

Question

Beer-Lambert law along with its limitations

Answer

The Beer-Lambert law is the linear relationship between absorbance and concentration of an absorbing species. The general Beer-Lambert law is usually written as:

$$A = a(\lambda) \cdot b \cdot c,$$

where A is the measured absorbance, $a(\lambda)$ is a wavelength-dependent absorptivity coefficient, b is the path length, and c is the analyte concentration.

When working in concentration units of molarity, the Beer-Lambert law is written as:

$$A = \epsilon \cdot b \cdot c,$$

where ϵ is the wavelength-dependent molar absorptivity coefficient with units of $M^{-1} \text{ cm}^{-1}$.

Limitations of the Beer-Lambert law

The linearity of the Beer-Lambert law is limited by chemical and instrumental factors. Causes of nonlinearity include:

- deviations in absorptivity coefficients at high concentrations (>0.01M) due to electrostatic interactions between molecules in close proximity
- scattering of light due to particulates in the sample
- fluorescence or phosphorescence of the sample
- changes in refractive index at high analyte concentration
- shifts in chemical equilibria as a function of concentration
- non-monochromatic radiation, deviations can be minimized by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band
- stray light