

Principles of Instrumental Analysis

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Preface

Instrumental methods of analysis have become the backbone of experimental chemistry. As a consequence, the practicing chemist has need for a broad understanding of the principles, the applications, and the limitations of these techniques. *Principles of Instrumental Analysis* has been prepared in an effort to fill this need.

We have chosen to stress principles throughout the text; information concerned with applications and with instrumentation has been selected with the aim of illustrating these principles. We agree with Sandell and Elving,¹ who have written:

It is important in any discussion of instrumentation and so-called instrumental methods of analysis to distinguish between instrumentation as an approach to the implementation of analytical techniques and methods, and as the manipulation of instruments. The latter is a minor result of the development of physical methods of analysis; the former is an extremely important aspect of analytical chemistry. Unfortunately, many writers on analytical chemistry, as well as many chemists in general, tend to think of instrumental analysis as being essentially the manipulation of black boxes.

Basically, in order to be able to apply instrumentation most efficiently to his problems, the analytical chemist must understand the fundamental relations of chemical species to their physical and chemical properties; he must know the scope, applicability, and limitations of physical property measurement in respect to qualitative and quantitative analysis. Knowing this, he can then call on the instrumentation expert to design an apparatus for the measurement—continuous or intermittent—of the desired properties with the needed precision. The analytical chemist does not necessarily need to be an electronics expert.

¹E. B. Sandell and P. J. Elving in I. M. Kolthoff and P. J. Elving, Eds., *Treatise on Analytical Chemistry*, Part I, Vol. 1 (New York: Interscience Publishers, Inc., 1959), p. 17.

The subject matter of this text is organized into two major and several minor sections. Chapters 2 through 14 are concerned with major analytical applications based upon the absorption or emission of electromagnetic radiation. Mass spectrometry is considered in Chapter 15; a survey of radiochemical methods is presented in Chapter 16. Chapters 17 through 22 cover the principal aspects of electroanalytical chemistry. A final section (Chapters 23 and 24) is devoted to separation techniques. Topic development in each section is sufficiently independent of other sections to provide the user with flexibility in selecting the order of presentation.

In the interests of imparting a reasonable size to the work, no attempt has been made to incorporate specific laboratory directions. The manuals by Meloan and Kiser² as well as by Reilley and Sawyer³ are recommended as sources for experimental work.

We wish to acknowledge the contributions of Professors Alfred Armstrong, William and Mary College, and John DeVries, California State College at Hayward, who have read the entire manuscript and have offered numerous valuable suggestions. Thanks are also extended to Professor R. M. Silverstein, State University of Forestry at Syracuse, who has reviewed the chapter concerned with nuclear magnetic resonance spectroscopy, to Professor Paul Kruger of Stanford University, who has offered comments with regard to the chapter on radiochemical methods, to Professor Richard H. Eastman of Stanford University, who has made suggestions concerning the material on absorption spectroscopy, and to Mr. Claude F. Mears of Stanford University who has provided answers to all problems and has verified the calculations that appear within the text.

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²C. E. Meloan and R. W. Kiser, *Problems and Experiments in Instrumental Analysis* (Columbus, Ohio: Charles E. Merrill Books, Inc., 1963).

³C. N. Reilley and D. T. Sawyer, *Experiments for Instrumental Methods* (New York: McGraw-Hill Book Company, Inc., 1961).

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1 Introduction

The goal of a chemical analysis is to provide information about the composition of a sample of matter. In some instances qualitative information concerning the presence or absence of one or more components of the sample suffices; in other instances quantitative data are sought. Regardless of the need, however, the required information is finally obtained by measuring some physical property that is characteristically related to the component or components of interest.

Classification of Analytical Methods

Analytical methods are ordinarily classified according to the property that is observed in the final measurement process. Table 1-1 lists the more important of these properties as well as the names of the methods that are based upon them. It is striking to note that until about 1920 nearly all analyses were founded on the first two properties listed—namely mass and volume. As a consequence, gravimetric and volumetric procedures have come to be known as *classical* methods of analysis. The remainder of the list comprises *instrumental* methods; it is with these that this book is concerned.

Few features clearly distinguish instrumental methods from the classical ones beyond the chronology of their development. Some instrumental techniques are more sensitive than classical techniques, but others are not. With certain combinations of elements or compounds an instrumental method may be more specific; with others a gravimetric or a volumetric procedure is less subject to interference. Generalizations on the basis of accuracy, convenience, or expenditure of time are equally difficult to draw. Nor is it necessarily true that instrumental procedures employ more

2 Introduction

Table 1-1 Physical Properties Employed for Analysis

<i>Physical Property Measured</i>	<i>Analytical Methods Based on Measurement of Property</i>
Mass	Gravimetric
Volume	Volumetric
Absorption of radiation	Spectrophotometry (x-ray, UV, visible, IR); colorimetry; atomic absorption, nuclear magnetic resonance, and electron spin resonance spectroscopy
Emission of radiation	Emission spectroscopy (x-ray, UV, visible), flame photometry, fluorescence (x-ray, UV, visible), radiochemical methods
Scattering of radiation	Turbidimetry, nephelometry, Raman spectroscopy
Refraction of radiation	Refractometry, interferometry
Diffraction of radiation	X-ray, electron diffraction methods
Rotation of radiation	Polarimetry, optical rotatory dispersion, and circular dichroism
Electrical potential	Potentiometry, chronopotentiometry
Electrical conductance	Conductimetry
Electrical current	Polarography, amperometric titrations
Quantity of electricity	Coulometry
Mass-to-charge ratio	Mass spectrometry
Thermal properties	Thermal conductivity and enthalpy methods

sophisticated or more costly apparatus; indeed, use of a modern automatic balance in a gravimetric analysis involves more complex and refined instrumentation than is required for many of the other methods listed in Table 1-1.

Separation Methods

More often than not, the analysis of a sample of matter requires one or more of the following steps preliminary to the final physical measurement: (1) sampling to provide a homogeneous specimen whose composition is representative of the bulk of the material; (2) preparation and solution of a measured quantity of the sample; and (3) separation of the species to be measured from components that will interfere with the final measurement. These steps are frequently more troublesome and cause greater errors than the final measurement itself.

Separation procedures are needed because the physical and chemical properties suited for the determination of concentration are ordinarily shared by more than one element or compound. In dealing with closely related substances the problem of separation becomes of major importance and requires such techniques as chromatography, fractional distillation, countercurrent extraction, or controlled potential electrolysis. These specialized separation methods also fall within the purview of this text.

Choice of Methods for an Analytical Problem

Table 1-1 suggests that the chemist who is faced with an analytical problem often has a bewildering array of methods from which to choose. The amount of time he must spend on the analytical work and the quality of his results are critically dependent on this choice. In making his decision the chemist must take into account the complexity of the materials to be analyzed, the concentration of the species of interest, the number of samples he must analyze, and the accuracy required. His choice will then depend upon a knowledge of the basic principles underlying the various methods available to him, and thus their strengths and limitations. The development of this type of knowledge represents a major goal of this book.

Instrumentation in Analysis

In the broadest sense an instrument for chemical analysis does not generate quantitative data but instead simply converts chemical information to a form that is more readily observable. Thus, the instrument can be viewed as a communication device. It accomplishes this purpose in several steps that include (1) generation of a signal, (2) transformation of the signal to one of a different nature (called transduction), (3) amplification of the transformed signal, and (4) presentation of the signal as a displacement on a scale or on the chart of a recorder. It is not necessary that all of these steps be incorporated in every instrument.

The signal employed in an instrument may be generated from the sample itself. Thus, the yellow radiation emitted by heated sodium atoms constitutes the source of the signal in a flame photometer. The gravitational force exerted by the species of interest (or a compound of that species) serves as the signal in a gravimetric method. With many instruments, however, the original signal is formed independently of the sample; it is the modification of this signal by the species of interest that is related to concentration. Thus, in a polarimeter the signal is a beam of plane-polarized light; it is the change in orientation of this plane by the sample that provides the desired information.

Many instruments employ a transducer, which serves to convert the original analytical signal to one that is more conveniently measured. For example, the photocell, the thermocouple, and the photomultiplier tube are transducers that convert radiant energy into electrical signals. A chemical coulometer is a transducer that transforms electrical signals into a related amount of a gas or a solid (which is subsequently measured).

The sensitivity of many instruments is increased by amplification of the original signal or its transduced form. Amplification is most commonly accomplished electronically, although mechanical amplification is also encountered as in, for example, the pointer of an analytical balance.

The transduced and amplified signal from an instrument is generally presented as a linear or angular displacement along a scale. The presentation will ordinarily consist of the deflection of a needle of a voltmeter, the deflection of a beam of light reflected from the mirror of a galvanometer, or a displacement of the meniscus in a buret.

The growth of instrumental analysis has closely paralleled developments of the field of electronics because the generation, transduction, amplification, and display of a signal can be rapidly and conveniently accomplished with electronic circuitry. Numerous transducers have been developed for the conversion of signals to electrical form, and enormous amplification of the resulting electrical signals is possible. In turn, the electrical signals are readily presented on meters, on recorders, or in digital form.

As a result of the appearance of so much electronic circuitry in the laboratory the modern chemist finds himself faced with the question of how much electronics he should know in order to make most efficient use of the equipment available to him for analysis. Is it more important for him to concentrate his attention on the instrument itself or should he devote the majority of his efforts to the chemical principles of the measurement and its inherent limitations and strengths? In this book we have chosen the latter course, and we discuss instrument details only to the extent that these play a direct, major role in the outcome of a measurement. Undoubtedly, a strong knowledge of electronics is advantageous to the experimental chemist, but we feel that a fundamental knowledge of the chemical aspects of chemical instrumentation is more important.

2 Electromagnetic Radiation and Its Interactions with Matter

Fundamental concepts and properties of electromagnetic radiation and its interaction with matter are reviewed in this chapter. The material serves as preparation for the instrumental methods discussed in Chapters 3 through 14.

PROPERTIES OF ELECTROMAGNETIC RADIATION

Electromagnetic radiation is a type of energy that is transmitted through space at enormous velocities. It takes many forms, the most easily recognizable being light and radiant heat. Less obvious manifestations include x-ray, ultraviolet, microwave, and radio radiations.

In order to characterize many of the properties of electromagnetic radiation it is convenient to ascribe a wave nature to its propagation and to portray these waves by such parameters as velocity, frequency, wavelength, and amplitude. However, in contrast to other wave phenomena such as sound, electromagnetic radiation requires no supporting medium for its transmission, and it readily passes through a vacuum.

The wave model for radiation fails completely to account for phenomena associated with the absorption or the emission of radiant energy; for these processes it is necessary to view electromagnetic radiation as discrete particles of energy called *photons*. The energy of a photon is proportional to the frequency of the radiation. These dual views of radiation as particles and as waves are not mutually exclusive. Indeed, the apparent duality is rationalized by wave mechanics and is found to apply to other phenomena, such as the behavior of streams of electrons or other elementary particles.

Wave Properties

Electromagnetic radiation is conveniently treated as an alternating electrical field in space; associated with the electrical force field, but at right angles to it, is a magnetic force field. The wave properties for the radiation can be represented by electrical and magnetic vectors as shown in Figure 2-1. The two vectors are sinusoidal and are perpendicular to the direction of propagation of the wave.

It is the electrical field of electromagnetic radiation that interacts with the electrons in matter; as a result, representation of radiation by the electrical vector alone suffices for most purposes.

Wave parameters. The time interval required for the passage of successive maxima past a fixed point in space is called the *period* p of the radiation. The *frequency* ν is the number of oscillations of the field that occur per second, and is equal to $1/p$.¹ It is of importance to realize that *the frequency*

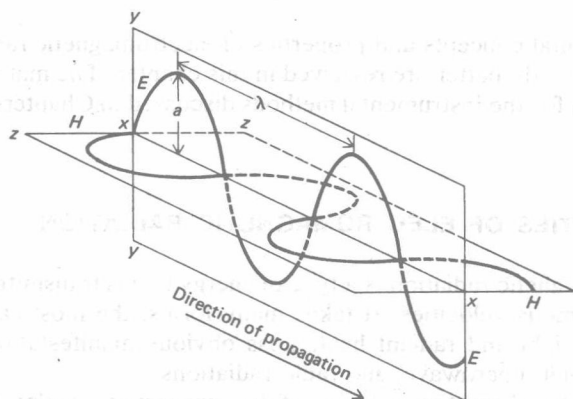


Figure 2-1. Electrical vector E and magnetic vector H of a plane-polarized electromagnetic wave of wavelength λ and amplitude a .

¹The common unit of frequency is the *hertz* Hz, which is equal to one cycle per second. The *fresnel* is 10^{12} Hz.

is determined by the source and remains invariant regardless of the media through which the radiation travels. In contrast, the *velocity* of propagation of a wave v_i is the rate at which the wave front moves through a medium, and is *dependent upon* both the medium and the frequency; the subscript i is employed to indicate this frequency dependence. Another parameter of interest is the *wavelength* λ_i , which is the linear distance between successive maxima or minima of a wave.² Multiplication of the frequency (in cycles per second) by the wavelength (in centimeters per cycle) gives the velocity of the radiation (in centimeters per second); that is,

$$v_i = \nu \lambda_i \quad (2-1)$$

In a vacuum the velocity of propagation of radiation becomes independent of frequency and is at its maximum; this velocity is given the symbol c . The value of c has been accurately determined to be 2.99792×10^{10} cm/sec. Thus, for a vacuum,

$$c = \nu \lambda \cong 3 \times 10^{10} \text{ cm/sec} \quad (2-2)$$

In any other medium the rate of propagation is less because of interaction between the electromagnetic field of the radiation and the bound electrons of the medium. Since the radiant frequency is invariant and fixed by the source, the *wavelength must decrease* as radiation passes from a vacuum to a medium containing matter (equation 2-1).

The *wave number* σ is defined as the number of waves per centimeter, and is yet another way of describing electromagnetic radiation. When the wavelength *in vacuo* is expressed in centimeters, the wave number is equal to $1/\lambda$.

The *power* P of a beam of radiation is the energy of the beam reaching a given area per second; the *intensity* I is the power per unit solid angle. These quantities are related to the square of the amplitude a of the beam (see Figure 2-1). Although it is not strictly correct, power and intensity are often used synonymously.

Interference. As with other wave phenomena, electromagnetic waves can under certain conditions interact with one another when superimposed to produce a resultant wave whose intensity is either amplified or diminished depending upon the phases of the component waves. The amplitude of the resultant wave can be obtained by vector addition as shown by the solid line in Figure 2-2. Maximum destructive interference occurs when two waves are 180 deg out of phase, and maximum constructive interference occurs when the waves are exactly in phase.

²The units commonly used for describing the wavelength of radiation differ considerably in the various spectral regions. For example, the Ångstrom unit Å (10^{-10} m) is convenient for x-ray and short ultraviolet radiation; the nanometer nm or the synonymous millimicron $m\mu$ (10^{-9} m) is employed with visible and ultraviolet radiation; the micron μ (10^{-6} m) is commonly employed for infrared radiation.

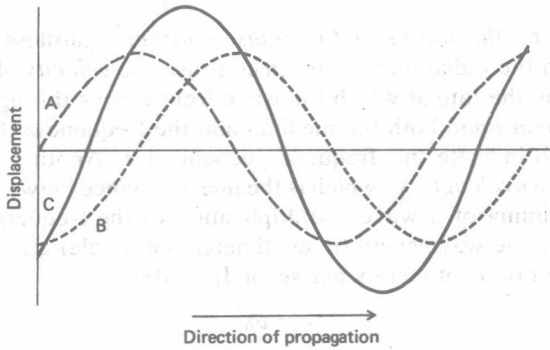


Figure 2-2. Illustration of interference. Curve B is 70 deg out of phase with Curve A. Curve C is the resultant wave.

Diffraction of radiation. Electromagnetic radiation normally travels in straight paths. However, when a beam passes a sharp edge or travels through a narrow opening, a part appears in areas that should be in the shadow of the object in its path of travel. This bending of radiation is a form of *diffraction*, and is a direct consequence of interference.

Figure 2-3(a) is a schematic drawing of a device that was used in 1800 by Thomas Young to demonstrate that light waves could interfere with one another in the same way as could other types of waves. Radiation is propagated from slit S_1 , illuminates slits S_2 and S_3 more or less equally, and then strikes a screen. If the radiation is monochromatic, a series of dark and light images or lines perpendicular to the plane of the paper is observed. If polychromatic radiation is employed, a central white band surrounded by colored fringes results. Note that the light band at E is in the shadow of the opaque material containing slits S_2 and S_3 , and that the paths BE and AE are identical in length. Thus, the waves arrive at this point completely in phase and reinforce one another.

With the aid of Figure 2-3(b) the conditions for maximum constructive interference that cause the other light bands are readily derived. The lines BD and AD represent the light paths from slits S_2 and S_3 to the point on the screen of maximum intensity D . Line BC is then drawn perpendicular to AD so that triangles ABC and BCD are similar. Thus, angle ABC is equal to the angle of diffraction θ and we may write

$$\overline{AC} = \overline{AB} \sin \theta$$

The relative dimensions in Figure 2-3 have been greatly distorted for the sake of clarity. In a real system the slit spacing \overline{AB} is extremely small when compared with the distance between the slit and the screen (\overline{OE}); that is, $\overline{OE} \gg \overline{AB}$. Under these conditions \overline{CD} closely approximates \overline{BD} , and the distance \overline{AC} then is a good measure of the difference in path lengths