

# QUANTITATIVE ANALYSIS

4<sup>TH</sup>  
EDITION

R. A. Day, Jr.

A. L. Underwood

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# PREFACE

Analytical chemistry has been taught in a variety of ways at different schools. At the present time, many schools offer a one-semester or one-quarter course emphasizing traditional topics following the general chemistry course, and a one-semester course in the senior year on instrumental topics with physical chemistry as a prerequisite. A third course, for students who do not expect to become professional chemists, is also offered at many schools. This course includes instrumental topics, and although it may be considered superficial, it has considerable value in showing students who will never study analytical chemistry again something of the field beyond the classical titrimetric and gravimetric techniques. The majority of the students in this course are premedical and pre dental; some anticipate graduate work in biomedical fields such as biochemistry, physiology, pharmacology, or microbiology. Biology majors may also take the course. At Emory University, we use this text for the first and third types of courses.

In revising the text, we have kept such a pattern of courses in mind. The major changes, both in reorganization of old material and in the introduction of new topics, are designed to improve the presentation of traditional topics for the introductory course. A clearer separation of gravimetric and titrimetric methods has been made, and a greater emphasis has been given to applications of these methods to practical analyses.

Changes in the later chapters have been fewer, and have been made primarily to update the material and improve the presentation. These chapters, which deal with such topics as electrical and spectroscopic methods of analysis and various aspects of chromatography, are not designed for the senior-level instrumental

course for professional chemistry students, although such students may find them useful as a starting point for reading more advanced material.

Specifically, we have made the following major changes. Separate chapters on titrimetric and gravimetric methods, covering mainly stoichiometric calculations, are included. Although the titrimetric chapter is presented first, the order of coverage can be reversed if the instructor desires. A new chapter on review of chemical equilibrium follows the stoichiometry chapters. This chapter covers all the types of equilibrium calculations encountered in the reactions used for analysis. The instructor can thus focus attention on equilibrium calculations before considering their applications to analysis. This chapter, which reviews the equilibrium treatment found in general chemistry texts, may be omitted if the class is well prepared. Chapters 6 through 11 then cover the traditional acid-base, complex formation, precipitation, and oxidation-reduction theory and applications. Chapter 11 is a new one discussing the numerous applications of oxidation-reduction reactions to analysis, and offers a respite from theory.

The chapters on spectrophotometry, flame emission and atomic absorption spectroscopy, solvent extraction, gas-liquid chromatography, and liquid chromatography have undergone less drastic changes. The chapters on electroanalytical chemistry, however, have been extensively rewritten in order to clarify points that students, in our own teaching experience, found troublesome in the earlier edition. A new chapter called "Real Analytical Chemistry" has been added in an effort to give a perspective regarding the importance and utility of the field of analytical chemistry.

Throughout the text, an attempt has been made to improve the questions and problems at the end of each chapter. In many cases involving fundamental concepts, two very similar problems are given consecutively, with answers furnished for the odd-numbered ones. This arrangement allows the student to check himself on one such calculation before attempting a problem for which the answer is not furnished.

One major departure from previous editions is the inclusion of laboratory directions in the last section of the text. This change has been made at the request of many users who find the cost of a separate laboratory manual excessive. In this laboratory section, we have included two chapters on general laboratory techniques and the analytical balance. Directions are then given for a large number of experiments which illustrate a wide variety of analytical applications. Most of the examples are taken from the classical areas of titrimetric and gravimetric methods and should provide ample coverage for the introductory, one-semester course. A few experiments are included in which a simple spectrophotometer or pH meter is employed. Several experiments of a "relevant" nature are included, such as the analysis of commercial antacids and bleaches, the determination of nitrites in water, and the identification of amino acids by potentiometric titration.

A separate laboratory manual will still be available for those teachers who may use the manual but not the text. This manual will include all of the laboratory experiments given in the text as well as exercises of a more advanced nature.



As with previous editions, teachers may obtain the *Solutions to Problems* manual from the publisher. This manual can also be made available to students through ordinary bookstore orders if the teacher wishes.

We express our sincere appreciation to the many users of the third edition who were kind enough to forward criticisms and suggestions for improvement. These include Professors Roger G. Bates, K. P. Li, and J. D. Winefordner, *University of Florida*; T. Dobbelsstein, Frederick W. Koknat, and F. W. Smith, *Youngstown State University*; Herschel Frye, *College of the Pacific*; Robert Glenn, *Hutchinson Community College*; Richard H. Groth, *Central Community College*; Howard L. Hodges, *University of Arkansas, Little Rock*; Gary D. Howard, *University of North Carolina, Charlotte*; Thomas A. Lehman, *Bethel College*; Charles A. Long, *Lake Forest College*; Richard McCreery, *Ohio State University*; David B. Moss, *Hiram College*; Daniel S. Polcyn, *University of Wisconsin, Oshkosh*; Lou R. Raasch, *East Tennessee State University*; Veronica L. Vogel, *Rutgers University*; and Hubert L. Youmans, *Western Carolina University*. Special thanks go to Professors Douglas G. Berge, *University of Wisconsin, Oshkosh*; M. Dale Hawley, *Kansas State University*; and Alfred A. Schilt, *Northern Illinois University*, who have read the entire manuscript and made numerous helpful suggestions.

Atlanta, Georgia

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# CHAPTER ONE

## introduction

### **ANALYTICAL CHEMISTRY**

It used to be possible to subdivide chemistry into several clear and well-defined branches—analytical, inorganic, organic, physical, and biological. Although there was always a certain overlap among these simple categories, it was not difficult to define the branches in terms that were acceptable to most chemists. It was generally fairly clear into which category any particular chemist fitted, and a label such as “organic chemist” usually implied a reasonably clear picture of the sorts of things such a chemist did.

One of the most prominent trends in chemistry in recent years has been a general blurring of the borders of its branches; actually, the boundaries between chemistry itself and other major sciences such as physics and biology are considerably less clear than they used to be. Fields such as chemical physics, biophysical chemistry, physical organic chemistry, geochemistry, and chemical oceanography have achieved recognition in at least a vague way, although precise definitions of these fields are exceedingly difficult to formulate.

During all of this change, chemistry courses in the undergraduate curriculum have largely retained their traditional titles, but they have undergone major changes in content. For example, it is not at all unusual to find such topics as molecular spectroscopy and chemical kinetics in organic chemistry courses. Solution thermodynamics, kinetics of electrode processes, and electronics appear in analytical courses at some schools. In most cases, the college freshman course has undergone drastic change, and interesting changes at the high school level have been initiated.

Analytical chemistry is as old, and as new, as the science of chemistry itself. It may be fairly said that analytical research, as opposed broadly to synthetic, ushered in the change from magic and alchemy to quantitative, scientific chemistry. Analytical work led directly to the revolution that overthrew the phlogiston theory, and rational experiments that would place chemistry on a sound basis of fact and theory became possible with the increasing use of the analytical balance. Careful analyses led to the laws of definite and multiple proportions, and made possible Dalton's great achievement—an atomic hypothesis grounded in fact rather than mystical speculation.

The late nineteenth and early twentieth centuries saw developments in organic and physical chemistry and in physics that were bound to dwarf other fields. During this time many analytical chemists concerned themselves with the chemical composition of various materials which were important in the commerce of a simple industrial society. In many universities, analytical chemistry was taught as a routine, cookbook subject, although a small number of excellent men kept the field alive as a science.

Roughly since World War II, an increasing sophistication of research in all areas of chemistry, physics, and biology and an explosive technological development have combined to create analytical problems which demand increasingly sophisticated knowledge and instrumentation for their solution. Typical examples of such problems are determining traces of impurities at the part per billion level in ultrapure semiconductor materials, deducing the sequence of some 20 different amino acids in a giant protein molecule, detecting traces of unusual molecules in the polluted atmosphere of a smog-bound city, determining pesticide residues at the part per billion level in food products, and determining the nature and concentration of complex organic molecules in, say, the nucleus of a single cell.

The solutions to a host of problems such as these have been developed by research workers of the most diverse backgrounds. For example, a biochemist received a Nobel Prize for working out the amino acid sequence in the protein insulin, and physicists were actively involved in the first semiconductor analyses by mass spectrometry. Research workers in many fields are constantly confronted by analytical problems, and in many cases they work out their own solutions. It is interesting to note that in a recent year, nearly 60% of the papers in the journal *Analytical Chemistry* were authored by people who did not consider themselves to be analytical chemists. The papers originated in a wide variety of laboratories associated with medical schools, hospitals, oceanographic institutes, agricultural experiment stations, physics departments, and many more.

The trends of recent years have drawn analytical chemistry into the forefront of research in many exciting areas, but this very intimacy has blurred the borders of the discipline and made it nearly impossible in many cases to decide what an analytical chemist is. In this connection we may quote from the Fisher Award Address of David N. Hume.<sup>1</sup>

<sup>1</sup> D. N. Hume, *Anal. Chem.*, **35**, 29A (1963).

One of the most difficult problems facing the analytical chemist today is explaining to others just what analytical chemistry is. Much of the difficulty derives from the changes in the nature of the profession and the fact that a given word may have a whole spectrum of meanings. . . . The increasing complexity of modern chemistry is to some extent the cause of this confusion, as is the fact that a chemist seldom works in only one branch of the subject, more often combining the techniques and approaches of several.

With this extensive overlap into a variety of fields, what distinguishes the analytical chemist from all others working in these areas? The analytical chemist has, usually, more interest in the methods and techniques in their own right. Physical, organic, and biochemists often need to develop new analytical methods for their own purposes, but their primary interests do not lie in the method itself. To the analytical chemist, developing the methods is the challenging part of the research. Because of his interest in the method per se, the analytical chemist is likely to be skeptical of data presented without a full disclosure of experimental details, and he retains a critical attitude toward results which some workers would like to accept so as to get on with other things. The analytical chemist deals with real, practical systems, and much of his effort is expended in an attempt to apply sound theory to actual chemical situations.

## QUANTITATIVE ANALYSIS

Analytical chemistry can be divided into areas called qualitative analysis and quantitative analysis. *Qualitative* analysis deals with the identification of substances. It is concerned with *what* elements or compounds are present in a sample. The student's first encounter with qualitative analysis is often in the general chemistry course, where he separates and identifies a number of elements by precipitation with hydrogen sulfide. In organic chemistry the student may identify his product of synthesis using such instrumental techniques as infrared and nuclear magnetic resonance spectroscopy.

*Quantitative* analysis is concerned with the determination of *how much* of a particular substance is present in a sample. The substance determined, often referred to as the *desired constituent* or *analyte*, may constitute a small or large part of the sample analyzed. If the analyte constitutes more than about 1% of the sample, it is considered a *major* constituent. It is considered *minor* if it amounts to 0.01 to 1% of the sample. Finally, a substance present to the extent of less than 0.01% is considered a *trace* constituent.

Another classification of quantitative analysis may be based upon the size of the sample which is available for analysis. The subdivisions are not clear-cut, but merge imperceptibly into one another, and are roughly as follows: When a sample weighing more than 0.1 g is available, the analysis is spoken of as *macro*; *semimicro* analyses are performed on samples of perhaps 10 to 100 mg; *micro* analyses deal with samples weighing from 1 to 10 mg; and *ultramicro* analyses involve samples of the order of a microgram ( $1 \mu\text{g} = 10^{-6} \text{ g}$ ).



## Steps in an Analysis

In the introductory course in quantitative analysis the student will deal mainly with major constituents of macro samples. He will seldom perform a *complete* quantitative analysis of a sample. A chemical analysis actually consists of four main steps: (1) sampling, that is, selecting a representative sample of the material to be analyzed; (2) conversion of the analyte into a form suitable for measurement; (3) measurement; and (4) calculation and interpretation of the measurements. Often the beginner carries out only steps 3 and 4 since these are usually the easiest ones.

In addition to the steps mentioned above, there are other operations that may be required. If the sample is a solid, it may be necessary to dry it before performing the analysis. Solids also need to be dissolved in an appropriate solvent before the measurement step. And an accurate measurement of weight of the sample (volume if it is a gas) must be made since quantitative results are usually reported in relative terms, for example, the number of grams of analyte per 100 g of sample (percent by weight).

At this time we shall make some general comments on the four steps of an analysis as well as the operation of dissolving the sample. In subsequent chapters these topics will be developed in much greater detail.

### Sampling

The beginning student seldom encounters the problem of sampling since the sample he is given is homogeneous, or nearly so. Nevertheless, he should be aware of the importance of sampling and he should know where to find proper directions when he is confronted with an unfamiliar problem.<sup>2</sup>

Coal is a particularly difficult material to sample, and we shall use it as an illustration of the problems and methods used to solve them.

The first step in the sampling procedure is to select a large portion of coal, called the *gross sample*, which though not homogeneous itself, represents the average composition of the entire mass. The size of the sample needed depends on such factors as particle size and homogeneity of the particles. In the case of coal the gross sample must be about 1000 lb if the particles are no greater than about 1 inch in any dimension.

There are many techniques used to obtain the gross sample. If the coal is in motion, on a conveyor of some type, a definite fraction may be continuously diverted to give the gross sample. If, on the other hand, the coal were being shoveled from a car, every fiftieth shovelful might be placed aside to form the sample.

After the sample has been selected, it is ground or crushed and systematically mixed and reduced in size. One method used for reducing the sample of coal involves piling the sample into a cone with a shovel, flattening the cone, and

<sup>2</sup> W. W. Walton and J. I. Hoffman, "Principles and Methods of Sampling," Chap. 4, p. 67, of I. M. Kolthoff and P. J. Elving, eds., *Treatise on Analytical Chemistry*, Part I, Vol. 1, Interscience Publishers, Inc., New York, 1959.

dividing it into four equal parts, two of which are discarded. A mechanical device for subdividing the sample is called a *riffle*. The riffle consists of a row of small sloping chutes arranged so that alternate chutes discharge the sample in opposite directions. In this manner the sample is halved automatically.

In the laboratory further grinding of the sample may be done with a mortar and pestle. It is often necessary to grind a sample to pass through a sieve of a certain mesh. The final laboratory sample, 1 g or so, is hopefully representative of the entire gross sample. The analytical data obtained cannot be better than the care exercised in the sampling procedure.

#### **Dissolving the Sample**

Many of the samples analyzed in the beginning course in quantitative analysis are soluble in water. Generally speaking, however, naturally occurring materials, such as ores, and metallic products, such as alloys, must be given special treatments to effect their solution. While each material may present a specific problem, the two most common methods employed in dissolving samples are (1) treatment with hydrochloric, nitric, sulfuric, or perchloric acid; and (2) fusion with an acidic or basic flux followed by treatment with water or an acid.

The solvent action of acids depends upon several factors:

1. The reduction of hydrogen ion by metals more active than hydrogen: for example,



2. The combination of hydrogen ion with the anion of a weak acid: for example,



3. The oxidizing properties of the anion of the acid: for example,



4. The tendency of the anion of the acid to form soluble complexes with the cation of the substance dissolved: for example,



Hydrochloric and nitric acids are most commonly used to dissolve samples. The chloride ion is not an oxidizing agent as is nitrate ion, but it has a strong tendency to form soluble complexes with many elements. A very powerful solvent, aqua regia, is obtained by mixing these two acids.

Many substances that are resistant to attack by water or acids are more soluble after fusion with an appropriate flux. Basic fluxes such as sodium carbonate are used to attack acidic materials such as silicates. Acidic fluxes such as potassium hydrogen sulfate are used with basic materials such as iron ores. Oxidizing or reducing substances can also be used in certain cases. Sodium peroxide, for example, is often employed as a flux.

### Conversion of the Analyte to a Measurable Form

Before a physical or chemical measurement can be made to determine the amount of analyte in the solution of the sample, it is usually necessary to solve the problem of "interferences." Suppose, for example, that the analyst wishes to determine the amount of copper in a sample by adding potassium iodide and titrating the liberated iodine with sodium thiosulfate. If the solution also contains iron(III) ion, this ion will interfere since it also oxidizes iodide to iodine. The interference can be prevented by adding sodium fluoride to the solution, converting iron(III) into the stable complex,  $\text{FeF}_6^{3-}$ . This is an illustration of a general method in which interferences are effectively "immobilized" by alteration of their chemical nature.

A second method involves physical separation of the analyte from the interferences. Suppose that one wishes to determine magnesium in a sample which also contains iron(III) ion and the magnesium is to be precipitated as the oxalate. The iron will interfere since it also forms a precipitate with oxalate. The iron can be precipitated as the hydroxide using ammonia at a pH of about 6.5. The magnesium is not precipitated at this pH, and hence the interference is removed.

In a *gravimetric* analysis the analyte is physically separated from all other components of the sample as well as from the solvent. For example, the chloride in a sample may be determined by precipitation of silver chloride, which is then filtered, dried, and weighed. Precipitation is one of the more widely used techniques for separating the analyte from interferences. Other important methods include electrolysis, solvent extraction, chromatography, and volatilization.

### Measurement

The measurement step in an analysis can be carried out by chemical, physical, or biological means. The laboratory technique which is employed has led to the classification of quantitative methods into the subdivisions *titrimetric* (*volumetric*), *gravimetric*, and *instrumental*. A *titrimetric* analysis involves the measurement of the volume of a solution of known concentration which is required to react with the analyte. In a *gravimetric* method the measurement is one of weight; an example was mentioned above in which chloride is determined by precipitating and weighing silver chloride. The term *instrumental* analysis is used rather loosely, originally referring to the use of a special instrument in the measurement step. Actually, instruments may be used in any or all steps of the analysis, and, strictly speaking, burets and analytical balances are instruments. Spectroscopy, both absorption and emission, is perhaps the most widely used instrumental method and is generally discussed in some detail in introductory texts. Other instrumental methods include potentiometry, polarography, coulometry, conductimetry, polarimetry, refractometry, and mass spectrometry.

### Calculation and Interpretation of the Measurements

The final step in an analysis is the calculation of the percentage of analyte in the sample. The principles involved in such calculations are normally straightforward.