

Instrumental Methods of Chemical Analysis

Galen W. Ewing

Professor of Chemistry
Seton Hall University

Fourth Edition

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Instrumental Methods of Chemical Analysis

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Chapter 1

Introduction

Analytical chemistry may be defined as the science and art of determining the composition of materials in terms of the elements or compounds contained. Historically, the development of analytical methods has followed closely the introduction of new measuring instruments. The first quantitative analyses were gravimetric, made possible by the invention of a precise balance. It was soon found that carefully calibrated glassware made possible considerable saving of time through the volumetric measurement of gravimetrically standardized solutions.

In the closing decades of the nineteenth century, the invention of the spectroscope brought with it an analytical approach that proved to be extremely fruitful. At first it could be applied only qualitatively; gravimetric and volumetric methods remained for many years the only quantitative procedures available for nearly all analyses. Gradually a few colorimetric and nephelometric methods were introduced. Then it was found that electrical measurements could be used to advantage to detect end points in titrations. Since about 1930, the rapid development of electronics has resulted in a major revolution in analytical instrumentation. Today the chemist, whether he calls himself an analytical specialist or not, must have a working knowledge of a dozen or so instrumental methods virtually unknown a generation ago.

Nearly any physical property characteristic of a particular element or compound can be made the basis of a method for its analysis. Thus, the absorption of light, the conductivity of a solution, or the ionizability of a gas can serve as an analytical tool. A whole series of related techniques depends on the varying electrical properties of different elements, as evidenced by their redox potentials. The phenomena of artificial radioactivity have led to several analytical methods of great significance. It is the purpose of this book to investigate the possibilities of many of these modern instrumental methods of analysis.

PHYSICAL PROPERTIES USEFUL IN ANALYSIS

The following is a list of physical properties that have been found applicable to chemical analysis. The list is not exhaustive, but it certainly includes all those properties that have been extensively investigated, as well as some not yet fully exploited.

EXTENSIVE PROPERTIES

1. Mass
2. Volume (of a liquid or gas)

MECHANICAL PROPERTIES

1. Specific gravity (or density)
2. Surface tension
3. Viscosity
4. Velocity of sound

PROPERTIES INVOLVING INTERACTION WITH RADIANT ENERGY

1. Absorption of radiation
2. Scattering of radiation
3. Raman effect
4. Emission of radiation
5. Refractive index and refractive dispersion
6. Rotation of the plane of polarized light and rotatory dispersion
7. Circular dichroism
8. Fluorescence and phosphorescence
9. Diffraction phenomena
10. Nuclear and electron magnetic resonance

ELECTRICAL PROPERTIES

1. Half-cell potentials
2. Current-voltage characteristics
3. Electrical conductivity
4. Dielectric constant

THERMAL PROPERTIES

1. Transition ~~temperatures~~
2. Heats of reaction
3. Thermal conductivity (of a gas)

NUCLEAR PROPERTIES

1. Radioactivity
2. Neutron cross section
3. Isotopic mass

METHODS OF SEPARATION PRIOR TO ANALYSIS

It would be desirable to discover analytical methods that are *specific* for each element or radical or class of compounds. Unfortunately only a few methods are completely specific, and it is therefore frequently necessary to perform quantitative separations with the objective of either isolating the desired constituent in a measurable form or removing interfering substances. Some methods of separation are:

1. Precipitation
2. Electrodeposition
3. Distillation
4. Solvent extraction or sublation
5. Partition chromatography
6. Adsorption chromatography
7. Ion exchange
8. Electrophoresis
9. Dialysis

ELECTRONICS

The fundamental task to be performed by an instrument is to translate chemical information into a form directly observable by an operator. It does this by means of a *transducer*, a component capable of transferring energy from one domain (chemical) to another (usually electrical). Then it is up to the electronics of the instrument to process the electrical signal (i.e., isolate it, amplify it, compare it with a standard, modify it functionally) and finally to read it out on a meter or an automatic recorder.

The great majority of laboratory instruments involve electronic devices. It is characteristic of analytical instruments that they are designed to be as sensitive as possible, and hence must be able to measure precisely the smallest signal that can be produced by the primary measuring element. Amplification is almost always required, and the most versatile way of achieving this amplification is through electronics.

In many methods it is necessary to apply some sort of stimulus to the chemical system (a beam of radiation, for example), and this stimulus is often produced or at least measured and regulated by additional electronic devices.

Because of these close relations with chemical instruments, the fundamentals of electronics form an integral part of any treatment of instrumentation. Fortunately, modern electronics has developed in the direction of modularization. A variety of amplifiers and logic elements is available as low-cost plug-in units that can be used as building blocks for the construction of most of the electronic equipment described in this book. Commercial equipment frequently does not make use of these building blocks as separate physical entities, but the principles involved are the same.

A short treatment of those aspects of electronics pertinent to our main subject is given in the concluding chapters of this book. This may be studied separately if desired, or used as resource material to aid in a better understanding of the instruments as they are taken up.

TITRATION

Titration is defined as the measurement of an unknown constituent by establishment of the exactly equivalent amount of some standard reagent. Physical measurements are involved in two ways: in the detection of the equivalence point, and in the measurement of the quantity of reagent consumed. Usually, and unless otherwise specified, the quantity of reagent is measured volumetrically with a buret. The chief exception is *coulometric titration*, in which the reagent is generated electrolytically on the spot as required, and its quantity determined by electrical measurements.

Many of the analytical methods described in this book can be used to follow the course of a titration, often with reduced demands on the instrumentation. Such applications are discussed toward the ends of the respective chapters.

NOTE ON UNITS

Worldwide agreement on units and their symbols is of prime importance to the future of science. A determined effort in this direction has been mounted by a number of international conferences with the cooperation of the National Bureau of Standards in the United States and corresponding offices in other countries. This effort has resulted in the *Système International d'Unités* (International System of Units, abbreviated SI). The system is described in a booklet published by the National Bureau of Standards.*

*C. H. Page and P. Vigoureux (eds.), *The International System of Units (SI)*, 1972. Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402; SD Catalog No. C 13.10:330/2; price 30 cents.

In the present text, SI units are used throughout. Where other units are widely employed, this fact will be pointed out. The chief difference so far this book is concerned is the abandoning of such well-known units as the angstrom, micron, gauss, and torr. Another point of departure from American custom is the spelling of metre. This form is preferred as obviating confusion between a unit (e.g., micrometre, 10^{-6} m) and an instrument (micrometer, a measuring tool).

The standard prefixes for multiples and submultiples of units are:

<i>Factor</i>	<i>Prefix</i>	<i>Symbol</i>
10^{12}	Tera	T
10^9	Giga	G
10^6	Mega	M
10^3	Kilo	k
10^2	Hecto	h
10^1	Deka	da
10^{-1}	Deci	d
10^{-2}	Centi	c
10^{-3}	Milli	m
10^{-6}	Micro	μ
10^{-9}	Nano	n
10^{-12}	Pico	p
10^{-15}	Femto	f
10^{-18}	Atto	a

BIBLIOGRAPHY

The student who wishes to pursue in greater depth any of the topics mentioned in this book has many avenues to which to turn. There are of course the general sources, such as *Chemical Abstracts*, applicable to all branches of chemistry.

In the analytical field there is a great proliferation of journals of primary interest. *Analytical Chemistry*, *Analytica Chimica Acta*, *Talanta*, *The Analyst* (including *Analytical Abstracts*), the *Zeitschrift für analytische Chemie*, and *Analytical Letters* attempt general analytical coverage. In specific fields are the *Journal of Electroanalytical Chemistry*, the *Journal of Chromatography*, the *Journal of Gas Chromatography*, *Spectrochimica Acta*, *Analytical Biochemistry*, and many others. With emphasis on instruments per se, one finds the *Review of Scientific Instruments*, the *Journal of Scientific Instruments*, and *Chemical Instrumentation*. The *Journal of Chemical Education* runs a monthly column on topics in chemical instrumentation, in addition to many articles of analytical interest.

On the theoretical side, the "Treatise on Analytical Chemistry," edited

by I. M. Kolthoff and P. J. Elving (Wiley-Interscience, New York), is invaluable, especially Part I. Many of the volumes of the series "Physical Methods of Chemistry," edited by A. Weissberger and B. W. Rossiter (Wiley-Interscience) present a wealth of information on analytical instrumentation. Also not to be overlooked is the series "Advances in Analytical Chemistry and Instrumentation," also published by Wiley-Interscience.

The *Annual Reviews* issue of *Analytical Chemistry*, published each April, contains critical reviews in all fields of analysis; in even years the reviews are classed by the analytical principles involved, and in odd years by field of application. The *CRC Critical Reviews in Analytical Chemistry* is another source of thorough treatment of selected topics.

An immense amount of useful information, with succinct reviews of theoretical principles, has been collected under the editorship of L. Meites in the "Handbook of Analytical Chemistry," published by McGraw-Hill, New York, 1963.

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Chapter 2

Introduction to Optical Methods

A major class of analytical methods is based on the interaction of radiant energy with matter. In the present chapter we shall review some of the pertinent properties both of radiation and of matter, and then discuss those features of optical instrumentation that apply to all or several spectral regions. In subsequent chapters each major spectral range (visible, ultraviolet, infrared, x-ray, microwave) will be considered separately, with respect to theory, instrumentation, and chemical applications.

THE NATURE OF RADIANT ENERGY

An investigation into the properties of radiant electromagnetic energy reveals an essential duality in our understanding of its nature. In some respects its properties are those of a wave, while in others it is apparent that radiation consists of a series of discrete packets of energy (*photons*). The photon concept is almost always required in the rigorous treatment of the interactions of radiation with matter, although the wave picture may be used to give approximately correct results when large numbers of photons are involved.

Radiant energy can be described in terms of a number of properties

or parameters. The *frequency* ν is the number of oscillations per second described by the electromagnetic wave; the usual unit of frequency is the *hertz* (1 Hz = 1 cycle per second). The *velocity* c of propagation is very nearly $2.9979 \times 10^8 \text{ m} \cdot \text{s}^{-1}$ for radiation traveling through a vacuum, and somewhat less for passage through a transparent medium.

The *wavelength* λ is the distance between adjacent crests of the wave in a beam of radiation. It is given by the ratio of the velocity to the frequency. The units of wavelength are the *micrometre* (1 $\mu\text{m} = 10^{-6} \text{ m}$; formerly called the *micron*, μ), and the *nanometre* (1 nm = 10^{-9} m ; formerly the *millimicron*, m μ). The *angstrom* (1 $\text{\AA} = 10^{-10} \text{ m}$) is widely used in spectroscopy. Another quantity which is often convenient is the *wave number* $\bar{\nu}$, the number of waves per centimetre.* The unit is the *reciprocal centimetre*, (cm^{-1}), sometimes called the *kaiser*.

The velocity, wavelength, frequency, and wave number are related by the expression

$$\nu = \frac{c}{\lambda} = c\bar{\nu} \quad (2-1)$$

The energy content E of a photon is directly proportional to the frequency:

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \quad (2-2)$$

where h is Planck's constant, very close to $6.6256 \times 10^{-34} \text{ J} \cdot \text{s}$. Thus there is an inverse relationship between energy content and wavelength, but a direct relation between energy and frequency or wave number. It is for this reason that the presentation of spectra in terms of frequency or wave number rather than wavelength is gaining in favor.

It is convenient, particularly with nuclear radiations and x-rays, to characterize the radiation by the energy content of its photons in *electron volts* (eV); 1 eV = $1.6020 \times 10^{-19} \text{ J}$, corresponding to frequency $\nu = 2.4186 \times 10^{14} \text{ Hz}$ or to the (in vacuo) wavelength $\lambda = 1.2395 \times 10^{-6} \text{ m}$. The multiples kilo-electron volt (keV) and mega-electron volt (MeV) are often encountered.

A beam of radiation carries energy which is emitted from a source and propagated through a medium or series of media to a receptor where

* It is unfortunate that the symbol $\bar{\nu}$ has been chosen to indicate the wave number, because of its likely confusion with ν for frequency; indeed, in certain areas of physics it is customary to use these symbols in exactly the opposite sense. Expressions such as "a frequency of 1600 wave numbers," though often found in the literature, are not correct. Frequency may be *proportional* to wave number, but cannot be equal to it, as the dimensions are unlike. Furthermore, a wave number is not a unit, so "1600 wave numbers" is no more correct than describing this page as "6 distances wide."

it is absorbed. On its way from source to ultimate absorber, the beam may undergo partial absorption by the media through which it passes, it may be changed in direction by reflection, refraction, or diffraction, or it may become partially or wholly polarized.

Since energy per unit time is power, one is often interested in the *radiant power* of the beam, a quantity often loosely referred to as intensity. *Intensity* more correctly refers to the power emitted by the source per unit solid angle in a particular direction. A photoelectric cell gives a response related to the total power incident on its sensitive surface. A photographic plate, on the other hand, integrates the power over the time of exposure to the beam, and hence its response (silver deposit) is a function of the total incident energy (rather than power) per unit area. In both photoelectric cells and photographic plates, as well as in the human eye, the sensitivity is a more or less complicated function of the wavelength.

SPECTRAL REGIONS

The spectrum of radiant energy is conveniently broken down into several regions, as shown in Table 2-1. The limits of these regions are determined by the practical limits of appropriate experimental methods of production and detection of radiations. The figures in the table are not in themselves especially significant, and should be considered only as rough boundaries.

The differentiation of spectral regions has additional significance for the chemist in that the interactions of the radiations with chemical systems follow different mechanisms and provide different kinds of information.

Table 2-1 Regions of the electromagnetic spectrum *

Designation	Wavelength limits		Frequency limits, Hz	Wave number limits, cm^{-1}
	Usual units	Metres		
X-rays	10^{-1} – 10^2 Å	10^{-12} – 10^{-8}	10^{16} – 10^{18}	
Far ultraviolet	10–200 nm	10^{-8} – 2×10^{-7}	10^{15} – 10^{16}	
Near ultraviolet	200–400 nm	2×10^{-7} – 4.0×10^{-7}	10^{15} – 7.5×10^{14}	
Visible	400–750 nm	4.0×10^{-7} – 7.5×10^{-7}	7.5×10^{14} – 4.0×10^{14}	25,000–13,000
Near infrared†	0.75–2.5 μm	7.5×10^{-7} – 2.5×10^{-6}	4.0×10^{14} – 1.2×10^{14}	13,000–4000
Mid infrared†	2.5–50 μm	2.5×10^{-6} – 5.0×10^{-5}	1.2×10^{14} – 6.0×10^{12}	4000–200
Far infrared†	50–1000 μm	5.0×10^{-5} – 1×10^{-3}	6×10^{12} – 10^{11}	200–10
Microwaves	0.1–100 cm	1×10^{-2} – 1	10^{11} – 10^8	10– 10^{-3}
Radio waves	1–1000 m	1 – 10^3	10^8 – 10^5	

* Where a numerical factor is omitted, it is because the precision of delineation of the region does not warrant a greater number of significant figures.

† The limits for the subdivisions of the infrared follow the recommendations of the Triple Commission for Spectroscopy; *J. Opt. Soc. Am.*, **52**:476 (1962).

The most important atomic or molecular transitions pertinent to the successive regions are:

.. X-ray	K- and L-shell electrons
Far ultraviolet	Middle-shell electrons
Near ultraviolet	Valence electrons
Visible	
Near and mid infrared	Molecular vibrations
Far infrared	Molecular rotations and low-lying vibrations
Microwave	Molecular rotations

INTERACTIONS WITH MATTER

Electromagnetic radiation originates in the deceleration of electrically charged particles, and can be absorbed by the reverse process, contributing its energy to accelerate particles. Hence an understanding of the interactions between matter and radiation can only be built on a knowledge of the electronic structure of atoms and molecules.

Figure 2-1 shows a few of the energy levels for the neutral sodium atom that apply to the outer (valence) electron. Under ordinary conditions essentially all the atoms in a body of sodium vapor are in the ground state, that is, their valence electrons lie in the $3s$ level. If irradiated with light containing the wavelengths 589.00 and 589.59 nm, the outer electrons of many of the atoms will absorb photons and be transferred to the $3p$ levels. (The two very close $3p$ levels differ only in their spin characteristics.) The excited electron has a strong tendency to return to its normal ($3s$) state, and in so doing emits a photon. This emitted photon possesses a very definite amount of energy, dictated by the spacing of the energy levels. In the present example, the emitted radiation constitutes the familiar yellow light of the sodium flame or lamp. This simple case, in which the outer electron is raised by one energy level and then returns, is known as *resonance absorption* and *radiation*. The important analytical technique of *atomic absorption* is based on this phenomenon.

If the electron is given more than enough energy to produce resonance, it may be raised to some higher level than $3p$, such as $4p$ or $5p$. In that case it will not drop back to $3s$ by a single process, but will pause at intermediate levels, like a ball rolling down steps. This situation no longer fits the definition of resonance radiation, but is more complex. For one thing, not all conceivable transitions are actually possible—some are “forbidden” by the selection rules of quantum mechanics.

With a highly energetic source, many electrons (not only the outermost) in any element can be excited to varying degrees, and the resulting radiation may contain up to several thousand discrete and reproducible

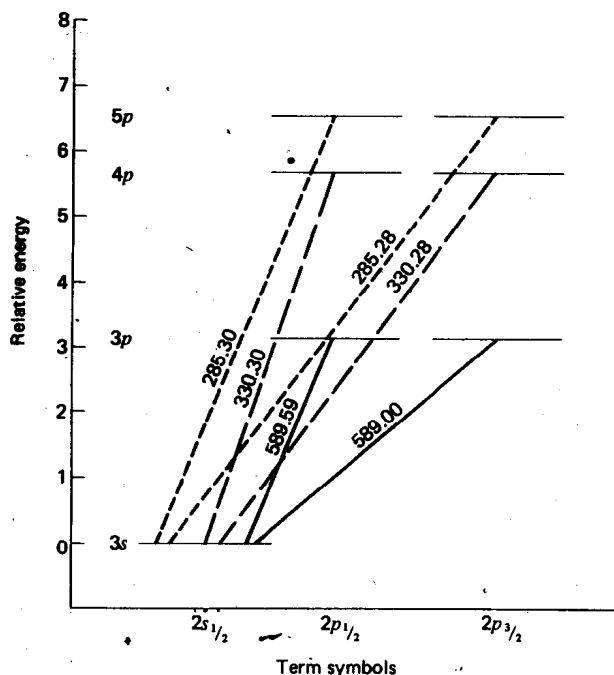


Fig. 2-1 Partial energy-level diagram for the valence electron in sodium.

wavelengths, mostly in the ultraviolet and visible regions. This is the basis of the analytical method of *emission spectroscopy*.

If the source of excitation provides even more energy, an inner electron can be torn entirely away from its atom. An electron from some higher level will then drop in to fill the vacancy. Since the energy change corresponding to this inner orbital transition is much greater than in the case of excited outer electrons, the photons radiated will be of much greater frequency and correspondingly shorter wavelength. This describes the emission of x-rays from atoms subjected to bombardment, for example, by a beam of fast-moving electrons.

MOLECULAR SPECTRA

In a typical molecule, as contrasted with an atom, the first few energy levels might show relations such as those of Fig. 2-2. The molecule to which this diagram applies has a singlet ground state designated S_0 , which

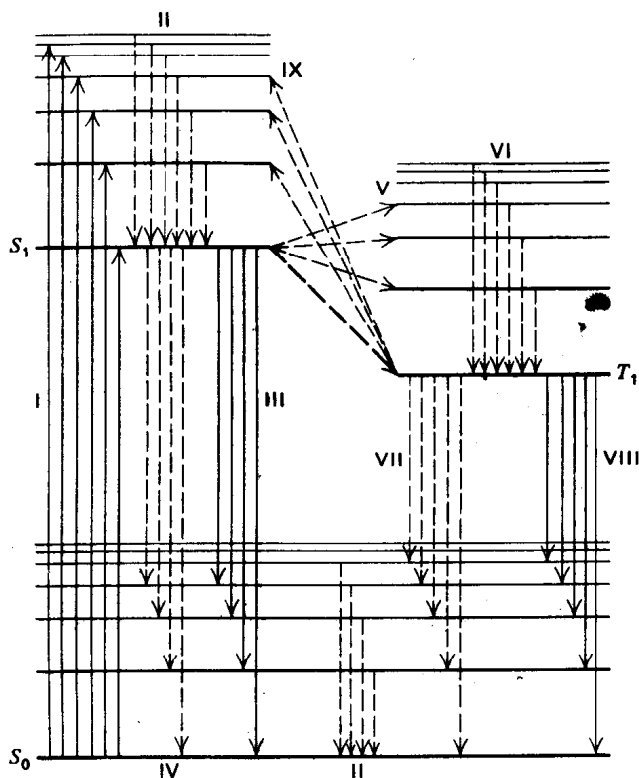


Fig. 2-2 Energy-level diagram of a typical organic molecule including only ground singlet, first excited singlet, and its corresponding triplet state. Solid lines indicate radiational transitions, and dashed lines indicate nonradiational transitions. Process I: absorption. Process II: vibrational deactivation. Process III: fluorescence. Process IV: quenching of excited singlet state. Process V: intersystem crossing to triplet state. Process VI: vibrational deactivation in the triplet system. Process VII: quenching of triplet state. Process VIII: phosphorescence. Process IX: intersystem crossing to excited singlet state. [Academic (1).]

represents its normal, unexcited condition. Two series of excited states exist, the *singlet* series, S_1, S_2, \dots , and the *triplet* series, T_1, T_2, \dots . These two series refer to a difference in the net electronic spin of atoms in the various levels. A triplet level always has less energy than the corresponding singlet. It is difficult to effect a change in electron spin, so the absorption of radiant energy can only raise an atom from S_0 to a high S level or sublevel. Triplet states can only be reached by an indirect