Preface

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As currently taught, the introductory course in analytical chemistry emphasizes quantitative (and sometimes qualitative) methods of analysis coupled with a heavy dose of equilibrium chemistry. Analytical chemistry, however, is more than equilibrium chemistry and a collection of analytical methods; it is an approach to solving chemical problems. Although discussing different methods is important, that discussion should not come at the expense of other equally important topics. The introductory analytical course is the ideal place in the chemistry curriculum to explore topics such as experimental design, sampling, calibration strategies, standardization, optimization, statistics, and the validation of experimental results. These topics are important in developing good experimental protocols, and in interpreting experimental results. If chemistry is truly an experimental science, then it is essential that all chemistry students understand how these topics relate to the experiments they conduct in other chemistry courses.

Currently available textbooks do a good job of covering the diverse range of wet and instrumental analysis techniques available to chemists. Although there is some disagreement about the proper balance between wet analytical techniques, such as gravimetry and titrimetry, and instrumental analysis techniques, such as spectrophotometry, all currently available textbooks cover a reasonable variety of techniques. These textbooks, however, neglect, or give only brief consideration to, obtaining representative samples, handling interferents, optimizing methods, analyzing data, validating data, and ensuring that data are collected under a state of statistical control.

In preparing this textbook, I have tried to find a more appropriate balance between theory and practice, between "classical" and "modern" methods of analysis, between analyzing samples and collecting and preparing samples for analysis, and between analytical methods and data analysis. Clearly, the amount of material in this textbook exceeds what can be covered in a single semester; it's my hope, however, that the diversity of topics will meet the needs of different instructors, while, perhaps, suggesting some new topics to cover.

The anticipated audience for this textbook includes students majoring in chemistry, and students majoring in other science disciplines (biology, biochemistry, environmental science, engineering, and geology, to name a few), interested in obtaining a stronger background in chemical analysis. It is particularly appropriate for chemistry majors who are not planning to attend graduate school, and who often do not enroll in those advanced courses in analytical chemistry that require physical chemistry as a pre-requisite. Prior coursework of a year of general chemistry is assumed. Competence in algebra is essential; calculus is used on occasion, however, its presence is not essential to the material's treatment.

Key Features of This Textbook

Key features set this textbook apart from others currently available.

- *A stronger emphasis on the evaluation of data.* Methods for characterizing chemical measurements, results, and errors (including the propagation of errors) are included. Both the binomial distribution and normal distribution are presented, and the idea of a confidence interval is developed. Statistical methods for evaluating data include the *t*-test (both for paired and unpaired data), the *F*-test, and the treatment of outliers. Detection limits also are discussed from a statistical perspective. Other statistical methods, such as ANOVA and ruggedness testing, are presented in later chapters.
- *Standardizations and calibrations are treated in a single chapter.* Selecting the most appropriate calibration method is important and, for this reason, the methods of external standards, standard additions, and internal standards are gathered together in a single chapter. A discussion of curve-fitting, including the statistical basis for linear regression (with and without weighting) also is included in this chapter.
- *More attention to selecting and obtaining a representative sample.* The design of a statistically based sampling plan and its implementation are discussed earlier, and in more detail than in other textbooks. Topics that are covered include how to obtain a representative sample, how much sample to collect, how many samples to collect, how to minimize the overall variance for an analytical method, tools for collecting samples, and sample preservation.
- *The importance of minimizing interferents is emphasized.* Commonly used methods for separating interferents from analytes, such as distillation, masking, and solvent extraction, are gathered together in a single chapter.
- *Balanced coverage of analytical techniques.* The six areas of analytical techniques—gravimetry, titrimetry, spectroscopy, electrochemistry, chromatography, and kinetics—receive roughly equivalent coverage, meeting the needs of instructors wishing to emphasize wet methods and those emphasizing instrumental methods. Related methods are gathered together in a single chapter encouraging students to see the similarities between methods, rather than focusing on their differences.
- *An emphasis on practical applications.* Throughout the text applications from organic chemistry, inorganic chemistry, environmental chemistry, clinical chemistry, and biochemistry are used in worked examples, representative methods, and end-of-chapter problems.
- *Representative methods link theory with practice.* An important feature of this text is the presentation of representative methods. These boxed features present typical analytical procedures in a format that encourages students to think about why the procedure is designed as it is.
- *Separate chapters on developing a standard method and quality assurance.* Two chapters provide coverage of methods used in developing a standard method of analysis, and quality assurance. The chapter on developing a standard method includes topics such as optimizing experimental conditions using response surfaces, verifying the method through the blind analysis of standard samples and ruggedness testing, and collaborative testing using Youden's two-sample approach and ANOVA. The chapter on quality assurance covers quality control and internal and external techniques for quality assessment, including the use of duplicate samples, blanks, spike recoveries, and control charts.

- *Problems adapted from the literature.* Many of the in-chapter examples and end-of-chapter problems are based on data from the analytical literature, providing students with practical examples of current research in analytical chemistry.
- *An emphasis on critical thinking.* Critical thinking is encouraged through problems in which students are asked to explain why certain steps in an analytical procedure are included, or to determine the effect of an experimental error on the results of an analysis.
- *Suggested experiments from the Journal of Chemical Education.* Rather than including a short collection of experiments emphasizing the analysis of standard unknowns, an annotated list of representative experiments from the *Journal of Chemical Education* is included at the conclusion of most chapters. These experiments may serve as stand alone experiments, or as starting points for individual or group projects.

The Role of Equilibrium Chemistry in Analytical Chemistry

Equilibrium chemistry often receives a significant emphasis in the introductory analytical chemistry course. While an important topic, its overemphasis can cause students to confuse analytical chemistry with equilibrium chemistry. Although attention to solving equilibrium problems is important, it is equally important for students to recognize when such calculations are impractical, or when a simpler, more qualitative approach is all that is needed. For example, in discussing the gravimetric analysis of Ag^+ as AgCl, there is little point in calculating the equilibrium solubility of AgCl since the concentration of Cl^- at equilibrium is rarely known. It is important, however, to qualitatively understand that a large excess of Cl^- increases the solubility of AgCl due to the formation of soluble silver-chloro complexes. Balancing the presentation of a rigorous approach to solving equilibrium problems, this text also introduces the use of ladder diagrams as a means for providing a qualitative picture of a system at equilibrium. Students are encouraged to use the approach best suited to the problem at hand.

Computer Software

Many of the topics covered in analytical chemistry benefit from the availability of appropriate computer software. In preparing this text, however, I made a conscious decision to avoid a presentation tied to a single computer platform or software package. Students and faculty are increasingly experienced in the use of computers, spreadsheets, and data analysis software; their use is, I think, best left to the personal choice of each student and instructor.

Organization

The textbook's organization can be divided into four parts. Chapters 1–3 serve as an introduction, providing an overview of analytical chemistry (Chapter 1); a review of the basic tools of analytical chemistry, including significant figures, units, and stoichiometry (Chapter 2); and an introduction to the terminology used by analytical chemists (Chapter 3). Familiarity with the material in these chapters is assumed throughout the remainder of the text.

Chapters 4–7 cover a number of topics that are important in understanding how a particular analytical method works. Later chapters are mostly independent of the material in these chapters. Instructors may pick and choose from among the topics

of these chapters, as needed, to support individual course goals. The statistical analysis of data is covered in Chapter 4 at a level that is more complete than that found in other introductory analytical textbooks. Methods for calibrating equipment, standardizing methods, and linear regression are gathered together in Chapter 5. Chapter 6 provides an introduction to equilibrium chemistry, stressing both the rigorous solution to equilibrium problems, and the use of semi-quantitative approaches, such as ladder diagrams. The importance of collecting the right sample, and methods for separating analytes and interferents are covered in Chapter 7.

Chapters 8–13 cover the major areas of analysis, including gravimetry (Chapter 8), titrimetry (Chapter 9), spectroscopy (Chapter 10), electrochemistry (Chapter 11), chromatography and electrophoresis (Chapter 12), and kinetic methods (Chapter 13). Related techniques, such as acid–base titrimetry and redox titrimetry, or potentiometry and voltammetry, are gathered together in single chapters. Combining related techniques together encourages students to see the similarities between methods, rather than focusing on their differences. The first technique presented in each chapter is generally that which is most commonly covered in the introductory course.

Finally, the textbook concludes with two chapters discussing the design and maintenance of analytical methods, two topics of importance to analytical chemists. Chapter 14 considers the development of an analytical method, including its optimization, verification, and validation. Quality control and quality assessment are discussed in Chapter 15.

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David Ballantine
Northern Illinois University

John E. Bauer
Illinois State University

Ali Bazzi
University of Michigan–Dearborn

Steven D. Brown
University of Delaware

Wendy Clevenger
University of Tennessee–Chattanooga

Cathy Cobb
Augusta State University

Paul Flowers
University of North Carolina–Pembroke

Nancy Gordon
University of Southern Maine

Virginia M. Indivero
Swarthmore College

Michael Janusa
Nicholls State University

J. David Jenkins
Georgia Southern University

Richard S. Mitchell
Arkansas State University

George A. Pearse, Jr.
Le Moyne College

Gary Rayson
New Mexico State University

David Redfield
NW Nazarene University

Vincent Remcho
West Virginia University

Jeanette K. Rice
Georgia Southern University

Martin W. Rowe
Texas A&M University

Alexander Scheeline
University of Illinois

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How to Contact the Author

Writing this textbook has been an interesting (and exhausting) challenge. Despite my efforts, I am sure there are a few glitches, better examples, more interesting end-of-chapter problems, and better ways to think about some of the topics. I welcome your comments, suggestions, and data for interesting problems, which may be addressed to me at DePauw University, 602 S. College St., Greencastle, IN 46135, or electronically at harvey@depauw.edu.