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CHEMICAL INSTRUMENTATION: A SYSTEMATIC APPROACH THIRD EDITION

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PREFACE

In the 15 years since the second edition of *Chemical Instrumentation*, the field of chemical methods of analysis has seen tremendous change. Measurements themselves have altered: sampling procedures have become more versatile, reliable, and automated and statistical and chemometric methods are being increasingly applied in order to obtain more information. In instruments, computers have become integral to the majority of models, advanced instruments increasingly are modular, and new sources such as lasers and new detectors such as photodiode arrays have come into more general use. Consequently, most established techniques have changed in methodology, instrumentation, and types of application. A parallel development has been that the central role of analytical chemistry in chemical measurements has been acknowledged.*

For the third edition of this book the goals have been to reflect these developments, include additional techniques, and present electroanalytical and column chromatographic methods more fully and authoritatively. In working toward these aims virtually all chapters in the second edition have been extensively revised. I have also developed new chapters and asked colleagues to write in other areas. The new chapters cover the following topics:

Microprocessors and microcomputers (Chapter 6)
Statistical control of measurement quality (Chapter 10)
Quantifying measurements and extracting information (Chapter 11)
X-ray fluorescence spectrometry (Chapter 21)
Surface spectrometric techniques (Chapter 22)
High performance liquid chromatography (Chapter 26)

Colleagues have contributed in several areas. Chapters 24–26 on chromatographic methods (Chapter 31, 2nd ed.) were written under the supervision of Dr. Ray P. W. Scott, who has recently retired as Director of Research, Perkin-Elmer Co. He wrote the chapter on chromatographic theory, and two of his colleagues, Dr. Kenneth Ogan and Mr. John D. Walters, wrote those on high performance liquid chromatography and gas chromatography, respectively. It has been especially satisfy-

ing to have the strong contributions of my co-author, Professor William R. Heineman of the University of Cincinnati, in the electroanalytical chemistry chapters, Chapters 27–30 (Chapters 23–26, 2nd ed.). Their fine contributions as well as the new chapters greatly improve the quality of coverage of principal analytical methods.

Some chapters of the second edition have also been omitted and others condensed or consolidated. One major concession to length was reluctantly made, the omission of the chapter on nuclear magnetic resonance spectrometry. With the advent of a bevy of high-powered nmr methods mainly applied through software, this technique has seemed best left to monographs primarily for organic chemists.

In first developing this text, I was guided by the conviction that the modern methods of analytical chemistry that are used in analysis and research can best be mastered if chemical instrumentation is studied in its own right. Accordingly, after beginning with a critical examination of the process of measurement, this book turns to a systematic treatment of instrument *design* and instrumental *methods*. The adequate consideration of the first theme has dictated the strong undercurrent of physics, engineering, and physical chemistry that is evident on inspection of this book. These disciplines provide the fundamentals that are needed to understand design and function. The pursuit of the second theme, modern methods of analytical chemistry, has required a running discussion of physical properties and behavior throughout. Throughout the book the emphasis is on fundamentals. Above all, as both author and editor, I have aimed for a good balance between physical theory and design on the one hand, and chemical theory and methods on the other.

Because one focus is on instrumentation, a substantial amount of physical theory has been introduced, much of it through the sections Basic Electronics, Basic Optics, and Basic Quantification, that comprise the early part of this volume. The first section, Chapters 2–6, deals with basic electricity and electronics and microprocessors/microcomputers. These chapters furnish background for discussion of the processing and electronic aspects of instrumentation and electroanalytical instruments. In the section on basic optics, Chapter 7 deals principally with physical optics, Chapter 8 with optical sources and detectors, and Chapter 9 with monochromators and polychromators. This group of chapters sets the stage for dealing with optical spectrometric methods. The last basic division, Chapters 10–12, is new and introduces theory on statistical assessment of error, ways of quantifying measurements to extract information, and signal/noise considerations. This block of chapters was written in response to a consensus reached at a June 1982 curriculum workshop that instrumentation should always be introduced along with the general statistical and mathematical aspects of measurement.*

Although the later chapters on specific techniques are largely complete in themselves, it is not intended that they be studied without the collateral or prior reading of the appropriate parts of chapters in the basic sections, or without some accom-

*Workshop on Instrumentation in the Undergraduate Chemistry Curriculum sponsored by the NSF Project, Scientific Instrumentation Information Network and Curricula, in June 1982 in Lexington, VA, directed by Prof. Frank A. Settle, Jr.

panying laboratory experiments or at least study of manufacturers' brochures on instruments. It is hoped that the cross referencing ensures that the reader who begins a study with any one of the methods is promptly directed to pertinent background theory. The index may also be used to facilitate reference to background.

While the graduate-advanced-senior-level approach of the second edition has been retained, a serious effort has been made to improve the tutorial quality of the text by increasing the quality and range of difficulty of worked-out examples and providing a good selection of exercises at the ends of chapters. The modular approach to instrumentation initiated in the first edition and strengthened in the second has now been sufficiently developed that it is the integrating structure for the book. This approach helps the instrument user to understand:

- How an instrument operates and how particular module(s) determine overall performance and specifications.
- Limitations to measurement that grow out of instrument and measurement design.
- Criteria by which one can select the model of instrument that will yield the desired measurements.
- Criteria by which one can select appropriate modules to build an instrument for research uses.

In addition, the value of this modular approach to instrumentation is that it takes one basic way of looking at instruments in many different fields and, by repeatedly applying this perspective, it teaches the reader a skill, how to look at a new instrument with comprehension. This consistent perspective is often absent elsewhere. For example, manufacturers seldom describe how their instruments carry out measurements and tend to stress data acquisition and computer-related aspects.

STYLE AND NOMENCLATURE

Information that is more esoteric (either more advanced or more technical) is presented in smaller type to indicate that it is for a special audience. Worked out examples continue to be set in smaller type.

Most *references* appear in footnotes, or when cited in examples, in the body of the example. Those references that are valuable as a general bibliography have been numbered and collected at the end of each chapter; some of them are cited in the text by number.

Choices in *nomenclature* were made on the basis of good usage and elegance. Thus, the term *analyte* is employed throughout rather than the somewhat wordy "substance of interest." Similarly, the terms *quantify* and *quantification* are used to refer to processes in which amounts or concentrations of substances are measured rather than "quantitate" and "quantitation" since the latter terms appear to ignore accepted routes of derivation of new words. In addition, *interferent* is used to identify any nonanalyte that affects a measurement.

ACKNOWLEDGMENTS

I especially appreciated having Bill Heineman join me as co-author. At the outset we talked at length about the content and emphasis of the third edition and ways to make the text more valuable to users. His ideas have been valuable at many points. As he gradually became busier, however, he had to limit his contribution to writing lucidly on electroanalytical methods.

Of the several others who have contributed advice, I especially thank Charles H. Lochmüller for his significant help in organizing the chromatography section, for his reading of first drafts of those chapters and commenting on them critically, and for simulating conversational advice at many stages as the chapters came to their final form. Peter C. Jurs helped by reading a late draft of Chapter 6 and recommending useful changes. Richard MacPhail read the section on lasers and provided good advice. George R. Dubay read through the mass spectrometry chapter and made suggestions about nomenclature and additional points that could be raised.

Darrel R. Wilder was kind enough to develop exercises for many chapters as well as answers, and John F. O'Keefe helped with some new exercises for the chapter on Raman spectrometry. And finally, I want to acknowledge the significant feedback from the many graduate students who used early versions of the electronics chapters and to undergraduates who used early versions of parts of Chapters 10 and 11. Student questions and suggestions helped materially in improving the approach and readability of the material. I wish also to acknowledge the real contribution of my wife, Shirley, for her forbearance during the long period of preparation of the third edition. Last, but not least, I am grateful to the many secretaries who were kind enough to enter original dictation in the wordprocessor and also to enter changes as editing occurred.

Bill Heineman wishes to acknowledge his indebtedness to John Kirchhoff and Hendrik Emons for reading Chapters 27–30 and commenting thereon, to Barbara Stallmeyer for typing these chapters, and to his wife, Linda.

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Durham, North Carolina
March 1988

PREFACE TO THE SECOND EDITION

Twelve years have passed since the appearance of the first edition of *Chemical Instrumentation*. Since the second edition represents a substantial rewriting, its main aspects deserve comment: its scope and aims, the ways in which the book has changed in response to developments in techniques and instrumentation, and some of the possibilities foreseen for use of this edition in courses.

Though a major revision has been carried out, the scope and aims of the book remain essentially the same. The volume treats a large number of the spectrometric, electrometric, and other physical methods that are important to chemists. What is lost by the omission of certain techniques (the book is long already) has—it is hoped—been compensated by the adoption of a consistent point of view.

The basic goal of the book is to offer a broad coverage of physical methods. The text reflects the conviction that such methods can best be mastered if the instrumentation necessary to measurement is studied in its own right. Thus equal emphasis is given to measurement principles and instrument design on the one hand and to techniques and their underlying theory on the other. The basic aim has also seemed best served by a semiquantitative approach, that is, by introducing mathematical expressions where necessary for good understanding but omitting most derivations of equations.

The other major goal is the development of a working mastery of the measurement process itself. It is easiest to describe the goal by suggesting criteria by which a working grasp can be recognized. Some of them are (a) facility in using instruments similar to or related to those one has studied; (b) an ability to devise and apply appropriate criteria for choosing an instrument (or a technique) for measurements on a given system; (c) facility in appreciating and mastering kinds of measurements that are unfamiliar. This aim has seemed best achieved by use of a modular approach* to instrumentation, a point that will be discussed below.

The second aim is actually also related to the time dimension of chemical measurement. One's grasp of physical methods must be sufficient to allow him to cope with the stream of new or modified instruments and techniques that appears. The questions that one must answer satisfactorily are: "What advantage(s) does the new instrument or technique offer over the present one?" and "How can the new

*A module is a subassembly or part that performs a particular function. Some examples are dc power supplies, monochromators, detectors, and amplifiers. When a modular point of view is taken, an instrument is represented by a block diagram.

device best be utilized in determinations of interest to me?'' Answering the queries should be a straightforward process, though not always an easy one, given a good grounding in measurement and techniques.

How does the second edition differ from the first? In the years that have elapsed since the publication of the first edition, there have been major changes in the field of measurement and analysis. Three of the most visible are (a) the well-nigh complete shift of electronics from vacuum tubes to semiconductor devices, (b) the increasing development of automatic instruments and tie-ins between instruments and computers, and (c) a growing acceptance of a modular or a ''systems'' view of instruments. All of these changes are reflected in this edition. Several chapters are given over to solid state electronics, and the older tube electronics is virtually excluded. Both automation and computer control are treated briefly and generally as they relate to instrument design. This discussion will be found in the parts of Chapters 1, 3, 9, and 17 that deal with the systems aspects of instruments. For reasons of brevity and because of rapid development in the field, little attempt is made to deal with automation and computer control in the discussion of individual instruments.

As noted above, a modular view of instrument design and function has been adopted. Its advantages deserve fuller comment. One is that it effects an economy both for the author and the reader. Modules are treated separately in early chapters where their characteristics can be explored with appropriate rigor and the most important different forms can be described and compared. Later, in chapters on techniques block diagrams are used for a particular instrument to show the modules that make it up and the pattern in which they are linked. For example, monochromators, optical sources, and detectors are discussed in Chapters 11 and 12, and the building up of spectrometers of various types is treated in Chapters 13–18, which deal with various spectroscopic methods. When an instrument is discussed, suitable choices of modules for it are suggested through examples and sometimes also through exercises at the ends of chapters. A very few modules that are peculiar to a single technique, such as burner-nebulizers in flame spectrometry, are discussed in chapters on techniques.

Some other advantages of a modular approach accrue to the instrument user. The most important is that he can understand an instrument on a ''macroscopic'' level. The types of components that make it up and their function can be perceived without the necessity of mastering a mass of detail. Further, manufacturer's specifications tend to become more intelligible since many aspects of the performance of an instrument are determined by the quality of particular modules. For example, the resolution of a spectrophotometer is mainly determined by the quality of its wavelength isolation device. A third advantage is that a ''systems'' approach is feasible. As a result, it becomes a fairly straightforward process to propose ways to optimize one or another aspect of instrument behavior, e.g., sensitivity, or to adapt it to new measurement situations.

The reader familiar with the first edition will observe other changes as well. He will find that the treatment of several topics has been expanded to chapter length (fluorometry, flame spectrometry, Raman spectrometry, and chromatography) and

several new topics are included (NMR spectrometry, single sweep and pulse polarography, mass spectrometry, operational amplifiers, signal-to-noise optimization, digital electronics, and monochromators). Further, the theoretical background of most measurement techniques is presented in greater depth. Finally, SI notation and units have been generally adopted (see Appendix C).

As a result of the way the book has been revised, the second edition can be used in at least three kinds of courses:

1. A junior–senior analytical chemistry course emphasizing physical methods. An appropriate selection of material would be Chapter 1, followed by chapters selected from the blocks 13 through 16 and 18 through 31. The index should prove helpful in locating pertinent analytical information. In such a course it is recommended that a problem book appropriate to the aims of the particular course be used also.

2. A senior or first-year graduate course in instrumentation that stresses electronics and electrical methods. Appropriate material would be Chapters 1 through 9, 23, and chapters selected from the block 24 through 28. Chapter 19 and perhaps also Chapter 17 could be included.

3. A senior or first-year graduate course in instrumentation that treats optical and spectral methods. Appropriate material would be Chapters 1 and 8, 10 through 12, 17, and chapters selected from the blocks 13 through 16 and 20 through 22. Selected sections from Chapter 2 through 7 could be included.

When used in courses the book will need to be supplemented by a laboratory manual. Since courses in modern analysis and instrumentation differ appreciably in aim and scope from school to school, it seemed wise to omit laboratory experiments from this edition. The teacher is accordingly referred to the many fine laboratory manuals that have appeared in the past several years. Some are the following:

1. C. N. Reilley and D. T. Sawyer, *Experiments for Instrumental Methods*. New York: McGraw-Hill, 1961.
2. L. P. Morgenthaler, *Basic Operational Amplifier Circuits for Analytical Chemical Instrumentation*, 2nd ed. Danville, Calif.: McKee-Pedersen Instruments, 1968.
3. G. G. Guilbault and L. G. Hargis, *Instrumental Analysis Manual*. New York: Marcel Dekker, 1970.
4. A. James Diefenderfer, *Basic Techniques of Electronic Instrumentation*. Philadelphia: Saunders, 1972.
5. C. E. Meloan and R. W. Kiser, *Problems and Experiments in Instrumental Analysis*. Columbus, Ohio: C. E. Merrill, 1963.
6. R. W. Hannah and J. S. Swinehart, *Experiments in Techniques of Infrared Spectroscopy*, rev. ed. Norwalk, Conn.: Perkin-Elmer, 1968.
7. Issues of *Journal of Chemical Education* (this journal publishes suitable experiments from time to time).

The teacher will also wish to know that names of manufacturers of a particular type of instrument have been omitted in this edition. Now there is at least one instrument listing that appears annually, an August issue of *Analytical Chemistry*, entitled "Laboratory Guide." Usually a late fall issue of *Science*, "Guide to Scientific Instruments," is also published. These compilations are up-to-date and inclusive, and instruments appear to be classified with care.

An annotated bibliography of important references appears at the end of each chapter. An additional collection of references too recent to be listed there has been organized in the same way and appears in Appendix D. Both listings should be consulted.

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I especially thank two colleagues—Dr. Maurice Bursey and Dr. Charles H. Lochmüller—for writing Chapters 30 and 31 on mass spectrometry and chromatography, respectively. Their share in this enterprise is considerable.

In addition, I am grateful to the host of authors from whose works I have learned. The group numbers too many to name, but they are acknowledged in the many references at the ends of chapters.

I thank sincerely Drs. Leon N. Klatt and John T. Bowman for reading and commenting on the entire manuscript. Warm appreciation is also due to Dr. Marvin M. Crutchfield, who performed the same function for the chapter on nuclear magnetic resonance spectrometry, to Gray F. Crouse, who assisted greatly in the preparation of illustrations, to many students, who after using some of these chapters in preliminary draft, offered criticism and thoughtful suggestions, to Cathy Penny, Gloria Powers, and Sandy Parker for typing the numerous drafts and the final manuscript, and to Scott A. Miller for his generous assistance in reading proof.

Finally, I solicit the assistance of readers of this book in identifying errors and in offering suggestions.

H.A.S.

Leicester, England
March 1972

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