CH 2252 Instrumental Methods of Analysis

Unit – I

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Beer-Lambert's Law

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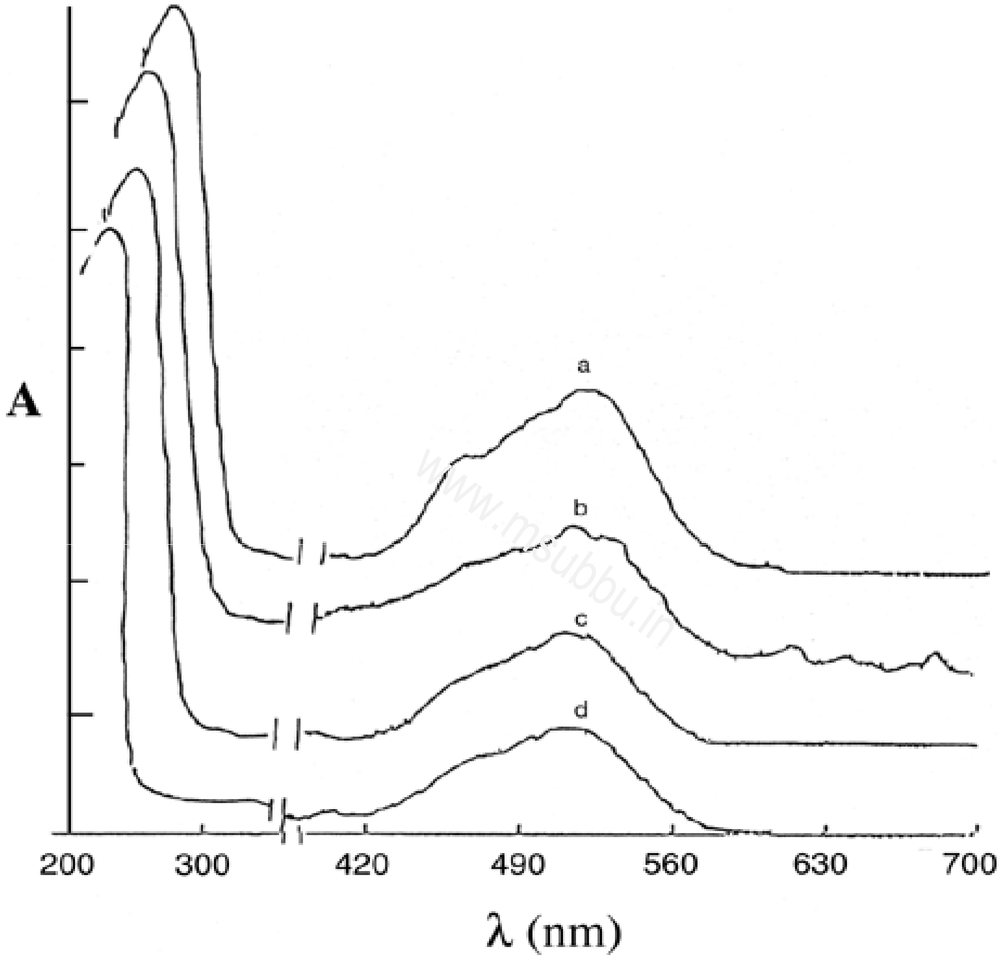
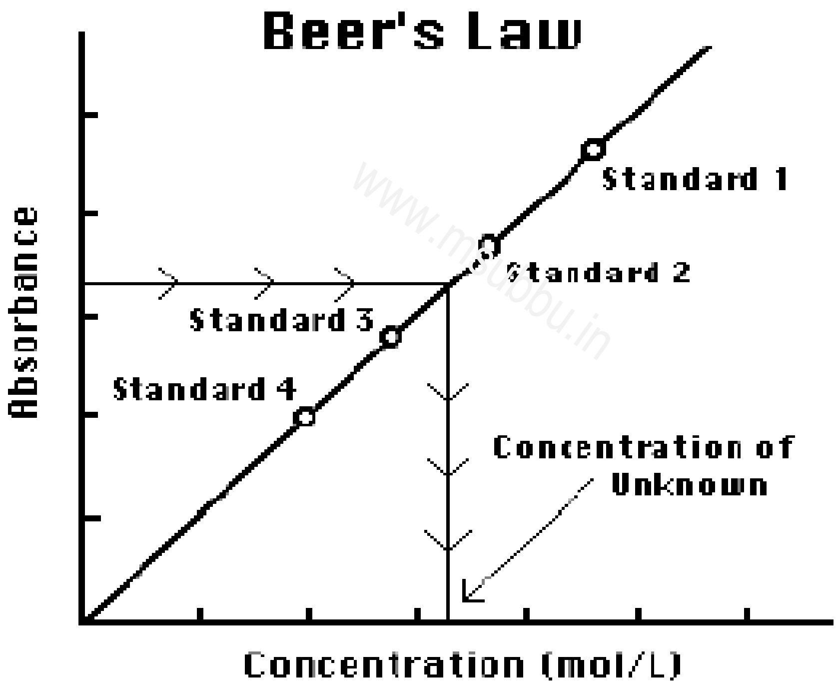
Contents

- Beer-Lambert's Law, Limitations, Deviations (Real, Chemical and Instrumental deviations), Estimation of inorganic ions such as Fe, Ni and Nitrite using Beer-Lambert's Law.

- Multi-component analysis


A
a
b
c
d
200
300
420
490
560
630
700
λ (nm)

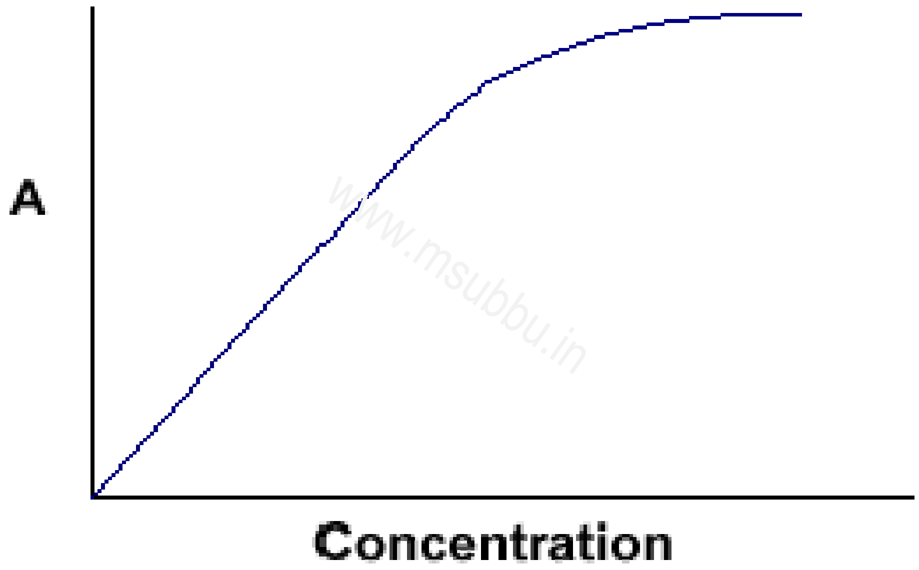
$$\log \frac{P_0}{P} = \varepsilon bc = A$$



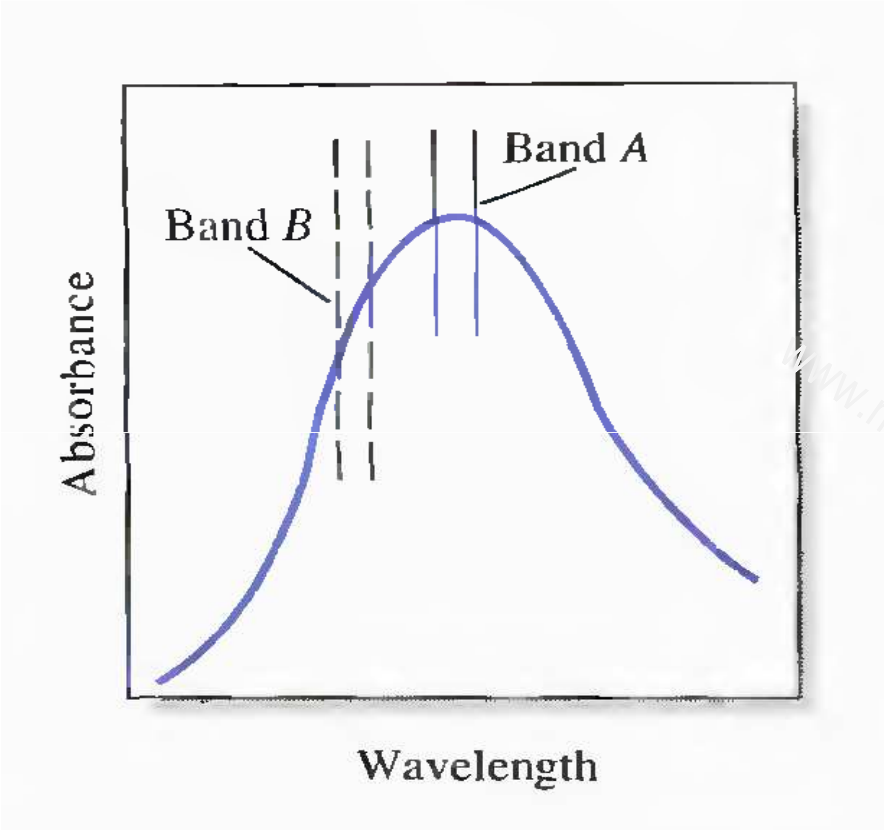
Deviations from Beer-Lambert's Law

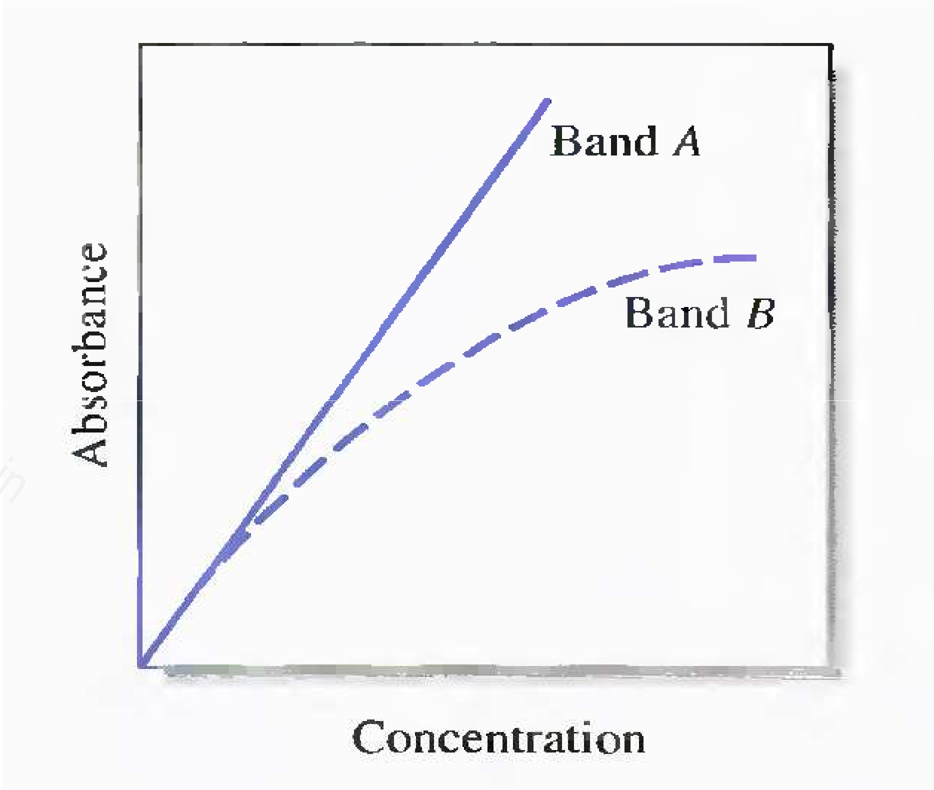
- Deviations in absorptivity coefficients at high concentrations (> 0.01 M) due to electrostatic interactions between molecules in close proximity
- Scattering of light due to particles in the sample
- Fluorescence or phosphorescence of the sample
- Changes in refractive index at high analyte concentration
- Shifts in chemical equilibrium as a function of concentration
- Non-monochromatic radiation
- Stray light

Beer-Lambert's law at high concentrations

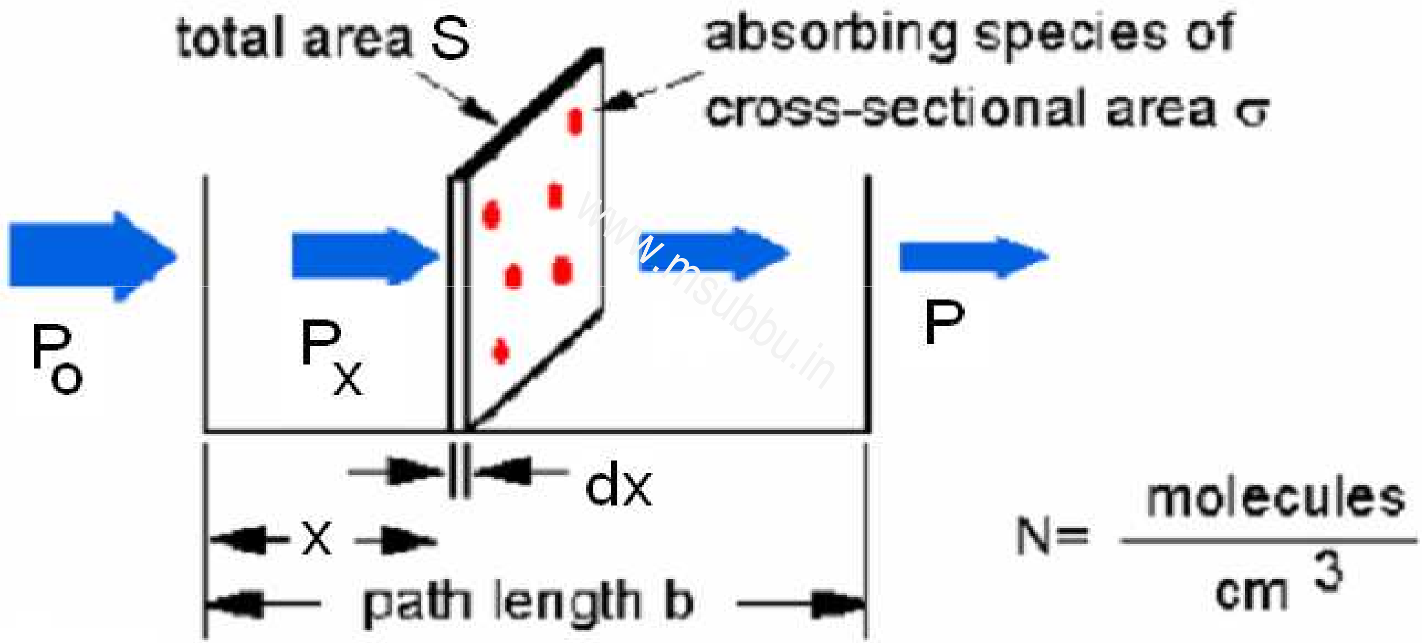


Polychromatic Radiation





Derivation of Beer-Lambert's law



$$-\frac{dP_x}{P_x} = \frac{\text{total opaque area in the slab}}{S} = \frac{dS}{S}$$

$$dS = \sigma(dxS) \times N$$

$$\frac{dS}{S} = \sigma N dx$$

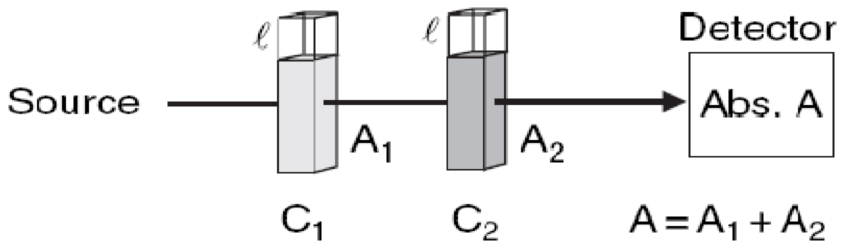
$$-\int_{P_o}^{P} \frac{dP_x}{P_x} = \int_0^b \sigma N dx$$

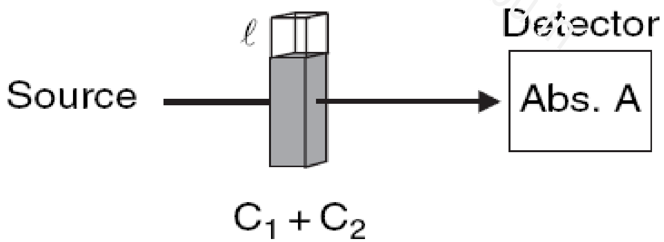
$$-ln \frac{P}{P_o} = \sigma b N$$

$$\text{number mol} = \frac{n \text{ particles}}{6.022 \times 10^{23} \text{ particles/mol}}$$

$$\log \frac{P_0}{P} = \varepsilon bc = A$$

Multi-component Analysis

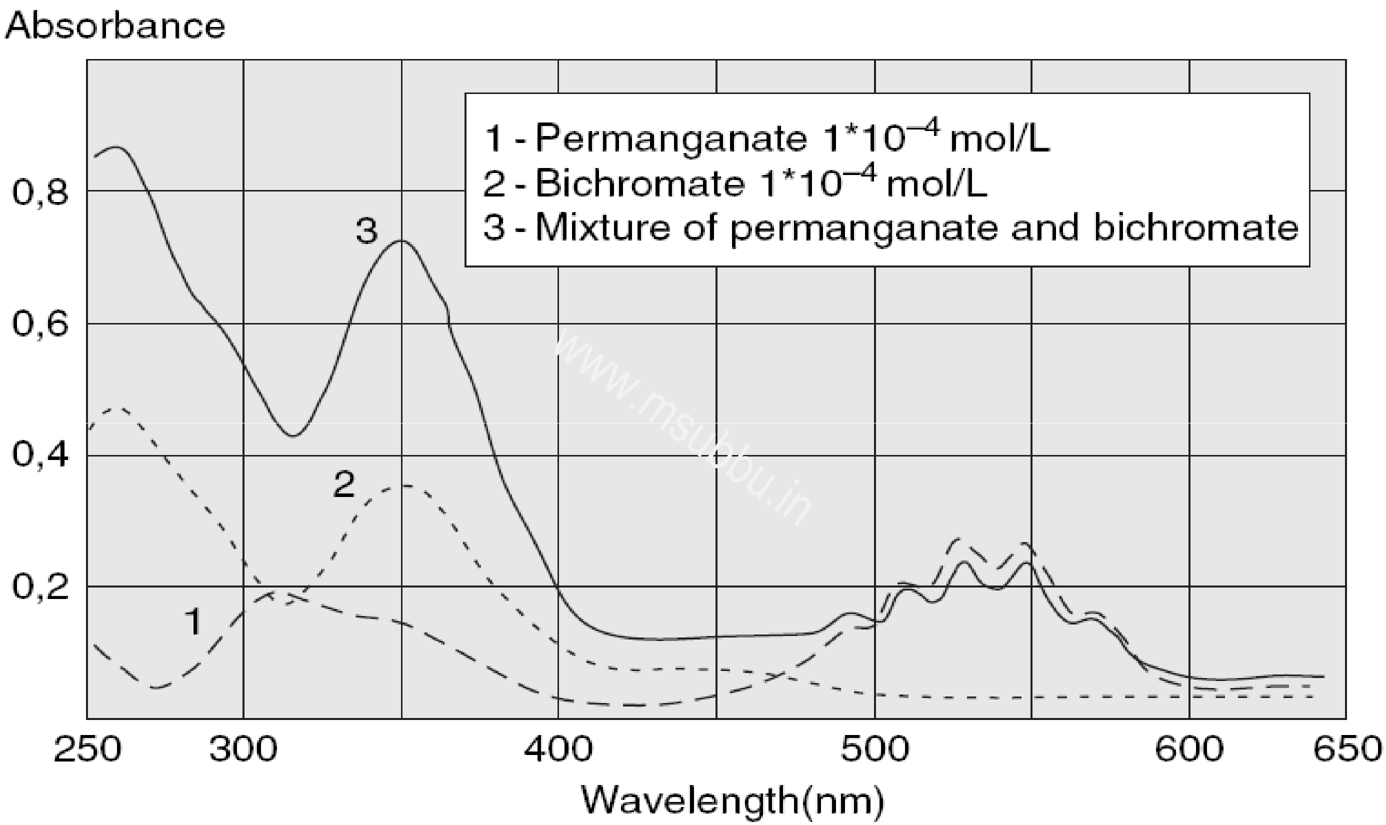




$$A_{\text{total}} = A_1 + A_2 + \cdots + A_n = \varepsilon_1 b c_1 + \varepsilon_2 b c_2 + \cdots + \varepsilon_n b c_n$$

$$\begin{aligned}
&\text{at } \lambda_1 \qquad && A_1 = \varepsilon_a^1 C_a + \varepsilon_b^1 C_b + \varepsilon_c^1 C_c \\
&\text{at } \lambda_2 \qquad && A_2 = \varepsilon_a^2 C_a + \varepsilon_b^2 C_b + \varepsilon_c^2 C_c \\
&\text{at } \lambda_3 \qquad && A_3 = \varepsilon_a^3 C_a + \varepsilon_b^3 C_b + \varepsilon_c^3 C_c
\end{aligned}$$

$$\begin{bmatrix} C_1 \\ C_2 \\ C_3 \end{bmatrix} = \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} \cdot \begin{bmatrix} \varepsilon_a^1 \varepsilon_b^1 \varepsilon_c^1 \\ \varepsilon_a^2 \varepsilon_b^2 \varepsilon_c^2 \\ \varepsilon_a^3 \varepsilon_b^3 \varepsilon_c^3 \end{bmatrix}^{-1}$$


Absorbance
0,8
0,6
0,4
0,2
3
2
1
1 - Permanganate 1*10^{-4} mol/L
2 - Bichromate 1*10^{-4} mol/L
3 - Mixture of permanganate and bichromate
250
300
400
500
600
650
Wavelength(nm)