QUANTITATIVE CHEMICAL ANALYSIS

FOURTH EDITION

I. M. KOLTHOFF

E. B. SANDELL

E. J. MEEHAN

STANLEY BRUCKENSTEIN

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I. M. KOLTHOFF
Professor Emeritus of Analytical Chemistry
Formerly Professor and Chief
Division of Analytical Chemistry
University of Minnesota

E. B. SANDELL
Professor of Analytical Chemistry
University of Minnesota

E. J. MEEHAN
Professor of Analytical Chemistry
University of Minnesota

STANLEY BRUCKENSTEIN
Professor of Chemistry
State University of New York at Buffalo

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Quantitative Chemical Analysis

Preface to the Fourth Edition

It is a very hard undertaking to seek to please everybody.—
PUBLILIUS SYRUS, *Maxim 675.*

The objectives and the organization of the fourth edition of this text remain much the same as in the earlier editions. Because of the introduction of some material that strictly does not fall under the heading of inorganic analysis, the title of the book has been changed. But most of its contents still deal with inorganic analysis or principles underlying both inorganic and organic analysis.

Among the additions that have been made in the revision, the following may be mentioned. The treatment of acid–base equilibria now includes a chapter dealing with these equilibria on a more advanced level; also, an introduction to acid–base equilibria in nonaqueous media is offered. New chapters have been needed to cover complex equilibria and compleximetric titrations adequately, with particular reference to metal–chelate and metal ion–indicator equilibria. Analytical separations, formerly discussed in one chapter, now require four. No one will be surprised to see that the section of the text dealing with physicochemical methods of analysis has been greatly expanded; familiarity with such methods is today required of every student majoring in chemistry. A discussion of the principles of electroanalysis and optical methods of analysis is followed by an experimental section in which a limited number of determinations are presented.

It seems to us that the scope of this textbook does not (and could not) call for a detailed exposé of all physicochemical and physical methods of analysis, but a number of such methods are surveyed. No doubt it is praiseworthy for a student to be familiar with nuclear magnetic resonance, for example, but there are many more mundane topics with which he should be acquainted before beginning the ascent to the more rarefied levels. We would be remiss if we slighted the fundamentals of quantitative analysis. We have encountered *graduate* students majoring in analytical chemistry who have not been able to calculate the calcium content of a sample from the titration of calcium oxalate with cerium(IV) or to detect chromium in chromite.

Some chapters have been set in reduced type to save space. To a large extent, these chapters cover material of a more or less advanced nature or that which is informational. Some of this material will need to be included in an elementary course, but since the scope of such a course will vary from one school to another, we have not attempted to indicate by type size the material that should or should not be included, which, after all, is a matter to be decided by the instructor. Proper attention to laboratory practice is always important and we have not neglected this aspect of the subject.

In the section on gravimetric analysis, as well as in other sections, more material is included than will be covered in any one course. This has been done in the belief that superior students, with a genuine interest in analysis, are likely to read chapters not formally assigned, and thus widen their knowledge. Moreover, when the treatment is not too parsimonious, the instructor can choose determinations most suitable for his course, and may, if he wishes, change determinations from one year to another. Need we say, in passing, that it is still essential for any but the most narrow of modern analysts to have some knowledge of *chemical* methods of analysis, either alone or in conjunction with physicochemical or physical methods? For example, chemical separations must often be applied in neutron activation analysis; indeed, gravimetric analysis may be a necessary part of such an analysis.

Analytical chemistry remains an essential part of a good chemistry curriculum. It is indispensable not only to chemistry but to other sciences and their applications as well. Believing this, we have thought it worth while once again to revise this book. We hope that the apportionment of space between theory and practice, and between the old and the new in analysis, represents a sound balance for instruction today. As much as anyone we regret the length of the revised edition, but the scope of modern chemical analysis and the need, as we see it, to treat the fundamentals with some thoroughness for the benefit of the serious student have not permitted a shorter treatment.

We are grateful to the many authors and editors of books, papers, and journals who have allowed us to use material in figures and tables. The source of the material has been indicated in each case. We are also indebted to the Arthur H. Thomas Company for the loan of cuts to illustrate certain laboratory apparatus.

Over the years, many users of the previous editions of this book have been very helpful and kind in offering comments and suggestions. We express our thanks for this interest and aid and welcome comments on this new edition.

The Authors

Minneapolis

From the Preface of the First Edition

An elementary textbook in quantitative analysis is necessarily limited in its scope, and many subjects of importance in this branch of chemistry cannot be treated. On the other hand, the advanced works in the field usually deal with highly specialized branches of the subject or selected topics, and there is little opportunity for the discussion of the broad fundamentals in a satisfactory way, at least not without repetition of much elementary matter which belongs in an introductory course. It seemed desirable to the authors to have available a book that could be used as an introductory text and which in addition would have the more or less comprehensive character of an advanced textbook, so that it would be suitable for use in beginning and advanced courses in analytical chemistry. With this aim in mind the authors have written the present work, in which there is contained material designed to make the student familiar with the fundamental theories of the subject, the practical methods of working, and the most important classical procedures. Highly specialized methods of analysis based on the measurement of physicochemical properties (conductometric and potentiometric titrations, gas analysis, nephelometry, spectrography, etc.) could naturally not be treated at length, but enough is said concerning these to enable the student to appreciate the advantages of such methods, and a sufficient number of references is given to serve as a starting point for him who is interested.

In writing this text, it has been our aim to offer a balanced outline of the theoretical and practical aspects of inorganic quantitative analysis. There appears to be a tendency to exaggerate the significance of "theory" at the expense of practical work in chemical analysis.

Theory and practice should go hand in hand. Many chemical students are faced in later life with analytical problems, of which the solution is not to be found in reference works, but which can be solved by a rational and intelligent application of the principles of the subject.

Taking into account the difficulties that the beginning student must encounter on being introduced to a subject which is entirely new to him, it seems to the authors that from the didactic point of view, gravimetric analysis should precede volumetric analysis. The theory of the former is much simpler than that of the latter. Therefore in beginning with gravimetric analysis the instructor can gradually develop the theoretical fundamentals of quantitative analysis without overburdening the student at the start. In general it is inadvisable to have the student make determinations before the theory underlying them has been offered.

No training in analytical chemistry can be considered satisfactory which does not give the student some opportunity to familiarize himself with the journal literature and standard reference books. For this reason rather frequent literature citations are given in this text. In advanced courses especially, the student should be encouraged to refer frequently to the original sources.

It does not seem to be generally realized that analytical chemistry is one of the fundamental branches of the science. The authors express the hope that books of the nature of the present one will aid in the recognition of the importance of quantitative analysis.

I. M. Kolthoff
E. B. Sandell

Minneapolis

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PART ONE

Theoretical Fundamentals

CHAPTER 1 *Introduction*

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

—WILHELM OSTWALD (1894)

Qualitative and quantitative analysis

Qualitative chemical analysis deals with the detection and identification of the constituents of a sample, quantitative chemical analysis with the determination of their amounts (usually relative amounts expressed as percentages). By *sample* is meant that portion of the material in question which is examined. The constituents to be detected or determined may be elements with or without regard to their state of combination or oxidation, radicals, functional groups (as in organic substances), compounds, or even phases which may or may not be compounds.

The greater part by far of chemical analysis is quantitative. More often than not, the qualitative composition of a sample is known from its source and a quantitative analysis can be carried out directly. Occasionally the qualitative composition of a sample may be unknown or imperfectly known, and it must be analyzed qualitatively before a quantitative analysis can be made. Qualitative tests may entail identification of the form of an element, as whether iron is present as Fe(II) or Fe(III), or sulfur is present as sulfide or sulfate. All qualitative tests are in some degree quantitative and give an indication of the amount of reacting constituent, whether by the quantity of a precipitate, the intensity of a color, the density of a spectral line on a photographic plate, etc. A qualitative analysis providing a rough indication of the amounts of the constituents present may be of great value in the choice of methods for their determination. Qualitative tests may also be of importance in revealing the presence of unexpected elements in a sample, which could lead to gross errors if disregarded in the quantitative procedure. The familiar "wet" scheme of inorganic qualitative analysis, modernized with organic reagent spot reactions, can be of good service in occasional qualitative analyses, which usually need not be complete. A spectrographic analysis provides a quick and sensitive means of recognizing many elements (particularly the metals) and allows an estimate to be made of their relative amounts. Qualitative organic analysis is likely to require the identification of *functional groups*, which may be roughly defined as reactive atoms or groups of atoms, such as carbonyl $\left(>CO\right)$, carboxyl (—COOH), azo (—N=N—), and one or two hundred others. Sometimes, the detection of an element, such as S or Cl, without regard to its form may suffice.

Qualitative tests of a nondestructive nature (not altering the physical or chemical identity of the sample or its amount) can be of great value. It may be of vital importance to learn whether or not a solid sample consists of more than one component (phase) and to obtain the identity of the components. A spectrographic or wet analysis might provide the gross composition of the sample but still leave the analyst ignorant of the actual composition, i.e., the number of components and their composition. Physical properties must, in general, be made the basis of such analyses. Microscopic examination (especially with a polarizing microscope) can show whether a finely divided solid is homogeneous or heterogeneous, and often permits identification of the components by their optical properties or from the measurement of their refractive indices. X-ray diffraction is of great value in the identification of solid phases. Simple tests such as determination of freezing point, boiling point, and refractive index can be of aid in identifying liquids.

The scope of quantitative chemical analysis

Science is essentially the study of quantitative relationships, and when these relationships involve the composition of substances, quantitative analysis must be brought in. It has played, and continues to play, a vital role in the development of chemistry and other sciences making use of chemistry. The formulation of the fundamental laws of chemistry has been based largely on the results of quantitative analyses. Our knowledge of the composition of the earth and all it contains and even of extraterrestrial matter has come from chemical analysis in one form or another. It has been said: "The sceptical chemist, and there is no other variety worthy of the name, draws conclusions regarding chemical materials under his scrutiny chiefly on the basis of quantitative chemical analysis, which in its proximate and ultimate forms, is the touchstone of all chemical hypothesis" (G. T. Morgan).

Chemical analysis is indispensable in many branches of science—in the earth sciences, in the biological sciences, even in archeology. Moreover, it finds constant application in technology and industry—in the analysis of raw materials and finished products, in the control of manufacturing processes—as well as in clinical medicine, agriculture, and other fields.

Quantitative chemical analysis is customarily divided into inorganic and organic. Both branches may be said to be based on essentially the same, or at least similar, fundamentals. However, just as inorganic analysis presupposes a knowledge of inorganic or general chemistry, so quantitative organic analysis presupposes some knowledge of organic chemistry and preferably of qualitative organic analysis. We do not on the whole[1] presuppose a knowledge of organic chemistry on the part of the student. Accordingly, this text deals almost wholly with inorganic or general quantitative analysis. The general principles of analysis can be illustrated very well by inorganic examples. Our treatment is in no way intended to belittle organic

[1] Certain sections of this book, as those on organic reagents and liquid-liquid extraction, can be read more meaningfully with an understanding of organic chemistry.

analysis, which in volume and perhaps in the importance of its applications over-shadows purely inorganic analysis. But organic quantitative analysis is best reserved for a later course, where it can be given full justice. A fair familiarity with inorganic analysis is a prerequisite for organic analysis.

The extent of modern inorganic analysis is so great that the whole subject cannot be treated, or even surveyed, in an introductory text such as this. Nor should it be. We shall stress the theoretical principles, especially of gravimetric and titrimetric analysis (which are still of fundamental importance), and illustrate them with a limited number of laboratory exercises. Some of these relate to samples of more or less complex composition, so that the aura of unreality tending to envelope academic analysis does not become all-pervasive. A number of physicochemical methods of analysis will be presented to demonstrate the usefulness of this type of analysis.

The general analytical process

The principal steps in an inorganic determination[2] may be outlined as follows:

1. Obtaining a representative sample of the material whose composition is desired. This may be no simple task when it is realized that a few tenths of a gram of material taken for analysis may be required to represent tons of parent material.
2. Bringing the weighed sample into solution or otherwise preparing it for analysis. In determinations by chemical methods the sample must in general be brought into complete solution. Dissolving the sample may not be necessary in determinations by physical methods, but some of these require other preparation of the sample.
3. Separating constituents that interfere in the determination of the desired constituent. This is an operation that is frequently required in applied analysis by chemical, and also by some physicochemical, and even physical, methods. Few if any methods are truly specific. Whenever possible, interfering substances are made innocuous by complexing or, less often, by a change in oxidation state. When such measures fail, separations must be made.
4. Carrying out the determination proper. The classification of methods of determination is considered in the next section.
5. Calculating the results. This step may include an evaluation of the precision and accuracy of the numerical result.

The methods of quantitative analysis

In quantitative chemical analysis we are almost always concerned with the relative amounts of constituents in a sample. The relative amounts, usually expressed as weight percentages, are obtained by finding the absolute amounts in a known amount of sample. A great variety of methods are available for this purpose. All methods of quantitative analysis are physical in the sense that the final step in a determination must involve the measurement of some physical property, the simplest being mass. However, in a more significant sense a distinction

[2] A point of terminology (and semantics): *Determination* is the process by which the amount of a given constituent is found in a sample. We say determination of calcium, not analysis *of* calcium. The latter means the determination of the constituents (there might be many) in a calcium sample. Determination of calcium is analysis *for* calcium. The term "determination" has also acquired, in some contexts, the connotation of the final step in an analysis, which has been preceded by separations or other treatment, and may then be used pejoratively (p. 10).