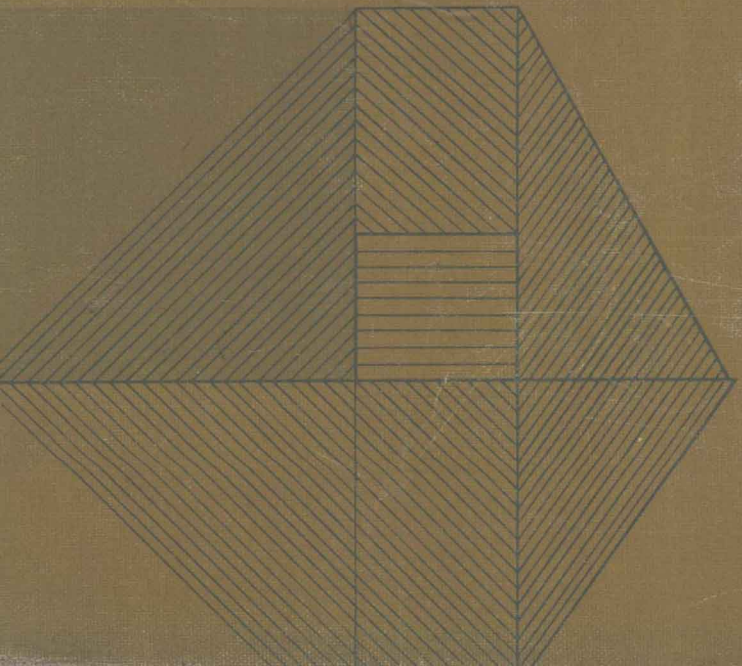
ELEMENTARY QUANTITATIVE ANALYSIS

Theory and Practice

Second Edition

W. J. Blaedel and V. W. Meloche



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Theory and Practice

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Harper & Row, Publishers
New York, Evanston, and London

Elementary Quantitative Analysis, Second Edition

Library of Congress catalog card number: 63-13613

PREFACE

This one-semester text should satisfy the requirements of a beginning course in inorganic quantitative analysis in the sophomore year. The topics of analytical chemistry are presented at two levels—in the text proper, and in the Supplement. The main body of the text is intended for study by both the chemistry major and the student majoring in other fields. Interesting proofs, details, and extensions of some topics in the main text are gathered into the Supplement, so that they will be available on an optional basis to those students and instructors who want them. This dual method of presentation will, we hope, lighten the teaching load of the instructor as well as the study load of the student.

Almost all the topics of elementary quantitative analysis are introduced in the text and the Supplement. Although prepared for the elementary course, the book contains more work than can be covered in the usual one-semester period. To facilitate the choice of study material by the student and the instructor, the text is organized in strict outline form.

Principles from other fields of science are involved in some subjects in quantitative analysis, such as statistics, equilibrium constants, electrode potentials, and instrumentation. We have attempted first to present these principles logically and independently, and then to apply them to quantitative analysis. Greater detail on topic sequence and organization is given in Chapter 1.

There is no arbitrary separation of theory, technique, and problem working, and an attempt has been made to stress all three equally. A rightful and necessary emphasis upon calculations is developed within the text, concurrently with the theoretical presentation of each topic. Insofar as is feasible, this is also done with experimental work.

The writing of a text is a humbling experience. In retrospect, we find that there are only a few ideas in this text which are our own. On each topic we have simply set down what seemed to us to be the best of the ideas of many people. Our methods and presentations have been greatly influenced by the concepts of other authors. It is impossible to express adequately our appreciation of the contributions of our colleagues,

graduate and undergraduate students, and secretaries, who gave so generously of their time, effort, and opinions. In particular, the help of Dr. Carter Olson in designing Experiment 22.1 is acknowledged.

Several important changes have been made in this second edition. Some modes of presentation have been altered or improved. Some topics of little general interest have been eliminated. Complexation and potentiometric titrations have been introduced. The problems after Chapter 3 have been very extensively revised.

This text should provide a core for the majority of work in the elementary analytical course. We know that our attempt to achieve depth in the Supplement has resulted in omission of a few topics that are considered important by some instructors. We hope that these omissions or inadequacies are few enough so that the usefulness of the text will not be impaired.

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1 THE STUDY OF QUANTITATIVE ANALYSIS

1A. PRIMARY OBJECTIVES

The study of analytical chemistry provides ideal training for nearly all scientists. A course in quantitative analysis equips the student with the ability to plan and to execute experimental work; it develops in him the ability to record and to interpret such work; and it trains him to understand and to communicate what he has done. These scientific abilities are extremely important; it is through them that the individual worker applies his knowledge and contributes to mankind's progress.

Furthermore, a course in quantitative analysis should impress upon the student the wide importance and the applicability of analytical chemistry and its relation to other branches of science.

Finally, and obviously, the course should extend the student's chemical knowledge and technique beyond the introductory level of general chemistry.

1A.1. Scientific Ability and Quantitative Analysis

Scientific ability is not a single characteristic, nor is it acquired without effort. It is a composite of many characteristics, acquired through many years of training, work, and concentration. It is more than the ability to assimilate theory, or to reason abstractly, or to plan well, or to use one's hands, or to convey ideas; it is the coordinated application of all these skills to the acquisition and extension of knowledge. The course in quantitative analysis is a very important link in the chain of

studies that develops this scientific ability in the chemist. With its multiple emphasis on theory, laboratory work, and high accuracy in the analysis of unknown samples, quantitative analysis is one of the most valuable courses in the student's training. No other chemistry course may be satisfactorily substituted for it.

1A.2. Importance of Quantitative Analysis

Quantitative analysis derives much of its knowledge from the other three divisions of chemistry. For example, knowledge of the properties of substances on which analyses are based is drawn from inorganic and organic chemistry. The methods and instruments used for measurement in analyses are drawn from physics and physical chemistry.

But, conversely, almost any study in chemistry has its analytical aspect, whether it is in research, development, or production. Analytical chemistry permeates the other fields of chemistry to such an extent that no chemist may consider himself free of its influences. With few exceptions, quantitative analysis is essential to all other areas of chemical science.

In spite of the importance of analytical chemistry to almost every chemical problem, workers often attempt to minimize or circumvent the analytical phase, for a reason that is understandable. Since the analytical effort is usually only a means to an end, there is often impatience with such a means, particularly if it is exacting or time consuming.

It is not the purpose of this text to extol the virtues of analytical chemistry. It is the purpose, however, to develop an awareness of the importance of analytical chemistry to all chemical problems, and to emphasize the fact that neglect of the analytical phase usually causes more confusion and loss of effort than is apparently saved by such negligence. The chemist who moves heaven and earth to avoid what he considers a mundane gravimetric analysis is not a good chemist. Also, the chemical engineer who takes a process into a pilot or semiworks stage without first making thorough provision for proper sampling and analysis at all steps materially increases the chances of confusion and failure of the process.

As far as practical importance is concerned, hundreds of millions of quantitative determinations are performed yearly in monitoring the processes and materials of American metallurgical industries alone. Comparable effort is expended in other chemical industries. Every individual who reads this text has probably undergone clinical tests and determinations; without the hundreds of millions of these that are performed yearly, our physicians and hospitals could not function properly. It is no exaggeration to say that without chemical analysis,

our industries and the civilization that they support could not exist as we know them today.

1B. ORGANIZATION OF THE TEXT

1B.1. Topic Sequence

There are four parts to this one-semester text: Part One, Introduction; Part Two, Gravimetric Analysis; Part Three, Volumetric Analysis; and Part Four, Special Topics. The theory, practice, and problem working of elementary quantitative analysis are integrated throughout, on the conviction that confusion arises in any attempt to separate or deemphasize one of them with respect to the other two.

The first five chapters include the prerequisite and introductory topics of quantitative analysis. This first chapter considers the study of quantitative analysis. The quantitative analytical process is outlined in an introductory way in Chapter 2. Chapters 3 and 4 summarize and review some essential aspects of elementary mathematics and chemistry. The fifth chapter introduces the concepts of accuracy, precision, computation, and the treatment of quantitative data.

In practice, laboratory work should begin immediately. It is therefore recommended that systematic study of the text begin with Chapter 6, and that the introductory chapters (1–5) be studied concurrently or intermittently, as the need arises. These two groups of chapters (1–5 and 6–13) are written with this necessity in mind. But the sooner the student masters the content of chapters 1 to 5, the more thoroughly will he understand the work of the rest of the course.

Chapter 6 introduces the student to laboratory work. Chapters 7 and 8 cover the analytical balance and gravimetric techniques. Chapters 9 and 10 deal with gravimetric calculations and analysis by evolution, which represents the simplest kind of gravimetric procedure. After these chapters the theory of gravimetric precipitation processes is presented, including solubility product (chapters 11, 12). A detailed description of two methods (for chloride and sulfate) and a summary of some others close the section on gravimetric analysis (Chapter 13).

After this, the transition to volumetric analysis by precipitation processes is easy (chapters 14–16). Acidimetry and alkalimetry (chapters 17, 18) follow, together with the quantitative treatment of acid-base equilibria, which are more complicated than those involving only solubility product. Redox titration, including study of the table of standard potentials, may be made the last topic of the elementary course (chapters 19, 20).

Part Four presents some topics that may be of interest to certain

groups of students and instructors. They include spectrophotometry (Chapter 21), instrumental methods of analysis (Chapter 22), complexation titrations (Chapter 23), and the literature of analytical chemistry (Chapter 24).

This sequence provides the opportunity to keep the lecture and laboratory work nearly abreast of each other and to distribute the introduction of new concepts evenly over the whole semester, as they increase in complexity.

1B.2. Use of the Supplement

The difference between teaching quantitative analysis to a chemistry major and to a student majoring in another field does not lie in the number or the kinds of topics studied, but only in the fact that the chemistry major studies some topics in greater detail. It is expected that this text will prove suitable for both kinds of students. By organization of the material according to the outline form, each topic is sharply delineated to facilitate study, reference, assignment, and review. The chemistry major or the advanced student who wishes to pursue any subject further than its elementary phase should make use of the Supplement. This is not itself readable with continuity, but is rather a series of notes that prove, amplify, or extend some of the topics of the text. The Supplement should aid the student to bridge the gap between the elementary phases of a subject and the advanced phases found in the voluminous and often bewildering array of chemical literature.

There are many illustrative examples throughout the text and Supplement. At the ends of the chapters discussion questions and problems are arranged according to sections. Problems in the Supplement are more challenging than those in the text. Answers are not given to the discussion questions, but are provided to about half of the problems, so that the student may have some check on his work as he proceeds.

1B.3. Experimental Work

As far as possible, the laboratory work is organized in such a way that the student will have some assurance of the correctness of his technique and equipment before he invests time in the analysis of unknown samples. For example, balance techniques and weights are checked before gravimetric analyses are undertaken. Volumetric equipment is calibrated, not so much to check the equipment as to check the student's technique in using it. Standard solutions are standardized by more than one method wherever this is possible. Failure to perform such checks faithfully is practically a guarantee of poor results on unknown

samples; furthermore, the time apparently saved by omission of such checks is generally lost several times over in attempts to rectify errors that could have been avoided by properly performing the checks. As many factors as possible should be checked before an analysis, rather than after.

Most of the usual determinations of elementary quantitative analysis are described in considerable detail, so that the student may work as independently as possible. They should be suitable for the greater part of the usual laboratory work, and not many special directions should have to be added for any particular instructor's purpose.

1C. THE STUDY OF QUANTITATIVE ANALYSIS

Both theoretical and experimental knowledge are fundamental to any science. Although separated for ease in teaching and study, these two kinds of knowledge are intimately related, and must constantly be correlated by the student during the learning process. In the laboratory it should be the student's constant effort to relate his actions to his theoretical knowledge. In the classroom, or when the text is being read, the process should be reversed, and the student should attempt to picture or interpret theoretical concepts in terms of concrete laboratory situations. If this is not done, the student's understanding of the subject will remain incomplete.

2 THE QUANTITATIVE ANALYTICAL PROCESS

2A. THE BRANCHES OF ANALYTICAL CHEMISTRY

Broadly speaking, *analytical chemistry* refers to all techniques and methods for discovering the identity and/or the amounts of the constituents in a sample. *Qualitative analysis* is concerned with the nature and the kinds of materials in the sample, without specific interest in the exact amounts present. *Quantitative analysis* is concerned with the amounts of various materials in the sample, and the results of such analysis are expressible only in terms of numbers. In general, the qualitative composition of a sample must be known before a quantitative analysis may be made; there is no point in trying to determine the amount of a constituent unless it is first known whether or not that constituent is present at all. Also, it must be known if interfering substances are present.

Quantitative analysis itself may be further divided into two branches. *Inorganic analysis* deals with the elements and their various inorganic compounds. This book is restricted almost entirely to inorganic analysis. *Organic analysis* deals with carbon compounds containing hydrogen, oxygen, and a small number of other elements. Procedures and techniques are considerably different from those of inorganic analysis, and are usually made the subject of a more advanced course of instruction.

In inorganic quantitative analysis some elements are encountered with much greater frequency than others. The methods of this text are restricted almost entirely to this class of common elements. The student who has had one semester of quantitative analysis should be conversant