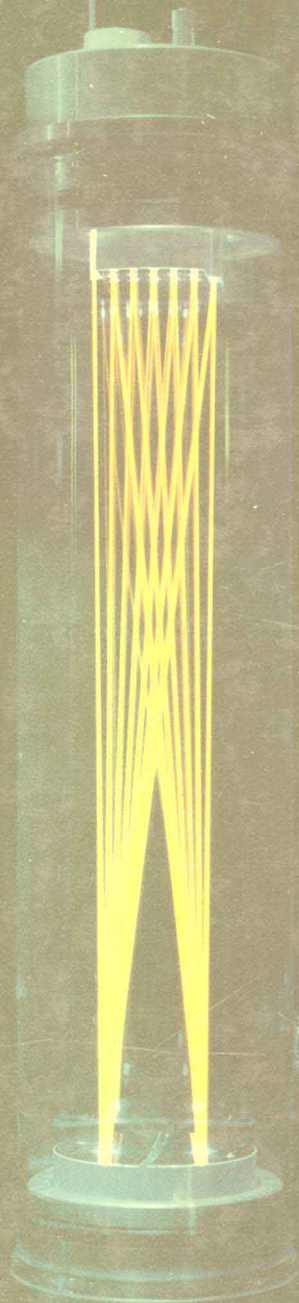


FUNDAMENTALS OF

# *Analytical Chemistry*

**Skoog  
West  
Holler**



*Fifth Edition*

008566  
FUNDAMENTALS OF

# **Analytical Chemistry**

FIFTH EDITION

DOUGLAS A. SKOOG

*Stanford University*

DONALD M. WEST

*San Jose State University*

F. JAMES HOLLER

*University of Kentucky*



*Saunders Golden Sunburst Series*

**Saunders College Publishing**

*New York Chicago San Francisco*

*Philadelphia Montreal Toronto*

*London Sydney Tokyo*

Copyrights © 1988, 1982, 1976, 1969, 1963 by W. B. Saunders Company

All rights reserved. No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopy, recording, or any information storage and retrieval system, without permission in writing from the publisher.

Requests for permission to make copies of any part of the work should be mailed to: Permissions, Holt, Rinehart and Winston, 111 Fifth Avenue, New York, New York 10003

Text Typeface: ITC New Baskerville  
Compositor: General Graphic Services  
Acquisitions Editor: John Vondeling  
Project Editor: Merry Post  
Copy Editor: Irene Nunes  
Art Director: Carol Bleistine  
Art Assistant: Doris Roessner  
Text Designer: Tracy Baldwin  
Cover Designer: Lawrence R. Didona  
Text Artwork: Larry Ward, Tom Mallon  
Production Manager: Harry Dean, Jr.  
Assistant Production Manager: Jo Ann Melody

Cover credit: A blue (488.0 nm) beam from an argon-ion laser enters a cell containing a minute quantity of  $\text{NO}_2$ , a brown gas found in smog. The beam, which is directed through the sample several times by mirrors, is absorbed by the  $\text{NO}_2$ . The gas subsequently fluoresces to give the bright orange color characteristic of  $\text{NO}_2$ . The intensity of the color is a measure of the concentration of the pollutant. This is a dramatic illustration of the very sensitive technique of laser-induced fluorescence, which is discussed in Chapter 20. The photo is courtesy of Professor Dennis J. Clouthier of the University of Kentucky.

Printed in the United States of America

Fundamentals of Analytical Chemistry, 5th edition

ISBN 0-03-14828-6

Library of Congress Catalog Card Number: 87-24411

## Preface

With the appearance of this edition—the fifth—*Fundamentals of Analytical Chemistry* enters its second quarter century as an introductory textbook on analytical chemistry designed primarily for a course for chemistry majors. During the lifetime of this text, the field of analytical chemistry has teemed with activity as never before: new instruments with previously unheard of sensitivities and selectivities have appeared; new methods for resolving the components of incredibly complex mixtures have been developed; and automation and computer control of the measurement process have become commonplace. Some of these developments have been incorporated in each new edition. Others have not, however, because the time allotted in most chemistry curricula for an introductory course in quantitative analysis is so limited.

In preparing each new edition, we have found ourselves facing the dilemma of what new developments to include and, equally important, what to delete from older editions to make space for the new. In making these decisions, we have adopted the general philosophy of avoiding superficiality by limiting the number of topics covered to those that we believe can be treated in sufficient depth so that the reader can develop a basic understanding of the principles upon which they are based.

Because disagreement is inevitable as to what topics should be included in an elementary analytical course, we have included more material than could possibly be covered in one or two semesters. We have tried to make chapters sufficiently independent so that some can be left out and the order of others changed without a loss in continuity. Thus, the text can be tailored to fit the tastes and prejudices of the individual instructor.

Much of the theoretical discussion in earlier editions of this text has centered on thermodynamics and the application of equilibrium calculations to analytical problems. With the appearance of automated instruments and the increasing importance of analytical methods for determining species of interest in medicine, biochemistry, and ecology, it is evident that a balanced analytical textbook must devote space not only to thermodynamic theory but also to the theory of reaction kinetics. Thus, the reader will find an entirely new chapter in this edition that deals with the kinetics and application of kinetic measurements in analytical chemistry.

Another significant change in this edition is the use of formula weights and molar concentrations in all volumetric calculations. The decision to abandon equivalent weights and normalities brings the text into line with current practice in most analytical journals. (We have, however, included a discussion of the use of normality and equivalent weight in Appendix 9.)

Other topics new to this edition include the operational definition of pH,

modern voltammetric techniques including pulse polarography and stripping methods, diode array detectors and multichannel spectroscopic instruments, dc plasma sources for atomic spectroscopy, flow injection methods, fused silica columns for capillary gas chromatography, supercritical-fluid chromatography, and electronic balances. We have also introduced a short section and a laboratory experiment involving a very old technique—weight titrations. With modern top-loading balances and plastic reagent dispensers, a weight titration can be carried out more efficiently and accurately than one based on volumetric measurements.

To provide space for these new topics, we have had to condense or delete several parts of earlier editions. Thus, we have reduced the number of laboratory experiments from 53 to 34. In addition, we have eliminated the chapter devoted to nonaqueous titrations and substituted a brief discussion of this subject in the chapter on applications of acid/base titrations. We have also omitted the discussion of the use of mercury(II) for complex formation titrations and shortened the discussions devoted to the theory of membrane electrodes and to the applications of oxidation/reduction titrations.

In addition to updating the text, we have extensively reorganized the introductory chapters in order to remove redundancies and to present the material in a more logical and concise way. To this end, we have integrated the material dealing with stoichiometry and chemical calculations into two early chapters (3 and 4) dealing with gravimetry and titrimetry (including weight titrimetry). Chapter 5 is devoted to aqueous solution chemistry including simple equilibrium calculations of all types and the use of activities and activity coefficients in such calculations. Chapter 6 extends the discussion of equilibrium to complex systems involving several competing reactions. The chapters that follow dealing with precipitation, neutralization, and complex formation titrations retain the organizational pattern of earlier editions. Many parts of these chapters have been rewritten to improve their clarity and readability, however.

The introductory chapter on oxidation/reduction equilibrium and electrochemical theory (Chapter 12) has been completely rewritten. In addition, the material on polarization phenomena has been moved to the chapter on coulometry where it first becomes of importance. We believe that these changes provide a clearer and more logical presentation of electrochemical theory that will make it more readily absorbed and understood by students. Chapter 15 on potentiometric methods has also undergone reorganization and extensive rewriting with a particular emphasis on clarification of the sign conventions that are used for indicator and reference electrodes.

The organization of the chapters dealing with spectroscopy, chromatography, and preliminary steps in an analysis are substantially the same as in earlier editions. Much of the material in these chapters has also been rewritten for clarity and readability.

The problem sets at the ends of chapters have all been rewritten and, in addition, sets of questions have been introduced. Answers to approximately half of the questions and problems are found at the end of the text. A solutions manual is also available for instructors, and about 60 to 70 transparencies have been developed for use in lectures.

We wish to acknowledge with thanks the comments and suggestions of the following who have reviewed the manuscript for this edition at various stages in its production: Professor John Ganchoff of Elmhurst College; Pro-



fessor Richard H. Hanson of the University of Arkansas at Little Rock; Professor T. J. Hauptert of California State University, Sacramento; Professor John L. Plude of University of Wisconsin, Oshkosh; and Professor Joseph J. Topping of Towson State University. We also wish to thank Professor Elizabeth W. Kleppinger of Berea College, who was kind enough to read page proofs for the first 11 chapters. In addition, we want to thank Professor David K. Roe of Portland State University for bringing to our attention an inconsistency in the sign convention for electrodes that was present in our earlier editions as well as in other analytical textbooks. Finally, we offer particular thanks to Professor Alfred Armstrong of The College of William and Mary in Virginia for again reviewing the manuscript in detail and to Professor Peter F. Linde of San Francisco State University for his thoughtful and cogent comments.

Douglas A. Skoog  
Donald M. West  
F. James Holler

# Contents Overview

1	Introduction	1
2	Evaluation of Analytical Data	6
3	Gravimetric Methods of Analysis	57
4	Titrimetric Methods of Analysis	84
5	A Review of Aqueous-Solution Chemistry	103
6	The Application of Equilibrium Calculations to Complex Systems	135
7	Precipitation Titrations	164
8	Titration Curves for Simple Acid/Base Systems	182
9	Titration Curves for Complex Acid/Base Systems	211
10	Applications of Neutralization Titrations	233
11	Complex-Formation Titrations	257
12	An Introduction to Oxidation/Reduction Equilibria and Electrochemical Theory	282
13	Theory of Oxidation/Reduction Titrations	315
14	Applications of Oxidation/Reduction Titrations	331
15	Potentiometric Methods	357
16	Electrogravimetric and Coulometric Methods	393
17	Voltammetry and Polarography	424
18	An Introduction to Spectroscopic Methods of Analysis	457
19	Instruments for Optical Spectroscopy	481
20	Molecular Spectroscopy	505
21	Atomic Spectroscopy Based on Ultraviolet and Visible Radiation	554
22	Kinetic Methods of Analysis	578
23	An Introduction to Chromatographic Methods	598
24	Gas-Liquid Chromatography	626
25	High-Performance Liquid Chromatography	644
26	The Analysis of Real Samples	667
27	Preparing Samples for Analysis	678
28	Decomposing and Dissolving the Sample	692
29	Eliminating Interferences	702
30	Chemicals, Apparatus, and Unit Operations of Analytical Chemistry	719
31	Selected Methods of Analysis	757

*Appendixes*

- 1 *Selected References to the Literature of Analytical Chemistry* 807
- 2 *Some Standard and Formal Electrode Potentials* 811
- 3 *Solubility-Product Constants* 815
- 4 *Dissociation Constants for Acids* 817
- 5 *Dissociation Constants for Bases* 818
- 6 *Stepwise Formation Constants* 819
- 7 *Designations and Porosities for Filtering Crucibles* 821
- 8 *Designations Carried by Ashless Filter Papers* 822
- 9 *Volumetric Calculations Using Normality and Equivalent Weight* 823
- 10 *The Potentiometer* 831
- 11 *The Method of Successive Approximations* 833
- 12 *Compounds Recommended for the Preparation of Standard Solutions of Common Elements* 835
- Answers to Questions and Problems* 837



# Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
1A	The Role of Analytical Chemistry in the Sciences	1
1B	Classification of Quantitative Methods of Analysis	2
1C	Steps in a Typical Quantitative Analysis	2
<b>2</b>	<b>Evaluation of Analytical Data</b>	<b>6</b>
2A	Definition of Terms	7
2B	Determinate Errors	13
2C	Gross Errors	16
2D	Indeterminate Errors	17
2E	The Uses of Statistics	26
2F	The Standard Deviation of Computed Results	43
2G	Methods for Reporting Analytical Data	47
<b>3</b>	<b>Gravimetric Methods of Analysis</b>	<b>57</b>
3A	A Review of Chemical Stoichiometry	57
3B	Properties of Precipitates and Precipitating Reagents	62
3C	A Critique of the Gravimetric Method	74
3D	Applications of Gravimetric Methods	75
<b>4</b>	<b>Titrimetric Methods of Analysis</b>	<b>84</b>
4A	Some General Aspects of Volumetric Titrimetry	84
4B	Standard Solutions	86
4C	Volumetric Calculations Based on Molar Concentrations	87
4D	Other Methods for Expressing Concentration	95
4E	Weight Titrimetry	98
<b>5</b>	<b>A Review of Aqueous-Solution Chemistry</b>	<b>103</b>
5A	The Chemical Composition of Aqueous Solutions	103
5B	Chemical Equilibrium	106
5C	The Effect of Electrolyte Concentration on Chemical Equilibria	122
<b>6</b>	<b>The Application of Equilibrium Calculations to Complex Systems</b>	<b>135</b>
6A	A Systematic Method for Deriving Algebraic Equations Describing Multiequilibrium Systems	136
6B	The Calculation of Solubility by the Systematic Method	139
6C	Separation of Ions by Control of the Concentration of a Precipitating Reagent	155

<b>7</b>	<b>Precipitation Titrations</b>	<b>164</b>
7A	Titration Curves in Titrimetric Methods	164
7B	Titration Curves for Precipitation Reactions	165
7C	Applications of Precipitation Titrations	177
<b>8</b>	<b>Titration Curves for Simple Acid/Base Systems</b>	<b>182</b>
8A	Solutions and Indicators for Neutralization Titrations	182
8B	Titration Curves for Strong Acids and Strong Bases	185
8C	Properties of Weak Acid and Weak Base Systems	188
8D	Properties of Buffer Solutions	193
8E	Titration Curves for Weak Acids	197
8F	Titration Curves for Weak Bases	202
8G	Common Types of Acid/Base Indicators	204
<b>9</b>	<b>Titration Curves for Complex Acid/Base Systems</b>	<b>211</b>
9A	Mixtures of Strong and Weak Acids or Strong and Weak Bases	211
9B	Equilibrium Calculations for Compounds with Multiple Acidic or Basic Functional Groups	214
9C	Titration Curves for Polyprotic Acids and Their Conjugate Bases	221
9D	The Composition of a Solution of a Polyprotic Acid as a Function of pH	227
<b>10</b>	<b>Applications of Neutralization Titrations</b>	<b>233</b>
10A	Reagents for Neutralization Reactions	233
10B	Typical Applications of Neutralization Titrations	238
10C	Application of Neutralization Titrations in Nonaqueous Media	245
<b>11</b>	<b>Complex-Formation Titrations</b>	<b>257</b>
11A	Complex-Formation Reactions	257
11B	Titrations with Aminopolycarboxylic Acids	259
11C	Titrations with Inorganic Complexing Agents	277
<b>12</b>	<b>An Introduction to Oxidation/Reduction Equilibria and Electrochemical Theory</b>	<b>282</b>
12A	Oxidation/Reduction Processes	282
12B	Electrochemical Cells	284
12C	Electrode Potentials	288
12D	Applications of Electrode Potentials	299
<b>13</b>	<b>Theory of Oxidation/Reduction Titrations</b>	<b>315</b>
13A	Electrode Potentials for Redox Titration Systems	315
13B	Oxidation/Reduction Indicators	325
13C	Potentiometric End Points	329
<b>14</b>	<b>Applications of Oxidation/Reduction Titrations</b>	<b>331</b>
14A	Auxiliary Oxidizing and Reducing Reagents	331
14B	Applications of Standard Oxidants	334
14C	Volumetric Applications of Reductants	341
14D	Some Specialized Oxidants	344

<b>15</b>	<b>Potentiometric Methods</b>	<b>357</b>
15A	Reference Electrodes	357
15B	Indicator Electrodes	359
15C	Instruments for the Measurement of Cell Potentials	374
15D	Direct Potentiometric Measurements	376
15E	Potentiometric Titrations	384
<b>16</b>	<b>Electrogravimetric and Coulometric Methods</b>	<b>393</b>
16A	The Effect of Current on Cell Potentials	393
16B	The Potential Selectivity of Electrolytic Methods	398
16C	Electrogravimetric Methods of Analysis	399
16D	Coulometric Methods of Analysis	407
<b>17</b>	<b>Voltammetry and Polarography</b>	<b>424</b>
17A	Polarographic Measurements	424
17B	Polarographic Currents	428
17C	Half-Wave Potentials	431
17D	Instrumentation	435
17E	Applications of Polarography	438
17F	Modified Voltammetric Methods	442
<b>18</b>	<b>An Introduction to Spectroscopic Methods of Analysis</b>	<b>457</b>
18A	Properties of Electromagnetic Radiation	457
18B	The Electromagnetic Spectrum	460
18C	Absorption of Radiation	460
18D	Emission of Electromagnetic Radiation	473
<b>19</b>	<b>Instruments for Optical Spectroscopy</b>	<b>481</b>
19A	Instrument Components	481
19B	Spectroscopic Instruments	498
<b>20</b>	<b>Molecular Spectroscopy</b>	<b>505</b>
20A	Ultraviolet and Visible Absorption Spectroscopy	505
20B	Infrared Absorption Spectroscopy	528
20C	Molecular Fluorescence Methods	534
20D	Automation of Photometric and Spectrophotometric Methods	538
<b>21</b>	<b>Atomic Spectroscopy Based on Ultraviolet and Visible Radiation</b>	<b>554</b>
21A	A Comparison of Atomic and Molecular Spectroscopic Methods	554
21B	Atomic Spectroscopy Based on Flame Atomization	555
21C	Atomic Absorption Methods with Electrothermal Atomizers	570
21D	Atomic Emission Methods Based on Atomization in Plasmas	571
<b>22</b>	<b>Kinetic Methods of Analysis</b>	<b>578</b>
22A	Rates of Chemical Reactions; Rate Laws	578
22B	The Determination of Reaction Rates	588
22C	Applications of Kinetic Methods	593

<b>23</b>	<b><i>An Introduction to Chromatographic Methods</i></b>	<b>598</b>
23A	<i>A General Description of Chromatography</i>	598
23B	<i>Migration Rates of Solutes</i>	602
23C	<i>Band Shapes and Band Broadening</i>	605
23D	<i>Optimization of Column Performance</i>	614
23E	<i>A Summary of Important Relationships for Chromatography</i>	620
23F	<i>Applications of Chromatography</i>	620
<b>24</b>	<b><i>Gas-Liquid Chromatography</i></b>	<b>626</b>
24A	<i>Principles of Gas-Liquid Chromatography</i>	627
24B	<i>Instruments for Gas-Liquid Chromatography</i>	627
24C	<i>Liquid Phases for Gas-Liquid Chromatography</i>	637
24D	<i>Applications of Gas-Liquid Chromatography</i>	638
24E	<i>Typical Applications of Gas Chromatography</i>	639
<b>25</b>	<b><i>High-Performance Liquid Chromatography</i></b>	<b>644</b>
25A	<i>Instruments for High-Performance Liquid Chromatography</i>	645
25B	<i>High-Performance Partition Chromatography</i>	648
25C	<i>High-Performance Adsorption Chromatography</i>	650
25D	<i>High-Performance Ion-Exchange Chromatography</i>	652
25E	<i>High-Performance Size-Exclusion Chromatography</i>	655
25F	<i>A Comparison of High-Performance Liquid Chromatography and Gas-Liquid Chromatography</i>	657
25G	<i>Supercritical-Fluid Chromatography</i>	658
25H	<i>Planar Chromatography</i>	662
<b>26</b>	<b><i>The Analysis of Real Samples</i></b>	<b>667</b>
26A	<i>Choice of Method for the Analysis of Real Samples</i>	669
26B	<i>The Accuracy Obtainable in the Analysis of Complex Materials</i>	674
<b>27</b>	<b><i>Preparing Samples for Analysis</i></b>	<b>678</b>
27A	<i>Sampling</i>	678
27B	<i>Moisture in Samples</i>	685
27C	<i>Determination of Water in Samples</i>	689
<b>28</b>	<b><i>Decomposing and Dissolving the Sample</i></b>	<b>692</b>
28A	<i>Some General Considerations</i>	692
28B	<i>Aqueous Reagents for Dissolving or Decomposing Samples</i>	693
28C	<i>Decomposition of Samples by Fluxes</i>	694
28D	<i>Decomposition of Organic Compounds for Elemental Analysis</i>	697
<b>29</b>	<b><i>Eliminating Interferences</i></b>	<b>702</b>
29A	<i>The Nature of the Separation Process</i>	702
29B	<i>Separation by Precipitation</i>	703
29C	<i>Extraction Methods</i>	706
29D	<i>Applications of Extraction Procedures</i>	710
29E	<i>Ion-Exchange Separations</i>	715
29F	<i>The Separation of Inorganic Species by Distillation</i>	716

<b>30</b>	<b><i>The Chemicals, Apparatus, and Unit Operations of Analytical Chemistry</i></b>	<b>719</b>
30A	<i>The Selection and Handling of Reagents and Other Chemicals</i>	719
30B	<i>The Cleaning and Marking of Laboratory Ware</i>	721
30C	<i>The Evaporation of Liquids</i>	721
30D	<i>The Measurement of Mass</i>	722
30E	<i>The Equipment and Manipulations Associated with Weighing</i>	731
30F	<i>Weight Titrations</i>	734
30G	<i>The Equipment and Manipulations for Filtration and Ignition</i>	735
30H	<i>The Measurement of Volume</i>	742
30I	<i>The Calibration of Volumetric Ware</i>	750
30J	<i>The Laboratory Notebook</i>	753
30K	<i>Safety in the Laboratory</i>	754
<b>31</b>	<b><i>Selected Methods of Analysis</i></b>	<b>757</b>
31A	<i>Gravimetric Methods of Analysis</i>	758
31B	<i>Precipitation Titrations</i>	762
31C	<i>Neutralization Titrations</i>	765
31D	<i>Complex-Formation Titrations with EDTA</i>	771
31E	<i>Oxidation/Reduction Titrations with Potassium Permanganate</i>	773
31F	<i>Iodimetric Titrations</i>	779
31G	<i>Iodometric Methods of Analysis</i>	781
31H	<i>Titrations with Potassium Bromate</i>	784
31I	<i>Potentiometric Methods</i>	786
31J	<i>Electrogravimetric Methods</i>	791
31K	<i>Coulometric Titrations</i>	792
31L	<i>Voltammetry</i>	794
31M	<i>Methods Based on the Absorption of Radiation</i>	796
31N	<i>Molecular Fluorescence</i>	800
31O	<i>Atomic Spectroscopy</i>	801
31P	<i>Separation of Cations by Ion Exchange</i>	803
31Q	<i>Gas-Liquid Chromatography</i>	805
<b>Appendix 1</b>	<b><i>Selected References to the Literature of Analytical Chemistry</i></b>	<b>807</b>
<b>Appendix 2</b>	<b><i>Some Standard and Formal Electrode Potentials</i></b>	<b>811</b>
<b>Appendix 3</b>	<b><i>Solubility-Product Constants</i></b>	<b>815</b>
<b>Appendix 4</b>	<b><i>Dissociation Constants for Acids</i></b>	<b>817</b>
<b>Appendix 5</b>	<b><i>Dissociation Constants for Bases</i></b>	<b>818</b>
<b>Appendix 6</b>	<b><i>Stepwise Formation Constants</i></b>	<b>819</b>
<b>Appendix 7</b>	<b><i>Designations and Porosities for Filtering Crucibles</i></b>	<b>821</b>
<b>Appendix 8</b>	<b><i>Designations Carried by Ashless Filter Papers</i></b>	<b>822</b>

<i>Appendix 9</i>	<i>Volumetric Calculations Using Normality and Equivalent Weight</i>	823
<i>Appendix 10</i>	<i>The Potentiometer</i>	831
<i>Appendix 11</i>	<i>The Method of Successive Approximations</i>	833
<i>Appendix 12</i>	<i>Compounds Recommended for the Preparation of Standard Solutions of Some Common Elements</i>	835
	<i>Answers to Questions and Problems</i>	837
	<i>Index</i>	873

# Introduction

Analytical chemistry is concerned with the separation, identification, and determination of the relative amounts of the components (the analytes) making up a sample of matter. A *qualitative analysis* provides information on the chemical identity of the analytes in the sample, whereas a *quantitative analysis* yields numerical information on the relative amount of one or more of these analytes. Generally, qualitative information is required before a quantitative analysis can be undertaken. A separation step is usually a necessary part of both a qualitative and a quantitative analysis.

The principal topics covered in this text are quantitative methods of analysis and methods of analytical separations, although references to qualitative methods appear from time to time.

1A

## The Role of Analytical Chemistry in the Sciences

Historically, analytical chemistry has played a vital role in the development of science. For example, in 1894 Wilhelm Ostwald wrote

Analytical chemistry, or the art of recognizing different substances and determining their constituents, takes a prominent position among the applications of science, since the questions which it enables us to answer arise wherever chemical processes are employed for scientific or technical purposes. Its supreme importance has caused it to be assiduously cultivated from a very early period in the history of chemistry, and its records comprise a large part of the quantitative work which is spread over the whole domain of science.

Since 1894, analytical chemistry has evolved from an art to a science, due in no small part to the work of Ostwald himself, and its importance still spreads over all domains of science and technology. To cite but a few examples, consider the following: The effectiveness of smog-control devices is determined by measuring the parts per million of hydrocarbons, nitrogen oxides, and carbon monoxide in the exhaust gases of automobiles. Hyperparathyroidism in human patients is diagnosed by quantitative measurements of ionized calcium in blood serum. The protein content, and thus the nutritional value of foods, is ordinarily established by quantitative determination of their nitrogen content. Periodic analysis of steel during its production permits adjustment in the concentration of such elements as carbon, nickel, and chromium to give a product that has a desired strength, hardness, corrosion resistance, and ductility. Household gas supplies are continuously monitored for their mercaptan content in order to ensure sufficient levels of odorant to warn of leaks. Modern farmers tailor their fertilization and irrigation schedules to meet changing plant needs during the growing season; these needs are



gauged from quantitative analyses of the plants and of the soil in which they grow.

In addition to everyday applications of the types just cited, quantitative analytical measurements play a vital role in many research areas in chemistry, biochemistry, biology, geology, and the other sciences. For example, chemists have learned much about mechanisms of chemical reactions through kinetic studies based upon periodic quantitative measurements that reveal the rates at which reactants are consumed or products are formed. Quantitative analyses for potassium, calcium, and sodium ions in the body fluids of animals have permitted physiologists to study the role these ions play in the conduction of nerve signals and the contraction and relaxation of muscles. Materials scientists, in their studies of the behavior of semiconductor devices, have relied heavily upon quantitative analyses of crystalline germanium and silicon for impurities in the concentration range from  $1 \times 10^{-6}$  to  $1 \times 10^{-10}$  percent. Archeologists have found it possible to identify sources of volcanic glasses (obsidian) based upon the concentrations of several minor elements in samples taken from various locations; this knowledge has made it possible to trace prehistoric trade routes for tools and weapons manufactured from obsidian.

Many chemists and biochemists devote a significant part of their time in the laboratory acquiring quantitative information about the systems in which they are interested. For such investigators, analytical chemistry serves as a tool in their scholarly efforts in much the same way that calculus and matrix algebra are tools of the theoretical physicist and ancient languages are tools of the classics scholar.

1B

### **Classification of Quantitative Methods of Analysis**

The results of a typical quantitative analysis are based upon two measurements. One is the weight or volume of sample to be analyzed. The second, which normally completes the analysis, is the measurement of some quantity that is proportional to the amount of analyte in that sample. Analytical methods are often classified according to the nature of this final measurement. In a *gravimetric method*, the mass of the analyte or that of some compound chemically related to the analyte is determined. In a *titrimetric method*, the quantity of reagent necessary to react completely with the analyte is measured. *Electroanalytical methods* involve the measurement of such properties as potential, current, resistance, and quantity of charge. *Spectroscopic methods* are based upon measurements of the interaction between electromagnetic radiation (including X-ray, ultraviolet, visible, infrared, microwave, and radio-frequency radiation) and analyte atoms or molecules or upon measurements of the amount of such radiation produced by analytes. Finally, there is a group of miscellaneous methods for completing analyses based upon measuring such properties as mass-to-charge ratio (mass spectrometry), rate of radioactive decay, heat of reaction, rate of reaction, thermal conductivity, optical activity, and refractive index.

1C

### **Steps in a Typical Quantitative Analysis**

A typical quantitative analysis involves a sequence of several steps:

1. Selecting a method of analysis
2. Sampling

3. Preparing a laboratory sample
4. Defining replicate samples
5. Preparing solutions of the sample
6. Eliminating interferences
7. Completing the analysis
8. Calculating results and estimating their reliability

In some instances, one or more of these steps can be dispensed with. Ordinarily, however, all play an important role in the success of an analysis.

The first 23 chapters of this text focus on the last two steps of this list. Step 7 involves measuring one of the physical properties mentioned in the previous section, preferably one that is proportional (in most cases) to the amount of analyte in a sample of known weight or volume. Step 8 consists of computing the relative amount of the analyte present in the samples and estimating the reliability of the results.

A brief description of each of these steps is provided at this juncture in order to give the reader an overall perspective on how quantitative chemical data are obtained.

---

**1C-1****Selecting a Method of Analysis**

Selecting which method will be used to solve an analytical problem is a vital first step in any quantitative analysis. The choice is sometimes difficult and requires experience as well as intuition on the part of the chemist. An important consideration in selection is the accuracy required. Unfortunately, high reliability nearly always entails a large expenditure of time; the method ultimately chosen may thus of necessity represent a compromise between accuracy and economics.

A second consideration, also related to economic factors, is the number of samples to be analyzed. If there are many, the chemist can afford to use a method that requires such preliminary operations as the assembling and calibrating of instrumental equipment and the preparing of standard solutions. On the other hand, with only a single sample or a few samples, it may be more expedient to select a procedure that avoids such preliminary steps.

Finally, the choice of method is always governed by the complexity of the sample being analyzed and by the number of components for which quantitative information is needed. Further details on choosing a method of analysis are given in Section 26A.

---

**1C-2****Sampling**

To produce meaningful information, an analysis must be performed on a sample whose composition faithfully reflects that of the bulk of material from which it is taken. Where the bulk is large and inhomogeneous, great effort is required to procure a representative sample. Consider, for example, a railroad car containing 25 tons of silver ore. Buyer and seller must come to agreement regarding the value of the shipment based primarily upon its silver content. The ore is inherently heterogeneous, consisting of lumps of various size as well as varying silver content. The assay of this shipment will be performed on a sample that has a mass of perhaps 1 g. For the analysis to have significance, it is essential that this small sample have a composition that is representative of the 25 tons (approximately 22,700,000 g) of ore in the shipment. The task of isolating 1 g with any confidence that its composition truly reflects the average composition of the nearly 23,000,000 g from which it is taken is clearly