
THIOPHENE and Its Derivatives

HOWARD D. HARTOUGH

*Socony-Vacuum Laboratories
Paulsboro, New Jersey*

With Special Chapters by

F. P. HOCHGESANG

Socony-Vacuum Laboratories, Paulsboro, New Jersey

and **F. F. BLICKE**

University of Michigan, Ann Arbor, Michigan

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and Its Derivatives

This is the third volume published in the series
THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

A SERIES OF MONOGRAPHS

ARNOLD WEISSBERGER, *Consulting Editor*



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INTRODUCTION TO THE SERIES

The Chemistry of Heterocyclic Compounds

The chemistry of heterocyclic compounds is one of the most complex branches of organic chemistry. It is equally interesting for its theoretical implications, for the diversity of its synthetic procedures, and for the physiological and industrial significance of heterocyclic compounds.

A field of such importance and intrinsic difficulty should be made as readily accessible as possible, and the lack of a modern detailed and comprehensive presentation of heterocyclic chemistry is therefore keenly felt. It is the intention of the present series to fill this gap by expert presentations of the various branches of heterocyclic chemistry. The subdivisions have been designed to cover the field in its entirety by monographs which reflect the importance and the interrelations of the various compounds, and accommodate the specific interests of the authors.

*Research Laboratories
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ARNOLD WEISSBERGER

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Preface

Since thiophene was discovered in 1882 by Victor Meyer its importance has increased at an accelerating rate. Although there has not been a year from 1883 to the present without publications concerning thiophene or its derivatives, there are three main periods in which the greater proportions of the publications were issued. The first of these was the Victor Meyer period of 1883 to 1888, which culminated in Victor Meyer's book *Die Thiophengruppe* (Braunschweig, 1888). The second period, which should be classified as the Steinkopf period, began in 1918 and continued until 1941. Again the work was summarized in a book by Wilhelm Steinkopf, *Die Chemie des Thiophens* (Verlag von Theodor Steinkopff, Dresden, 1941). The present period of accelerated research, initiated by the commercial availability of thiophene, began in 1945 and promises to continue into the next decade.

The rapid strides in thiophene chemistry between 1944 and 1950 have created the need for the present volume. For example, the subject matter of Chapter IX, one of the longest in the book, is covered in less than a page in *Die Chemie des Thiophens*. I once commented before an American Chemical Society meeting that thiophene chemistry was merely in its infancy, since there were still so many problems to be undertaken and solved before we could know its true character. The remark came back from the floor that, while this was probably true, thiophene chemistry was certainly enjoying a robust and healthy childhood.

The present book was begun in 1947 but so many references appeared in 1947 and 1948 that it was necessary to rewrite most of the chapters as many as three times. The text originally included references up to January 1, 1949. Several hundred references appearing in *Chemical Abstracts* between January 1 and October 1, 1949, were inserted into the completed text but in a number of cases it was not possible to handle these later references in detail. Since October 1, 1949, about four hundred additional articles and patents have been published.

The treatise was designed to cover critically all phases of thiophene chemistry and to point out some of the existing problems yet to be solved. In order to achieve this goal, Dr. F. F. Blicke, Head of the Pharmacy School, University of Michigan, contributed Chapter II on toxicological and pharmacological properties of thiophene, and Mr. F. P. Hochgesang of the Physics Division of the Socony-Vacuum Laboratories reviewed the spectrochemical and related properties of thiophene. In addition,

Chapter IV includes a complete summary of the unpublished data obtained in the Socony-Vacuum Laboratories. These data should be of particular value to petroleum chemists, as well as to organic chemists, in identifying natural-source thiophenes and synthetic thiophenes. The literature was reviewed with the intention of including every significant reference and every derivative of thiophene. It will be appreciated that this is a rather formidable task, and I shall be most grateful to those users of the book who will bring to my attention deficiencies of which they become aware.

In addition to the contributions mentioned above, I am deeply indebted to Drs. A. A. O'Kelly and D. E. Badertscher for their encouragement during the writing period. Dr. S. L. Meisel and Dr. E. M. Crane were especially helpful in proofreading the manuscript and in offering critical comments. Great credit goes to Dr. W. P. Hawthorne for his painstaking proofreading and critical review of the contents of this volume which have immeasurably improved its quality and organization. Special thanks are due to Dr. R. Bulkley, Dr. L. A. Hamilton, and Mr. J. J. Dickert, Jr., who graciously volunteered to help in the tedious task of checking references.

The writing of this book was greatly facilitated by private communications to the author from friends in this country and abroad. Sincere thanks are due Dr. Robert Levine of the University of Pittsburgh, Dr. C. D. Hurd of Northwestern University, Dr. F. F. Nord of Fordham University, and many others. Dr. Otto Dann of the University of Erlangen, Germany, was instrumental in maintaining contact for the author with Dr. Steinkopf and in supplying biographical data about Dr. Steinkopf. He also transmitted information concerning his own work in thiophene chemistry. Dr. Frederick Challenger of the University of Leeds, England, has been helpful in forwarding copies of his articles submitted for publication in English journals many months prior to their availability in this country.

Originally this volume was to include fused ring systems containing thiophene rings such as thianaphthene and dibenzothiophene. To expedite publication of thiophene data, the data on condensed ring systems containing thiophene rings are now scheduled for publication in a separate volume by the present author and Dr. S. L. Meisel which should appear in 1952 or 1953.

*Hercules Experiment Station
Wilmington, Delaware
August, 1951*

H. D. H.

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CHAPTER I

General Discussion

I. History of Thiophene

The history of thiophene does not actually begin with the discovery and isolation of thiophene in 1882. It begins in 1844 with the synthesis of thionessal (tetraphenylthiophene) by Laurent, although the structure of that compound was not proved until many years later. Dibenzothiophene was discovered in 1870 by Stenhouse, but here again the structure was not fully established until a later date.

Three years before the discovery of thiophene Claisen found that coal tar benzene produced a violet color with phenylglyoxylic acid when concentrated sulfuric acid was added. This was later found by Victor Meyer to be due to the presence of thiophene. In a similar manner, the "indophenine test" for aromatic compounds had been developed by von Baeyer. This test had been accepted for some time as characteristic for aromatic hydrocarbons and was directly responsible for the series of events that led to the discovery of thiophene.

The actual discovery of thiophene by Victor Meyer at Zürich followed from a series of events well worthy of relating again. In 1882 Meyer's good friend, Prof. Wilhelm Weith, died. Meyer was called upon that autumn to present the special series of lectures on aromatic chemistry at Zürich, previously given by Weith. Victor Meyer's generous use of demonstrations in his brilliant lectures called for the use of von Baeyer's indophenine test with "pure benzene" from coal tar. This test consisted of treating benzene and a trace of isatin with a little sulfuric acid, whereby the blue color of indophenine developed. However, at this particular lecture, T. Sandmeyer, Meyer's assistant, preparing the lecture table, substituted synthetic benzene from the dry distillation of calcium benzoate. This material, to Victor Meyer's consternation, failed to give the characteristic test. Sandmeyer called Meyer's attention to the fact that synthetic benzene had been used. In Meyer's own words¹: "However, the riddle was not completely resolved thereby, and, while I disclosed the

¹ V. Meyer, *Die Thiophengruppe*. Braunschweig, 1888, pp. 1-2.

striking phenomenon to my class room, I added the observation that here lay a problem whose experimental solution would certainly yield important information." Victor Meyer set out the same day to investigate this phenomenon and taking the purest commercial benzene available (sold under the name of *Benzol purissim. crystallisatum*) treated it with sulfuric acid and found the "indophenine test," *i.e.*, the test with isatin and sulfuric acid, to be much weaker than with the unpurified product. He then prepared an extract of the commercial benzene by regenerating from the sulfonic acid that was called "activated benzene," since it gave a greatly intensified indophenine test. At this point Meyer surmised that two forms of benzene existed—an "active form" and an "inactive form" in regard to the indophenine test. He also considered that the sulfonic acid of this "active form" of benzene was undergoing the color transformation with isatin and began work on that basis.

Further treatment of ten liters of commercial benzene by "extraction" with sulfuric acid followed by dry distillation of the lead salt of the sulfonic acid contained in the sulfuric acid layer gave Victor Meyer a "single cubic centimeter of a light, water-clear, mobile liquid, that boiled at about 83°, that appeared similar to benzene, yet did not solidify in ice-water and showed very considerable sulfur content." This material gave the most intense indophenine test obtained so far and Meyer then abandoned his theory of an "activated benzene" in favor of a reaction of isatin with a sulfur compound.

At that time a study of the chemistry of dyes such as indophenine and bromoindophenine was being undertaken in von Baeyer's laboratories in an intensive manner and Victor Meyer received considerable encouragement from that source. Von Baeyer sent Meyer samples of indophenine and bromoindophenine and Meyer was able to point out to von Baeyer that they contained sulfur and were formed from the reaction of isatin and thiophene in the presence of sulfuric acid.

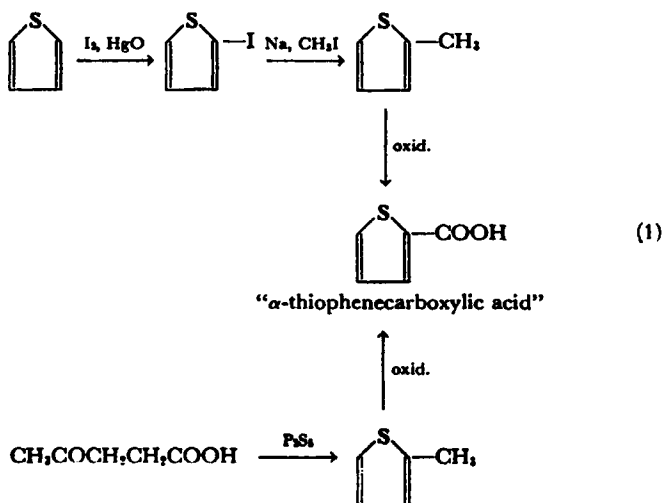
Through friends, R. Bindschedler and R. Gnehm, Victor Meyer was able to persuade the Farbenfabrik Bindschedler, Busch and Co. to extract some 250 liters of benzene with 25 liters of concentrated sulfuric acid. The "black-acid" received by this process was converted to the lead salt and dry distillation of this salt with ammonium chloride gave a "crude thiophene." The thiophene received by this treatment, 140 g. from a 2660 g. portion of the lead salt, was found to boil at 84° and contain about 28% sulfur (the sample was about 70% thiophene and 30% benzene). A portion, 70 g., was brominated and a dibromo derivative, which analyzed as $C_4H_2Br_2S$, was obtained. Victor Meyer then could surmise that the original material, before bromination, was C_4H_4S . The dibromothiophene resisted dehydrobromination in boiling alcoholic

potassium hydroxide and the bromo groups could not be removed by reduction. Its properties were similar to those of the bromobenzenes and Victor Meyer quickly grasped its aromatic nature. The history of the naming of the C_4H_4S compound is described by Thorpe.² He states that Meyer's first inclination was to use the name *thianthren*, then *thiophan*, next *thiol*, and finally *thiophen*, to denote that it was a sulfur-containing compound giving derivatives analogous to those of the phenyl series.

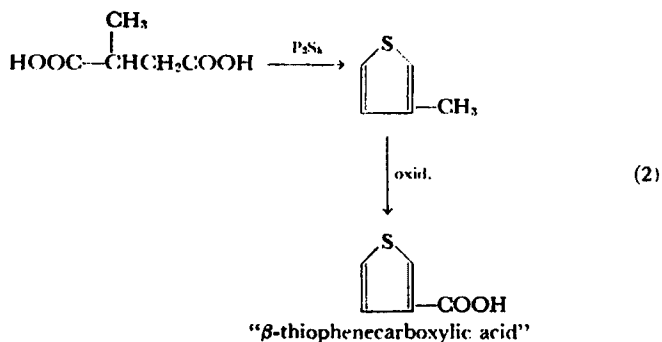
With the cooperation of the Fabrik Griesheim Co. at Frankfurt am Main and the Anilinfarbenfabrik Gans und Co., some 2000 kg. of pure, half-degree benzene was treated with 100 kg. of concentrated sulfuric acid, and 1944 g. of pure thiophene of sulfur content 38.02% (38.1% is the theoretical) was obtained. Victor Meyer then set out to determine the chemistry of thiophene. Its structure was established by a ring-closure synthesis from the reaction of succinaldehyde or succinic acid with phosphorus pentasulfide.

After the process for the extraction of thiophene from benzene was announced, the Schuchardt Co. in Görlitz made thiophene available at 130 marks per kilogram. Victor Meyer indicates that after obtaining 1 kg. from that source he abandoned it in favor of his own synthetic methods by ring closure.

The methylthiophenes were isolated from coal tar toluene in much the same manner and were eventually synthesized by ring closure of levulinic acid (2-methylthiophene) and methylsuccinic acid (3-methylthiophene).



² Thorpe, *J. Chem. Soc.*, 77, 169 (1900). British Chemical Society's Victor Meyer Memorial Lecture.



Orientation in the thiophene series was carried out with the methylthiophenes as shown in equations (1) and (2) above.

In *Die Thiophengruppe*,¹ Meyer summarizes the approach he and his students took to the problem. The conclusions reached at that time concerning the structure of thiophene have not changed to the present day. In 1888, when Victor Meyer completed his book after five years of active research, 106 publications on thiophene chemistry had been released from his laboratories at the Universities of Zürich (1882–1885) and Göttingen (1885–1888). Only 25 publications appeared from other laboratories during that period.

From the time of publication of *Die Thiophengruppe* until the Victor Meyer Memorial Lecture was given by Thorpe² in 1900, an additional 50 articles appeared in the literature. This attests to the interest aroused by the new chemistry of thiophene.

In 1910 Dr. Wilhelm Steinkopf at Karlsruhe University (later at the Dresden Technical Academy) began what developed into a lifetime study of thiophene chemistry. He published consistently during the thirty years until his retirement in 1940, primarily in *Liebig's Annalen*. Approximately 65 lengthy articles have appeared under his name that have greatly advanced the chemistry of thiophene. His book *Die Chemie des Thiophens*³ published in 1941 summarized the chemistry of thiophene up to that date. Steinkopf used synthetic thiophene as his starting material and describes in his book the apparatus in which almost daily runs were made with phosphorus sulfides and disodium succinate. To say that Steinkopf centered his work on any one branch of thiophene chemistry would be an understatement, since reference to his work will be found in nearly all of the chapters of this book. He contributed prolifically to the mercuration of thiophene, the halogenation of thiophene, and the synthesis of many new thiophene derivatives. His work

³ Steinkopf, *Die Chemie des Thiophens*. Steinkopff, Leipzig, 1941. Lithoprinted by Edward Brothers, Ann Arbor, Mich.

was primarily involved with syntheses rather than theoretical aspects of thiophene chemistry, although contributions in the latter field are not lacking.

Wilhelm Steinkopf was born in Stassfurt on June 28, 1879. He attended grammar school there and in Bernburg where the family moved after his mother's early death. He matriculated at Heidelberg where he attended lectures of Curtius. After three semesters at Heidelberg, he transferred to Karlsruhe and studied under Engler, Bunte, LeBlanc, Haber, Scholl, and the physician, O. Lehmann. He received his Dr.-Ing. degree in 1909 and upon graduation became a member of the staff at Karlsruhe. During World War I, 1915 to 1918, he worked at the Kaiser Wilhelm Institute for Physical and Electro-chemistry. He returned briefly to Karlsruhe and then was called to the Institute for Organic Chemistry at the Dresden Technical Academy. In 1934 he became director, and in 1940 retired as *professor emeritus*. Until his death on March 12, 1949, Dr. Steinkopf had lived in Niebelsbach, Swabia, near the Black Forest in Germany.

The present commercial process for the synthesis of thiophene, developed in the Socony-Vacuum Laboratories in the early 1940's, adds another case of serendipity to the history of thiophene. A. N. Sachanen, R. C. Hansford, and H. E. Rasmussen, in studying methods of dehydrogenating butane to butadiene, examined the dehydrogenation of butane with sulfur and discovered that thiophene was being formed in the process. After suitable modifications of the sulfur-butane feed streams, it was found that a feasible process for the production of thiophene was at hand. At that time no practical uses of thiophene were apparent. In 1943, J. H. McCracken prepared a literature survey of the field of thiophene chemistry. Although this failed to uncover potential commercial uses, the survey was used as the basis of the literature search made by the present author. Almost at the time of completion of McCracken's survey, Steinkopf's book, which had been unavailable due to the war, was obtained.³ This also failed to disclose any practical commercial uses for thiophene. For that reason, some preliminary studies of the alkylation of thiophene were undertaken very early in these Laboratories. The author's connection with this project began in 1944 and active work was continued for a little more than three years.

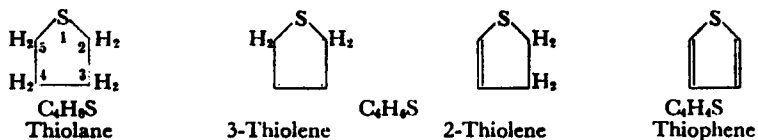
Sample distribution of thiophene began late in 1944 and the response of the drug industry, resin industry, dye industry, chemical industry, and the universities in this country and abroad led the Socony-Vacuum Oil Co., Inc., to plan to market thiophene on a modest scale. Initially, samples were supplied from a 100-pound-per-day unit which began production in September, 1945, and later demands required the construction of a 1000-pound-per-day unit which was put into operation in 1947. During 1946 and 1947 approximately 100 derivatives of thiophene

were distributed by Socony-Vacuum to several hundreds of interested parties to facilitate their research. These samples ranged in quantity from one gram to several pounds. 2-Acetylthiophene, *tert*-butylthiophene, di-*tert*-butylthiophene, and 2-benzoylthiophene, as well as 2- and 3-methylthiophenes, have been available in pilot plant scale.

At the present writing, the only commercial use for the thiophenes is in the form of intermediates for the production of antihistaminic drugs (see Chapters II and IX for more specific details). Their use in the dye industry is being considered seriously, but production has not yet started. Thiophene has been considered as a dewaxing solvent, paint remover, intermediate in phenol-formaldehyde plastics, resin intermediate, and as an intermediate in preparation of antispasmodic drugs. Fundamentally, thiophene looks quite promising in the resin industry because of its difunctional characteristics due to the extreme activity of positions 2 and 5, but until the present time this work has been discouraging due to light instability of the thiophene unit in the resins. It is possible that this color instability can be overcome, but no study of the subject has been made.

II. Nomenclature of Thiophene Compounds

The *Ring Index*, system 114, refers to C_4H_4S as *thiophene*, thiofuran, thiole, thiofurfuran, thiotetrole, and divinylene sulfide. Its tetrahydro form, C_4H_8S , is named *thiolane*, tetramethylene sulfide, and thiacyclopentane. No name is assigned to the dihydro form, C_4H_6S . *Chemical Abstracts* uses *thiophene* for C_4H_4S , tetrahydrothiophene for C_4H_8S , and dihydrothiophene for C_4H_6S . Since the di- and tetrahydrothiophene names are cumbersome to use, the American Chemical Society Subcommittee for Heterocyclic Nomenclature has accepted tentatively the author's suggestion that the three proper names of thiophene and its hydrogenated forms shall be as follows:

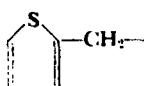


This same Subcommittee has not yet recommended any major changes in thiophene nomenclature over that now in current use by *Chemical Abstracts*. The nomenclature used by *Chemical Abstracts* is not always the most convenient nor the most accurate and the author has taken some liberties in this book in order to render a more usable form.

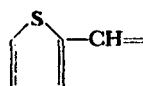
Unfortunately, there are no hard and fast rules for thiophene nomenclature, and thiophene takes on peculiar root and prefix forms that are rather foreign to the basic name thiophene and their origin is subject to practically no rules of nomenclature. It is to be hoped that the nomenclature can be systematized and adhered to more closely than in the past. In general, the following roots can be used systematically applying standard nomenclature rules:



2-Thienyl



2-Thenyl



2-Thenal or 2-Thenylidene

Table I-1 lists the nomenclature as it appears in *Chemical Abstracts*, as found in this book, and less common terms which have been used, in some instances, incorrectly.

Thiophene nomenclature has undergone a number of changes. Originally, Victor Meyer labeled the sulfur atom as the α -position and the other positions β , γ , β' , γ' as follows:



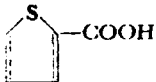
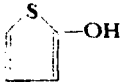
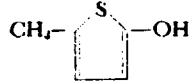
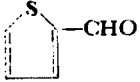
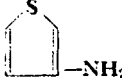
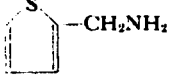
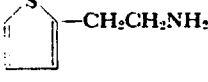
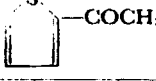
A few years later this was changed to the α , β , α' , β' nomenclature used for many years, *i.e.*, the 2,5-positions were designated as α, α' and the 3,4-positions became β, β' :



This type of positional designation is now obsolete.

A recent communication to the author from S. S. Kurtz, Jr., Chairman of the Nomenclature Committee, Division of Petroleum Chemistry regarding nomenclature to be used in A. P. I. Project #48 reports states in part: "Compounds containing the thiophene ring shall be named in such a manner that 'thiophene' forms the base of the name. Thus benzothiophene rather than thianaphthene. Radical names such as thenyl and thienyl shall be recognized. Fully or partially hydrogenated thiophenes as well as any other sulfur-containing cyclic compounds, other than those containing thiophene, shall be named using the thia system." This last portion on hydrogenated thiophenes is not in accord with the recommendations of the A. C. S. Subcommittee on Heterocyclic Nomenclature and it further serves to point out the need for a standard, systematic nomenclature,

TABLE I-1. Nomenclature of Thiophene Compounds

Compound	Chemical Abstracts	This book	Other nomenclature
	2-Thiophenecarboxylic acid	2-Thiophenecarboxylic acid	α -Thienylcarboxylic acid 2-Thenoic acid 2-Thiophenoic acid
	Thiophene-2-ol	2-Hydroxythiophene	2-Thienol
	5-Methylthiophene-2-ol	5-Methyl-2-hydroxythiophene	Thiotenol
	2-Thiophenecarboxaldehyde	2-Thiophenealdehyde	α -Thiophenealdehyde 2-Thenaldehyde
	3-Aminothiophene	3-Aminothiophene	3-Thiophenine
	2-Thenylamine	2-Thenylamine	2-Aminomethylthiophene 2-Thienylmethylamine
	β -(2-Thienyl)ethylamine	2-(2-Thienyl)ethylamine	2-Aminoethylthiophene
	2-Thienyl methyl ketone 2-Acetylthiophene	2-Acetylthiophene	2-Acethiothienone α -Acethiothienone




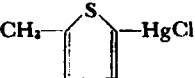






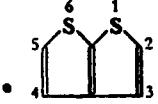
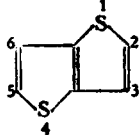
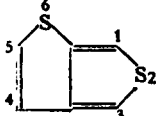
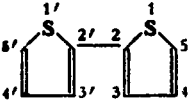
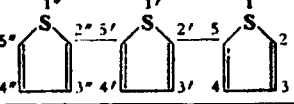
Compound	Chemical Abstracts	This book	Other Nomenclature
 <chem>CCCCCCCCC(=O)c1sccc1</chem>	2-Thienyl octyl ketone	2-Nonanoylthiophene	2-Pelargonthienone
 <chem>CCCCC(=O)c1sccc1</chem>	ϵ -Oxo-2-thiophenecaproic acid	5-(2-Thienyl)pentanoic acid	—
 <chem>C=CC(=O)c1sccc1</chem>	2-Thienylacrylic acid	2-Thienylacrylic acid	—
 <chem>Cc1sccc1[Hg]Cl</chem>	5-Methyl-2-thiophenemercurochloride	5-Methyl-2-thiophenemercurochloride	—
 <chem>N#Cc1sccc1</chem>	2-Thiophenecarbonitrile	2-Thiophenitrile	α -Cyanothiophene
 <chem>S=Cc1sccc1</chem>	3-Thiophenethiol	3-Thiophenethiol	—
 <chem>S=C(S)c1sccc1</chem>	3,4-Thiophenedithiol	3,4-Thiophenedithiol	—
 <chem>S=C(S)C=C1SCC1</chem>		3,4-Thiolanedithione	—
 <chem>C1=CC=CS1</chem>	Selenophene	Selenophene	Selenofuran

TABLE I-1 (Continued)

Compound	Chemical Abstracts	This book	Other nomenclature
	Tellurophene	Tellurophene	Tellurofuran
	Thieno[2,3- <i>b</i>]thiophene	Thieno-[2,3- <i>b</i>]thiophene	Thiophthene (liquid)
	Thieno[3,2- <i>b</i>]thiophene	Thieno-[3,2- <i>b</i>]thiophene	Thiophthene (solid)
		Thieno-[3,4- <i>b</i>]thiophene	—
	2,2'-Bithiophene	2,2'-Dithienyl	α -Dithienyl
	2,2'-5',2''-Terthiophene	2,2'-5',2''-Terthienyl	α -Terthienyl

III. Occurrence of Thiophene Compounds in Nature

There is no definite proof that thiophene compounds actually exist, as such, in natural products. They apparently are the end products of thermal or catalytic treatment of carbonaceous deposits. Victor Meyer's discovery of thiophenes in coal tar in 1882 and 1883 has led to a variety of investigations which have shown that a great number of thiophene homologs exist in products derived from natural sources. The source of these products is normally in carbonaceous deposits of lignite, peat, shale, coal, and crude oil. Naturally, the amount of sulfur-bearing products varies with the source, but, usually, the thiophenes represent a portion of the sulfur-containing constituents of any of the light oils from carbonaceous deposits. Whenever thiophene is found, its homologs are present in higher fractions of the distillable oils. It is open to question if thiophene compounds actually exist in crude oils or whether they are formed by refining processes such as high temperature distillation or catalytic cracking (where they may be formed by dehydrogenation of thiolanes). In fact, several authorities have questioned the structure of the "alkylthiolanes" obtained from Canadian crude oil.¹ Challenger² states: "It was not proved, however, that the tetrahydrothiophene or thiophane ring was present in any of these compounds, which ranged in boiling point from 125 to 295°. The use of the term 'thiophane' was then hardly justified."

In summary, it can be stated that all types of thiophene homologs have been found in products obtained from natural sources. All of the possible methylthiophenes (mono-, di-, tri-, and tetra-) have been isolated from coal tar or shale oils. Other homologs such as ethyl-, propyl-, and butyl thiophenes have been isolated. Compounds closely related to thiophene, such as thianaphthene, dibenzothiophene, and dithienyl, are also found.

Specifically, thiophene has been isolated from coal tar,³⁻⁶ lignite tar,^{6,7} and shale oil⁸⁻¹¹; the methylthiophenes from coal tar^{1,4,12} lignite tar,¹³

¹ Mabery and Quayle, *Am. Chem. J.*, **35**, 404 (1906).

² Challenger, *J. Soc. Chem. Ind. (London)*, **48**, 622 (1929).

³ V. Meyer, *Ber.*, **16**, 1465 (1883).

⁴ V. Meyer, *Ber.*, **16**, 2970 (1883).

⁵ Weissgerber, *Ber.*, **61**, 2116 (1928).

⁶ Heusler, *Ber.*, **28**, 494 (1895).

⁷ Saladini, *Ann. chim. applicata*, **18**, 337 (1928).

⁸ Challenger, Jinks, and Haslam, *J. Chem. Soc.*, **127**, 162 (1925).

⁹ Challenger, *J. Soc. Chem. Ind.*, **48**, 622 (1929).

¹⁰ Challenger, *et al.*, *J. Inst. Petroleum Technol.*, **12**, 106 (1926).

¹¹ Dodonow and Soschestwenskaja, *Ber.*, **59**, 2202 (1926).

¹² V. Meyer and Kreis, *Ber.*, **17**, 787 (1884).

¹³ Pfaff and Kreutzer, *Z. angew. Chem.*, **36**, 437 (1923).

shale oil,^{8-11,14} crude oil,¹⁵ and bituminous limestone¹⁶; the dimethylthiophenes from coal tar,^{5,17-19} lignite tar,¹³ shale oil,^{8-10,20-23} and bituminous limestone¹⁶; the trimethylthiophenes from coal tar⁵ and shale oil^{8-10,14}; and tetramethylthiophene from coal tar.⁵ Other alkylthiophenes found in similar sources are 2-ethylthiophene,^{8-11,14,20} 3-ethylthiophene,¹⁴ isomeric (iso- and normal) propylthiophenes,^{8-10,14,23,24,25} and butylthiophenes.²⁴ Thiolane has been isolated in several instances.^{8-10,15} Dithienyl has been isolated directly from coal tar.²⁶ Thianaphthene²⁷⁻³⁰ and dibenzothiophene^{27,28} have also been obtained from this source.

Austrian, Russian, and French shale oils are particularly high in thiophene content. Picon³¹ recently summarized the data on these materials and described methods of separation of thiophene and its homologs from shale oils obtained in the Tyrol and Ain districts of France. Shale oils from the Ain contains about 16% sulfur, mostly in the form of thiophenes. Shale oil from Rifle, Colorado, contains less than 1% sulfur. Oils obtained from Indiana and midwestern shales contained 1-2% sulfur.

McKittrick³² extracted a thermally cracked California naphtha with sulfur dioxide and subsequently treated the extract with aniline to produce a concentrate high in sulfur content. The concentrate was carefully fractionated and the fractions were treated with mercuric chloride and sodium acetate. In this manner, thiophene, 2-methylthiophene, 3-methylthiophene, 2,3-dimethylthiophene, 2-ethylthiophene, and 3-ethylthiophene were isolated as mercurichloride derivatives.

¹⁴ Steinkopf and Nitschke, *Arch. Pharm.*, **278**, 360 (1940).

¹⁵ Teutsch and Herzenberg, *Petroleum*, **30**, No. 20, 1 (1934).

¹⁶ Chabrier, Tchoubar, and Le Tellier-Dupre, *Bull. soc. chim.*, 332 (1946).

¹⁷ Schulze, *Ber.*, **17**, 2852 (1884).

¹⁸ Messinger, *Ber.*, **18**, 563, 1636 (1885).

¹⁹ Keiser, *Ber.*, **28**, 1804 (1895); **29**, 2560 (1896).

²⁰ Stadnikov and Weizmann, *Brennstoff-Chem.*, **8**, 343 (1927).

²¹ Vozzhinskaya, *Chimika toredogo Topliva*, **6**, 250 (1935).

²² Leclere and Leclere, *Compt. rend.*, **194**, 286 (1932).

²³ Scheibler, *Ber.*, **48**, 1815 (1915).

²⁴ Scheibler and Rettig, *Ber.*, **59**, 1198 (1926).

²⁵ Haines, *et al.*, *U. S. Bur. Mines R. I.* **4060** (1946).

²⁶ Nahnsen, *Ber.*, **17**, 789 (1884).

²⁷ Weissgerber, *Brennstoff-Chem.*, **2**, 1 (1921).

²⁸ Boes, *Apoth.-Ztg.*, **17**, 565, 638 (1902).

²⁹ Weissgerber and Kruber, *Ber.*, **53**, 1552, 1566 (1920).

³⁰ Fricke and Spilker, *Ber.*, **58**, 24, 1589 (1925).

³¹ Picon, *Compt. rend.*, **228**, 251 (1948); *Bull. soc. chim.*, **1949**, 289, 296; *Compt. rend.*, **227**, 1381 (1948).

³² McKittrick, *Ind. Eng. Chem.*, **21**, 585 (1929).

IV. Color Reactions of Thiophene Compounds

Many color tests have been developed for thiophene compounds, but there is no single color test which is specific for members of the thiophene series. Usually the same test can be used for the five-membered heterocyclics, in general, but with some gradation in color.

Only in rare instances is there any appearance of specific colors to distinguish isomers. For example, the ceric nitrate test¹ listed below gives isomer color specificity in regard to 2- and 3-methylthiophene and these compounds are readily distinguishable by the test. The dimethylthiophenes also give characteristic colors (see Table I-2). Similarly, 2-acetyl-3-methylthiophene and 2-acetyl-4-methylthiophene give specific colors in this same test to the extent that the transient blue color of the

TABLE I-2. Color Reaction of Thiophene Compounds with Ceric Nitrate

Compound	Color in organic layer	Color change in inorganic layer
Thiophene	None to light brown	Brown ppt.
Alkylthiophene		
2-Methyl-	Brown	Bright purple ppt
3-Methyl-	Brown	Deep blue ppt.
2- <i>n</i> -Propyl-	Red	None
2- <i>n</i> -Butyl-	Red	None
2- <i>tert</i> -Butyl-	Red	None
3- <i>tert</i> -Butyl-	Light orange	None
2,5-Di-(<i>tert</i> -butyl)-	None	None
2,3-Dimethyl-	Green	Green-brown ppt.
2,4-Dimethyl-	Red → purple	Red ppt.
3,4-Dimethyl-	Deep blue	Deep blue ppt.
2,5-Dimethyl-	Purple	Purple ppt.
2-Ethyl-	Red → red ppt.	None
2,3,4-Trimethyl-	Green → brown → purple ppt.	None
2,3,5-Trimethyl-	Purple → brown ppt.	None
2,3,4,5-Tetramethyl-	Blue → red → red-brown ppt.	None
Di-(5-methyl-2-thienyl)methane	Deep red	Red ppt.
Tri-(5-methyl-2-thienyl)methane	Bright-orange	Yellow
2- <i>tert</i> -Amyl-	Red	Colorless
1-(2-Thienyl)-(1,1,3,3-tetramethylbutane)	Yellow	Yellow
2-Pinyl-	Yellow ^b	Colorless
2-Benzyl-	Brown	Blue ppt.

Table Continued

TABLE I-2 (Continued)

Compound	Color in organic layer	Color change in inorganic layer
Alkylenethiophene		
2-(α -Methylvinyl)thiophene	Blue \rightarrow brown	Colorless
Acylthiophenes		
2-Acetyl-	Red	Colorless
2-Acetyl-3-methyl-	Red	Colorless
2-Acetyl-4-methyl-	Blue \rightarrow red	Colorless
2-Acetyl-5-methyl-	Red	Colorless
2-Acetyl-3,4-dimethyl-	Red \rightarrow brown \rightarrow lt. red	Colorless
2-Acetyl-3,5-dimethyl-	Red \rightarrow brown \rightarrow pale yellow	Colorless
2-Acetyl-4,5-dimethyl-	Red \rightarrow tan \rightarrow lt. red	Colorless
2-Acetyl-5-ethyl-	Cherry red \rightarrow tan \rightarrow lt. red	Colorless
2-Acetyl-3,4,5-trimethyl-	Purple \rightarrow brown \rightarrow lt. red	Colorless
3-Acetyl-2,5-dimethyl-	Pink \rightarrow tan \rightarrow pink	Colorless
2-Acetyl-5- <i>tert</i> -butyl-	Deep red	Colorless
2-Acetyl-5-chloro-	Orange ^a	Light yellow
2-Acetyl-2,5-dichloro-	None	None
2-Acetyl-2,5-di- <i>tert</i> -butyl-	None	None
2-Propionyl-	Red \rightarrow deep brown	Colorless
2-Butanoyl-	Orange	Colorless
2-(2-Ethylbutanoyl)-	Light yellow	Yellow
2-Benzoyl-	Light yellow	Yellow
2-Thenoyl-	Yellow to tan	Colorless
2-(2-Thenoyl)-3-(4)-methyl-	Green	Colorless
Halothiophenes		
2-Chloro-	Light red ^a	Yellow
2-Bromo-	Brown	Yellow
2,3-Dichloro-	Orange	Yellow
2,4-Dichloro-	Light yellow	Yellow
2,5-Dichloro-	None	None
2,5-Dibromo-	None	None
3,4-Dichloro-	Light yellow	Yellow
2,3,4-Trichloro-	Light yellow	Yellow
2,3,4,5-Tetrachloro-	None	—
2,2,3,4,5,5-Hexachlorothiolenane	None	—
2,2,3,4,5,5-Hexachloro-3-thiolene	None	—
Thiophenecarbinols		
2-Thiophenecarbinol	Deep purple	—
2-(2-Thienyl)ethanol	Brown	—
2-(4-Methyl-2-thienyl)ethanol	Deep red \rightarrow brown	—
2-(5-Chloro-2-thienyl)ethanol	Deep red	—

Table Continued

TABLE I-2 (Continued)

Compound	Color in organic layer	Color change in inorganic layer
Miscellaneous		
2-Thenylamine ^c	Brown ppt. ^d	Brown ppt. ^d
3-Methyl-2-thenylamine	Dissolves	Red
5-Methyl-2-thenylamine	Dissolves	Red
Di-(2-thenyl)amine	Brown ppt. ^d	Brown ppt. ^d
Di-(5-methyl-2-thenyl)amine	White ppt. ^d	—
2-Thiophenealdehyde	Red ^d	Colorless
5-Methyl-2-thiophenealdehyde	Deep red ^d	Colorless
2-Thiophenecarboxylic acid	None ^a	None
Ethyl 2-thiophenecarboxylate	Light green → blue ^a	•
2-Nitrothiophene	None	—
3-Thiophenethiol	Brown	Brown ppt.

^a On warming. ^b Red on warming. ^c 2-Aminomethylthiophene. ^d Heat of reaction. ^e Colors aqueous layer of reagent yellow. On warming, aqueous layer turns red, yellow, and colorless within a few seconds. Final color of organic layer is pink.

latter can be detected in mixtures with as little as 1 part of the 2-acetyl-4-methylthiophene to 10 parts of 2-acetyl-3-methylthiophene. Since these derivatives often are formed together in the acylation of 3-methylthiophene, this test has some merit.

The sodium nitroprusside test is convenient for the alkanoylthiophenes up to a 5-carbon alkane chain and is very sensitive with 2-acetylthiophene, 2-propanoylthiophene, and 2-butanoylthiophene. 1 part of 2-acetylthiophene can be detected in 10,000 parts of thiophene. For example, it has been used in our laboratory in studying new catalysts for the acylation of thiophene; if about 0.2 ml. of the reaction mixture is withdrawn periodically the formation of even very small amounts of the alkanoylthiophenes can be detected by the test.

The isatin test is sensitive to small amounts of thiophene compounds in crude mixtures but it seems to have no specificity for given series of compounds. It is reported to fail in testing for thiophenes in shale oils in the presence of large amounts of unsaturates.²

The more common color tests are described below in detail:

1. *Ceric Nitrate*.¹ Equal volumes, 0.1 to 1.0 ml., of ceric nitrate alcohol reagent³ and the thiophene derivative to be tested are placed in a small test tube. Normally the color change takes place at the interface and spreads rapidly through

¹ Hartough, *Ind. Eng. Chem., Anal. Ed.*, **20**, 860 (1948), and unpublished data.

² Challenger, Jinks, and Haslam, *J. Chem. Soc.*, **127**, 162 (1925).

³ Duke and Smith, *Ind. Eng. Chem., Anal. Ed.*, **12**, 201 (1940).

the organic layer. Agitation is necessary to develop the final color. These colors are listed in Table I-2. If the samples to be tested are solids melting below 100°, the mixture is warmed in a steam bath or in boiling water. Diluents change colors somewhat, but in some cases they can be used. *Dioxane must not be used as a solvent*, since very often variations of color are obtained.

2. *Sodium Nitroprusside Test for Alkanoylthiophenes.*⁴ A modification of the method of Feigl and Zapport⁵ was adopted for this test. To 1.0 ml. of a saturated solution of sodium nitroprusside in alcohol is added one drop of 2-acetylthiophene. The mixture is diluted with 1.0 ml. of water and a few drops of 10% KOH in alcohol is added. An intense red to purple color forms. Change of the color to an intense blue upon addition of a few drops of glacial acetic acid is specific for the —COCH₃ grouping; —COCH₂R groups give no color change upon addition of acetic acid. Sensitivity of the test decreases rapidly with increase of the size of the R group; 2-butanoylthiophene gives a well-defined red color, but 2-decanoylthiophene and 2-benzoylthiophene fail to give the test.

3. *The Isatin Test (Indophenine Reaction).* About 1 ml. of a dilute solution of the compound in benzene, or an inert solvent, is mixed with a few milligrams of isatin and 1 ml. of concentrated sulfuric acid. Development of a blue color indicates the presence of a thiophene compound. There has been no systematic study of the limitations of this test and it has been used, for the most part, in detecting small amounts of thiophene and its homologs in benzene and coal tar distillates.

4. *The Laubenheimer Reaction.*⁶⁻⁸ The test is best run in the following manner. A few milligrams of phenanthraquinone are dissolved in 1-2 ml. of glacial acetic acid. One drop of the compound to be tested is added to this solution followed by the addition of about one ml. of concentrated H₂SO₄. A blue to blue-green precipitate indicates the presence of a thiophene compound. No systematic study of the test has been made.

5. *The Liebermann Test.*⁹⁻¹² If 2-3 drops of the thiophene compound is dissolved in 1 ml. of thiophene-free benzene with 1 ml. of 8% KNO₂-concentrated sulfuric acid mixture, a blue to blue-green color develops on shaking. No systematic study of the test has been carried out.

6. *Miscellaneous Color Tests.* There are a variety of color reactions of thiophene that have not received appreciable attention. The thallin-nitric acid

⁴ Hartough and Kosak, unpublished work.

⁵ Feigl, *Spot Tests*, 3rd Ed., Elsevier, New York, 1946, p. 350.

⁶ Laubenheimer, *Ber.*, **8**, 224 (1875).

⁷ V. Meyer, *Ber.*, **16**, 2971 (1883).

⁸ Odernheimer, *Ber.*, **17**, 1338 (1884).

⁹ Liebermann, *Ber.*, **20**, 3231 (1887).

¹⁰ Liebermann and Plcus, *Ber.*, **37**, 2461 (1904).

¹¹ Claisen and Manasse, *Ber.*, **20**, 2197 (1887).

¹² Schwalbe, *Ber.*, **37**, 324 (1904).

¹³ Kreis, *Chem. Ztg.*, **26**, 523 (1902).

¹⁴ Fletcher and Hopkins, *J. Physiol. (London)*, **35**, 247 (1907).

¹⁵ Fearon, *Biochem. J.*, **12**, 179 (1918).

¹⁶ Christomanos, *Biochem. Z.*, **229**, 248 (1930).

¹⁷ Deniges, *Bull. soc. chim.*, [4] **5**, 649 (1909).

¹⁸ Hilpert and Wolf, *Ber.*, **46**, 2215 (1913).

method of Kreis¹³ gives an intense violet color and is said to be sensitive to one part in 100,000 in detecting thiophene in benzene. A deep red color develops when thiophene is treated with copper sulfate, lactic acid, and concentrated sulfuric acid.¹⁴⁻¹⁶ Methylglyoxal and nascent bromine give a transient red color changing to violet, blue, and green.¹⁷ Antimony pentachloride treatment of benzene containing small amounts of thiophene gives a transient reddish-yellow color slowly changing to green.¹⁸ Sulfuric acid gives various colors with thiophene compounds and numerous unrelated color reactions are reported in the literature. However, there has been no attempt to correlate the diffuse and sometimes conflicting colors produced with various concentrations of this acid. The Liebermann test seems to produce more uniform results.

V. Estimation of Thiophene

The most recent compilation and comparison of methods for determining small amounts of thiophene in benzene by Claxton and Hoffert¹ shows that the method of Deniges² is very suitable if unsaturates are absent. The reproducibility was $\pm 0.005\%$ of thiophene. Unsaturates such as amylene, cyclohexene, or indene cause a considerable error by their reaction with Deniges' reagent, a mercuric sulfate solution. When an excess of the reagent is shaken with benzene containing a small amount of thiophene, a complex of thiophene and basic mercuric sulfate, $C_4H_4S \cdot HgS_2O_6$, is precipitated which can be filtered off, dried, and weighed. Results usually are high if unsaturates are present.

The American Society for Testing Materials tentatively recommended a method for the determination of thiophene in benzene which involves comparison of the color developed by an isatin - ferric chloride - sulfuric acid reagent with color standards made from known concentrations of thiophene in benzene.³ Somewhat similar colorimetric methods for the estimation of thiophene in gasoline^{4,5} and in gas samples⁶ have been developed.

Other methods are as follows: (1) a gravimetric method⁷ based on the precipitation of tetraacetoxymercurithiophene of which several modifications have been made⁸⁻¹⁰ (a good description of the procedure is

¹ Claxton and Hoffert, *J. Soc. Chem. Ind.*, **65**, 333 (1946).

² Deniges, *Compt. rend.*, **120**, 628, 781 (1895); *Bull. Soc. Chim.* (3) **13**, 537 (1895).

³ *A.S.T.M. Supplements*, 1947, Part III-A, D931-47T, pp. 279-281.

⁴ McKee, Herndon, and Withrow, *Anal. Chem.*, **20**, 301 (1948).

⁵ Hakewill, Paper presented before Division of Fuel and Gas, A. C. S., Sept., 1948. See also Hakewill and Rueck, *Am. Gas Assoc. Proc.*, **28**, 529 (1946).

⁶ Brady, *Anal. Chem.*, **20**, 512 (1948).

⁷ Dimroth, *Ber.*, **32**, 759 (1899).

⁸ Schwalbe, *Chem.-Ztg.*, **29**, 895 (1905).

⁹ Paolini, *Gazz. chim. ital.*, **37**, 58 (1907).

¹⁰ Paolini and Silbermann, *Atti accad. nazl. Lincori*, **24**, 209 (1915).

given by Spielmann and Schotz¹¹); (2) the Deniges method adapted to a volumetric determination¹²; (3) the isatin test developed by Schwalbe⁸ into a semiquantitative method; and colorimetric determinations based on colors produced with (4) nitric acid and thallin,¹³ (5) amyl nitrite and sulfuric acid,¹⁴ (6) with alloxan and sulfuric acid,¹⁵ and (7) lactic acid, sulfuric acid, and copper sulfate.^{16,17}

Other recent methods are of the combustion type in which benzene containing thiophene is burned in hydrogen over a hydrogenation catalyst and the resulting hydrogen sulfide is determined by standard techniques.¹⁸ Combustion with oxygen in which the sulfur is oxidized to sulfur dioxide, which is determined by standard methods, appears to be satisfactory if other sulfur compounds are absent.^{19,20} Methods such as complex formation with aluminum chloride,²¹ and conversion to 2-benzoylthiophene by use of benzoyl chloride catalyzed with titanium or tin tetrachlorides^{22,23} have been used, but these methods are not specific for thiophene.

Physical methods of analysis, now in the process of development in many petroleum laboratories, involve the use of the mass spectrograph and infrared spectrograph. Ultraviolet absorption methods are also under development. Chapter IV summarizes some of the preliminary work along this line undertaken in the Socony-Vacuum Laboratories. Eventually, it is anticipated that these physical methods will outmode the wet-chemical methods of analysis.

Methods of identification and determination of antihistaminic drugs of the thenyl series have recently been described.²⁴ The methods involve identification of the products by their optical crystallographic properties or by colorimetric methods with various alkaloidal reagents such as Marquis' reagent, Buckingham's reagent, Frohde's reagent, and Mandelin's reagent.

¹¹ Spielmann and Schotz, *J. Soc. Chem. Ind.*, **38**, 189T (1919).

¹² Meyer, *Compt. rend.*, **169**, 1402 (1919).

¹³ Kreis, *Chem.-Ztg.*, **26**, 523 (1902).

¹⁴ Leibermann, *Ber.*, **20**, 3231 (1887).

¹⁵ Ekkert, *Pharm. Centralblatt*, **71**, 625 (1930).

¹⁶ Christomanos, *Biochem. Z.*, **229**, 248 (1930).

¹⁷ Fearon, *Biochem. J.*, **12**, 179 (1918).

¹⁸ Gillo, *Ann. chim.*, **12**, 281 (1939).

¹⁹ Thomas, Ivis, Abersold, and Hendricks, *Ind. Eng. Chem., Anal. Ed.*, **15**, 287 (1943).

²⁰ Reisz and Wohlberg, *Am. Gas Assoc. Proc.*, **25**, 259 (1943).

²¹ Sabrou and Renaudic, International Benzene Conference, Rome, 1935.

²² Stadnikov and Kashtanov, *J. Russ. Phys.-Chem. Soc.*, **60**, 1117 (1926).

²³ Stadnikov and Goldfarb, *J. Ber.*, **61**, 2341 (1928).

²⁴ Haley and Keenan, *J. Am. Pharm. Assoc. (Sci. Ed.)*, **38**, 85 (1949).

VI. Removal of Thiophene and Its Homologs from Coal Tar Aromatics and Petroleum Stocks

Table I-3 is a compilation of methods for the removal of thiophene and its homologs from coal tar or petroleum. Its abundance in these sources varies from approximately 0.1 to several weight percent, being most prevalent in cracked fractions of "high-sulfur" crude oils and in shale oils. It would be most difficult to assess the methods and state that any one of them is the best. Suffice it to say, that Victor Meyer's original method involving a "sulfuric acid wash" is probably the most convenient one and that it is still in wide use today. Other methods, such as high-temperature catalysis, are more applicable to refining techniques in the petroleum industry.

TABLE I-3. Removal of Thiophene and Its Homologs from Coal Tar Aromatics and Petroleum Stocks

Material containing thiophenic contamination	Method of removal	Ref.
Coal tar benzene.....	Sulfuric acid wash	1-4
Raw toluene and xylene.....	Sulfuric acid wash	5
Raw benzene.....	H ₂ SO ₄ , an unsat. alicyclic or heterocyclic hydrocarbon	6
Coal tar distillates.....	H ₂ SO ₄ , NaNO ₂	7
Tar oils.....	90% H ₂ SO ₄	8
Benzene.....	66° Bé. H ₂ SO ₄ , "starch yielding substances"	9
Benzene.....	95% H ₂ SO ₄ , an alkylating agent for benzene	10
Benzene.....	H ₂ SO ₄ , an aldehyde or phthalic anhydride	11
Petroleum stocks.....	H ₂ SO ₄	12

Table continued

¹ V. Meyer, *Ber.*, **17**, 2641 (1884).

² Schulze, *Ber.*, **18**, 497 (1885).

³ Gillies, *Gas World*, **104**, No. 2700, *Coking Sect.*, 52 (1936); *Chem. Abstr.*, **30**, 4657 (1936).

⁴ Hoffert, Claxton, and Hancock, *Gas J.*, **214**, 103, 167 (1936).

⁵ Schulze, *Ber.*, **17**, 2853 (1884).

⁶ Kopelevich and Brodovich, *Russ. Pat.* 39,096 (1934); *Chem. Zentr.*, **1935**, **11**, 3619.

⁷ Schwalbe, *Zeit. Farb. Tex. Ind.*, **3**, 461 (1904); *J. Chem. Soc. Abstr.*, **1905**, 124.

⁸ Weissgerber, *Ber.*, **B61**, 2111 (1928).

⁹ von Lauer and Ponchaud, *U. S. Pat.* 2,346,524 (1944).

¹⁰ Bullard, Anderson, and McAllister, *Brit. Pat.* 579,781 (1946).

¹¹ Badische-Anilin und Soda Fabrik., *Ger. Pat.* 211,239 (1909).

¹² Wood, Lowy, and Faragher, *Ind. Eng. Chem.*, **16**, 1116 (1924).

TABLE I-3 (Continued)

Material containing thiophenic contamination	Method of removal	Ref.
Naphtha.....	Fuming H ₂ SO ₄ and 66° BÉ. H ₂ SO ₄ , 53° BÉ. H ₂ SO ₄ was ineffective	13
Shale oil distillates.....	96.5% H ₂ SO ₄	14
Lignite oils.....	Concd. H ₂ SO ₄	15
Bituminous primary distillates.....	Dil. H ₂ SO ₄	16,16a
Shale oil.....	Concd. H ₂ SO ₄	17
Schist and peat oils.....	H ₂ SO ₄ -H ₃ PO ₄	18
Russian petroleum stocks.....	CH ₂ O and "naphthasulfonic acids"	19
Petroleum stocks.....	Sulfur dioxide	20
Naphtha.....	Sulfur dioxide extracted; the extract treated with aniline	21
Coal tar distillates.....	HgCl ₂ , NaOOCCH ₃	22
Coal tar distillates.....	HgSO ₄ , HgO	23
Coal tar distillates.....	Hg(OOCCH ₃) ₂	24
Raw benzene.....	Hg(OOCCH ₃) ₂	25-27
Raw benzene.....	HgSO ₄ , HgO	28
Raw benzene.....	HgO, stearic acid	29
Sulfur rich oils.....	Mercury salts	30
Kimmeridge shale oils.....	Hg(OOCCH ₃) ₂	31
Gasoline.....	Hg(NO ₃) ₂	32,32a
Cracked rubber distillates.....	Hg(OOCCH ₃) ₂	33

Table continued

¹³ Wood, Shelly, and Trusty, *Ind. Eng. Chem.*, **18**, 169 (1926).¹⁴ Leclere and Leclere, *Compt. rend.*, **194**, 286 (1932).¹⁵ Ruhemann and Baumbach, *Braunkohle*, **31**, 549, 565 (1932).¹⁶ French Pat. 721,698 (1930); *Chem. Abstr.*, **26**, 4069 (1932).^{16a} Picon, *Compt. rend.*, **228**, 251 (1948); *Bull. soc. chim.*, **1949**, 289, 296.¹⁷ Reichert, *Arch. Pharm.*, **276**, 316 (1938).¹⁸ Hahn and Nielsen, Danish Pat. 51,230 (1936); *Chem. Abstr.*, **30**, 6171 (1936).¹⁹ Stadnikov and Weizmann, *Brennstoff-Chem.*, **8**, 343 (1927).²⁰ Challenger, *Ind. Chemist*, **2**, 445 (1926); *Chem. Abstr.*, **21**, 646 (1927).²¹ McKittrick, *Ind. Eng. Chem.*, **21**, 585 (1929).²² Heusler, *Ber.*, **28**, 488 (1895).²³ Deniges, *Bull. soc. chim.*, [3] **13**, 537 (1885); *Compt. rend.*, **120**, 628, 781 (1895).²⁴ Paolini and Silbermann, *Gazz. chim. ital.*, **45**, 11, 385 (1915).²⁵ Dimroth, *Ber.*, **32**, 760 (1899).²⁶ Schwalbe, *Ber.*, **38**, 2208 (1905).²⁷ Dimroth, *Ber.*, **35**, 2032 (1902).²⁸ Jones, *J. Soc. Chem. Ind.*, **37**, 324T (1918).²⁹ Ardagh and Furber, *J. Soc. Chem. Ind.*, **48**, 73T (1929).³⁰ Scheibler, Brit. Pat. 155,259 (1920).³¹ Challenger, Haslam, Bramball, and Walden, *J. Inst. Petroleum Technol.*, **12**, 106 (1926).³² Ball, *U. S. Bur. Mines, Rept. Investigations*, **3591** (1942); *Chem. Abstr.*, **36**, 1763 (1942).^{32a} Mixer, *Chem. Eng. News*, **26**, 2434 (1948).³³ Midgley, Henne, and Shepard, *J. Am. Chem. Soc.*, **54**, 2953 (1932).