STANDARD METHODS OF CHEMICAL ANALYSIS

SIXTH EDITION

Volume One—The Elements

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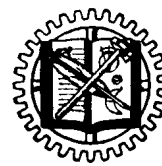
IN COLLABORATION WITH MANY CONTRIBUTORS
(SEE LIST ON PAGES FOLLOWING)



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PREFACE

Throughout its various editions this work has been a source of analytical information of proven value for general use in the chemical laboratory. For more than fifty years it has been consulted by chemists as a reference for standard methods of analysis—those most widely accepted and readily applied. All of its characteristics—the plan of organization, the detail of presentation and even its selection of methods—have been determined by this function as a general, practical reference book.

Thus, it contains chapters of two kinds: (1) those dealing with a single element or a single class of substances, as exemplified by the chapters on aluminum or lead or uranium, and those on petroleum or plastics or water analysis; and (2) those chapters dealing with a single type of analytical method, as exemplified by the chapters on microanalysis or ion exchange or spectrographic analysis.

These characteristics of earlier editions have been maintained in the Sixth Edition. This has required, in view of the great advances of the intervening years, the addition of the third volume, devoted entirely to chapters on physical and instrumental methods and their applications. It has also necessitated the publication of the three volumes separately, at approximately annual intervals. However, the established policy has been followed by seeking as contributors men of wide specialized experience, either with individual elements and types of substances, or with particular methods of analysis. Furthermore, the basic organization of the chapters and within the chapters has been maintained, with certain minor changes made necessary by the extensive additions of new methods and new information.

In Volume I, the elements are taken up, chapter by chapter, in alphabetical order except for certain logical groupings of elements. Thus, tellurium is treated in the chapter with selenium, tantalum with niobium, technetium with rhenium, the rare earths with cerium, and the alkali metals in the first chapter of the book. An alphabetical listing of the elements, giving the page number of the chapter in which each element is treated, follows the comprehensive table of contents.

In Volume I on the elements the reader will note the omission of the analytical chemistry of the transuranium elements which is available in full detail only to those having access to classified information. The methods of determining the inert gases (helium family), are to be found under gas analysis, and under the mass spectrographic and spectral analysis in Volumes II and III, respectively.

Each chapter is arranged, for convenient reference, in accordance with a uniform sequence, that has been followed throughout the book. It is as follows:

Physical Properties. Atomic weight; specific gravity; melting-point; boiling-point; oxides.

Detection. Characteristic reactions leading to the recognition of the element.

Estimation. The subject is introduced with such information as is useful to the analyst.

Preparation and Solution of the Samples. Here directions are given for the preparation and decomposition of characteristic materials in which the element

occurs. Recommendations to the best procedures are included to assist the analyst in his choice.

Separations. This section is devoted to procedures for the removal of substances, commonly occurring with the element, that may interfere with its estimation. In the absence of such substances, or in case methods are to be followed by which a direct estimation of the element may be made in the presence of these substances, this section in separations may be omitted in the course of analysis. Here the discretion of the chemist is necessary, and some knowledge of the substance examined.

Gravimetric Methods of Determination
Titrimetric Methods of Determination
Colorimetric/Photometric Methods of Determination
Other Methods of Determination
Determinations in Other Substances

Under each of these headings are grouped those methods of determination which are most widely accepted, most certain to give consistent results and, in the case of analyses of other substances, most frequently to be needed by the chemist. Where a decision has been necessary as to where to include a method in Volume I, or one of the other two volumes of the book, the rule followed has been to place in Volume I those methods which, though used for special substances, are sufficiently general to be applicable to other materials, and to plan to include in the other volumes those methods used primarily for a single class of substances, as well as those requiring highly specialized equipment.

It is fortunate that the 1961 Table of Atomic Weights of the I.U.C. was published before the Sixth Edition of STANDARD METHODS OF CHEMICAL ANALYSIS, so that the values and factors throughout this volume have been recalculated accordingly.

In addition to the contributors listed in these pages, whose work has gone so far to make this book possible, acknowledgment is due to the American Society of Testing Materials for their generous permission to reproduce their methods; to Mr. W. R. Minrath, Vice President of D. Van Nostrand Company, without whose aid in the selection of contributors and in editing the progress of the work would have lagged immeasurably due to the critical illness of the editor at that time; and to Professor Morris B. Jacobs of Columbia University, for his help in evaluation and for his extensive contributions of material.

INTRODUCTION

The fundamental importance of analytical chemistry is shown by the urgent demands on this branch of chemistry. Our present-day knowledge of elements has been made possible by analysis. The separations in metallurgy are dependent upon analytical principles. Startling discoveries in medicine have been dependent on accurate analysis and the same is true in regard to experimental research, where analytical methods are employed for ascertaining the composition of the products formed. The importance of analysis for control of chemical industrial processes has created a demand for rapid methods so that there is a constant effort on the part of the analytical chemist to simplify procedures of analysis. On the other hand our extended knowledge of the nature of substances and their chemical reactions has shown errors in former methods of procedure and the necessity for modifications which are being developed to take care of interferences. This accounts for the large number of specialized methods that appear in chemical literature and the vast amount of work that has been done for coupling accuracy with simplicity, wherever this is possible. Research demands accuracy in analytical procedures with sacrifice of simplicity and rapidity, should these be impossible; on the other hand rapid methods are essential to the economic control of chemical industrial processes.

A correct evaluation of materials for one or more of the substances desired, necessitates careful sampling, for obtaining representative portions for analysis. Ores and minerals of uniform composition are exceptions; even in the case of alloys, where a uniform composition would be expected, segregation of elements of the molten mixtures during the process of cooling is known to take place. Sampling of solutions is no exception to the necessity of careful procedure.

An early training in the chemical laboratory, generally starting in the high school and carried on in the college or university, has acquainted the chemist with the common apparatus employed in the analytical laboratory. He is familiar with the different forms of containers—beakers, casseroles, flasks, crucibles—closed or perforated forms, made of porcelain, silica or other refractory materials, or of metals—iron, nickel, platinum and certain resistant alloys. The chemist is familiar with different types of measuring apparatus—the balance, burette, measuring flasks, pipettes, etc. He has used different forms of heating or combustion apparatus—drying ovens, burners and furnaces. He has become familiar with laboratory operations and technique, details of which appear in elementary texts of analytical chemistry, used in his preparation for a professional career. It has been considered unnecessary to give such details here. Throughout the work attention is called to special apparatus and cautions in technique and operations where these are considered necessary. A chapter appears in the later portion of this volume on special apparatus and calibration methods that will be found useful.

In the preparation and decomposition of the material for analysis care must be exercised to avoid loss by volatilization or separation; for example the volatility of mercury compounds, silicon and fluorine in presence of each other during the acid attack, stannic chloride, boron in certain combinations; the precipitation of cer-

tain radicals with silica during the action of strong acids, and the co-precipitation of a number of substances with aluminum hydroxide (the ammonia precipitate). Throughout the text precautions are given to avoid such losses and attention is called to the steps where such losses are apt to occur. In the mechanical preparation of the material fine grinding of refractory substances is generally advisable. It must be remembered, however, that chemical changes may take place, for example oxidation of sulfide ores leading to low results. Then again contamination by abrasion of the grinding apparatus must be guarded against.

The amount of the sample required for analysis depends not only upon the percentage of the element or substance in the material, but also upon the delicacy of the method, that is to be used. In the determination of the more common elements in ores and minerals a 0.5 gram sample is generally sufficient. In micro-methods, a few milligrams are sufficient, while in the determination of the so-called "traces" of impurities much larger samples may be required.

In complete analysis of substances it may be advisable to take separate samples for individual estimations, as in case of carbon dioxide in carbonates, the estimation of carbon, fluorine, and chlorine. On the other hand combinations may be better, for example the determination of silica, titanium, manganese and nickel in the same sample; chromium and vanadium; barium and zirconium; iron, aluminum, titanium, vanadium, zirconium and the phosphate radical in the same sample. Procedures in the text indicate the best conditions for accuracy, and the operations necessary for removal of interfering substances.

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The first four editions of STANDARD METHODS OF CHEMICAL ANALYSIS were prepared under the Editorship of Dr. Wilfred W. Scott, Professor of Chemistry at the University of Southern California. After his death, the Fifth Edition was edited by Dr. N. Howell Furman, then Professor of Chemistry at Princeton University. Professor Furman also edited Volume I of the Sixth Edition, and is Advisory Editor of Volume II, which is edited by Dr. Frank J. Welcher of the University of Indiana. Volume III is edited by Dr. Seymour Z. Lewin of New York University.

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