A Graduated Cylinder Colorimeter: An Investigation of Path Length and the Beer–Lambert Law

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In most introductory chemistry courses, students are exposed to the Beer–Lambert law: $A = \varepsilon bC$. The experiments typically involve determination of the concentration of an analyte at a particular wavelength, usually in the UV or visible portion of the electromagnetic spectrum. However, the Beer–Lambert law has been shown to hold true for spectrophotometric investigations outside of the UV–vis region including gamma rays (*1*) and IR (*2*). Occasionally attention is given to the path length term in the relationship (*3–6*).

The premise of these experiments is based on work from August Beer and Johann Lambert, who demonstrated that the intensity of light exiting a medium (I), as compared to the intensity of light entering the medium (I_0), decreases exponentially with increases in concentration (Beer) or path length (Lambert). Beer's and Lambert's relationships are often combined and expressed in a common logarithmic form

$$-\log T = -\log(I/I_0) = \varepsilon bC = A$$

where the ratio of $I{:}I_0$ is the transmittance (T) and A is the absorbance of the medium.

In this experiment, a very simple apparatus was constructed using a 10-mL graduated cylinder as a variable path-length cell. The apparatus design can be seen in Figure 1. The light source and monochromator was a light emitting diode (LED), and the detector was a voltage divider composed of a photoresistor (CdS) in series with a fixed resistor. Texas Instrument's Calculator Based Laboratory systems interfaced to a Vernier colorimeter along with other reported colorimeters (*7, 8*) use LEDs as light sources. This colorimeter was constructed by students and is suitable for use in introductory chemistry courses in which the fundamentals of spectrophotometric analysis are addressed. This experiment is also suitable for chemistry and physics courses in which basic electronics are discussed because of the detector configuration.

Students gain an understanding of the components and operation of spectrometers and explore the relationship of absorbance and transmittance to path length and concentration. They discover the logarithmic relationship between absorbance and path length or concentration by observing the exponential decay of transmittance with path length and/or concentration. Students who have constructed a colorimeter have commented on their increased ability to understand the function of components in higher-end models of spectrometers that before had merely been black boxes to them.

Procedure

A 10-mL Pyrex graduated cylinder with a removable base was used as the centerpiece for the apparatus. A cork stopper was fitted snugly into the top. An appropriately colored LED (Radio Shack, 5 mm, V_f = 2.1 V) was secured into the cork stopper and powered by a 9-V battery. A potentiometer (Radio Shack, Bourns 3006P 103, 15 turn, 10-kW Trimpot) regulated the voltage to the LED to 2 V. The photoresistor (Radio Shack, cadmium sulfide photocell) detector was secured in the base of the graduated cylinder and placed in series with a 1-kW (fixed) resistor and a 9-V battery. The resistors in series acted as a voltage-divider circuit. All voltage measurements were made across the fixed resistor. As light struck the photoresistor, its resistance decreased, which led to an increase in the voltage across the fixed resistor. This design allowed the measured voltage to follow changes in transmittance.

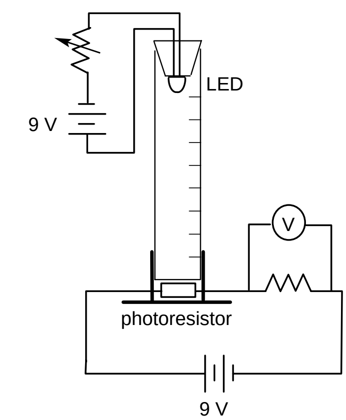

Figure 1. Diagram of the graduated cylinder colorimeter and associated electronics.

The entire assembly was covered with a box before each measurement to provide a stable and dark background. A measure of the "dark" voltage (V_{dark}) was made without the LED lit. A voltage measurement corresponding essentially to the 100% transmittance value (V_{water}) was made with the LED lit after the addition of distilled water in 1-mL increments from 0 to 5 mL. Finally, with the graduated cylinder emptied and dried, the voltage across the fixed resistor was recorded after each milliliter addition of colored test solution (V_{sample}) from 0 to 5 mL. To calculate the absorbance the following relationship was used:

$$A = -\log T = -\log\left(\frac{I}{I_0}\right) = -\log\left(\frac{V_{sample} - V_{dark}}{V_{water} - V_{dark}}\right)$$

Hazards

The solutions of tetraamminecopper(II) and permanganate should be handled with care and disposed of properly.

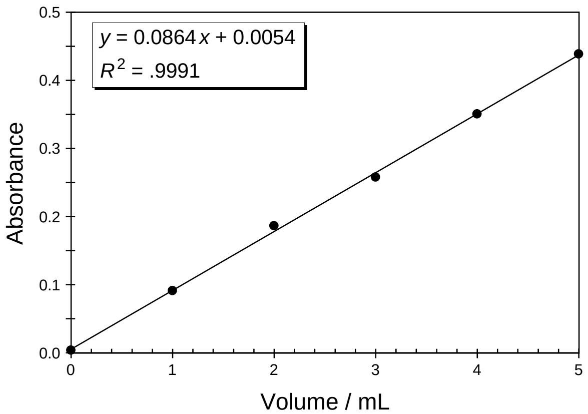

Figure 2. A plot of absorbance versus volume of 2.95×10^{-4} M permanganate in the 10-mL graduated cylinder colorimeter.

Results and Discussion

The green LED used for the permanganate solution had a maximum wavelength emission of 565 nm, which corresponds well with a wavelength of significant absorbance for the permanganate ion. Figure 2 is a plot of absorbance versus volume of permanganate in the graduated cylinder. The concentration of permanganate used in this experiment was 2.95×10^{-4} M. As expected, there is a linear relationship between absorbance and volume because height, which in this case represents path length, increases linearly with volume in a graduated cylinder.

A study of the relationship between absorbance and concentration also was performed with this instrument using solutions of permanganate ion and the same green LED. Five solutions (1.2×10^{-3} to 7.4×10^{-5} M) were prepared. Absorbance was measured for the addition of 2 mL of each solution to the colorimeter. Again a linear relationship was found (r^2 = .9997).

A second solution containing 0.010 M tetraamminecopper(II), $Cu(NH_3)_4^{2+}$, was studied with the colorimeter. A yellow LED (emission λ_{max} = 580 nm) was used as the light source because of the significant overlap between the emission spectrum of the LED and the absorbance spectrum of the $Cu(NH_3)_4^{2+}$ (absorbance λ_{max} = 595 nm). Again, the linear relationship between absorbance and path length was observed (R^2 = .99).

Conclusion

This low-cost, low-tech, versatile device is useful for demonstrating the rarely discussed relationship between absorbance and cell path length and the relationship between absorbance and concentration for different solutions. The incorporation of elementary electronics concepts makes this an easily constructed, explained, and understood exercise for introductory chemistry or physics courses as well as advanced chemistry course.

Acknowledgment

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ʷSupplemental Material

Details of the construction and use of the apparatus are available in this issue of *JCE Online*.

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