

# Transient-Absorption Spectroscopy of Cis–Trans Isomerization of *N,N*-Dimethyl-4,4'-azodianiline with 3D-Printed Temperature-Controlled Sample Holder

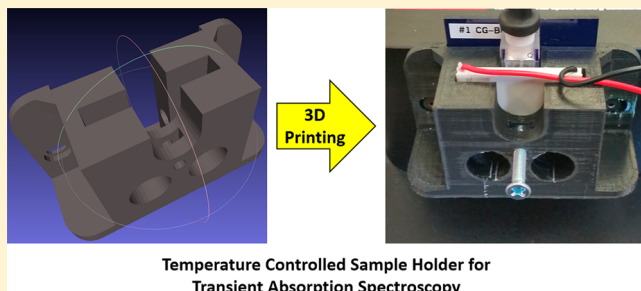
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**S** Supporting Information

**ABSTRACT:** The laboratory unit demonstrates a project-based approach to teaching physical chemistry laboratory where upper-division undergraduates carry out a transient-absorption experiment investigating the kinetics of cis–trans isomerization of *N,N*-dimethyl-4,4'-azodianiline. Students participate in modification of a standard flash-photolysis spectrometer by adding a temperature-controlled sample holder. The sample holder design is open-source and can be reproduced with the 3D-printing technology. Students build the experimental setup, perform the transient spectroscopy experiment, and analyze the obtained kinetics data to estimate the activation energy, enthalpy, entropy, and Gibbs free energy of cis–trans isomerization of *N,N*-dimethyl-4,4'-azodianiline.

**KEYWORDS:** Upper-Division Undergraduate, Physical Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Laboratory Equipment/Apparatus, Photochemistry, UV–Vis Spectroscopy



Temperature Controlled Sample Holder for Transient Absorption Spectroscopy

## INTRODUCTION

The proposed laboratory unit continues our work,<sup>1</sup> reported in this journal, on revising the Physical Chemistry Laboratory curriculum at Monmouth University. Our goal is to develop a project-based approach to teaching laboratory courses and integrate research projects into the curriculum. It has been shown that undergraduate research serves as a powerful teaching and curriculum development tool in addition to advancement of a faculty research program.<sup>2</sup> The present experiment is aimed to bring novel technologies into the undergraduate laboratory without oversimplifying or hiding chemical processes behind the technological advancements.<sup>1,3</sup>

### Azobenzenes Photoswitches

In the current experiment, kinetics of isomerization of *N,N*-dimethyl-4,4'-azodianiline (DMADA, Figure 1), which belongs to the class of azobenzenes, is investigated. Azobenzenes consist of two phenyl rings linked by an N=N double bond.

The lowest energy trans conformation is dominant in solution at room temperature. Irradiation with light induces photoisomerization of azobenzene to its high energy cis conformation around the N=N double bond. Over time, the molecule slowly returns back to its lowest energy trans isomer at the expense of thermal energy in the dark, or it can be switched back to its trans conformation with the light of a longer wavelength than the excitation wavelength. The two isomers have distinct molecular structures and, thus, different UV–vis spectra. Azobenzene photoswitches have photochromic properties. They may undergo the reversible change

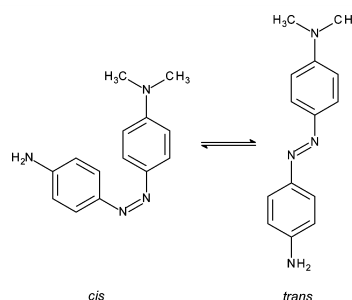
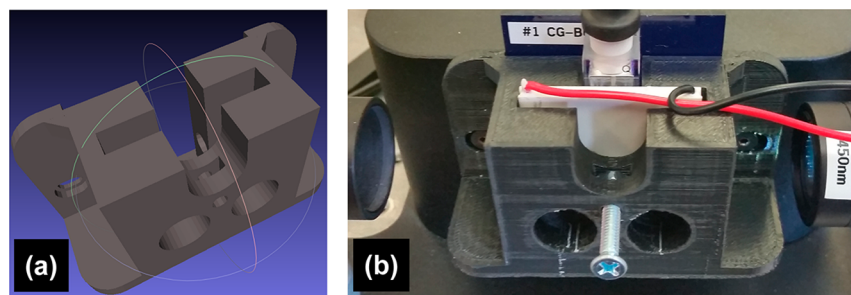


Figure 1. Cis and trans isomers of *N,N*-dimethyl-4,4'-azodianiline (DMADA).

of the UV–vis absorption spectrum under external stimulation with light. That feature enables applications of azobenzenes as photoswitches (PS) in neuroscience.<sup>4</sup> Azobenzene photoswitches covalently attached to ion channels of a live neuron act as photo controlled channel blockers. Upon the exposure to light, a PS undergoes photoisomerization, such that the PS blocking moiety opens or closes an ion channel pore. Neurons become directly sensitive to light that enables a real-time probing of cells, so that specific signaling events in neural networks can be detected and controlled.<sup>4</sup> Azo-based photochromic materials were also suggested for recording optical

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**Figure 2.** Temperature-controlled sample holder for transient-absorption experiments with flash-photolysis spectrometer: (a) 3D-model; (b) fully assembled unit.

information with two-photon fluorescence micropatterning.<sup>5</sup> Furthermore, azobenzenes are used in liquid crystal systems<sup>6</sup> and as nonlinear optical materials.<sup>7</sup>

### Transient-Absorption Spectroscopy

The kinetics of photoinduced isomerization of azobenzenes is investigated with transient-absorption spectroscopy in the presented laboratory unit. This type of spectroscopy measures the change in the light absorbance of a sample measured as a function of time following excitation of a sample with a pulse of light. The transient-absorption spectroscopy is often used to study kinetics of photochemical processes. These include ultrafast photochemical processes at pico- and femtosecond scales. Unlike ultrafast techniques that are not commonly available in an undergraduate laboratory, flash-photolysis spectrometers with Xe-flash pump and LED probe light sources, suitable for simple transient-spectroscopy experiments, offer more affordable options.<sup>8,9</sup>

### Isomerization of *N,N*-Dimethyl-4,4'-azodianiline

The advantage of DMADA as an example of a model photoswitch used in the proposed experiment is 2-fold: its transient absorption under cis–trans isomerization changes in visible spectral range, and time of isomerization is within the range of 1–25 s (depending on temperature). Thus, DMADA is an ideal model to study with an educational flash-photolysis spectrometer.<sup>9</sup>

In the presented experiment the trans form of DMADA in ethanol solution, being irradiated with an Xe-flash lamp pulse, is nearly instantly transformed into the cis conformation, and then it slowly transforms backward into the trans form. The kinetics of that backward cis-to-trans transformation is registered as a change of transient absorption of DMADA.

Measurements of the transient absorption change in the course of isomerization enables direct calculations of the rate of the isomerization process. However, if these kinetic measurements are performed at different temperatures, a deeper insight into the mechanism of DMADA isomerization is achieved. Students use the Arrhenius method to estimate activation energy and then evaluate enthalpy, entropy, and Gibbs free energy of activation based on kinetic measurements at different temperatures.<sup>10,11</sup>

### 3D-Printed Temperature-Controlled Sample Holder

A standard KRONOS flash-photolysis spectrometer used in the proposed experiment does not include an option for the temperature control of a sample. A recently proposed work-around, to equilibrate a sample in a thermal bath and then quickly transfer it to the spectrometer to take measurements at the desired temperature,<sup>11</sup> is not convenient for DMADA.

In order to take measurements at desired temperature, a temperature-controlled (TC) sample holder for a flash-photolysis spectrometer has been designed and built with a 3D-printing technology (Figure 2).

A TC sample holder can be made of standard plastic filaments on a 3D-printer. A source file for the holder design in freely available for use and modification in Supporting Information to this paper (Section S1). A TC sample holder can be assembled from readily available off-the-shelf components that include a 3D-printed body, Peltier thermoelectric element, and temperature sensor.

Applications of 3D-printing technology in chemical education has received attention recently. 3D-printing technology used for building and printing of physical models of molecules, orbitals, and potential energy surfaces has been reported in this journal.<sup>12–20</sup> In the present laboratory unit, we employ an approach where the design of a desired instrument or attachment is made available for a wide academic community and can be reproduced with 3D-printing technology. A similar approach to make a photocatalysis reactor<sup>21</sup> and spectrophotometer<sup>22</sup> with 3D-printing technology has been recently reported in this journal.

### Learning Outcomes

The laboratory unit offers students to solve a problem of measurement of activation parameters of isomerization of DMADA. In this laboratory experiment students formulate a problem, propose a solution, carry out the experiment, critically evaluate the obtained results, and propose improvements to the experimental setup. Upon completion of the laboratory unit, students learn how to assemble a TC sample holder and carry out a transient-absorption experiment with temperature control. Participating in this experiment, students apply their theoretical knowledge from chemical kinetics and transition state theory to estimate activation parameters of the isomerization reaction. The methods learned in this project can also be used by students to build laboratory instrumentation, to design advanced transient-absorption experiments, and to measure and evaluate thermodynamic functions based on spectroscopic measurements.

### MATERIALS

A detailed description of the required materials is given in Table S1. The access to 3D-printing service or a 3D-printer is required to make a TC sample holder. It is assumed that common undergraduate chemistry laboratory glassware needed for solution preparation is available. A brief summary of required materials is provided below:

- Flash photolysis spectrometer

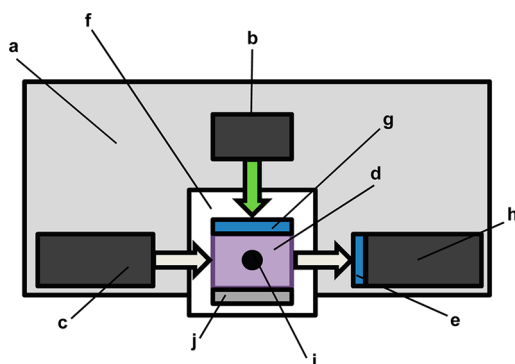
- Digital DC power supply 12 V
- Peltier thermoelectric element
- Temperature sensor
- Quartz cuvette with cap
- Wires and connectors
- Machine screw and nut
- Caliper
- DMADA
- Ethanol

## LABORATORY UNIT OVERVIEW

The detailed description of the transient-absorption experiment is given elsewhere,<sup>23</sup> and detailed laboratory procedures are provided in Section S2. A brief description of the experimental setup and procedures is given below.

### Transient-Absorption Experiment

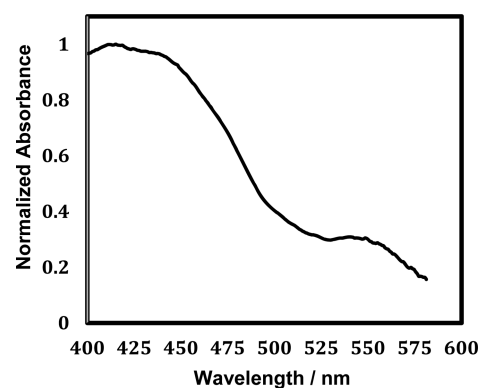
In the experiment, a sample of DMADA (concentration  $5.5 \times 10^{-5}$  M in ethanol) is placed in a 1 cm quartz cuvette. A flash-photolysis KRONOS spectrometer is used in this experiment. In the experimental setup (Figure 3), a sample is exposed to a



**Figure 3.** Scheme of the transient-absorption experiment with a TC sample holder: (a) flash-photolysis spectrometer; (b) Xe flash pump lamp; (c) white light LED probe; (d) cuvette with a sample; (e) optical interference filter (450 nm); (f) TC sample holder; (g) excitation bandpass color glass filter; (h) detector; (i) temperature sensor; (j) Peltier thermoelectric element; (h) detector.

flash of an Xe-pump lamp with a bandpass (350–600 nm) color glass filter. The spectral range for investigation of cis–trans isomerization of azobenzenes with transient-absorption has been previously established as 300–600 nm.<sup>23–25</sup> A white light continuous wave output LED and diode photodetector is used for probing transient-absorption at a fixed wavelength. The transient-absorption wavelength 450 nm is selected to maximize the signal-to-noise ratio with a standard set of optical interference filters supplied with the KRONOS spectrometer. Photoinduced transient cis-isomers of DMADA cause reduction of absorption at 450 nm as compared to absorption before flash excitation. Absorption at this wavelength is monitored over 25 s.

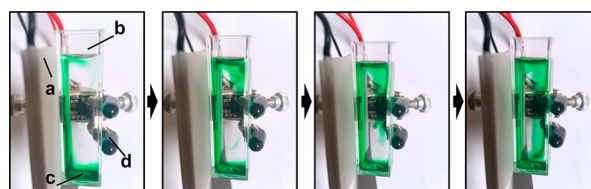
The kinetics of the transient absorption change associated with thermally induced cis–trans backward transition is collected with the KRONOS software, stored in a CSV file, and then analyzed. The maximum of steady state absorption of the trans form of DMADA at room temperature is close to 420 nm (Figure 4). An advantage of DMADA use in this experiment is determined by a significant transient absorption change for cis and trans forms at 450 nm.



**Figure 4.** Visible steady state absorption of the trans form of DMADA in ethanol at room temperature.

### Temperature-Controlled Sample Holder

Before building an actual TC sample holder, students have built a simple prototype which was not suitable for transient-absorption measurements, however, it helped students to the Peltier thermoelectric element and observe convection flows in the cuvette that affected the temperature distribution and solution mixing. A prototype TC sample holder (Figure 5) was assembled with a three-pronged clamp and Peltier element.



**Figure 5.** Convection flow in a prototype TC sample holder: (a) Peltier element; (b) cuvette; (c) green dye; (d) three-pronged clamp.

Students observed convection flows in a cuvette and were able to switch hot and cold sides of the Peltier element with switching its polarity. A common question asked by students was if heating of one vertical wall of the cuvette was sufficient to maintain the desired temperature in the entire volume of the sample. This question is related to transport properties of a sample solution.

In order to access this issue, a small amount of dye solution was injected with a syringe to the bottom of a cuvette with a sample (see Section S2 for complete details). Upon turning on the Peltier element, conventional flows can be seen in the cuvette (Figure 5). This simple experiment visualizes mixing of the sample and illustrates the mechanism of heat transfer in the cuvette. When students have gained conceptual understating of a prototype TC unit, they can start working with an actual TC sample holder.

### Building a TC Sample Holder with 3D-Printing Technology

A TC sample holder (Figure 2) with an excitation filter slot, sample compartment, Peltier element slot, and compression screw is made out of acrylonitrile butadiene styrene (ABS) black plastic on a 3D-printer (MakerBot Replicator 2X, 0.1 mm resolution). Before printing a TC sample holder, it is highly recommended to take measurements of all components (e.g., a Peltier element, cuvette, optical filters, mounting holes on the spectrometer used, machine screws, nuts, etc.) with a caliper with the precision of  $\pm 0.1$  mm. The 3D-design is created with

free online software TinkerCAD.<sup>26</sup> The software works in a web browser and does not require special training in computer-aided design (CAD) software. The printing process may take 6–12 h. So, a sample holder has to be made in advance. The TC sample holder design is first created by an instructor and then can be modified by students. An STL file that can be directly send to a 3D-printer is freely available for download and modification (Section S1). One can make adjustments to the design and print the final unit from ABS plastic. The TC sample holder is installed with two mounting screws to the KRONOS spectrometer, replacing the standard sample holder. The detailed instructions for assembly of the unit are given in Section S2.

Two research students worked over one semester for 1–2 h per week on the building of the experimental setup. Then, the experiment was integrated into the Physical Chemistry laboratory course.

We believe that the proposed approach to build an attachment for laboratory equipment with 3D-printing technology opens new opportunities for customization and production in-house equipment for undergraduate laboratory experiments beyond transient-absorption spectroscopy. For example, temperature control can be added to vibrational spectroscopy techniques, etc.

## HAZARDS

### Electrical Hazard

- Flash-photolysis spectrometer has an internal high-voltage power supply. Always follow safety instructions of the flash-photolysis spectrometer.
- Peltier thermoelectric element uses an outside power source (1–12 VDC). Electrical tape or thermo-shrink isolation should be used to insulate wire connections of the thermoelectric element.
- The experimental setup should not be installed in locations where flammable vapors or other easily ignitable materials are present.

### Fire Hazard

- Ethanol vapors are flammable. Properly seal the cuvette and stock solution flask. Immediately clean up any spills of ethanol. Remember, an electric spark may ignite ethanol vapors.
- Peltier thermoelectric element may overheat, burn, and cause a fire hazard if improperly used. Stay within the recommendations by the thermoelectric element specification values of allowed voltage and current. Never leave powered thermoelectric element unattended.

### Chemical Hazard

- DMADA may causes skin irritation, serious eye irritation, and respiratory irritation.
- When working with chemicals safety goggles, gloves, and a lab coat must be worn to prevent direct skin and eye contact.

## DESCRIPTION OF LABORATORY SESSIONS

There are two parts of the laboratory unit. In the first part, research students who were taking the Research in Chemistry course worked on the development of the presented experiment. The second part of the unit was integrated into the

Physical Chemistry Laboratory course and carried out by students taking the course. This approach is flexible and facilitates integration of project-based laboratory units into a traditional chemistry laboratory curriculum.

Two research students participated in the first part of the unit. The instructor created the initial design of a TC sample holder. Students assembled and adjusted the TC sample holder, made their suggestions, and implemented them (e.g., adjusted a temperature probe). Then, students prepared stock solutions and samples to be studied. Next, students studied the kinetics of isomerization with the experimental setup and determined the optimal collection time for given temperature.

The second part of the unit was carried out by 8 students taking the Physical Chemistry Laboratory course. The students worked in pairs. They were provided with a TC sample holder and stock solutions. The students had to prepare their samples and assemble and tune up the experimental setup. They recorded a visible steady-state absorption spectrum of a DMADA sample and studied the kinetics of the isomerization with the transient-absorption method. The experiment was carried out over one 3 h laboratory session.

## DATA ANALYSIS

Intensity of light passed through the sample is recorded as a time-series  $I(t)$  measured in mV. The absorption change  $\Delta A(t)$  at time  $t$  can be calculated as

$$\Delta A(t) = -\log \frac{I(t)}{I_0} \quad (1)$$

where  $I_0$  is the initial intensity before the excitation flash. The first order reaction kinetics model can be used to describe the isomerization process:

$$\Delta A(t) = A_f + (A_i - A_f)e^{-t/\tau} \quad (2)$$

where  $A_i$  is the initial absorption difference right after the flash,  $A_f$  is the final absorption when the kinetic curve levels-off, and  $\tau$  is the time-constant of the isomerization process. The exponential fitting is performed by students using Excel spreadsheet software with Solver add-in (standard Excel trendline tool is not suitable for this analysis). The detailed instructions for the exponential fitting are given in Section S3.

Based on estimated time-constants at different temperatures the Arrhenius equation and associated plot can be used to determine the activation energy ( $E_a$ ) of isomerization according to the equation:

$$k = \frac{1}{\tau} = Ae^{-E_a/RT} \quad (3)$$

where  $k$  is the rate constant of a reaction,  $R$  is the gas constant,  $T$  is the absolute temperature in Kelvin, and  $A$  is the pre-exponential Arrhenius factor. The activation enthalpy and entropy is calculated using the transition state theory:<sup>11</sup>

$$\Delta H^\ddagger = E_a - RT \quad (4a)$$

$$\Delta S^\ddagger = R \ln \left( \frac{hA}{ek_B T} \right) \quad (4b)$$

where  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are the activation enthalpy and entropy, respectively,  $e$  is the base of the natural logarithm,  $k_B$  is the Boltzmann constant,  $h$  is the Planck constant. The activation

enthalpy and entropy calculation eqs 4a and 4b are used to estimate the Gibbs free energy of activation ( $\Delta G^\ddagger$ ):

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (5)$$

## RESULTS AND DISCUSSION

Transient absorption at 450 nm of sample containing  $5.5 \times 10^{-5}$  M solution of DMADA in ethanol were collected over 28–55 °C temperature range. A sample transient-absorption curve is shown in Figure 6 (see also Section S5). The

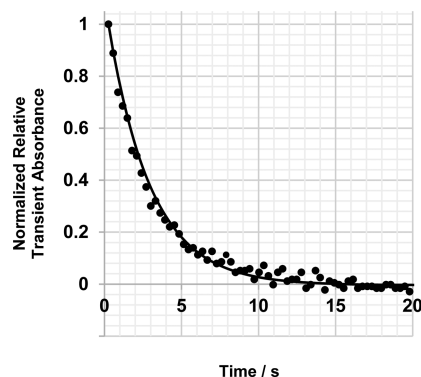


Figure 6. Sample measured transient-absorption kinetics (dots) and exponential fitting curve (solid line) at 47 °C.

temperature measurements used in the thermodynamics analysis are obtained as direct readings of the temperature probe during the kinetic measurement. An average of 6 measurements with duration of 25 s were obtained at each temperature.

The corresponding sample Arrhenius plot is shown in Figure 7. The data analysis gives the averaged values of the standard

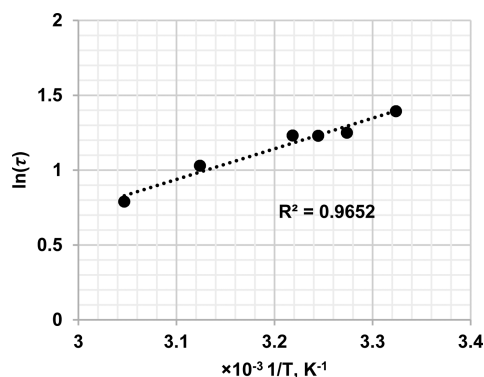


Figure 7. Arrhenius plot shows sample analysis of kinetic measurements used to determine the activation energy and pre-exponential factor.

activation energy  $3.82 \pm 0.57$  kcal/mol, activation enthalpy  $3.2 \pm 0.6$  kcal/mol, activation entropy  $-52.6 \pm 3.5$  cal/(mol K), and activation Gibbs free energy  $18.9 \pm 1.1$  kcal/mol. The results can be qualitatively classified as an endothermic step of the isomerization, based on positive values of enthalpy and Gibbs free energy. This step corresponds to the transition to a sterically restricted transition state structure, which is reflected by the negative estimated value of the activation entropy.

The activation parameters are close to those previously reported<sup>25</sup> for a series of polyhydroxy-substituted azobenzenes

in ethanol:  $\Delta H^\ddagger = 3.6$ – $22.7$  kcal/mol and  $\Delta S^\ddagger = -6.0$  to  $-44.5$  cal/(mol K). The structural differences of DMADA and polyhydroxy-substituted azobenzenes may explain the differences in the activation parameters.

Based on in-class observations, interviews with students, and their laboratory reports it has been found that building and adjusting the TC sample holder was the most engaging part of the laboratory unit for many students. Some students were excited with the opportunity to design the equipment while others asked for more directions from the instructor on how to complete the assignment. The measurements of kinetic curves were more as a standard chemistry laboratory and students were well prepared for this assignment. The most challenging step that required the most effort from the students was the data analysis. Students completed nonlinear fitting of kinetic curves using the proposed procedure. However, they had to make an assessment of obtained results in terms of nature of the activation process under study. On multiple occasions students sought for the instructor's help and had to go back to their lecture notes in order to rationalize the obtained results or repeat the calculations if the data analysis was performed incorrectly. It was observed that successful completion of the data analysis depended primarily on the level of preparation of a student in the associated lecture course.

## CONCLUSIONS

The proposed laboratory unit was carried out initially by undergraduate research students and then integrated into the standard Physical Chemistry Laboratory curriculum. The experiment provides students with hands-on experience in designing, building, and experimenting with laboratory equipment. Students specifically acquired working skills in transient-absorption spectroscopy and investigation of the cis-trans isomerization kinetics process of DMADA. Furthermore, students get practice in manipulations with the results of measurements that include nonlinear fitting and estimation of rates and time-constants of the cis-trans isomerization of DMADA. Also, students reinforce their knowledge learned at the Physical Chemistry lecture course on transport properties of solutions, chemical kinetics, and the Arrhenius method.

This experiment integrated into the Physical Chemistry laboratory curriculum provides a project-based approach to teaching laboratories when multiple stages of the experiment are accomplished by students over the course of multiple weeks. The development and preparation of the experiment by research students and execution of the experiment by the entire Physical Chemistry class provides a flexibility and is advantageous for the integration of new laboratory units into the traditional physical chemistry curriculum.

The use of 3D-printing technology provides means for a fast and inexpensive way to build and share new laboratory equipment to design new or improve existing experiments in an undergraduate laboratory. In this approach, improvements and modifications to laboratory units can be developed and shared with a broader academic community.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00121.

Detailed materials list, design of the TC sample holder, experimental procedures, and datasheet are provided (PDF, DOCX)

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### Notes

The authors declare no competing financial interest.

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