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Chapter 1
Introduction

A quantitative analysis provides numerical information about the amount of some species (the *analyte*) that is contained in a measured quantity of matter (the *sample*). The results of a quantitative analysis are ordinarily expressed in relative terms, such as parts per hundred (that is, as a percentage), parts per thousand, parts per million, or perhaps parts per billion of the sample. Other ways of expressing results include the weight (or the volume) of analyte per unit volume of sample, as well as the mole fraction.

Chemistry in general, and analytical chemistry in particular, will only be peripheral to the intellectual goals of many readers of this book; indeed, the need for study in this area may be questioned. In 1984, Wilhelm Ostwald wrote,

> Analytical chemistry, or the art of recognizing different substances and determining their constituents, takes a prominent position among the applications of 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 science.

The amount of our chemical knowledge has increased enormously since 1894; these words, nevertheless, are as apt today as they were then. The fact is that few (if any) areas of manufacture, and few (if any) of the physical sciences, escape the need for quantitative chemical information. The amount of protein in foodstuffs, for example, is commonly established by a quantitative analysis for nitrogen content. The analysis of soils and the needs of plants provide the farmer with the information that will maximize yields through the judicious application of fertilizers. The properties of alloys depend in large measure upon composition, which, in turn, is monitored by chemical analysis. The effectiveness of devices for the control of automotive and industrial pollution is likewise established by analysis. Physicians rely upon the chemical analysis of body fluids as an important aid in diagnosis. A listing such as this is virtually endless.

1A CLASSIFICATION OF QUANTITATIVE METHODS

Quantitative methods can be subdivided into several groups, based upon the nature of the final measurement in the analysis, the magnitude of which is proportional to the amount of analyte in the sample. The final measurement in a *gravimetric* analysis involves a determination of mass. Likewise, the final measurement of a typical *volumetric* analysis consists of measuring the volume of a solution that contains sufficient reagent to react completely with the analyte. *Electroanalytical* methods are based upon the measurement of such electrical quantities as volts, amperes, ohms, and coulombs. *Spectroscopic* methods are based upon measurements of the interaction of electromagnetic radiation (X-ray, ultraviolet, visible, infrared, and radio radiation) with analyte atoms or molecules or upon the production of such radiation by the analyte.

1B STEPS IN A CHEMICAL ANALYSIS

In most analyses, the measurement step just described must be preceded by several preliminary steps, which are often more time consuming and more formidable than the final measurement itself. Indeed, this final step is likely to be the most straightforward part of the entire analytical process. The preliminary steps that are common to most analytical procedures are described in this section.

Definition of the Problem At the outset, the analyst must have a clear understanding of the accuracy that is needed in the results of an analysis. The selection of a method and the care with which it is performed are critically dependent upon the accuracy that is required. It is safe to state that an increase in the reliability of a measurement is likely to require an exponential increase in the time and effort needed to perform the measurement. An analysis that is incapable of providing the required reliability will clearly be a waste of time. Equally wasteful is the performance of an analysis at a level of accuracy that exceeds by very much the demands made upon the data. For example, numerous methods exist for the analysis of chlorine. A very simple (but not very accurate) method is sufficient to establish whether the chlorine content of swimming pool water is high enough to provide safety and yet not so high as to cause eye irritation. In contrast, investigation of a reaction mechanism in which chlorine is a participant is likely to require a method of measurement that possesses a far greater degree of reliability. A compromise may also be required between the accuracy that can be attained and the time available for performing the analysis. A physician with a critically ill patient cannot afford to wait hours (or perhaps days) for the results of an elegant analysis; here the demands of time may dictate the use of a method that will provide the needed guidance at the expense of the ultimate in accuracy.

Sampling[1] Fundamental to any chemical analysis is the acquisition of a sample with a composition that is representative of a larger quantity of matter. In general, the more finely divided and homogeneous the material, the easier it is to obtain such a sample. At one extreme is a well mixed gas or solution where inhomogeneity exists only at the molecular level. Here, one can be confident that even the smallest sample will be truly representative of a much larger mass of material. An example of the other extreme would be a 25-ton shipment of silver ore where buyer and seller must come to agreement as to its average silver content. The ore, however, is inherently heterogeneous, consisting of particles that range in size from a few tenths of a millimeter to several centimeters. Furthermore, the silver content of these particles may range from zero to several percent depending upon their particle size. The assay of this shipment will be performed on a sample that weighs something on the order of 1 g. The composition of this sample must be the same as the average for the entire 25 tons (or 22,700,000 g) in the shipment. The task of isolating 1 g with any confidence that its composition truly reflects that of the nearly 23,000,000 g from which it was taken is a nontrivial undertaking that requires a systematic manipulation of the entire shipment.

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[1] For a detailed discussion of sampling, see: C. A. Bicking, in *Treatise on Analytical Chemistry*, 2nd ed., I. M. Kolthoff and P. J. Elving, Eds., Part I, Vol. 1, Chapter 6. New York: John Wiley & Sons, 1978.

Many sampling problems will be less formidable than the one just described. Regardless of difficulty, however, assurance is needed that the sample that is employed in the analysis is truly representative of the whole before proceeding further.

Preparation of the Laboratory Sample for Analysis Most solid materials must be ground to decrease particle size and then thoroughly mixed to ensure homogeneity. Moreover, the adsorption or desorption of water from the atmosphere will cause the percent composition of the sample to depend upon the humidity of its surroundings. This source of difficulty is ordinarily overcome by putting the sample through some sort of drying cycle.

We have noted that quantitative analytical results are commonly reported in relative terms (such as percentage); it is therefore necessary to determine the weight or volume of the sample upon which the analysis is perfomed.

Solution of the Sample[2] Most (but certainly not all) analyses are performed on solutions of the sample. Ideally, the solvent should dissolve the entire sample (not just the analyte) rapidly and under sufficiently mild conditions that loss of the analyte does not occur. Solvents with these properties simply do not exist for many of the materials that are of interest to the scientist—a silicate mineral, a high-molecular-weight polymer, or a sample of animal tissue, for example. For such materials, the conversion to a soluble form is often difficult and time consuming.

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[2] For a detailed treatment of decomposition and solution of samples, see: R. Bock, *A Handbook of Decomposition Methods in Analytical Chemistry*. New York: John Wiley & Sons, 1979; and D. C. Bogen, in *Treatise on Analytical Chemistry*, 2nd ed., P. J. Elving, E. Grushka, and I. M. Kolthoff, Eds., Part I, Vol. 5, Chapter 1. New York: John Wiley & Sons, 1982.

Separation of Potential Interferences Few chemical or physical properties of analytical importance are unique to a single chemical species; instead, the reactions used and the properties measured are shared by several elements or compounds. This lack of specificity adds greatly to the difficulties faced by the analyst because a scheme must be devised for isolating the species of interest from all others in the sample that can influence the final measurement. Substances that prevent the direct measurement of the analyte concentration are called *interferences;* their elimination prior to the final measurement is an important step in most analyses. No hard and fast rules exist for the elimination of interferences; this problem is frequently the most demanding aspect of the analysis. Separation methods are treated in Chapters 17 and 18.

Completion of the Analysis All preliminary steps in an analysis are undertaken to ensure that the final measurement is a true gauge of the quantity of analyte in the sample. The foregoing survey of the steps in an analysis suggests, correctly, that this final measurement is frequently the least difficult step.

Many types of final measurements are discussed in the chapters that follow, along with the principles upon which such measurements are based.

1C CHOICE OF METHOD FOR AN ANALYSIS

The chemist or scientist who needs analytical data is frequently confronted with numerous methods that can, in principle, provide the desired information. The success or failure of an analysis can be critically dependent upon the choice of method. Speed, sample composition, convenience, accuracy, availability of equipment, number of analyses, amount of sample available for analysis, and likely concentration range of the analyte are all factors that will influence this choice. There is no substitute for experience in making the decision.

Analytical Chemistry: An Introduction deals with (1) the chemical principles upon which all analytical methods are based; (2) the accuracy and precision of quantitative analyses; (3) the principles of gravimetric, volumetric, electroanalytical, and certain spectroscopic and chromatographic methods; and (4) unit operations, such as weighing, measuring volumes, drying, and evaporating, which are part of all analytical methods. In addition, specific directions for several typical methods of analysis are provided. Mastery of this material will permit the student to perform useful chemical analyses and will also provide a background that will aid in the selection of procedures for solving analytical problems.

Chapter 2
Review of Some Elementary Concepts

The analyte in a typical quantitative analysis will ordinarily exist in solution at one stage or another. Thus, familiarity with solution chemistry as well as an understanding of mass relationships between reactants and products in solution is fundamental to the study of analytical chemistry. This chapter provides a brief review of these topics.

2A SOLUTIONS AND THEIR COMPOSITION

2A-1 Electrolytes

Solutes that dissociate to produce conducting solutions are classed as electrolytes. *Strong electrolytes* are ionized completely, or nearly so, while *weak electrolytes* are only partially ionized. Table 2-1 is a compilation of solutes that act as strong and as weak electrolytes in aqueous solution.

2A-2 Acids and Bases

The concept of acid-base behavior—as proposed independently by Brønsted and Lowry in 1923—is of particular importance to the analytical chemist.[1]

Table 2-1 Classification of Electrolytes

Strong Electrolytes	Weak Electrolytes
1. The inorganic acids HNO_3, $HClO_4$, H_2SO_4* HCl, HI, HBr, $HClO_3$, $HBrO_3$	1. Many inorganic acids such as H_2CO_3, H_3BO_3, H_3PO_4, H_2S, H_2SO_3
2. Alkali and alkaline-earth hydroxides	2. Most organic acids
3. Most salts	3. Ammonia and most organic bases
	4. Halides, cyanides, and thiocyanates of Hg, Zn, and Cd

* H_2SO_4 is completely dissociated into HSO_4^- and H_3O^+ ions and for this reason is classified as a strong electrolyte. However, it should be noted that the HSO_4^- ion is a weak electrolyte, being only partially dissociated.

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[1] For a thorough treatment of the various acid-base concepts, see: I. M. Kolthoff, in *Treatise on Analytical Chemistry,* 2nd ed., I. M. Kolthoff and P. J. Elving, Eds., Part I, Vol. 2, Chapter 17. New York: John Wiley & Sons, 1979.

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