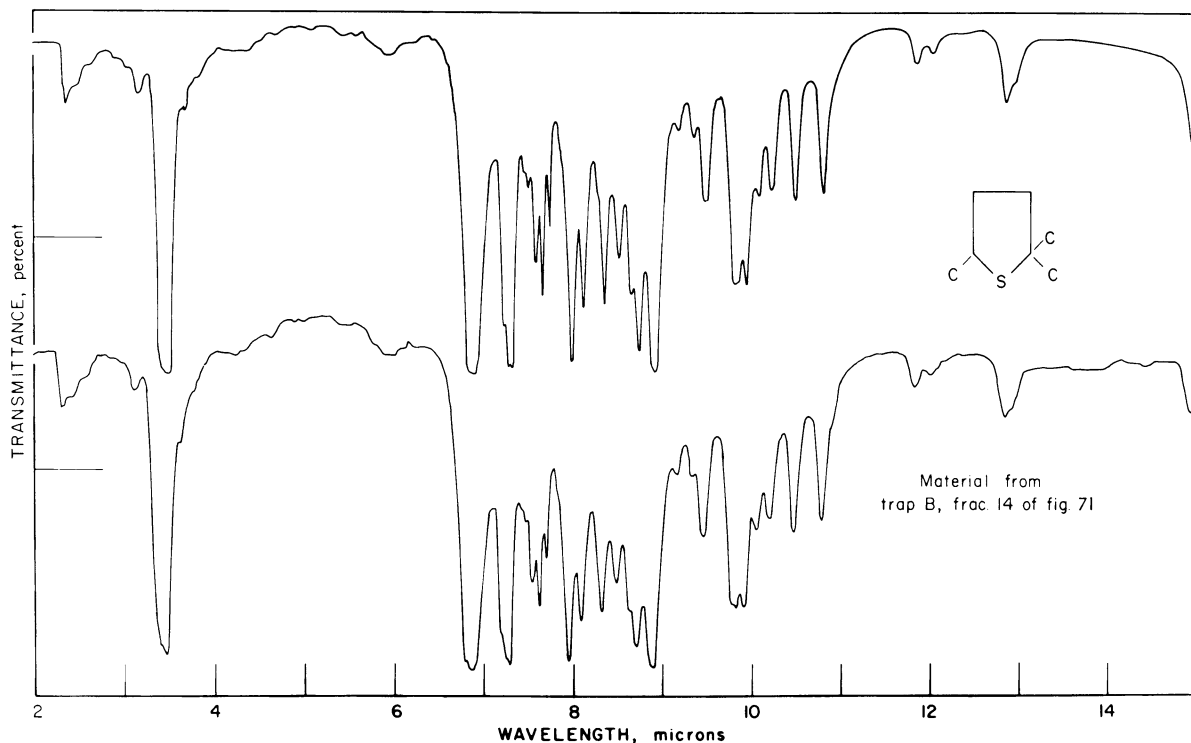
Figure 76.—Comparison of infrared spectrum of 2,2,5-trimethylthiacyclopentane
with spectrum of sulfide isolated from Wasson crude oil.

strate proved to be the most suitable for resolving the difficultly separable pair of cyclic sulfides, 2,2-dimethylthiacyclopentane and trans-2,5-dimethyl-thiacyclopentane.

Eighteen cyclic sulfides were identified in this Wasson 111° to 150° C (232° to 302° F) distillate by means of the various separation and identification techniques discussed above.

Identification of Thiols

Figure 72 shows the chromatograms of thiol distillation fractions 1, 10, and 18 of figure 69, with appropriate retention time markers for some of the identified thiols. The complexity of these thiol fractions is evident from the numerous retention time data points, particularly since these compounds do not represent a complete listing The GLC column (DC–550 silicone oil) and operating conditions used to produce the chromatograms in this figure are the same as for the cyclic sulfide study. Here too, as in the cyclic sulfide study, many of the GLC peaks contained more than one component, and thus required rechromatographing on other columns of different polarity for the most effective separations. Many such separation problems

existed for these thiol fractions; but in all instances, resolution and identification of the individual thiols were possible. For instance, rechromatographing a portion of the thiols of the GLC peak at 30 + minutes on a more polar column ($\frac{1}{4}$ in OD, 40-ft-long di-2-ethylhexyltetraphenylphthalate column; 20 g/100 g weight ratio of stationary phase on 30- to 42-mesh GC–22 "Super-Support") effectively resolved 2,3-dimethyl-2-butanethiol from 1-pentanethiol. These compounds had identical retention times on the DC–550 silicone oil column. The phthalate column also was effective for isolating cyclopentanethiol, 1-methyl-1-cyclopentanethiol, and other thiols described in an earlier publication (79). However, this paper illustrates only one specific instance of trapping and rechromatographing on a different column.

Thiol distillation fraction 18 was relatively complex, especially compared with fraction 21 which was almost solely cyclohexanethiol. The shaded GLC peak C of figure 72 represented but one of the peaks requiring trapping from the DC–550 silicone oil column and rechromatographing in other more polar GLC columns to effect satisfactory separations and unambiguous identifications. Trapping during
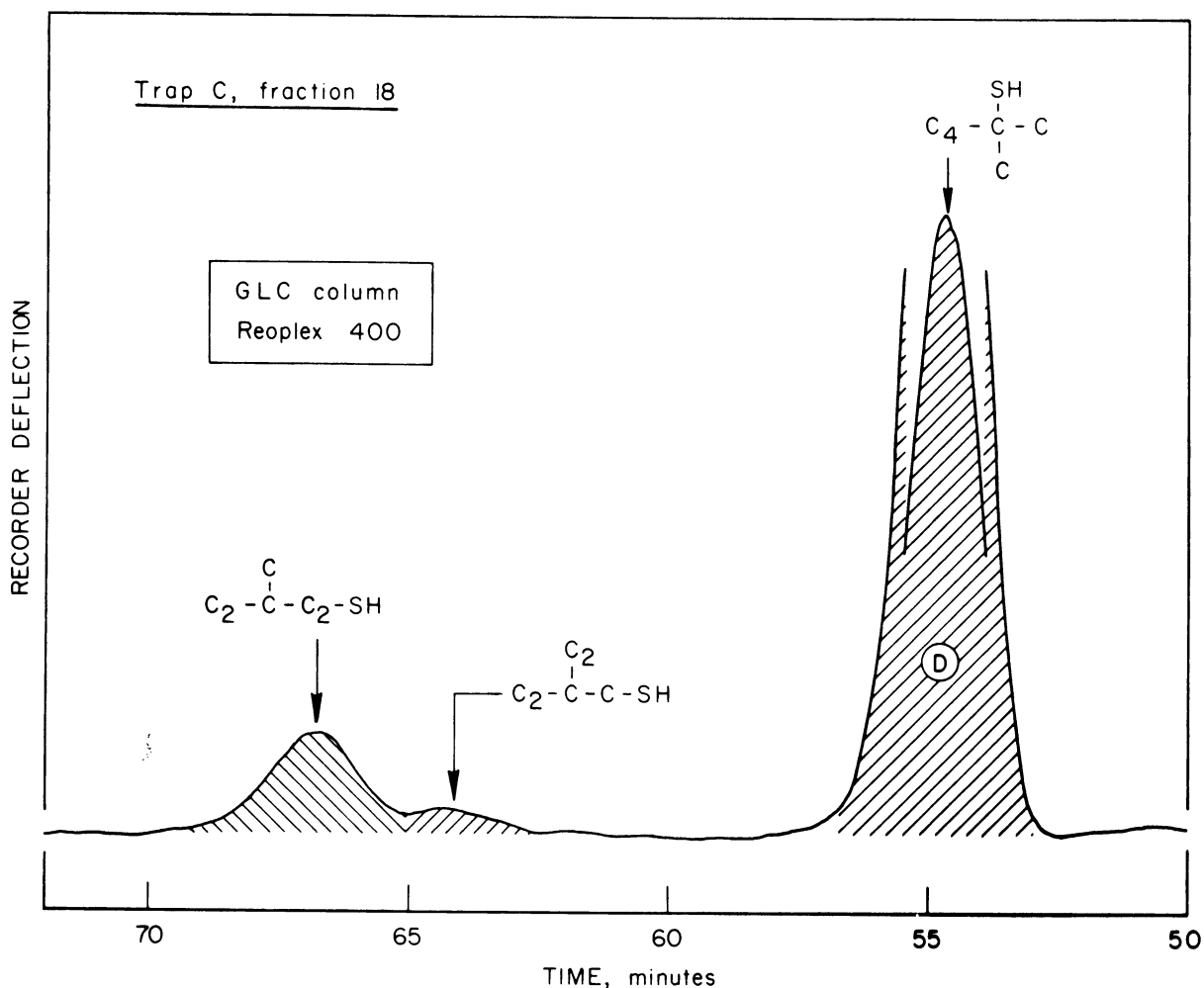
Figure 77.—Gas-liquid chromatogram of material trapped from peak C, fraction 18, figure 72.

the time interval which included the shaded peak C of fraction 18 in figure 72 and rechromatographing in a ¼-in-OD, 40-ft-long Reoplex 400 column produced the chromatogram shown in figure 77. Retention time data for the DC–550 silicone oil column indicated the distinct possibility of the presence of three compounds occurring during the time interval denoted by the shaded peak C. However, microdesulfurization of the material in trap C produced only two hydrocarbons. These latter data indicate an ambiguity that occasionally occurs when two compounds in the same peak desulfurize to give the same hydrocarbon. In this instance, 2-methyl-2-hexanethiol produced 2-methylhexane upon desulfurization, while both 2-ethyl-1-butanethiol and 3-methyl-1-pentanethiol produced the single hydrocarbon, 3-methylpentane, upon desulfurization. Other thiol precursors could

produce these particular hydrocarbons upon desulfurization, but boiling point and retention time considerations adequately resolved any possible ambiguity.

Final proof of identification rested upon an infrared spectral comparison of a known reference compound with material isolated with the GLC column. For example, the identification of 2-methyl-2-hexanethiol merely involved retrapping during the time interval denoted by the shaded peak D of figure 77, analyzing the resulting material by infrared, and comparing the resulting spectrum with that of the known compound, as illustrated in figure 78.

Employment of similar procedures resulted in the identification of 36 thiols.

This systematic separation and identification study on the Wasson 111° to 150° C (232°–302° F)
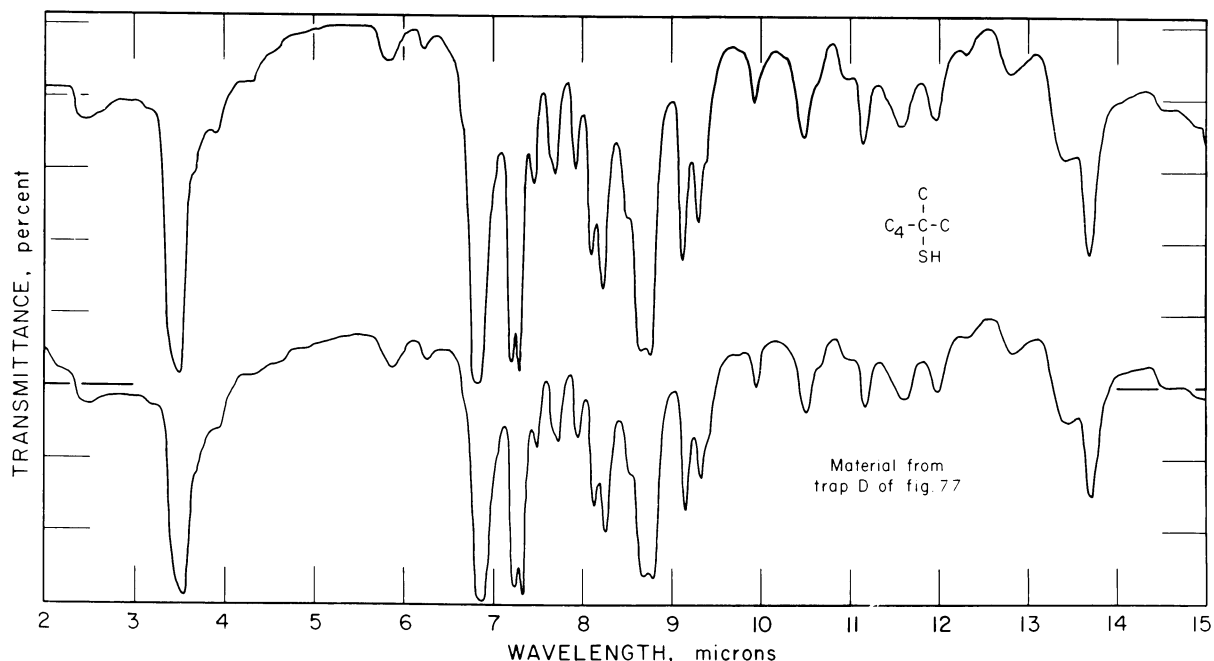
Figure 78.—Comparison of infrared spectrum of 2-methyl-2-hexanethiol with spectrum of thiol isolated from Wasson crude oil.
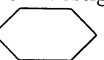
distillate resulted in the identification of 23 chain sulfides, 18 cyclic sulfides, and 36 thiols. These 77 individual sulfur compound identifications represent a detailed study of the sulfur compounds present in a given petroleum fraction. The separation and identification techniques discussed should materially aid other researchers interested in similar studies.

150° to 220° C Boiling Range

The sulfur compounds in the 150° to 220°F (302° to 428°C) boiling range were not investigated to the extent that the sulfur compounds were in the lower boiling ranges. This results in part from pressure of other work, the increased number of isomers, and the limited number of reference compounds.

Identification of Alkyl Cycloalkyl Sulfides

The fact that chain sulfides of the structure R—S—R' constitute an appreciable part of the sulfur content of some crude oils is well established (*37, 81, 427*). Cyclic sulfides, such as thiacyclohexanes and thiacyclopentanes, in which the sulfur is in the ring, are even more abundant

(*25, 37, 422*). However, before this specific investigation, alkyl cycloalkyl sulfides, R—S— or R—S—, had not been identified in any crude oil. Five individual alkyl cycloalkyl sulfides have been identified in a Wasson crude oil distillate boiling 150° to 220° C. The concentration of the alkyl cycloalkyl sulfides found in this distillate was very small. Why the quantities of chain and cyclic sulfides are comparatively large, among the sulfur components of many oils when the concentrations of alkyl cycloalkyl sulfides are so meager, is presently unknown.

A sulfide concentrate in which the alkyl cycloalkyl sulfides were identified was prepared by isothermal distillation, vacuum fractionation, alumina percolation, and chemical treatment. The purpose of the final chemical treatment was to separate and recover the sulfides from a thiol-free aromatic-sulfur compound concentrate. The procedure used was based on a sulfide oxidation method developed by Bateman and Hargrave (*30*), modified by S. F. Birch (private correspondence), and varied further by the authors to meet their needs.

Based on sample treatment and mass spectral analyses, the concentrate studied was known to be a thiol-free sulfide conc: ;trate that contained about 69 percent cyclic sulfide , 18 percent chain sulfides,

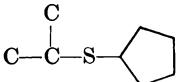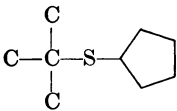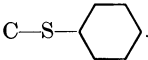and small amounts of other types of sulfur compounds and some aromatics.
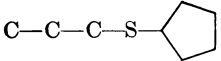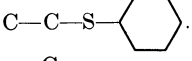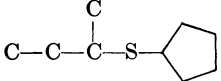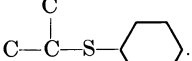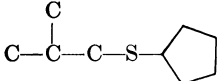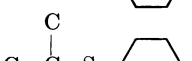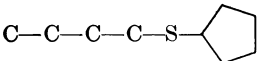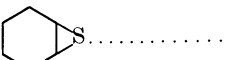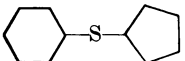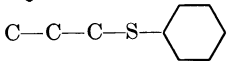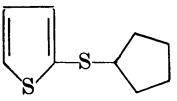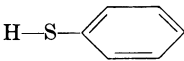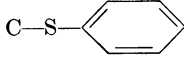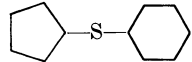
A GLC chromatogram of this concentrate indicated the composition of the sample to be quite complex—containing some 30 individual compounds. The retention time of one reasonably well separated peak at about 22 minutes agreed with the retention times of several alkyl cycloalkyl sulfides. To obtain some of this material for desulfurization studies, the effluent emerging between 21 and 22.5 minutes was collected in a series of repetitive runs and then rechromatographed and retrapped over a time interval between 19.2 and 24.5 minutes.

The light products of desulfurization of this material were found to contain methane, ethane, propane, isobutane, and n-butane. The heavier products of desulfurization were, among other compounds, cyclopentane, methylcyclopentane, and cyclohexane. With the columns and conditions employed, these identifications are certain and free from conflict with other paraffins or cycloparaffins. The number of sulfur compounds in petroleum that could produce cyclopentane or cyclohexane upon desulfurization and also have a retention time in agreement with the trapped area is very limited. Table 37 lists a series of compounds that meet these requirements; among them several that will produce the required hydrocarbons but have retention times somewhat outside that of the trapped area. All other sulfur compounds that would produce the required hydrocarbons upon desulfurization can be eliminated.

Individual alkyl cycloalkyl sulfides were not present in sufficient quantity for spectral study.

Table 37.—Possible sulfur compound precursors of cyclopentane and cyclohexane

Cyclopentane		Cyclohexane	
Compound	Retention time minutes	Compound	Retention time minutes
C—C—S—⬠ (with C on second carbon)	15.0	⬡ S (thiabicyclo)	16.8
C—C—S—⬠ (with two C on second carbon)	16.3	C—S—⬡	18.8
C—C—C—S—⬠	19.5	C—C—S—⬡	22.1
C—C—C—S—⬠ (C branch on middle)	21.1	C—C—S—⬡ (C branch)	22.0
C—C—C—S—⬠ (C branch on second)	21.7	C—C—S—⬡ (two C branch)	22.8
C—C—C—C—S—⬠	27.8	⬡ S (bicyclo)	24.2
⬡—S—⬠	94.0	C—C—C—S—⬡	29.0
thiophene—S—⬠	211.0	H—S—⬡ (aromatic)	32.1
		C—S—⬡ (aromatic)	47.4
		⬠—S—⬡	94.0
		⬡ S (bicyclo)	(1)

[1] Compound highly reactive and not available for testing. Reported (40) to be unstable in acid and therefore if originally present would not have survived chemical treatment to which sample was subjected.

However, by microdesulfurization and GLC data, the absence of thiols, bicyclic sulfides, dicycloalkyl sulfides, and cycloalkyl thienyl sulfides in the trapped and desulfurized material is indicated from determined retention times as shown in table 37 and by deductive reasoning. This leaves only alkyl cycloalkyl sulfides as possible precursors of the identified cyclopentane and cyclohexane. Having established that cyclopentane and cyclohexane were produced by desulfurization of alkyl cycloalkyl sulfides and that methane, ethane, propane, isobutane, and n-butane were also produced, it is now necessary to consider the retention times of possible precursors of these hydrocarbons and to pair the individual fragments.

In table 37 only five compounds—ethylcyclohexyl sulfide, isopropylcyclohexyl sulfide, tert-butylcyclohexyl sulfide, isobutylcyclopentyl sulfide, and sec-butylcyclopentyl sulfide—have retention times that include them within or near the initial trapping time interval of 21.0 to 22.5 minutes and in the rerun and retrapping at 19.2 to 24.5 minutes. From a qualitative and quantitative evaluation of the data, the identification of ethylcyclohexyl sulfide, isopropylcyclohexyl sulfide, and sec-butylcyclopentyl sulfide is well established. The other two sulfides, tert-butylcyclohexyl sulfide and isobutyl cyclopentyl sulfide, are identified only on a conditional basis as the small amount of isobutane found in the light products of desulfurization could have been combined with either the cyclohexane or cyclopentane, or both, to form their respective alkyl cycloalkyl sulfides. However, in other work on the same concentrate, isobutylcyclopentyl sulfide, having a retention time of 102 minutes, and tert-butylcyclohexyl sulfide, having a retention time of 114 minutes, were isolated. Upon desulfurization, isobutane was identified in both instances, indicating the presence of both sulfides in Wasson crude oil. Therefore, these five sulfides, and only these compounds, must be precursors of the identified hydrocarbons.

A sulfide concentrate prepared from another sample of the same distillate and one prepared from a slightly higher boiling distillate by sulfonium salt formation (186), a method not requiring acid treatment, also gave evidence, upon desulfurization of the entire concentrate, of the presence of alkyl cycloalkyl sulfides; hence it is improbable that any chemical treatment was involved in their formation.

Using a combination of separation and identification techniques, the following individual alkyl cycloalkyl sulfides were identified: ethylcyclohexyl sulfide, isopropylcyclohexyl sulfide, tert-butylcyclo-

hexyl sulfide, sec-butylcyclopentyl sulfide, and isobutylcyclopentyl sulfide. This represents the first reported identification of this type of compound in any crude oil. Here, as in other ring types, the six-member ring appears to predominate over the five-member ring. The concentrations, on a crude oil basis, of the five compounds identified range from 0.00000003 to 0.000009 percent. This represents but 0.3 to 90 parts per billion. These are minimum values influenced possibly by significant but not unreasonable processing losses. If the amounts detected in Wasson crude oil are indicative of that present in other oils, it is understandable that they had not been identified previously.

200° to 250° C Boiling Range

In the 200° to 250°F (392° to 482°C) boiling range, 46 sulfur compounds were identified; these included 2 thienothiophenes, 18 thiaindans, 4 alkyl aryl sulfides, and 22 benzo[b]thiophenes.

Identification of Thienothiophenes

The source material used in this study was an aromatic-sulfur compound fraction from an alumina percolation of a thiol-free, 200° to 250° C (392° to 482° F) Wasson crude oil distillate. From this fraction, easily crystallizable materials (mostly naphthalenes) were removed by crystallization from cold n-butane, after which sulfides were precipitated by saturating with anhydrous hydrogen iodide (186) at −78° C. A concentrate was then obtained from this residue by adduct formation with trinitrobenzene (TNB). Naphthalenes and benzothiophenes were readily adducted at room temperature and removed by filtration. Chilling of the filtrate to −78° C caused formation of a second adduct which also was recovered by filtration.

The principal component of the second adduct was identified by GLC and spectral analyses as biphenyl. Mass spectral data also indicated the presence of another substance of molecular weight 154, containing two sulfur atoms per molecule, which was suspected of being a methylthienothiophene. An additional concentration step involving crystallization of biphenyl, yielded about 0.05 ml of a yellow liquid for further study. Desulfurization of this sample and GLC analysis of the resulting hydrocarbons produced the chromatogram shown in the center panel of figure 79. The upper panel of this figure is the chromatogram of the n-pentane solvent used to dissolve the products of desulfurization from the trap in which they were collected, and the bottom panel is the chromatogram of the
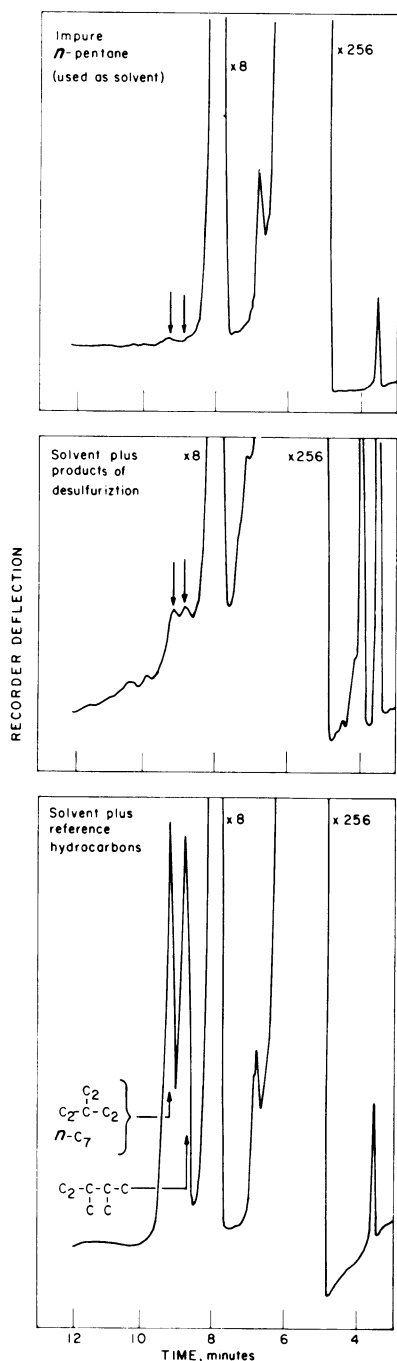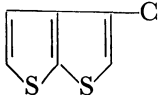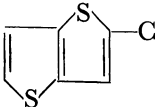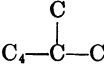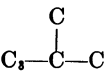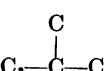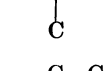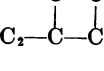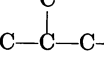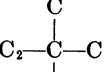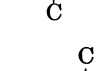
Figure 79.—Chromatograms indicating the possible presence of [structure] and [structure] in Wasson crude oil.

Table 38.—Boiling points and GLC retention times of C₇ paraffins

Formula	Boiling point, °C	Retention time,[1] minutes
n-C₇	98.4	9.2
C₄—C—C (with C above)	90.1	8.1
C₃—C—C₂ (with C above)	92.0	8.6
C₃—C—C (with C above and C below)	79.3	7.1
C₂—C—C—C (with C, C above)	89.8	8.8
C—C—C—C—C (with C, C above)	80.6	7.1
C₂—C—C₂ (with C above and C below)	86.1	8.5
C—C—C—C (with C above, C C below)	80.9	8.0
C₂—C—C₂ (with C₂ above)	93.5	9.2

[1] GLC column and operating conditions:
  Column: aluminum tubing, 40 feet long, ¼ inch OD.
  Column packing: 16.7 percent Reoplex 400 and GC–22 Super Support.
  Helium flow rate: 60 ml/min.

solvent to which small quantities of n-heptane and 2,3-dimethylpentane were added. Table 38 lists the GLC retention times of all possible C₇ paraffins. These data and those of figure 79 indicate that only 2,3-dimethylpentane emerged from the column used in these experiments at 8.8 minutes, the retention time of the first peak, and that only two compounds, n-heptane and 3-ethylpentane, emerged at 9.2 minutes, the retention time of the second peak. From boiling point considerations, no C₆ or C₈ paraffins have a retention time agreeing with either of the peaks. The available evidence indicates that the materials producing the two peaks in the chromatogram of the center panel (fig. 79) were correctly identified.
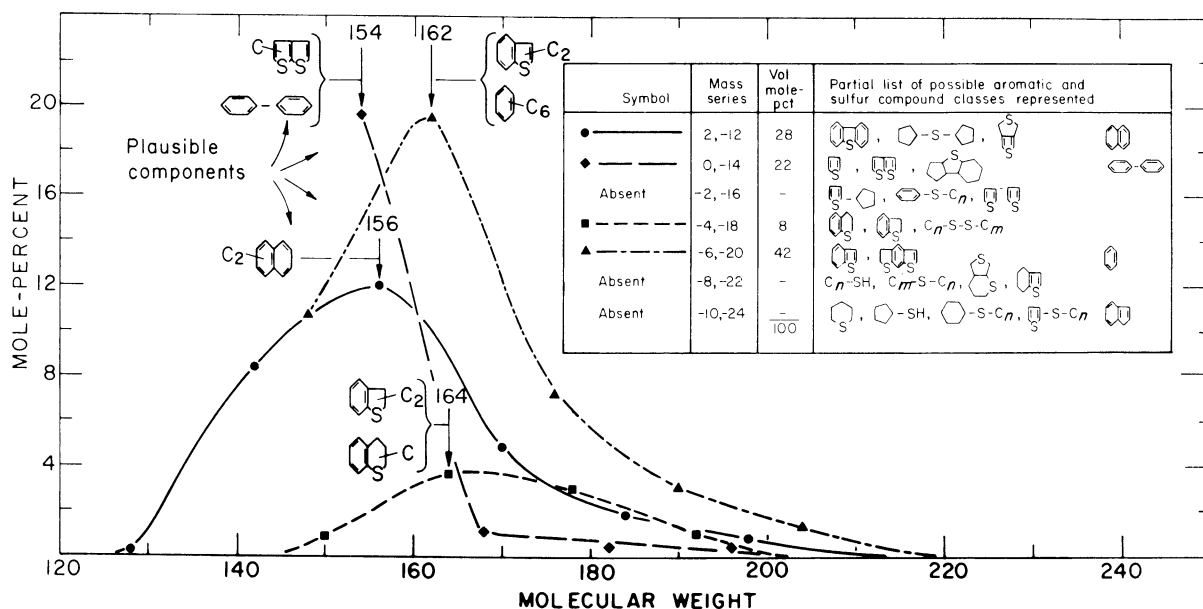
Figure 80.—Mass analysis data giving concentration versus molecular weight for various classes of sulfur compounds present in a Wasson crude oil fraction.

The results of a low-voltage mass spectral analysis made on the concentrate before removal of biphenyl are plotted in figure 80. An important feature of these data is the absence of those sulfur compounds making up mass series -2, -16; -8, -22; and -10, -24, indicated in the table of figure 80. This absence is not unexpected, because chemical treatment of the sample would have removed such compounds as thiols, chain and cyclic sulfides, and other related compounds, and the mass analysis accurately reflected the effectiveness of this chemical treatment. The sample still retained considerable amounts of such aromatic types as methyl naphthalenes and biphenyls, accounting for the peak in the series $+2$, -12 (C_2-naphthalenes of molecular weight 156) and 0, -14 (biphenyl at molecular weight 154). As mentioned, biphenyl was readily separated from the sample, and its identification was confirmed by its infrared spectrum. The formulas shown in the key of figure 80 are typical and representative of each mass series most likely to be present in the concentrate. However, the presence of all these types is not implied.

Table 39 lists possible sulfur compound precursors of the hydrocarbons 2,3-dimethylpentane, n-heptane, and 3-ethylpentane, which are the hydrocarbons resulting from the desulfurization of the sample (fig. 79). Although table 39 is not complete, it includes most of the compound types that

are thought to exist in virgin petroleum. The following consideration of each individual compound permits the identification of thienothiophenes in petroleum.

Row A.—This row lists the four thienothiophenes that, upon desulfurization, can yield the hydrocarbon heading the columns in which they appear. With reservations (because of instability) about the presence in petroleum of [structure] in column 1 and [structure] in column 3, it is believed that the other two thienothiophenes in the first and second columns are the precursors of the hydrocarbons shown at the head of their respective columns. All other structures can be effectively eliminated from consideration or seriously questioned as potential precursors.
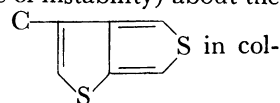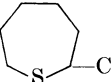
Row B.—Only one monomethylthiacycloheptane 2-methylthiacycloheptane, exists that can produce n-heptane on desulfurization. Chemical treatments should have removed this compound (see discussion, row C), and low-voltage mass spectrometry (LVMS) indicated that this class of sulfur compounds (series -10, -24) was absent from the concentrate. Thiacycloheptane has never been iso-

Table 39.—Possible sulfur compound precursors of the hydrocarbons 2,3-dimethylpentane, *n*-heptane, and 3-ethylpentane

lated from petroleum but has been actively sought; therefore, the presence of a derivative in crude oil was questionable from that point of view. Furthermore, although the boiling point of the 2-methyl derivative was not known, it was estimated as follows:

Compound	Boiling point, °C	Compound	Boiling point, °C
(thiacyclohexane)	141.8	(thiacycloheptane)	173
(methylthiacyclohexane)—C	153.0	(methylthiacycloheptane)—C	[1] 184

[1] Estimated.

This boiling point is too low to allow inclusion of the compound in the concentrate which has a boiling range of 200° to 250° C (392° to 482° F).

Row C.—Chemical treatment, precipitation by hydrogen iodide, and nonadductibility with TNB should have separated the thiacycloalkanes from the sample, and LVMS indicated that such compounds (series −10, −24) were absent. Boiling points of all of the compounds shown in row C are not known; however, that of 2-*n*-propylthiacyclopentane, 179.5° C (356° F), is probably the highest. Thus, on the basis of boiling point, all of the structures shown are excludable from the concentrate.

Row D.—The highest boiling point of all alkylthiophenes shown is 173° C (344° F) (2,3,4-trimethylthiophene), which is sufficient for excluding C$_7$ thiophenes from the concentrate. By LVMS the alkylthiophenes might have been present (series 0, −14); however, the lowest molecular-weight compound indicated (fig. 80) is 154, corresponding to a C$_9$ thiophene. This circumstance excluded C$_7$ thiophenes from this particular concentrate. Bearing incidentally on this matter, neither the parent compound, thiophene (*424*), nor any of its methyl or ethyl derivatives have been found in Wasson crude oil, although there is evidence of the presence of thiophenes as a class.

Row E.—The dithiabicycloalkanes (series −8, −22) are absent by LVMS. The fused thiacycloalkane-thiophene type shown in the second section of row E could be present as they fall in the mass series +2, −12. Their molecular weight would be 156. It is thought that these compounds would react chemically as cyclic sulfides and would be removed by the treatment given the concentrate. Some of the structures shown in which the sulfide

sulfur is one carbon removed from a thiophene ring, are expected to be highly unstable by analogy with the known 2-thiaindan, particularly toward atmospheric O$_2$. It is also doubtful that any of these structures would adduct with TNB.

Row F.—Compounds of the mass series −6, −20, to which alkylthiacycloalkyl sulfides belong, are in the concentrate. However, chemical treatment of the concentrate should have eliminated these alkylthiacycloalkyl sulfides. Thus, the compounds representing the −6, −20 series are probably all benzothiophenes and alkylbenzenes.

Thienyl sulfides (series −10, −24) were not indicated by mass spectrometry. This was expected, because they also should have been eliminated from the concentrate by the chemical treatment. However, a member of this type, methyl-3,4,5-trimethyl-2-thienyl sulfide, which produces 2,3-dimethylpentane upon hydrogenolysis, is known to be present in crude oil (*424*).

Row G.—Thiols should not be present in the concentrate because of chemical treatment of the sample, and LVMS verified the absence of these thiols (series −8, −22, absent).

Alkyl sulfides should have been eliminated from the sample by chemical treatment, and LVMS substantiated their absence (series −8, −22, missing).

Alkyl disulfides are members of the mass series −4, −18 and as such might be present in the concentrate. Disulfides presumably are minor sulfur compound constituents of some petroleums and may not exist at all in many crude oils. However, the several disulfides tested in this investigation (*n*-butyldisulfide, isoamyldisulfide, and *tert*-amyldisulfide) failed to form adduction products with TNB, and thus it is presumed that this class of compounds is absent from the concentrate.

While the data do not provide the rigorous proof available for many other identifications, they do seem adequate to establish the presence in Wasson crude oil of thienothiophenes as a class and to identify two individual thienothiophenes, namely 3-methylthieno[2,3-*b*]thiophene and 2-methylthieno[3,2-*b*]thiophene. Other sulfur compounds (table 39) which could give the observed products of desulfurization produced by the concentrate, were considered. These were eliminated as possible precursors on the basis of mass spectral analysis and chemical and physical properties. One or more additional methylthienothiophenes are possibly present, but the limited amount of sample available prevented their identification. Thienothiophenes are not quantitatively an important class of petroleum sulfur compounds; however, the identification

of any class of sulfur compounds containing two sulfur atoms is of real interest.

Identification of Thiaindans

The apparent absence of thiaindans in petroleum has long been of interest to petroleum chemists. Because of a close similarity in structure to the relatively abundant benzothiophenes, their presence in petroleum was expected but not established by any investigation prior to this study.

Employing isothermal and molecular distillation, vacuum fractionation, silica gel and alumina adsorption, and chemical treatment, as shown in

figures 81 and 82, all part of a broad and systematic effort, several distillates and concentrates of interest to the project were prepared. The thiaindan concentrate, shown in the lower right block of figure 82, was the subject of this specific investigation. Early mass spectral analyses showed that this concentrate contained 60 percent of a molecular weight of 136 to 200, 23 percent alkylbenzenes, 9 percent naphthalenes, and small amounts of other sulfur compounds. Preliminary desulfurization work indicated the presence of thiaindans and prompted a detailed study which resulted in the positive identification of three thiaindans and the tentative identification of 15 other alkylthiaindans (421).

A GLC evaluation of the thiaindan concentrate using a $\frac{1}{4}$-inch by 40-foot column packed with
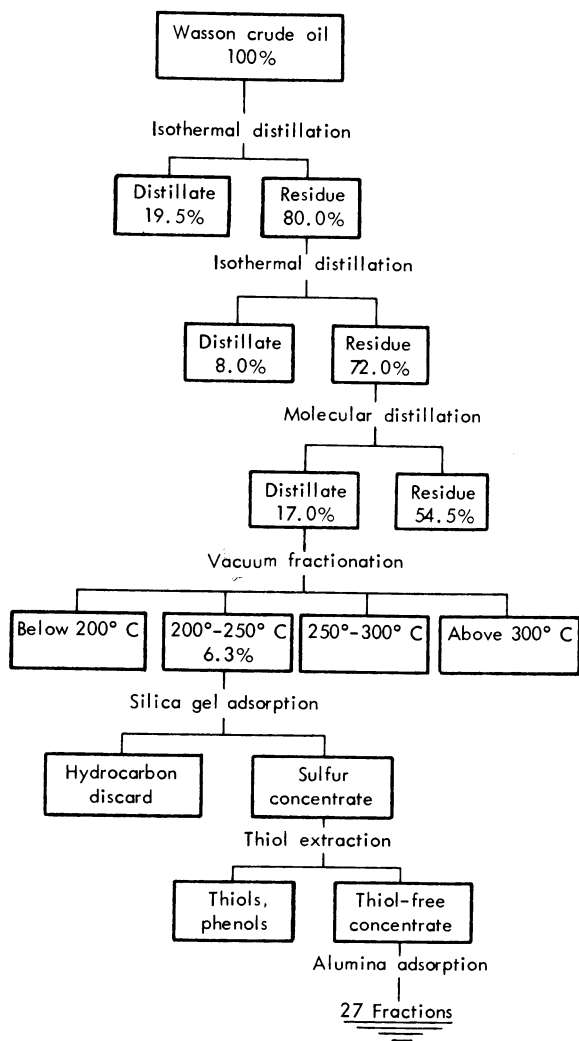
Figure 81.—Outline of treatment of Wasson crude oil to produce adsorption fractions.

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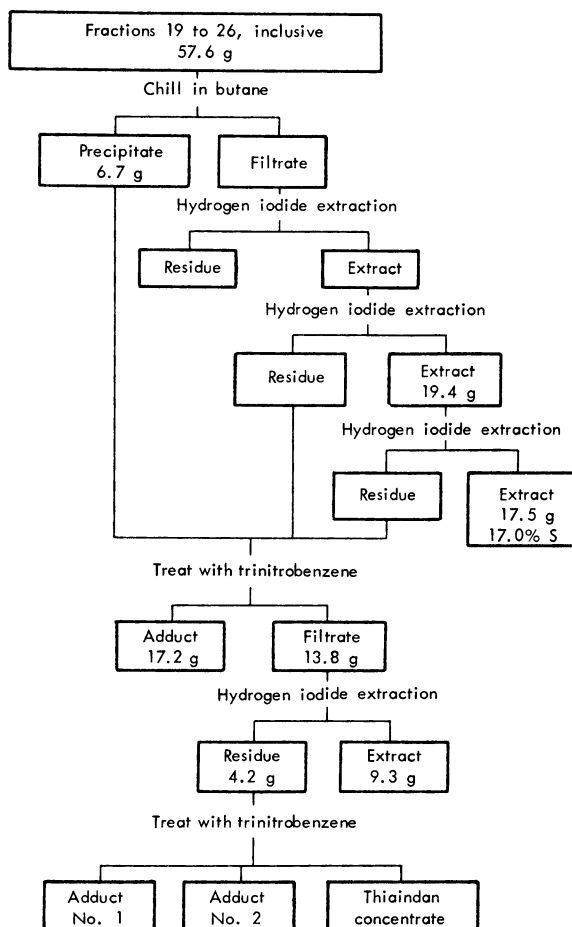
Figure 82.—Treatment of Wasson 200° to 250° C adsorption fractions.

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30–40 mesh GC–22 support impregnated with silicone rubber SE–30 is shown in figure 83. A comparison of the retention times of the peaks in this chromatogram with the retention times of reference thiaindans, suggests the possible presence of 2-methyl-1-thiaindan emerging during the time interval encompassed by the shaded peak at 42 minutes.

Raney nickel desulfurization of this trapped material produced three products—n-propylbenzene, isobutylbenzene, and n-butylbenzene. To find a symmetrical chromatographic peak containing two or more components is not surprising, although often disturbing, and such was the case in finding three components here. However, capitalizing on the resolving power of GLC, and specifically upon the effectiveness of the alternate use of nonpolar and polar stationary phases, it was possible to isolate a fraction of essentially pure 2-methyl-1-thiaindan. The excellent agreement of the infrared spectrum of this material, isolated from the crude oil, with the spectrum of the reference 2-methyl-1-thiaindan, as shown in figure 84, is unequivocal proof of the presence of this compound in Wasson crude oil. Similar data were obtained on 1-thiaindan and 2,2-dimethyl-1-thiaindan. Mass spectrometry, desulfurization, and GLC data also supported these firm identifications.

The absence of reference thiaindans other than 1-thiaindan, 2-methyl-1-thiaindan, and 2,2-dimethyl-1-thiaindan precluded additional positive identifications. However, by a combination of gas-liquid chromatography and Raney nickel desulfurization, data were acquired to permit the tentative identification of additional thiaindans. The individual alkylbenzenes produced by Raney

nickel desulfurization were isolated by GLC trapping techniques, and those present in sufficient quantity were identified by infrared and mass analyses. The minor components were identified by GLC retention times. These data are shown in table 40. By way of explanation, the aromatic produced by desulfurization and labeled peak 2 in this table was identified by mass and infrared analyses as isopropylbenzene. 3-Methyl-1-thiaindan is the only precursor of the identified isopropylbenzene and is so indicated in column 4 of this same table. Like treatment of 15 peaks produced 15 tentative identifications in addition to the three identifications positively established earlier by spectral comparison. Some six individual aromatics could have been produced from two different thiaindans, and these are listed in the table on an "and/or" basis and reported as a single identification. Traces of aromatics could have been produced from the desulfurization of trace amounts of aryl sulfides or benzothiophenes present in the thiaindan concentrate. However, the identifications reported would not be invalidated by such trace amounts of aromatics derived from other classes of sulfur compounds.

In a systematic study employing the procedures described, the following 18 thiaindans were identified: 1-thiaindan, 2-methyl-1-thiaindan, 3-methyl-1-thiaindan, 5-methyl-1-thiaindan and/or 7-methyl-1-thiaindan, 3,3-dimethyl-1-thiaindan, 2,3-dimethyl-1-thiaindan and/or 3-ethyl-1-thiaindan, 2,2-dimethyl-1-thiaindan, 3,5-dimethyl-1-thiaindan and/or 3,7-dimethyl-1-thiaindan, 3,6-dimethyl-1-thiaindan, 2,5-dimethyl-1-thiaindan and/or 2,7-dimethyl-1-thiaindan, 2-ethyl-1-thiaindan, 2,6-dimethyl-1-thiaindan, 2-methyl-3-ethyl-
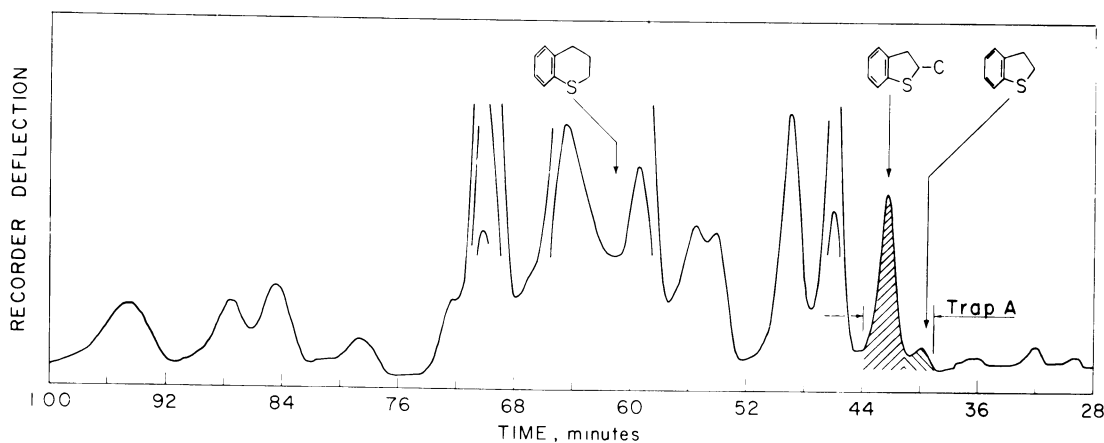
Figure 83.—Gas-liquid chromatogram of a thiaindan concentrate from Wasson crude oil.

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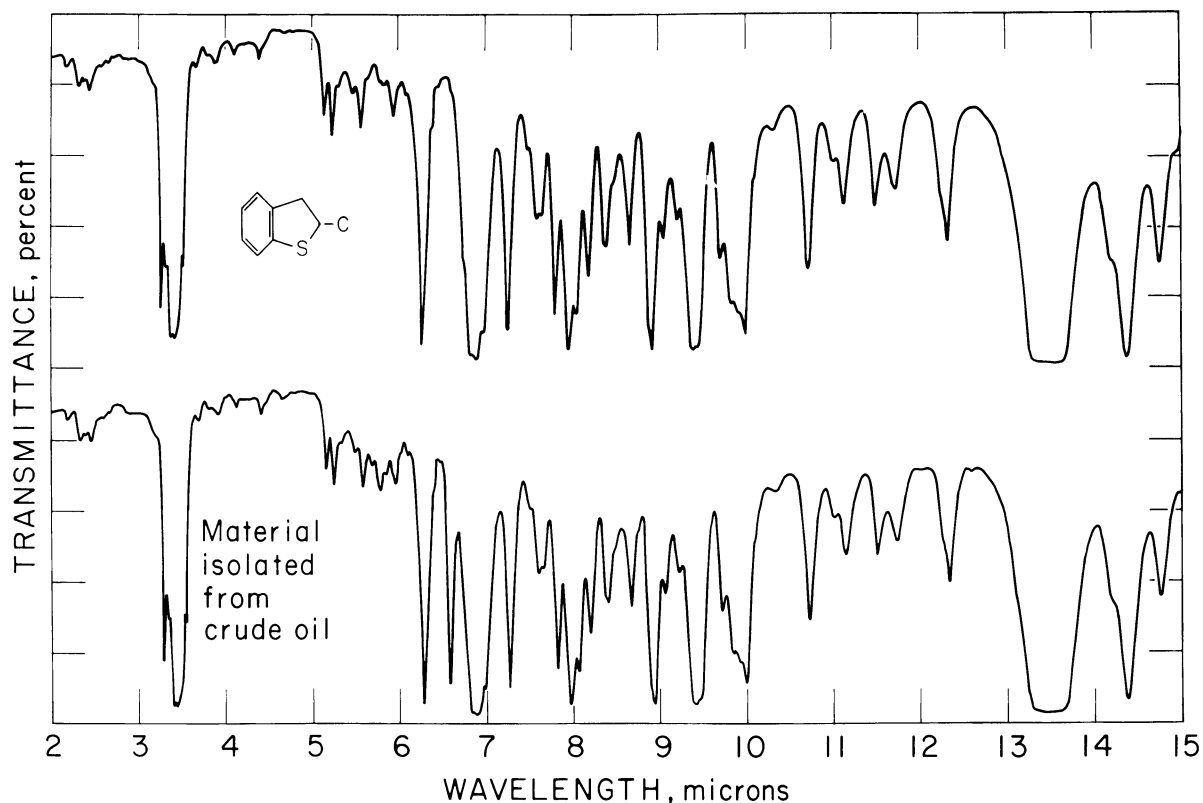
Figure 84.—Comparison of infrared spectrum of 2-methyl-1-thiaindan with spectrum of material isolated from Wasson crude oil.

(Reproduced by permission from reference 73.)

1-thiaindan, 2,4-dimethyl-1-thiaindan, 2,2,5-trimethyl-1-thiaindan and/or 2,2,7-trimethyl-1-thiaindan, 2,3,4-trimethyl-1-thiaindan and/or 3-ethyl-4-methyl-1-thiaindan, 2,2,4-trimethyl-1-thiaindan, and 2-methyl-2-ethyl-1-thiaindan.

While thiaindans, as a class, are not quantitatively a major constituent of petroleum, they do represent a significant part of the sulfur-containing material of Wasson crude oil in the 200° to 250° C (392° to 482° F) boiling range and are of concern in studies investigating the origin of petroleum. Of the thiaindans identified, 2-methyl-1-thiaindan is the most abundant, followed by 3-methyl-1-thiaindan, and probably 2,2-dimethyl-1-thiaindan and 2-ethyl-1-thiaindan, in that order.

Identification of Alkyl Aryl Sulfides

As a byproduct of the thiaindan studies just described, four alkyl aryl sulfides were identified in Wasson crude oil. This result was accomplished concurrently with the trapping of 1-thiaindan, 2-methyl-1-thiaindan, and 2,2-dimethyl-1-thiain-

dan on a nonpolar GLC column. The trapped material was then rerun on a polar GLC column (¼ inch by 25 feet, packed with 45–50 mesh Chromosorb G coated with about 6 percent Reoplex 400) and resolved into four major peaks as shown in figure 85. The shaded peak at 28 minutes in figure 85 represents the material of interest in this discussion; the other major peaks at 36, 46, and 54 minutes were produced by thiaindans.

The material producing the peak at 28 minutes was analyzed by mass and infrared spectrometry. The mass spectrum indicated a molecular weight of 166, two units higher than the thiaindans previously identified in this same concentrate fraction. A parent mass of 166 could result from several classes of sulfur compounds such as cycloalkyl thiophenes, dithienyls, alkyl tetrahydrobenzothiophenes, benzenethiols, and alkyl aryl sulfides. By a combination of mass and infrared spectral data, GLC retention time data, and knowledge of previous sample treatment, it was possible to eliminate from consideration all sulfur compound classes except the alkyl aryl

Table 40.—Data pertaining to Raney nickel desulfurization products from thiaindan concentrate as shown in chromatogram of figure 83, trap A

Peak No.	Identity of material producing peaks		Precursor of identified aromatic
	As indicated by GLC	As determined by infrared	
1			
2			
3			
4		(1)	
5		(1)	
6			
7		(1)	
8		(1)	

See footnotes at end of table.

Table 40.—Data pertaining to Raney nickel desulfurization products from thiaindan concentrate as shown in chromatogram of figure 83, trap A—Continued

Peak No.	Identity of material producing peaks		Precursor of identified aromatic
	As indicated by GLC	As determined by infrared	
9			
10			
11		(1)	
12		(1)	
13			
14			
15			

[1] Sample of insufficient size to permit infrared analysis.
[2] Unidentified.
NOTE.—Slash indicates "and/or".
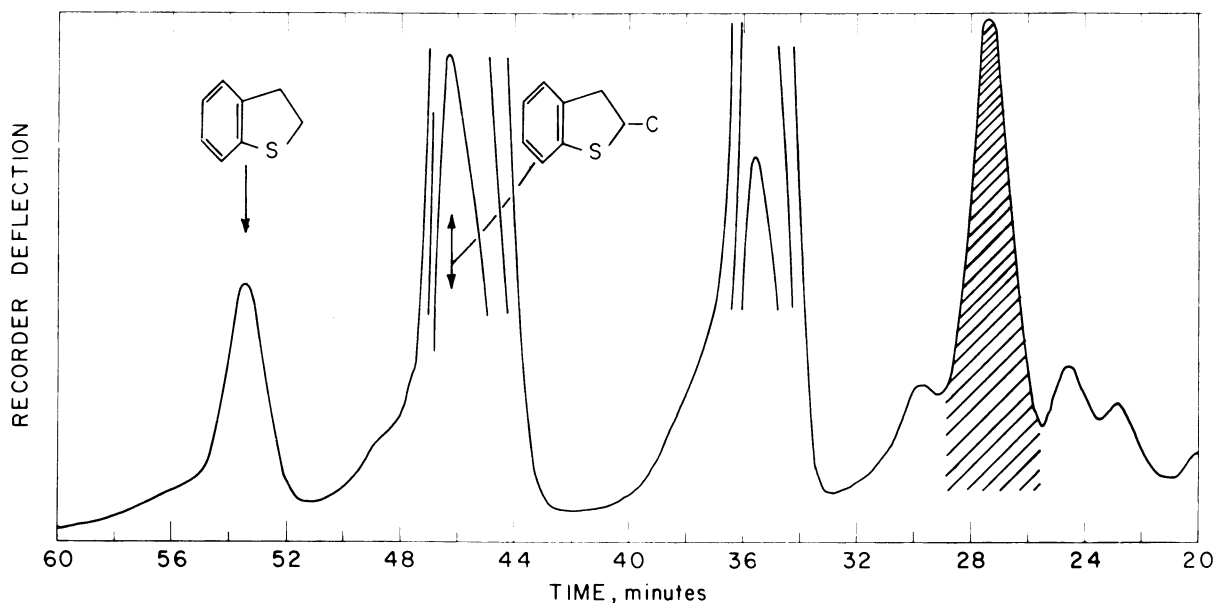
**Figure 85.—Gas-liquid chromatogram of material trapped during
39 to 44-minute interval on nonpolar column.**

sulfides. A detailed consideration of individual members of these classes and the circumstances that permit the elimination of all but the alkyl aryl sulfides is described in a report by Hopkins and others (190). Once it was established that this class of compounds was present in the material producing the peak at 28 minutes, additional investigation was necessary to identify the individual compounds, since both the mass and infrared data indicated the material to be at least a three- and possibly a four-component mixture.

It was determined from the mass spectral data that the sulfur atom in the alkyl aryl sulfides was attached directly to the benzene ring, and that either propyl or butyl side chains were attached to the sulfur. Further, the mass spectral data pertaining to the material isolated from the oil show intense ions at m/e 110, 124, and 166. Ten alkyl aryl sulfides have such spectra, but only four were found to have retention times compatible with the trapping time interval on both polar and nonpolar columns, thereby eliminating the other six.

Spectral data (mass and infrared) suggest that all four sulfides; namely, (2-methyl-1-thiabutyl)-benzene, 2-methyl-1-(2-methyl-1-thiapropyl)ben-zene, 3-methyl-1-(2-methyl-1-thiapropyl)benzene, and 4-methyl-1-(2-methyl-1-thiapropyl)benzene are present in the material isolated from the crude oil. Experimental blends were prepared containing these four alkyl aryl sulfides in quantitative propor-

tions suggested by earlier spectral data. Table 41 shows the composition of the blend in closest agreement with the sample spectrum.

**Table 41.—Composition of synthetic
blend of alkyl aryl sulfides**

Percent	Composition
49...................	⟨benzene⟩—S—C(—C)—C—C
32...................	C⟨benzene⟩—S—C(—C)—C
11...................	⟨benzene, C⟩—S—C(—C)—C
8...................	C—⟨benzene⟩—S—C(—C)—C

The infrared spectra of the four sulfides, the material isolated from the crude and the four-component blend, are reproduced in figure 86. Infrared absorption bands in the spectrum of the isolated sulfides at 12.4 and 12.9 microns were
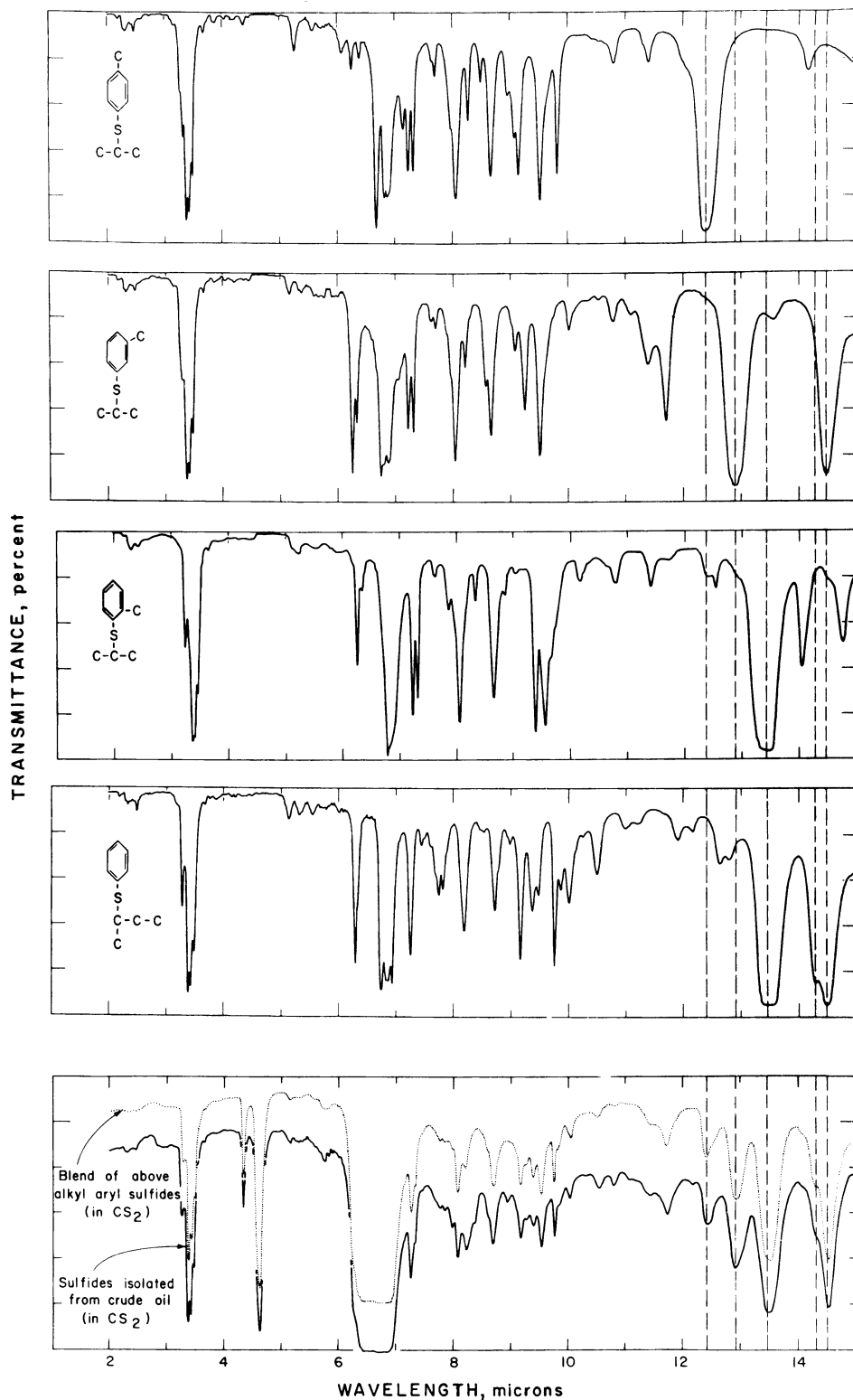
Figure 86.—Infrared spectra establishing the presence of alkyl aryl sulfides in Wasson crude oil.

assigned to 1,4- and 1,3-disubstituted aromatics, respectively. These two bands are evident in the spectra of the sample and of the blend shown in the lower panel of this figure. The doublet at 13.5 and 14.5 microns was assigned to monosubstituted aromatics, and these bands are present in the spectrum of (2-methyl-1-thiabutyl)benzene (2d panel from bottom, fig. 86) and are prominent in the spectrum of the blend and of the sample. The spectrum of 2-methyl-1-(2-methyl-1-thiapropyl)-benzene, a minor component of some 8 percent, contributes very little to the spectrum of the blend or of the sample; however, a small enhancement of

the peaks at 9.35 and 9.50 microns is produced by the doublet in the spectrum of the compound at about 9.48 microns.

A careful study of the spectra of the sample, blend, and individual compounds shows that the absorption bands match favorably in both wavelength and intensity. While the agreement is not perfect and the presence of small amounts of other compounds is evident in the spectrum of the isolated material, there is little doubt of the presence of the four named alkyl aryl sulfides in Wasson crude oil.

These sulfide identifications were further supported by the desulfurization of a sample of
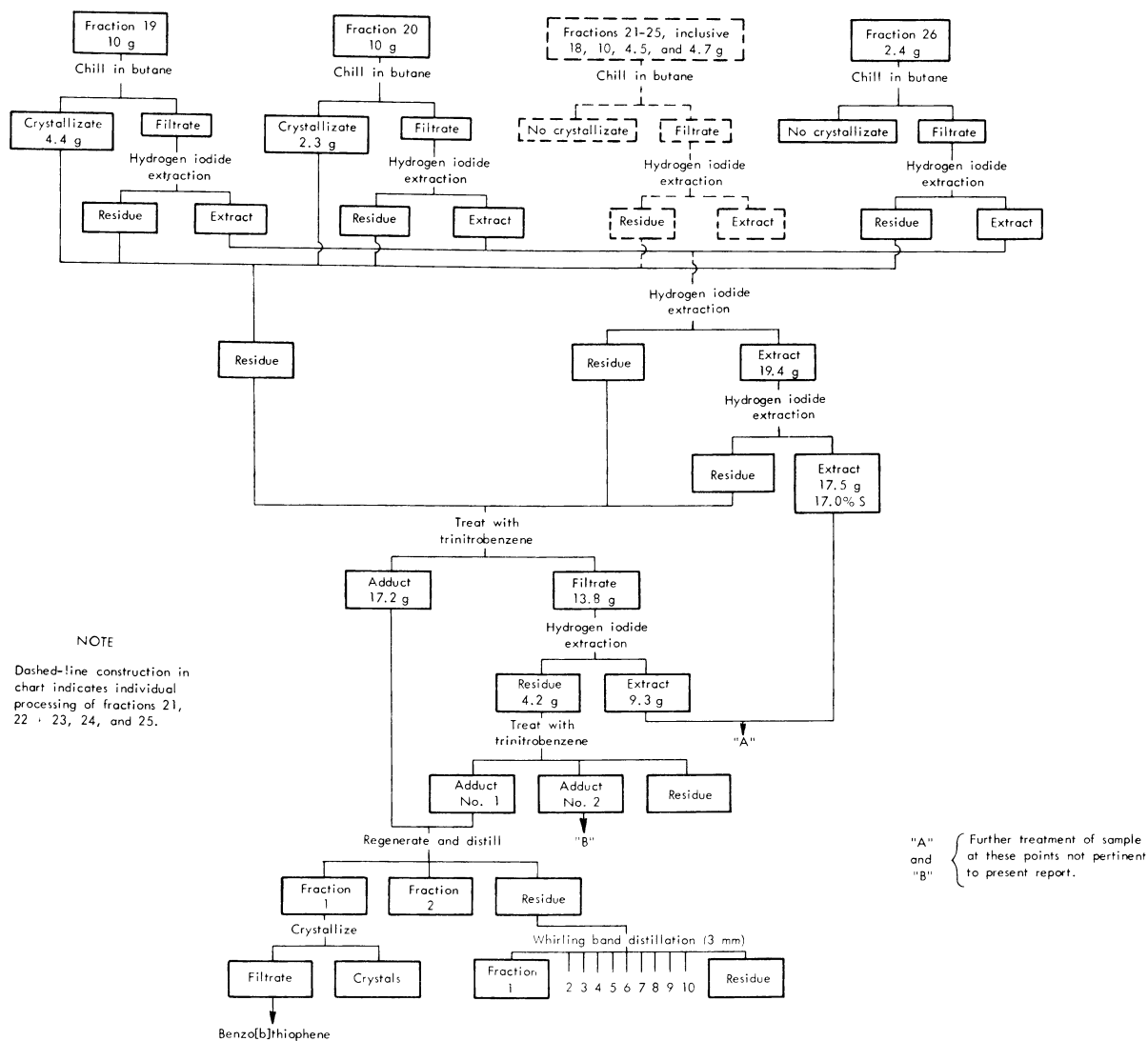
Figure 87.—Treatment of Wasson 200° to 250° C (392° to 482° F) adsorption fractions.

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the isolated material and the generation of the hydrocarbons expected from their desulfurization; namely: propane, butane, cyclohexane, and methylcyclohexane.

The identification of (2-methyl-1-thiabutyl)benzene, 2-methyl-1-(2-methyl-1-thiapropyl)benzene, 3-methyl-1-(2-methyl-1-thiapropyl)benzene, and 4-methyl-1-(2-methyl-1-thiapropyl)benzene demonstrate the advantages and often the necessity of applying diverse disciplines, such as GLC, desulfurization, and mass and infrared spectral techniques in a systematic effort to isolate and identify individual compounds in a small amount of a complex mixture.

Using these techniques, good spectral (mass and infrared) agreement was shown between the reference blend and the isolated material. GLC retention times for the four identified sulfides were in agreement with the trapped area on both the polar and nonpolar columns. All other sulfides of the proper molecular weight and producing the correct hydrocarbons on desulfurization were eliminated because of retention time incompatability with the trapping time intervals used on one or both of the columns. Qualitative identification of the proper hydrocarbons was achieved upon desulfurization.

The possibility of blending compounds, other than the four identified sulfides, to meet the separation and identification requirements discussed above is most limited, and the combination of data leaves little doubt as to the qualitative composition of the isolated material.

While alkyl aryl sulfides are present only in minor concentration, their identification in petroleum is of interest.

Identification of Benzo[b]thiophenes

Benzo[b]thiophenes represent a major class of sulfur compounds in petroleum. In spite of their abundance, few individual members of this class of sulfur compounds had been identified prior to this study. Richter and others (342) identified benzo[b]thiophene in a California crude oil and more recently Coleman and others (74) identified benzo[b]thiophene, 2-methyl-, and 3-methylbenzo[b]thiophenes in Wasson, Texas, crude oil.

It was not until the development of more sophisticated separation and identification techniques that other individual alkylbenzo[b]thiophenes could be separated from associated naphthalenes and identified. In addition to GLC, chemical derivative formation with Raney nickel desulfurization and reduction to benzenethiols by calcium in liquid ammonia proved to be particularly useful.

Benzo[b]thiophenes are desulfurized with Raney

nickel to alkylbenzenes without changing the carbon structure. These benzenes can then be separated by GLC and identified spectrally. For example, the identification of n-propylbenzene in the products of desulfurization of a benzo[b]thiophene concentrate would quite specifically point to 2-methylbenzo[b]thiophene as the only possible precursor. Reduction with calcium in liquid ammonia was useful in distinguishing between certain isomers which produce the same benzene by Raney nickel desulfurization. Use of the calcium hexamine method was especially helpful in differentiating between 7-methyl- and 5-methylbenzo[b]thiophenes, both of which yield 1-ethyl-3-methylbenzene by Raney nickel desulfurization but produce different benzenethiols by calcium reduction.
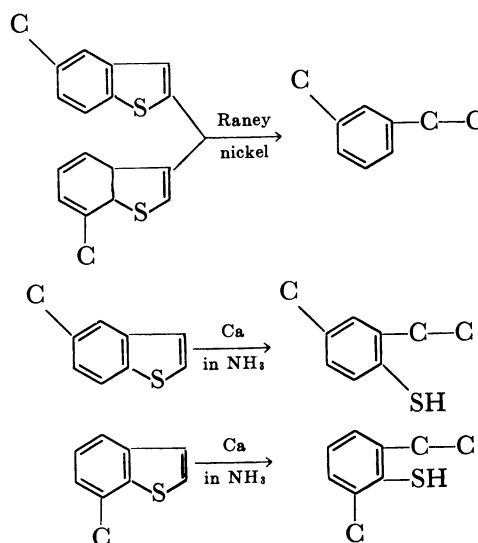
The benzo[b]thiophene study reported herein was made on a 200° to 250° C (392° to 482° F) distillate prepared from Wasson crude oil in a series of isothermal and fractional distillations. The benzo[b]thiophenes were concentrated by adsorption over silica gel followed by graded elution over H-41 alumina. The sulfides were then removed by treatment with anhydrous hydrogen iodide (186) at −78° C. Subsequently the benzothiophenes were further resolved by adduction with 1,3,5-trinitrobenzene, recovered by adsorption, and distilled into 10 fractions using a 50-plate whirling band column. These chemical separation steps are shown in figure 87.

The resulting distillation fractions were too complex to permit direct isolation and identification of any individual benzo[b]thiophene by GLC alone. Therefore, the 10 distillation fractions were individually examined by both Raney nickel desul-

furization and reduction by calcium in liquid ammonia. The separation of the reaction products by GLC and their identification by GLC and spectral (mass, infrared, and ultraviolet) techniques permitted the identification of 22 benzo[b]thiophenes in Wasson, Tex., crude oil. With but few exceptions, the identified alkylbenzenes or aromatic thiols, or both, left no doubt as to the identity of the benzo[b]thiophene precursor. Five of the identifications are ambiguous in that the identified alkylbenzene could be produced from two or more benzothiophenes and their complete resolution was beyond the scope of this study. Because of this ambiguity, these identifications are listed as "and/or" and each pair or group is listed as a single tentative identification. The individual benzothiophenes that were identified and their concentration in the crude oil are reported in table 42.

Table 42.—Benzo[b]thiophenes identified in Wasson crude oil [1]

Benzo[b]thiophenes	Weight-percent in crude	Weight-percent of benzothio-phenes
Benzo[b]thiophene	....	([2])
3-Methyl-	0.00095	9.2
2-Methyl-	.00248	24.0
4-Methyl-	....	([2])
7-Methyl-	.00010	1.0
2,3-Dimethyl-	} .00306	29.0
3-Ethyl-		
3,7-Dimethyl-; possibly 3,5-dimethyl-	.00020	1.9
3,6-Dimethyl-	.00009	.9
2,7-Dimethyl-; possibly 2,5-dimethyl-	.00101	9.8
2-Ethyl-	.00037	3.6
2,6-Dimethyl-	.00013	1.2
2,4-Dimethyl-	.00094	9.1
4,7-Dimethyl-	.00004	.4
2-Methyl-3-ethyl-	.00006	.6
3-Ethyl-5-methyl- and/or 3-ethyl-7-methyl- and/or 2,3,5-trimethyl- and/or 2,3,7-trimethyl-	.00038	3.7
2,3,6-trimethyl- and/or 3-ethyl-6-methyl-	....	....
2-Methyl-5-ethyl- and/or 2-methyl-7-ethyl- and/or 5-propyl- and/or 7-propyl-	....	....
2-Methyl-4-ethyl- and/or 4-propyl-	....	....
2,4,7-Trimethyl-	....	....
2-Ethyl-5-methyl- and/or 2-ethyl-7-methyl-	....	....
2-Ethyl-4-methyl-	....	....
Total, fractions 17–22	.00051	5.0
Total	.01032	100.0

To provide the reader with some measure of the type of data obtained in the identifications reported, figure 88 shows a comparison of the infrared spectrum of a reference thiol and the spectrum of a thiol produced by reduction with calcium in liquid ammonia of a benzothiophene isolated from the sample. The agreement between spectra leaves no doubt as to the identity of the produced thiol which, in turn, points conclusively to 7-methylbenzo[b]thiophene as the only possible benzothiophene precursor. Also in table 43, as an

Table 43.—Products of desulfurization and benzo[b]thiophene precursors

Alkylbenzene	Identified by—	Precursor
sec-Butylbenzene	GLC, UV	2,3-Dimethyl- and 3-ethylbenzo[b]-thiophene.[1]
1-Ethyl-2-methyl-benzene	GLC	4-Methylbenzo[b]-thiophene.
1-Methyl-4-isopro-pylbenzene	GLC, IR	3,6-Dimethylbenzo-[b]thiophene.

[1] Both 2,3-dimethyl- and 3-ethylbenzo[b]thiophenes were identified by selective trapping followed by desulfurization. The 2,3-dimethyl-isomer predominates.

example, several alkylbenzenes from the Raney nickel desulfurization of the sample are shown, together with the method used to identify them and the precursor from which they were derived.

Employing a combination of chromatographic, chemical, and spectroscopic methods, 22 benzo[b]-thiophenes were identified in a 200° to 250° C (392° to 482° F) distillate of Wasson crude oil. Details of this systematic study were reported by R. L. Hopkins and others (187) in 1969.

Five compounds, 2-methyl-; 2,3-dimethyl-; 3-methyl-; 2,7-dimethyl-; and 2,4-dimethylbenzo[b]thiophenes represent 82 percent of the total benzothiophenes identified and indicate a preference for alkylation in the two position followed by the three and then the seven position. Most of the ring structures and substitutional patterns noted in the benzothiophenes were also found in the thiaindans previously described. The principal difference is the existence of geminal disubstitution in the thiaindans which cannot exist in the benzothiophenes, a point not to be taken lightly by researchers interested in the genesis of petroleum.

The relative concentration of benzothiophenes varies from crude oil to crude oil, but based on the results of this study and other recent available information, this sulfur-compound class
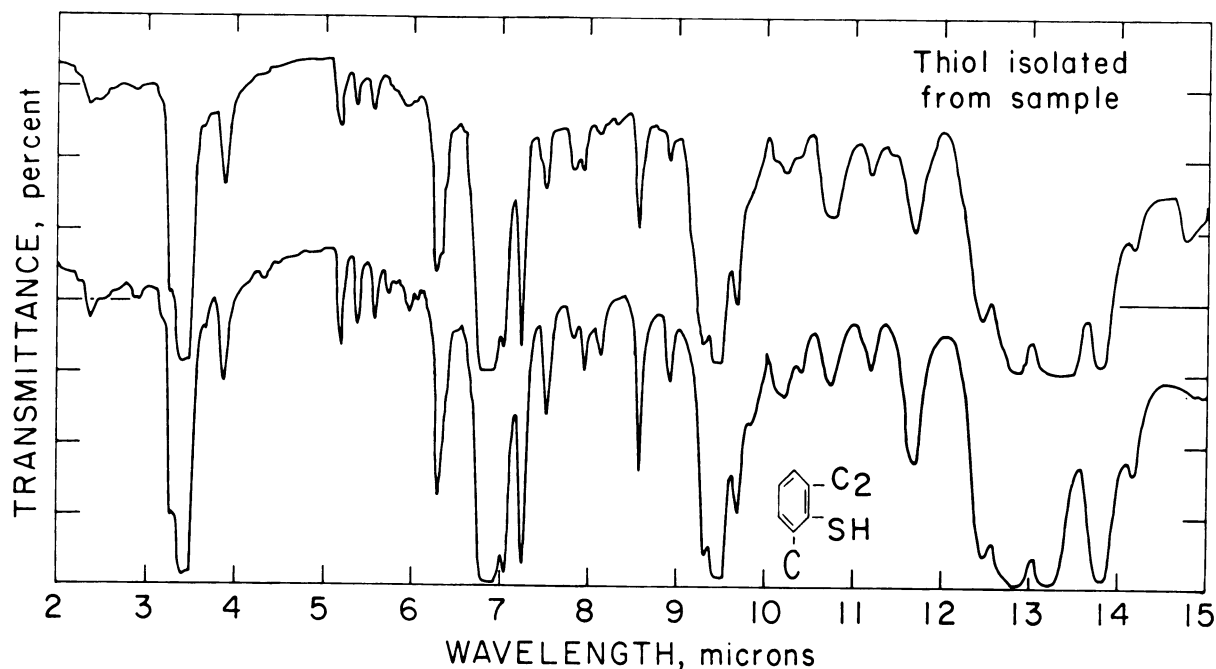
Figure 88.—Comparison of infrared spectrum of reference thiol and spectrum
of thiol produced from a benzothiophene isolated from crude oil.

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undoubtedly represents a most significant and important class of sulfur compounds in almost all crude oils.

WILMINGTON, CALIFORNIA, CRUDE OIL

Although the Wasson crude oil from West Texas was the object of major study, interest developed in applying separation and identification procedures to other crude oils for comparison purposes. Wilmington, California, crude oil, having been selected for investigation by API Research Project 52, which was studying the naturally occurring nitrogen compounds in crude oil, it was reasoned that basic data determined with respect to sulfur compounds in this particular crude oil should be complementary to the nitrogen studies. Wilmington crude oil, geologically, is from a Tertiary age formation and is classified as a youthful oil (less than 70 million years old), whereas the Wasson, Texas, crude oil is from formation of Permian age and is classified as a mature oil (225 to 600 million years old).

The first work done on the Wilmington crude oil by the Bureau of Mines at Bartlesville was to conduct a thermal stability test (late 1949) in a manner

developed by this Research Center and applied to numerous crude oils (80). Comparative results of this test (80, fig. 2) indicated that the sulfur compounds of Wilmington crude oil were comparatively stable. Relatively, the Wilmington crude contained 1.53 percent sulfur, while the Wasson crude had 1.85 percent sulfur. However, the difference in total sulfur did not explain the difference in the thermal stability patterns which was attributed to the presence of different sulfur-compound types. Later separation and identification studies did show major differences in the relative abundance of principal sulfur-compound types in Wilmington and Wasson crude oils.

The actual separation and identification studies on a Wilmington crude oil distillate began in the middle of 1954 with a large-scale isothermal distillation of Wilmington crude as denoted in figure 89. This particular investigation involved a charge of about 50 gallons (165.37 kg) of Wilmington crude oil to the steam-heated, glass isothermal still operating at atmospheric pressure. Although details of still construction and experimental operation are given elsewhere in the text, this particular run utilized a charge rate of about 35 ml per minute and a helium sweep gas flowrate of 9.3 liters per minute over a steam-heated (100° C (212° F)) rotating glass
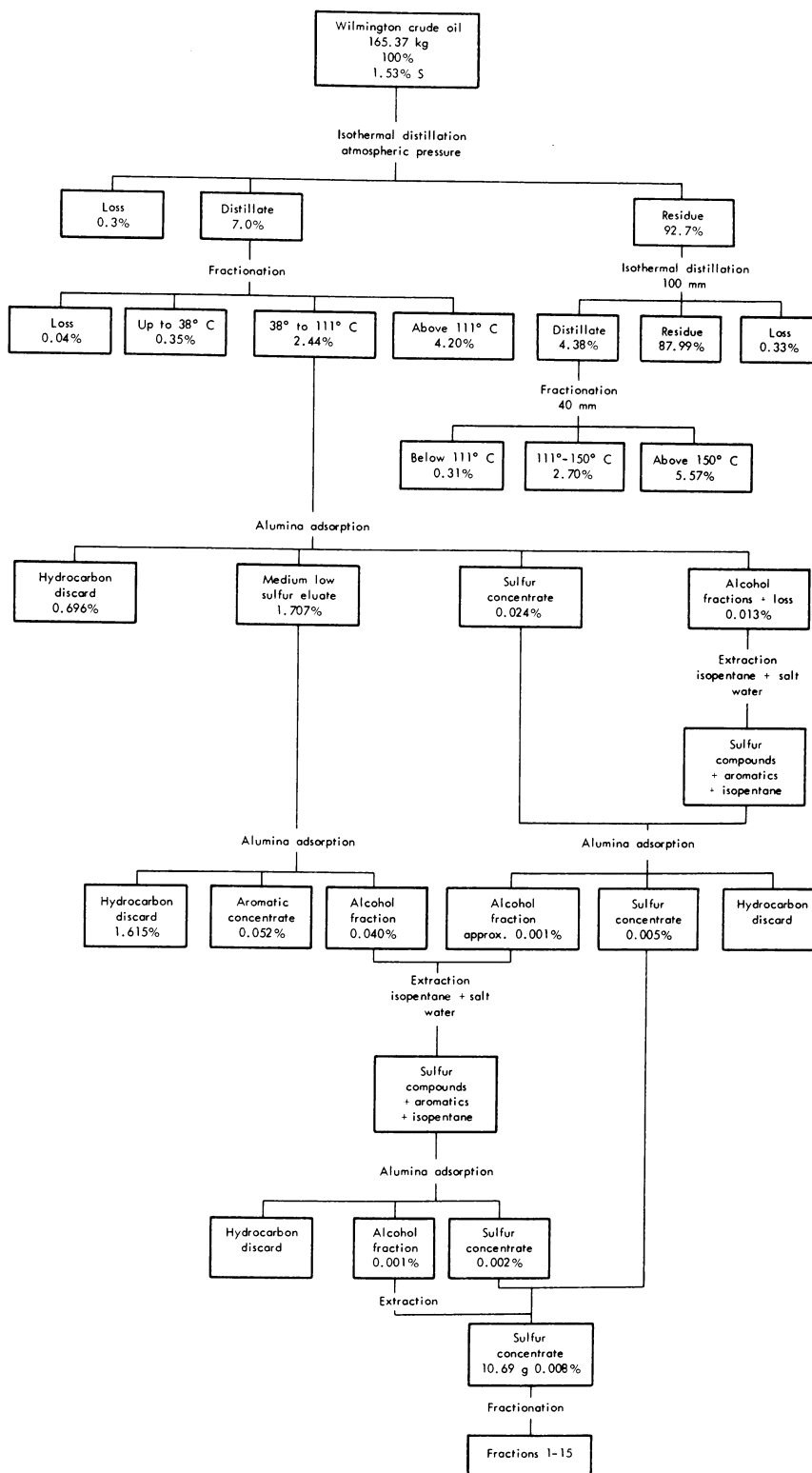
Figure 89.—Summary of processing of Wilmington crude oil with emphasis on the 38° to 111° C boiling range distillate.

drum. The operation yielded a distillate essentially complete through 111° C (232° F) constituting 7.0 weight-percent of the original crude oil charge. Charging the resulting residue through the iso-thermal still at a reduced pressure of 100 mm provided an additional quantity of distillate representing 4.4 percent of the Wilmington crude oil.

An all-glass, 30-plate Oldershaw column was used to fractionate these respective distillates into distinct boiling ranges of 38° to 111° C (100° to 232° F) and 111° to 150° C (232° to 302° F). In this processing step, stillpot temperatures were maintained below 100° C (212° F) by reduction of pressure stepwise during the distillation, starting at atmospheric pressure and ending at 200 mm during distillation of the 38° to 111° C (100° to 232° F) fraction. For the 111° to 150° C (232° to 302° F) fraction, the distillation was begun at 80 mm and ended at 20 mm. The 100° C (212° F) stillpot temperature limitation was an optimum guideline adopted from early thermal stability studies to avoid thermal degradation.

Although the crude oil contained 1.53 percent sulfur, most of this sulfur occurred in the high-boiling range as indicated by a sulfur content of only 0.010 percent for the 38° to 111° C (100° to 232° F) distillate and of 0.038 percent for the 111° to 150° C (232° to 302° F) distillate. The concentration of sulfur compounds in both fractions involved batchwise percolation of the respective distillates through spray-dried, fully activated H–41 alumina. The initial adsorption work on 3.5 kg of the 38° to 111° C (100° to 232° F) distillate consisted of three fairly large-scale (about 1,500 ml) batch runs. The comparatively heavy sample loading of about 1,100 grams of distillate to about 1,500 to 1,600 ml of alumina gel was feasible because the sample contained fairly low amounts of sulfur and aromatics. Successive rechromatographing of the initial sulfur-aromatic concentrate yielded a final concentrate of 10.69 grams, representing 0.008 percent of the original crude oil. For the sake of simplicity, figure 89 shows these successive adsorption runs as a single step. While the sulfur content of the final concentrate was only slightly greater than 1 percent, this concentration of sulfur represented a hundredfold increase over that of the starting distillate. On the basis of one atom of sulfur per molecule in this molecular weight range, the 1-percent-sulfur value represents approximately 2.5 percent sulfur compounds and a preliminary examination by mass spectrometry substantiated this assumption. These data showed the samples to contain roughly 29 percent benzene and 69 percent toluene as major contaminants plus 0.4 percent thiophene and 2.0 percent methylthiophenes.

38° to 111° C Boiling Range

The early work with the 38° to 111° C (100° to 232° F) boiling range Wilmington distillate began in the last half of 1954, before the acquisition of gas chromatography equipment by the project. Distillation of a 5-ml aliquot portion of this concentrate fraction with an all-glass concentric-tube column into fractions adequately separted benzene and thiophene from toluene and the methylthiophenes. Analysis of the initial distillate fraction by both mass and infrared spectroscopy established the presence of thiophene to the extent of roughly 1.1 percent, or a minimum concentration of 0.000032 percent of the total crude oil.

Methylthiophenes also were found, not only in the later semimicro distillation fractions, but also in the total 38° to 111° C (100° to 232° F) distillate. 2-Methylthiophene was found to be the predominant isomer (0.00010 percent of crude) with but traces of the 3-methylthiophene. Thus, the first published identifications of sulfur compounds in Wilmington crude oil (426) listed only thiophene and 2-methylthiophene as definitely identified. The presence of 3-methylthiophene was suspected, but it was not until the acquisition of GLC equipment that its identification could be established with certainty in the presence of the more abundant 2-methyl isomer. In those early days of GLC, the state of the art was seriously lacking with respect to sensitive detectors, knowledgeable selection of stationary phases, and other operational procedures. Despite these handicaps, GLC usage, combined with supplementary mass and infrared data, was more than adequate to resolve the 3-methylthiophene problem, both qualitatively and semiquantitatively, for publication in late 1959 (430).

GLC operating parameters involved were as follows: Column, ¼-inch by 6-foot copper tubing packed with 40- to 50-mesh acid-washed firebrick coated (20/100 wt ratio) with Dow-Corning 550 silicone oil, temperature 38° C (100° F), helium flowrate of 60 ml/min. A thermistor detector was used.

Because of the limited quantity of sulfur concentrate available from the processing of the low-boiling, 38° to 111° C (100° to 232° F), low-sulfur distillate, further concentration with the limited equipment and techniques then in common usage seemed unwise. As a result, the 3-methylthiophene concentration in the crude oil is not known with certainty, but it is estimated to be about 0.00006

weight-percent. The quantitative data for thio-phene, 2-methylthiophene, and 3-methylthiophene balances the sulfur value for the entire distillate. This is even more meaningful, too, in that such a quantitative balance left no latitude for other sulfur compounds, and indeed none were found! Thus, the first study of the Wilmington crude oil distillate indicated the sulfur to be thiophenic which is quite unlike the Wasson distillates that had been studied.

111° to 150° C Boiling Range

Extension of this study to the next higher boiling range Wilmington crude oil distillate, 111° to 150° C (232° to 302° F), did not occur until approximately 4 years later. At that time significant progress had been made in a number of analytical techniques, such as the various aspects of GLC including improved stationary phases column selection and usage and methods of trapping (75); development of a microhydrogenation technique to help characterize skeletal structure of many sulfur compounds (428); the improvement in micro techniques for both mass and infrared spectroscopy (226); and the improvement of liquid-solid chromatographic techniques (333).

```
          ┌────────────────────────┐
          │  Wilmington crude oil  │
          │       distillate       │
          │    111° to 150° C      │
          │        2.70%           │
          │       0.038% S         │
          └────────────────────────┘
                      │
          Liquid-solid chromatography
                 on alumina
          ┌───────────────┬────────────────┐
  ┌───────────────┐         ┌───────────────┐
  │ Aromatic-sulfur│         │  Hydrocarbon  │
  │   compound     │         │   discard     │
  │  concentrate   │         │    2.657%     │
  │    0.043%      │         └───────────────┘
  └───────────────┘
          │
  Liquid-solid chromatography
         on alumina
```
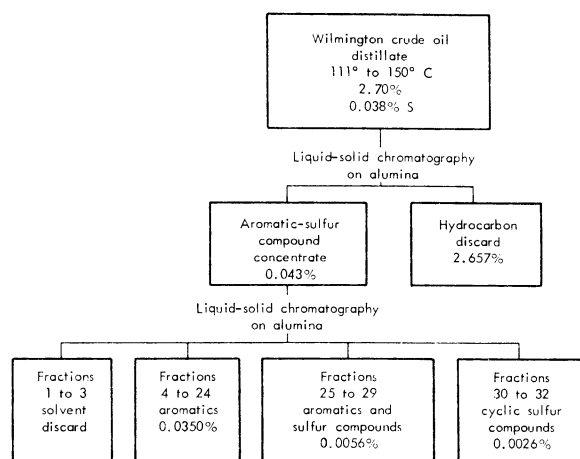
Figure 90.—Outline of distillate treatment used in producing sulfur-compound concentrates.

(Reproduced by permission from reference 76.)

Figure 90 shows that the Wilmington 111° to 150° C (232° to 302° F) distillate represented 2.70 percent of the original crude oil and contained only 0.038 percent sulfur. Previous discussion of liquid-solid chromatography covers the adsorption work on this distillate quite thoroughly as an example of

the use of improved techniques in obtaining separations previously considered impossible. This discussion points out the details of the two major adsorption steps utilized in separating well concentrated sulfur-containing fractions as depicted in the lower right-hand blocks of figure 90. The main emphasis used in these steps was to maintain adequate gel-to-sample ratios and to apply precision chromatography through the use of extremely high height-to-diameter ratios (1,000 to 1). These conditions were served by a 12-mm-ID by 12,200-mm-long column containing 1,350 ml of gel for the final concentration step on 28 grams of a sulfur and aromatic compound concentrate. Since this particular adsorption run utilized some dilution with isooctane (36 grams), the eluate from the bottom of the column was collected in a total of 32 fractions ranging in size from 0.7 to 1.5 grams. Generally, the order of elution was isooctane, followed by aromatics, alkylthiophenes and, finally, alkyl-substituted cyclic sulfides. There were small adsorptive differences between various compounds within each class which are discussed in the section on liquid-solid chromatography.

The fine differences in adsorptivity between individual compounds within a given class became quite obvious through careful GLC analyses that separated every compound. Note, though, that such GLC separations did not always occur with the use of a single stationary phase. In many instances, single compound resolution required trapping and rechromatographing on a second and even a third column. The section on gas-liquid chromatography describes several examples of this technique as applied to the studies of thiophenes and cyclic sulfides in Wilmington crude oil and to cyclic sulfides, benzothiophenes, etc., in Wasson crude oil.

The initial GLC survey of all the resulting adsorption subfractions involved the use of a Perkin-Elmer Model 154–D chromatograph equipped with a standard "Column R" (¼-inch by 6-foot column packed with polypropylene glycol coated diatomaceous earth) operating at 90° C (194° F) with a helium flow rate of 50 ml per minute. By comparing the GLC chromatograms of successive adsorption fractions, it became quite obvious when a given compound began to elute from the adsorption column and when it ended. Thus, the resulting chromatograms obtained with this particular GLC column showed the first definite appearance of nonaromatics occurring in adsorption fraction 28 as evidenced by the peak labeled D at about 76 minutes in figure 91. The large peak at 51 minutes, labeled B, coincident with meta- and paraxylenes in previous fractions, was of special interest because
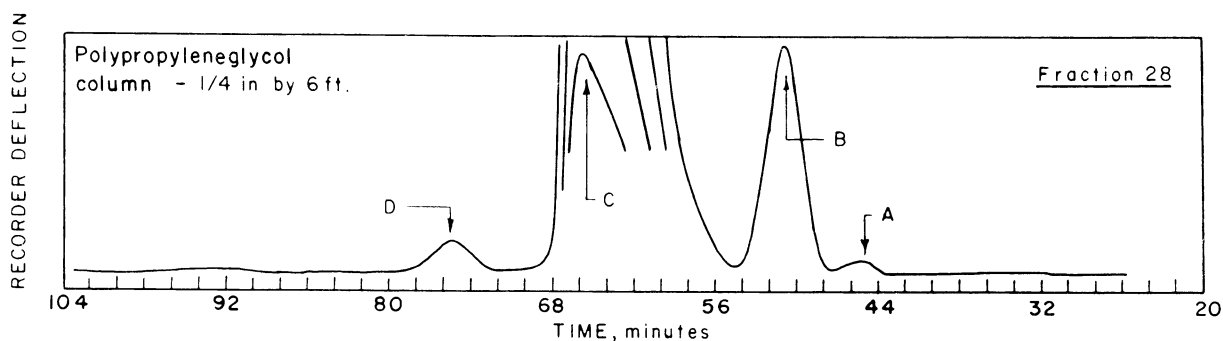
Figure 91.—Gas-liquid chromatogram of main thiophene concentrate
fraction as obtained in a preliminary survey.

of its thiophenelike odor. Trapping and desulfuriz-
ing the material produced *n*-hexane, an important
indication of the presence of a C_6-sulfur-containing
compound. Repeated trapping yielded sufficient
sample for a mass spectrometric analysis that proved
the presence of both 2-ethyl- and 2,5-dimethyl-
thiophene in this single peak. The slight distortion
on the leading edge of the large peak labeled *C* was
additional evidence of other nonhydrocarbons.

Even though the polypropylene glycol column
was useful in preliminarily detecting the presence of
sulfur compounds, it did not resolve the number of
peaks expected from the complexity of the fraction.

The next procedural step was to construct many
GLC columns packed with specially selective sta-
tionary phases. Although the top chromatogram of
figure 92, as obtained on a ¼-in by 40-ft poly-
epichlorohydrin column, was significantly better
than that of figure 91 in indicating separating
ability, other stationary phases proved much more
valuable for isolating the individual compounds, as
is discussed in more detail under the section on
gas-liquid chromatography.

Figure 92 shows applications of different GLC
stationary phases for separating given compounds
and the efficacy of the microdesulfurization tech-
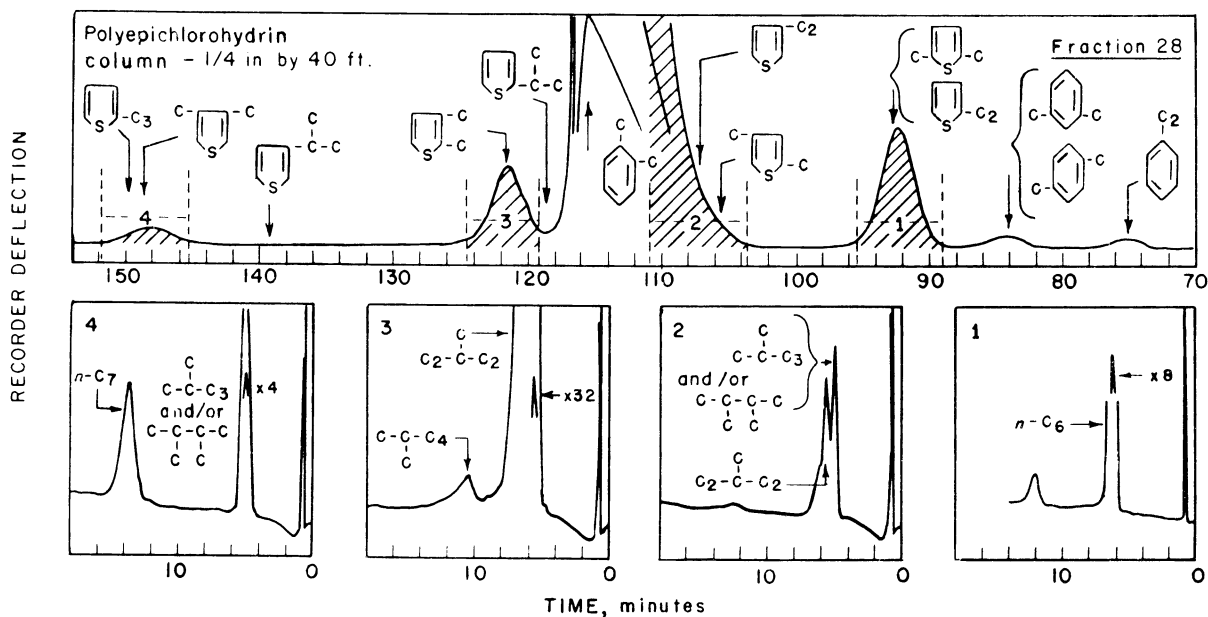
Figure 92.—Gas-liquid chromatograms of thiophene concentrate fraction
and of desulfurization products from labeled GLC subfractions.
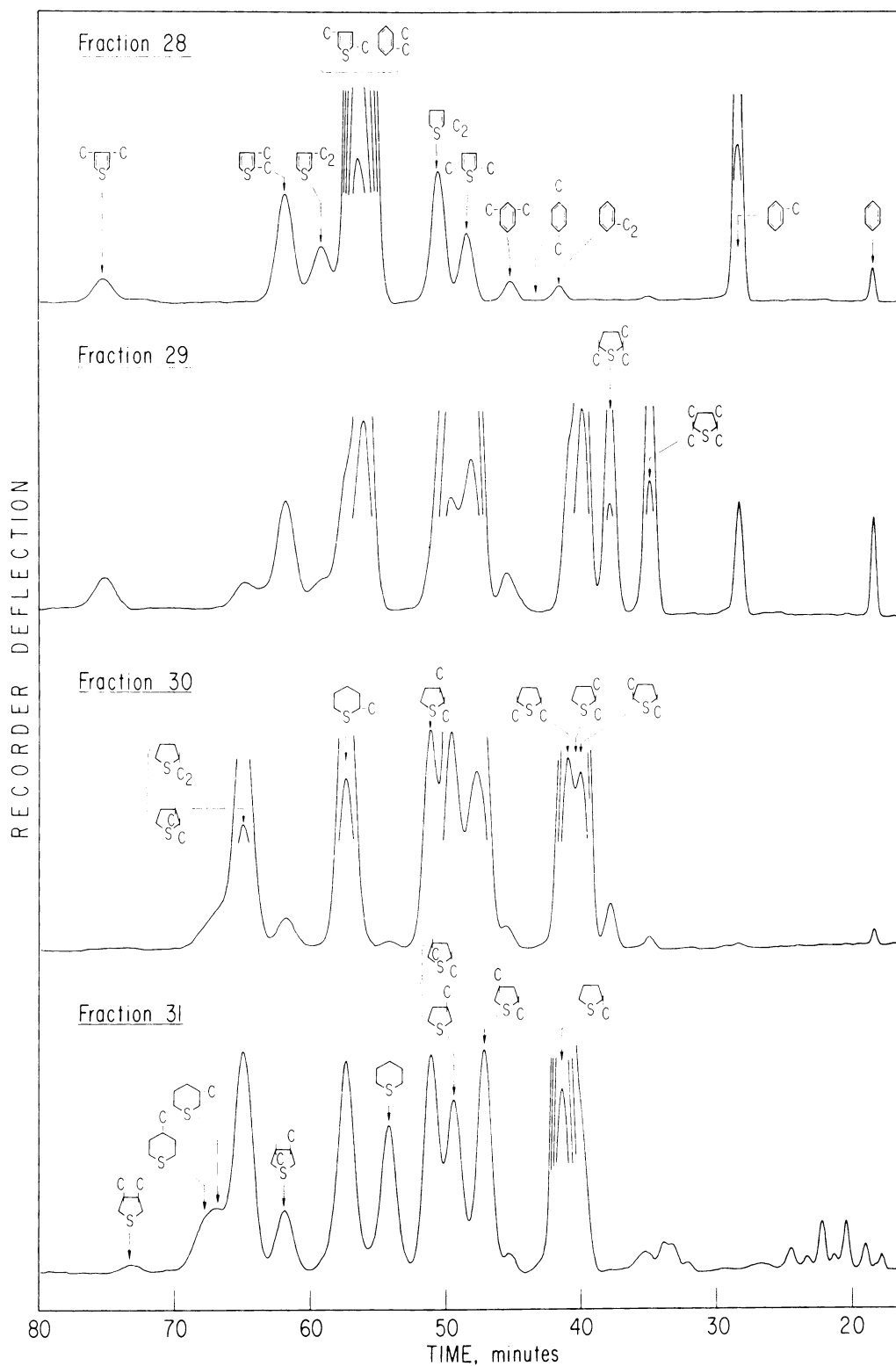
Figure 93.—Gas-liquid chromatograms showing change in concentration of thiophenes, aromatics, and cyclic sulfides in alumina adsorption fractions 28 through 31.

(*Reproduced by permission from reference 76.*)
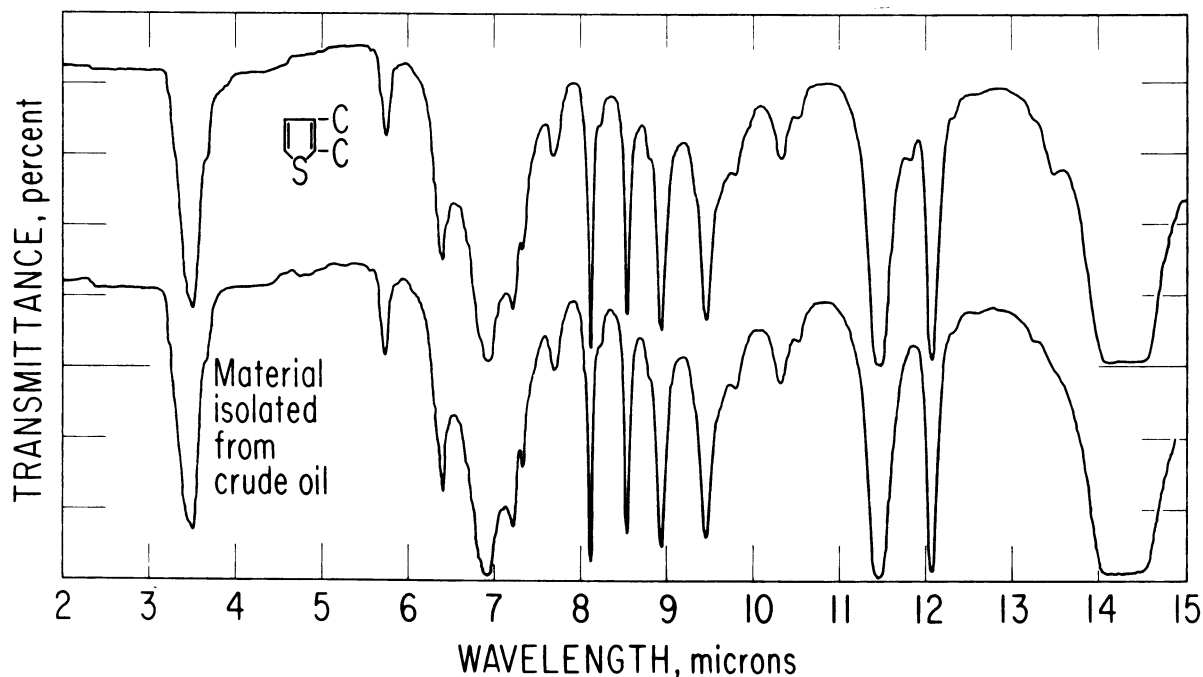
Figure 94.—Comparison of infrared spectrum of 2,3-dimethylthiophene with spectrum of material isolated from Wilmington crude oil.

(Reproduced by permission from reference 77.)

nique for the identification of sulfur compounds in given GLC subfractions. Specifically, the material eluting over a time interval of roughly 89 to 96 minutes in the top chromatogram of figure 92, when desulfurized and rechromatographed on a different column, produced the chromatogram in the lower right panel labeled 1. This latter GLC analysis proved the main constituent of the desulfurized fraction to be *n*-hexane, which information, combined with some known retention time data, pointed to both 2-ethyl- and 2,5-dimethylthiophene as the sulfur compounds of the fraction. These identifications were uncomplicated by interference of *meta*- and *para*xylene in the trapped material. Additional trapping and microhydrogenation experiments related to the GLC separation of adsorption fraction 28 proved each peak to be a mixture that needed further resolution for optimum identifications.

2-Ethyl- and 2,5-dimethylthiophene were resolved into two distinct peaks by the use of a Reoplex 400 (polypropylene glycol adipate) column which also separated 3-ethyl-; 2,3-dimethyl-; and 3,4-dimethylthiophene as individual peaks, as illustrated in the top panel of figure 93. Such individual compound resolution with GLC materially simpli-

fied identifications through the use of infrared spectral comparisons of material isolated from the crude oil distillates with a known reference compound; for example, 2,3-dimethylthiophene in figure 94. In this instance, as in most identifications, the isolated material was trapped as effluent from a GLC column and charged to a Barnes Engineering Co. Type D ultramicro cavity cell of 0.05-mm path length for determination of infrared spectrum on a Perkin-Elmer Model 21 spectrophotometer equipped with a Perkin-Elmer 4X beam condenser.

Resolution of individual compounds by GLC also provided an excellent basis for quantitation and for determining exact elution points for the individual compounds from the alumina adsorption column, which, in turn, provided much desirable relative-adsorbability data as discussed in the text under liquid-solid chromatography. Applying this knowledge, four alkylthiophenes were isolated by GLC from appropriate adsorption fractions and the weight-percent of each plotted against grams of eluant. The resulting plot, figure 95, shows relative and absolute abundance and the relative adsorptivity of each thiophene. These data, and the chromatograms of figure 93, indicate that adsorption fraction 29 is a transitional fraction containing
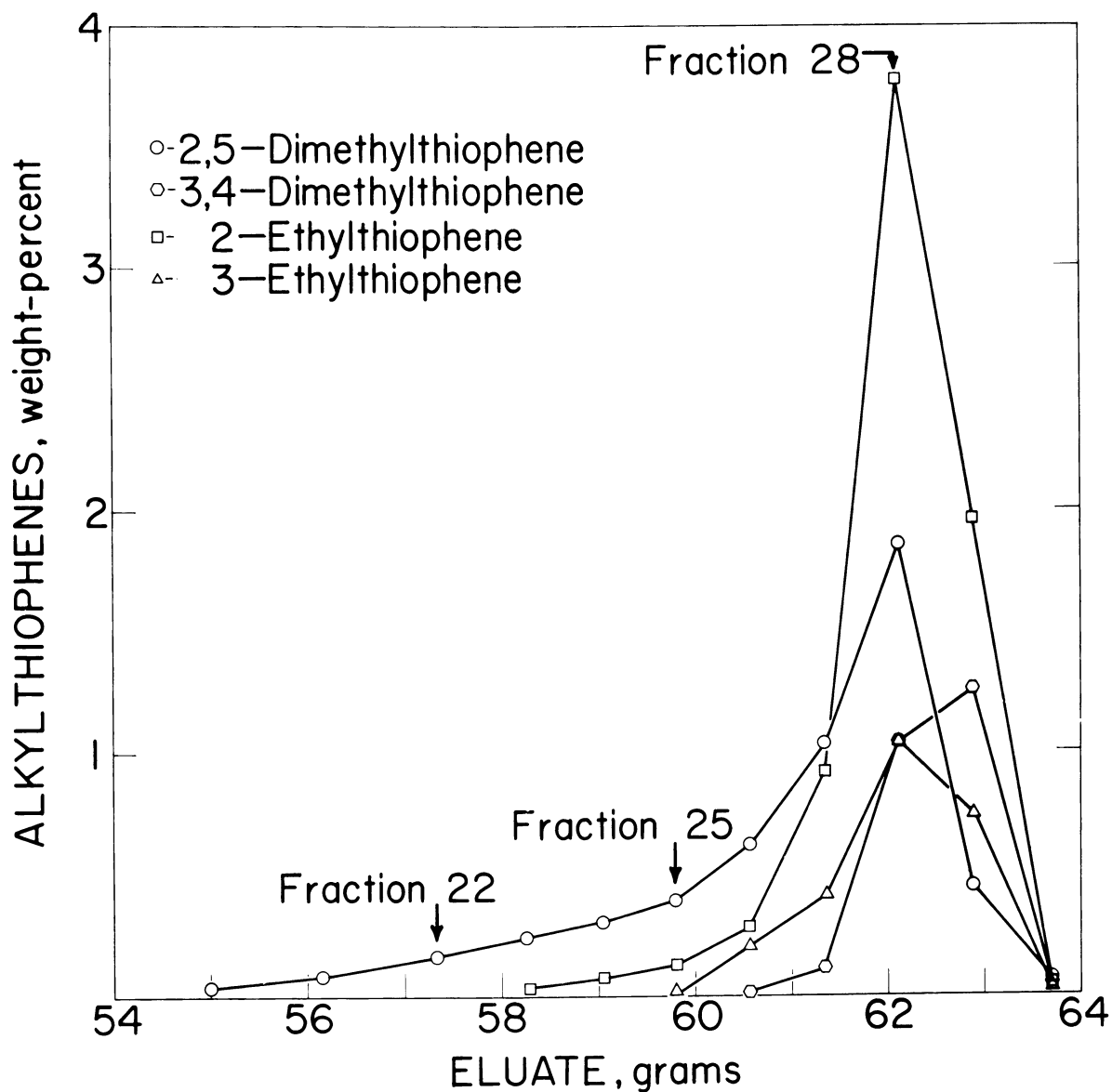
Figure 95.—Quantitative distribution curves for selected
alkylthiophenes in alumina adsorption fractions.

the last appreciable quantity of alkylthiophenes, and the first and least strongly adsorbed cyclic sulfides. Obviously, the final concentrating adsorption run successfully produced a relatively sharp separation between thiophenes and cyclic sulfides with but one small 0.8-gram transition fraction (No. 29) containing both compound types. Because of the limited number of possible alkylthiophenes in the Wilmington distillate, the separation and quantitation of these compounds proved to be rela-tively simple compared with that for the more numerous alkyl substituted cyclic sulfides, many of which were present as cis- and trans-isomers.

Identifications of cis- and trans-alkyl-substituted cyclic sulfides were especially troublesome because, in addition to the greater number of possible com-pounds, cis- and trans- forms are indistinguishable by microdesulfurization and almost so by mass spectrometry. Despite such handicaps, GLC studies with different stationary phases showed that each

isomer in this investigation is separable and once separated, can be analyzed and compared with a known reference compound. Some of these separations by GLC are quite pronounced on the chromatograms of adsorption fractions 29, 30, and 31 of figure 93. Quite fortuitously, the only stereoisomeric cyclic sulfides contained in this distillate were 2,3-; 2,4-; and 3,4-dimethylthiacyclopentane, all of which were separated and identified.

The peaks of two cyclic sulfides that stood out quite conspicuously in the chromatogram of adsorption fraction 29, and only in fraction 29 (see figure 93), were 2,2,5,5-tetramethylthiacyclopentane at 34.5 minutes, and 2,2,5-trimethylthiacyclopentane at 37.5 minutes. These two cyclic sulfides, with their specially placed multimethyl substitutions, of course, do not have *cis-* or *trans-*isomers (true of 2,2-dimethylthiacyclopentane also), but from the standpoint of adsorption on alumina and elution time on the specially selective Reoplex 400 GLC column, they were exceptionally conspicuous. These two highly substituted cyclic sulfides were identified during a related GLC study that involved steric hindrance effects of alkyl substitution around the sulfur atom of cyclic sulfides. The analytical techniques used for identifying these cyclic sulfides are described in a preliminary publication (*422*) and discussed in greater detail in two later papers (*76, 77*).

This sulfur compound identification study on the Wilmington 111° to 150° C (232° to 302° F) distillate represents an investigation that employed several techniques for separation and identification. Distillation provided material of a limited molecular-weight range. Liquid-solid chromatography separated the sulfur compounds from most of the associated hydrocarbons and concentrated them according to type (e.g., fractions 28–31 of fig. 93). Gas-liquid chromatography selectively isolated individual compounds from extremely complex mixtures. Microdesulfurization provided clues to carbon skeletal structure and mass spectrometry gave molecular weight and additional structural detail. Finally, comparison of the infrared spectra with that of reference compounds generally provided the information necessary for identification.

The 30 sulfur compounds identified in this limited boiling range study on Wilmington, crude oil are listed in table 44 in order of increasing boiling point. Quantitative data are also given for the thiophenes and for two of the more easily isolatable cyclic sulfides. Some additional quantitative insight can be derived by close inspection of the chromatograms of figure 93 from which one may draw some obvious conclusions. For example,

Table 44.—Sulfur compounds identified in Wilmington, California, crude oil and estimated weight-percent present where known

Name	Boiling point, ° C	Weight-percent in crude oil
Thiophene	84.1	0.000032
2-Methylthiophene	112.5	.00010
3-Methylthiophene	115.4	.00006
2-Methylthiacyclopentane	133.2	....
2-Ethylthiophene	134.0	.000080
3-Ethylthiophene	136.0	.000027
2,5-Dimethylthiophene	136.7	.000061
2,2-Dimethylthiacyclopentane	138.4	....
3-Methylthiacyclopentane	138.7	....
2,4-Dimethylthiophene	140.7	.000058
2,3-Dimethylthiophene	141.6	.000094
Thiacyclohexane	141.8	....
trans-2,5-Dimethylthiacyclopentane	142.0	....
cis-2,5-Dimethylthiacyclopentane	142.3	....
3,4-Dimethylthiophene	145.0	.000028
trans-2,5-Dimethylthiacyclopentane	148.0	....
cis-2,4-Dimethylthiacyclopentane	148.0	....
trans-2,3-Dimethylthiacyclopentane	148.0	....
cis-2,3-Dimethylthiacyclopentane	148.0	....
2-Methylthiacyclohexane	153.0	....
2-Isopropylthiophene	153.0	.000006
trans-3,4-Dimethylthiacyclopentane	156.0	....
cis-3,4-Dimethylthiacyclopentane	156.0	....
3-Methylthiacyclohexane	158.0	....
2,2,5-Trimethylthiacyclopentane	[1] 158.0	.000070
2-Ethylthiacyclopentane	......	....
2-*n*-Propylthiophene	158.5	.000009
4-Methylthiacyclohexane	158.6	....
2,4,4-Trimethylthiacyclopentane	.....	....
2,2,5,5-Tetramethylthiacyclopentane	.....	.000085

[1] Estimated.

the peak at 57 minutes in the chromatograms of fractions 30 and 31 corresponding to 2-methylthiacyclohexane is obviously in excess of the single peak at 34.5 minutes for 2,2,5,5-tetramethylthiacyclopentane identified in adsorption fraction 29 as being present to the extent of 0.000085 weight percent of the original crude. A true quantitative value for 2-methylthiacyclohexane is clouded by its presence in some measure in fraction 29 (not actually determined) as a trailing shoulder on a larger nonsulfur compound peak (last of the *o*-xylene). It is observed also that there is less of the parent compound, thiacyclohexane (54.5 minutes in the chromatogram of fraction 31), than 2-methylthiacyclohexane mentioned above.

One of the more interesting observations resulting from this limited comparative study on Wilmington crude oil was the existence of significant differences in types and quantities of sulfur compounds present in different crude oils. For example, the Wasson crude oil distillate boiling up to 150° C (302° F) contained large amounts of thiols, chain sulfides, and of course, cyclic sulfides, but little or no alkylthiophenes. On the other hand,

the comparable Wilmington crude oil distillate contained alkylthiophenes and cyclic sulfides but no thiols or chain sulfides. Such differences in crude oil composition certainly denote important differences either in origin or geologic history or both, but the interpretation of such differences needs more data and study before logical explanations can be derived.

In conclusion one may note that of the 30 sulfur compounds boiling below 150° C identified in Wilmington crude oil and listed in table 44, 11 are thiophenes and 19 are cyclic sulfides. These compounds include all theoretically possible thiophenes within this boiling range and all but one cyclic sulfide, thiacyclopentane, which should occur in a lower boiling distillation fraction not examined.

AGHA JARI, IRAN, CRUDE OIL

38° to 100° C Boiling Range

In a dual effort to evaluate separation and identification procedures previously developed and apply them to other crude oils, a qualitative study was made of the sulfur compounds found in the 38° to 100° C (100° to 212° F) fraction of Agha Jari crude oil (81).

The outline of sample treatment required to secure the distillate investigated is given in figure 96. Approximately 20 gallons, or 63,849 grams of Agha Jari crude oil was processed through the steam-heated isothermal still at atmospheric pressure to yield 11,792 grams of distillate that represented 18.5 percent of the original charge. As this distillate contained both light and heavy ends that were not needed for this study, it was vacuum fractionated in an all-glass Oldershaw column to yield 4,135 grams of a 38° to 100° C (100° to 212° F) distillate. This distillate contained only 0.066 percent sulfur which would yield, if recovery were 100 percent, 2.6 grams of sulfur or roughly 7.4 grams of sulfur compounds based on an average molecular formula of C_4H_{10}.

A 3,980-gram sample of the 38° to 100° C (100° to 212° F) distillate was percolated through alumina to concentrate the sulfur compounds. For this operation, the distillate was divided into six aliquot portions and separately filtered through jacketed columns that held approximately 1,750 ml of fluid-grade H–41 alumina. The sulfur concentrate obtained was repercolated twice to concentrate the sulfur compounds further by selective elution of the aromatics. After percolation through alumina, the 3,980 grams of original distillate had been reduced to about 8.0 grams of a sulfur compound-aromatic

concentrate that contained about 35 percent aromatics. At no time during processing was the crude oil or any of its fractions subjected to a temperature higher than 100° C (212° F). The conditions employed were such that the sulfur compounds subsequently found are thought to have been present in the crude oil and not produced in any processing steps.

Because of the relatively small amount of concentrate on hand for study, the availability of gas-liquid chromatography (GLC) was opportune. In the mid 1950's, when this work was being done, the technique of GLC was in its infancy. Equipment was in a state of rapid development, and only laboratory or custom-constructed apparatus was available. With present sophisticated equipment and techniques, it would be possible now to make more complete and quantitative analyses in much less time, but the identifications reported here can hardly be challenged because of the use of equipment that now would be considered outmoded. Many of the improved chemical and GLC techniques developed and used later could have separated the thiols and chain sulfides of the Agha Jari distillate into separate fractions free of aromatics, while judicious use of improved GLC columns could have isolated each individual compound for trapping and positive identification, not only by mass spectrometry, as was done on Wasson, but also by microhydrogenation and infrared spectrometry.

To effect the identifications reported, a 0.02-ml sample of the sulfur compound-aromatic concentrate indicated in the final block of figure 96 was examined by gas-liquid chromatography, and the chromatogram shown in figure 97 (top panel) was obtained. The retention times of the sulfur compounds in the boiling range of 38° to 100° C had been determined in various GLC columns, and with this information, a tentative identification could be assigned to most of the compounds producing the peaks in this chromatogram. The addition of small amounts of pure sulfur compounds to small separate samples enhanced the suspected peaks and produced no extraneous peaks (fig. 97, center and bottom panels), thus corroborating their presence in the concentrate. Final proof of compound identity was obtained by trapping, in liquid air-cooled traps, the compounds that emerged from the column during formation of a peak and analyzing the trap contents by mass spectrometry. Although not labeled in the chromatograms of figure 97, the material producing the last peak, retention time of roughly 74 minutes, was identified as toluene. The other possibly present aromatic, benzene, eluted with 2-butanethiol.
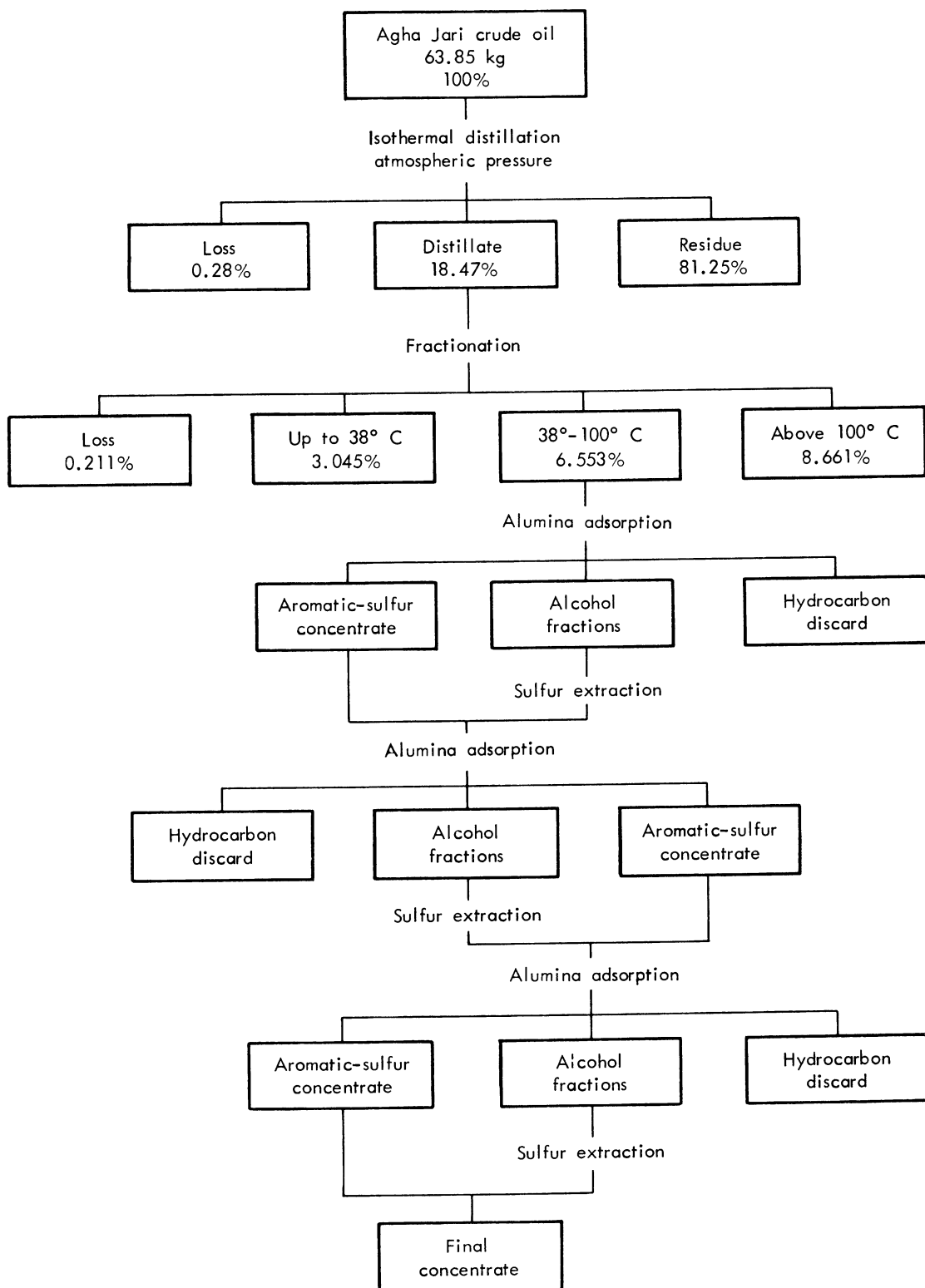
Figure 96.—Summary of processing of Agha Jari, Iran, crude oil.

Figure 97.—Gas-liquid chromatographic analysis of Agha Jari 38° to 100° C sulfur concentrate.

Table 45.—Sulfur compounds identified in Agha Jari, Iran, crude oil [1]

Compound	Boiling point, °C
Identified:	
2-Propanethiol	52.56
2-Methyl-2-propanethiol	64.22
2-Thiabutane	66.65
3-Methyl-2-thiabutane	84.8
2-Butanethiol	85.0
3-Thiapentane	92.10
2-Thiapentane	95.6
2-Methyl-3-thiapentane	107.38
Tentatively identified:	
1-Propanethiol	67.8
2-Methyl-1-propanethiol	88.5
2,2-Dimethyl-1-propanethiol	103.7

[1] Reprinted from Anal. Chem., v. 30, Oct. 1958, p. 1594.
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The eight sulfur compounds definitely identified are listed in table 45 in order of increasing boiling point. These compounds are listed in table 46 in order of increasing concentration in the crude oil,

Table 46.—Sulfur compounds definitely identified in Agha Jari crude oil, approximate concentration

Compound	Approximate concentration in crude oil, weight-percent
2-Methyl-2-propanethiol	0.00002
2-Propanethiol	.00009
2-Methyl-3-thiapentane	.00043
2-Butanethiol	.00065
3-Methyl-2-thiabutane	.00074
2-Thiapentane	.00134
2-Thiabutane	.00220
3-Thiapentane	.00571

with approximate quantitative values given. While the quantitative results of this work are subject to improvement, the approximate values do give some conception as to the relative abundance of the compounds identified.

The presence of three compounds identified by retention time and peak enhancement could not be confirmed conclusively by mass spectrometry of trapped fractions because of insufficient sample. The identification of these compounds must remain
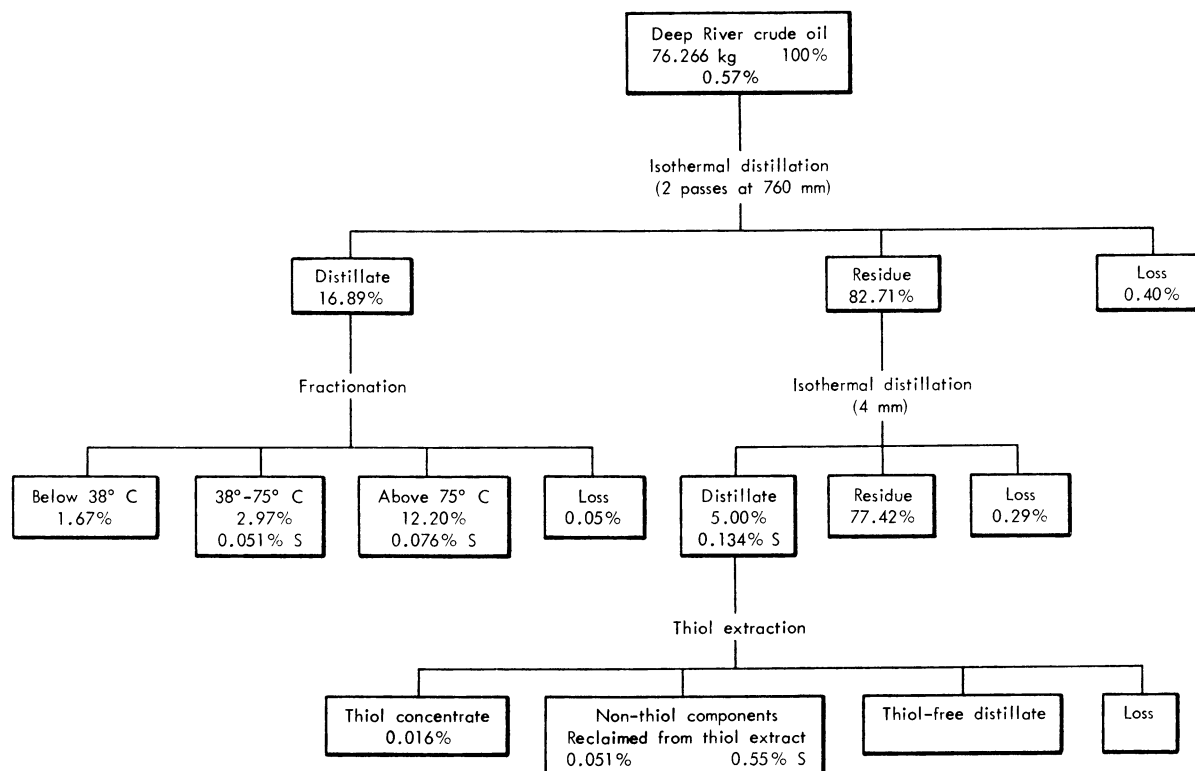
Figure 98.—Summary of the processing of Deep River, Michigan, crude oil.
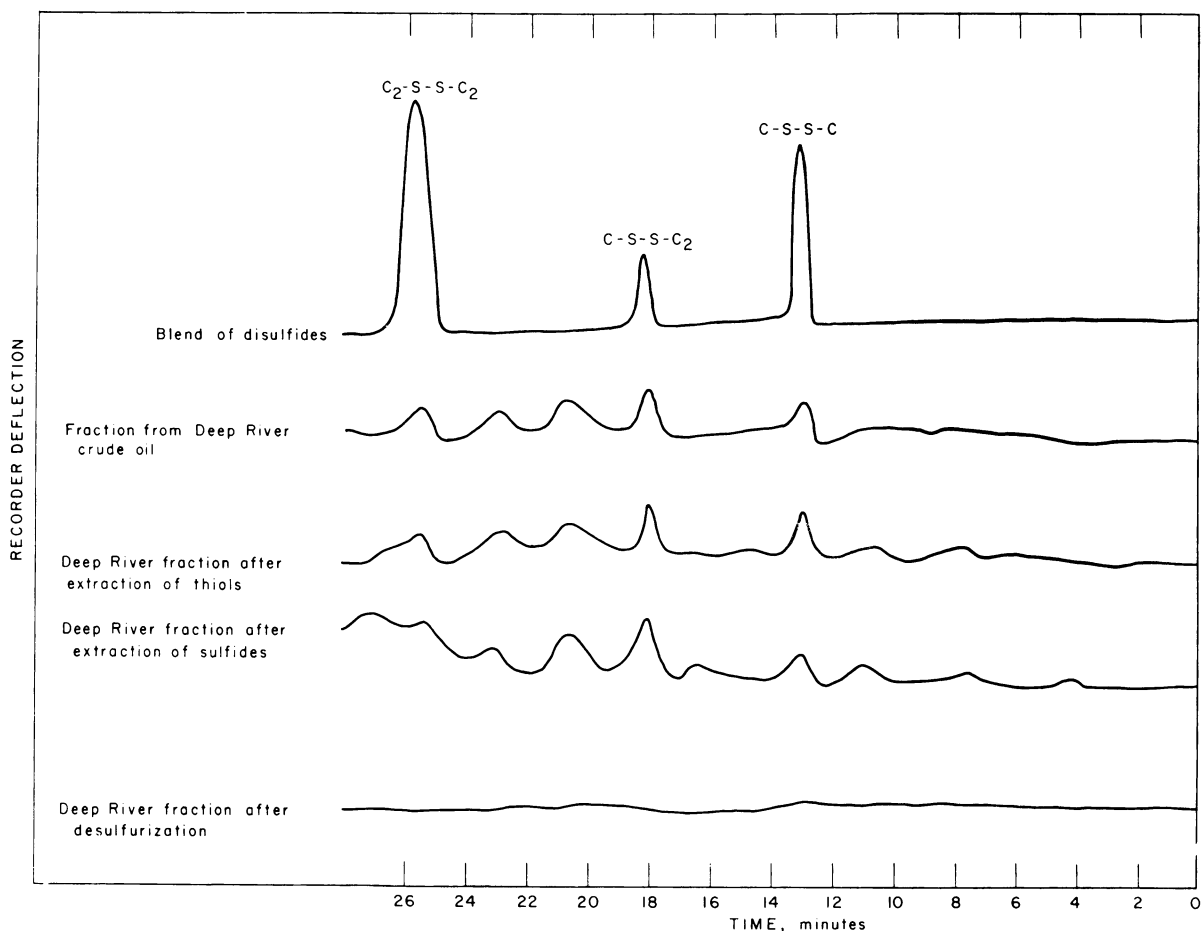
Figure 99.—Gas-liquid chromatograms (electron capture) suggesting
presence of disulfides in Deep River crude oil fraction.

tentative (see table 45) until confirmatory proof of their presence is secured by independent means.

Three other compounds, 1-butanethiol, 98.4° C (208° F), 2-methyl-2-butanethiol, 99.2° C (210° F), and 3,3-dimethyl-2-thiabutane, 99.0° C (210° F), were sought but not found. The retention time of each of these three compounds coincides with a major component in the concentrate, and trace amounts would be most difficult to separate and identify by GLC techniques available at that time. These compounds have been identified in small or trace amounts in Wasson crude oil and are believed to be present only in trace amounts in Agha Jari crude oil.

DEEP RIVER, MICHIGAN, CRUDE OIL

The presence of disulfides in virgin crude oils had long been suspected but never unequivocally confirmed before this investigation. Early work of the project in the identification of sulfur compounds, by type, in a series of crude oils, pointed to the Deep River field of Michigan as one that would merit more detailed study as to the possible presence of disulfides. Toward this end several samples of crude oil were collected, in the absence of air, from wells in the Deep River, Michigan, field. This field is in Arenac County and is a quite narrow field lying diagonally in Deep River Township for a length of 6 miles. The crude oil sample investigated is from a well, Werblo No. 4, in the extreme northwest end of the field near the discovery well. It's sulfur content is 0.57 percent. Twenty-five gallons of this crude oil was obtained from the "heater-treater," into which the well production emptied, operating at atmospheric temperature and at several pounds positive gas pressure. The sampling drum was flushed with nitrogen to remove air

although the abundant natural gas present in the crude oil made this precaution almost superfluous. Extra care was employed to prevent exposure of the crude oil and its fractions to air. Related studies have shown that, at most, only traces of thiols are oxidized to disulfides when refluxed for several hours under purified nitrogen. These data are reassuring, indicating that the disulfides subsequently found were indigenous to the crude oil and were not formed during processing.

The sample of crude oil (25 gallons) was processed (three passes) through the isothermal still to produce two distillates. The distillate produced in the third and final pass (at 4 mm) through the isothermal still was chemically treated to extract the thiols. This treatment produced a thiol concentrate, a thiol-free distillate, and a small (36-g) hydrocarbon non-thiol fraction which was dissolved or entrained in the thiol extraction solvent and recovered by back extracting the extract solution. Most of the disulfides appear to have been concentrated in this fraction, probably through preferential solvent extraction. A flow chart indicating all processing steps is shown in figure 98.

With an electron-capture detector, a chromato-gram was obtained on the fraction that contained the non-thiol components reclaimed from the thiol extract. The electron-capture detector responds specifically to disulfides (306) and is not sensitive to other types of sulfur compounds likely to be present in the fraction under examination. The chromatogram obtained (see fig. 99) showed small peaks at retention times in agreement with those of 2,3-dithiabutane, 2,3-dithiapentane, and 3,4-dithiahexane. These peaks were eliminated from the chromatogram by desulfurization of the fraction, enhanced in the chromatogram by addition to the fraction of the suggested disulfides, and not affected by the chemical removal from the fraction of thiols, sulfides, and thiophenes (see fig. 99), thereby providing data of sufficient certainty for the tentative identification of these disulfides in Deep River crude oil. While the data are not as conclusive as isolation of the individual compounds and their identification by their properties (spectra), the authors feel that there is no doubt of the presence of this class of sulfur compounds in Deep River crude oil. These identifications represent the first of this class of sulfur compounds to be found in virgin petroleum.

During this research the major study was on Wasson, Texas, crude oil. Being investigated to a lesser degree were crude oils from these fields: Wilmington, California; Agha Jari, Iran; and Deep River, Michigan. Table 47 summarizes the data of tables 48 and 49 in terms of types and numbers of compounds identified in all four crude oils during the life of the project.

The sulfur compounds identified by the Bureau of Mines-American Petroleum Institute Research Project 48 in the four crude oils are listed in tables 48 and 49 in order of increasing boiling points. The quantitative data are minimum values that reflect handling losses throughout the complicated processing steps required for individual compound identification.

For thiols and low-boiling sulfides, the values are thought to be low by no more than 10 percent. For sulfides boiling above 111° C (232° F), the values reported may be low by as much as 50 percent because of processing losses. Total sulfur content, by weight-percent, for the original crude oils were Wasson, 1.85 percent; Wilmington, 1.38 percent; Agha Jari, 1.36 percent; and Deep River, 0.58 percent.

Table 47.—Number and type of sulfur compounds identified by Bureau of Mines–API Research Project 48 in four crude oils [1]

	Wasson	Wilming-ton	Agha Jari	Deep River	Total
Thiols:					
Alkyl	40	....	6	....	46
Cyclic	6	....	....	....	6
Aromatic	[2] 1	....	....	....	1
Sulfides:					
Dialkyl	38	....	5	....	43
Alkylcycloalkyl	5	....	....	....	5
Alkylaryl	4	....	....	....	4
Cyclic	21	19	....	....	40
Thiaindans	18	....	....	....	18
Disulfides	1	....	....	3	4
Thiophenes:					
Alkyl	0	11	....	....	11
Benzo-	22	....	....	....	22
Thieno-	2	....	....	....	2
Dibenzo-	2	....	....	....	2
Total identifications	160	30	11	3	204
Unduplicated identifications	160	14	0	2	176

[1] Reproduced by permission from reference 73.
[2] Uncertain.

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Table 48.—Sulfur compounds identified in Wilmington, Deep River, and Agha Jari crude oils and estimated weight-percent present where known [1]

Name	Boiling point, ° C	Weight-percent in crude oil
WILMINGTON CRUDE OIL		
Identified:		
Thiophene	84.1	0.000032
2-Methylthiophene	112.5	.00010
3-Methylthiophene	115.4	.00006
2-Methylthiacyclopentane	133.2	....
2-Ethylthiophene	134	.000080
3-Ethylthiophene	136	.000027
2,5-Dimethylthiophene	136.7	.000061
2,2-Dimethylthiacyclopentane	138.4	....
2,4-Dimethylthiophene	140.7	.000058
2,3-Dimethylthiophene	141.6	.000094
Thiacyclohexane	141.8	....
trans-2,5-Dimethylthiacyclopentane	142.0	....
cis-2,5-Dimethylthiacyclopentane	142.3	....
3,4-Dimethylthiophene	145	.000028
trans-2,4-Dimethylthiacyclopentane	148	....
cis-2,4-Dimethylthiacyclopentane	148	....
trans-2,3-Dimethylthiacyclopentane	148	....
cis-2,3-Dimethylthiacyclopentane	148	....
2-Methylthiacyclohexane	153	....
2-Isopropylthiophene	153	.000006
trans-3,4-Dimethylthiacyclopentane	156	....
cis-3,4-Dimethylthiacyclopentane	156	....
3-Methylthiacyclohexane	158.0	....
2,2,5-Trimethylthiacyclopentane	[2] 158	.000070
2-Ethylthiacyclopentane	.....	....
2-n-Propylthiophene	158.5	.000009
4-Methylthiacyclohexane	158.6	....
2,2,5,5-Tetramethylthiacyclopentane	.....	.000085
Tentatively identified:		
3-Methylthiacyclopentane	138.7	....
2,4,4-Trimethylthiacyclopentane	.....	....

DEEP RIVER CRUDE OIL

Name	Boiling point, ° C	
Tentatively identified:		
2,3-Dithiabutane	115	....
2,3-Dithiapentane	[2] 133	....
3,4-Dithiahexane	152.6	....

AGHA JARI CRUDE OIL

Name	Boiling point, ° C	
Identified:		
2-Propanethiol	52.6	....
2-Methyl-2-propanethiol	64.2	....
2-Thiabutane	66.7	....
3-Methyl-2-thiabutane	84.8	....
2-Butanethiol	85.0	....
3-Thiapentane	92.1	....
2-Thiapentane	95.6	....
2-Methyl-3-thiapentane	107.4	....
Tentatively identified:		
1-Propanethiol	67.8	....
2-Methyl-1-propanethiol	88.5	....
2,2-Dimethyl-1-propanethiol	103.7	....

[1] Reproduced by permission from reference 73.
[2] Estimated.

Table 49.—Sulfur compounds identified in Wasson, Texas, crude oil and estimated weight-percent present, where known

Name	Boiling point, °C	Weight-percent	
		In crude oil [1]	Of total sulfur in crude oil
IDENTIFIED			
Methanethiol.	5.9	0.00240	0.0865
Ethanethiol.	35.0	.00530	.1478
2-Thiapropane.	37.4	.00088	.0245
2-Propanethiol.	52.6	.00199	.0453
2-Methyl-2-propanethiol.	64.2	.00055	.0106
2-Thiabutane.	66.7	.00222	.0505
1-Propanethiol	67.8	.00041	.0093
3-Methyl-2-thiabutane	84.8	.00064	.0123
2-Butanethiol.	85.0	.00386	.0742
2-Methyl-1-propanethiol	88.5	.00003	.0006
2-Thiapentane	92.1	.00075	.0144
2-Thiapentane.	95.6	.00030	.0058
1-Butanethiol.	98.4	Trace	Trace
3,3-Dimethyl-2-thiabutane.	99.0		
2-Methyl-2-butanethiol.	99.2	.00064	.0106
2-Methyl-3-thiapentane.	107.4		
3-Methyl-2-butanethiol.	109.8		
2-Pentanethiol.	112.4	.0014	.023
3-Pentanethiol.	113.9	.00057	.0095
4-Methyl-2-pentanethiol.			
3-Methyl-3-pentanethiol.			
3-Thiahexane.	118.5	.00012	.0020
2,4-Dimethyl-3-thiapentane.	120.0	.00053	.0078
2,2-Dimethyl-3-thiapentane.	120.4	.000058	.0008
Thiacyclopentane.	120.9	.000077	.0015
2-Thiahexane.	123.5	.000077	.0013
2,3-Dimethyl-2-butanethiol.	124.0		
1-Pentanethiol.	126.6		
2-Methyl-3-thiahexane.	132.0	.000078	.0011
Cyclopentanethiol.	132.1		
2-Methylthiacyclopentane.	133.2	.0023	.039
4-Methyl-3-thiahexane.	133.6	.00050	.0073
2-Methyl-3-pentanethiol.	²134.5		
3-Methylthiacyclopentane.	134.7		
2-Hexanethiol.	138.7	.00046	.0078
3-Methyl-2-thiahexane.	138.9	.0028	.041
	139.		

Name	Boiling point, °C	Weight-percent	
		In crude oil [1]	Of total sulfur in crude oil
IDENTIFIED—Continued			
3-Ethyl-2-thiapentane.			
3-Hexanethiol.			
Thiacyclohexane.	141.8	0.00032	0.0054
trans-2,5-Dimethylthiacyclopentane.	142.0	.0025	.037
cis-2,5-Dimethylthiacyclopentane.	142.3	.0024	.036
2,4-Dimethyl-3-thiahexane.	²142.3		
2-Methyl-2-hexanethiol.			
3-Thiaheptane.	144.2	.000078	.0011
trans-2-Methylcyclopentanethiol.	145		
3-Methyl-3-hexanethiol.			
cis- and/or trans-2,3-Dimethylthiacyclopentane.	148		
trans-2,4-Dimethylthiacyclopentane.	148		
cis-2,4-Dimethylthiacyclopentane.	148		
cis-2-Methylcyclopentanethiol.	152		
2-Methylthiacyclohexane.	153.0	.0029	.043
cis- and/or trans-3,4-Dimethylthiacyclopentane.	156		
2,2,5-Trimethylthiacyclopentane.	²158		
2-Ethylthiacyclopentane.			
3-Methylthiacyclohexane.	158.0	.000024	.0004
4-Methylthiacyclohexane.	158.6	.000048	.0007
Cyclohexanethiol.	158.7	.0012	.018
4-Heptanethiol.			
3-Heptanethiol.			
2-Heptanethiol.			
3,5-Dimethyl-4-thiaheptane.	165		
2,4-Dimethyl-3-thiaheptane.			
2-Methyl-4-ethyl-3-thiahexane.			
2-n-Propylthiacyclopentane.			
Benzo[b]thiophene.	219.9		
(2-Methyl-1-thiabutyl)benzene.			
1-Thiaindan.	235.6	.00248	
2-Methylbenzo[b]thiophene.	²243.0	.00010	
7-Methylbenzo[b]thiophene.		.00095	
3-Methylbenzo[b]thiophene.	²246.0		
2-Methyl-1-thiaindan.			
Dibenzothiophene.			

See footnotes at end of table

Table 49.—Sulfur compounds identified in Wasson, Texas, crude oil and estimated weight-percent present, where known—Continued

Name	Boiling point, °C	Weight-percent In crude oil [1]	Weight-percent Of total sulfur in crude oil
TENTATIVELY IDENTIFIED			
2,2-Dimethyl-1-propanethiol	103.7	......	......
3-Methyl-2-thiapentane	112	......	......
2,2-Dimethyl-1-butanethiol	......	......	......
2-Methyl-1-butanethiol	118	......	......
3,3-Dimethyl-2-butanethiol	......	......	......
3,3-Dimethyl-2-thiapentane	² 131	......	......
2,3-Dithiapentane	² 133	......	......
5-Methyl-3-thiahexane	134.2	......	......
3,4-Dimethyl-2-thiapentane	......	......	......
3,3-Dimethyl-1-butanethiol	......	......	......
2,2-Dimethyl-3-thiahexane	......	......	......
3-Methyl-2-pentanethiol	......	......	......
2,2-Dimethylthiacyclopentane	138	......	......
2-Methyl-1-pentanethiol	² 142	......	......
2,3-Dimethyl-1-butanethiol	......	......	......
1-Methylcyclopentanethiol	......	......	......
4-Methyl-1-pentanethiol	......	......	......
2-Ethyl-1-butanethiol	......	......	......
3-Methyl-1-pentanethiol	142.7	......	......
4-Thiaheptane	......	......	......
2,5-Dimethyl-3-thiahexane	......	......	......
4,4-Dimethyl-3-thiahexane	......	......	......
3,3-Dimethylthiacyclopentane	² 145	......	......
2-Thiaheptane	145	......	......
1-Hexanethiol	......	......	......
cis- and/or trans-3-Methylcyclopentanethiol	......	......	......
4-Heptanethiol	......	......	......
4,5-Dimethyl-3-thiahexane	......	......	......
2-Methyl-3-thiaheptane and/or 3-methyl-4-thiaheptane	......	......	......
2-Methyl-4-thiaheptane	......	......	......
4-Ethyl-3-thiaheptane	......	......	......
5-Methyl-4-thiaoctane and/or 3-ethyl-4-thiaheptane	......	......	......
4-Methyl-3-thiaoctane	......	......	......
2-Methyl-4-thiaoctane	......	......	......
3-Methyl-3-thiaoctane	......	......	......
2,2,5,5-Tetramethylthiacyclopentane	......	......	......
Benzenethiol	169.1	......	......
1-Heptanethiol	......	......	......
2-Octanethiol	186.4	......	......
trans-2,5-Diethylthiacyclopentane	......	......	......
cis-2,5-Diethylthiacyclopentane	......	......	......
(1-Thiapropyl)cyclohexane	......	......	......
(2-Methyl-1-thiapropyl)cyclohexane	......	......	......
(2-Methyl-1-thiabutyl)cyclopentane	......	......	......
(3-Methyl-1-thiabutyl)cyclopentane	......	......	......
2-Methyl-1-(2-methyl-1-thiapropyl)benzene	......	......	......
3-Methyl-1-(2-methyl-1-thiapropyl)benzene	......	......	......
4-Methyl-1-(2-methyl-1-thiapropyl)benzene	......	......	......
(2,2-Dimethyl-1-thiapropyl)cyclohexane	² 228	......	......

Name	Boiling point, °C	Weight-percent In crude oil [1]	Weight-percent Of total sulfur in crude oil
TENTATIVELY IDENTIFIED—Continued			
4-Methylbenzo[b]thiophene	......	......	......
3-Methyl-1-thiaindan	......	......	......
5-Methyl-1-thiaindan and/or 7-methyl-1-thiaindan	......	......	......
2-Methylthieno[3,2-b]thiophene	......	......	......
3-Methylthieno[2,3-b]thiophene	......	......	......
2-Ethylbenzo[b]thiophene	......	0.00037	......
2,3-Dimethylbenzo[b]thiophene	......	.00094	......
3-Ethylbenzo[b]thiophene	......	.00101	......
2,4-Dimethylbenzo[b]thiophene	......	.00013	......
2,5- and/or 2,7-Dimethylbenzo[b]thiophene	......	.00009	......
2,6-Dimethylbenzo[b]thiophene	......	......	......
3,6-Dimethylbenzo[b]thiophene	......	......	......
3,7-Dimethylbenzo[b]thiophene	......	.00020	......
4,7-Dimethylbenzo[b]thiophene	......	.00004	......
2,2-Dimethyl-1-thiaindan	......	......	......
3,3-Dimethyl-1-thiaindan	......	......	......
2,5-Dimethyl-1-thiaindan and/or 2,7-dimethyl-1-thiaindan	......	......	......
2,3-Dimethyl-1-thiaindan and/or 3-ethyl-1-thiaindan	......	......	......
2,4-Dimethyl-1-thiaindan	......	......	......
2,6-Dimethyl-1-thiaindan	......	......	......
3,5-Dimethyl-1-thiaindan and/or 3,7-dimethyl-1-thiaindan	......	......	......
3,6-Dimethyl-1-thiaindan	......	......	......
2-Ethyl-1-thiaindan	......	......	......
2,3,6-Trimethylbenzo[b]thiophene and/or 3-ethyl-6-methylbenzo[b]thiophene	......	......	......
2,4,7-Trimethylbenzo[b]thiophene	......	......	......
2-Ethyl-4-methylbenzo[b]thiophene	......	......	......
2-Methyl-3-ethylbenzo[b]thiophene	......	......	......
2-Methyl-2-ethyl-1-thiaindan	......	......	......
2-Ethyl-5-methylbenzo[b]thiophene and/or 2-ethyl-7-methylbenzo[b]thiophene	......	.00006	......
3-Ethyl-5-methyl and/or 3-ethyl-7-methyl and/or 2,3,5-trimethyl and/or 2,3,7-trimethylbenzo[b]thiophene	......	......	......
4-n-Propylbenzo[b]thiophene and/or 2-methyl-4-ethylbenzo[b]thiophene	......	......	......
2-Methyl-5-ethyl and/or 2-methyl-7-ethyl and/or 5-propyl and/or 7-propylbenzo[b]thiophene	......	......	......
2,2,5-Trimethyl-1-thiaindan and/or 2,2,7-trimethyl-1-thiaindan	......	......	......
2,2,4-Trimethyl-1-thiaindan	......	......	......
2,3,4-Trimethyl-1-thiaindan and/or 3-ethyl-4-methyl-1-thiaindan	......	......	......
2-Methyl-3-ethyl-1-thiaindan	......	......	......
2-Methyldibenzothiophene and/or 4-methyldibenzothiophene	......	......	......

[1] These are minimum values. For the thiols boiling below 100° C and sulfides boiling above 100° C and for thiols boiling above 111° C may be low by 50 percent because of processing losses, the values are thought to be 90 to 95 percent correct. The values reported for some cyclic and chain sulfides boiling above 111° C may be low by 50 percent because of processing losses.

² Estimate.

SOME AREAS FOR FUTURE RESEARCH

Sulfur compounds are the most important non-hydrocarbons in petroleum, not only because they are present in the largest percentages, but also because of their corrosive nature and their deleterious effects on petroleum products. Much research was done before 1948 on the development of processes to remove sulfur compounds from petroleum products or to neutralize their effects, but little research was done through a systematic study to identify the types of sulfur compounds in petroleum or through scientific studies of the properties of these compounds. Thus, the science of petroleum sulfur compounds dates back only about 25 years. While the information developed since 1948 added to our knowledge of petroleum sulfur chemistry, it also pointed out new areas of research that should be explored.

The development of more data on the types of sulfur compounds in petroleum has led petroleum chemists and geochemists to study these data for an explanation of the source of these sulfur compounds and to determine if they provide clues to the origin of petroleum. There are two general theories regarding the source of sulfur compounds in petroleum. The first theory is that the sulfur compounds were derived either directly or indirectly from the original source material for petroleum. According to this theory, the oil that first forms contains sulfur compounds which disappear later during the long process of maturation. From this it would follow that geologically young oils would be rich in sulfur and ancient oils would be deficient in sulfur. This theory is not consistent in that many Tertiary oils contain almost no sulfur, while some ancient oils are high in sulfur (102).

While the probability exists that some sulfur compounds may be derived from the original petroleum source material, most investigators favor the second theory that the sulfur compounds were produced by secondary reactions after the oil was formed. This theory is based on experimental data demonstrating that certain microorganisms under anaerobic conditions are capable of oxidizing hydrocarbons to carbon dioxide, using oxygen derived from sulfate rocks, and producing hydrogen sulfide and sulfur as byproducts. Calculations by Smith (373, pp. 110–113) show that the reactions of n-alkanes with sulfur to form hydrogen sulfide and alkenes are not thermodynamically feasible below 460° K (370° F). Therefore, this reaction probably is not the predominant source of hydrogen sulfide

in crude oils. However, these reactants will form alkanethiols and sulfides at temperatures low enough to be consistent with reservoir conditions.

The origin of cyclic sulfides presents a more complex explanation as few natural products are known that contain thiacyclopentanes or thiacyclohexanes. However, the analogous oxygen and nitrogen compounds are abundant in nature. Birch (37) suggested the cyclic sulfides may be products of the reactions of hydrogen sulfide with heterocyclics, such as pyrrolidine and tetrahydrofuran. The same types of reactions might occur with the heterocyclics indole and carbazole to form benzothiophene and dibenzothiophene. Smith's calculations show these reactions to be thermodynamically feasible.

The reactions suggested above could account for most of the types of sulfur compounds found in petroleum, but more definitive information is desirable for relating probable petroleum sulfur compounds with the reservoir environment. Some geochemists believe that sulfur isotope ratios of a range of selected crude oils, reservoir rocks, and possible source beds, will provide valuable clues to the origin of petroleum, as well as the sulfur compounds.

These are four naturally occurring stable sulfur isotopes: ^{32}S, ^{33}S, ^{34}S, and ^{36}S. The ratios of the two most abundant, ^{32}S and ^{34}S, are used in examining natural materials. Thode and coworkers (412) have made extensive studies of the $^{34}S/^{32}S$ ratios of a variety of crude oils and found they vary by about 4.5 percent. Their data show variations in a single pool are very small and there is only a narrow range in comparisons of oil pools in the same reservoir rock within a large sedimentary basin. In contrast, oil pools in reservoir rocks of different geological age show a wide range. They conclude that the sulfur isotope ratio for any given oil does not change with time. Thus, the sulfur isotope ratio may give information about the isotope ratio of the source sulfur at the time of petroleum formation, the type of environment, and oil migration. For example, marine oils in the same zones in a sedimentary basin would be expected to have similar isotope ratios. Evidence shows this is generally true, but variations exist through the possible introduction of other sources of sulfur during migration in the reservoir rock. In contrast, nonmarine oils show no relationship to the isotope ratios of contemporaneous oceans (411).

Petroleum chemists have long been intrigued by the similarity of Middle East oils from different formations (*108*). Sulfur isotope ratio studies of the prolific oilfields in Northern Iraq by Thode and Rees (*413*) reveal similar ratios for oils from the Tertiary, Upper, Middle, and Lower Cretaceous formations. They concluded that all of these oils had a common source in the Jurassic or Lower Cretaceous and that they migrated vertically upwards to where they were trapped in their present reservoir rocks. However, the source beds have not yet been identified.

Thode and Rees (*413*) have made extensive studies of the sulfur isotope ratios of Middle East oils, and they are intrigued by unusually large differences in the isotope ratios between these oils and those of the possible parent oceans, which indicate larger than usual fractionation in the bacterial reduction of sulfate to sulfide. They speculate that there may be a relationship between the unusual conditions of sulfate reduction and the prolific oil formation which occurred at the same time in that area.

Analyses of more than 8,000 crude oils by the Bureau of Mines have shown that all crude oils contain sulfur, ranging from a few hundredths percent to as much as 14 percent. Studies of sulfur distribution in crude oils show that sulfur content increases progressively with boiling range.

Early efforts of the project were directed to the identification of the sulfur compounds in the lower boiling ranges. With the development of improved techniques and the availability of more reference sulfur compounds, these studies were extended into the next higher boiling ranges. Our knowledge of the more volatile (below 150° C, 302° F) sulfur compounds is good for Wasson, Texas, and Wilmington, California, crude oil and fair for Agha Jari, Iran, oils. Some compositional data are available for the higher boiling ranges of the Wasson crude oil.

These studies show major differences in sulfur compound composition between crude oils and significant differences between boiling ranges. The Wasson fraction boiling below 200° C (392° F) was found to contain thiols and sulfides, both chain and cyclic, but no thiophene or alkylthiophenes. Above 200° C (392° F) the predominant sulfur compounds were benzothiophenes, dibenzothiophenes, and polybenzothiophenes.

In contrast, Wilmington naphtha contained thiophene, alkyl thiophenes, and cyclic sulfides but no thiols or alkyl sulfides. The heavier distillates appear to be largely benzothiophenes and their benzologs.

The Agha Jari distillate below 110° C (230° F) contained only alkanethiols and sulfides.

Since a more intensive study was made of the Wasson crude oil, it is anticipated that more sulfur compound types would be identified. Alkyl cyclo-alkyl sulfides, alkyl aryl sulfides, bicyclic sulfides, thienothiophenes, and thiaindans were identified in Wasson but not reported in other crudes studied by Bureau of Mines–API RP 48.

Consideration of sulfur content and average molecular weight shows that some crude oils will average more than one sulfur atom per molecule. However, most sulfur studies have been made on the more volatile fractions, so only a few multisulfur atom compounds have been identified. Only one disulfide has been identified in Wasson (*73*) and three in Deep River crude oil (*73*). Nondisulfide types include a thienyl sulfide (*39*) in an Iranian crude, two thienothiophenes (*193*) in Wasson, and a benzodithiophene in an unidentified crude oil (*251*).

The few crude oils that have been studied show interesting differences in the types of sulfur compounds present. Studies of additional crude oils to obtain quantitative information on the types of sulfur compounds present, particularly high molecular weight compounds, should be a fruitful field for research.

A study of the naturally occurring sulfur compounds in petroleum requires special precautions because of the reactivity and the thermal instability of certain types of compounds. Thermal stability studies by Coleman and others (*80*) showed significant evidence of instability at about 150° C (302° F) for crude oils that contained elemental sulfur. The naturally occurring sulfur compounds in Wasson and Slaughter crude oil, started to break down at about 200° C (392° F), but those in Wilmington were stable up to about 260° C (500° F). Little is known of the reactions of sulfur with hydrocarbons or with heterogeneous compounds, but a study of this type in a simulated geological environment might give significant clues to the origin not only of sulfur compounds, but also to the origin of petroleum. For example, Douglas and Mair (*105*) show that sulfur reacts readily with cholesterol at 150° C (302° F) to form aromatic-type compounds, some with a benzene, some a naphthalene, and some a phenanthrene ring system as part of the molecule.

Thermodynamic equilibria data available on sulfur compounds, as compared to amounts of these compounds found in Wasson, are more confusing than enlightening so far as giving clues to the origin of petroleum. Equilibria data obtained by Scott and others (*363*), on isomeric alkanethiols, sulfides,

and thiophenes show that the concentration of total sulfides relative to the thiols is much higher than equilibrium concentrations at any reasonable temperature. Evidently the more reactive thiols were not formed in equilibrium amounts or were altered by chemical reaction after formation. Also, lack of thermodynamic equilibrium in Wilmington crude is shown by the preponderance of 2-methylthiophene over the thermodynamically favored 3-methylthiophene. Quantitative data on individual sulfur compounds in more crude oils and additional thermodynamic data on these compounds should provide useful leads to better theories on the origin of petroleum and would provide rigorous tests of proposed theories. These data and those obtained in a study of the reactive systems under geologic conditions would provide a better basis for developing theories on the origin of sulfur compounds in petroleum.

The chemistry of petroleum sulfur compounds has been advanced appreciably during the past 25 years, but research in this field should be expanded to include quantitative data on more crude oils. Techniques are now available for almost routine investigation of the sulfur compounds boiling up to about 250° C (482° F), but research on the sulfur compounds in the higher boiling fractions has been neglected. Although a few high molecular weight sulfur compounds have been synthesized, more data are needed to provide reference data for individual or type compound identification. Correlative studies on sulfur isotope ratios for sulfur compounds may provide clues as to the origin of the sulfur in petroleum and of petroleum itself.

Advances made in the chemistry of petroleum sulfur compounds have indicated where additional research is needed. The application of recently developed analytical instruments and instruments yet to be developed will provide the means to probe into the higher molecular weight regions.

Speculation on the origin of petroleum fascinates all who research this valuable natural resource, and more information on trace components, of which sulfur is the most prevalent, may well provide the necessary clues.

SUMMARY

The wide occurrence of sulfur and sulfur compounds in petroleum is a major problem. All facets of petroleum production, transportation, storage, processing, and use are adversely affected in varying degrees by the sulfur indigenous to it.

While meaningful progress has been made in the past 20 years in all areas of petroleum sulfur studies, much work remains to be done to permit man to develop and control more effectively his petroleum resources and the environmental conditions affected by petroleum.

The work reported in this Bulletin has significantly extended available knowledge of petroleum sulfur composition, developed unique and effective separation and identification methods, and laid the groundwork for more sophisticated studies. Major accomplishments of the work can be summarized as follows:

1. The identification of 200 sulfur compounds in four crude oils. These compounds represent 13 different classes of sulfur compounds, four of which, alkyl cycloalkyl sulfides, disulfides, alkyl aryl sulfides, and thiaindans, had not been identified previously in petroleum. Similarly, the presence of elemental sulfur was established for the first time in virgin crude oils. Thienothiophenes were tentatively identified in Wasson, Texas, crude oil.

2. Some 11 analytical (separative or identification) procedures which are applicable to any petroleum fraction were developed or extended. These include isothermal distillation, liquid-solid adsorption chromatography, extraction of thiols, microtrapping procedures, unique gas-liquid chromatographic methods, catalytic vapor phase hydrogenolysis, microscale Raney nickel desulfurization, extraction of sulfides by hydrogen iodide adduction, reduction of benzothiophenes to thiols with calcium in liquid ammonia, trinitrobenzene adduction, and spectral correlations. Of these new methods, the catalytic vapor phase hydrogenolysis of GLC fractions was most helpful to the program and has received worldwide attention, no doubt because of its simplicity and its power in aiding structure determination.

3. Approximately 150 sulfur compounds and related hydrocarbons were synthesized. Since many of these compounds were previously unavailable in any laboratory, their spectra were obtained and submitted to API Project 44 for inclusion in the spectral catalog.

4. The data from these studies, both the identifications and the analytical procedures, have been reported in 58 published papers, which are listed in appendix C.

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APPENDIX A.—ADVISORY COMMITTEE MEMBERS
API RESEARCH PROJECT 48

Name	Representing	Tenure		
W. N. Axe	Phillips Petroleum Co., Bartlesville, Okla.	July	1957–July	1966
P. D. Caesar	Socony Mobil Oil Co., Paulsboro, N.J.	January	1957–July	1966
R. G. Capell	Mellon Institute, Pittsburgh, Pa.	July	1951–January	1956
W. N. Catchpole	British Petroleum Co., Ltd., New York, N.Y.	July	1961–July	1963
W. H. Claussen	California Research Corp., Richmond, Calif.	January	1949–July	1957
K. S. Cuddington	British Petroleum Co., Ltd., New York, N.Y.	January	1958–July	1960
J. H. Dove	Anglo-Iranian Co., Ltd.,[1] New York, N.Y.	January	1951–January	1952
C. J. Egan	California Research Corp., Richmond, Calif.	July	1957–July	1962
F. E. Frey[2]	Phillips Petroleum Co., Bartlesville, Okla.	July	1948–January	1954
G. N. Griffiths	British Petroleum Co., Ltd., New York, N.Y.	July	1960–July	1961
W. E. Hanson	Mellon Institute, Pittsburgh, Pa.	January	1956–July	1966
H. D. Hartough	Socony-Vacuum Oil Co., Paulsboro, N.J.	January	1950–January	1951
	Hercules Powder Co., Wilmington, Del.	January	1951–July	1955
	Houdry Process Corp., Marcus Hook, Pa.	July	1955–July	1957
C. J. Helmers	Phillips Petroleum Co., Bartlesville, Okla.	January	1954–July	1957
G. P. Hinds, Jr.[3]	Shell Oil Co., Houston, Tex.	July	1951–July	1966
P. D. Holmes	British Petroleum Co., Ltd., New York, N.Y.	January	1965–July	1966
D. A. Howes	Anglo-Iranian Oil Co., Ltd.,[1] New York, N.Y.	July	1948–January	1951
C. E. Johnson[4]	Standard Oil Co. (Ind.), Whiting, Ind.	July	1954–January	1959
R. H. Kozlowski	California Research Corp., Richmond, Calif.	July	1962–July	1966
G. R. Lake	Union Oil Co. of California, Brea, Calif.	January	1950–July	1966
A. P. Lien	Standard Oil Co. (Ind.), Whiting, Ind.	July	1951–July	1954
H. T. Lorne	Anglo-Iranian Oil Co., Ltd.,[1] New York, N.Y.	January	1952–July	1953
A. R. Mercer	British Petroleum Co., Ltd., New York, N.Y.	November	1956–January	1958
E. P. Oke	Anglo-Iranian Oil Co., Ltd.,[1] New York, N.Y.	July	1954–November	1956
A. A. Rawlins	Anglo-Iranian Oil Co., Ltd.,[1] New York, N.Y.	July	1953–July	1954
F. P. Richter	Socony-Vacuum Laboratories, Paulsboro, N.J.	July	1951–January	1957
W. D. Seyfried[5]	Humble Oil and Refining Co., Baytown, Tex.	July	1948–November	1956
J. C. Schiller	Humble Oil and Refining Co., Baytown, Tex.	November	1956–July	1966
M. E. Spaght	Shell Development Co., San Francisco, Calif.	July	1948–January	1949
H. Sutherland	Shell Development Co., Modesto, Calif.	January	1949–July	1951
R. W. Walker	Sinclair Res., Inc., Harvey, Ill.	July	1963–July	1966
A. W. Weitkamp	Standard Oil Co. (Ind.),[6] Whiting, Ind.	January	1959–July	1966
A. A. Yeo	British Petroleum Co., Ltd., New York, N.Y.	July	1963–January	1965

[1] Now British Petroleum Co., Ltd.
[2] Deceased.
[3] Chairman of Advisory Committee, January 1959–July 1966.
[4] Chairman of Advisory Committee, January 1956–January 1959.
[5] Chairman of Advisory Committee, July 1948–January 1956.
[6] Now American Oil Co.

APPENDIX B.—TECHNICAL STAFF OF SEPARATION AND IDENTIFICATION SECTION OF API RESEARCH PROJECT 48

Name	Title			
N. G. Adams	Petroleum chemist.	August	1948–July	1952
M. G. Barker	Petroleum chemist.	April	1949–November	1951
W. R. Blackburn	Chemical engineer.	January	1949–July	1949
H. J. Coleman	Research chemist.	April	1949–July	1966
Loyetta K. Curnutte	Physical science aid.	October	1953–October	1961
J. E. Dooley	Chemist.	August	1965–July	1966
B. H. Eccleston	Physical chemist.	April	1950–November	1954
D. Eccleston	Student trainee (chemical engineering).	June	1961–September	1961
N. G. Foster	Physical chemist.	March	1957–January	1963
J. H. Hale	Petroleum engineer.	August	1948–August	1950
R. W. Higgins [1]	Organic chemist.	June	1955–September	1955
D. E. Hirsch	Chemist.	July	1958–September	1961
F. L. Ho	Chemical engineer.	July	1959–September	1959
R. L. Hopkins	Research chemist.	August	1950–July	1966
Joan Juneau	Chemist.	January	1954–August	1956
R. F. Kendall	Physicist.	September	1957–July	1966
L. Mikkelsen	Physicist (general).	July	1952–May	1956
Marilyn Morrison	Analytical chemist.	January	1951–November	1952
H. T. Rall	Research chemist.	April	1949–July	1966
Dorothy Richardson	Analytical chemist.	{ November	1951–August	1954
		July	1958–July	1961
A. C. Smith	Physicist.	June	1954–September	1954
H. M. Smith	Petroleum chemist.	August	1948–December	1954
C. J. Thompson	Research chemist.	September	1949–July	1966
Pearl Tribble	Mathematics aid.	July	1957–July	1958
M. L. Whisman	Analytical chemist.	January	1952–October	1958
C. C. Ward	Chemical engineer.	January	1955–July	1966
Don Yee	Physical chemist.	July	1954–April	1957

[1] Deceased.

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APPENDIX D.—SULFUR COMPOUNDS AND RELATED HYDROCARBONS SYNTHESIZED BY SEPARATION AND IDENTIFICATION SECTION

THIOLS

1. 2-Octanethiol
2. 5-Ethyl-2-nonanethiol
3. 3-Methyl-2-butanethiol
4. 3-Hexanethiol
5. 3-Methyl-1-pentanethiol
6. 2-Methyl-1-butanethiol
7. 2-Ethyl-1-butanethiol
8. 3-Methyl-2-pentanethiol
9. 2-Phenyl-1-propanethiol
10. 2-Methyl-1-hexanethiol
11. 3,3-Dimethyl-2-butanethiol
12. *cis-* and *trans*-2-Methylcyclopentanethiols
13. *cis-* and *trans*-3-Methylcyclopentanethiols (mixture)
14. Cyclopentylmethanethiol
15. 2,2-Dimethyl-1-butanethiol
16. 2-Heptanethiol
17. 3-Heptanethiol
18. 4-Heptanethiol
19. 2-Methyl-2-hexanethiol
20. 2-Methyl-1-hexanethiol
21. 2-Methyl-3-hexanethiol
22. 3-Methyl-3-hexanethiol
23. 2-Methylcyclohexanethiol (probably mixture *cis-* and *trans-*)
24. 3-Methylcyclohexanethiol (probably mixture *cis-* and *trans-*)
25. 4-Methylcyclohexanethiol (probably mixture *cis-* and *trans-*)
26. 4-Ethylbenzenethiol
27. 2,3-Dimethyl-1-butanethiol
28. 2,5-Dimethylbenzenethiol
29. Cyclopentanethiol
30. Cyclohexanethiol
31. 3,3-Dimethyl-1-butanethiol

AROMATIC SULFIDES

1. 2,3-Cyclopentano-1-thiaindan
2. 1,2,3,4,4a,4b-Hexahydrodibenzothiophene
3. Phenylisobutyl sulfide
4. Phenyl *sec*-butyl sulfide
5. *m*-Tolyl isopropyl sulfide
6. *p*-Tolyl isopropyl sulfide
7. *o*-Tolyl propyl sulfide
8. *p*-Tolyl propyl sulfide
9. Phenyl methallyl sulfide
10. Phenyl *t*-butyl sulfide
11. 1-Thiaindan
12. 4-Ethylphenyl ethyl sulfide

CHAIN SULFIDES

1. 2,2,4,4-Tetramethyl-3-thiapentane (*t*-butyl sulfide)
2. 3,5-Dimethyl-4-thiaheptane (*sec*-butyl sulfide)
3. 2,2,4-Trimethyl-3-thiapentane (isopropyl *t*-butyl sulfide)

4. 2,5-Dimethyl-3-thiahexane (isopropyl isobutyl sulfide)
5. 2,4-Dimethyl-3-thiahexane (isopropyl *sec*-butyl sulfide)
6. 2-Methyl-3-thiaheptane (isopropyl *n*-butyl sulfide)
7. 3,3-Dimethyl-2-thiapentane (methyl *t*-amyl sulfide)
8. 5-Methyl-2-thiaheptane (methyl isoamyl sulfide)
9. 4-Methyl-2-thiahexane (methyl active amyl sulfide)
10. 4,4-Dimethyl-2-thiapentane (methyl neopentyl sulfide)
11. 3-Methyl-6-thiadecane
12. 3,7-Dimethyl-4-thianonane
13. 2,2,6-Trimethyl-3-thiaoctane
14. 2,3-Dimethyl-5-thianonane
15. 3,6,7-Trimethyl-4-thiaoctane
16. 2,2,5,6-Tetramethyl-3-thiaheptane
17. 3,4-Dimethyl-5-thianonane
18. 3,5,6-Trimethyl-4-thiaoctane
19. 2,2,4,5-Tetramethyl-3-thiaheptane
20. 3-Ethyl-3-methyl-4-thiaoctane
21. 3-Ethyl-3,5-dimethyl-4-thiaheptane
22. 2,2,4-Trimethyl-4-ethyl-3-thiahexane
23. 3-Methyl-4-thiaheptane (propyl *sec*-butyl sulfide)
24. 2-Methyl-4-thiaheptane (propyl isobutyl sulfide)
25. 6-Methyl-3-thiaheptane (ethyl isoamyl sulfide)
26. 5-Methyl-3-thiaheptane (ethyl active amyl sulfide)
27. 4,4-Dimethyl-3-thiahexane (ethyl *t*-amyl sulfide)
28. 4,5-Dimethyl-3-thiahexane (ethyl *sec*-isoamyl sulfide)
29. 4-Methyl-3-thiaheptane (ethyl 2-pentyl sulfide)
30. 4-Ethyl-3-thiahexane (ethyl-3-pentyl sulfide) (mixture resolvable on GLC)
31. 4-Thianonane (propyl *n*-amyl sulfide)
32. 3-Thiaheptane (ethyl *n*-butyl sulfide)
33. 2,2-Dimethyl-3-thiahexane (propyl *t*-butyl sulfide)
34. 3-Methyl-2-thiahexane (methyl 2-pentyl sulfide)
35. 3-Ethyl-2-thiapentane (methyl 3-pentyl sulfide)
36. 2,2-Dimethyl-3-thiapentane (ethyl *t*-butyl sulfide)
37. 4-Methyl-3-thiaheptane (ethyl 2-pentyl sulfide)
38. 4-Ethyl-3-thiahexane (ethyl-3-pentyl sulfide)
39. 4-Methyl-3-thiahexane (ethyl *sec*-butyl sulfide)
40. 5-Methyl-3-thiahexane (ethyl isobutyl sulfide)
41. 2-Methyl-3-thiahexane (isopropyl propyl sulfide)
42. 3-Ethyl-2-thiahexane (methyl-3-hexyl sulfide)
43. 5-Methyl-2-thiaheptane
44. 4,5-Dimethyl-2-thiahexane
45. 4-Ethyl-2-thiahexane
46. 3,4-Dimethyl-2-thiahexane
47. 3-Ethyl-3-methyl-2-thiapentane
48. 3,3-Dimethyl-2-thiahexane
49. 5,5-Dimethyl-2-thiahexane
50. 4,4-Dimethyl-2-thiahexane
51. 3,4,4-Trimethyl-2-thiapentane

CYCLOALKYL SULFIDES

1. Cyclopentyl ethyl sulfide
2. Cyclopentyl propyl sulfide
3. Cyclopentyl isopropyl sulfide
4. Cyclopentyl butyl sulfide
5. Cyclopentyl isobutyl sulfide
6. Cyclopentyl *sec*-butyl sulfide

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7. Cyclopentyl *t*-butyl sulfide
8. Cyclopentyl pentyl sulfide
9. Cyclopentyl cyclohexyl sulfide
10. Cyclohexyl *sec*-butyl sulfide
11. Cyclohexyl *t*-butyl sulfide
12. 2-Methylcyclopentyl methyl sulfide
13. 2-Methylcyclopentyl ethyl sulfide
14. 2-Methylcyclopentyl isopropyl sulfide
15. 2-Methylcyclopentyl propyl sulfide
16. Dicyclopentyl sulfide
17. Cyclohexyl-1-hexyl sulfide
18. Cyclohexyl methyl sulfide
19. Dicyclohexyl sulfide
20. Cyclopentyl-1-hexyl sulfide

PARAFFINS AND CYCLOPARAFFINS

1. 2,5-Dimethylhexane
2. 2-Methylhexane
3. 2,2-Dimethylpentane
4. 3,3-Dimethylpentane
5. 2,3-Dimethylhexane
6. 4-Methylheptane
7. 2,4-Dimethylhexane
8. 3-Ethyl-2-methylpentane
9. 2-Methylbicyclohexyl
10. 3-Methylbicyclohexyl
11. 4-Methylbicyclohexyl
12. 3,4-Dimethylhexane

AROMATIC HYDROCARBONS

1. 1-Methyl-3-propylbenzene
2. 1,3-Dimethyl-5-ethylbenzene
3. 1-Methyl-4-propylbenzene
4. 1-Methyl-2-propylbenzene
5. 1,4-Dimethyl-2-ethylbenzene
6. 1,3-Dimethyl-4-ethylbenzene
7. 3-Phenylpentane
8. 1-Ethyl-3-isopropylbenzene
9. 1-Ethyl-2-isopropylbenzene
10. 2-Phenylpentane
11. 1-Methyl-3-*sec*-butylbenzene
12. 1,3-Dimethyl-5-isopropylbenzene
13. 1-Methyl-2-*sec*-butylbenzene
14. 1,4-Dimethyl-2-isopropylbenzene
15. 1-Ethyl-4-isopropylbenzene
16. 1-Methyl-4-*sec*-butylbenzene
17. Isopentylbenzene
18. 1,3-Dimethyl-4-isopropylbenzene
19. 1,2-Dimethyl-4-isopropylbenzene
20. 1,3-Dimethyl-5-propylbenzene
21. 1-Ethyl-2-propylbenzene
22. 1,4-Dimethyl-2-propylbenzene
23. 1-Ethyl-4-propylbenzene
24. 1-Methyl-3-butylbenzene
25. 1,3-Dimethyl-4-propylbenzene
26. 1-Methyl-4-butylbenzene
27. 1-Methyl-2-butylbenzene
28. 1,2-Dimethyl-4-propylbenzene
29. 1,2,4-Trimethyl-5-ethylbenzene
30. 1,2,3-Trimethyl-5-ethylbenzene
31. 1-Methyl-3-*t*-butylbenzene
32. 1-Methyl-4-*t*-butylbenzene
33. 1-Methyl-3-isobutylbenzene
34. 1-Methyl-4-isobutylbenzene
35. 1-Methyl-2-isobutylbenzene
36. 1-Phenyl-2-methylbutane
37. 3-Methyldiphenylmethane
38. 4-Methyldiphenylmethane