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Laboratory Experiment

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Decay Kinetics of UV-Sensitive Materials: An Introductory Chemistry Experiment

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S Supporting Information

ABSTRACT: First-order kinetic decay rates can be obtained by measuring the time-dependent reflection spectra of ultraviolet-sensitive objects as they returned from their excited, colored state back to the ground, colorless state. In this paper, a procedure is described which provides an innovative and unique twist on standard, undergraduate, kinetics experiments. Specifically, UV-sensitive beads and threads are utilized as the time changing system, as opposed to more conventional wet chemical systems. The spectral data is collected and analyzed by the students during a standard laboratory session, and the class results are pooled so that the reflection spectra and decay curves of all colors for both UV sensitive beads and threads can be compared. This new approach to a kinetics experiment increases student interest in a safe, inexpensive, and environmentally friendly way.

KEYWORDS: *First-Year Undergraduate/General, Laboratory Instruction, Hands-On Learning/Manipulatives, Kinetics, Spectroscopy*

INTRODUCTION

Kinetics experiments are often performed in high school chemistry classes or in second semester of college general chemistry courses. Traditional laboratory exercises often involve the mixing of two or more chemicals and then observing a time-dependent spectroscopic signal.[1−3] More novel ways of teaching introductory kinetics involve unusual systems such as light sticks,[4] candy,[5] or other common items.[6] In this experiment, UV sensitive beads and threads are utilized and they represent a system that is inexpensive, safe, environmentally friendly, and most importantly, fun and exciting for undergraduate students. UV sensitive beads and threads are objects which turn color in the presence of UV light but return to white when the UV source is removed.

This experiment consists of two general procedures. In the first, a fiber optically coupled SpectroVis Plus spectrometer is used to measure the reflection spectrum from an incandescent bulb off of a UV sensitive bead or thread, both in its excited (immediately after UV irradiation) and unexcited state (only incandescent illumination). The raw intensity data is exported into Excel, or a similar data analysis program, and is manipulated to yield a reflection spectrum of the object. Students will observe that the absorbed color is complementary to the color of the object.

The LoggerPro software package provided by Vernier is perfectly capable of performing the analysis. Exporting the data into Excel is optional, but students are largely more comfortable with Excel and it allows them to do the analysis on their own computer.

The second procedure consists of the kinetic runs, in which the object is irradiated by a UV lamp for 1 min and afterward the intensity of reflected incandescent light is measured as a function of time. The absorbance of visible light will slowly decrease as the item returns to the unexcited, colorless state. The data is again exported into Excel and processed to give the absorbance of the sample as a function of time. The decay process follows a first-order kinetics relationship, so a plot of the natural log of the time changing absorbance will produce a linear curve. The negative slope of this line is the decay rate constant for a specific color for either the UV-sensitive bead or thread. The recording of data and subsequent analysis takes only a few minutes, so multiple trials of different items may be performed in one laboratory session.

All of the UV-sensitive materials have their reflection spectra recorded and decay rates measured by assigning each pair of students a different color of bead or thread. The results of all groups are compiled so that the class can then analyze the larger data set. Students can then deduce if the beads and threads have the same dye molecules, and if any of the items contain a mixture of dyes.

The specific identity of the chromophores (dye molecules) is beyond the scope of this experiment, and generally are proprietary information. The dyes usually consist of two planar organic rings that are orthogonal in the unexcited state.[7] When excited by UV light, the rings become coplanar with a concomitant increase in the conjugation in the molecule. The long conjugation in the molecule causes the absorption of visible light. Once the excitation source is removed, the molecules relaxes slowly back to the orthogonal form. Without knowing the actual identity of the dye molecules, it is impossible to conclude with complete certainty if any dyes are the same between the two substrates or if any of the objects contain a mixture of dyes. However, items that have multiple absorbance maxima are thought to have multiple chromo-

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phores, and a comparison of decay rates to the other UV sensitive items can help confirm this hypothesis.

■ EXPERIMENTAL SECTION

This laboratory exercise uses UV-sensitive beads (Educational Innovations) and UV-sensitive thread (Solar Active). Each pair of students will analyze one bead color, and one thread color. To do this, they will use a Venier SpectroVis Plus spectrometer connected to a standard PC laptop capable of running the LoggerPro software and data analysis program such as Excel, and fiber optic detection system. Finally, an incandescent light source and UV light source (any UV−B (300−360 nm) lamp, such as Spectroline's medium wave E-Series lamps) are also needed, but multiple pairs of students can share the two light sources. Finally, a standard 1 cm^2 cuvette is used to calibrate the SpectraVis Plus; a plastic, disposable cuvette with DI water is appropriate for this.

For this experiment, students work in pairs as some of the physical manipulation involved in recording the data may be challenging for one person. However, initially students do a visual test of the UV-sensitive objects, and several pairs of students can perform this semiqualitative test simultaneously. Each pair of students then completes the rest of the lab independently.

Learning Outcomes

The student learning outcomes of this experiment are the following:

- To learn about visible reflection spectroscopy and complementary colors.
- To record kinetics data using a quick, safe, and inexpensive chemical system.
- To perform data analysis involving background subtraction, intensity to absorbance conversions, and first order decay plots.
- To support predicted outcomes with quantitative data.

Visual Test

Working in teams of four or six, the students place one of each of the five UV-sensitive beads under the UV lamp and switch on the lamp for 1 min. The beads will turn from white to their colored form. They then turn off the lamp and watch the beads slowly revert back to white. The students will record which reverts the quickest and slowest and how long they take using a timer. They repeat the process using the seven UV-sensitive threads.

Spectroscopic Data

Each pair of students is assigned one UV bead and thread color to monitor spectroscopically. The students mount the object (thread or bead) in a 3-fingered clamp. The fiber optic probe leading to the SpectroVis Plus spectrometer is held by another 3-fingered clamp and positioned a few inches away from the object in the same horizontal plane (Figure 1). The incandescent lamp is placed so the emitted light will reflect off the object and into the fiber optic probe. Finally, the UV light source is mounted above the object.

As this setup may not be intuitive to first-year students, a sample setup is created that the students can copy.

After starting the LoggerPro software, the students calibrate the spectrometer using a 1 cm^2 cuvette filled with DI water. The fiber optic probe is then inserted into the cuvette holder. The incandescent light is switched on, and the students observe the reflected spectrum being collected in real time. Small adjustments can be made to the position of the incandescent lamp or fiber optic probe to maximize the reflected light signal. Once a satisfactory spectrum of the unexcited sample is observed, it is saved and exported into Excel (Column A, Wavelength; Column B, Intensity) for later analysis.

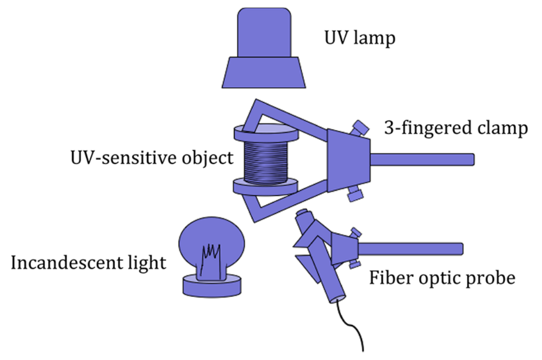

Figure 1. Experimental setup showing the UV-sensitive object (thread), fiber optic probe, and incandescent and UV light sources.

The UV lamp is then turned on, and the item is allowed to change color for 1 min. The UV lamp is then turned off, and with the incandescent lamp running, the reflection spectrum is quickly recorded before the color has faded too much. This new spectrum will show an intensity minimum at the color complementary to what is observed on the thread or bead (i.e., the red object will have a minimum at a blue wavelength). The low percent reflection indicates a high amount of absorbance at that wavelength, which gives rise to the characteristic color observed. This new reflection spectrum (excited state) is also exported into Excel (Column C). The wavelength and intensity values at the highly absorbance wavelength for both the excited and unexcited spectra are noted for later use. To convert the intensity measurements to a more familiar absorbance spectrum, unexcited spectrum (Column B) is divided by the UV excited spectrum (Column C) and the Log_{10} of this result is taken (Column D).

Note: The green and blue threads will show two minimum "peaks" in their reflection spectra (Figure 2). One pair of students should be assigned each peak for the next portion so that kinetics data is collected for both of them.

Kinetics Data

The spectrometer is then configured to record a time-dependent intensity at a single wavelength. The wavelength selected will correspond to the wavelength of minimum intensity in the absorbance spectrum. The UV lamp will be switched on for 1 min to excite the sample. The UV lamp is switched off, and with the incandescent lamp on, the time dependent intensity is measured for 2 min. The resulting data is exported into a new Excel spreadsheet (Column A, Time; Column B, Intensity).

To analyze the data as first-order decay kinetics, the time-dependent intensity values need to be converted into absorbance values. Dividing the intensity values by the reflected intensity of the unexcited sample at that same wavelength and multiplying by 100 gives the percent light reflected (results in Column C). Taking the $\log_{10}$ of the percent reflected value yields a more familiar absorbance (Column D).

Now it is possible to obtain rate constants by plotting the natural log of the absorbance (Ln of Column D) versus time, with the negative of the slope equaling the rate constant for the color decay process.

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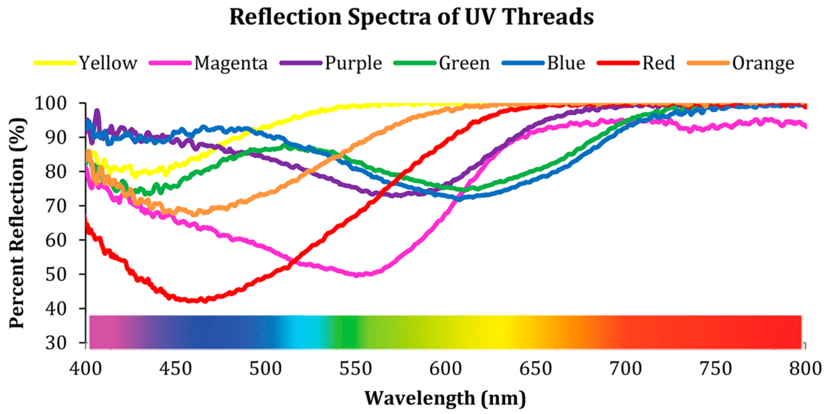

Figure 2. Reflection spectrum of the UV threads.

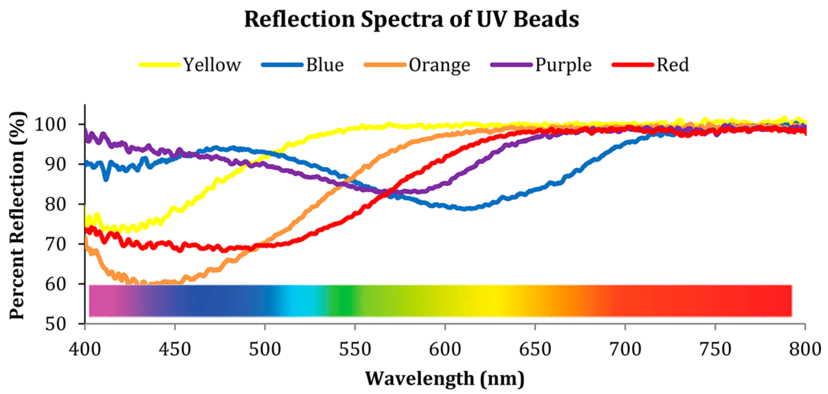

Figure 3. Reflection spectrum of the UV beads.

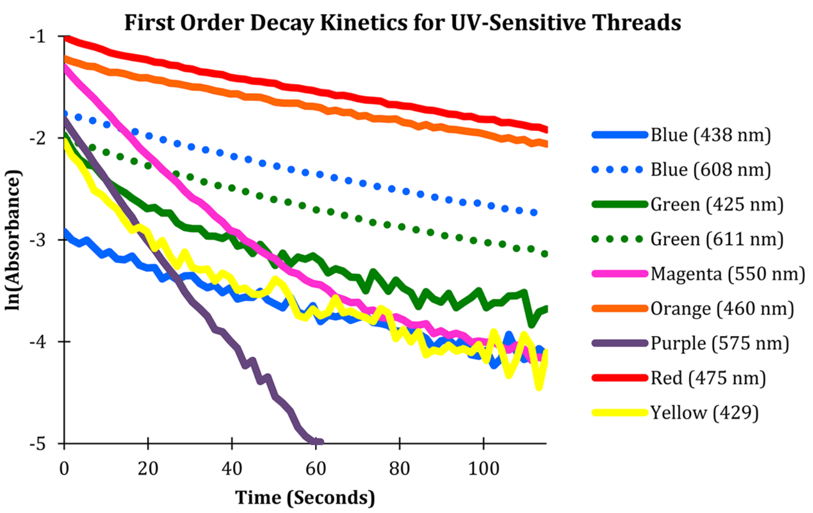

Figure 4. First-order decay curves for the UV threads.

The first trial and analysis will take roughly an hour, but all subsequent trials and their analysis will go much faster. Students should do three trials in a row for both bead and then thread. Each group enters its reflected absorbance spectrum and average rate constants for each object into a master spreadsheet that is made available to the class.

HAZARDS

Avoid prolonged exposure to the ultraviolet light source. All other materials are safe to use with reasonable precautions.

DISCUSSION

The results of the first visual analysis will depend on external factors such as the ambient lighting, and the student's ability for color perception. Commonly, the purple thread and bead will return to white the quickest, and the red and orange thread and bead are the slowest. The purpose of this exercise is to have the students witness for themselves what the spectrometer will be measuring, and to heighten their interest in the experiment by trying to predict the results.

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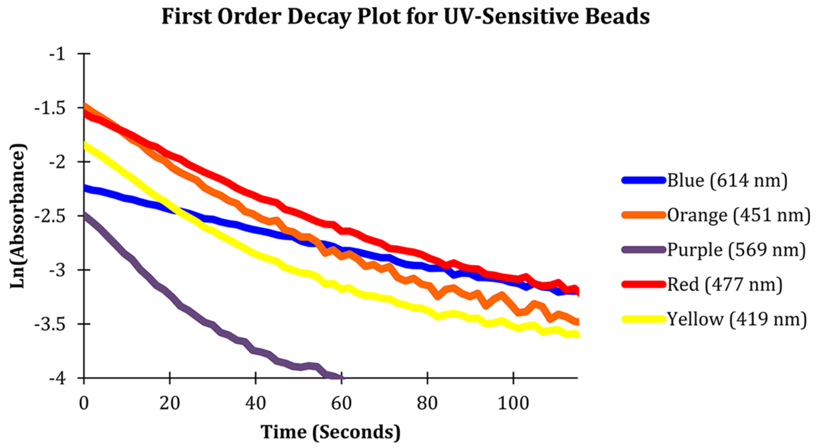

Figure 5. First-order decay curves for the UV beads.

The visible absorption spectra for both the threads and beads are shown below (Figures 2 and 3). For the UV threads, all the colors except green and the blue thread appear to have one reflection minimum, though some of the reflection minimum "peaks" are rather broad. At this point, the students could think that the green color is a combination of blue and yellow. On the basis of peak position and width, they may also speculate that the orange is mixture of red and yellow, due to its broad minimum that encompasses both of the other two colors. To confirm these combinations, the decay rates must be equal. For example, if the decay rate of the green thread at 610 nm is the same as the blue thread at the same wavelength, it would be reasonable to conclude that they have the same dye. An examination of the compiled class data will allow the students to make these conclusions.

Shown below are the decay curves for the threads and beads (Figures 4 and 5). A table of first-order decay rate constants for each item is also shown (Tables 1 and 2). The constants were obtained from a linear fit of the first 115 s of the decay curve, except for the purple object which were fit for only 60 s, due its rapid decay rate. The decay constants represent the averaged values of 3 trials, along with the standard deviation and percent deviation. A larger error is seen in measuring decay curves at lower wavelengths due to the decreased sensitivity of the spectrometers in that spectral region.

Table 1. UV Color-Changing Thread Decay Constant Analysis, Average of 3 Trials

Thread Color	Peak Wavelength,[a] nm	Decay Constant, 1/s	Standard Deviation	Relative Standard Deviation	Average *R*-Squared
Blue	438	0.0102	0.0011	11	0.914
Blue	607	0.0086	0.0022	26	0.997
Green	425	0.0129	0.0009	7	0.893
Green	611	0.0096	0.0017	18	0.988
Magenta	550	0.0242	0.0015	6	0.936
Orange	460	0.00700	0.00021	3	0.994
Purple	575	0.052	0.019	37	0.975
Red	475	0.0074	0.0009	12	0.992
Yellow	429	0.020	0.008	38	0.802

[a]Peak wavelength represents minima reflection wavelengths, as seen in Figure 2.

The first-order decay plots for some of the dyes do appear to be nonlinear, but this is most likely due to the weak absorbance signal at the longer decay times. Shorter decay times can be used for data collection for those items that exhibit this weaker absorbance signal (i.e., the magenta thread), or they could be omitted from the objects tested by a class section.

Table 2. UV Color-Changing Bead Decay Constant Analysis, Average of 3 Trials

Bead Color	Peak Wavelength,[a] nm	Decay Constant, 1/s	Standard Deviation	Relative Standard Deviation	Average *R*-Squared
Blue	614	0.0084	0.0023	27	0.990
Orange	451	0.017	0.004	24	0.953
Purple	569	0.0248	0.0019	8	0.952
Red	477	0.0142	0.0008	6	0.973
Yellow	419	0.0125	0.0022	18	0.869

[a]Peak wavelength represents minima reflection wavelengths, as seen in Figure 3.

From the decay graphs and tables of decay constants, it can be seen that the red and orange threads have nearly identical decay rates. It is very likely that they have the same dye molecule. The green thread being a combination of yellow and blue dyes is less convincing. While decay rate of the green at the longer wavelength is similar to the blue rate, there is a larger difference between the shorter wavelength decay rate and the yellow decay rate. This difference in rates is probably due to the reduced sensitivity of the spectrometer at the lower wavelengths. The reflection spectra show more noise at those wavelength values. It is the opinion of the authors that the green thread does contain a mixture of dyes seen in the blue and yellow threads.

Given the vastly different values for many of the same colors of threads and beads (only blue has a similar decay rate between the two substrates), and that the decay rates are not different by a constant amount, it can be argued that the two substrates have different dye molecules. It is not possible to draw any more definitive conclusions based on only the reflection spectra and decay rates. Any further determination is beyond the scope of this experiment.

■ CONCLUSION

UV-sensitive materials provide a quick, inexpensive, easy to use, and safe medium for kinetics experiments. Reflection spectroscopy is employed to monitor the decay of an absorption signal from the excited state. Spectral analysis and first-order kinetics

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rate constants allow students to qualitatively compare the dyes used in two different substrates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed instructions for the student, notes on setup and where to purchase UV-sensitive materials for the instructor, along with a set of sample data with analysis. 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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