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Simultaneous Equations as a Tool in the Spectrophotometric Analysis of Two Non-interacting Substances in a Binary Mixture: Senior Undergraduate Physical and Physical-Organic Chemistry Laboratory Experiment

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Abstract A simple and lucid spectrophotometric way of analyzing a mixture of two compounds is explained in this article for senior undergraduate level students. The essential feature of this method is that there should be at least 30-40 nm difference in the λ_{max} of the two compounds so that there will not be any overlap of the two individual spectra of the two compounds when recorded together in a mixture.

Keywords Analysis of Binary Mixtures, Spectrophotometric Analysis, Simultaneous Equations

1. Introduction

Interest in the analysis of drugs and some organic compounds in binary mixtures by spectrophotometric method have become seriously interesting among analytical chemists and pharmacists. As a sample some references are given at the end of the article[1-8]. In all these articles the aim of the authors was much focused on the determination of the concentration/purity of the two components in the mixture. Therefore we have tried to make the analysis much lucid and simple for a senior undergraduate laboratory experiment using the method of solving simultaneous equations[9].

2. Experimental

All the chemicals were of analytical grade. $KMnO_4$ and $K_2Cr_2O_7$ are from Aldrich (Bangalore, India). Distilled water used was from all glass still. The UV-visible spectra are recorded on UVIKON-323 (Italy) spectrophotometer. All the analytical data were stored in a personal computer and analyzed using KaleidaGraph software (Synergy Software, Reading, PA, USA).

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3. Theory

3.1. Discussion

According to Beer-Lambert law[10]

$$\text{Absorbance} = \varepsilon\, t\, C \qquad (1)$$

where '**ε**' is the molar absorptivity of any substance, '**t**' is the path length in cm of the cuvette through which light passes and '**C**' is the concentration of the substance taken. The conditions that need to be fulfilled in order for Beer-Lambert law to be valid are also to be valid here[10]. The conditions are: The absorption spectra of the two components must be independent of each other i.e. non-interfering, the solutions must be homogeneous, the incident radiation must be monochromatic, and the radiation must not do any photochemistry or photophysics with the substances. For all practical purposes to make the situation simple let a cuvette of 1 cm path length be chosen so that equation (1) becomes

$$\text{Absorbance} = \varepsilon\, C \qquad (2)$$

Let a mixture contain two compounds say **A** and **B**. Let the compounds **A** and **B** have their λ_{max} at λ_1 and λ_2. Figure 1 shows the UV-Vis absorption spectrum of compound **A** with maximum absorbance at its λ_{max} i.e. λ_1 and a small absorbance at λ_2 which is the λ_{max} of compound **B**.

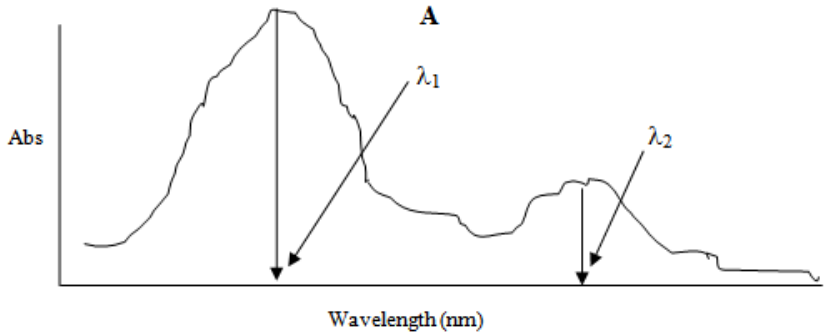

Figure 1.

Let $\mathbf{Abs_1}$ and $\mathbf{Abs_2}$ be the absorbencies of compound **A** at $\boldsymbol{\lambda_1}$ and $\boldsymbol{\lambda_2}$ respectively. Therefore according to equation 2, the absorbencies at $\boldsymbol{\lambda_1}$ and $\boldsymbol{\lambda_2}$ are:

$$\mathrm{Abs}_1 = \boldsymbol{\varepsilon}_{\mathbf{A}}^{\mathbf{1}} C_A \quad \text{at } \lambda_1 \tag{3}$$

$$\mathrm{Abs}_2 = \boldsymbol{\varepsilon}_{\mathbf{A}}^{\mathbf{2}} C_A \quad \text{at } \lambda_2 \tag{4}$$

Similarly Figure 2 shows the UV-Vis absorption spectrum of compound **B** with maximum absorbance at its $\boldsymbol{\lambda_{max}}$ i.e. $\boldsymbol{\lambda_2}$ and a small absorbance at $\boldsymbol{\lambda_1}$ which is the $\boldsymbol{\lambda_{max}}$ of compound **A**.

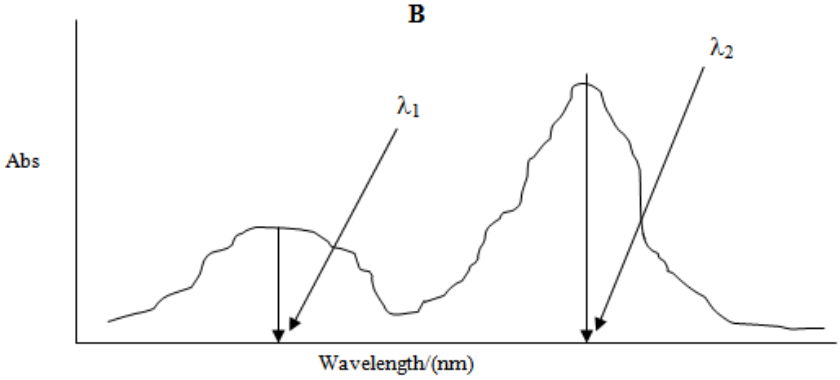

Figure 2.

Let $\mathbf{Abs_3}$ and $\mathbf{Abs_4}$ be the absorbencies of compound **B** at $\boldsymbol{\lambda_1}$ and $\boldsymbol{\lambda_2}$ respectively. Therefore again according to equation 2, the absorbencies at $\boldsymbol{\lambda_1}$ and $\boldsymbol{\lambda_2}$ are:

$$\mathrm{Abs}_3 = \boldsymbol{\varepsilon}_{\mathbf{B}}^{\mathbf{1}} C_B \quad \text{at } \lambda_1 \tag{5}$$

$$\mathrm{Abs}_4 = \boldsymbol{\varepsilon}_{\mathbf{B}}^{\mathbf{2}} C_B \quad \text{at } \lambda_2 \tag{6}$$

Figure 3 shows the UV-Vis absorption spectrum of the mixture of compounds **A** and **B**.

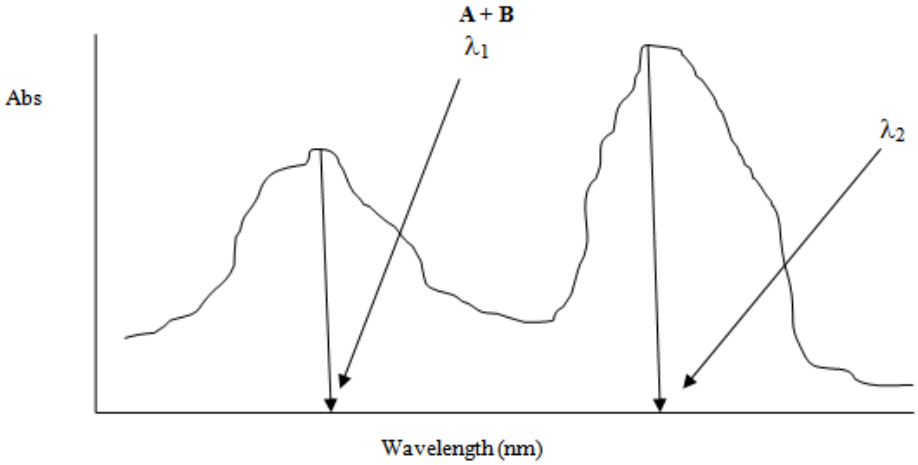

Figure 3.

Let $\mathbf{Abs_5}$ be the total absorbance of the mixture of the compounds **A** and **B** at $\boldsymbol{\lambda_1}$ and $\mathbf{Abs_6}$ is the total absorbance of the mixture of the compounds **A** and **B** at $\boldsymbol{\lambda_2}$ respectively. Therefore again according to equation 2, the total absorbencies of the two components in the mixture at $\boldsymbol{\lambda_1}$ and $\boldsymbol{\lambda_2}$ are:

$$Abs_5 = \boldsymbol{\varepsilon_A^1} C_A + \boldsymbol{\varepsilon_B^1} C_B \quad \text{at } \lambda_1 \qquad (7)$$

$$Abs_6 = \boldsymbol{\varepsilon_A^2} C_A + \boldsymbol{\varepsilon_B^2} C_B \quad \text{at } \lambda_2 \qquad (8)$$

$\boldsymbol{\varepsilon_A^1}$, $\boldsymbol{\varepsilon_A^2}$, $\boldsymbol{\varepsilon_B^1}$ and $\boldsymbol{\varepsilon_B^2}$, the molar absorptivities are independently experimentally determinable quantities of compounds **A** and **B** using equation 2 from the concentration dependencies of absorbvity, the so called Beer-Lambert law. $\mathbf{Abs_5}$ and $\mathbf{Abs_6}$ are also experimentally determinable quantities from figure 3. Now equations 7 and 8 are two simultaneous equations with two unknowns in the mixture i.e. $\mathbf{C_A}$ and $\mathbf{C_B}$. Using simple algebra one can eliminate one unknown to calculate the other. So first let $\mathbf{C_B}$ be eliminated. To do this let equation 7 be multiplied by $\boldsymbol{\varepsilon_B^2}$ and equation 8 by $\boldsymbol{\varepsilon_B^1}$. Therefore we get

$$\boldsymbol{\varepsilon_B^2} \bullet Abs_5 = \boldsymbol{\varepsilon_B^2}\,\boldsymbol{\varepsilon_A^1} C_A + \boldsymbol{\varepsilon_B^2}\,\boldsymbol{\varepsilon_B^1} C_B \qquad (9)$$

$$\boldsymbol{\varepsilon_B^1} \bullet Abs_6 = \boldsymbol{\varepsilon_B^1}\,\boldsymbol{\varepsilon_A^2} C_A + \boldsymbol{\varepsilon_B^1}\,\boldsymbol{\varepsilon_B^2} C_B \qquad (10)$$

Subtraction of equation 10 from equation 9, the quantities $\boldsymbol{\varepsilon_B^2}\,\boldsymbol{\varepsilon_B^1}\mathbf{C_B}$ and $\boldsymbol{\varepsilon_B^1}\,\boldsymbol{\varepsilon_B^2}\mathbf{C_B}$ would be canceled and we get

$$\boldsymbol{\varepsilon_B^2} \bullet Abs_5 - \boldsymbol{\varepsilon_B^1} \bullet Abs_6 = C_A[\boldsymbol{\varepsilon_B^2}\,\boldsymbol{\varepsilon_A^1} - \boldsymbol{\varepsilon_B^1}\,\boldsymbol{\varepsilon_A^2}] \qquad (11)$$

$$\text{Therefore } C_A = \frac{\boldsymbol{\varepsilon_B^2} \bullet \mathbf{Abs_5} - \boldsymbol{\varepsilon_B^1} \bullet \mathbf{Abs_6}}{[\boldsymbol{\varepsilon_B^2}\boldsymbol{\varepsilon_A^1} - \boldsymbol{\varepsilon_B^1}\boldsymbol{\varepsilon_A^2}]} \qquad (12)$$

Knowing all the quantities on right hand side of equation 12, $\mathbf{C_A}$, the concentration of the compound **A** in the mixture could be obtained. Substituting $\mathbf{C_A}$ in either the equation 9 or 10 and knowing other quantities, $\mathbf{C_B}$, the concentration of the compound **B** in the mixture could be calculated.

4. Practice

4.1. UV-Vis Spectra of $KMnO_4$, $K_2Cr_2O_7$ and the Mixture of the Two

As a specific example for the practice in the laboratory we have performed the experiments using $KMnO_4$, $K_2Cr_2O_7$ and the mixture of the two. First we have recorded the spectra of $KMnO_4$ (4.0 X 10^{-4} M), $K_2Cr_2O_7$ (4.8 X 10^{-4} M) and the mixture (containing 2.0 X 10^{-4} M of $KMnO_4$ and 2.40 X 10^{-4} M of $K_2Cr_2O_7$) so that it is necessary to identify the wavelengths where the analysis is to be carried out. Figure 4 shows the spectra of these solutions in the range 250 nm to 650 nm. But unfortunately there was no absorbance at 525 nm for $K_2Cr_2O_7$ which is the λ_{max} of $KMnO_4$. So it was thought worthwhile to choose another range of wavelength region for the analysis. Figure 5 is the reproduction of part of the figure 4 which shows that there are appreciable absorbvities for the two samples of solutions and the mixture.

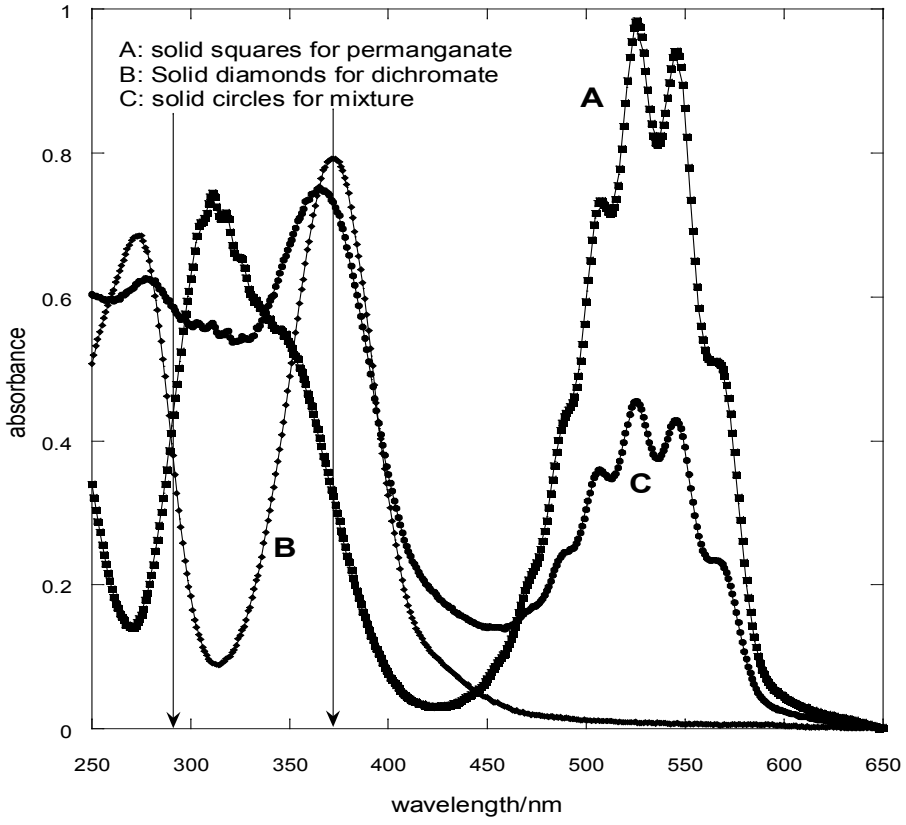

Figure 4. UV-VIS spectra of $KMnO_4$, $K_2Cr_2O_7$ and the mixture

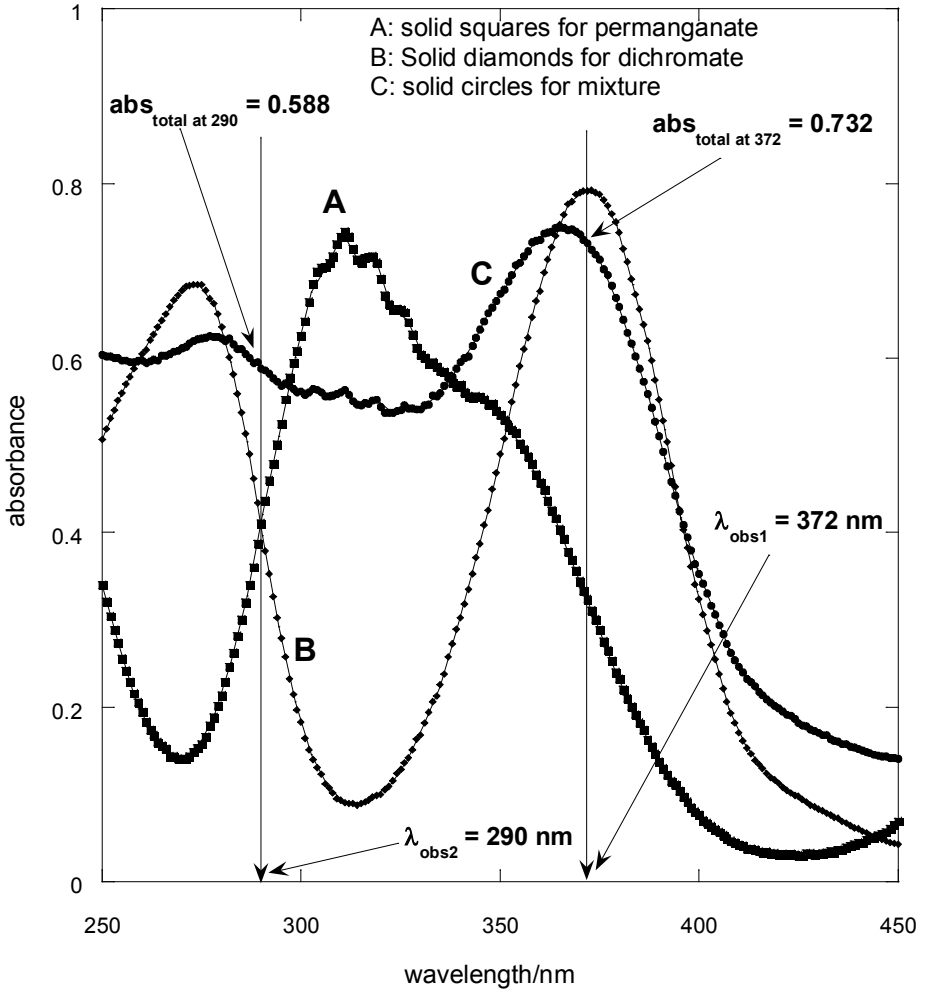

Figure 5. UV-Vis spectra of $KMnO_4$ and $K_2Cr_2O_7$ and the mixture

From figure 5 two wavelengths were identified λ_{obs1} (372 nm) and λ_{obs2} (290 nm) at which all the individual samples and the mixture have absorbencies[11]. First it is necessary to determine the molar absorbance of $KMnO_4$ and $K_2Cr_2O_7$. These were determined at 372 nm and 290 nm for both the samples. In recording the spectra the 1 cm path length optical quartz cuvettes were used. Hence to determine the molar absorbencies **(ε)** again equation 2 is used. Figures 6 and 7 show the Beer-Lamberts law plots of $KMnO_4$ and $K_2Cr_2O_7$. From the slopes of these plots molar absorbencies **(ε)** of $KMnO_4$ and $K_2Cr_2O_7$ were obtained. They were 805 mol^{-1} cm^{-1} ($\boldsymbol{\varepsilon^1_{KMnO_4}}$) at 372 nm, 1030 mol^{-1} cm^{-1} ($\boldsymbol{\varepsilon^2_{KMnO_4}}$) at 290 nm for $KMnO_4$. And for $K_2Cr_2O_7$ they were 1652 mol^{-1} cm^{-1} ($\boldsymbol{\varepsilon^1_{K_2Cr_2O_7}}$) at 372 nm and 853 mol^{-1} cm^{-1} ($\boldsymbol{\varepsilon^2_{K_2Cr_2O_7}}$) at 290 nm.

From figure 5, for the mixture abs_{total} at 372 nm is 0.732. Therefore

$$0.732 = \varepsilon^1_{KMnO_4} \bullet C_{KMnO_4} + \varepsilon^1_{K_2Cr_2O_7} \bullet C_{K_2Cr_2O_7} \quad (13)$$

$$0.732 = 805 \text{ X } C_{KMnO_4} + 1652 \text{ X } C_{K_2Cr_2O_7} \quad (14)$$

And at 290 nm

$$0.588 = \varepsilon^2_{KMnO_4} \bullet C_{KMnO_4} + \varepsilon^2_{K_2Cr_2O_7} \bullet C_{K_2Cr_2O_7} \quad (15)$$

$$0.588 = 1030 \text{ X } C_{KMnO_4} + 853 \text{ X } C_{K_2Cr_2O_7} \quad (16)$$

Therefore equations 14 and 16 are two simultaneous equations with two unknowns i.e. C_{KMnO_4} and $C_{K_2Cr_2O_7}$. First to eliminate $C_{K_2Cr_2O_7}$ equation 14 is multiplied by 853 and equation 16 is multiplied by 1652. Then one would get

$$853 \text{ X } 0.732 = 853 \text{ X } 805 \ C_{KMnO_4} + 853 \text{ X } 1652 \ C_{K_2Cr_2O_7} \quad (17)$$

And

$$1652 \text{ X } 0.588 = 1652 \text{ X } 1030 \ C_{KMnO_4} + 1652 \text{ X } 853 \ C_{K_2Cr_2O_7} \quad (18)$$

Subtracting equation 17 from equation 18, the second terms on right hand side of the both equations would be cancelled out and rearranging for the concentration of permanganate, we get $C_{KMnO_4} = 3.38 \text{ X } 10^{-4}$ M. The concentration of permanganate actually taken in the mixture is only $2.0 \text{ X } 10^{-4}$ M. The deviation in this case most probably be due to the wavelength used is not the λ_{max} of $KMnO_4$. And substituting this value either in Equation 13 or 14 we get $C_{K_2Cr_2O_7} = 2.8 \text{ X } 10^{-4}$ M. And the concentration of dichromate used in the mixture is $2.4 \text{ X } 10^{-4}$ M which is in good agreement with analysis of the mixture.

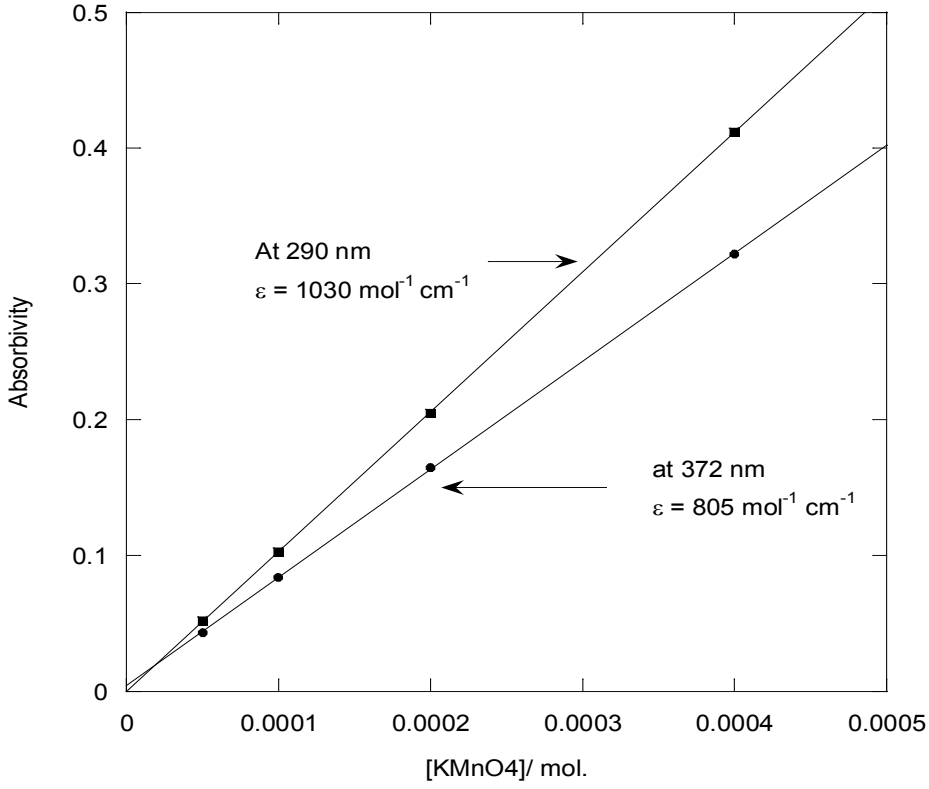

Figure 6. Determination of molar absorbivity of $KMnO_4$

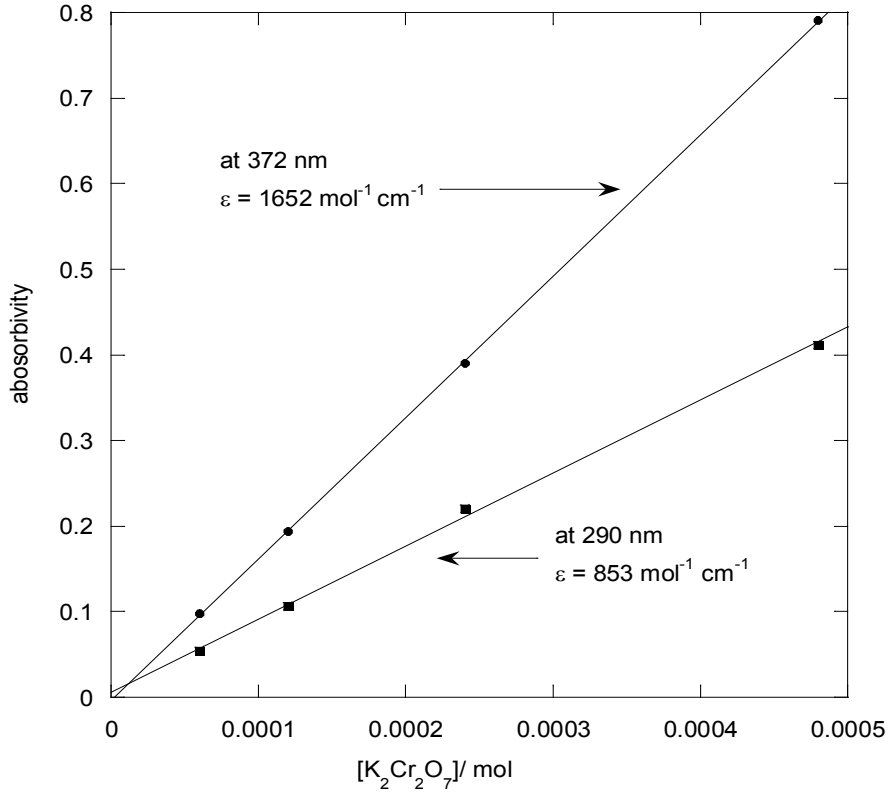

Figure 7. Determination of molar aborvity of $K_2Cr_2O_7$

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[11] It is not necessary to perform the analysis at the max of the samples. This is possible only when first sample has appreciable absorbance at the max of the second sample and vice-versa. If the analysis is carried out at other convenient wavelengths then one can call those wavelengths as obs.