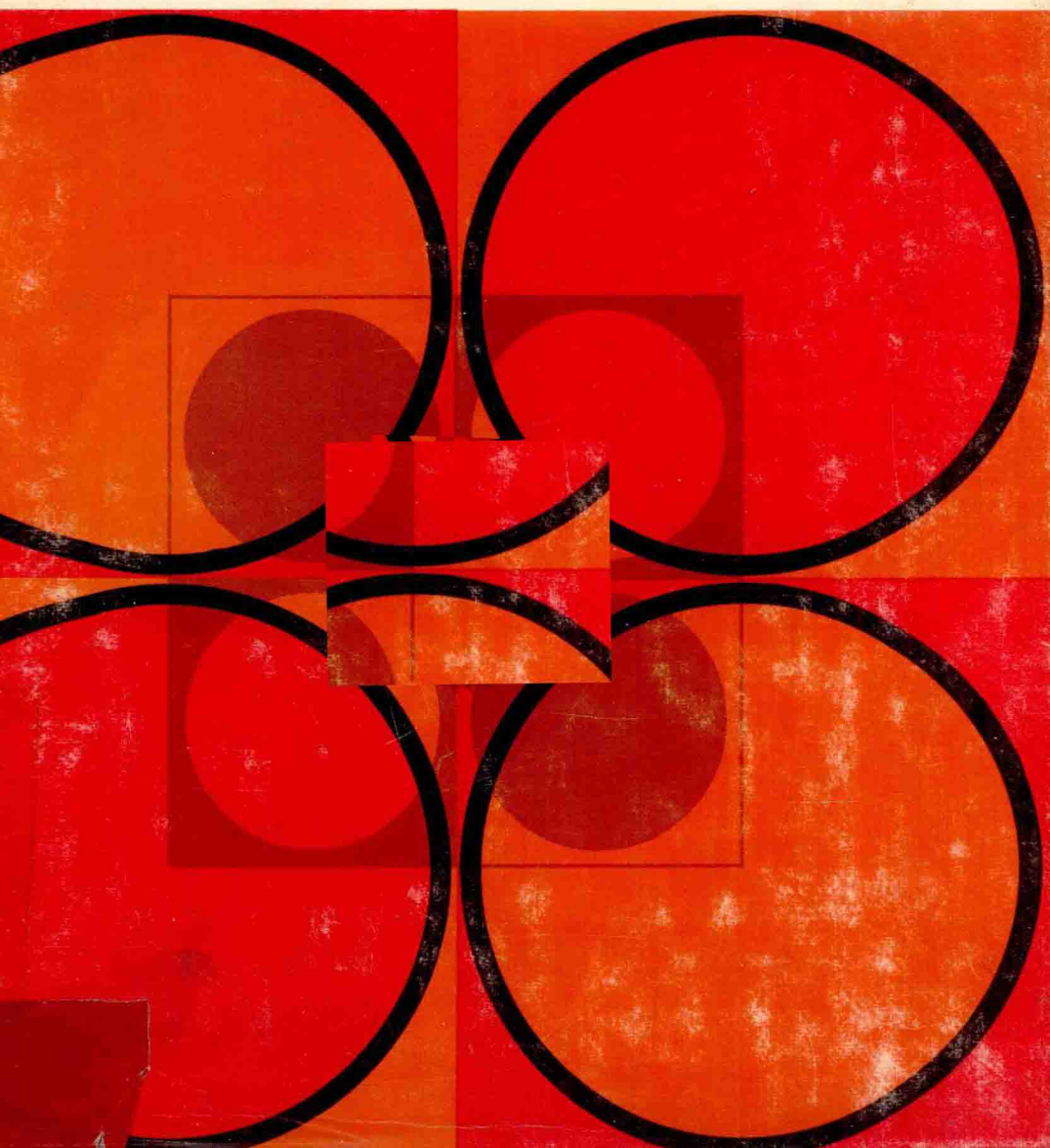


The Analytical Chemistry of Sulfur and its Compounds

Part I Edited by J. H. KARCHMER



The Analytical Chemistry of Sulfur and its Compounds

PART I

J. H. Karchmer

EDITOR

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PREFACE

It is becoming increasingly apparent that sulfur compounds play an important role in our technological and scientifically oriented society. Specific effects in numerous commercial processes and the physical and chemical attributes of many products have been traced not merely to the presence of total sulfur but more specifically to a particular sulfur functional group. In pharmaceutical chemistry and biochemistry the role of sulfur compounds is of no less importance.

Just as the publication of good texts in analytical chemistry has lagged behind the explosive development of instrumental analytical techniques witnessed during the last twenty years, so has the publication of analytical methods for sulfur compounds lagged behind their actual development. Many useful methods that employ a diversity of techniques, classical and instrumental are in current use in many research institutions, manufacturing plants, control laboratories, and universities. However, there is no single source in which a chemist or engineer, confronted with a problem involving sulfur chemistry, can find a comprehensive treatment of the analytical chemistry of a large number of compounds. There are several good general analytical books that also contain chapters on sulfur compounds as well as excellent books and review articles devoted to the chemistry of sulfur compounds (see below). Although these articles and books are extremely useful, they do not preclude the need for a single *analytically* oriented book of pertinent facts about sulfur compounds, their chemical and physical properties, usages, means of detection, and means of determination.

In pursuance of this objective the most frequently encountered sulfur compound types were classified and fitted into a general subject-matter outline. Of necessity, the classification and the resulting outline were somewhat arbitrary; however, there was no major deviation from established traditional classification. For each of the major divisions covering a distinguishable sulfur compound type or group competent chapter authors, qualified by experience and scholarship, were selected from academic institutions and industry.

In order to achieve some degree of uniformity in the format and amount of information provided in each chapter, a detailed general contents outline was supplied to each author. The prime topics suggested were background chemistry, nomenclature, occurrence, physical properties, physical measurements, analytically significant chemical and physical properties, interfering materials, and recommended procedures.

In general, this type of material will be found in each of the chapters expressed in a format and original style preferred by each author and fitted to the particular characteristics of the subject matter of each chapter.

The chapters provide many analytical procedures now existing in widely scattered sources, including information about the scope, limitations, lower limit of sensitivity, accuracy, and reproducibility of selected procedures. The main emphasis is on the presentation of discussions in depth of the principles underlying the analytical methods. This treatment provides the analytical chemist with the means of devising his own method to solve his particular problem and to avoid the disastrous effects of possible interfering materials.

Since this book is directed to chemists who have at least the equivalent of a bachelor's degree and have available some literary facilities, no background information is included on classical or instrumental analytical techniques.

Initially this book was intended to be a single volume, but length of the various individual contributions has made it necessary to divide it into two parts. This volume, which presents the first six chapters, is concerned primarily with the inorganic sulfur compounds, although it cannot be properly so titled because the chapters on total sulfur and sulfur-containing gases are concerned with some organic materials. Since this clear-cut division between inorganic and organic sulfur compounds could not be made, it was decided to include in this volume the chapter on thiols.

Part II, which will be issued shortly, will be devoted exclusively to organic sulfur compounds. There are chapters on sulfides, disulfides and polysulfides, thiophenes, sulfur analogs of carbonyls, carboxylic and carbonic acids, other divalent sulfur compounds, tetra- and hexavalent sulfur compounds, and a survey of the nuclear magnetic resonance of sulfur compounds.

Baytown, Texas

J. H. KARCHMER

General Analytical Books Containing Chapters on Sulfur Compounds

Kolthoff, I. M., and P. J. Elving, *Treatise on Analytical Chemistry*, Interscience, New York, 1966, Part II, Vol. 12, p. 57 and Vol. 13, p. 337.

- Meites, Louis, *Handbook of Analytical Chemistry*, McGraw-Hill, New York, 1963, pp. 12-125 to 12-177.
- Mitchell, John, I. M. Kolthoff, E. S. Proskauer, and A. Weissberger, *Organic Analysis*, Interscience, New York, 1961.
- Siggia, Sidney, *Quantitative Organic Analysis Through Functional Groups*, Wiley, New York, 1963.
- Stone, K. G., *Determination of Organic Compounds*, McGraw-Hill, New York, 1956.

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- Gilman, Henry, *Organic Chemistry, An Advanced Treatise*, Wiley, New York, 1942.
- Kharasch, N., *Organic Sulfur Compounds*, Vol. I, Pergamon, New York, 1961.
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- Pryor, William A., *Mechanisms of Sulfur Reactions*, McGraw-Hill, New York, 1962.
- Reid, E. E., *Organic Chemistry of Bivalent Sulfur*, Vols. I-V, Chemical Publishing, New York.

The Analytical Chemistry of Sulfur and its Compounds

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CHAPTER 1

ELEMENTAL SULFUR

William N. Tuller

Freeport Sulphur Company

1.1 Uses and Sources

1.1.1 TECHNICAL IMPORTANCE

Sulfur is the only nonmetal that is cheaply available in the elemental form, which can be easily oxidized, and whose oxide forms a strong acid. Elemental sulfur can also be easily reduced. It can be used, therefore, either as an oxidizing agent or as a reducing agent, depending upon the environment to which it is subjected. As a result of these facts, sulfur is one of the most widely used elements in industry. It is essential, in one way or another, for the manufacture of nearly everything that our present civilization produces.

Figure 1.1 shows the distribution of sulfur among its various uses in the United States. The world distribution of uses is very similar.

Sulfur is used directly in the elemental form in the manufacture of paper and pulp, carbon disulfide, rubber and other elastomers, and for crop dusting.

It is most used in industry in the form of sulfuric acid. Sulfuric acid manufacture consumes about 85 % of the elemental sulfur used in the United States. The acid enters into the manufacture of fertilizer, chemicals, pigments, iron and steel, rayon, film, and petroleum products.

Fertilizer manufacture is its largest single consumer. In the form of sulfuric acid, sulfur has no important competitor for the manufacture of phosphate fertilizers from phosphate rock, and it is used in the manufacture of some of the nitrogen fertilizers. So the food supply of the world depends heavily on the supply of sulfur. About 45 % of all the sulfur used is for this purpose.

1.1.2 SOURCES

The largest deposits of elemental sulfur are found approximately 2000 ft below ground, in sedimentary deposits of anhydrite, gypsum, and calcite, on top of salt domes along the coast of the Gulf of Mexico in