which have different refractive indexes and are in optical contact with each other. The spectrum obtained is similar to that of a transmission spectrum of a material. This technique is used extensively for analyzing coatings, pastes, paints, fibers, and fabrics.

Near-infrared spectrophotometry. This designates work carried out between 0.78 and 3 μm. The absorption bands in this region are mainly overtones (harmonics) of bands in the infrared region. These bands are quite sharp and are of great value in quantitative analysis for various functional groups, particularly those containing hydrogen atoms.

Visible spectrophotometry. The visible region of the spectrum covers the narrow range from about 380 to 780 nm. The spectrophotometers for this region use tungsten lamps as light sources, glass or quartz prisms or gratings in the monochromators, and photomultiplier cells as detectors. Within this narrow portion of the electromagnetic spectrum, a majority of the spectrophotometric analyses are made. Figure 2 shows a typical visible absorption spectrum. The substance, peroxytitanate ion, absorbs light in the region below 500 nm; that is, it absorbs violet, blue, and green light and transmits red, orange, and yellow. For analytical work, the wavelength of maximum absorption is usually used, in this case 410 nm.

Ultraviolet spectrophotometry. The spectral region from 200 to 400 nm, called the near ultraviolet, is commonly used in chemical analysis. Ultraviolet spectrophotometers usually have a hydrogen lamp as a radiation source; a quartz prism, or a grating in the monochromator; and a photomultiplier tube as a detector. Simple inorganic ions and their complexes as well as organic molecules can be detected and determined in this region.

Filter photometry. In filter photometry, the monochromator of the spectrophotometer is replaced by a filter. This filter passes a band of light of a much wider range of wavelengths than those passed by even the poorest monochromator. The filter is chosen so as to transmit best the light which the sample absorbs most. Filter photometers are generally much less expensive than spectrophotometers. By careful use of calibration curves, filter photometers can give sufficiently accurate and precise results for a wide variety of applications. *See* ANALYTICAL CHEMISTRY; MOLECULAR STRUCTURE AND SPECTRA; OPTICAL METHODS OF CHEMICAL ANALYSIS. [J.N.L.]

Spectroscopy An analytic technique concerned with the measurement of the interaction (usually the absorption or the emission) of radiant energy with matter, with the instruments necessary to make such measurements, and with the interpretation of the interaction both at the fundamental level and for practical analysis.

A display of such data is called a spectrum, that is, a plot of the intensity of emitted or transmitted radiant energy (or some function of the intensity) versus the energy of that light. Spectra due to the emission of radiant energy are produced as energy is emitted from matter, after some form of excitation, then collimated by passage through a slit, then separated into components of different energy by transmission through a prism (refraction) or by reflection from a ruled grating or a crystalline solid (diffraction), and finally detected. Spectra due to the absorption of radiant energy are produced when radiant energy from a stable source, collimated and separated into its components in a monochromator, passes through the sample whose absorption spectrum is to be measured, and is detected. Instruments which produce spectra are variously called spectroscopes, spectrometers, spectrographs, and spectrophotometers. *See* SPECTRUM.

Interpretation of spectra provides fundamental information on atomic and molecular energy levels, the distribution of species within those levels, the nature of processes involving change from one level to another, molecular geometries, chemical bonding, and interaction of molecules in solution. At the practical level, comparisons of spectra provide a basis for the determination of qualitative chemical composition and chemical structure, and for quantitative chemical analysis.

Origin of spectra. Atoms, ions, and molecules emit or absorb characteristically; only certain energies of these species are possible; the energy of the photon (quantum of radiant energy) emitted or absorbed corresponds to the difference between two permitted values of the energy of the species, or energy levels. (If the flux of photons incident upon the species is great enough, simultaneous absorption of two or more photons may occur.) Thus the energy levels may be studied by observing the differences between them. The absorption of radiant energy is accompanied by the promotion of the species from a lower to a higher energy level; the emission of radiant energy is accompanied by falling from a higher to a lower state; and if both processes occur together, the condition is called resonance.

Instruments. Spectroscopic methods involve a number of instruments designed for specialized applications.

An optical instrument consisting of a slit, collimator lens, prism or grating, and a telescope or objective lens which produces a spectrum for visual observation is called a spectroscope.

If a spectroscope is provided with a photographic camera or other device for recording the spectrum, the instrument is called a spectrograph. *See* SPECTROGRAPHY.

A spectroscope that is provided with a calibrated scale either for measurement of wavelength or for measurement of refractive indices of transparent prism materials is called a spectrometer.

A spectrophotometer consists basically of a radiant-energy source, monochromator, sample holder, and detector. It is used for measurement of radiant flux as a function of wavelength and for measurement of absorption spectra.

An interferometer is an optical device that measures differences of geometric path when two beams travel in the same medium, or the difference of refractive index when the geometric paths are equal. Interferometers are employed for high-resolution measurements and for precise determination of relative wavelengths. *See* INTERFEROMETRY.

Methods and applications. Since the early methods of spectroscopy there has been a proliferation of techniques, often incorporating sophisticated technology.

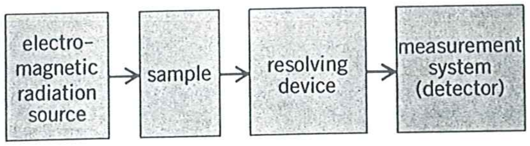
Astronomical spectroscopy involves the study of radiant energy emitted by celestial objects by combined spectroscopic and telescopic techniques to obtain information about their chemical composition, temperature, pressure, density, magnetic fields, electric forces, and radial velocity. *See* ASTRONOMICAL SPECTROSCOPY.

Atomic absorption and fluorescence spectroscopy is a branch of electronic spectroscopy that uses line spectra from atomized samples to give quantitative analysis for selected elements at levels down to parts per million, on the average. *See* FIRE ASSAYING; TRACE ANALYSIS.

Attenuated total reflectance spectroscopy is the study of spectra of substances in thin films or on surfaces obtained by the technique of attenuated total reflectance or by a closely related technique called frustrated multiple internal reflection. In either method the sample is penetrated by a radiant-energy beam one or more times. The technique is employed primarily in infrared spectroscopy for qualitative analysis of coatings and of opaque liquids.

Electron paramagnetic spectroscopy is a microwave technique, based on the splitting of electronic energy levels in a magnetic field, and is used to establish structures of species containing unpaired electrons. *See* ELECTRON PARAMAGNETIC RESONANCE (EPR) SPECTROSCOPY.

Electron spectroscopy includes a number of subdivisions, all



Schematic diagram of the basic spectrometric experiment.

flame, or an applied voltage, or momentum from mechanical motion. The sample then emits the gained energy as photons (packets, quanta) of radiation.

The next stage of the experiment separates all the wavelengths of radiation present so that they may be measured independently of all others. Finally, there is a device for detecting the amount of radiation present (emission or luminescence) or absent (absorption). The identity of the wavelengths gives qualitative information. The amount of radiation gives quantitative information. *See* GAMMA-RAY DETECTORS; GEIGER-MÜLLER COUNTER; PHOTOTUBE; SPECTROSCOPY; TRANSDUCER. [A.T.Z.]

Spectrography The use of photography to record the electromagnetic spectrum displayed in a spectroscope. The technique is used mainly in atomic and molecular physics, in analysis of the chemical composition of materials, and in astronomical photography. *See* ASTRONOMICAL PHOTOGRAPHY; SPECTROCHEMICAL ANALYSIS; SPECTROSCOPY. [W.Cl.]

Spectroheliocope An instrument for the monochromatic visual observation of the Sun. A telescope projects an image of the Sun on the first slit of a powerful spectroscope. The resulting spectrum is imaged in the plane of a second slit which permits only a single line element of the spectrum to emerge from the instrument. The emergent line element is a monochromatic image of that part of the Sun that falls on the first slit. When the two slits are vibrated synchronously at high frequency, persistence of vision permits monochromatic observation of an area of the solar surface. The slits may also be moved at a slow rate and the image recorded photographically. This modification of the spectrohelioscope is a simple form of the spectroheliograph. [R.R.McM./J.W.E.]

Spectrophotometric analysis A method of chemical analysis based on the absorption or attenuation by matter of electromagnetic radiation of a specified wavelength or frequency. The region of the electromagnetic spectrum most useful for chemical analysis is that between 200 nanometers and 300 micrometers. Since the sample being analyzed absorbs the radiation, spectrophotometric analysis is sometimes referred to as absorptimetric analysis.

The instruments used in this work are referred to as spectrophotometers. A simple spectrophotometer consists of a source of radiation, such as a light bulb; a monochromator containing a prism or grating which disperses the light so that only a limited wavelength, or frequency, range is allowed to irradiate the sample; the sample itself; and a detector, such as a photocell, which measures the amount of light transmitted by the sample.

In most quantitative analytical work, a calibration or standard curve is prepared by measuring the absorption of known amounts of the absorbing material at the wavelength at which it strongly absorbs. Such a calibration curve is shown in Fig. 1 for the absorbing material whose absorption spectrum is shown in Fig. 2. The absorbance of the sample is read directly from the measuring circuit of the spectrophotometer.

When the transmittance or the absorbance of a sample is measured and plotted as a function of wavelength, an absorption spectrum is obtained. The spectrum shown in Fig. 2 indicates that the sample transmits the least light at 410 nm and transmits the most around 700 nm.

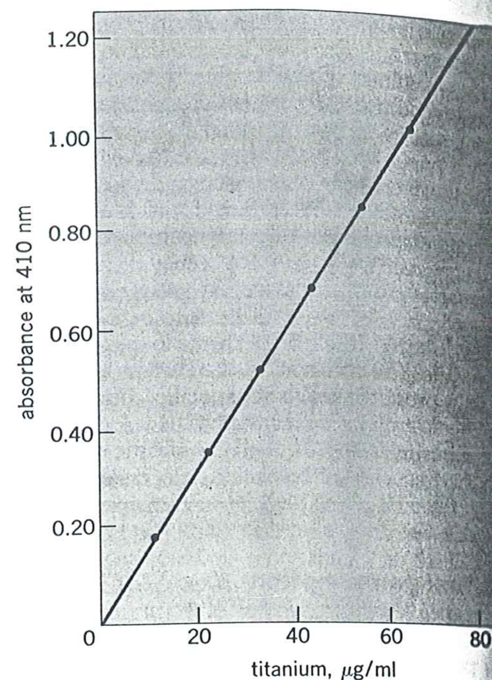


Fig. 1. Calibration curve for determination of titanium by color formed with hydrogen peroxide.

Infrared spectrophotometry. The interaction with of electromagnetic radiation of wavelength between 1 μm (infrared region) induces either rotational or vi energy level transitions, or both, within the molecules The frequencies of infrared radiation absorbed by a are determined by its rotational energy levels and by constants of the bonds in the molecule. Since these en els and force constants are usually unique for each so also the infrared spectrum of each molecule unique. Because of their individuality, infrared sp organic compounds are considered equivalent to, or to, the preparation of chemical derivatives for the ider of species in organic chemistry. For this reason the portion of the spectrum is often called the fingerprint

Attenuated total reflectance. This is a technique the infrared spectrum of a surface can be obtained wi chemical treatment of the sample; its principle is bas phenomenon of energy reflection at the interface of t

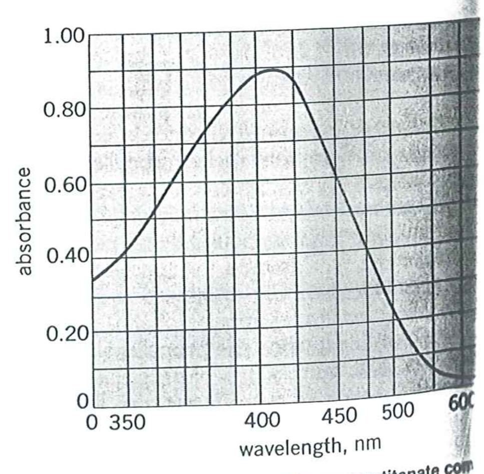


Fig. 2. Absorption spectrum of the peroxytitanate com region 340–700 nm.