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Laboratory Experiment

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From Voltage to Absorbance and Chemical Kinetics Using a Homemade Colorimeter

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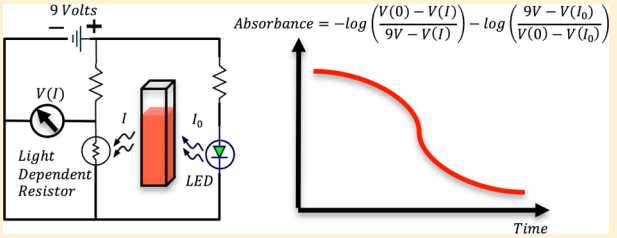
Supporting Information

ABSTRACT: The use of the Beer–Lambert law in spectroscopy is the core of standard methods for determining a chromophore concentration in a solution. Its application requires an understanding about interaction of light with a colored solution and the use of light emission and light detection devices. We build here a simple electronic circuit formed of light-emitting diodes and light-dependent resistors that can be used for measuring chromophore concentrations during experiments focused on chemical kinetics: decolorizing of phenolphthalein in a basic solution, and reduction of methylene blue by ascorbic acid. From the chemical point of view, the goal is to determine experimentally the rate law. In addition, students understand, using inexpensive electronics, the basic design of a spectrophotometer to achieve successful measurements of absorbance.



KEYWORDS: *Second-Year Undergraduate, Laboratory Instruction, Kinetics, Interdisciplinary/Multidisciplinary*

A measurement frequently involves a device where electronics plays an important role. Absorbance is not an exception. A controlled light-emitting source and a light-sensitive detector are important components of a spectrophotometer. On the other hand, for chemistry students, the application of the Beer–Lambert law[1] commonly starts after a spectrum is obtained. Even good software, where absorbance is computed from intensity, does not give to the student an insight about the way electronics provides that intensity measurement. The experiments proposed here help to understand the way in which a basic electronic circuit is designed to get an absorbance measurement, as well as to make use of nonconventional variables as voltage for obtaining relevant information in chemistry. The goal is to determine, using a homemade colorimeter and measuring voltage, the order of reaction of two well-known reactions: the conversion of phenolphthalein to its colorless carbinol form in a sodium hydroxide solution and the reduction of methylene blue by ascorbic acid in an acidic solution. We found that this experience is appropriate as a pair of Lab Sessions in a course of Elementary Kinetics or in a course of Electronics, both oriented to students of Chemical Engineering.

MATERIALS AND METHODS

Design of the colorimeter

After an idea proposed in the *Journal of Chemical Education*,[2] we develop a colorimeter that can be built by the students as observed in Figure 1a. The core of it is a set of six discrete elements. These elements, as Figure 1a also presents, are light emitting diodes (LEDs) aligned opposite to light-dependent resistors (LDRs). After the sample absorbs light coming from the LED, the LDR senses the change in light intensity, which is expressed as a change in the output voltage from a voltage divider working at constant input voltage. Therefore, when the equation of a voltage divider and a multimeter is used, it is possible to quantify the absorbance.

The schematic diagram of the electronic circuit designed for the colorimeter is shown in Figure 1b. The Supporting Information provides a detailed guide for building it. A LED-selector terminal helps to decide on the color of the LED to be used: green, yellow, or red. To achieve this, the LED-selector terminal should be connected to the positive source of voltage (Vcc in the diagram). The source of voltage or power source is also connected to a resistor (100 Ω) and a LDR in series. Notice that there is a LDR for each LED and that they are aligned one opposite to each other. Between the 100 Ω resistor and the LDR, a test probe is placed to obtain a voltage divider circuit:[3] the probe is connected to the multimeter on the positive relative connector meanwhile the multimeter negative relative connector is connected to the ground terminal GND. All components are housed on a PVC box, which allows keeping the electronics away during experiments, but more importantly, it gives a stable position for the cuvette. To select a LED and perform the measurements, a female DB-9 terminal collects all wires to be connected to a DC Power Source (Matrix Technology Inc., Model MPS-3005L-3, Shenzhen, China) or a multimeter (MUL-600, Steren Inc.) as observed in Figure 1. It is also possible to use a 9 V DC battery instead of the Power Source, but we have observed that batteries discharge after only three or four experiments, drifting the voltage during an experiment and hampering good results.

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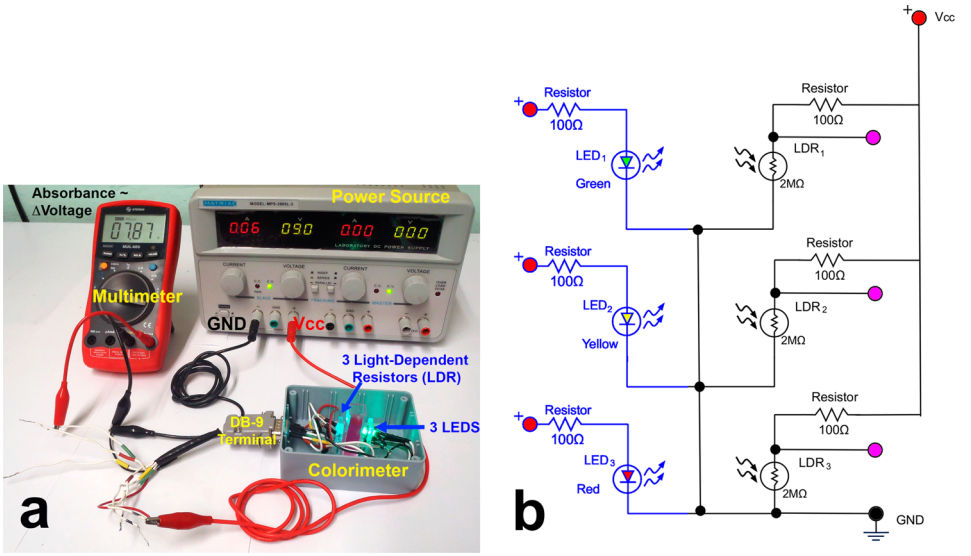

Figure 1. (a) Schematic picture of the experimental setup built to measure the absorbance of a solution using a colorimeter: A power source of 9 V is used to energize a circuit, where a LED and a Light-Dependent Resistor (LDR) are used as a light source and a light detector, respectively. With the use of a multimeter, the changes of light intensity on the LDR that produces a change in the circuit voltage can be used to compute the absorbance of the solution as explained in the text. (b) Schematic diagram of the electronic circuit designed for the colorimeter. Colors in the circuit correspond to the parts of the circuit held on each one of the acrylic pieces inside the colorimeter: the blue part at left corresponds to the line of 3 LEDS, and the black part at right corresponds to the line of 3 Light-Dependent Resistors; both marked in panel a.

Fabrication of the Colorimeter

Usually, students working in pairs need a first 3 h lab session to finish a functional colorimeter. The Supporting Information provides a detailed guide to build it. A second lab session is necessary to perform absorbance measurements using this colorimeter. In the first session, a lab instructor for each three or four pairs of students avoids common errors as defecting soldering or incorrect diagram interpretation. At the end of the first session, they have to check that the color LED to be used can be selected properly. To do that, they have to switch on the Power Source using zero voltage and zero current intensity. Then, they have to increase DC voltage and current intensity slowly until 9 V are achieved at the minimum possible current intensity. If current intensity is deliberately high, LEDs can be damaged and they have to be replaced. Once one LED is switched on, the voltage of the correspondent LDR should be less than the voltage imposed in the circuit (less than 9 V) as we are going to explain below.

Checking the Linear Response of the LDR Resistance with Light Intensity

We compare results obtained in our colorimeters with results from a commercial USB650-UV spectrophotometer from Ocean Optics, controlled by a computer interface using the OceanView software. This spectrophotometer was also operated for testing the LDR performance used in the colorimeters. Its software allows counting the total light intensity on the detector in photons per squared centimeters per second [(photons/cm^2)/s]. In such a way, when an LDR is blocking the pathway between the light emission source and the light detector at different emission intensities, we are able to determine the resistance of the LDR as a function of the light intensity on it. Integration over the total wavelength range measured by the spectrophotometer light detector, from 200 to 850 nm, gave us (photons/cm^2)/s on the LDR. According to Figure 2, the nominal LDR resistance value of 2 MΩ is not observed because even a small amount of light on the LDR

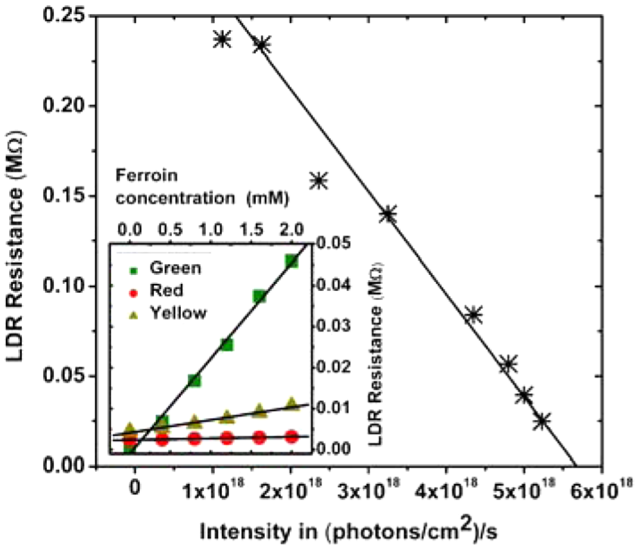

Figure 2. LDR resistance as a function of the total incident light. The black continuous line is a linear fit with R^2 = 0.970. Inset: LDR resistance for a solution of ferroin measured with different color LEDS detailed in the legend. All linear fittings (black continuous lines), exhibit a square correlation coefficient higher than 0.983.

produces a large resistance decrement and easily sends the LDR resistance vs light intensity dependence to a linear regime kept until high intensity values: the highest intensity observed in this figure is the maximum intensity of the spectrophotometer light source.

A chromophore can also be used to test the linearity of the LDR resistance vs light intensity; since changing its concentration, it can act as a graduated color filter . Figure 2 (inset) shows the resistance value of a LDR measured using different LED colors hosted in the colorimeter as a function of ferroin standard solutions (using dilutions of a Ferroin indicator solution 0.025 M from Sigma-Aldrich). As expected,

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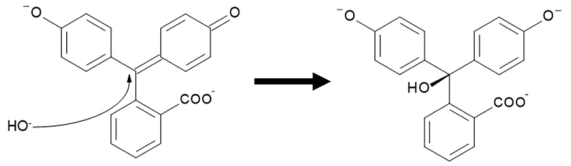
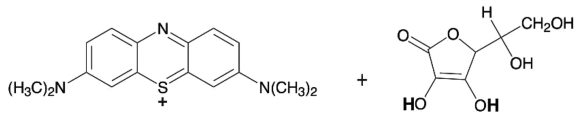
it is by far better to use a green LED, i.e., a color near the ferroin maximum of absorption (around 500 nm). Other LED colors can also be used, although as observed in the same figure, the sensitivity of the colorimeter for a specific chromophore cannot be as good as it could be necessary.

Chemical Reactions

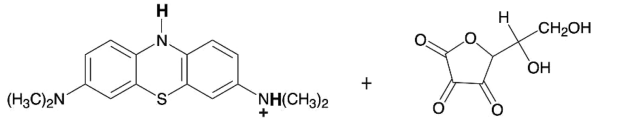
Two reactions were tested using the colorimeter. The conversion of phenolphthalein to its colorless carbinol formed in a sodium hydroxide solution



and the reduction of methylene blue by ascorbic acid:



Methylene blue (blue) Ascorbic acid



Leucomethylene blue (colorless) Dehydroascorbic acid

For the first experiment, a stock solution of phenolphthalein was prepared according to literature; dissolving 0.1 g of the reagent in 80 mL of ethanol and 20 mL of distilled water.[4] At the beginning of an experiment, 1−3 drops of this indicator were added directly in the spectrophotometer cuvette previously filled with 2 mL of a solution of NaOH 0.5 M freshly prepared to avoid reaction with ambient CO_2. Please note that NaOH is in great excess with respect to phenolphthalein.

For the second experiment, stock solutions of methylene blue (0.1338 mM), sulfuric acid (1.0 M), and ascorbic acid (0.454 M) were prepared. A sample to be measured is prepared mixing 1 mL of the sulfuric acid solution and 10 μL of the ascorbic acid solution in a cuvette. Once the solution is in the cuvette, ready to be measured inside the colorimeter, 1 mL of the methylene blue solution was rapidly added to it using a micropipette. In such conditions, ascorbic acid is in great excess with respect to the amount necessary to react with the methylene blue present (reaction needs 1:1 stoichiometry). The solution was permanently stirred during an experiment.

Phenolphthalein, ascorbic acid, NaOH (pellets), concentrated sulfuric acid, and absolute ethanol, all of them at their highest available grade of purity, were purchased from Karal. Methylene blue was purchased to Sigma-Aldrich.

HAZARDS

Sulfuric acid and sodium hydroxide are corrosive and should be handled with care. Sodium hydroxide can cause serious eye damage. Methylene blue is a skin and eye-irritating agent. Protective gloves and goggles must be worn when handling these chemicals. In addition, methylene blue powder inhalation or ingestion is potentially dangerous and a dust mask must be worn when handling this chemical.

RESULTS AND DISCUSSION

Equations that Govern the Colorimeter

The LDR resistance, R vs light intensity follows a linear relationship as observed in Figure 2, from which we can propose

$$R(I) = R_0 - fI \tag{1}$$

Here, f is a constant factor related with the sensitivity of the LDR to the light intensity "I" and R_0 are the resistance at null intensity ($I = 0$). In the voltage divider circuit detailed in Figure 1b, the multimeter voltage measurement across it is given by

$$V_{out} = \left(\frac{R(I)}{R(I) + 100\ \Omega}\right)V_{in} \tag{2}$$

In our case, V_{in} = 9 V and 100 Ω is the resistor in parallel to the LDR observed in the right (black) part of Figure 1b. Clearly V_{out} varies only when the light intensity on the LDR does, so we can redefine V_{out} as $V(I)$. Combining the previous equations, it is easy to obtain an equation for the intensity on the LDR resistance:

$$I = \frac{(R_0 + 100)(V(0) - V(I))}{f(9\ \text{V} - V(I))} \tag{3}$$

where

$$V(0) = \left(\frac{R_0}{R_0 + 100\ \Omega}\right) \times 9\ \text{V} \tag{4}$$

In the next subsection, we will show how to use these expressions to compute absorbance.

Chemical Kinetics Using the Colorimeter

We are ready now to follow the kinetics of a reaction using our assembled colorimeter. First, we have to choose one LED. The LED having the complementary color of the chromophore is the right one because it provides the highest light absorption of the sample and as a consequence, the lowest light intensity on the LDR at the beginning of an experiment. In such a way, we will get the largest difference in voltage from the beginning to the end of the experiment. If we do not have that color among LEDs, we should use the closest color to the complementary one. In the case of phenolphthalein, with a maximum point of absorption at 552.8 nm (according to ref 5), we use the green LED which has its maximum of absorption at 523 nm. At 552.8 nm, the green LED light emission is a quarter of that emitted at 523 nm (see the LED emission profile in the Supporting Information). Although it is good enough to consider as a first approach a fractional loss of light intensity due to absorption when an infinitesimal increase is made in phenolphthalein concentration (Beer's Law), a mismatch between the LED maximum emission and the chromophore maximum absorption wavelengths limits the use of the Beer's Law[1] as we suggest and explain later on in this manuscript.

Now, and under stirring, 1−3 drops of phenolphthalein are added in the cuvette. It is important to be sure that mixing is complete, using, if necessary, a Pasteur pipet. We should immediately notice a decrease in voltage (V_{out}).

The measured voltage, as a function of the light intensity on the LDR, $V(I)$, changes in time because the light intensity on

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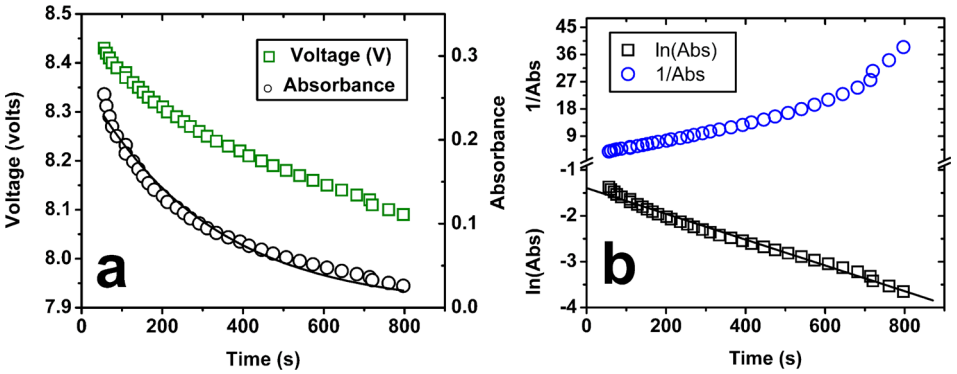

Figure 3. (a) Voltage and absorbance vs time for an experiment where a colored solution of phenolphthalein (Ph) reacts with NaOH, producing an uncolored carbinol. As reaction goes on, the absorption of the green light emitted by a LED, and the absorbance, in consequence, decrease as a result of the [Ph] decrement. Absorbance was computed from voltage according to eq 6. The line of tendency is a nonlinear fitting of absorbance vs time using eq 9. (b) Using the same absorbance data, we compute ln(Abs) and 1/(Abs) functions to know the order of the reaction with respect to [Ph]. A linear fitting is observed for ln(Abs) data. For the fitting, the square of the Correlation Coefficient is 0.988.

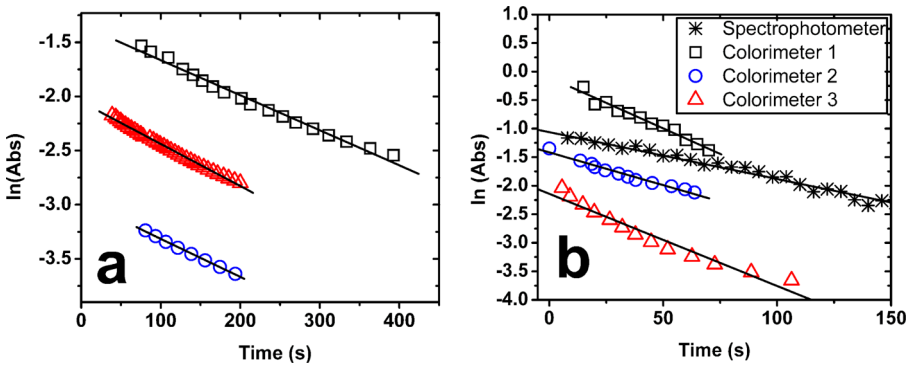

Figure 4. Plots of ln(Abs) vs time coming from three different homemade colorimeters for the reaction of phenolphthalein (Ph) with NaOH. Ph reacts with NaOH, producing an uncolored carbinol. Absorbance was computed from voltage according to eq 1. Linear fittings are observed for each set of data. From the upper to the lower curve, slope values obtained from linear fittings are −0.00324, -0.00388^{-1}, and $-0.00352\ s^{-1}$. In all cases, the squared Correlation Coefficient was higher than 0.987. (b) Plots of ln(Abs) vs time for the methylene blue reduction by ascorbic acid. Results come from a set of three homemade colorimeters and a commercial spectrophotometer. Linear fittings are observed. The squared Correlation Coefficient was higher than 0.951 for the colorimeters and 0.982 for the spectrophotometer.

the LDR, $I(t)$, does as a function of phenolphthalein concentration. To compute absorbance (Abs), we need the ratio of the temporal intensity $I(t)$ to the intensity of the incident radiation I_0. To get I_0, we use a cuvette filled with a 0.5 M NaOH solution. From eq 3,

$$I_0 = \frac{(R_0 + 100)(V(0) - V(I_0))}{f(9\ \mathrm{V} - V(I_0))} \tag{5}$$

Then, voltage differences are sufficient to compute absorbance using its definition[1]

$$\mathrm{Abs} = -\log\left(\frac{I}{I_0}\right) = -\log\left(\frac{V(0) - V(I)}{9\ \mathrm{V} - V(I)}\right) - \log\left(\frac{9\ \mathrm{V} - V(I_0)}{V(0) - V(I_0)}\right) \tag{6}$$

Notice that intensity ratios do not depend on f and R_0 because these terms cancel each other. We can now understand why it is enough to know voltage differences for computing absorbance and why it is important to determine $V(0)$ and $V(I_0)$ to avoid the necessity to determine R_0. We have explained how to obtain $V(I_0)$ from a cuvette filled with 0.5 M NaOH solution. On the other hand, $V(0)$ is determined by blocking the path of light between the LDR and the LED. In this study, blockage was done using a plastic black block with the LED switched on. Since even small amounts of light on the LDR surface fulfills $R(I) = R_0 - fI$, students should not worried about a "perfect" light blockage that sends $R(I)$ out of this regime.

Finally, it is important to notice that absorbance has two logarithmic terms, one of them constant (the second one in eq 6) once $V(0)$ and $V(I_0)$ are determined.

The Beer−Lambert law and the kinetic law for phenolphthalein concentration consumption ([Ph] consumption), $\mathrm{Abs} = \varepsilon l[\mathrm{Ph}]$ and $-(\mathrm{d}[\mathrm{Ph}]/\mathrm{d}t) = k'[\mathrm{Ph}]^n$, respectively, now come into play. Here, absorbance is the product of the molar absorptivity ε, the cuvette path length l, and the molar concentration of phenolphthalein [Ph]. The consumption in [Ph] placed as a negative time derivative is captured in the kinetic law as a product of a constant k' and an explicit dependence of [Ph] to the coefficient "n", i.e., the order of reaction[6] with respect to [Ph]. Combining both laws, we get the folowing:

$$\frac{\mathrm{dAbs}}{\mathrm{d}t} = -\frac{k'\varepsilon l}{(\varepsilon l)^n}(\mathrm{Abs})^n \tag{7}$$

The solution of this differential equation depends on the order of reaction "n". For $n = 0$, the solution is

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$$\mathrm{Abs} - \mathrm{Abs}_0 = -k'\varepsilon l t \quad (8)$$

For $n = 1$, we have an independent solution of the product "εl":

$$\mathrm{Abs} = \mathrm{Abs}_0\, e^{-k't} \quad (9)$$

For $n = 2$, the solution of eq 2 depends on the product "εl":

$$\frac{1}{\mathrm{Abs}} - \frac{1}{\mathrm{Abs}_0} = \frac{k't}{\varepsilon l} \quad (10)$$

We do not consider higher orders of reaction because kinetic theory marks collisions of three or more molecules as extremely improbable.[6]

Student Data

Figure 3a plots voltage and absorbance (Abs) for the temporal [Ph] consumption in a 0.5 M solution of NaOH (first experiment). A nonlinear fitting of Abs data using eq 4 (i.e., considering $n = 1$) is also presented. Evidently, Abs data do not suggest a zero order of reaction, and in Figure 3b, we contrast the temporal variation of ln(Abs) and 1/(Abs). According to eqs 9 and 10, those functions are linear in time for $n = 1$ and $n = 2$, respectively. The linear plot is obviously the one obtained using $n = 1$, as literature points out.[7] Figure 4a shows data of this experiment using three different colorimeters. It is remarkable to get in all of them almost the same slope ($0.00354 \pm 0.00032\ s^{-1}$), which means that results coming from different similar devices are reproducible to some extent as we will discuss below.

In Figure 4b, using the same three colorimeters reported in Figure 3b and a commercial spectrophotometer (USB650UV, Ocean Optics), we compare plots of ln(Abs) coming from experiments where ascorbic acid (AA) is oxidized in an acidic solution by methylene blue (MB). In this experiment, we measured [MB] using the colorimeter red LED. The maximum absorption wavelength for MB is 665 nm, [8] near the maximum wavelength emission of the red LED. As observed, a plot of ln(Abs) vs time, considering that this is a first-order reaction ($n = 1$) with respect to MB, gives a straight line as reported in literature.[9] The slope value of that line gives us directly the first-order decay constant k'. k' varies as much as in a ratio of two running this experiments in our three different devices, from 0.01149 to $0.01613\ s^{-1}$ (using the spectrophotometer, $k' = -0.00822\ s^{-1}$). Furthermore, we can see that straight lines (ln(Abs) vs time), when a colorimeter is used, show a downward bending. This is also observed in the first experiment with phenolphthalein (Figure 3b and 4a). At the moment, we do not have a conclusive explanation for such deviation, but reasons can be multiple. An evident complication is the use of LEDs with a broad emission spectrum: they send a broad wavelength spectrum on the sample and compromise the validity of Beer's law over a wide range of absorbance. Light response of a LDR could also be not exactly linear. Nonetheless, measurements of absorbance are good enough to illustrate already known kinetics of a reaction, and to give to the student an insight of the way electronics provides absorbance.

CONCLUSION

We developed a set of experiments where second-year undergraduate students built and used a colorimeter. They learn to use basic electronics to test kinetics of simple chemical reactions from absorbance data. Those data were good enough to distinguish different orders of reaction and to get a rough idea of decay constant values.

We consider that the use of basic commercial off-the-shell electronic components as LDR and LEDs, and the revision of basic concepts in electricity as a voltage divider, to get a valid result in chemistry, perfectly illustrates the common need for interdisciplinary approach to solve technological problems. For us, the development of a colorimeter was also of importance because of our limited budget to attend to medium-size groups of engineering chemistry students: we only have one available spectrophotometer.

ASSOCIATED CONTENT

Supporting Information

A detailed guide for building a colorimeter as the one used in this paper. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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