1.5: Multicomponent Samples

We can extend Beer's law to a sample that contains several absorbing components. If there are no interactions between the components, then the individual absorbances, A_i, are additive. For a two-component mixture of analyte's X and Y, the total absorbance, A_{tot}, is

$$A_{tot} = A_X + A_Y = \varepsilon_X b C_X + \varepsilon_Y b C_Y$$

Generalizing, the absorbance for a mixture of n components, A_{mix}, is

$$A_{mix} = \sum_{i=1}^{n} A_i = \sum_{i=1}^{n} \varepsilon_i b C_i \tag{1.5.1}$$

Determining Concentrations from Spectra

Simultaneous determination of concentration of two simultaneously present absorbers (B and C) is possible from measuring @ two wavelengths, λ_1 and λ_2. In a 1 cm pathlength cell,

$$A_1 = A(\lambda_1) = \varepsilon_b(\lambda_1)c_b + \varepsilon_c(\lambda_1)c_c$$

$$A_2 = A(\lambda_2) = \varepsilon_b(\lambda_2)c_b + \varepsilon_c(\lambda_2)c_c$$

Simultaneous solutions of this linear system of equations are possible provided

$$\det \begin{vmatrix} \varepsilon_B(\lambda_1) & \varepsilon_C(\lambda_1) \\ \varepsilon_B(\lambda_2) & \varepsilon_C(\lambda_2) \end{vmatrix} \neq 0$$

If this is 0 (or close to it), then the equations are **linearly dependent** and no unique solution for c_b and c_b possible. The wavelengths, λ_1 and λ_2 should be chosen to yield a large value for the determinant.

Isosbestic Points

If there are only two species present in solution that absorbs, S and ES, for instance, and they have overlapping spectra, there will be at least one wavelength, λ_o, where

$$\varepsilon_S(\lambda_o) = \varepsilon_{ES}(\lambda_o).$$

The absorbance @ λ_o will be constant irrespective of the condition of the sample (in equilibrium or out of equilibrium) assuming constant sum of populations.

$$\begin{aligned} A(\lambda)_o) &= x\varepsilon_S(\lambda_o) + y\varepsilon_S(\lambda_o) \\ &= (x+y)\varepsilon_S(\lambda_o) \end{aligned}$$

λ_o defines an **isobestic point**. If we know the spectrum of S and ES, λ_o can be determined.

Example 1.5.1: p-nitrophenol vs. p-nitrophenolate

You need a spectrometer to produce a variety of wavelengths because different compounds absorb best at different wavelengths. For example, p-nitrophenol (acid form) has the maximum absorbance at approximately 320 nm and p-nitrophenolate (basic form) absorbs best at 400 nm (Figure 1.5.3).

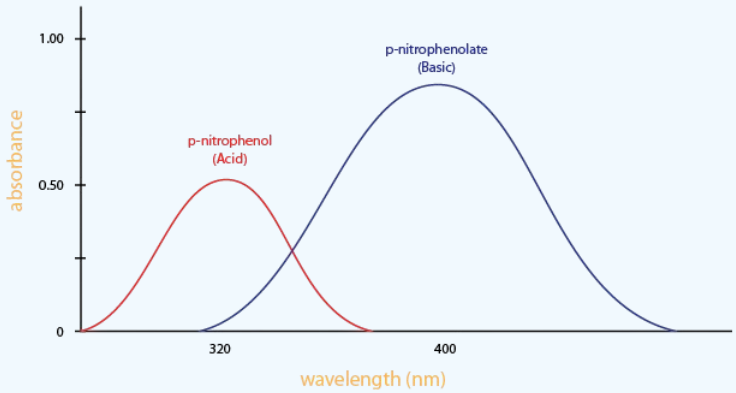

Figure 1.5.3: Absorbance of two different compounds. (CC BY 4.0; Heesung Shim via LibreTexts)

Looking at the graph that measures absorbance and wavelength, an isosbestic point can also be observed. An **isosbestic point** is the wavelength in which the absorbance of two or more species are the same. The appearance of an isosbestic point in a reaction demonstrates that an intermediate is NOT required to form a product from a reactant. Figure 1.5.4 shows an example of an isosbestic point.

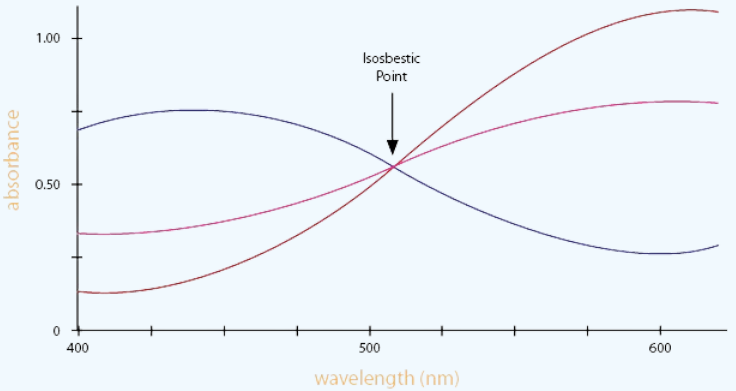

Figure 1.5.4: An example of isosbestic point. (CC BY 4.0; Heesung Shim via LibreTexts)