INSTRUMENTAL METHODS OF CHEMICAL ANALYSIS

Fifth Editior

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PREFACE

As in previous editions, the general objective of this book is to survey the theory and practice of modern analytical instrumentation. Emphasis is placed on the possibilities and limitations inherent in the various methods.

The text is planned for use in upper-level undergraduate or first-year graduate classes. To be most effective, this course should follow work in elementary quantitative analysis and a year of physics; it may follow or run concurrently with physical chemistry. The treatment is not highly mathematical, but elementary calculus is employed where needed.

It is always difficult to decide what to include and what to omit. The words "analytical" and "instrumental" are not amenable to objective definition. With respect to the former, H. A. Laitinen has written: "The vital point here is that if the research is aimed at methods of solution of a measurement problem, it is properly classified as analytical chemistry, whereas the interpretation of the results of the measurements infringes upon other fields of chemistry." [Editorial, *Anal. Chem.*, **1966**, *38*, 1441.] I have attempted to include just enough interpretive material to suggest the areas in which a method can be useful.

With respect to detailed coverage, I have tried to be led primarily by usefulness to chemistry students, with due consideration to their expected background. Thus it is assumed that the principles of the analytical balance have been treated in prior courses.

A treatment of photoacoustic spectroscopy has been added as a separate chapter, since its applications cannot be restricted to either the infrared or ultraviolet–visible spectral regions.

The chapter on electronic circuitry has been expanded to include material on analog-to-digital conversion and related techniques leading toward computer interfacing. The treatment of computers in analytical chemistry has been expanded considerably, with emphasis on the significance of the monumental increase in

the incorporation of microprocessors in commercial instruments. Enough material is presented to give a picture of how these devices function, and their limitations.

As in previous editions, the electronics chapter is placed at the end of the book, and is cross-referenced in the text as needed. The instructor can easily introduce this material at the start of the course if desired.

The SI system of units is used throughout. Other conventional units that are still frequently encountered in the literature are defined and used occasionally in problems to give students practice in interconversion.

Mention of the products of individual manufacturers does not necessarily imply that I consider them superior to competing items. The aim is to describe instruments typical of their class or possessing some special features of interest, not to write a complete catalog of analytical apparatus.

I wish to express my sincere appreciation to my colleagues and students over the years, who have offered advice and pointed out shortcomings. Particular thanks go to the following individuals who have read the manuscript with care and provided most helpful critiques: Professors Richard J. Cook, Frank A. Guthrie, Arno Heyn, Joseph Jordan, and Edward H. Piepmeier. I am greatly indebted also to the personnel of instrument companies and distributors, too numerous to list, without whose cooperation the book could not be a success.

Some of the work on this edition was performed while I was visiting professor at Carleton College, and I wish to acknowledge the use of library and other facilities at Carleton during my very pleasant stay there.

Galen W. Ewing

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CHAPTER

ONE

INTRODUCTION

Analytical chemistry may be defined as the science and art of determining the composition of materials in terms of the elements or compounds contained in them. Historically, the development of analytical methods has followed closely the introduction of new measuring instruments. The first quantitative analyses were gravimetric, made possible by the invention of a precise balance. In the closing decades of the nineteenth century, the invention of the spectroscope brought with it an analytical approach that proved to be extremely fruitful. At first it could be applied only qualitatively, gravimetric and volumetric methods remaining for many years the only quantitative procedures available. Gradually a few colorimetric and turbidimetric methods were introduced. Then it was found that electrical measurements could be used to advantage to detect end points in titrations. Since about 1930, the rapid development of electronics has resulted in a major revolution in analytical instrumentation. Today the chemist, whether he calls himself an analytical specialist or not, must have a working knowledge of a dozen or so instrumental methods virtually unknown a generation ago.

Nearly any physical property characteristic of a particular element or compound can be made the basis of a method for its analytical determination. A quick summary of the topics included in this book will indicate the great variety of such methods. In successive chapters we will consider first a whole series of spectroscopic techniques involving the absorption or emission of radiant energy in all regions of the electromagnetic spectrum. Then we will turn to a survey of electrochemical

methods, followed by a treatment of chromatography as applied to both gas and liquid phases. Chapters on thermometric and nuclear methods conclude the treatment of analytical disciplines.

In recent years, several techniques have evolved that combine two or more methods into one. These "hyphenated" techniques are described arbitrarily under one of the methods involved and cross-referenced under the others. One of the earliest of these hybrid areas to be developed involved the marriage of a mass spectrometer (MS) with a gas chromatograph (GC), hence is referred to as "GC/MS"; it is treated in Chap. 20.

Many features of analytical methods are similar or identical from one to another. To avoid excessive duplication, some of these are treated together in Chap. 26. Here will be found, for example, a discussion of the method of standard additions, which is a technique for the calibration of an analytical procedure that is used in several of the subject areas of earlier chapters.

Before proceeding to these substantive topics, some general remarks concerning the objectives of instrumentation and the means of attaining them are in order.

The fundamental task to be performed by an instrument is the translation of chemical information into a form that is directly observable by an operator. It does this by means of a *transducer*. This is a component whereby the information is caused to control or "modulate" an electric current. The succeeding electronic circuitry must then extract the information from the carrier current, amplify it if necessary, and display it on a readout device.

ELECTRONICS

Analytical instruments are usually designed to be as sensitive as practicable, so that they are able to measure precisely the smallest signal that can be produced by the transducer. Provision for logical or arithmetic processes, such as the automatic subtraction of a background, are frequently included in the electronics package.

In many methods it is necessary to apply some sort of stimulus to the system (a beam of radiation, for example), and this stimulus is often produced, measured, and regulated with the aid of additional electronic circuitry.

Because of these close relations with chemical instruments, the fundamentals of electronics form an integral part of any treatment of instrumentation. Fortunately, modern electronics has developed in the direction of modularization. A variety of amplifiers and logic elements are available as low-cost plug-in units that can be used as building blocks for the construction of most of the electronic circuitry described in this book.

A short summary of those aspects of electronics pertinent to our main subject is given in Chap. 27. This may be studied separately if desired, or used as resource material to aid in a better understanding of the various instruments as they are treated.