

Instrumental Methods of Chemical Analysis

Third Edition

GALEN W. EWING

Professor of Chemistry
Seton Hall University

MCGRAW-HILL BOOK COMPANY

New York St. Louis San Francisco
Toronto London Sydney

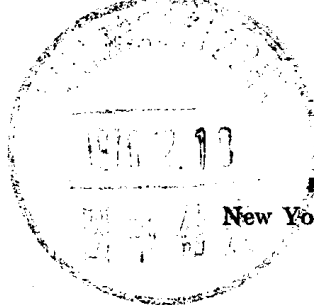
54.6
E. 15

Instrumental Methods of Chemical Analysis

Third Edition

GALEN W. EWING
Professor of Chemistry
Seton Hall University

5503420



McGRAW-HILL BOOK COMPANY

New York St. Louis San Francisco
Toronto London Sydney

**INSTRUMENTAL METHODS OF
CHEMICAL ANALYSIS**

Copyright © 1960, 1969 by McGraw-Hill, Inc. All Rights Reserved. Copyright 1954 by McGraw-Hill, Inc. All Rights Reserved. Printed in the United States of America. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior written permission of the publisher.

Library of Congress Catalog Card Number 68-25651
19851

1234567890MAMM7543210698

DR 68/02

To Two Inspiring Teachers

WILLIAM GEORGE GUY

The College of William and Mary

and

THOMAS FRASER YOUNG

The University of Chicago

Preface

As in previous editions, the general objective in this book is to survey modern analytical instruments and techniques and to present sufficient theory for their comprehension. Emphasis is placed on the possibilities and limitations inherent in the various methods.

The text is planned for use in upper-level undergraduate or first-year graduate classes. To be taught most effectively, this course should follow work in elementary quantitative analysis and a year of physics; it may follow or run concurrently with physical chemistry.

It is always a difficult matter to decide what to include and what to omit. The words "analytical" and "instrumental" are not amenable to objective definition. With respect to the former, H. A. Laitinen has written: "The vital point here is that if the research is aimed at methods of solution of a measurement problem, it is properly classified as analytical chemistry, whereas the interpretation of the results of the measurements infringes upon other fields of chemistry." (Editorial, *Anal. Chem.*, **38**, 1441, 1966.) I have attempted to include just enough interpretive material to suggest the areas in which a method can be useful.

With respect to the term "instrumental," I have tried to be led more by usefulness to the chemistry student than by a strict definition of the term. Thus such an important instrument as the analytical balance is not discussed, whereas paper chromatography is.

The principal changes in the third edition are a reduction in space devoted to the theory of potentiometric and conductometric titrations, to refractometry, and to classical emission spectrography. Much more attention is given to gas chromatography and to recent modifications of polarography and related techniques. A unified treatment is attempted in the analytical applications of flames. Similarly many of the techniques of separation are grouped together to emphasize their basic similarities. Optical rotatory dispersion, circular dichroism, microwave absorption, and chronopotentiometry are subjects newly introduced.

The chapter on electronics is expanded and updated, with increased emphasis on solid-state devices and particularly on the unique and valuable properties of operational amplifiers. This chapter is self-supporting, and some instructors may wish to use it to introduce the course.

Stylistically, it seems appropriate to let *cuvette* follow *pipette* and *burette* in dropping the final two letters. *Millimeter-of-mercury* has given way to *torr*, *cycle-per-second* to *hertz*, and *millimicron* to *nanometer* (which, along with *kilometer*, should be pronounced more like *centimeter* than like *thermometer*).

Mention of the products of individual manufacturers does not necessarily imply that I consider them superior to competing items. The aim is to describe instruments typical of their class or possessing some special features of interest, not to write a complete catalog of analytical apparatus.

I wish to express my sincere appreciation to my colleagues and students, past and present, who have offered advice and pointed out errors. Especial thanks go to Professors J. M. Fitzgerald and R. F. Hirsch, who have read carefully and critically many chapters of manuscript. My thanks also to the personnel of instrument companies and distributors, too numerous to list, without whose cooperation the book could not be a success.

Galen W. Ewing

Contents

Preface vii

- 1 Introduction 1
- 2 Introduction to Optical Methods 6
- 3 The Absorption of Radiation: Ultraviolet and Visible 48
- 4 Fluorimetry and Phosphorimetry 105
- 5 The Absorption of Radiation: Infrared 119
- 6 The Scattering of Radiation 151
- 7 Emission Spectroscopy 164
- 8 Flame Spectroscopy 176
- 9 X-ray Methods 195
- 10 Polarimetry and Optical Rotatory Dispersion 224
- 11 Introduction to Electrochemical Methods 234
- 12 Potentiometry 248
- 13 Voltammetry, Polarography, and Related Techniques 275
- 14 Electrodeposition and Coulometry 316
- 15 Conductimetry 336

16	Radioactivity as an Analytical Tool	354
17	Mass Spectrometry	380
18	Magnetic Resonance Spectroscopy	404
19	Thermometric Methods	420
20	Introduction to Interphase Separations	436
21	Gas Chromatography	450
22	Liquid Chromatography	475
23	Solvent Extraction and Related Methods	494
24	Electrical Separation Methods	505
25	General Considerations in Analysis	513
26	Electronic Circuitry for Analytical Instruments	523
	Laboratory Experiments	567
	Appendix	609
	Name Index	611
	Subject Index	619

Introduction

Analytical chemistry may be defined as the science and art of determining the composition of materials in terms of the elements or compounds which they contain. 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 which 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, principally for substances for which other techniques were unknown or unreliable. Then it was found that electrical measurements could detect end points in titrations. In the years since about 1930, the rapid develop-

5503420

ment of the vacuum-tube amplifier and the photoelectric tube, and more recently, of transistors and other semiconductor devices, has resulted in the establishment of many analytical methods based upon them. Today the chemist, whether he calls himself an analytical specialist or not, must have a working knowledge of a dozen or so instruments which were 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 each serve as an analytical tool. A whole series of related techniques depends upon 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 extremely 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 which have been found applicable to chemical analysis. The list is not exhaustive, but it certainly includes all those properties which have been extensively investigated, as well as some not yet fully exploited.

EXTENSIVE PROPERTIES

1. Mass
2. Volume (of a liquid or a 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. Electric conductivity
4. Dielectric constant
5. Magnetic susceptibility

THERMAL PROPERTIES

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

NUCLEAR PROPERTIES

1. Radioactivity
2. Isotopic mass

METHODS OF SEPARATION PRIOR TO ANALYSIS

It would be desirable to discover analytical methods which 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 either of isolating the desired constituent in a measurable form or of removing interfering substances. Some methods of separation are the following:

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

FUNDAMENTAL AND DERIVED PHYSICAL QUANTITIES

Fundamental physical quantities that can be measured directly are surprisingly few. Most of the measurements which we make in the laboratory consist essentially in the observation of linear or angular displace-

* An example of an analysis which is specific is the resonance absorption of radiation by atoms of the same element giving rise to the radiation (atomic absorption).

ment, by comparison with some kind of scale. In using the analytical balance, we actually note the displacement of a pointer or its equivalent, and adjust the weights to bring the displacement to zero. The buret is read by observation of the linear displacement of the meniscus from its initial to its final position. Electrical measurements are made through the angular displacement of meter needles or of potentiometer dials, and so on. Many other quantities, such as the intensities of light or sound, must serve only as null indicators unless a device is available to convert the quantity to a form which can be read on a meter. It is the function of the instrument to translate chemical composition into information directly observable by the operator. In nearly all cases, the instrument acts either directly or indirectly as a *comparator*, in that the unknown is evaluated relative to a standard.

Most of the analytical methods to be described rest on sound mathematical theory. Occasionally there is reported an experimental procedure which is mostly empirical, with little theoretical background. Such a method may be usable for analytical purposes, but it must be proved valid by exhaustive study and independent checking of data so that the analyst may have certain knowledge of what he is actually measuring.

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 the *coulometric titration*, where the reagent is generated electrolytically on the spot as required, and its quantity determined by electrical measurements; *photochemical* generation has recently been demonstrated as suitable for titrations.

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* (which includes *Analytical Abstracts*), and the *Zeitschrift für*

analytische Chemie 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*, *Instrumentation Technology* (formerly the *Instrument Society of America Journal*), and the *Instrument Society of America Transactions*. 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 (Interscience Publishers, Division of John Wiley & Sons, Inc.), is invaluable, especially Part I. Also not to be overlooked is the series *Advances in Analytical Chemistry and Instrumentation*, edited by C. N. Reilley (and, for vol. 5, F. W. McLafferty), and published by the same house.

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 fields of application. The *Treatise on Analytical Chemistry* and the *Annual Reviews*, taken together, provide the best entry into a new field.

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 Book Company in 1963.

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 pertinent properties, both of radiation and of matter, and then discuss those features of optical instrumentation which apply to all or several spectral regions in common. In subsequent chapters each major spectral range (visible, ultraviolet, infrared, x-ray, microwave) will be considered separately, with respect to instrumentation and chemical application.

THE NATURE OF RADIANT ENERGY

An investigation into the properties of radiant 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 the 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 units of frequency are the *hertz* (1 Hz = 1 cycle-sec⁻¹) and the *fresnel* (10¹² Hz). The *velocity* c of propagation is very nearly 2.998×10^8 m-sec⁻¹ for radiation traveling through a vacuum, and somewhat less for passage through various transparent media.

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 *angstroms* (1 Å = 10⁻¹⁰ m), *microns* (1 μ = 10⁻⁶ m), or *nanometers* (1 nm = 10⁻⁹ m = 10⁻³ μ = 10 Å). The nanometer is also designated the millimicron (mμ); the term nanometer follows the recommendations of the National Bureau of Standards in 1963.¹⁰ Another quantity which is convenient in some circumstances is the *wave number* λ^{-1} which is the number of waves per centimeter.* The unit for wave number is the *reciprocal centimeter* (cm⁻¹), for which the name *kaiser* (K) has been suggested.

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

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

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

$$E = h\nu = h \frac{c}{\lambda} = hc\lambda^{-1} \quad (2-2)$$

where h is Planck's universal constant, very close to 6.6256×10^{-27} erg-sec.¹⁰ 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 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 = 1.602×10^{-12} erg, and corresponds to fre-

* It is unfortunate that the symbol $\bar{\nu}$ is often used to indicate the wave number, because of possible confusion with ν for frequency; in certain areas of physics it is usual to interchange these symbols. In this book we will use the slightly cumbersome but unambiguous symbol λ^{-1} . There can be no justification for expressions such as "a frequency of 1600 cm⁻¹," which is all too often found in the literature; frequency *must* have the dimensions of reciprocal time, *never* reciprocal distance.

quency $\nu = 2.4186 \times 10^{14}$ Hz or to the (in vacuo) wavelength

$$\lambda = 1.2395 \times 10^{-6} \text{ m}$$

The multiples keV and MeV are frequently encountered.

A beam of radiation consists of energy which is emitted from a source and propagated through a medium or series of media to a receptor where it is absorbed. On its way from source to ultimate absorber, the beam may suffer partial absorption by the media through which it passes, it may be changed in direction by reflection, refraction, or diffraction, and it may become partially or wholly polarized.

Since energy per unit time is power, it is correct to speak of 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 upon its sensitive surface. A photographic plate, on the other hand, integrates the power over the period of 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, and this must be taken into consideration in their use.

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 deter-

Table 2-1 Regions of the electromagnetic spectrum*

Designation	Wavelength limits		Frequency limits, Hz†	Wave number limits, $\text{cm}^{-1}\ddagger$
	Usual units	Meters		
X-rays	10^{-2} – 10^2 Å	10^{-12} – 10^{-8}	10^{16} – 10^{18}	
Far ultraviolet	10–200 nm	10^{-8} – 2×10^{-7}	10^{16} – 10^{18}	
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 μ	7.5×10^{-7} – 2.5×10^{-6}	4.0×10^{14} – 1.2×10^{14}	13,000–4000
Mid infrared‡	2.5–50 μ	2.5×10^{-6} – 5.0×10^{-5}	1.2×10^{14} – 6.0×10^{12}	4000–200
Far infrared‡	50–1000 μ	5.0×10^{-5} – 1×10^{-1}	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 – 10^4	

* 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.

† Calculated from $\nu = c/\lambda$, where $c = 3.0 \times 10^8$ m/sec.

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

mined by the practical limits of appropriate experimental methods of production and detection of radiations. The figures quoted 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 to the chemist in that the physical interactions follow different mechanisms and provide different kinds of information. 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 and visible....	Valence electrons
Near and mid-infrared	Molecular vibrations
Far infrared	Molecular rotations and low-lying vibrations
Microwave	Molecular rotations

These will now be considered in detail.

INTERACTIONS WITH MATTER: ATOMIC SPECTRA

Electromagnetic radiation originates in the deceleration of electrically charged particles and can be absorbed by the reverse process, contributing its energy to produce acceleration. Hence an understanding of the interactions between matter and radiation can only be built upon a knowledge of the structure of atoms and molecules. Figures 2-1 and 2-2 show typical energy-level diagrams for an atom and a molecule, respectively.

Consider first the energy levels of an atom, which are represented by horizontal lines in Fig. 2-1. The vertical lines in this figure indicate permitted electronic transitions between the various levels. The greater the vertical distance between two levels, the greater the energy difference, and the greater energy a photon must have to be emitted or absorbed in such a transition.

In a normal (i.e., unexcited) atom, the electrons occupy as many levels as needed, starting with the lowest ($1s$) and proceeding upward according to the well-known quantum rules. Sodium, for example, has 11 electrons, designated $1s^2$, $2s^2$, $2p^6$, $3s^1$. The $3s$ electron is the least strongly held and hence can easily be pushed upward from the $3s$ to the $3p$ level, which is an example of electronic excitation. This can be accomplished by providing energy in any one of a number of forms. The excited electron has a strong tendency to return to its normal state, the $3s$ level, and in doing so emits a quantum of radiation (a photon). This