SPECTROSCOPY

Spectroscopy is the study of the interaction of electromagnetic radiation (EMR) and matter. It is a tool that can be used to evaluate structure, concentration, composition and vibration. There are two main types of spectroscopy: absorption and emission. The signal for spectroscopy is the measurement in change of number of photons reaching a dictation device.

Absorption Spectroscopy

Light energy in the form of photons are used to excite the particles of a material, if the energy of the photon matches the energy required for the electrons in the matter to "jump" to a higher state the photon will be absorbed. The lack of the returning photon is measured and reported as absorbance.

Emission spectroscopy

Energy from a variety of possible sources, like a flame or electricity, is used to excite the electrons in a material. Because electrons will not remain in the excited state energy is released when they return to a lower state, this energy released is measured and reported as emission.
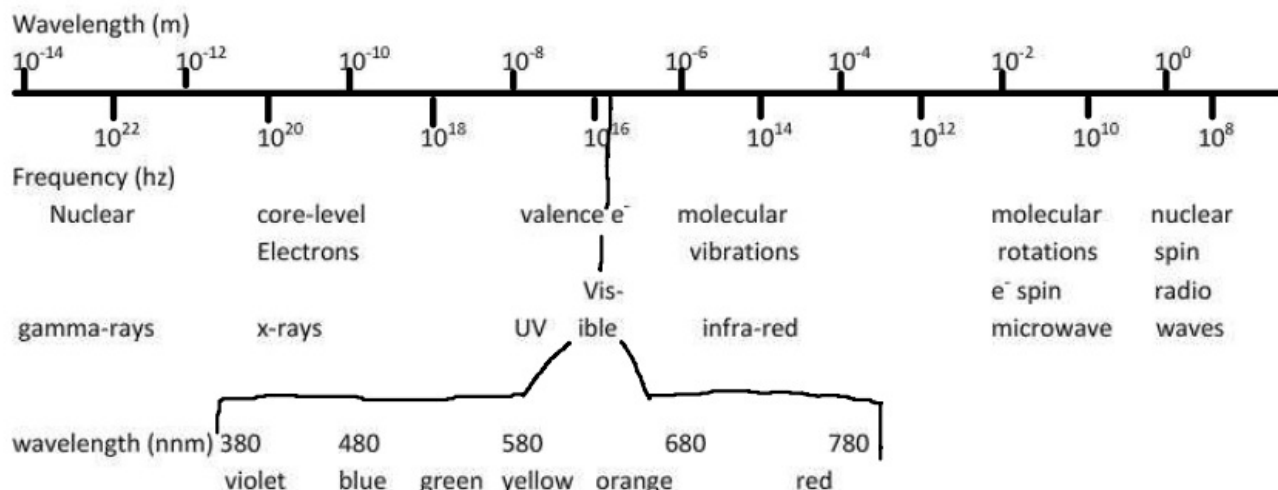
Absorbance – the attenuation of photons as they pass through a sample. (A)

Absorbance spectrum – a graph of a sample's absorbance of EMR vs. wavelength (or frequency).

Emission – the release of a photon when an analyte's electrons return to a lower energy state after having been in an higher-excited energy state.

Emission Spectrum – a graph of emission intensity vs. wavelength (or frequency).

Electromagnetic Radiation (EMR) – or light in the form of photons that have both wave-like behavior and are particles (DeBroglie – Dual Nature). These photons move in 3 directions simultaneously: up/down waves represent the electrical field, side to side waves represent the magnetic field all while moving with forward progression. Light waves move through a space with constant velocity, in a vacuum EMR travels at the speed of light, 3.0×10^8 m/s.

Wavelength (m)

10^{-14} 10^{-12} 10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{0}

10^{22} 10^{20} 10^{18} 10^{16} 10^{14} 10^{12} 10^{10} 10^{8}

Frequency (hz)

| Nuclear | core-level Electrons | valence e⁻ | molecular vibrations | | molecular rotations e⁻ spin | nuclear spin radio |

Vis-ible

gamma-rays   x-rays   UV   ible   infra-red   microwave   waves

wavelength (nnm) 380   480   580   680   780

violet   blue   green yellow   orange   red

wavelength (λ) is equal to the speed of light (c) divided by the frequency (v)

1m = 1 000 000 000 nm   1m = 10⁹nm

wavelength is generally measured in meters or nanometers
speed of light is 3.0 x 10^8 m/s
frequency is the number of cycles per second, labeled as 1/s, s^{-1}, or Hertz (hz)

Planck's equation = Energy (E) = planck's constant (h) x frequency (v)
          Where planck's constant is 6.626 x 10^{-34} J·s

Types of Spectroscopy
Light spectroscopy – which includes visible, ultra-violet, infra-red and near infra-red (NIR) – specimens are used in the gas or liquid phases, specific wavelengths of light are directed towards a sample that is in the pathway in front of a detector (meter) that will give a reading of the absorbance of the photons of the light source.

Atomic Absorption spectroscopy (AA) – a low intensity flame is used to vaporize the sample but not excite the electrons, a series of lamps that are designed to shine through the vapor at various wavelengths will excite the electrons. The absorbance is then determined based on the number of photons continuing through to the meter.

x-ray spectroscopy – x-rays of sufficient frequency are directed towards a sample energizing the inner shell electrons causing them to jump to higher energy levels or to be removed completely ionizing the atom. The remaining holes are filled by outer energy level electrons by the loss of energy. This de-excitation process is emitted as radiation.

Mass Spectroscopy – A sample is converted to ions so that they can be moved about and manipulated by external electric and magnetic fields. A small sample is ionized, usually to cations by loss of an electron. The ions are sorted and separated according to their mass and charge. The separated ions are then measured, and the results displayed on a chart.

In one common procedure, ionization is effected by a high energy beam of electrons, and ion separation is achieved by accelerating and focusing the ions in a beam, which is then bent by an external magnetic field. The ions are then detected electronically and the resulting information is stored and analyzed in a computer.

Atomic Emission spectroscopy – electrons are excited uses a high intensity flame (commonly a total consumption burner). Because the electrons are excited by the heat of the flame no additional lights are required. A high resolution polychromator can be used to produce an emission intensity vs. wavelength spectrum over a wide range of wavelengths showing multiple element excitement lines. Conversely, a monochromator can be set for a specific wavelength to concentrate on the analysis of a single element and emission line. (aka flame emission spectroscopy) **Plasma Emission spectroscopy** is the most currently used variation of this method. Plasma emission spectroscopy uses a direct-current plasma (DCP), created by an electrical discharge between two electrodes, to excite the electrons.

Spark or arc Emission spectroscopy – a solid sample is analyzed for the presence of metallic elements. An electric arc or spark is passed through the sample, heating it to high temperatures in order to excite the electrons. The excited analyte atoms glow, emitting light at various wavelengths that can be detected and analyzed.

There are almost as many types of spectroscopy as there are ways to excite electrons. Some additional methods are listed below:

Raman	Nuclear Magnetic Resonance (NMR)
Electron Tunneling	Electron Paramagnetic
Electron Spin Resonance	Neutron Scattering
Attenuated Total Reflectance	Gamma Ray activation analysis
Fourier transform	Hadron
Frequency modulated	microwave
Vibrational	Transmission or conversion-electron Mossbauer (CEMS)

Formulas:

Transmittance (T) $T = \dfrac{P_T}{P_o}$ (light emerging through sample)
P_o (light intensity through blank)

Absorbance (A) $A = -\log T$

Planck's Law $E = h \cdot v$

Wavelength (λ) $= \dfrac{\text{speed of light (c)}}{\text{Frequency (v)}}$ speed of light $= 3.0 \times 10^8$ m/s

Absorbance (A) $A = \varepsilon \cdot l \cdot C$ ε = molar absorptivity l = cell path length   C = solution concentration

Slope $= \varepsilon \cdot l$

$C_1 / C_2 = A_1 / A_2$

The wavelength of maximum absorption is λ max.

Beer's Law: (aka Beer-Lambert Law)

Evaluating the absorptivity and molar absorptivity give the probability that an analyte will absorb a photon of given energy. As a result absorption values are dependent on wavelength. There is a direct relationship between a sample's concentration and its absorbance. Therefore a graphing of absorbance and concentration will establish a linear relationship that can be later used as a calibration curve.

Mathematics of Spectroscopy

① $\nu = \dfrac{c}{\lambda} = \dfrac{3.00 \times 10^8 \frac{m}{s}}{4.65 \times 10^7 m} = \boxed{6.45 \times 10^{14}\ hz}$

$E = (6.626 \times 10^{-34}\ J \cdot s)(6.45 \times 10^{14}\ hz) = \boxed{4.27 \times 10^{-19}\ Joules}$

② $T\% = \dfrac{P_T}{P_0}$ $68\% = \dfrac{P_T}{520\ ph/sec}$ $P_T = \boxed{350\ photons/sec}$

③ $\dfrac{651\ ph/sec}{877\ ph/sec} \times 100 = \boxed{74.2\%\ T}$