ANALYTICAL CHEMISTRY

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SECOND EDITION

ANALYTICAL CHEMISTRY

2nd Edition

UNIVERSITY OF WASHINGTON

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PREFACE

to the Second Edition

With today's familiar cry by students for "relevance" in course work, analytical chemistry stands out as one example of a practical and useful subject. Chemical analysis is used in many fields of science, from the clinical laboratory, the biochemist's laboratory, and the physiologist's laboratory to the engineer's laboratory. It is used as an intrinsic tool in geology, oceanography, and air and water pollution. Rare is the chemist who does not rely frequently upon analytical chemistry for the solution of his problems.

The wide utility of analytical chemistry is sufficient reason alone for treating it as an individual course. Another reason, nearly as important, is that the analytical chemistry course is one of the few where the student learns careful and quantitative laboratory skills and techniques. These skills are critically important for the nurse, the physician, the dentist, the pharmacist, and for those in many other professions. Analytical chemistry becomes a little more exciting when the student realizes that an incorrect blood analysis may endanger a patient's life, or that an error in quality-control analysis may result in serious financial loss for a manufacturer.

The emphasis of this second edition of *Analytical Chemistry* remains the same as in the first. It is for the nonchemistry major, with emphasis on the life sciences applications of analytical chemistry. A practical approach is retained with a deemphasis of complex equilibria as much as is practical. Some sections on equilibria have been expanded somewhat, however, in order to make the discussions less intuitive in nature. The section on complexation equilibria, for example, is expanded so that tabulated formation constants (added in Appendix C) can be used in calculations. The discussion of solubility product equilibria has been moved from Chapter 13, "Precipitation and Complexometric Titrations," to Chapter 6, "Gravimetric Analysis," since the equilibria are useful in understanding the precipitation phenomena.

The organization of the text remains essentially the same, following the orderly sequence of an analysis. The major change is placing Chapter 4, "Data Handling," toward the front of the text, since these skills are required early in the laboratory experiments. Major sections have been kept sufficiently separated from each other that they can be covered in different sequence. Some instructors, for example, may prefer to delay the teaching of separation methods until the student has a more thorough grounding in the basic equilibria that are covered in the chapters on volumetric measurement.

New chapters on nonaqueous titrations and drug analysis have been added. Acid-base theories have been moved to Chapter 12, "Nonaqueous Titrations," so that the student will be well grounded in the more familiar Arrhenius theory first.

A number of sections have been expanded and new ones added. Tests of significance are included in Chapter 4, since they are widely used in the life sciences. A description of multiple extractions (countercurrent distribution) has been added to Chapter 7, "Solvent Extraction," a logical lead-up to chromatographic separations in Chapter 8. An important addition to that chapter is a major section on the new technique of high-speed liquid chromatography.

The concept of normality is introduced in Chapter 9, "Principles of Volumetric Analysis." Dimensional units are included in calculations throughout the text to give the student a better feel for the proper setting up of problems. Also,

new homework problems have been added. The more challenging problems are marked with an asterisk. As before, a solutions manual is available containing detailed calculations for problems and answers for questions; this should serve as a reinforcing aid for the student.

The review of balancing redox reactions has been moved to Chapter 14, "Reduction-Oxidation Titrations," which uses a simpler method for balancing that does not require knowledge of the changes in oxidation states. The discussion of potentiometric titrations now includes derivative titrations and Gran's plot titrations (the latter a particularly useful technique for use with ion selective electrodes).

In Chapter 17, "Spectrometry," an expanded section has been added on the relationship of absorption spectra to molecular structure, and the quantitative analysis of mixtures of substances with overlapping spectra is also covered. A discussion of nonflame atomization techniques has been added to the section on atomic absorption spectrophotometry.

The discussion of the principles of enzyme rate methods is expanded in Chapter 19, "Kinetic Methods of Analysis," for a more thorough understanding of the capabilities of the techniques. A section on enzymes in diagnosis of disease is also included in Chapter 23, "Clinical Chemistry," along with the new technique of radioimmunoassay. Chapter 20, "Radiochemical Methods of Analysis," includes a description of solid-state semiconductor detectors, and the centrifugal analyzer is described in Chapter 22, "Automation in the Laboratory." Chapter 25, "Pollution Analysis," now includes descriptions of sampling procedures and summaries of representative analyses.

In order to make room for the new material, some topics had to be eliminated. The chapter on laboratory safety was deleted, and hopefully the instructor will have the necessary information available in the laboratory anyway. The less-used chapters on miscellaneous methods of separation and optical rotatory dispersion were taken out. The chapter on sampling was eliminated (with essential parts retained in other chapters), since this is frequently not covered and adequate treatment is better left to more advanced texts. The same is true of the chapter on the development of an analytical procedure, although the description of the literature of analytical chemistry is included in Appendix A. The section on classical methods of gas analysis was deleted since gas chromatography is now widely used in place of these methods. Also, it was felt that proper treatment of the use of computers in analytical chemistry is better handled in a more advanced text or a separate course.

Eight of the old experiments have been eliminated while 14 new ones have been added, for a total of 51 experiments. A gravimetric nickel-dimethylglyoxime experiment was added as an alternative to the more expensive silver chloride experiment. Similarly, a precipitation titration of sulfate in urine is included as an alternative to the more expensive mercurimetric titration of blood or urine chloride. A number of environmentally related experiments have been added. These include the determination of sulfur dioxide in air, mercury in air, nitrate in water, detergents in water, and lead on leaves. Many of these can be used in place of other spectrophotometric experiments. Additional new experiments include thin-layer chromatography of amino acids, two nonaqueous titrations, potentiometric determination of fluoride in water, spectrophotometric determination of a mixture of chromium and man-

ganese, fluorometric determination of riboflavin, atomic absorption determination of copper in urine, and ultraviolet analysis of APC tablets.

Ion-exchange chromatography experiments and solvent extraction experiments have been integrated with experiments in later chapters, since titrations or spectrophotometric measurements are required to complete the analyses.

All experiments have been reorganized. More detailed descriptions of the principles are given, along with chemical reactions involved. The directions are organized with more subheadings to identify each step, and instructions are given in each experiment in order to be prepared to complete the experiment during one laboratory session. Most of the experiment footnotes in the first edition have been included in the text of the experiments, since many were an integral part. The experiments in the earlier chapters dealing with fundamentals of different analytical techniques include directions for calculations. But the later experiments in the applications chapters have these omitted, since the student should be better equipped to handle calculations at this stage.

Several experiments again require the use of either blood or urine. Various sources of blood are available, including freeze-dried standard serum samples or outdated blood-bank blood. Animal blood is usually satisfactory. Various types of animal blood preparations can be obtained from Animal Blood Centre, Inc., P.O. Box 2, Dewitt Branch, Syracuse, New York.

The suggestions of a number of colleagues have aided greatly in the revision of the text. The author would like to express his appreciation to Professors T. R. Dickson, Robert L. Grob, Janan Hayes, Calvin O. Huber, Harold M. McNair, Robert L. Osburn, Gordon A. Parker, and Robert L. Pecksok. Dr. Larry H. Thomas and Linda Marshall checked all the calculations for the solutions manual, an arduous but much appreciated task. I especially thank my students and other users of the text who have contributed comments and suggestions for changes.

Solutions Manual. A comprehensive solutions manual is available for use by students in which all problems are completely worked out. Also, all questions are answered, summarizing the appropriate material in the text with the corresponding text page numbers given.

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PART ONE

PRINCIPLES OF ANALYTICAL CHEMISTRY

Chapter 1

Introduction to Analytical Chemistry

CHAPTER One

Introduction

Analytical chemistry can be thought of as comprising two branches, qualitative and quantitative. Qualitative analysis deals with finding *what* constituent or constituents are in an analytical sample, and quantitative analysis deals with the determination of *how much* of a given substance is in the sample. In the latter case, a history of the sample composition will generally be known; or else the analyst will have performed a qualitative test. With today's instrumentation and with the large variety of chemical measurements available, specificity or sufficient selectivity[1] can often be achieved so that the quantitative measurement serves as a qualitative measurement. However, simple qualitative tests are usually more rapid than quantitative procedures.

Qualitative analysis is composed of two fields: inorganic and organic. The former is usually covered in introductory chemistry courses, whereas the latter is best left until after the student has had a course in organic chemistry. This text deals principally with quantitative analysis. In the consideration of applications of different techniques, emphasis is placed on situations that the life scientist may be expected to encounter. However, discussions are sufficiently broad to include other areas of general interest.

1.1 THE ANALYTICAL PROCESS

The analytical process involves a logical sequence: (1) defining the problem, (2) obtaining and dissolving the sample, (3) performing the required separations, (4) making the appropriate measurements, and (5) data presentation. The unit operations of analytical chemistry that are common to most types of analyses are considered in more detail below.

1.1.1 Defining the Problem

In defining the analytical problem, the analyst asks himself such questions as: What information is required? How sensitive must the method be? How accurate and precise[2] must it be? What interferences are likely and what separations are required? How soon must the results be available? How many samples must be run? What equipment is available? What is the cost?

Examples of the manner in which the analysis of particular types of samples are made are given in Chapters 23-25 at the end of the text. These chapters describe commonly performed clinical, drug, and pollution analyses. The various techniques described in this text are utilized for the specific analyses. Hence, it will be useful for you to read through these chapters after completing the majority of this course to gain an appreciation of what goes into analyzing real samples and why the analyses are made.

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[1] A clear distinction should be made between the terms *specific* and *selective*. A specific reaction or test is one that occurs only with the substance of interest, while a selective reaction or test is one that can occur with other substances but exhibits a degree of preference for the substance of interest. Few reactions are specific but many exhibit selectivity.

[2] *Accuracy* is the degree of agreement between a measured value and a true value. *Precision* is the degree of agreement between replicate measurements of the same quantity and does not necessarily imply accuracy. These terms are discussed in more detail in Section 4.3.