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Chemical Kinetics using a Smartphone Spectrometer

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Honors Research Project

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Abstract:

In a time where many high school science classes are lacking in quality laboratory education, there is a need for accessible chemical equipment that enhance teaching fundamental concepts of chemistry with ease and at a low cost. The DualSpec handheld smartphone spectrometer aims to be a quality open-source spectroscopic instrument that can easily be made and used at home by people of any scientific level. This research sought to show that the DualSpec could be used to teach higher level spectroscopic concepts such as those used in chemical kinetics. The DualSpec was compared to a commercial spectrometer using the commonly taught crystal violet experiment. Both instruments showed that the reaction with sodium hydroxide was a first-order reaction with respect to the crystal violet concentration, with comparable time constants of 0.288 (± 0.00279) and 0.363 (± 0.00107) min^{-1}. This shows that the DualSpec can be utilized as a teaching tool for high school chemistry classes to prepare students for undergraduate chemistry curricula by providing accessible and quality hands-on experiments.

Introduction:

For years, scientists have been studying the benefits of teaching science via laboratorial experimentation, and it has been readily acknowledged that experimentation plays a fundamental role in forming well-rounded scientists.[1,2] Due to its hands-on nature, it is nearly impossible for science of any kind to be fully understood without some practice of analytical, theoretical, and critical thinking which comes from laboratory experiments. This practice may be summed up using the word “inquiry”, as defined by the diverse ways in which scientists study the natural world, propose ideas, and explain and justify assertions based on evidence derived from scientific work.[3] Thanks to advancements in technology more opportunities for scientific inquiry are available, and the view of science education is continuing to change.[3]

Although it is agreed that laboratory practices are needed for proper education in science, one fatal drawback that often prevents aspiring students from getting the experiences they need is monetary costs. In many cases, universities are able to find funding for the purchase of instruments which cost multiple thousands of dollars, but most public secondary education institutions would never be able to afford similar instruments. Opensource equipment, or that which is free and readily available to the public, could bridge this gap. By sharing ideas and software files especially on the internet, smaller groups are saved from spending commercially-high costs or reinventing the wheel, and ideas can be improved by collaboration much more quickly.[4]

The overall goal of my honors project was to provide more open-source experimental equipment in order to increase the number of prospective scientists with access to quality experiential learning. Specifically, my research was to further the development of a portable, handheld, 3D-printable spectrophotometer that utilizes smartphone cameras to take spectroscopic data in the UV/visible range.[5] Previous research showed that basic spectroscopic theory could be taught using this device, such as the Beer-Lambert law.[5] The focus of this project is to show that even higher levels theories, such as kinetic reaction decay experiments, can be successfully accomplished on this device.

Spectroscopy studies the interactions between radiation and matter.[6] It is one area of chemistry that is often taught in undergraduate chemistry curriculum due to its wide array of applications and could easily be transitioned into secondary education with the right processes. There are many different spectroscopic methods, and some of those most commonly used are nuclear magnetic resonance (NMR), infrared (IR), and Ultra Violet/Visible (UV-Vis) spectroscopy. As indicated by their names, the different methods are separated by the region of the electromagnetic spectrum used or produced by their use. Spectroscopy is especially useful for quantitative experiments because of its speed and flexibility in instrumentation, and UV-visible spectroscopy is a favored technique.[7] A UV-vis spectrometer is the instrument used to collect spectral data from compounds that absorb or emit light in the UV/visible regions of the electromagnetic spectrum.

Some basic knowledge of spectroscopy is necessary to understand how this experiment functions. As monochromatic light passes through a colored sample, some of it will be absorbed by the sample and some will be transmitted with an intensity, I. The initial intensity of the light is given by I_0.[8] The ratio of these light intensities transmitted through the sample is known as transmittance, T. Rather than thinking about the quantity of light being transmitted through the sample, one normally considers the ability of a sample to absorb light, or its absorbance, A. Absorbance can be determined by light intensity or transmittance via the following relationships:

$$T = \left(\frac{I}{I_0}\right) \qquad \textbf{Eq. 1}$$

$$A = \log\left(\frac{I_0}{I}\right) = \log\left(\frac{1}{T}\right) = -\log(T) \qquad \textbf{Eq. 2}$$

The Beer-Lambert Law (Eq. 3) shows the direct relationship between the absorbance of a sample, the length of the path that the light must travel, b, and the sample concentration, c:[6]

$$\mathrm{A = \varepsilon bc} \qquad \textbf{Eq. 3}$$

In this equation, ε is the molar absorptivity, or extinction coefficient, of the compound in units of $\mathrm{M^{-1}cm^{-1}}$. It is a constant for a given molecule at a given wavelength.[8] Typically the path length (or the length of the cuvette) is 1 cm. Graphing absorbance values versus the corresponding solution concentration gives a Beer-Lambert plot, where the value of the slope is the extinction coefficient.[6] Since this is a direct relationship, the higher the concentration of the sample (or the darker the color), the higher the absorbance.

Another facet of UV-vis spectroscopy is that of chemical kinetics, which studies the rates of chemical reactions. One commonly taught kinetics experiment is the crystal violet kinetics experiment. Crystal violet (CV) is a cationic organic dye of a deep purple color. When it reacts with hydroxide ion (commonly provided by sodium hydroxide solution), its color fades due to the formation of its neutral hydrolyzed product.[9] Its structure before and after the reaction is shown in **Figure 1**.

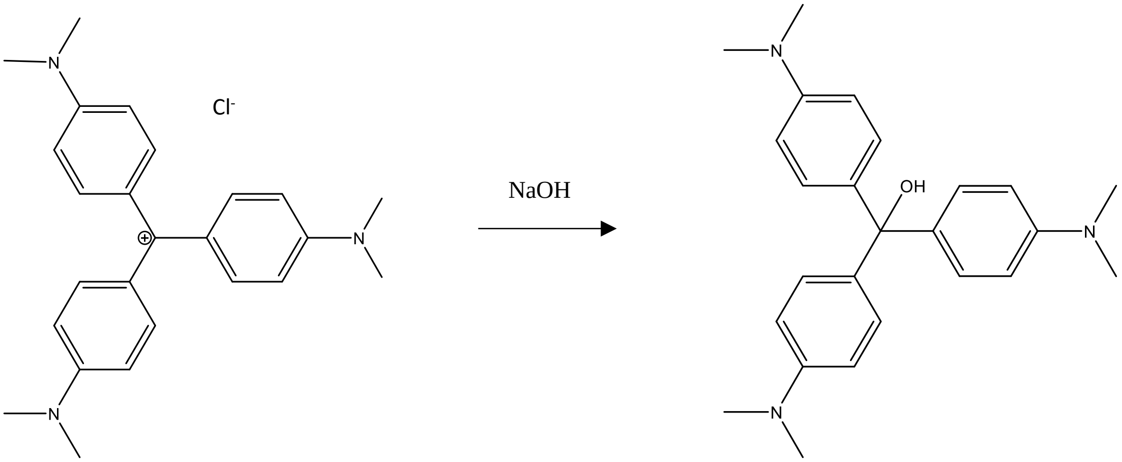

Fig. 1. The structure of crystal violet before and after reaction with sodium hydroxide. The first structure gives a purple color, while the second is colorless.

This reaction can be shown as:

$$CV^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow CVOH_{(aq)}$$

And the rate law for this reaction is given by:[9]

$$\text{rate} = k[CV^{+}]^{m}[OH^{-}]^{n}$$

where k is the rate constant, and m and n are the orders of the reaction with respect to each reactant. The rate of the reaction with respect to CV can be determined by plotting absorbance data versus time as the reaction proceeds. This is only possible if the concentration of hydroxide ion is significantly higher than the concentration of CV.

Chemical kinetics is taught in most undergraduate chemistry curricula, where colleges and universities have the equipment and students have the background experimental and mathematical knowledge necessary to run the experiments designed for one- to two-week lab periods. There are some kinetics experiments designed for high school students, but they typically include more watching than hands on experimentation, and do not go deep into the concepts behind the experiments.[10] The crystal violet experiment is commonly taught in secondary levels of education using small colorimeters.[11,12] While these experiments allow for the basic idea of color decay to be applied to the concept of reaction kinetics, more can be done to enhance student comprehension. In addition, the 3D-printed DualSpec spectrophotometer could open up the possibilities of teaching the basic principles of chemical kinetics to students at the high school level.

Materials and Methods

Sample Preparation:

Crystal violet solution (1%, Sigma-Aldrich) and solid sodium hydroxide (Sigma-Aldrich) were used to prepare the solutions for this experiment. One hundred twenty microliters of crystal violet solution were diluted in 50 mL nanopore water to give a solution that was 5.76×10^{-5} M crystal violet. Solid sodium hydroxide (1.0 g) was dissolved in 250 mL of nanopore water to give a solution that was 0.1 M NaOH. Considerations for the safe and intended completion of these experiments can be found in **Appendix 1.**

Data Collection:

The commercial spectrometer used for this research was a Thermo Scientific Genesys 6 UV-Visible Spectrometer. The experiments were performed using the Basic ATC function of the instrument. Because crystal violet absorbs at 590 nm, the absorbance readings were taken at this wavelength. One clear plastic cuvette was filled with nanopore water and placed in the indicated slot, and the instrument was blanked. In the other cuvette was added 2 mL of the prepared crystal violet solution. This cuvette was then placed in the instrument while a pipette was filled with 2 mL of the prepared NaOH solution. When the experiment was ready to be performed, the NaOH was added to the sample cuvette, the solution was mixed, a timer was started, the instrument was covered, and data collection began. Because the instrument shows the absorbance on a screen, the absorbance data was collected manually in an Excel spreadsheet every 15 seconds for approximately 12 minutes. The points of absorbance versus time were then plotted on a graph.

Data collection on the DualSpec apparatus was performed using an iPhone 7s, its camera function, and an incandescent-bulb lamp. The lamp was approximately 60 cm away from the instrument, and this was adjusted until the light shone through the parallel beams evenly so the spectra could be seen clearly. Calibration videos were taken in order to account for any background noise from the light in the room. Three five-second videos were taken: one with the slits and the fluorescent lights on, one with only the lamp and the slits, and one with the lamp on and nanopore water in both cuvettes. During the actual experiment, the left beam contained the blank (nanopore water), and the right was the sample. The crystal violet-sodium hydroxide reaction was performed in the same way and using the same concentrations as with the commercial instrument. There was a 15-20 s dead time between when the NaOH was added to the cuvette and when the video was actually started. Twelve-minute videos were taken for each run, and these videos were analyzed using MatLab software to give the curves. The iPhone 7s camera has a frame rate of 30 frames per second (fps) for videos. This was converted to minutes to give a total of more than 21,000 frames per 12-minute video. The entire data set was used to plot the kinetic traces of the absorption decay versus time, while every 1000th frame was used to plot the intensity and absorption spectrographs versus pixel position.

Results and Discussion

Commercial Spectrometer:

Absorbance data for the crystal violet and sodium hydroxide reaction was plotted versus time to give the curve in **Figure 2**. To determine the order of the reaction, the absorbance data was manipulated following basic rules of kinetics. Plotting the natural logarithm of the absorbance values versus the respective times gave a linear plot, concluding that this was a first order reaction with respect to crystal violet, as seen in **Figure 3.** The linearized equation for the reaction is $y = -0.288x + 0.7333$. The slope of this plot is the negative of the rate constant, *k*, which is shown to be $0.288 \pm 0.00279 \text{ min}^{-1}$. The standard deviation for the slope of the line was determined using the complete least squares fitting function in Excel. To determine the order with respect to the hydroxide anion, additional testing would have needed to be done using different concentrations of sodium hydroxide. Doing the additional experiments could be a way to extend the educational value of this experiment.

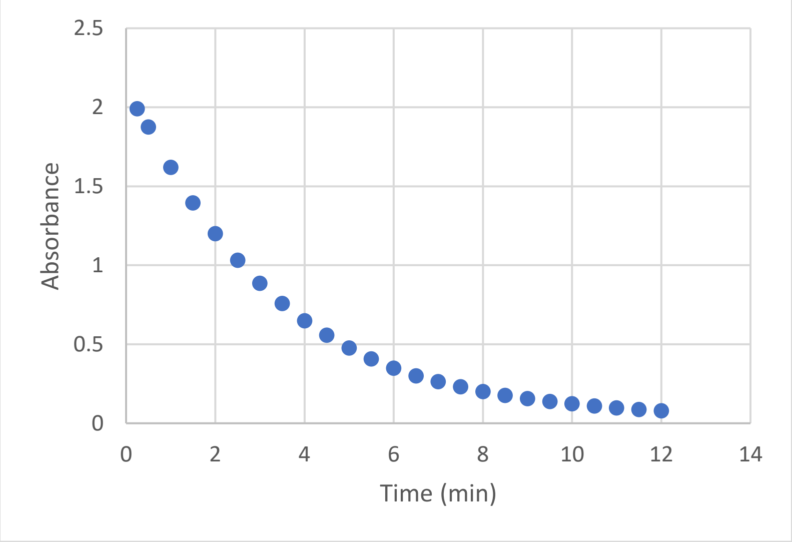

Fig. 2. The crystal violet absorbance decay over time on the Genesys6 spectrometer.

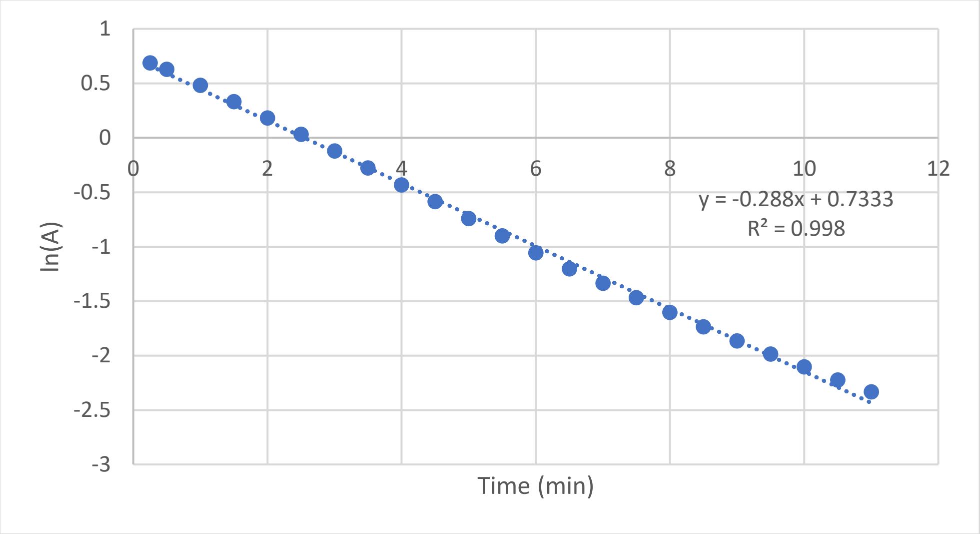

Fig. 3. Plot of ln(*A*), where *A* is the crystal violet absorbance from the Genesys6 Spectrometer. Because the fit is a straight line, this is a first order reaction with respect to crystal violet, and the rate constant, *k*, is the negative of the slope, 0.288 min^{-1}. The standard deviation is ± 0.00279 min^{-1}.

DualSpec:

The videos that were taken on the iPhone 7s in the DualSpec apparatus showed the spectral changes as the reaction proceeded. This is something that is unique to the use of the smartphone spectrometer. The spectra appeared as two rectangles on the phone screen: one for the reference water cuvette and one for the sample cuvette. The spectrum for the reference cuvette showed the band of colors in the visible spectrum. The crystal violet sample cuvette was mainly darkened out, because the solution absorbed most of the visible light. When the sodium hydroxide was added to the solution and the reaction began, the progress of the reaction could visibly be observed on the screen as the band of colors appeared on the spectrum. This was due to the amount of light absorbed by the solution decreasing as the clear carbinol was formed. Screenshots of the videos taken by the iPhone 7s in the DualSpec apparatus in an experimental run are shown below in **Figure 4**.

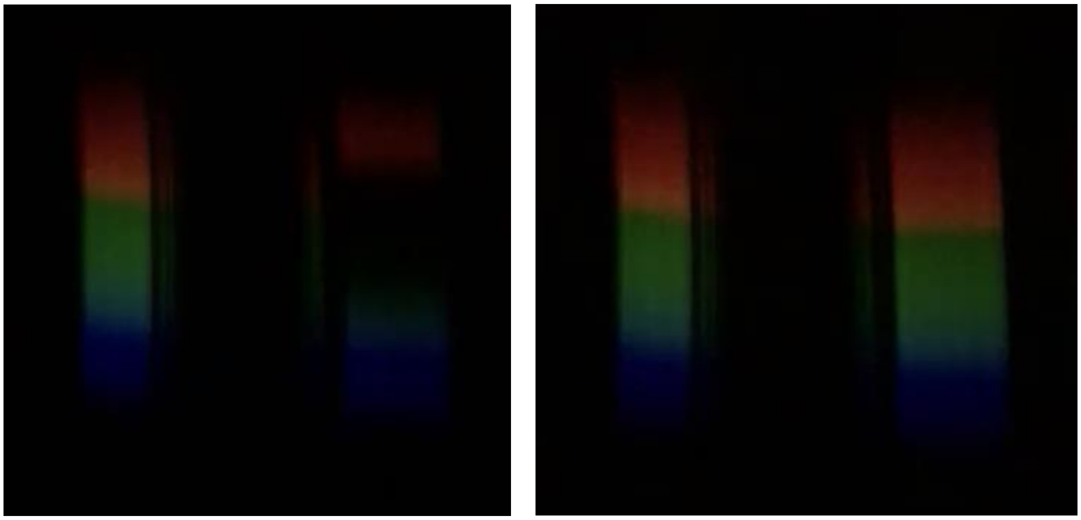

Fig. 4. Screenshots of the crystal violet reaction video at ~t_0 and t ~11.5 minutes, respectively. The crystal violet sample is in the right cuvette, with the water reference in the left cuvette. At t_0 it absorbs most of the light compared to the reference, while at t ~11.5 the purple color has faded and absorbs little to no light.

The video data were analyzed using MatLab software to give the relative intensities at the respective pixel positions, shown in **Figure 5A**. Any background subtraction or other corrections were then done before transferring the intensity data to obtain the absorption spectra (**Figure 5B)** using the relationship in **Eq. 2**, $A = \log\left(\frac{I_0}{I}\right)$. The spectra show a maximum at approximately pixel position 415. This could be corrected using MatLab to show the maximum absorbance in terms of nanometers. These spectral lines were then converted to give one curve using the rate of frames per minute for the camera. This absorbance curve is shown in **Figure 5C.** Finally, this curve was manipulated using the same rules of kinetics by graphing ln(A) versus time (**Figure 5D)**. The fit proved to be as expected, showing the reaction as first-order with respect to crystal violet as seen in the commercial spectrometric experiments. The time constant for the plot was found to be 0.363 min^{-1} with a standard deviation of 0.001066 min^{-1}. This value is comparable to the time constant of 0.288 min^{-1} from the commercial spectrometer.

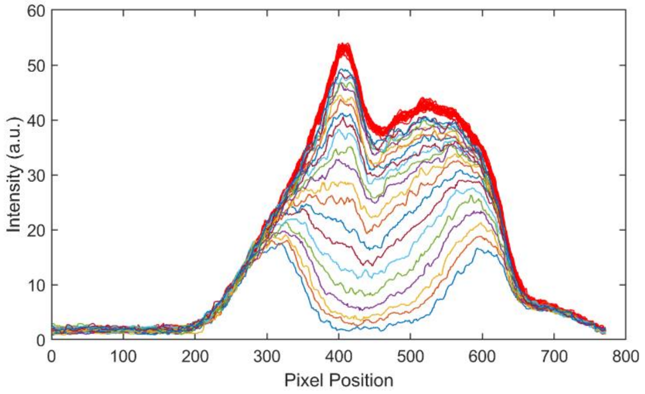

Fig. 5A. The resulting spectrographs from the 12-minute video are shown. A water sample is shown in the top (red) path, and the absorbing crystal violet solution in the bottom path.

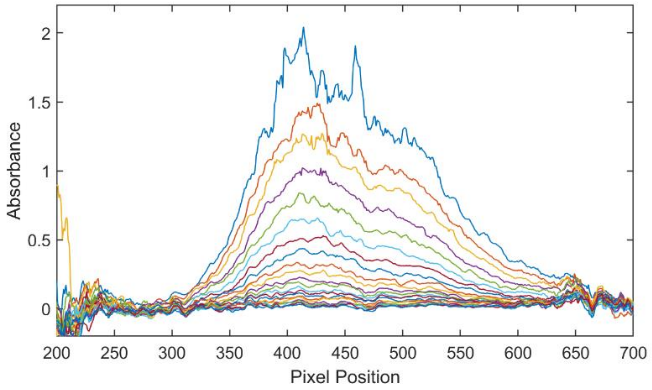

Fig. 5B. The absorption data for the crystal violet solution at each pixel position from the video, calculated from the intensity spectra in Fig. 4A.

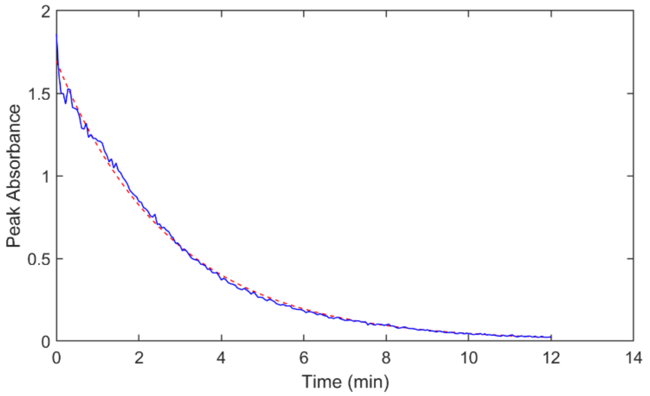

Fig. 5C The absorption decay curve plotted versus time, calculated from the absorption data in Fig. 4B.

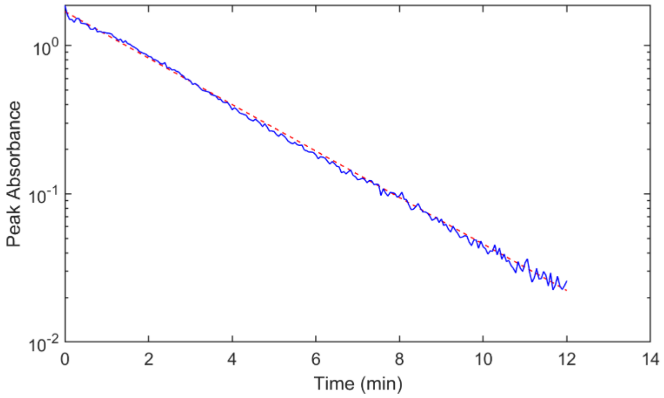

Fig. 5D Plot of ln(A) versus time, showing a first-order relationship with respect to crystal violet concentration and a time constant of 0.363 min^{-1}. y = -0.3633x + 0.5207

Literature values for the crystal violet time constant fell between 0.194 and 0.418 min^{-1}.[13,14] Both the commercial and DualSpec spectrometers gave constants that fell within this range. It should be noted that the smartphone camera attached to the DualSpec takes 30 frames of data per second, greatly surpassing the rate of the commercial instrument. This could have had an impact on the rate constant and caused the slight difference between the two values. Overall, it is extremely encouraging that the reaction rate with respect to crystal violet proved to be the same using both instruments, and even more so that the rate constants were comparable.

Conclusions

In high school science classrooms today, there is room for improvement regarding the amount and quality of experimental experiences provided to students. It has already been agreed that learning through experimentation is crucial for forming well-rounded scientists who can think analytical and draw conclusions on their own. As technology advances, there is a growing market for open-source chemical equipment that can be used for teaching fundamental concepts of chemistry to students before they reach college. This research sought to show that the DualSpec handheld 3D-printed smartphone spectrometer could be one such piece of equipment, and that it could be used to teach not only static concepts of spectroscopy such as the Beer-Lambert law, but chemical kinetics as well.

The commonly utilized crystal violet and sodium hydroxide reaction was used in this research to compare the quality of kinetics data taken on the DualSpec with that taken on a commercial-grade spectrophotometer. The Genesys6 spectrophotometer showed that the reaction was first order with respect to crystal violet with a rate constant of 0.288 (± 0.00279) min^{-1}. The DualSpec apparatus also showed that the reaction was first order with respect to crystal violet, with a rate constant of 0.363 (± 0.00107) min^{-1}. Both values fell within the range of 0.194 to 0.418 min^{-1} from literature.

This shows that for basic educational kinetics experiments, the DualSpec can be utilized to obtain spectroscopic data at or near the caliber of a commercial-grade spectrophotometer. This could very easily increase the accessibility of higher-level chemical experimentation in high schools, preparing students for college even more than ever before. Additionally, the DualSpec offers more opportunities for visual concept learning than a commercial spectrometer. The raw data is a unique learning aspect, because the videos allow real spectral color changes to be seen while the experiment proceeds. Students can consider the theory behind absorption, transmittance, and light intensity while they watch these quantities change in real-time. They also have the chance to learn how to 3D-print and run software such as MatLab, which are skills that could be leveraged in other areas of learning or future work. Overall, providing opensource 3D-printing files for the DualSpec allows anyone to be able to make their own low-cost, handheld spectrophotometer at home and use it to learn chemical kinetics.

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Appendix 1: Safety Considerations

Various considerations were made to ensure the safe and intended completion of these experiments for any person participating in them. Two of the most important considerations were in the handling of the 1% crystal violet solution and the sodium hydroxide, as well as the proper disposal of any waste.

The hazards listed for the crystal violet solution from the Safety Data Sheet (SDS) included acute toxicity, acute and chronic aquatic toxicity, carcinogenicity, and serious eye damage. Because of these hazards, preventative measures were taken to limit personal exposure to the solutions. Proper personal protective equipment was always worn in the lab. This included eye glasses with side shields, nitrile gloves, long pants, and closed toed shoes. These safety measures also sufficed to protect from skin irritation that can be caused by exposure to sodium hydroxide solutions. As an additional precaution, student researchers washed their hands at the end of every lab session.

Another consideration that was made during these experiments was the disposal of crystal violet solutions at the end of the experiments. Following the recommendations in the SDS, any unused crystal violet was treated with sodium hydroxide solution (~0.1 M) until the color disappeared. The resulting clear solution was treated with acetic acid until the pH was neutral, and the waste was discarded down the drain.