

AN  
INTRODUCTION  
TO  
CHEMICAL ANALYSIS

HARRIS / KRATOCHVIL

**WALTER E. HARRIS**

Professor of Analytical Chemistry  
University of Alberta

**BYRON KRATOCHVIL**

Professor of Analytical Chemistry  
University of Alberta

AN  
**INTRODUCTION**  
TO  
**CHEMICAL ANALYSIS**



**SAUNDERS GOLDEN SUNBURST SERIES**

SAUNDERS COLLEGE PUBLISHING  
Philadelphia

SAUNDERS COLLEGE PUBLISHING/CBS

Educational and Professional  
Publishing, A Division of CBS Inc.

Address Orders to: 383 Madison Ave.,  
New York, NY 10017

Address Editorial correspondence to:  
West Washington Square  
Philadelphia, PA 19105

*The cover.* One of the rewards of analytical chemistry is the opportunity it affords to work with a variety of colors. The items displayed suggest both the instrumental and noninstrumental sides of analysis. The visible region of the spectrum on the spine represents the important role of spectral methods in analysis. The other items displayed are: a molecular model of the magnesium-calmagite indicator complex; mixing coils from an automatic analyzer; an inductively coupled plasma flame during the measurement of a 1000-ppm solution of barium chloride; bromocresol green acid-base indicator at 0.2 pH intervals from pH 3.0 to 5.8; a liquid-liquid extraction separation of lead dithizone; titration of iron(II) with dichromate using diphenylaminesulfonate indicator; and a gas-chromatographic column.

An Introduction to Chemical Analysis

ISBN 0-03-056882-X

Copyright ©1981 by Saunders College Publishing. Copyright under the International Copyright Union. All rights reserved. This book is protected by copyright. No part of it may be reproduced, stored in a retrieval system, or transmitted in any form or by any means — electronic; mechanical, photocopying, recording, or otherwise — without written permission from the publisher. Made in the United States of America. Library of Congress catalog number 80-53930

1234 005 987654321

CBS COLLEGE PUBLISHING

## PREFACE

Our goals in writing this textbook are several: (1) to present analytical chemistry that is both accurate and current; (2) to provide laboratory procedures that emphasize workable, student-tested experiments; and (3) to present a readable, consistent level of theory with the student in mind.

We have aimed for a logical and concise style of presentation, illustrated often by examples that employ real data. The level of the material is designed for students who have a background in general chemistry and have sufficient appreciation of the need for high-quality experimental work to benefit from an intensive course in chemical measurements. Our overall objective is to develop in students a justified confidence in the quality of their experimental work, while providing them with the related theoretical background. The questions and problems at the end of each chapter are intended to serve as a systemic review of the material. For convenience in use, the examples and experiments have been set in a different format.

To reflect the practice of teaching a combination of noninstrumental and instrumental topics in introductory analytical courses, this book treats the two areas with about equal emphasis. It is designed to provide both the theoretical basis for analysis and a set of tested experiments on a level consistent with the description of the principles. No prior analytical experience is assumed; the book begins with basic analytical operations and builds progressively to current instrumental techniques. Our aim throughout is to give the reader a sense of the practical and its relation to theory. In explaining the fundamental basis of titrimetry we illustrate the calculated theoretical curves with data obtained in the laboratory. Such quantities as formal potentials and conditional equilibrium constants are of greater practical use than the more fundamental concepts of standard potential and thermodynamic equilibrium constants. Similarly, distribution ratios and partition ratios are more useful to the working analyst than distribution constants. The theory of sampling error is not only discussed, but its measurement is illustrated by an experiment.

Our experience indicates that student satisfaction and competence are enhanced when appropriate attention is paid initially to the fundamental techniques of measurement of weight and volume. Accordingly, more than usual detail on these topics is included. Also, we have emphasized polarography over more advanced electroanalytical methods in the belief that a student who understands direct-current polarography can quickly understand the more sophisticated techniques.

The detailed instructions for the procedures have been chosen, tested, and refined over a period of years. Unknown samples are used throughout; there is objective evidence that they increase both teaching effectiveness and student interest. We have attempted to recognize the realities of the marketplace by deleting a well-worked-out experiment because of the escalating cost of silver

nitrate; in other procedures more dilute solutions of silver are used with, we trust, minimal loss of instructional benefit.

As far as practical, SI units, with the exceptions listed in *Analytical Chemistry*, and the nomenclature, symbols, and abbreviations recommended by IUPAC have been adopted. In certain cases awkward situations arise. For instance, in chromatography the symbol  $D_m$  is widely used to denote diffusion coefficient in the mobile phase, while the same symbol is proposed for the mass distribution ratio. To reduce confusion we use the symbol  $k$  for mass distribution ratio (partition ratio).

The accompanying instructors' manual gives both philosophy and practical suggestions on the teaching of introductory analytical chemistry. It provides information on techniques for the development of workable procedures, valid samples, and sound grading scales.

Colleagues and associates have been more than liberal with their assistance. Extraordinary appreciation must be expressed to Lu Ziola and Phyllis Harris. Ms. Ziola's knowledge of TEXTFORM programming and computer typesetting carried the book through to the completion of pages. This allowed us to make changes up to the last minute, with a substantial saving in publication time.\* Phyllis Harris enhanced the quality in matters of style, clarity, and consistency and edited the copy.

Professor Fred Cantwell of the University of Alberta not only taught from the draft manuscript for a year but also willingly reviewed the manuscript twice. In both contexts he provided innumerable incisive comments and suggestions that we deeply appreciate. Dorothy Cox made many contributions, particularly in the laboratory experiments and discussions, and in writing the problems.

Appreciation is also expressed to those who reviewed the manuscript, Gary Asleson of the College of Charleston, James Anderson of the University of Georgia, and Stanley Pons of the University of Alberta; to Cathy Johnson for assisting with manuscript preparation, particularly with the figures and problems; and to Faye Nagle for drafting services. We also wish to thank John Vondeling and Lee Walters of Saunders for their encouragement and assistance in allowing us total responsibility for the book including typesetting at the University of Alberta.

Finally, we acknowledge the contributions of many others, including the teaching assistants and students with whom we have had the pleasure of working over the years. We welcome comments, suggestions, and criticisms.

W. E. HARRIS  
B. KRATOCHVIL

August, 1980



\*Writing and entry of material was begun in July, 1979, class material was produced as required throughout the following academic year, the first draft was completed in May, 1980, the revised manuscript on August 18, and page composition on September 30.

# I. PERIODIC CHART OF THE ELEMENTS

|          |        |          |         |          |         |          |          |          |          |          |         |          |        |          |         |        |          |         |          |          |          |         |          |        |
|----------|--------|----------|---------|----------|---------|----------|----------|----------|----------|----------|---------|----------|--------|----------|---------|--------|----------|---------|----------|----------|----------|---------|----------|--------|
| 1A       |        | 2A       |         |          |         |          |          |          |          |          |         |          |        |          |         |        |          |         | 3A       | 4A       | 5A       | 6A      | 7A       | 2      |
| 3        | Li     | Be       |         |          |         |          |          |          |          |          |         |          |        |          |         |        |          |         |          |          |          |         |          | He     |
| 11       | Na     | Mg       |         |          |         |          |          |          |          |          |         |          |        |          |         |        |          |         |          |          |          |         |          | 10     |
| 19       | K      | Ca       | Sc      | 21       | 22      | 23       | 24       | 25       | 26       | 27       | 28      | 29       | 30     | 31       | 32      | 33     | 34       | 35      | 36       | 37       | 38       | 39      | 40       | Ne     |
| 39       | 0983   | 40.08    | 44.9559 | 47.90    | 50.9415 | 51.996   | 54.9380  | 55.847   | 58.9332  | 58.70    | 63.546  | 65.38    | 69.72  | 72.59    | 74.9216 | 78.96  | 79.904   | 83.80   | 85.47    | 87.62    | 88.9059  | 91.22   | 92.9064  | 95.94  |
| 37       | Rb     | Sr       | Y       | 39       | 40      | 41       | 42       | 43       | 44       | 45       | 46      | 47       | 48     | 49       | 50      | 51     | 52       | 53      | 54       | 55       | 56       | 57      | 58       | 59     |
| 85       | 46.78  | 87.62    | 88.9059 | 91.22    | 92.9064 | 95.94    | 98.9062  | 100.9062 | 102.9055 | 106.4    | 107.868 | 112.41   | 114.82 | 118.69   | 121.75  | 127.60 | 126.9045 | 131.30  | 132.9054 | 137.33   | 138.9055 | 140.12  | 140.9077 | 144.24 |
| 55       | Cs     | Ba       | La      | 57       | 58      | 59       | 60       | 61       | 62       | 63       | 64      | 65       | 66     | 67       | 68      | 69     | 70       | 71      | 72       | 73       | 74       | 75      | 76       | 77     |
| 132.9054 | 137.33 | 138.9055 | 140.12  | 140.9077 | 144.24  | 145.9176 | 150.9196 | 151.964  | 157.25   | 158.9254 | 162.50  | 164.9304 | 167.26 | 168.9342 | 171.934 | 173.04 | 174.967  | 176.931 | 178.49   | 180.9479 | 183.85   | 186.207 | 188.9059 | 190.2  |
| 87       | Fr     | Ra       | Ac      | 89       | 90      | 91       | 92       | 93       | 94       | 95       | 96      | 97       | 98     | 99       | 100     | 101    | 102      | 103     | 104      | 105      | 106      | 107     | 108      | 109    |
| 223      | 223    | 226      | 227     | 227      | 228     | 232      | 233      | 237      | 244      | 247      | 251     | 252      | 257    | 261      | 265     | 269    | 272      | 285     | 289      | 293      | 297      | 301     | 305      | 309    |
| Fr       | Ra     | Ac       | Th      | Pa       | U       | Np       | Pu       | Am       | Cm       | Bk       | Cf      | Es       | Fm     | Md       | No      | Lr     | La       | Ce      | Pr       | Nd       | Pm       | Sm      | Eu       | Gd     |
|          |        |          |         |          |         |          |          |          |          |          |         |          |        |          |         |        |          |         |          |          |          |         |          |        |

For B, C, H, Pb, Sm, and S, the precision of the atomic weight is limited by variations in the isotopic abundances in terrestrial samples. For B, Li, and U, variations in atomic weights in processed material may occur because of commercial isotopic separations. Values are reliable to  $\pm 1$  in the last digit, or  $\pm 3$  if the last digit is smaller. Mass numbers in brackets are for most stable or best known isotope.

# CONTENTS

|                                                                                           |    |
|-------------------------------------------------------------------------------------------|----|
| CHAPTER 1. INTRODUCTION .....                                                             | 1  |
| 1-1 The Nature of Analytical Chemistry .....                                              | 1  |
| 1-2 Analytical Chemistry and Problems in Society. Public<br>Perceptions of Toxicity ..... | 2  |
| 1-3 Steps in Analysis .....                                                               | 4  |
| 1-4 Management of Experimental Data .....                                                 | 6  |
| 1-5 Statistics for Small Sets of Numbers .....                                            | 11 |
| PROBLEMS .....                                                                            | 13 |
| REFERENCES .....                                                                          | 15 |
| CHAPTER 2. BASIC LABORATORY OPERATIONS .....                                              | 16 |
| 2-1 Measurement of Weight .....                                                           | 16 |
| 2-2 Measurement of Volume .....                                                           | 24 |
| 2-3 Background for Beginning Laboratory Work .....                                        | 30 |
| 2-4 The Laboratory Notebook .....                                                         | 33 |
| 2-5 Preliminary Operations .....                                                          | 33 |
| 2-6 Use of the Analytical Balance .....                                                   | 37 |
| 2-7 Use of the Top-Loading Balance .....                                                  | 41 |
| 2-8 Calibration of Burets .....                                                           | 42 |
| 2-9 Calibration of Pipets .....                                                           | 44 |
| 2-10 Use of Pipets and Volumetric Flasks .....                                            | 45 |
| 2-11 Measurement Techniques and Line Widths .....                                         | 47 |
| PROBLEMS .....                                                                            | 47 |
| REFERENCES .....                                                                          | 50 |
| CHAPTER 3. Chemical Equilibrium. Introduction to Titrimetry .....                         | 51 |
| 3-1 Review of Chemical Equilibrium .....                                                  | 51 |
| 3-2 Titrimetric Methods .....                                                             | 55 |
| 3-3 Calculations in Titrimetric Analysis .....                                            | 59 |
| PROBLEMS .....                                                                            | 63 |
| REFERENCES .....                                                                          | 64 |
| CHAPTER 4. PRECIPITATION EQUILIBRIA AND TITRATIONS .....                                  | 65 |
| 4-1 Equilibria in Precipitation Titrations .....                                          | 65 |
| 4-2 Detection of the End Point: Methods and Indicators .....                              | 71 |
| 4-3 Applications .....                                                                    | 75 |
| 4-4 Argentimetric Determination of Chloride .....                                         | 75 |

|                                                              |                                                                                                                               |     |
|--------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------|-----|
| 4-5                                                          | Titrimetric Determination of Sulfate with Barium Using an Adsorption Indicator .....                                          | 79  |
|                                                              | PROBLEMS .....                                                                                                                | 81  |
|                                                              | REFERENCES .....                                                                                                              | 84  |
| CHAPTER 5. ACID-BASE EQUILIBRIA AND TITRATIONS .....         |                                                                                                                               | 85  |
| 5-1                                                          | Review of Fundamental Concepts .....                                                                                          | 85  |
| 5-2                                                          | Calculation of pH in Solutions of Acids, Bases, and their Salts. Calculation of Concentrations of Species at a Given pH ..... | 89  |
| 5-3                                                          | Buffer Solutions .....                                                                                                        | 99  |
| 5-4                                                          | Acid-Base Titrations .....                                                                                                    | 102 |
| 5-5                                                          | Molecules with Both Acidic and Basic Properties. Amino Acids .....                                                            | 111 |
| 5-6                                                          | Acid-Base Indicators .....                                                                                                    | 111 |
| 5-7                                                          | Titriments and Primary Standards .....                                                                                        | 114 |
| 5-8                                                          | Applications .....                                                                                                            | 116 |
| 5-9                                                          | Titration of Potassium Acid Phthalate .....                                                                                   | 121 |
| 5-10                                                         | Determination of Sodium Carbonate .....                                                                                       | 123 |
|                                                              | PROBLEMS .....                                                                                                                | 125 |
|                                                              | REFERENCES .....                                                                                                              | 129 |
| CHAPTER 6. ACID-BASE TITRATIONS IN NONAQUEOUS SOLVENTS ..... |                                                                                                                               | 130 |
| 6-1                                                          | Properties of Solvents .....                                                                                                  | 131 |
| 6-2                                                          | Titriments and Solvents .....                                                                                                 | 135 |
| 6-3                                                          | Detection of the End Point .....                                                                                              | 138 |
| 6-4                                                          | Applications .....                                                                                                            | 139 |
| 6-5                                                          | Nonaqueous Titration of Oxine .....                                                                                           | 140 |
| 6-6                                                          | Nonaqueous Photometric Titration of Oxine .....                                                                               | 142 |
| 6-7                                                          | Titration of Acetylsalicylic Acid .....                                                                                       | 145 |
|                                                              | PROBLEMS .....                                                                                                                | 146 |
|                                                              | REFERENCES .....                                                                                                              | 148 |
| CHAPTER 7. COMPLEXATION EQUILIBRIA AND TITRATIONS .....      |                                                                                                                               | 150 |
| 7-1                                                          | Equilibria with Unidentate Ligands .....                                                                                      | 152 |
| 7-2                                                          | Calculation of Concentrations of Species in Metal-Ligand Systems .....                                                        | 153 |
| 7-3                                                          | Multidentate Ligands. Ethylenediaminetetraacetic Acid (EDTA) .....                                                            | 156 |
| 7-4                                                          | EDTA Titration Curves .....                                                                                                   | 161 |
| 7-5                                                          | Indicators .....                                                                                                              | 163 |
| 7-6                                                          | Applications of EDTA Titrations .....                                                                                         | 166 |
| 7-7                                                          | Determination of Calcium and Magnesium in Limestone with EDTA .....                                                           | 169 |

|                                                                  |                                                                                                    |     |
|------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|-----|
| 7-8                                                              | Determination of Hardness of Water with EDTA .....                                                 | 171 |
|                                                                  | PROBLEMS .....                                                                                     | 172 |
|                                                                  | REFERENCES .....                                                                                   | 175 |
| CHAPTER 8. GRAVIMETRIC ANALYSIS .....                            |                                                                                                    | 176 |
| 8-1                                                              | Atomic Weights: A Historical Overview .....                                                        | 177 |
| 8-2                                                              | Properties of Precipitates .....                                                                   | 180 |
| 8-3                                                              | Precipitation from Homogeneous Solution .....                                                      | 189 |
| 8-4                                                              | Stoichiometry .....                                                                                | 190 |
| 8-5                                                              | Techniques of Filtration, Washing, and Ignition .....                                              | 191 |
| 8-6                                                              | Applications: Precipitation .....                                                                  | 195 |
| 8-7                                                              | Applications: Volatilization .....                                                                 | 196 |
| 8-8                                                              | Organic Reagents .....                                                                             | 198 |
| 8-9                                                              | Determination of Nickel as Nickel Dimethylglyoxime .....                                           | 200 |
| 8-10                                                             | Determination of Chloride as Silver Chloride .....                                                 | 201 |
| 8-11                                                             | Determination of Sulfate as Barium Sulfate .....                                                   | 203 |
|                                                                  | PROBLEMS .....                                                                                     | 204 |
|                                                                  | REFERENCES .....                                                                                   | 208 |
| CHAPTER 9. OXIDATION-REDUCTION REACTIONS AND<br>EQUILIBRIA ..... |                                                                                                    | 209 |
| 9-1                                                              | Definitions .....                                                                                  | 210 |
| 9-2                                                              | Equations for Oxidation-Reduction Reactions .....                                                  | 211 |
| 9-3                                                              | Standards of Potential. The Nernst Equation .....                                                  | 215 |
| 9-4                                                              | Oxidation-Reduction Equilibria .....                                                               | 223 |
| 9-5                                                              | Precision and Accuracy of Potentials. Formal Potentials .....                                      | 228 |
|                                                                  | PROBLEMS .....                                                                                     | 229 |
|                                                                  | REFERENCES .....                                                                                   | 232 |
| CHAPTER 10. OXIDATION-REDUCTION TITRATIONS .....                 |                                                                                                    | 233 |
| 10-1                                                             | Titration Curves .....                                                                             | 233 |
| 10-2                                                             | Detection of the Equivalence Point .....                                                           | 241 |
| 10-3                                                             | Reagents for Preliminary Oxidation or Reduction .....                                              | 243 |
| 10-4                                                             | Titriments and Primary Standards .....                                                             | 246 |
| 10-5                                                             | Other Oxidants and Reductants .....                                                                | 252 |
| 10-6                                                             | Note on Organic Analysis .....                                                                     | 254 |
| 10-7                                                             | Dichromate Determination of Iron in an Ore .....                                                   | 255 |
| 10-8                                                             | Permanganometric Determination of Iron in an Ore .....                                             | 258 |
| 10-9                                                             | Iodimetric Determination of Copper in Brass .....                                                  | 260 |
| 10-10                                                            | Organic Functional-Group Analysis: Determination of Ethylene<br>Glycol by Periodate Cleavage ..... | 262 |
|                                                                  | PROBLEMS .....                                                                                     | 266 |
|                                                                  | REFERENCES .....                                                                                   | 269 |

## CHAPTER 11. ELECTROANALYTICAL METHODS: POTENTIOMETRY AND SELECTIVE ELECTRODES ..... 270

|       |                                                                              |     |
|-------|------------------------------------------------------------------------------|-----|
| 11-1  | Potentials at Interfaces .....                                               | 271 |
| 11-2  | Measurement of Potential .....                                               | 273 |
| 11-3  | Junction Potentials .....                                                    | 275 |
| 11-4  | Reference Electrodes .....                                                   | 276 |
| 11-5  | Cells in Potentiometry .....                                                 | 279 |
| 11-6  | Direct Potentiometry .....                                                   | 280 |
| 11-7  | Selective Electrodes .....                                                   | 283 |
| 11-8  | Potentiometric Titrations .....                                              | 295 |
| 11-9  | Potentiometric Titration of an Acid Mixture .....                            | 299 |
| 11-10 | Potentiometric Titration of Cerium(IV) with Potassium<br>Ferrocyanoide ..... | 303 |
| 11-11 | Potentiometric Titration of NTA in a Detergent .....                         | 306 |
|       | PROBLEMS .....                                                               | 307 |
|       | REFERENCES .....                                                             | 310 |

## CHAPTER 12. OTHER ELECTROANALYTICAL METHODS ..... 311

|      |                                                                                                         |     |
|------|---------------------------------------------------------------------------------------------------------|-----|
| 12-1 | Quantitative Electrolysis: Coulometry and<br>Electrodeposition .....                                    | 311 |
| 12-2 | Polarography .....                                                                                      | 320 |
| 12-3 | Amperometric Titrations .....                                                                           | 328 |
| 12-4 | Other Electroanalytical Techniques .....                                                                | 332 |
| 12-5 | Conductometry .....                                                                                     | 336 |
| 12-6 | Constant-Current Coulometric Titration of Cyclohexene with<br>Electrochemically Generated Bromine ..... | 337 |
| 12-7 | Electrolytic Determination of Copper in Brass .....                                                     | 340 |
| 12-8 | Amperometric Titration of Arsenic(III) Using a Rotating<br>Platinum Electrode .....                     | 341 |
|      | PROBLEMS .....                                                                                          | 343 |
|      | REFERENCES .....                                                                                        | 345 |

## CHAPTER 13. REACTION-RATE METHODS IN ANALYSIS. RADIOCHEMISTRY ..... 347

|      |                                                                                                             |     |
|------|-------------------------------------------------------------------------------------------------------------|-----|
| 13-1 | The Concept of Rate of Reaction .....                                                                       | 347 |
| 13-2 | Enzyme-Catalyzed Reactions .....                                                                            | 351 |
| 13-3 | Applications of Rate Methods .....                                                                          | 352 |
| 13-4 | Radiochemistry .....                                                                                        | 355 |
| 13-5 | Applications of Radiochemistry to Analysis .....                                                            | 358 |
| 13-6 | Carrier Precipitation: Separation of Thorium-234 from<br>Uranium-238 and Measurement by Radioactivity ..... | 360 |
|      | PROBLEMS .....                                                                                              | 367 |
|      | REFERENCES .....                                                                                            | 369 |

**CHAPTER 14. INTRODUCTION TO SPECTRAL METHODS:  
ULTRAVIOLET AND VISIBLE SPECTROPHOTOMETRY ..... 370**

|       |                                                                                               |     |
|-------|-----------------------------------------------------------------------------------------------|-----|
| 14-1  | Characteristics of Electromagnetic Radiation .....                                            | 371 |
| 14-2  | Absorption and Emission of Photons .....                                                      | 374 |
| 14-3  | Absorption and Intensity Information .....                                                    | 378 |
| 14-4  | Precision of Measurements .....                                                               | 382 |
| 14-5  | Instrument Components for the UV and Visible Regions ....                                     | 384 |
| 14-6  | Spectrophotometers .....                                                                      | 392 |
| 14-7  | Quantitative Methodology .....                                                                | 396 |
| 14-8  | Fluorescence and Phosphorescence .....                                                        | 397 |
| 14-9  | Applications of Ultraviolet and Visible Methods .....                                         | 401 |
| 14-10 | Photometric Titrations .....                                                                  | 404 |
| 14-11 | Ammonia by the Nessler Standard-Series Method .....                                           | 406 |
| 14-12 | The Spectronic 20 and Sample-Tube Matching .....                                              | 410 |
| 14-13 | Spectrophotometric Determination of Trace Iron as Bipyridine<br>Complex .....                 | 412 |
| 14-14 | Simultaneous Spectrophotometric Determination of Cobalt and<br>Nickel as EDTA Complexes ..... | 415 |
| 14-15 | Photometric Titration of Iron(III) with EDTA .....                                            | 417 |
|       | PROBLEMS .....                                                                                | 419 |
|       | REFERENCES .....                                                                              | 423 |

**CHAPTER 15. OTHER SPECTRAL METHODS OF ANALYSIS ..... 424**

|      |                                                                                 |     |
|------|---------------------------------------------------------------------------------|-----|
| 15-1 | Infrared Spectrophotometry .....                                                | 424 |
| 15-2 | Nuclear Magnetic Resonance (NMR) .....                                          | 430 |
| 15-3 | X-Ray Fluorescence Analysis .....                                               | 433 |
| 15-4 | Raman Spectroscopy .....                                                        | 434 |
| 15-5 | Arc and Spark Emission Spectroscopy .....                                       | 436 |
| 15-6 | Flame Emission Spectroscopy .....                                               | 437 |
| 15-7 | Atomic Absorption .....                                                         | 439 |
| 15-8 | Atomic-Absorption Determination of Trace Copper in Nickel<br>Metal .....        | 443 |
| 15-9 | Infrared Spectrophotometric Determination of Four Substituted<br>Benzenes ..... | 447 |
|      | PROBLEMS .....                                                                  | 449 |
|      | REFERENCES .....                                                                | 452 |

**CHAPTER 16. SEPARATIONS IN ANALYSIS: SINGLE-STAGE AND  
OTHER TECHNIQUES ..... 453**

|      |                                                                                                                   |     |
|------|-------------------------------------------------------------------------------------------------------------------|-----|
| 16-1 | Background and Classification .....                                                                               | 453 |
| 16-2 | Liquid-Liquid Extraction .....                                                                                    | 455 |
| 16-3 | Determination of Trace Nickel by Liquid-Liquid Extraction<br>from Copper and Spectrophotometric Measurement ..... | 465 |

|                                                   |                                                                                                                   |     |
|---------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|-----|
| 16-4                                              | Determination of Aluminum by Liquid-Liquid Extraction from Iron and Titration with EDTA .....                     | 467 |
| 16-5                                              | Determination of Aluminum by Liquid-Liquid Extraction from Iron and Precipitation from Homogeneous Solution ..... | 471 |
|                                                   | PROBLEMS .....                                                                                                    | 473 |
|                                                   | REFERENCES .....                                                                                                  | 476 |
| CHAPTER 17. INTRODUCTION TO CHROMATOGRAPHY .....  |                                                                                                                   | 477 |
| 17-1                                              | Basic Concepts .....                                                                                              | 477 |
| 17-2                                              | Band Broadening .....                                                                                             | 482 |
| 17-3                                              | The Separation of Mixtures: Resolution .....                                                                      | 490 |
|                                                   | PROBLEMS .....                                                                                                    | 491 |
|                                                   | REFERENCES .....                                                                                                  | 493 |
| CHAPTER 18. GAS CHROMATOGRAPHY .....              |                                                                                                                   | 494 |
| 18-1                                              | Factors Affecting Separation .....                                                                                | 494 |
| 18-2                                              | Detection and Identification .....                                                                                | 499 |
| 18-3                                              | Quantitative Analysis .....                                                                                       | 502 |
| 18-4                                              | Temperature Programming .....                                                                                     | 505 |
| 18-5                                              | Separation and Analysis of a Mixture of Benzene and Cyclohexane .....                                             | 506 |
|                                                   | PROBLEMS .....                                                                                                    | 508 |
|                                                   | REFERENCES .....                                                                                                  | 510 |
| CHAPTER 19. LIQUID CHROMATOGRAPHY .....           |                                                                                                                   | 511 |
| 19-1                                              | Ion-Exchange Chromatography .....                                                                                 | 512 |
| 19-2                                              | Adsorption Chromatography .....                                                                                   | 519 |
| 19-3                                              | Liquid-Liquid Chromatography .....                                                                                | 521 |
| 19-4                                              | Exclusion Chromatography .....                                                                                    | 521 |
| 19-5                                              | High-Pressure Liquid Chromatography .....                                                                         | 523 |
| 19-6                                              | Thin-Layer and Paper Chromatography .....                                                                         | 525 |
| 19-7                                              | Determination of Total Salt in a Mixture by Ion Exchange .                                                        | 528 |
| 19-8                                              | Zinc and Nickel by Ion-Exchange Separation and Complexation Titration .....                                       | 530 |
| 19-9                                              | <i>ortho</i> - and <i>para</i> -Nitroaniline in a Mixture by Liquid Chromatography .....                          | 533 |
|                                                   | PROBLEMS .....                                                                                                    | 536 |
|                                                   | REFERENCES .....                                                                                                  | 538 |
| CHAPTER 20. AUTOMATION IN CHEMICAL ANALYSIS ..... |                                                                                                                   | 539 |
| 20-1                                              | Automation of Single Operations .....                                                                             | 540 |
| 20-2                                              | Continuous Analysis .....                                                                                         | 541 |
| 20-3                                              | Determination of Glucose by Automatic Analysis .....                                                              | 546 |

|                                                                              |     |
|------------------------------------------------------------------------------|-----|
| PROBLEMS .....                                                               | 549 |
| REFERENCES .....                                                             | 550 |
| CHAPTER 21. SAMPLING. PRELIMINARY STEPS IN ANALYSIS .....                    | 551 |
| 21-1 Obtaining Representative Samples .....                                  | 552 |
| 21-2 Errors in Sampling .....                                                | 553 |
| 21-3 Preliminary Treatment of Samples .....                                  | 556 |
| 21-4 Experimental Determination of Sampling Error .....                      | 559 |
| PROBLEMS .....                                                               | 562 |
| REFERENCES .....                                                             | 563 |
| CHAPTER 22. EVALUATION OF EXPERIMENTAL DATA .....                            | 564 |
| 22-1 Indeterminate (Random) Error and the Gaussian-Distribution Curve .....  | 564 |
| 22-2 Testing Whether Two Means Differ .....                                  | 567 |
| 22-3 Testing Whether Two Standard Deviations Differ .....                    | 569 |
| 22-4 Fitting Straight-Line Relations .....                                   | 570 |
| 22-5 Uncertainty in a Result from a Calibration Curve .....                  | 573 |
| 22-6 Correlation Coefficients .....                                          | 575 |
| 22-7 Evaluation of Prejudice in Data .....                                   | 577 |
| PROBLEMS .....                                                               | 580 |
| REFERENCES .....                                                             | 582 |
| CHAPTER 23. ANALYTICAL PROBLEM SOLVING. USE OF THE CHEMICAL LITERATURE ..... | 583 |
| 23-1 Approaching an Analytical Problem .....                                 | 583 |
| 23-2 The Literature of Analytical Chemistry .....                            | 584 |
| 23-3 Consulting the Chemical Literature .....                                | 587 |
| 23-4 A Problem in Literature Searching .....                                 | 588 |
| PROBLEMS .....                                                               | 590 |
| REFERENCES .....                                                             | 593 |
| ANSWERS TO NUMERICAL PROBLEMS .....                                          | 594 |
| APPENDIX .....                                                               | 598 |
| INDEX .....                                                                  | 602 |

# LIST OF EXPERIMENTS

| Section Number | Experiment                                                                  | Page |
|----------------|-----------------------------------------------------------------------------|------|
| 2-6            | Use of the Analytical <b>Balance</b> .....                                  | 37   |
| 2-8            | Calibration of <b>Burets</b> .....                                          | 42   |
| 2-9            | Calibration of <b>Pipets</b> .....                                          | 44   |
| 2-10           | Use of <b>Pipets and Volumetric Flasks</b> .....                            | 45   |
| 4-4            | Argentimetric Determination of <b>Chloride</b> .....                        | 75   |
| 4-5            | Titrimetric Determination of <b>Sulfate</b> .....                           | 79   |
| 5-9            | Titration of <b>Potassium Acid Phthalate</b> .....                          | 121  |
| 5-10           | Determination of <b>Sodium Carbonate</b> .....                              | 123  |
| 6-5            | Nonaqueous Titration of <b>Oxine</b> .....                                  | 140  |
| 6-6            | Nonaqueous Photometric Titration of <b>Oxine</b> .....                      | 142  |
| 6-7            | Titration of <b>Acetylsalicylic Acid</b> .....                              | 145  |
| 7-7            | Determination of <b>Calcium and Magnesium</b> in Limestone .....            | 169  |
| 7-8            | Determination of <b>Hardness in Water</b> with EDTA .....                   | 171  |
| 8-9            | Determination of <b>Nickel</b> as Nickel Dimethylglyoxime .....             | 200  |
| 8-10           | Determination of <b>Chloride</b> as Silver Chloride .....                   | 201  |
| 8-11           | Determination of <b>Sulfate</b> as Barium Sulfate .....                     | 203  |
| 10-7           | Dichromate Determination of <b>Iron</b> in an Ore .....                     | 255  |
| 10-8           | Permanganimetric Determination of <b>Iron</b> in an Ore .....               | 258  |
| 10-9           | Iodimetric Determination of <b>Copper</b> in Brass .....                    | 260  |
| 10-10          | Determination of <b>Ethylene Glycol</b> .....                               | 262  |
| 11-9           | Potentiometric Titration of an <b>Acid Mixture</b> .....                    | 299  |
| 11-10          | Potentiometric Titration of <b>Cerium(IV)</b> .....                         | 303  |
| 11-11          | Potentiometric Titration of <b>NTA</b> in a Detergent .....                 | 306  |
| 12-6           | Coulometric Titration of <b>Cyclohexene</b> .....                           | 337  |
| 12-7           | Electrolytic Determination of <b>Copper</b> in Brass .....                  | 340  |
| 12-8           | Amperometric Titration of <b>Arsenic(III)</b> .....                         | 341  |
| 13-6           | Determination of <b>Thorium-234</b> in Uranium-238 .....                    | 360  |
| 14-11          | <b>Ammonia</b> by the Nessler Standard-Series Method .....                  | 406  |
| 14-12          | The Spectronic 20 and <b>Sample-Tube Matching</b> .....                     | 410  |
| 14-13          | Spectrophotometric Determination of <b>Trace Iron</b> .....                 | 412  |
| 14-14          | Spectrophotometric Determination of <b>Cobalt and Nickel</b> .....          | 415  |
| 14-15          | Photometric Titration of <b>Iron(III)</b> with EDTA .....                   | 417  |
| 15-8           | Determination of <b>Trace Copper</b> in Nickel .....                        | 443  |
| 15-9           | Determination of Four <b>Substituted Benzenes</b> .....                     | 447  |
| 16-3           | Determination of <b>Trace Nickel</b> in Copper .....                        | 465  |
| 16-4           | Determination of <b>Aluminum</b> with EDTA .....                            | 467  |
| 16-5           | Determination of <b>Aluminum</b> by Precipitation .....                     | 471  |
| 18-5           | Determination of <b>Benzene and Cyclohexane</b> .....                       | 506  |
| 19-7           | Determination of <b>Total Salt</b> by Ion Exchange .....                    | 528  |
| 19-8           | Determination of <b>Zinc and Nickel</b> by Ion Exchange .....               | 530  |
| 19-9           | Determination of <i>ortho</i> - and <i>para</i> - <b>Nitroaniline</b> ..... | 533  |
| 20-3           | <b>Glucose</b> by Automatic Analysis .....                                  | 546  |
| 21-4           | Experimental Determination of <b>Sampling Error</b> .....                   | 559  |
| 22-7           | Evaluation of <b>Prejudice</b> in Data .....                                | 577  |
| 23-4           | A Problem in <b>Literature Searching</b> .....                              | 588  |

# 1

## INTRODUCTION

When it has once been given a man to do some sensible things, afterwards his life is a little different.

A. Einstein

### 1-1 THE NATURE OF ANALYTICAL CHEMISTRY

*Analytical chemistry* deals with the identification, characterization, and measurement of the chemical species present in a sample. It may also be involved in the characterization of a sample through measurement of its physical properties, such as the viscosity of an oil or the crystal structure of a mineral. The scope of modern analytical chemistry is thus extremely broad, and it continues to expand as society and technology impose new demands on it. These demands extend from the identification and measurement (typically at the part-per-billion level) of environmental contaminants in water, air, and soil, or of impurities in materials for semiconductors in electronics, to continuous monitoring of the levels of critical substances in the bloodstream of hospital patients. To meet such demands has required the development of a host of new analytical techniques and instruments.

Analytical chemistry is a dynamic, challenging field called upon to solve many kinds of problems with technology that constantly provides new measurement tools. For example, more and more substances are being found whose concentration levels in the human body serve as indicators of health or of specific disorders. In pharmacology, accurate adjustment of a drug dose for an individual may necessitate the determination of its levels in the bloodstream. Because these measurements must be made rapidly and in large numbers, the development of efficient automated methods is important. Thus the role of an analytical chemist is essential not only to chemical science but also to allied areas in biology, food science, medicine, biochemistry, and engineering.

That part of analytical chemistry dealing with the measurement of the quantity of a substance present in a material is termed *quantitative analysis*, and is the area considered in this book. Training in this area includes more than an introduction to various methods of analysis. It involves evaluation of problems from the standpoints of proper acquisition of samples, selection of

analytical methods, consideration of possible interfering substances, and sound interpretation of results. It also fosters an appreciation of the care necessary in laboratory operations and provides experience in logic and planning that is valuable in all fields.

## 1-2 ANALYTICAL CHEMISTRY AND PROBLEMS IN SOCIETY. PUBLIC PERCEPTIONS OF TOXICITY

Analytical chemistry sits at the core of all regulations designed to protect the public from chemical exposure that may present a significant health risk.

J. G. Rodricks

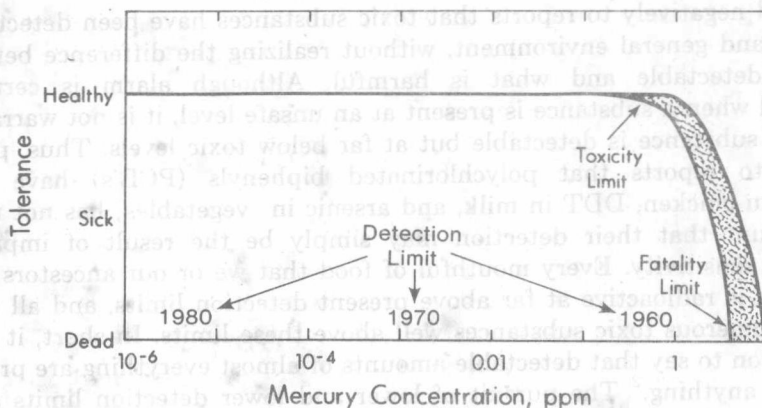
Analytical chemistry, because it permeates almost every aspect of society, has profound implications for human welfare. An example is the analysis of materials for chemicals of possible toxicity to man. Threats to health, whether perceived or real, are of intense concern to the public. In the setting, monitoring, and enforcing of regulations regarding toxic substances, analytical chemistry plays a key role.

When foods were tested in past decades for toxic materials, they were presumed safe if such materials were not detected. Today, all foods can be shown to contain detectable amounts of a host of toxic materials. Such information is unsettling to the public. Nevertheless, food now is probably generally safer and of better quality than ever before. What has happened? To clarify this seeming contradiction, two terms relating to toxicity and one concerning the limit of analytical measurement should be described. The *fatality limit*<sup>1</sup> is the level of chemical exposure that when maintained for any length of time results in death. This limit depends on the nature of the chemical, the type of exposure, and on individual human factors such as size, age, general health, and smoking habits. The *toxicity limit* is the limit where well-being is first noticeably affected. This limit also depends on the chemical, the type of exposure, and individual human factors. It cannot be sharply defined. For benzene the toxicity limit is about 25 ppm, for the refrigerant gas freon about 1000 ppm, and for the fungal metabolite aflatoxin about 0.03 ppm.

Between the fatality limit and the toxicity limit an individual's health is affected. For the many chemicals essential to normal health (including water, oxygen, potassium, fluoride, selenium, and chromium) intake must not be reduced too far or health is affected by deficiency, which in the limit is fatal also.

The *detection limit* is the minimum amount of a substance that can be determined by a laboratory test procedure. This limit depends on the state of the art in analytical laboratories. The detection limit is completely independent of the other two and is continually being lowered as knowledge

<sup>1</sup>Both fatality and toxicity limits may be either acute or chronic. The acute limit is that for an exposure of short duration; the chronic limit is for exposures of long duration. Chronic limits are lower than acute limits. Types of exposure include inhalation, ingestion, and skin contact.



**Figure 1-1.** Schematic diagram illustrating the relation between the fatality and toxicity limits and the changing detection limits with time for mercury.

of chemistry improves and more sensitive instrumentation is developed.

The difference between detection limit and fatality or toxicity limit is not significant as long as the detection limit is below the toxicity limit. One of the greatest differences exists for the detection of radioactive substances, where the detection limit is billions of times lower than the toxicity limit. The levels of radioactivity normally present in our bodies from such atoms as carbon-14 and potassium-40 are easily measurable by present techniques.

Two or three decades ago, detection limits and toxicity limits for many materials were in the same range. But now detection limits have dropped far below toxicity limits. Unfortunately, misinterpretation of these greatly decreased detection limits has resulted in serious abuses in the use and interpretation of modern analytical information.

### EXAMPLE 1-1

Twenty years ago detection and toxicity limits for mercury were about the same, and the detection of mercury in food was cause for justifiable concern. Since then detection limits have been dramatically lowered. Figure 1-1 depicts schematically the relation between the fatality limit, toxicity limit, and changing detection limits for mercury. A decade ago calls for the banning of food products were made because mercury had been detected in them — even though the amount was well below the toxicity limit.

Toxicity limits are established from the evaluation of numerous medical records. As indicated in Figure 1-1, the toxicity curve in the region of the toxicity limit shows a gradual rather than a sharp change, indicating the limit to be somewhat arbitrary. This applies to all substances. The value of this limit is unlikely to change substantially in the future. On the other hand, as analytical knowledge and techniques improve, detection limits will undoubtedly continue to fall, but never reach zero.

The general public and even many scientists have been slow to recognize the significance of the dramatic changes in detection limits brought about by improved analytical methods. Instead of being reassured by more precise information on levels of potentially hazardous substances, they have often