Instrumental Analysis

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This book has been written as a text for a course in instrumental analysis given to senior and graduate chemistry students at Rensselaer Polytechnic Institute. The course is designed to familiarize the students with the operation of the major analytical instruments and the possible applications of these instruments to their research problems and their future work in the field of chemistry.

A great deal of instrumentation is used in the modern courses in physics and physical chemistry, but this equipment is usually constructed or assembled in the laboratory and the emphasis is on the system being measured rather than on the instruments themselves. The present course recognizes that, in general, the analytical chemist uses commercial instruments for the determination of various elements or compounds. Therefore, the emphasis is less on the particular system being measured than on the utility of the several types of instruments and on a broad picture of the field of commercial instruments. The student who has this training will be in a position to select instruments for a particular problem with some idea of the advantages and disadvantages of the types that are available.

The selection of the equipment to be included in the text has been decided by the actual units available at Rensselaer. The simple instruments whose analytical uses are considered in the usual undergraduate courses in physical and organic chemistry have not been discussed again. An attempt has been made to describe the principles that are basic to the various types of instrumental analysis and to describe some of the commercial models of instruments that are presently available. Although the rapid changes and improvements being made in commercial instruments may make some of the descriptions obsolete, the principles learned should carry over to new equipment as it appears on the market.

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The theoretical discussions in the body of the text are limited to the needs of the analytical chemist. A knowledge of physical and general analytical chemistry is assumed as a prerequisite, so that, unless some particular analytical viewpoint is to be emphasized, much elementary material has been omitted. The applications of instrumental analysis are presented only generally, since the literature, particularly *Analytical Chemistry*, contains a large number of articles on the applications of instrumental methods of analysis. The experienced analytical chemist, therefore, will not find new or unpublished techniques in this book. Instead we have striven for clarity in explaining the common techniques. If the material presented is completely understood by the student, the objective of preparing an introductory text will have been fulfilled.

Since it is realized that the instructors will devise their own or modify the suggested experiments, the instructions for laboratory work in Chapter 22 are purposely kept brief. Wherever possible, a minimum amount of chemical manipulation is required so as to make more time available for working with the equipment. Since the average laboratory does not have all types of the more expensive pieces of equipment, such as spectrographs, spectrometers and X-ray diffraction units, actual operating instructions have been given for only a few instruments which are likely to be available in all academic laboratories. We have used mimeographed instruction sheets for operation of the instruments in the laboratory. These are merely adapted from the operating instructions written by the manufacturer. Sample instructions are given in the chapter on laboratory experiments. Such a system is flexible in that it may be added to as new equipment becomes available.

We have received excellent co-operation from instrument manufacturers and suppliers in the presentation of particular instruments. We should like to express our appreciation to Professor Lewis G. Bassett of Rensselaer for his continued encouragement to us in the setting up of the course, obtaining of equipment, and the writing of the text. We are indebted to Miss Rose D'Alessandro and Mrs. Anne Wagner for their time and effort in the preparation of the text.

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January 1954

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Introduction

In instrumental analysis, a physical property of a substance is measured to determine its chemical composition. Instrumental methods may be used by the analytical chemist to save time, to avoid chemical separations, or to obtain increased accuracy. Other reasons may indicate their use in particular cases.

The time-saving features of instrumental analysis are most fully realized in routine analysis, or where a considerable number of determinations are to be made. These methods usually require a standardization or calibration procedure to determine the relationship between the measured value of the physical property and the chemical composition. In some cases this relationship may be found in books of tables or in the literature, but in others the relationship must be determined in the laboratory. Therefore, for a few samples the use of a standard gravimetric or volumetric procedure is less time-consuming, whereas for routine work the time required for the initial calibration is negligible.

It must be emphasized that the accuracy of some instrumental methods is dependent upon the accuracy with which the classical or "wet" chemical analysis can be made. Therefore, improvement in classical methods of analysis will mean further improvement in the accuracy of instrumental analysis. For example, a reliable direct spectrographic method is not available for the determination of very low concentrations of aluminum in steel because existing "wet" methods of analysis do not yield results reliable enough to establish accurate values for spectrographic standards.

Physical properties may be classified as specific (emission spectra for example) or nonspecific (specific gravity, refractive index, etc.), just as chemical reagents or tests are classified. If the measured property is specific for the substance being determined, a direct measurement is possible. If no specific property is available, the

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measurement of two or more nonspecific properties may allow correction for interfering substances. A specific reagent may be employed to form a new system allowing direct measurement, or a specific chemical reaction may be combined with an instrumental endpoint measurement to give a specific volumetric method. In other cases, a chemical separation of interfering substances must precede the measurement.

It is a common fallacy that in instrumental analysis the analytical chemist pushes a button and the machine does the rest. It is true that technicians may run routine analyses instrumentally and that our instrument makers are trying to eliminate the human element. However, in most instrumental work, a higher order of technique is required than in conventional methods, and considerable skill is needed to interpret the results.

The accuracy of instrumental methods of analysis is usually less than that of sound "wet" methods for concentrations above 1%. However, the fact that a physical measurement may maintain a constant relative rather than absolute error allows increased accuracy in determining low percentages.

The considerable interest in instrumental methods at the present time may be best observed in the current journals on analytical chemistry. The proportion of determinations using physical methods of analysis is increasing every year.

A bibliography of a general nature is appended, the articles by R. H. Müller being specially recommended for a general picture of the field.

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Spectral Theory

The following discussion of spectral theory is intended to give the student analyst a concept of the production of spectra. The treatment is not rigorous or complete but should be sufficient for the purpose. A list of references at the end of the chapter will point out possible further study.

2.1 The electromagnetic spectrum. The electromagnetic spectrum is the complete system of radiant energy, that is, of energy propagated in wave form. An electromagnetic wave consists of an oscillating electric field and a similar magnetic field so completely connected that each depends upon the other for its existence. The two fields oscillate at right angles to one another and to the direction of propagation of the wave. Each component vibrates with the same frequency and is in equal phase with the other in free space. Electromagnetic waves travel in free space with a constant velocity, c, where c equals 3.0×10^{10} cm per second. The velocity of electromagnetic waves in a given medium, such as glass, is not necessarily c, but may vary with the frequency, and this variation is termed dispersion. Hence, a glass prism disperses the electromagnetic waves of visible light into a series of different frequencies which are seen by the human eye as different colors. Such a series of different wavelengths is termed a spectrum.

Electromagnetic waves are usually described in terms of (a) the length of the cycle or wave (wavelength, λ), (b) the number of cycles or waves in a unit distance (wave number, ν'), and (c) the number of cycles or waves passing a point in space in a unit time (frequency, ν). These units are related by the equation

$$c = \lambda \nu$$

where c is the speed of light, equal to 3.0×10^{10} cm per second. Figure 2.1 shows a graphical illustration of these terms.
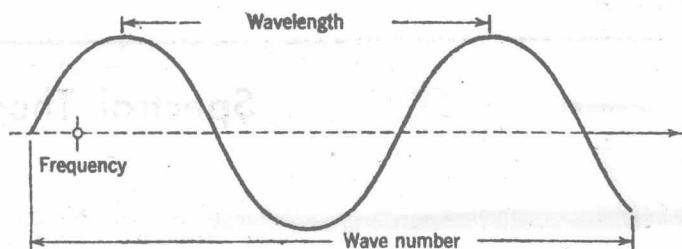
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Fig. 2.1 Relationship among wavelength, wave number, and frequency (Reproduced by permission of W. R. Brode, *Chemical Spectroscopy*, 2nd ed., John Wiley, New York, 1947)

The approximate limits of wavelength and frequency for the various types of radiation, including the frequency range of sound waves, are shown in Table 2.1. The table demonstrates that the funda-

TABLE 2.1

Radiation	Wavelength, cm	Frequency, cycles/sec
Sound		1.6×10^1 –2.0×10^4
Hertzian	3.0×10^6 –1.0×10^{-2}	1.0×10^4 –3.0×10^{12}
Infrared	6.0×10^{-1}–7.5×10^{-5}	5.0×10^{10}–4.0×10^{14}
Visible	7.5×10^{-5}–4.0×10^{-5}	4.0×10^{14}–7.5×10^{14}
Ultraviolet	4.0×10^{-5}–1.0×10^{-6}	7.5×10^{14}–3.0×10^{16}
X rays	1.0×10^{-6}–1.0×10^{-9}	3.0×10^{16}–3.0×10^{19}
Gamma rays	1.0×10^{-8}–1.0×10^{-11}	3.0×10^{18}–3.0×10^{21}
Cosmic rays	$<1.0 \times 10^{-11}$	$>3.0 \times 10^{21}$

mental units would have very awkward values for some of the ranges indicated. Therefore, other, more convenient, units are used as illustrated in Fig. 2.2, which shows the complete electromagnetic spectrum. The units given in this figure will be described in the sections where they are applicable.

The purely wave theory of light has been modified to admit the existence of corpuscular units of radiant energy. These corpuscular units, or quanta, are propagated in wave form, and the energy involved may be expressed as

$$\epsilon = h\nu$$

where ϵ = energy content of the quantum in ergs, h = Planck's constant, 6.6×10^{-27} erg-second, ν = frequency in vibrations per second.

This formula implies that radiant energy is made up of discrete

units of definite energy content (quanta) and states that their magnitude is dependent on the frequency of the radiation.

Wavelength λ (meters)		Frequency ν
	Cosmic rays	

10^{-14}
-13 — 10^{22}
-12 — 21
-11 — 20 — Gamma rays
19
1 angstrom — -10 — 18
1 millimicron — -9 — 17 — X rays
-8 — 16
-7 — Ultraviolet
15
1 micron — -6 — 14 ←— Visible
-5 — 13 — Infrared
-4 — 12
1 millimeter — -3 — 11 — 1 fresnel
-2 — 10
-1 — 9 — Hertzian waves
1 meter — 0 — 8
1 — 7
2 — 6
1 kilometer — 3 — 5 — Radio waves — 1 megacycle
4 — 4
5 — 3
6 — 2 — Audible frequencies — 1 kilocycle
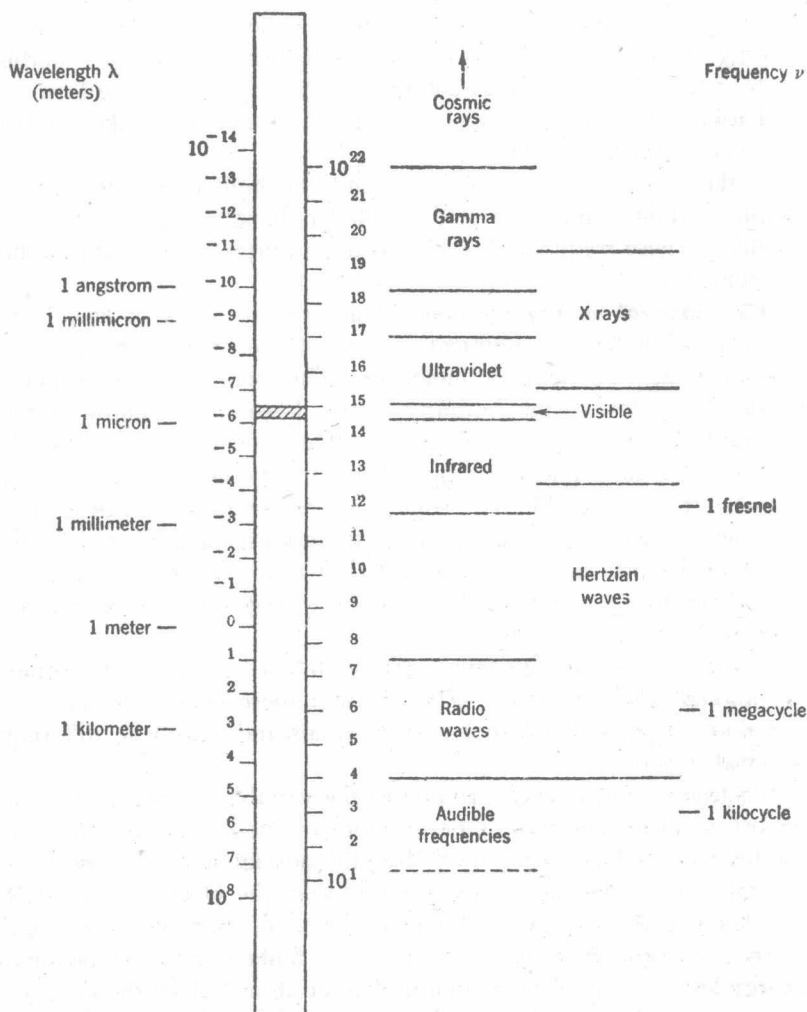7 — 10^1
10^8

Fig. 2.2 The electromagnetic spectrum

2.2 Principles of spectral analysis. Spectral analysis is based on the measurement of the radiant energy absorbed or emitted by atoms or molecules. The frequency of this radiation is determined by the formula

$$\Delta E = h\nu$$

where ΔE is the change in internal energy of the atom or molecule. Thus it appears that the radiant energy is quantized; that is, the absorption or emission is in discrete units of definite frequency.

An atom or molecule may be excited by the addition of sufficient energy in any form and thus raised to a higher energy state. If this state is unstable, the excess energy may be released in the form of radiation. The various frequencies of this radiation make up the emission spectrum of the substance.

If the added energy is radiant, and the higher energy state is stable, certain frequencies of the added radiant energy may be absorbed. These frequencies make up the absorption spectrum of the substance.

2.3 Spectral energy changes. The modern theory of wave mechanics precludes any physical picture of the energy changes occurring within an atom or molecule. Therefore in an elementary treatment no loss in intelligibility occurs if we speak simply of the energy levels in an atom or molecule. The concept of energy levels is necessary to explain the quantized energy changes mentioned above. It is reasonable to assume that, for certain definite energy changes to occur within a substance, there must be definite possible levels of internal energy, and that a shift from one level to another would produce a corresponding energy change and an equivalent spectral frequency absorbed or emitted.

Three types of energy level exist within a molecule, electronic, vibrational, and rotational. The shifts in these energy levels have different causes and different energy values and appear in different spectral regions.

Electronic energy levels are due to the variable energy content of an extranuclear electron. One or more of these electrons may be excited to a higher energy level than the normal state by absorbing energy, and, if the higher state is unstable, the electron may shift to a lower stable energy level and, in doing so, emit radiant energy.

From the quantum theory, there are a finite number of possible energy levels for an electron in a particular atom. Since the changes from one level to another need not occur stepwise, the number of possible energy changes for a particular electron is the mathematical combination of levels for the electron,[*] and the number of possible energy changes for an atom is the sum of the numbers for each electron in the atom. Each possible energy change will give rise to a spectral frequency.

[*] Certain transitions do not occur, but they may be neglected in this discussion.

In an atom with several extranuclear electrons, it is more difficult to shift an electron whose sphere of action lies nearer to the nucleus than one farther from the nucleus. (These will be spoken of as "inner" and "outer" electrons.) The energy involved is of a different order of magnitude, and the radiation is in a different portion of the spectrum, as shown in Table 2.2.

TABLE 2.2

Process	Typical Energy, ergs	Frequency, vib/sec	Region
"Inner" electron shift	4.0×10^{-9}	6×10^{17}	X ray
Ionization	4.0×10^{-11}	6×10^{15}	Far ultraviolet
"Outer" electron shift	6.6×10^{-12}	1×10^{15}	Near ultraviolet
	3.3×10^{-12}	5×10^{14}	Visible
Vibration	4.0×10^{-13}	6×10^{13}	Near infrared
Rotation	2.0×10^{-14}	3×10^{12}	Far infrared

It is possible to remove an electron from an atom completely, and, although this is really just another energy level for the electron, the nature of the change is ionization, and is treated as a special case.

The atoms in a molecule are held together by attractive forces or bonds. There is a certain average equilibrium position of the atoms, but their actual position at any instant may vary considerably from the average. These positional or vibrational energy levels may be changed by quantized absorption or emission. The energy involved in the vibrational shifts is determined by the mass of the atoms and the nature and magnitude of the bonding forces; therefore spectra are produced that are characteristic of these factors.

The molecule as a whole may rotate about its center of gravity or any axis. The modes and rates of rotation are quantized, any energy change corresponding to a change in angular momentum and producing a spectral frequency.

Finally, the atom or molecule may have energy of translation. A change in the energy of translation will result in a change in temperature of the substance. This latter change is not ordinarily considered to be quantized, but is continuously variable.

Table 2.2 shows the approximate magnitude of the energies involved and the spectral region in which the corresponding fundamental radiation occurs.

2.4 Continuous, line, and band spectra. If a solid is heated to incandescence, it produces a continuous spectrum, that is, light con-

taining all the visible wavelengths. Similar effects may be obtained by other means in various regions of the electromagnetic spectrum. Any instrument designed to measure radiation frequencies would show that radiation was occurring at all frequencies over a considerable range. The relative amount of energy may vary in this range, but all frequencies are present.

On the other hand, the emission spectrum of the vapor produced and excited by an electric arc between two electrodes is discontinuous; that is, the radiation is confined to discrete wavelengths. Our measuring instrument would distinguish radiant energy at particular frequencies, with large gaps where no radiation appears. These particular frequencies are usually spoken of as lines, due to their appearance when registered on a photographic plate by a spectrograph. They are due to excited atoms or ions emitting energy by electronic energy-level shifts and are found in the visible and ultraviolet regions.

The emission spectrum of a molecular substance may be complicated by vibrational and rotational changes being superimposed on the electronic energy-level shifts of the atoms involved. This results in slight changes in the quantity of energy involved, and a consequent slight shift in the wavelength of the line. On a photographic plate, a fine structure of closely spaced lines would appear.

It should be noted that it is difficult to excite a substance sufficiently to produce an electronic-emission spectrum without disrupting the molecular structure, as well as vaporizing the substance. Therefore most emission spectra used for analytical purposes are those of atoms or ions in the vapor state.

If a molecular substance is not excited sufficiently to produce an electronic spectrum, the vibrational spectrum may still appear. As the total energy is small, the radiation appears in the infrared only. The rotational energy changes may be superimposed on the vibrational, giving the spectrum a fine structure. If the excitation is still less, only the rotational energy may be involved, and the rotational spectrum appears alone in the far infrared.

Though the above discussion has been devoted to emission spectra, similar considerations apply to the absorption of radiant energy. Also, we have considered only the vapor state, and, as we generally measure the absorption spectra of substances in their state at normal temperatures, we must extend our ideas to liquids and solids.

When light from a continuous source passes through a substance in the vapor state, absorption may occur. This absorption is the exact

reverse of the emission described above, is bound by the same possible energy changes, and occurs in the same spectral regions. The added restriction is that the higher energy state must be stable. As an example, the Fraunhofer lines in the spectrum of the sun are dark lines caused by absorption of certain frequencies by the vapor atmosphere of the sun. These frequencies may also be found in the emission spectra of the same elements when excited under normal conditions.

In pure liquids or solutions and in solids, the relatively close packing and resultant intermolecular or interionic forces cause a broadening of the lines. These broad lines or bands appear in the portion of the spectrum corresponding to the fundamental energy change involved.

2.5 Molecular bonds and absorption spectra. Ionic compounds are held together by the electrostatic forces on the charged particles. No one ion is permanently bound to another, but rather each ion may be considered to be in an electric field, due to the charges and positions of all the other ions in the system. There is no molecular structure or molecular spectrum; the only effect of this community interaction is the broadening of the electronic-absorption bands.

The spectral range in which the absorption occurs depends on the magnitude of the energy change. Colored ions (absorption in the visible range) are characteristic of the transition and rare-earth elements, as their electronic configuration allows electron shifts of moderate energy content. It should be noted that the absorption bands for the rare-earth ions are comparatively narrow, as the electron shifts occur in inner levels protected from interionic forces.

In its simplest case, the covalent or electron-sharing bond links together two atoms so that they have an equilibrium position with respect to each other. Unless disruption of the molecule occurs, the two atoms remain together as a unit, with the ability to absorb energy of vibration or rotation.

The bonding may consist in sharing two, four, or six electrons, corresponding to the single, double, or triple bond. Single bonds show absorption only in the infrared if the two atoms are the same, for example C—C, and in some cases where dissimilar atoms are joined, as C—OH and C—O—C. Other singly bonded groups like C—Cl, C—Br, C—I and C—NH$_2$ as well as doubly and triply bonded groups absorb in the visible or ultraviolet as well as in the infrared. This means that an electronic shift is occurring, and this shift is due to the phenomenon of resonance.