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Edition

# Analytical Chemistry

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# ANALYTICAL CHEMISTRY

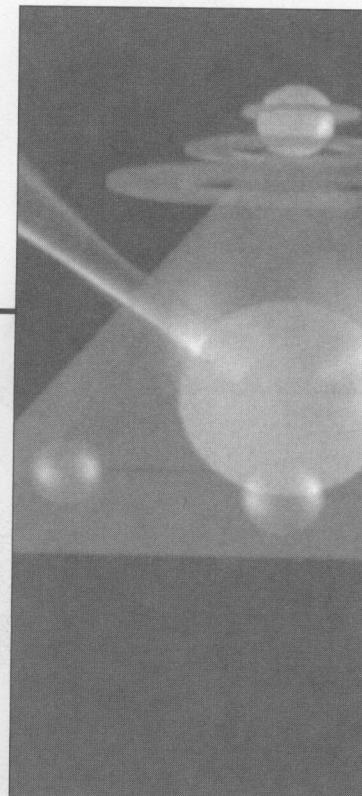
Sixth Edition

Gary D. Christian

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To

Sue—for decades of joy and for her amazing grandmothering  
Tanya and Taffy—for the sunshine they bring in our lives

"Teachers open the door, but it is up to you to walk through it." — Albert Einstein

Dr. Charles E. Sorenson grew up in Oregon and has had a lifelong interest in teaching. He earned his B.S. degree from the University of Oregon and his M.S. degree from the University of Maryland, where he earned an appreciation of the excitement of research from his mentor, Bill Furb. He began his career as a research analyst at the Naval Research Laboratory, where he developed an interest in chemical and biochemical chemistry. He joined the University of Kentucky in 1967 and in 1975 moved to the University of Washington. He was Divisional Head of Sciences during 1993-2001.

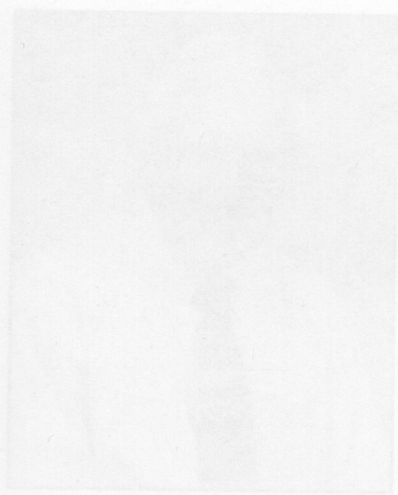
Dr. Sorenson worked the first edition of this book in 1971. He is the author of over 200 research papers and has authored five other books, including *Analytical Chemistry: A Practical Approach*, and *How to Write a Thesis*. He has a strong interest in the interdisciplinary nature of chemistry, and has been a member of the American Chemical Society (ACS) Division of Analytical Chemistry since 1971. He was a recipient of the ACS Division of Analytical Chemistry Award for Excellence in Teaching and the ACS Fisher Award in Analytical Chemistry, a top recognition for contributions in analytical chemistry. He was a Fulbright Scholar and received the Lammie Gold Medal, University of Kentucky, and the University of Washington Commemorative Medal, and has been a recipient of the ACS Division of Analytical Chemistry Award for Excellence in Research. He is joint editor-in-chief of *Journal of Analytical Chemistry*, an international journal of analytical chemistry, and serves on the editorial boards of numerous other journals. He served as Chairman of the ACS Division of Analytical Chemistry.

Dr. Sorenson chaired preparation of the ACS Examination on Analytical Chemistry and was a preparer for the Chemistry Test for the GRE. He was a member of the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Pure and Applied Chemistry (IUPAC) Commission on Analytical Chemistry. He is a member of the American Chemical Society, the Society for Applied Spectroscopy, the Society for Environmental Chemistry, and the Society for Environmental Chemistry. He is currently living in Seattle, Washington, with his wife of 11 years, Sue, and their two children, Tanya and Taffy.

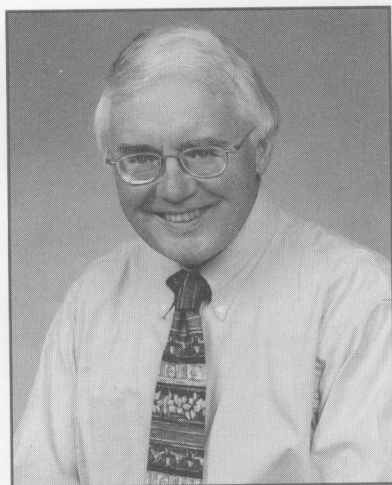
Dr. Sorenson designed this book for both courses. He thought it would be interesting to you that are not formally covered. They can certainly serve as a reference in the future.

## WHAT IS THE SAME?

This sixth edition of *Analytical Chemistry* is extensively revised and updated (more on that below), but many features from previous editions remain. Each chapter is



## About the Author



**G**ary Christian grew up in Oregon and has had a lifelong interest in teaching, inspired by a great high school science teacher in a rural school, Harald Platou. He received his B.S. degree from the University of Oregon and Ph.D. degree from the University of Maryland, where he gained an appreciation of the excitement of research from his mentor, Bill Purdy. He began his career as a research analytical chemist at Walter Reed Army Institute of Research, where he developed an interest in clinical and bioanalytical chemistry. He joined the University of Kentucky in 1967 and in 1972 moved to the University of Washington. He was Divisional Dean of Sciences during 1993–2001.

Gary wrote the first edition of this book in 1971. He is the author of over 300 research papers and has authored five other books, including *Instrumental Analysis*. His research interests include electroanalytical chemistry, atomic spectroscopy, process analysis, and flow injection analysis.

He was recipient of the American Chemical Society (ACS) Division of Analytical Chemistry Award for Excellence in Teaching and the ACS Fisher Award in Analytical Chemistry, a top recognition for contributions in analytical chemistry. He was a Fulbright Scholar and received the Talanta Gold Medal, Université Libre de Bruxelles Medal of Honor, Charles University Commemorative Medal, and University of Ghent Honorary Certificate of Research. He is joint editor-in-chief of *Talanta*, an international journal of analytical chemistry, and serves on the editorial boards of numerous other journals. He served as Chairman of the ACS Division of Analytical Chemistry.

Gary chaired preparation of the ACS Examination on Analytical Chemistry and was a preparer for the Chemistry Test for the GRE. He was a member of the team that prepared the exam for the International Chemistry Olympiad when it was held in the United States. He is a member of the American Chemical Society, Society for Applied Spectroscopy, Spectroscopy Society of Canada, and Society for Electroanalytical Chemistry.

Gary lives in Medina, Washington, with his wife of 41 years, Sue, and their wonderful granddaughters, Tanya and Taffy.

# Preface

*"Teachers open the door, but it is up to you to enter"* —Anonymous

**A**nalytical chemistry is concerned with the chemical characterization of matter, both qualitative and quantitative. It is important in nearly every aspect of our lives because chemicals make up everything we use. The late Charles N. Reilley said "analytical chemistry is what analytical chemists do." You will learn in this text what they do.

This text is designed for college students majoring in chemistry and fields related to chemistry. It deals with the principles and techniques of quantitative analysis, that is, how to determine how much of a specific substance is contained in a sample. You will learn how to design an analytical method, based on what information is needed, how to obtain a laboratory sample that is representative of the whole, how to prepare it for analysis, what measurement tools are available, and the statistical significance of the analysis. Chapters 24–26 illustrate applications of techniques you have learned to the fields of clinical chemistry, genomics and proteomics, and environmental sampling and analysis.

Examples of the use of analytical chemistry techniques are drawn from such areas as life sciences, clinical chemistry, air and water pollution, and industrial analyses. Analytical chemistry becomes meaningful when you realize that an incorrect blood analysis may endanger a patient's life, or that an error in quality control analysis may result in serious financial loss for a manufacturer. Millions of dollars are saved in the chemical industry by performing on-line automated analyses of chemical processes, to assure maximum efficiency in chemical production.

## WHO SHOULD USE THIS TEXT?

The text is written for an undergraduate quantitative analysis course. It necessarily contains more material than normally can be covered in a one-semester or one-quarter course, so that your instructor can select those topics deemed most important. Some of the remaining sections may serve as supplemental material. Depending on how a quantitative analysis and instrumental analysis sequence is designed, it could serve for both courses. In any event, I hope you will take time to read some sections that look interesting to you that are not formally covered. They can certainly serve as a reference in the future.

## WHAT IS THE SAME?

This sixth edition of *Analytical Chemistry* is extensively revised and updated (more on that below), but many features from previous editions remain. Each chapter is

introduced with a summary paragraph that lists the topics to be covered, giving you a broad overview of each subject. **Boldface type** is used for key terms, and important equations are boxed to aid in review. *Margin notes* are generously used to further emphasize important concepts and aid in review.

Dimensional analysis is emphasized throughout to give you a better feel for the proper setting up of problems. SI units or symbols (e.g., L, mL, mol, and s) are used throughout. The concept of normality and equivalents is introduced, but emphasis remains on the use of molarity and moles. The presentation of normality is done in a way that allows it to be ignored if your instructor chooses not to assign it.

Problems and Recommended References are grouped by topic, for ease in assignment. References have been extensively updated, and numerous new problems added. There are 673 questions and problems for you to practice answering (there is Solutions Manual for these—see below).

A number of new topics were introduced in the prior edition, and most remain as important features of the text. Some are:

- Statistics of small sets of data
- Statistics of sampling
- Systematic approach to equilibrium calculations (mass and charge balance)
- Heterogeneous equilibria
- Logarithmic diagrams for describing multiple equilibria species (the preparation of these using spreadsheets is now introduced)
- Diode array spectrometers
- Fourier transform infrared spectroscopy
- Near-IR spectroscopy
- Fiber-optic sensors
- Gas chromatography–mass spectrometry

## WHAT IS CHANGED?

Some chapters have been reordered to better tie together related topics. The chapter on basic tools and operations in analytical chemistry has been moved to the front of the text (Chapter 2), at the suggestion of a number of users. Different sections of it can be assigned by your instructor as needed for the laboratory. The chapter on gravimetric analysis and precipitation equilibria (Chapter 10) has been moved to just before the one on precipitation reactions and titrations, which better aligns these related topics.

Chromatography, a major analytical tool for analyzing mixtures of analytes, has undergone significant growth in recent years, with improved capabilities, and so the coverage of chromatographic techniques has been expanded and updated, comprising three chapters on principles of chromatography, gas chromatography, and liquid chromatography (Chapters 19–21). Older techniques such as paper chromatography have been deleted.

## WHAT IS NEW?

This revision follows publication of the fifth edition of *Analytical Chemistry* by nearly a decade, a result of being a dean too long! Much has changed in that time. This sixth edition presents a number of new topics, new chapters, and changes in presentation. Major additions include:

- Color added to the text, for a more pleasing layout
- Spreadsheets (using Excel) introduced and used throughout the text for performing computations, statistical analysis, and graphing.

Many titration curves are derived using spreadsheets, as are the calculations of  $\alpha$ -values and plots of  $\alpha$ -pH curves, and of logarithm concentration diagrams. The spreadsheet presentations are given in a “user-friendly” fashion to make it easier for you to follow how they are set up. The way in which spreadsheet calculations are performed is by entering formulas in specific cells, e.g., cell B11 may contain a formula to calculate the ratio of numbers entered in cells A2 and A3, and the formula is (=A2/A3). The answer appears in cell B11 where the formula is entered. Cells that have formulas entered in them are **boldfaced**. Usually, you have to “reverse engineer” the cell entries to determine the equations from which they were derived, for example, the equation dividing one number by another to obtain the fraction. This is very awkward for complicated equations. To avoid this, the actual equations used for deriving the cell formulas are given in the documentation section below the spreadsheet setups; the formula to be entered in the identified cell number is given just below the equation. You will better understand and appreciate this when you begin studying the use of spreadsheets.

- New chapter on Good Laboratory Practice: Quality Assurance of Analytical Measurements

This aspect of the practice of analytical chemistry has become increasingly important as government agencies have established rather complex and stringent guidelines to assure that analytical measurements are accurate, for establishing or enforcing policy. Any budding analytical chemist will find that knowledge of these guidelines will be viewed favorably by an employer. This chapter serves as an introduction and reference to current practices, and includes:

- Validation of analytical methods
  - Quality assurance
  - Laboratory accreditation
  - Electronic records and electronic signatures (the new 21 CFR, Part 11 regulations)
- New chapter on Genomics and Proteomics

Analytical chemistry played a key role in the completion of the historic Human Genome Project. You should know what that is. The technologies have become routine for DNA sequencing of complex organisms, for forensic science, and so forth. We now move into the realm of protein profiling (proteomics), an even more challenging analytical endeavor, and an introduction to this emerging field is given. This chapter discusses:

- The Human Genome Project
- How genes are sequenced
- The polymerase chain reaction (PCR)
- DNA chips
- 2-D PAGE and MALDI-TOF for protein profiling

A number of new topics throughout the text include:

- Calibration of glassware
- Accelerated and microwave extraction and digestion
- Solid-state ISFET electrodes
- Spectral databases—web-based: commercial and free
- Solid-phase extraction (SPE) expanded; solid-phase microextraction (SPME)
- Chromatography nomenclature: IUPAC-recommended terms and symbols used
- Theory of chromatography column efficiency expanded
- Chromatography simulation software for method development
- Capillary gas chromatography (GC) columns: updated and expanded
- Headspace, thermal desorption, and purge and trap GC analysis
- Fast gas and liquid chromatography
- High performance liquid chromatography-mass spectrometry (HPLC-MS)
- Mass analyzers for GC-MS and LC-MS
- HPLC stationary phases updated; narrowbore columns for high sensitivity
- Capillary electrophoresis expanded; capillary electrochromatography

## EXPERIMENTS

There are 40 experiments illustrating most of the measurement techniques presented in your text. Experiments are grouped by topic. Each contains a description of the principles and chemical reactions involved, so you gain an overview of what is being analyzed and how. Solutions and reagents to prepare in advance of the experiment are listed, so experiments can be performed efficiently; your instructor will have prepared many of these. Experiments are designed where possible to avoid the use of asbestos, chloroform, carbon tetrachloride, or benzene, consistent with occupational health and safety. All experiments, particularly the volumetric ones, have been designed to minimize chemical waste by preparing the minimum volumes of reagents, like titrants, required to complete the experiment.

**Deleted.** Three experiments that use mercury have been deleted. The paper chromatography experiment is deleted because thin-layer chromatography is predominantly used in its place today. For space reasons, the presentation of catalytic methods and the corresponding experiment are deleted from the text in favor of enzymatic kinetic methods. Also, the anion chromatography separation of cobalt and nickel is omitted.

**New.** A new microscale titration experiment is included, provided by Professor John Richardson from Shippensburg State University, for the analysis of hard-water samples (Experiment 18). The tools and techniques used for that experiment could be used to design similar experiments for other titrations if desired. (If your instructor tries this with you, I may include your experiment in the next edition!) Two **team experiments** are added (Experiments 39 and 40) to illustrate the principles presented in Chapter 4 on statistical validation. One is on method validation and quality control, in which different members of teams perform different parts of the validation for a chosen experiment. The other is on proficiency testing, in which you calculate the  $z$ -values for all the student results of one or more class experiments and you compare your  $z$ -value to see how well you have performed.

**Spreadsheets.** You are encouraged (actually instructed) to use spreadsheets in your experiments to prepare calibration curves and to perform statistical analysis on your experimental results.

## CD-ROM

Your textbook includes a CD-ROM that contains useful supplemental material to complement the text. When opening the CD-ROM, click first on “Read me” for details of the contents. There are files on chapter auxiliary data, chapter spreadsheet figures, chapter text spreadsheets, laboratory apparatus, spreadsheet problem solutions, and website URLs. There are useful hints for using the spreadsheets.

## A WORD ABOUT WEBSITES

There are over 100 websites given throughout the text for access to useful supplemental material. I have heavy fingers when typing URLs, and the Web is unforgiving of typos. To efficiently access the websites, a list of all the URLs is posted on the Wiley website for your text, by chapter in order of appearance, including margin notes. You can use this list to access the websites without typing the URLs.

Click on the URL to open the site. If this does not work, copy it to your clipboard and then paste into your browser **Address** and then click on **Go** (or **Enter** on your keyboard). Sometimes a linked site won't open, but if you input just the homepage portion of the URL, you can open this and then link to the final URL. For company homepages, you may need to go to the Product link. Or try the site's search engine. Some URLs will change or be deleted with time. If you have trouble getting a website to open, or if it is changed, try going to a search engine, such as Google, and search for the company or topic.

## TEXT WEBSITE

John Wiley & Sons, Inc. maintains a website for *Analytical Chemistry* that contains additional supplemental material, which may be updated or added to from time to time. Any text errors that are noted will be posted on this site. Materials on the website include supplemental materials for different chapters that expand on abbreviated presentations in the text. Chapters from *The Encyclopedia of Analytical Chemistry* on “Literature Searching Methodology” and “Analytical Problem Solving: Selection of Analytical Methods” are included. The website URLs in the text are also listed on this site and may be updated. **All figures and tables in the text are posted on the website and can be downloaded for preparation of transparencies.** You may access the website at: [www.wiley.com/college/christian](http://www.wiley.com/college/christian).

## THANKS

The production of your text involved the assistance and expertise of numerous people. Special thanks go first to the users of the text who have contributed comments and suggestions for changes and improvements; these are always welcome. A number of colleagues served as reviewers of the text and manuscript and have aided immeasurably in providing specific suggestions for revision. They, naturally, express opposing views sometimes on a subject or placement of a chapter or section, but collectively have assured a near optimum outcome that I hope you find easy and enjoyable to read and study. Special mention goes to Professors Dennis Anjo (California State University at Long Beach), Kevin Chambliss (Baylor University),

Michael DeGrandpre (University of Montana), Jinmo Huang (The College of New Jersey), Ira Krull (Northeastern University), Gary Long and Harold McNair (Virginia Tech), Jody Redpenning (University of Nebraska), John Richardson and Thomas Schroeder (Shippensburg State University), Benjamin Rusiloski (Delaware State University), James Rybarczyk (Ball State University), Cheryl Klein Stevens (Xavier University of Louisiana), and Phillip Voegel (Midwestern State University). Professor Norman Dovichi (University of Washington) provided valuable input on Chapter 25 on genomics and proteomics. And thanks to Mack Carter for his computer wizardry, and Sheila Parker for helping keep my head above water.

The professionals at John Wiley & Sons have been responsible for producing a high-quality book. David Harris and Deborah Brennan, Acquisitions Editors, shepherded the process from beginning to end. Their assistant, Cathy Donovan, handled the whole review process and attended to many details. Elizabeth Swain was the production editor, arranging copyediting to printing. Sandra Rigby was the illustration editor responsible for the artwork in your text. Ernestine Franco at Pern Editorial Services was a real professional in copyediting the manuscript for a smooth printing. It has been a real pleasure working with this team and others in a long but rewarding process.

My wife and best friend, Sue, has been my strongest supporter during this two-year exercise. She kept the process on schedule by her efficient translation and typing of my scribbled handwritten pages. Thanks, thanks, thanks!

## SOLUTIONS MANUAL

A comprehensive solutions manual is available for use by instructors and students in which all problems are completely worked out and all questions are answered. Answers for spreadsheet problems, which include the spreadsheets, are given in your CD-ROM. Answers to even-numbered problems are given in Appendix F.

GARY D. CHRISTIAN

January, 2003

Seattle

*"To teach is to learn twice." —Joseph Joubert*

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