MODERN ORGANIC ELEMENTAL ANALYSIS

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Library of Congress Cataloging in Publication Data

Ma, Tsu Sheng, [Date]
Modern organic elemental analysis.

Includes bibliographical references and indexes.
1. Chemistry, Analytic--Quantitative. 2. Chemistry, Organic. I. Rittner, Robert C., [Date] joint author.
II. Title.
QD271.7.M29 547'.34 79-11573
ISBN 0-8247-6786-1

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

Printed in the United States of America

Preface

The purpose of this book is to organize in a single volume the methods of organic elemental analysis applicable to different sample sizes and the techniques for the determination of all of the elements in organic materials. It is intended for various groups of users including (a) chemists in small laboratories who occasionally perform organic analysis; (b) practicing analysts in large establishments who may encounter difficult samples; (c) research analysts who wish to have a comprehensive review of the existing methods; (d) graduate students in analytical and organic chemistry who should have some knowledge of the evolution and current status of organic analysis; (e) teachers of advanced quantitative techniques who need a textbook containing a large variety of experiments; and (f) organic chemists who do not analyze their samples but wish to know how the analysis can be done.

At the present time, it can be said that there is a method for the determination of any element which may be present in an organic substance. The book is written to assist the reader in finding the method and in choosing the best method if more than one is available. The individual elements are systematically treated in Chaps. 2-9. Chapter 10 deals with the simultaneous determination of two or more elements using one sample. The basic principles for each method of analysis are fully discussed, as well as the applications and limitations. Most of the procedures described are at the milligram level, which is the current practice. However, some macro procedures are also mentioned, such as Kjeldahl determination of nitrogen. Chapter 11 presents methods using less than milligram amounts of sample; such methods are recommended when a larger quantity of the working material cannot be obtained. Finally, Chap. 12 deals with trace analysis of specific elements which, understandably, involves the use of large samples.

Experimental details are given separately in the last part of each chapter. This arrangement is convenient for the practicing chemist who wishes to try out a procedure and for the student who uses this book as a laboratory manual.

In the selection of laboratory experiments, I have tried to include both classical and new methods. Procedures using elaborate instrumentation and physicochemical measurement devices are presented. On the other hand, determinations that can be accomplished by means of simple equipment and techniques are also described; these methods can be employed with advantage in small laboratories. Most of the experiments have been thoroughly tested by my students or are being used in the laboratory of Dr. Robert C. Rittner. Dr. Rittner contributed a great deal in the experimental sections of this book. He took my course in quantitative organic analysis at New York University 25 years ago and has since been in charge of several analytical laboratories in industry.

It should be noted that this book is not limited to the experimental methods of one school. A number of detailed procedures are based on information that I obtained from other analytical laboratories; these procedures were confirmed by the original workers named in the respective experimental sections.

My involvement in organic analysis began in 1934 when I entered the University of Chicago to study organic synthesis under Professor Julius Stieglitz. In our first meeting, the professor told me about the Pregl combustion trains that Oskar Wintersteiner had recently introduced at the laboratory and advised me to learn the microchemical techniques which should be taught in the Orient some day. Consequently, by the time I received by Ph.D I was already well-versed in organic analysis. During World War II, I was supervisor of the microchemical laboratory at the University of Chicago, where I saw thousands of samples processed and many new methods developed.

After the war, I had the opportunity to lecture in Europe and Asia and made four extended lecture tours in the last fifteen years. On those tours, I visited numerous laboratories, observed the operations of many practicing and research analysts, and discussed the merits and drawbacks of various methods. The consensus of our discussions was that (1) the analyst can no longer restrict himself to procedures for only one range of sample sizes because he now deals with pure organic compounds as well as complex mixtures containing minute amounts of elements of interest; (2) the types of samples received for analysis vary from laboratory to laboratory; and (3) the facilities and maintenance services available differ greatly from one location to another. These discussions and conclusions stimulated the idea of a book to meet the needs implied. At the invitation of my revered friend Dr. Maurits Dekker, this book was begun. Dr. Dekker deserves the credit if this book is a success, while I shall bear responsibility if it does not fulfill our expectations.

I wish to express my heart-felt appreciation to my colleagues in organic analysis who have generously shared with me their experience and expertise. I thank the many journals, publishers, and instrument manufacturers for their kind permission to reprint the illustrations in this book; the source of each illustration is indicated under the figure caption.

I am deeply indebted to my wife Gioh-Fang whose encouragement and patience have been indispensable for the progress of my work. Our children Chopo and Mei-Mei helped in typing my manuscripts and reading proofs.

T. S. Ma

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Introduction

1.1 OBJECTIVES OF ORGANIC ELEMENTAL ANALYSIS

Organic elemental analysis is concerned with the determination of the elements present in organic materials. Generally speaking, the objectives of such quantitative measurements can be classified into three categories.

(1) The analysis may be carried out on a single compound (known as the pure sample) for the purpose of determining its elemental composition. If the sample is a synthetic product formed in a known reaction, the analytical data can be checked against the values calculated from the expected molecular formula. Usually the determination of one or two elements in the compound suffices. On the other hand, if the sample is a new substance (e.g., obtained from nature, or an unexpected synthetic product), determination of all elements present is recommended so that the sum total of elemental composition adds up to 100%.

(2) The analysis may be performed on a mixture for the purpose of finding out the content of a particular element, or the amount of certain compounds, in the analytical sample. For example, fertilizers are analyzed for nitrogen by the Kjeldahl method; sulfur determinations are carried out in the petroleum industry in crude oils and gasolines; nonprotein nitrogen (NPN) analysis is made on certain biological fluids. Similarly, the amount of fluoroacetic acid in plant leaves is usually measured by the fluorine content of the material, while the extent of chlorobiphenyl residue left in the field which has been sprayed by these insecticides is indicated by organic chlorine analysis.

(3) The analysis may be undertaken for the purpose of assessing the purity of the organic substances in question, such as pharmaceutical preparations, fine chemicals, and high-quality solvents. In this case, the element to be analyzed is usually the one which is present in the contaminant and not in the pure product. It should be noted that product purity is

frequently determined by functional group analysis [1,2] or by chromatography [3]. There are occasions, however, when quantitative elemental analysis provides a simple method to attain this objective. For instance, the determination of sulfur serves to indicate the amount of thiophene in benzene.

1.2 HISTORICAL BACKGROUND

Quantitative analysis of the elements in organic substances was initiated by Lavoisier [4] two centuries ago. After learning the experimental technique from Priestly [4] in 1774 to prepare oxygen, Lavoisier burned alcohol and other combustible organic compounds in oxygen; from the weight of water and carbon dioxide produced, he calculated their compositions. Understandably, Lavoisier's results were imperfect, partly because of impurities in the substances investigated, partly because of defects in his methods, and partly in consequence of his incorrect values for the compositions of water and carbon dioxide. About five decades later, Liebig [5] developed the method for the determination of carbon and hydrogen (1831) by combustion in the presence of copper oxide, while Dumas [5] analyzed nitrogen (1830) in organic compounds by measurement of the nitrogen gas produced. It is of interest to note, however, that much emphasis had been given to the quantitative aspects of organic analysis prior to the publication of the procedures of Liebig and Dumas. Thus, in the "Handbuch der Allgemeinen und technischen Chemie" published in 1829, discussion of each organic compound was accompanied by its elemental percentage composition as reported by the investigators. For example, the data for urea were as follows [6]:

Investigators	%C	%H	%N
Fourcroi and Vauquelin	14.7	13.3	32.5
Prout	19.975	6.650	46.650
Berard	18.9	9.7	45.2
Ure	18.57	5.93	43.68
Prevost and Dumas	18.23	9.89	42.23

When compared with the currently accepted values [7] (CH_4N_2O: C, 20.00%, H, 6.71%, N, 46.65%), we can appreciate the remarkably accurate results obtained 150 years ago by Prout who analyzed a sample of urea which was dried over concentrated sulfuric acid in a vacuum desiccator.

The methods for determining sulfur and halogens were developed by Carius [8] (1860) who discovered that heating organic compounds with nitric acid in a sealed tube quantitatively converted these elements into ionic forms (see Chaps. 5 and 6). For many decades, the Liebig, Dumas, and Carius procedures were standard techniques practiced by organic chemists. It should be mentioned that the determination of oxygen was not performed, although oxygenated compounds were the first crop of organic substances isolated by Scheele [5, 9] in 1770.

A great advance in organic elemental analysis took place at the turn of this century when Pregl [10] worked out micromethods using milligram quantities of samples. Much of Pregl's contribution is discussed in the succeeding chapters. It is interesting to note, however, that the general acceptance of the Pregl micromethods has deprived most students of organic chemistry of the opportunity to acquire the experimental skill of quantitative analysis.

1.3 RECENT DEVELOPMENTS

A. Modification and Expansion of Pregl Procedures

The Pregl school for organic elemental analysis was characterized by detailed directions and precise laboratory operations. The apparatus and reagents to be employed, as well as the experimental procedures, were strictly prescribed and followed. Such precisely defined instructions were essential in order to attain the same precision and accuracy using a 3- to 5-mg sample as in elemental analysis using a 200- to 500-mg sample. Consequently, the Pregl school tended to discourage variations and innovations. Modifications of the Pregl procedures began during World War II because of various reasons: (1) the unavailability of the Pregl apparatus from Europe led to the production of microbalances and microapparatus in America; (2) the increase in the number of samples to be analyzed fostered the development of rapid methods (e.g., the micro Kjeldahl procedure developed by Ma and Zuazaga [11]); (3) the dearth of chemists having delicate manipulative skill necessitated the introduction of less demanding experimental operations. Thus, workers in several countries including Czechoslovakia [12], Germany [12a], Japan [13, 14], UK [15, 15a], USA [16], and USSR [17, 18] have published their respective modifications of the Pregl micromethods.

The field of organic elemental analysis has expanded in recent years. First, the methods for the determination of oxygen and fluorine, respectively, have been perfected; thus it is now possible to determine any and every element that may be present in an organic sample. Secondly, the rapid increase of interest in the study of organometallic compounds has created new problems since these compounds are not always amenable to

the existing methods of analysis [19]. Thirdly, public attention on pollution control and environmental protection has demanded reliable methods for trace analysis in complex systems [20]. Finally, it may be mentioned that some macromethods using decigram or larger samples are still recognized as official procedures, e.g., the Kjeldahl procedure in US Pharmacopeia [20a].

B. Development of Rapid and Automated Procedures

Rapid procedures of organic elemental analysis are usually achieved by eliminating certain operations and/or devising techniques for fast decomposition of the sample and measurement of the reaction products. For example, in the micro Kjeldahl procedure (see Sec. 3.3), distillation of ammonia by means of a rapid stream of water vapor and absorption of ammonia in 2% boric acid instead of standardized 0.01 N hydrochloric acid shortens the experiment considerably [11]. Decomposition of halogenated compounds in the closed flask (see Sec. 5.3) is practically instantaneous, compared to the slow operation of oxidation by means of nitric acid or in a current of oxygen [21]. Simultaneous determination of more than one element using a single weighed sample (see Chap. 10) frequently eliminates some duplicate operations and hence speeds up the entire analytical process.

Automated procedures were designed to relieve the manipulative strain of the analyst [22]. They are also labor-saving and faster than manual operations. The commercial automated machines for C, H, N determinations are described in Chap. 2. Recently Ubik and co-workers have proposed methods for automatic determination of oxygen [23] and for simultaneous determination of oxygen and nitrogen [24]. The scheme of the apparatus for nitrogen analysis [25] is shown in Fig. 1.1. The procedure involves pyrolytic decomposition of the organic compound in a stream of hydrogen at 1000-1100°C; the hydropyrolytic products are then passed through layers of Mn(II) oxide and nickel at 950°C. Nitrogen gas is liberated on the nickel. After removal of interfering substances (CO, H_2O, hydrogen halide), the amount of nitrogen formed is measured by thermal conductivity. Thus the basic Dumas principle to convert organic nitrogen to elementary nitrogen is retained. Ebel [26] has published a comprehensive survey on automated C, H, N determinations. Salzer [27] has reviewed the physicochemical measuring methods which are amenable to automation [28]. Scheidl and Toome [29] have described an automated potentiostatic procedure for the determination of chlorine, bromine, or iodine. A combustion furnace, a buret and a titrator are modified and connected to an apparatus. A solid-state programmer using monostable and multivibrator circuits to generate various time delays completes a halogen determination in 4 min. Fraisse and Richard [29a] have fabricated an automated introduction device that can be used for various determinations.