

---

---

---

# QUANTITATIVE ANALYTICAL CHEMISTRY

fourth edition

**JAMES S. FRITZ**

Iowa State University

**GEORGE H. SCHENK**

Wayne State University

---

---

---

# QUANTITATIVE ANALYTICAL CHEMISTRY

fourth edition

**JAMES S. FRITZ**  
Iowa State University

**GEORGE H. SCHENK**  
Wayne State University

ALLEN AND BACON, INC. — BOSTON, LONDON, SYDNEY, TORONTO

---

Production Editor David Dahlbacka  
Interior Designer Libby Griffiths  
Manufacturing Buyer Karen Mason



Copyright © 1979, 1974, 1969, 1966 by Allyn and Bacon, Inc.,  
470 Atlantic Avenue Boston, Massachusetts 02210

All rights reserved. No part of the material protected by this  
copyright notice may be reproduced or utilized in any form or by  
any means, electronic or mechanical, including photocopying,  
recording, or by any information storage and retrieval system,  
without written permission from the copyright owner.

*Library of Congress Cataloging in Publication Data*

Fritz, James Sherwood, 1924-  
Quantitative analytical chemistry.

Bibliography p.

Includes index.

I. Chemistry. Analytic. Quantitative. I. Schejnk,  
George H. Joint author. II. Title.  
QD101 .F74 1979 545 78-21616

ISBN 0-205-06527-9

ISBN 0-205-06590-2 (International)

*Printed in the United States of America*

---

## PREFACE

A new edition of any textbook gives the authors an opportunity to add new material to keep the book current. At the same time, subject matter that has become of limited value can be condensed or eliminated. But apart from keeping the text material up-to-date, we think that a new edition ought to be a definite improvement over the previous book. Explanations should be made more clear and logical; difficult concepts should be made more understandable. These principles have been our guide in preparing this fourth edition. Above all, we have tried to produce a book that is modern in outlook and covers the material in a manner that is clear and easy to understand.

Part I in particular has been carefully gone over. Many changes have been made, although the general format remains unchanged except for addition of a new chapter (Chapter 10) on acid-base titrations in nonaqueous solvents. Chapter 5 on spectrophotometry has been completely rewritten to include more examples, a modern treatment of all instrumental components, and a discussion of approaches to spectrophotometric determinations. Some marginal topics have been eliminated from Chapter 7 and the treatment of chemical equilibrium has been made clearer and contains more worked-out examples. Chapters 8 and 9 have been reorganized and contain a unique new treatment of acid-base titration curves that is more logical and easier to understand than the usual presentations. Chapter 11 on precipitate-formation titrations has been shortened somewhat from the previous edition. Chapter 12 on complexes and complex-formation titrations has been rewritten; the discussion of equilibrium constants is easier to follow and includes numerous worked examples.

The first fourteen chapters provide the fundamentals for a short course in quantitative analytical chemistry. However, a sound, modern course or course sequence should certainly include at least some of the topics covered in the later chapters of Part I. In this edition, Chapter 16 on electrochemistry has been reorganized and has a new and clearer treatment of polarography. A new section on gas-sensing electrodes has been added to Chapter 17. Reflecting the ever growing importance of chromatography in practical analysis, our coverage of chromatography in Chapters 19–22 remains unusually strong. All of these chapters have been revised and updated, and Chapter 20 on gas chromatography has been completely rewritten.

Spectrophotometry continues to grow in usefulness as a method for quantitative analysis. In Chapter 23, the theory of fluorescence methods has been revised and a section on infrared instrumentation has been added. New sections on inductively coupled plasma in emission spectroscopy and on flameless atomic absorption have been added to Chapter 24. To complete the revisions in Part I, new examples of actual analytical problems have been incorporated into Chapter 25.

Several changes have been made in Part II. A new experiment, Experiment 15 on determining Vitamin C in dehydrated juice solids, has been added. In addition, theoretical material on choosing sample size in Chapter 28 has been moved to Chapter 2; new material on handling a student sample has been substituted for the former. An appropriate form for reporting the gravimetric chloride has been included in Chapter 26 to guide students who do a gravimetric experiment as their first experiment. Finally, we have included only directions for weighing on a single-pan balance, in recognition of the universal use of single-pan balances.

There are many new questions and problems at the end of the chapters in Part I. In almost every case, these are grouped under various headings to provide more convenient selection for assignments or self-study. Answers to approximately half the numerical problems are given in the back of the book. An answer book with worked-out solutions to problems is available for instructors.

The authors wish to thank Robert L. Grob, Larry G. Hargis, Bruno Jaselskis, and John E. Roberts, who read and commented on the manuscript, and Dennis Johnson for his valuable comments on the electrochemistry chapters. We are also grateful to our graduate students and associates who contributed data for figures and assisted us in other ways. Finally, we wish to acknowledge the excellent editorial assistance of David Dahlbacka.

**James S. Fritz**  
**George H. Schenk**

# **FORMULA WEIGHTS**

(Arranged alphabetically according to atomic symbol. All weights rounded to relative uncertainties between 0.2 and 0.02 ppt.)

AgBr	187.78
AgCl	143.32
AgI	234.77
AgNO <sub>3</sub>	169.88
Al(C <sub>6</sub> H <sub>5</sub> NO) <sub>3</sub> (aluminum oxinate)	459.46
Al <sub>2</sub> O <sub>3</sub>	101.96
As <sub>2</sub> O <sub>3</sub>	197.84
As <sub>2</sub> O <sub>5</sub>	229.84
BaCl <sub>2</sub>	208.25
BaCl <sub>2</sub> ·2H <sub>2</sub> O	244.27
BaCO <sub>3</sub>	197.35
BaCrO <sub>4</sub>	253.33
BaO	153.34
BaSO <sub>4</sub>	233.40
CHCl <sub>3</sub>	119.38
CO <sub>2</sub>	44.011
C <sub>2</sub> H <sub>4</sub> (OH) <sub>2</sub> (ethylene glycol)	62.07
C <sub>4</sub> H <sub>9</sub> OOH ( <i>t</i> -butyl hydroperoxide)	90.13
C <sub>6</sub> H <sub>5</sub> Br (bromobenzene)	157.02
CaCO <sub>3</sub>	100.09
CaC <sub>2</sub> O <sub>4</sub>	128.10
CaMg(CO <sub>3</sub> ) <sub>2</sub>	184.41
CaO	56.08
Ca(OH) <sub>2</sub>	74.10
CaSO <sub>4</sub>	136.14
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	310.18
Ce <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>	544.47
CeF <sub>3</sub>	197.12
Cr <sub>2</sub> O <sub>3</sub>	152.00
CuO	79.54
CuS	95.60
CuSO <sub>4</sub> ·5H <sub>2</sub> O	249.68
FeO	71.85
FeS	87.91
FeSO <sub>4</sub> ·C <sub>2</sub> H <sub>4</sub> (NH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> ·4H <sub>2</sub> O	382.18
FeSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	392.15
FeS <sub>2</sub>	119.97
Fe <sub>2</sub> O <sub>3</sub>	159.69
Fe <sub>3</sub> O <sub>4</sub>	231.54
2Fe <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O	337.38
HCO <sub>2</sub> CH <sub>3</sub> (acetic acid)	60.05
HCO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (benzoic acid)	122.12
HfC <sub>10</sub> H <sub>15</sub> O <sub>7</sub> N <sub>2</sub>	388.66

HCl	36.46
HIO <sub>4</sub> (periodic acid)	191.91
HNO <sub>3</sub>	63.02
HSO <sub>3</sub> NH <sub>2</sub> (sulfamic acid)	97.09
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (oxalic acid)	90.04
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O (oxalic acid)	126.07
H <sub>2</sub> S	34.08
H <sub>2</sub> SO <sub>3</sub>	82.08
H <sub>2</sub> SO <sub>4</sub>	98.08
H <sub>3</sub> PO <sub>4</sub>	98.00
H <sub>5</sub> IO <sub>6</sub> (periodic acid)	227.94
HfO <sub>2</sub>	210.49
HgCl <sub>2</sub>	271.50
HgO	216.59
Hg <sub>2</sub> Cl <sub>2</sub>	472.13
KBr	119.01
KBrO <sub>3</sub>	167.01
KCl	74.56
KClO <sub>4</sub>	138.55
KHC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	218.16
KHC <sub>8</sub> H <sub>4</sub> O <sub>4</sub> (KHP)	204.23
KI	166.01
KIO <sub>3</sub>	214.00
KIO <sub>3</sub> ·HIO <sub>3</sub>	389.93
KMnO <sub>4</sub>	158.04
KOH	56.11
KSCN	97.18
K <sub>2</sub> CrO <sub>4</sub>	194.20
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	294.19
K <sub>2</sub> O	94.20
K <sub>2</sub> SO <sub>4</sub>	174.27
La <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>	541.89
MgCl <sub>2</sub>	95.22
MgCO <sub>3</sub>	84.32
MgNH <sub>4</sub> PO <sub>4</sub>	137.32
MgO	40.31
Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	222.57
MnO <sub>2</sub>	86.94
MoO <sub>3</sub>	143.94
NH <sub>2</sub> CO <sub>2</sub> NH <sub>2</sub> (urea)	60.05
NH <sub>2</sub> (C <sub>4</sub> H <sub>9</sub> O <sub>3</sub> ) (THAM)	121.14
NH <sub>2</sub> (C <sub>5</sub> H <sub>7</sub> N)	
(4-aminopyridine)	94.11
NH <sub>3</sub>	17.031
NH <sub>4</sub> Cl	53.49

NH <sub>4</sub> OH	35.05
(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	124.10
(NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>	548.23
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132.14
NaAl(SiO <sub>3</sub> ) <sub>2</sub>	202.14
NaBr	102.90
Na(CH <sub>3</sub> CO <sub>2</sub> ) (sodium acetate)	82.04
Na(C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> )	
(sodium benzoate)	144.10
NaCl	58.44
NaF	41.99
NaHCO <sub>3</sub>	84.01
NaH <sub>2</sub> PO <sub>4</sub>	119.98
NaOH	40.00
Na <sub>2</sub> CO <sub>3</sub>	105.99
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	134.00
Na <sub>2</sub> H <sub>2</sub> Y·2H <sub>2</sub> O (EDTA)	372.24
Na <sub>2</sub> O	61.98
Na <sub>2</sub> SO <sub>4</sub>	142.04
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	248.19
Ni(C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> N <sub>2</sub> ) <sub>2</sub> (Ni-DMG <sub>2</sub> )	288.94
P <sub>2</sub> O <sub>5</sub>	141.95
PbCl <sub>2</sub>	278.10
PbCrO <sub>4</sub>	323.19
PbO <sub>2</sub>	239.19
PbSO <sub>4</sub>	303.25
Pb <sub>3</sub> O <sub>4</sub>	685.57
SO <sub>2</sub>	64.06
SO <sub>3</sub>	80.06
SiO <sub>2</sub>	60.09
SnCl <sub>2</sub>	189.61
SnO <sub>2</sub>	150.69
SrCO <sub>3</sub>	147.63
SrSO <sub>4</sub>	183.68
ThO <sub>2</sub>	264.04
TiO <sub>2</sub>	79.90
UO <sub>2</sub> (C <sub>10</sub> H <sub>13</sub> AsN <sub>2</sub> O <sub>5</sub> )	388.16
U <sub>3</sub> O <sub>8</sub>	842.09
V <sub>2</sub> O <sub>5</sub>	181.88
Y <sub>2</sub> O <sub>3</sub>	225.81
Yb <sub>2</sub> O <sub>3</sub>	394.08
ZnO	81.37
ZrO <sub>2</sub>	123.22

---

# CONTENTS

*Preface* ix

## **PART I PRINCIPLES AND THEORY 1**

### **CHAPTER 1 INTRODUCTION 3**

1-1 The Nature of Analytical Chemistry • 3    1-2 Some Fundamental Concepts • 6

### **CHAPTER 2 STEPS IN A CHEMICAL ANALYSIS 15**

2-1 Plan of Analysis • 15    2-2 Sampling • 15    2-3 Drying the Sample • 18    2-4 Measuring the Sample • 19    2-5 Dissolving the Sample • 19    2-6 Separating Interfering Substances • 21  
2-7 Measuring the Desired Substance • 21    2-8 Calculating and Evaluating the Results • 21

### **CHAPTER 3 TREATMENT OF ANALYTICAL DATA 24**

3-1 Error and Deviation • 25    3-2 Significant Figures • 26    3-3 The Central Tendency of a Set of Results • 29    3-4 Precision • 30  
3-5 Accuracy of an Analysis: Confidence Limits • 35    3-6 Handling Small Sets of Data • 37

### **CHAPTER 4 GRAVIMETRIC METHODS OF ANALYSIS 46**

4-1 Mechanism of Precipitation • 47    4-2 Conditions for Analytical Precipitation • 48    4-3 Precipitation from a Homogeneous Solution • 51  
4-4 Impurities in Precipitates • 53    4-5 Washing and Filtering Precipitates • 55    4-6 Heating the Precipitate • 56    4-7 Calculating the Results • 57    4-8 Examples of Precipitation Methods • 59

### **CHAPTER 5 SPECTROPHOTOMETRIC METHODS OF ANALYSIS 69**

5-1 Absorption of Radiant Energy • 70    5-2 Beer's Law • 76  
5-3 Measurement of Radiant Energy Absorption • 83    5-4 Spectrophotometric Methods Using Light • 90    5-5 Ultraviolet Spectrophotometric Methods • 104



<b>CHAPTER 6 TITRIMETRIC (VOLUMETRIC) METHODS OF ANALYSIS</b>	<b>116</b>
6-1 General Principles • 116      6-2 Calculations with Molarity • 121	
6-3 Calculations with Normality • 125	
<b>CHAPTER 7 CHEMICAL EQUILIBRIUM</b>	<b>134</b>
7-1 Equilibrium and Equilibrium Constants • 134      7-2 Ionization of Weak Acids • 136      7-3 Formation of Complexes • 139      7-4 Solubility of Precipitates: Calculations with the Solubility Product • 140      7-5 Simultaneous Equilibria: Use of Conditional Constants • 142      7-6 Activity Coefficients and Chemical Equilibrium • 146	
<b>CHAPTER 8 ACID-BASE EQUILIBRIA</b>	<b>150</b>
8-1 Acid-Base Theory • 150      8-2 Acidity of Solutions; pH • 152	
8-3 Calculation of pH: Solutions of Strong Acids and Bases • 154	
8-4 Calculation of pH: Solutions of Weak Acids and Bases • 155	
8-5 Ionization of Polyprotic Acids • 158      8-6 Buffers • 162	
<b>CHAPTER 9 ACID-BASE TITRATIONS</b>	<b>170</b>
9-1 Preparation and Standardization of Titrants • 170      9-2 Titration Curves • 172      9-3 Acid-Base Indicators • 179      9-4 Some Acid-Base Methods • 182	
<b>CHAPTER 10 ACID-BASE TITRATIONS IN NONAQUEOUS SOLVENTS</b>	<b>193</b>
10-1 Solvents • 194      10-2 Titrants • 197      10-3 Titration of Bases • 199      10-4 Titration of Acids • 202	
<b>CHAPTER 11 PRECIPITATE-FORMATION TITRATIONS</b>	<b>206</b>
11-1 Potentiometric Titrations with Silver(I) • 206      11-2 Mohr Method for Halides • 208      11-3 Volhard Method • 209      11-4 Adsorption Indicator Method for Halides • 210      11-5 Adsorption Indicator Method for Sulfate • 211	
<b>CHAPTER 12 COMPLEXES AND COMPLEX FORMATION TITRATIONS</b>	<b>214</b>
12-1 Formation of Complexes • 214      12-2 Theory of Complexometric Titrations • 220      12-3 Determination of Calcium and Magnesium: Water Hardness • 229      12-4 Other EDTA Titration Methods • 233	

<b>CHAPTER 13</b>	<b>THEORY OF OXIDATION-REDUCTION REACTIONS AND TITRATIONS</b>	<b>240</b>
13-1	Oxidation-Reduction Reactions • 240	
13-2	Electrode Potentials • 242	
13-3	Variation of Electrode Potential with Concentration • 244	
13-4	Combining Half-Reactions to Form a Complete Reaction • 247	
13-5	Potentiometric Titrations • 249	
13-6	Oxidation-Reduction Indicators • 252	
13-7	Limitations of Oxidation-Reduction Theory • 253	
13-8	Rates and Mechanisms of Oxidation-Reduction Reactions • 254	
<b>CHAPTER 14</b>	<b>OXIDATION-REDUCTION TITRATIONS</b>	<b>265</b>
14-1	Calculations • 265	
14-2	Titration Involving Strong Oxidizing Agents • 266	
14-3	Determination of Iron • 272	
14-4	Titration Involving Iodine • 273	
<b>CHAPTER 15</b>	<b>THE USE OF REACTION RATES</b>	<b>283</b>
15-1	Kinetic Theory: Rate Constants • 283	
15-2	Kinetics of Enzyme-Catalyzed Reactions • 287	
15-3	Relative Rates of Two Organic Reactions • 291	
15-4	Determination of Catalysts • 293	
<b>CHAPTER 16</b>	<b>ELECTRICAL METHODS OF SEPARATION AND ANALYSIS</b>	<b>297</b>
16-1	Principles of Electrolysis • 297	
16-2	Electrodeposition • 304	
16-3	Coulometric Methods of Analysis • 308	
16-4	Polarography • 313	
<b>CHAPTER 17</b>	<b>POTENTIOMETRIC DETERMINATIONS WITH ION-SELECTIVE ELECTRODES</b>	<b>327</b>
17-1	Practical Measurement of Potential • 328	
17-2	Glass Electrodes • 331	
17-3	Liquid-Membrane Electrodes • 335	
17-4	Solid-State Membrane Electrodes • 339	
17-5	Enzyme Electrodes • 341	
17-6	Gas-Sensing Electrodes • 342	
17-7	Applications • 344	
<b>CHAPTER 18</b>	<b>LIQUID-LIQUID EXTRACTION</b>	<b>347</b>
18-1	General Principles • 347	
18-2	Completeness of Extraction • 348	
18-3	Extraction of Metal-Organic Complexes • 350	
18-4	Extraction of Ion-Association Complexes • 354	
<b>CHAPTER 19</b>	<b>PRINCIPLES OF CHROMATOGRAPHY</b>	<b>359</b>
19-1	Basic Principles • 359	
19-2	Plate Theory of Chromatography • 366	

<b>CHAPTER 20</b>	<b>GAS CHROMATOGRAPHY</b>	<b>376</b>
20-1	Introduction and Overview · 376	
20-2	Theory of Gas-Liquid Chromatography · 378	
20-3	Selection of Conditions · 380	
20-4	Qualitative and Quantitative Analysis · 387	
20-5	Applications of Gas Chromatography · 389	
<b>CHAPTER 21</b>	<b>LIQUID CHROMATOGRAPHY</b>	<b>395</b>
21-1	Systems · 395	
21-2	Column Chromatography · 397	
21-3	Plane Chromatography · 405	
<b>CHAPTER 22</b>	<b>ION EXCHANGE IN ANALYTICAL CHEMISTRY</b>	<b>412</b>
22-1	Ion-Exchange Resins and Equilibrium · 412	
22-2	Analytical Applications of Ion Exchange · 415	
22-3	Ion-Exchange Chromatography · 416	
<b>CHAPTER 23</b>	<b>ELECTRONIC ABSORPTION SPECTRA, FLUORESCENCE AND INFRARED SPECTROSCOPY</b>	<b>428</b>
23-1	Theory of Electronic Absorption Spectra · 428	
23-2	Fluorescence Analysis · 435	
23-3	Infrared Methods and Chemical Structure · 444	
<b>CHAPTER 24</b>	<b>ANALYTICAL APPLICATIONS OF ATOMIC SPECTROMETRY</b>	<b>463</b>
24-1	Emission Spectrometry (Electrical Excitation) · 464	
24-2	Emission Spectrometry (Flame Excitation) · 473	
24-3	Atomic Absorption Spectrometry · 481	
<b>CHAPTER 25</b>	<b>ANALYSIS OF REAL SAMPLES: ANALYTICAL PROBLEM SOLVING</b>	<b>493</b>
25-1	Selecting an Analytical Method · 493	
25-2	Examples of Actual Analytical Problems · 494	
<b>PART II</b>	<b>LABORATORY TECHNIQUES AND PROCEDURES</b>	<b>501</b>
<b>CHAPTER 26</b>	<b>INTRODUCTION TO LABORATORY WORK</b>	<b>503</b>
26-1	Laboratory Notebook · 503	
26-2	Planning Laboratory Work · 505	
26-3	Cleanliness and Order · 505	
26-4	Reagents · 506	
<b>CHAPTER 27</b>	<b>THE ANALYTICAL BALANCE</b>	<b>509</b>
27-1	Accuracy and Precision · 509	
27-2	Principles of the Equal-Arm Balance · 510	
27-3	Construction of the Equal-Arm Balance · 511	
27-4	Direct-Reading Balances · 513	
27-5	Analytical Weights · 517	

27-6	General Rules for Use of Balance	518	27-7	Weighing Procedure for Single-Pan Balance (Mettler)	519	27-8	Errors in Weighing	520
Experiment 1: Weighing an Object				520				
Experiment 2: Statistical Evaluation of Weighing Data				521				
CHAPTER 28 SAMPLES, WEIGHING OPERATIONS, AND GRAVIMETRIC TECHNIQUES								523
28-1		Samples	523	28-2		Weighing Operations	523	
28-3		Gravimetric Techniques	527					
CHAPTER 29 GRAVIMETRIC PROCEDURES								532
Experiment 3: Gravimetric Determination of Chloride				532				
Experiment 4: Gravimetric Determination of Aluminum				535				
Experiment 5: Gravimetric Determination of Sulfate				537				
CHAPTER 30 VOLUMETRIC GLASSWARE								540
30-1		Calibration	540	30-2		Accuracy and Precision	540	
30-3		Volumetric Flasks	542	30-4		Pipets and Their Use	542	
30-5		Burets and Their Use	544					
Experiment 6: Calibrating a 25-ml Pipet				547				
CHAPTER 31 TITRIMETRIC PROCEDURES								548
Experiment 7: Standardization of NaOH and Determination of Total Acidity				549				
Experiment 8: Standardization of HCl and Determination of Sodium Carbonate				551				
Experiment 9: Perchloric Acid Nonaqueous Titrations				553				
Experiment 10: Determination of Chloride Using an Adsorption Indicator				555				
Experiment 11: Determination of Sulfate Using an Adsorption Indicator				557				
Experiment 12: EDTA Determination of Water Hardness Using Calmagite				559				
Experiment 13: EDTA Determination of Water Hardness Using Arsenazo				561				
Experiment 14: Iodometric Determination of Arsenic and Study of the Arsenic-Iodine Reaction				563				
Experiment 15: Determination of Vitamin C in Dehydrated Juice Solids				567				
Experiment 16: Iodometric Determination of Copper				568				
Experiment 17: Periodate Determination of Ethylene Glycol				571				
Experiment 18: Dichromate Determination of Iron Ore; Analysis of a Razor Blade				574				
Experiment 19: Permanganimetric Determination of Iron				577				

CHAPTER 32 SPECTROPHOTOMETRIC INSTRUMENTS AND PROCEDURES	582
32-1 Operating Principles • 583      32-2 Operating Procedures • 584	
Experiment 20: Spectrophotometric Determination of Manganese in Steel      585	
Experiment 21: Near-Infrared Determination of Water in Acetic Acid-Water Mixtures      588	
Experiment 22: Photometric Titrations of Copper(II) With EDTA      590	
Experiment 23: Fluorometric Determination of Vitamin D      594	
CHAPTER 33 ELECTROANALYTICAL PROCEDURES	598
Experiment 24: Potentiometric Determination of the Equivalent Weight and $K_a$ for a Pure Unknown Weak Acid      598	
Experiment 25: Determination of the Formula and Stability Constant of a Silver Complex Ion      601	
Experiment 26: Electrodeposition of Copper      603	
Experiment 27: Coulometric Titration of Arsenic      606	
Experiment 28: Amperometric Titration of Mercaptans      607	
CHAPTER 34 SEPARATION PROCEDURES	611
Experiment 29: Solvent Extraction of Zinc      611	
Experiment 30: Quantitative Gas Chromatographic Analysis of a Multicomponent Mixture      614	
Experiment 31: Separation of Metal Ions by Paper Chromatography      617	
Experiment 32: Thin-Layer Chromatographic Separation of Nitroanilines on Fluorescent Sheets      619	
Experiment 33: Anion-Exchange Separation of Iron, Cobalt, and Nickel      621	
APPENDICES	
1. Literature of Analytical Chemistry      625	
2. Equilibrium Constants      629	
3. Standard Electrode Potentials      634	
4. Balancing Oxidation-Reduction Equations      636	
5. Least-Squares Method for Linear Plots      638	
6. Solving Quadratic Equations      639	
7. Logarithms and Antilogarithms      641	
8. Four-Place Logarithms      643	
Answers to Selected Questions and Problems      647	
Index      655	

---

## PART I • PRINCIPLES AND THEORY

---



---

# CHAPTER 1 • INTRODUCTION

---

## 1-1. THE NATURE OF ANALYTICAL CHEMISTRY

**What Is Analytical Chemistry?** Analytical chemistry is the branch of chemistry dealing with the separation and analysis of chemical substances. Traditionally, analysis has been concerned largely with chemical *composition*, but it is coming more and more to include the determination of chemical *structure* and the measurement of physical properties. Analytical chemistry includes both qualitative and quantitative analysis. Qualitative analysis is concerned with *what* is present, quantitative analysis with *how much*. This book deals almost entirely with quantitative analysis. However, it might be appropriate to comment briefly on the qualitative methods used to identify the substances present in a chemical mixture.

The systematic hydrogen sulfide qualitative scheme is helpful in learning and organizing some chemical reactions, but it is no longer used widely as a practical analytical method. The emission spectrograph (see Chapter 24) is a rapid and useful way of detecting the elements present in inorganic samples. Sensitive, selective chemical spot tests have been worked out to detect many ions and molecules. Chromatography is an extremely valuable method of separating and detecting both organic and inorganic substances (see Chapters 19-22). For example, paper and thin-layer chromatography have been used to rapidly identify subgroups in blood [1] and by police laboratories to identify the many inks used in ballpoint pens. Infrared spectra serve as excellent "fingerprints" for identifying organic and many inorganic compounds (see Chapter 23). These, together with other ingenious methods, are the techniques of modern qualitative analysis.

Courses in quantitative analysis traditionally have dealt almost exclusively with the analysis of inorganic material. Nevertheless, analytical chemistry properly includes the analysis of organic material too. Analytical chemistry finds extensive application in the analysis of organic compounds, pharmaceuticals, biochemicals, body fluids, hair, the atmosphere, polluted water, foods, soils, and in many other areas.

[1] "Scientific Methods of Crime Investigation," *Chemistry*, 43, 12 (1969).



**What Is an Analytical Chemist?** A true analyst, or analytical chemist, has several characteristics. He or she has a knowledge of the methods and instruments used for analysis. He understands the principles of analysis, so that he can apply and, if necessary, modify analytical methods to solve a particular problem; frequently he is a research chemist who studies the theory of analytical processes or develops completely new methods of analysis. He can evaluate and interpret the results of a quantitative analysis.

Above all, an analytical chemist is a problem solver. It has been said that if you can state a problem clearly, it can be solved. An analytical chemist must do just this. By asking questions and gathering information, he or she determines what the actual problem *is*, then uses experience and cleverness to map out a scheme for solving it.

Thus, an analytical chemist is a skilled, well-trained chemist—in sharp contrast with the more numerous technicians or “determinators,” who simply twist the dials of an instrument or follow “cookbook” analytical procedures.

**What Information Does Chemical Analysis Provide?** *Qualitative analysis* may be used to indicate the presence or absence of certain elements, ions, or molecules. For example, the first step in “screening” a suspicious solid sample for lysergic acid diethylamide (LSD) is to examine it under ultraviolet light [1]. Most hallucinogens such as LSD show up as fluorescent or discolored areas that can then be dissolved and tested further. A *structural determination* may be used to define the entire structure of a new drug or to verify only the structure or stereochemistry of a certain part of a newly synthesized molecule.

The most important aspect of analysis is still *quantitative analysis*, with which this book is mainly concerned. A quantitative analysis provides data regarding the chemical composition of matter. These data may be quite detailed, or they may be incomplete and general. The types of quantitative analysis may be classified as follows:

**Complete Analysis.** The amount of each constituent of the sample is determined quantitatively. For example, a complete analysis of a gasoline sample would tell the percentage of each compound present (hydrocarbons, tetraethyllead, tricresyl phosphate, etc.). In many samples, such an analysis would be a waste of time; instead a “complete” analysis is run for a select number of species. For example, in clinical laboratories, a “complete” blood analysis may involve the determination of eight or twelve species: glucose,  $\text{Na}^+$ ,  $\text{K}^+$ , bilirubin, alkaline phosphates, etc. [2].

**Ultimate Analysis.** The amount of each element in a sample is determined without regard to the actual compounds or ions present. An ultimate analysis of a gasoline sample would tell the percentage of carbon, hydrogen, oxygen, lead, phosphorus, etc.

**Partial Analysis.** The amount of a certain selected constituent in a sample is determined. A partial analysis of gasoline might tell the percentage of tetraethyl-

[2] L. T. Skeggs, *Anal. Chem.*, 38, 31A (May, 1966).