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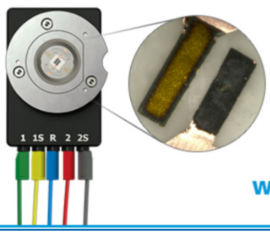

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A Thermoelectric Temperature Control Module for a Portable Fluorescent Sensing Platform

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Fluorescent portable monitoring systems provide real-time and on-site analysis of a sample solution, avoiding transportation delays and solution degradation. However, some applications, such as environmental monitoring of bodies of water with algae pollution, rely on the temperature control that off-site systems provide for adequate solution results. The goal of this research is the development of a temperature stabilization module for a portable fluorescent sensing platform, which is necessary to prevent inaccurate results. Using a Peltier device-based system, the module heats/cools a solution through digital-to-analog control of the current, using three surface-mounted temperature modules attached to a copper cuvette holder, which is directly attached to the Peltier device. This system utilizes an in-house algorithm for control, which effectively minimizes temperature overshooting when a change is enacted. Finally, with the use of a sample fluorescent dye, Rhodamine B, the system's controllability is highlighted through the monitoring of Rhodamine B's fluorescence emission decrease as the solution temperature increases.
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Fluorescent detection has become one of the most widely used methods in understanding the vitality of bodies of water in regions affected by pollution, whether from natural or manmade sources. However, in order to effectively interpret the status of the environment, scientists often collect samples and return to their labs to process, sacrificing time and the vitality of the samples as a function of the distance travelled and the travelling conditions. Moreover, on-site detection methods, although effective, are subject to environmental factors on which fluorescent detection is dependent, such as temperature. In a continuation of the development of a portable fluorescent sensor platform discussed in Refs. 1, 2, the development of a temperature stabilization module to ensure controllability of environmental factors in on-site monitoring is explored. This is a problem in fluorescence, especially in the chemical compounds that lose fluorescence as the temperature changes, such is the case with some algae and cyanobacteria. Many algae species, such as the cyanobacteria *Spirulina*, are subject to changes in behavior, such as decreased fluorescence, at different temperatures.[3] Chemiluminescence, which is the effect of chemical reactions that release photons, also suffer from temperature dependence, as also reported with electrogenerated chemiluminescence of $Ru(bpy)_3^{2+}$.[4]

There are two types of fluorescent measurement implementations: on-site and laboratory-based testing. The laboratory-based monitoring systems are mostly bulky and expensive, requiring researchers to tow their specimens to an off-site location for analysis. This is inefficient and can result in the loss of viable samples as time is sacrificed in transportation, which can result in further degradation to the body of the sample already in question. Portable fluorometers, on the other hand, currently lack much needed controllability of sample temperatures, resulting in inaccurate reporting.

To analyze a sample's fluorescence, a wavelength of excitation, which is particular to the substance, is shone at the sample. Fluorescence occurs following the absorption of a photon, which excites the molecule into an excited state, as seen in Fig. 1. Fluorescence is emitted during the vibrational relaxation process, where the molecule losses energy and the excess vibrational energy is converted to heat.[5] Depending on how temperature sensitive a solution is, heat may yield inaccurate results and decrease the fluorescence. Temperature is critical to monitor in these on-site solutions to ensure that time is conserved, and accurate findings are reported. In this work, a custom-made copper cuvette holder is proposed, joined with a temperature controller platform using a Peltier device for stable reading of fluorescence emission from on-site solutions to combat inaccurate temperature-sensitive solutions. To validate the system's efficiency in temperature control, Rhodamine B, which is one of the widely used fluorescence standards and probes in bioscience, is used.[6] Fluorescence dyes are widely used in biomolecule detection/quantification, flow tracing reference for gases and liquids, pathogen detection, and other life science applications.[7–10] However, fluorescence emission efficiency of the dyes is easily affected by several parameters, such as temperature. Therefore, it is essential to monitor and control these parameters for reliable and accurate measurements, as shown with this device.

Design and Experiments

System components.—For the development of the temperature stabilization module, a novel method for a lightweight, compact, and power-conservative module is designed. Controllability in over both heating and cooling of the system allows the solution's temperature to be a controlled variable. The system consists of ten major components in its current state, as highlighted in Fig. 2. The major components of this system are described below.

Quartz cuvette.—The quartz cuvette can hold up to 30 ml of solution. Quartz was selected due its low heat capacity and wide range of optical transparency for the wavelength between 190 and 2500 nm.

Copper cuvette holder.—A copper cuvette holder was manufactured with combination of 3D-printing and resin casting technologies (i.materialise, Belgium). First, the holder was 3D-printed with a resin that melts under certain temperature condition. The 3D-printed resin model was then placed in the plater mold to create the cavity for the copper casting. After removing the resin within the plaster by applying heat, the molten copper was poured back in to fill the cavities left in the plaster. Finally, the plaster is cooled and broken up to extract the copper model out. For the material, copper was selected due to the relatively high thermal conductivity (399 W/(m-K)).

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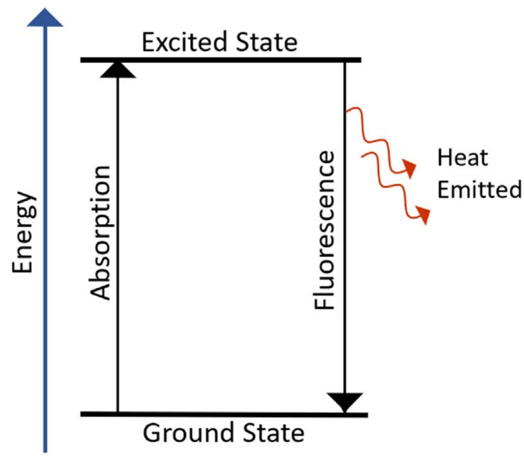

Figure 1. An overview of the process of fluorescence. Here, a molecule absorbs some energy, which elevates the molecule to an excited state. As the molecule relaxes to the lowest vibrational state, it emits heat. Then, the molecule will emit both florescence and heat as it returns to the ground state.

Temperature monitoring printed circuit board (PCB) module.—For the temperature monitoring of the copper body, digital temperature IC sensor, MCP9808 (Microchip Technology, USA), was used. It was selected due to several benefits such as small formfactor (3 mm × 3 mm), low power consumption (active mode: 0.66 mW sleep^{-1} mode: 0.33 μW), and ease of use. The sensor provides the temperature detection capacity in the range of −20 °C < T < + 100 °C with ±0.25 °C accuracy. For the communication protocol, the sensor has industry standard 2-wire, SMBus/I2C compatible serial interface with 400 kHz speed. A custom-designed PCB boards were used to solder the surface-mount device (SMD) temperature sensors for a compact design. Three surface-mounted temperature modules were attached via silver epoxy to the surface of the copper holder to monitor the temperature of three different regions of its body. The measured values through these digital temperature sensors were cross-validated with a type K thermocouple attached directly on the surface of the holder body, and the temperature variations between two types of sensors were below 1 °C.

Infrared (IR) temperature sensor.—An IR temperature sensor (MLX90614, Melexis, Belgium) was mounted above the quartz cuvette for contactless temperature monitoring of the sample solution. The sensor provides the temperature detection capacity in the range of −20 °C < T < +120 °C with ±0.14 °C accuracy and 5° of field of view (FOV). Conventional temperature controlling systems may fail to measure an accurate temperature reading of the solution in the cuvette because the sensors are only reporting the temperatures of the heating element or the metal holder body. Therefore, the IR temperature sensor was selected to directly monitor the solution temperature for the higher accuracy. The temperature reading of the solution was cross validated with a waterproof digital temperature sensor (DS18B20, Adafruit Industries, USA), and the variations between two sensors were below 1 °C.

Peltier device.—A thermoelectric device, specifically a Peltier device (71035–506, Laird Thermal Systems, USA), is attached to the bottom portion of the copper cuvette holder. The Peltier device allows maximum power of 4.4 W with 2.1 A of drive current and the maximum temperature difference between the hot and cold sides is 67 °C (@ 25 °C). The Peltier device was controlled with a microcontroller and a temperature stabilization algorithm.

Peltier current controller.—An LED driver IC (AL8843SP-13, Diodes Incorporated, USA) was selected to supply constant current to our Peltier device with ±4% output accuracy. The output current can be adjusted linearly by applying the voltage to the control pin in the range of 0–2.5 V. A digital-to-analog (DAC) module (MCP4725, Microchip, USA) was utilized to offer 12-bit digital steps of resolution (1.22 mV bit^{-1}) with an output voltage range of 0 to 5 volts. The maximum output current of the IC was determined by an external sensing resistor. An H-bridge circuit was utilized to switch the polarity of current applied to the Peltier.

Magnetic stirrer module.—In order to offer a rapid horizontal and vertical mixing of the solution, simple DC motor (3 V, 6600 rpm) was assembled with a 3D-printed housing and a magnet to fabricate a stirrer module. The speed of DC motor was controlled by PWM signal generated from a microcontroller and the module was placed underneath the quartz cuvette. For the mixer, disposable PTFE-based magnetic bars (6 mm × 3 mm) were selected.

Water coolant system (water-cooling block, water-reservoir, cooling fan with radiator, and pump).—When a Peltier device is being used to lower the temperature of the solution, the temperature of the opposite side of the device will increase since the heat

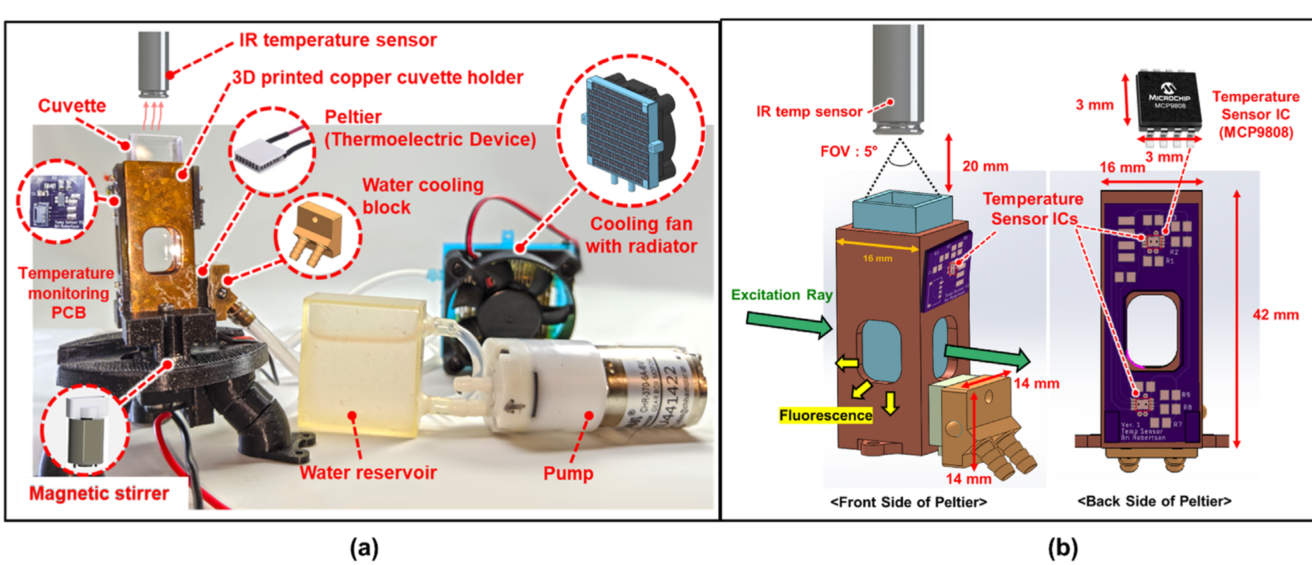

Figure 2. Schematic illustration and photograph of the fabricated thermoelectric temperature control module: (a) Images of the module with an exploded view of each component and (b) Illustrations of the temperature monitoring IR sensor and a temperature sensor IC.

(or charge) is being moved from the cold side to the hot side. To protect the device from being damaged from the excessive heat, it requires a proper cooling system.[10] A water-cooling system was selected over the air-cooling system to provide design flexibility for the end users. The pump pushes water through the water-cooling block (copper), which removes heat collected on the side of the Peltier device. The heated water is then pumped into the radiator with the fan to lower the water temperature. Later the cooled water is pumped into the 3D-printed water reservoir to get pumped back to the cooling block.

To achieve controllability, an in-house temperature stabilization algorithm, depicted in Fig. 3, was developed with a microcontroller-based system, linearly controlling the output of the current through a Peltier current controller and a DAC control module with 12-bit digital steps of resolution, which gives a current resolution of approximately 1 mA per bit. The current supplied to the Peltier device is in the range of 0–1.8 A at room temperature (25 °C). In Fig. 4, the output of the DAC module to the current measured flowing through the Peltier device is compared. A strong linear relationship of the digital control voltage and the current through the Peltier device yields controllability over how quickly the solution changes temperature, which is an essential component of developing an algorithm that adequately reacts to an external stimulus (user inputted temperature T_d, ambient temperature change) that requires a temperature change. Monitoring the ambient temperature is essential in understanding the range of temperature for a system, for the cold side of the Peltier module is dependent on the ambient temperature.[11]

The algorithm operating the Peltier system is based on the amount of current required to raise the temperature in some amount of time, with aims to minimize power consumption. For this application, the quickest amount of time to change the temperature is selected, but time remains an input to the algorithm. Temperature is checked every half second, thus allowing continuous monitoring of the solution and system stabilization points. The temperature is declared stable when the temperature remains at $T_d \pm 0.25$ °C. Since the bottom of the copper cuvette heats/cools quicker than the rest of the cuvette due to proximity to the Peltier device, overshooting is prevented through monitoring the difference between ambient and Back Bottom temperatures, and accounting for that difference in the algorithm.

As the current supplied to the Peltier device increases, the rate of temperature change increases. This algorithm design aims to reduce power consumption through determining what output current will be sufficient to achieve temperature stabilization in the quickest time possible while limiting overshoot. Since this method approaches the current output problem in a similar way to pulse-width modulation (PWM), a degradation to Peltier performance is not expected.[11]

Fluorescence Performance

The module's performance is tested by stabilizing the temperature of Rhodamine B, a common temperature-dependent fluorophore widely used in environmental monitoring.[6] For excitation, $\lambda_{ex} = 553$ nm was utilized for stimulating the Rhodamine B. The Peltier device was controlled with different levels of direct current (DC) to demonstrate the temperature controlling capability of the device, and fluorescence efficiency of the Rhodamine B was tested with a varying temperature level: 25 °C to 55 °C. For our device, the temperature is monitored by temperature sensors that are attached at three different points of the copper body for uniform temperature heating of the solution in the copper cuvette. Using these three temperature sensors, the uniformity of the temperature across the copper cuvette holder indicates that the temperature is maintained within 1 °C. The solution temperature is monitored directly with the use of an infrared temperature sensor positioned down at the opening of the cuvette. A type K thermocouple monitors the ambient temperature. An analysis of several different temperature components of the device allows for a better interpretation of what is happening in the system. Moreover, when cooling the solution, the implementation of a water-cooling apparatus allows for a way to lower the temperature of the opposite side of the Peltier, preventing the device from being destroyed. These features allow for the sample to be monitored efficiently, allowing for proper stabilization techniques and the ability to fluctuate the temperature when required of an application.

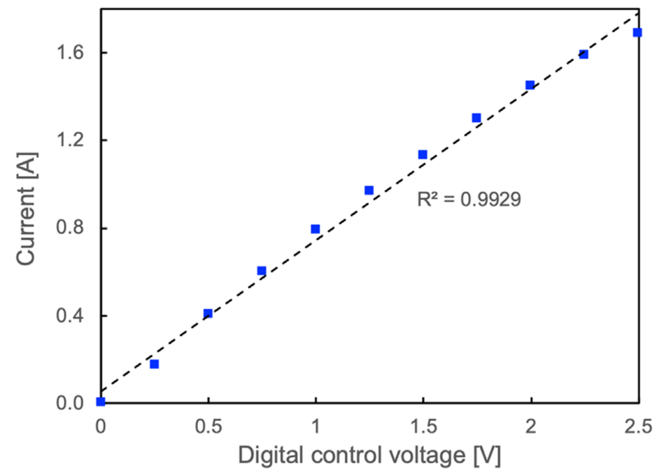

Figure 4. The current across the Peltier device is directly related to the digital control voltage, which is in the range of 0–2.5 V.

Results and Discussion

In Fig. 5, the temperature distribution across the copper cuvette is illustrated at stabilization. One concern for the module was uneven temperature distribution of solution at stabilization; however, not much variance (<2 °C) was observed, but higher solution temperatures (>55 °C) were subject to non-uniformity in the temperature profile of the copper cuvette. As the temperature difference between the ambient temperature and the desired temperature increases, the Peltier device struggles with maintaining the temperature because the temperature difference between the two junctions decreases.[11]

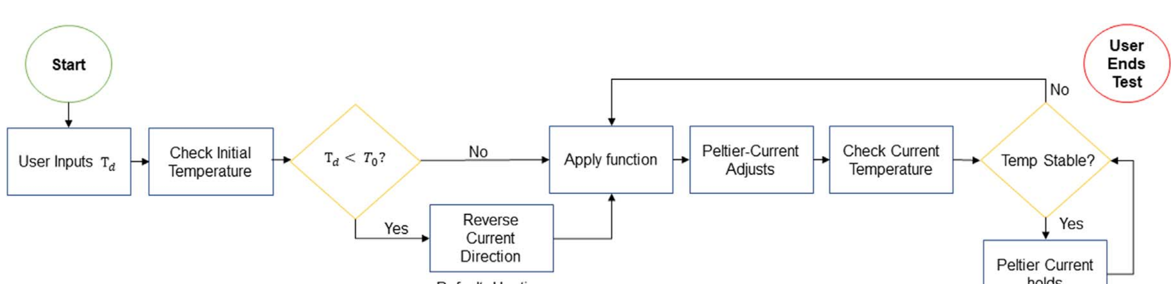

Figure 3. Algorithm flowchart illustrating the stabiliztion process.

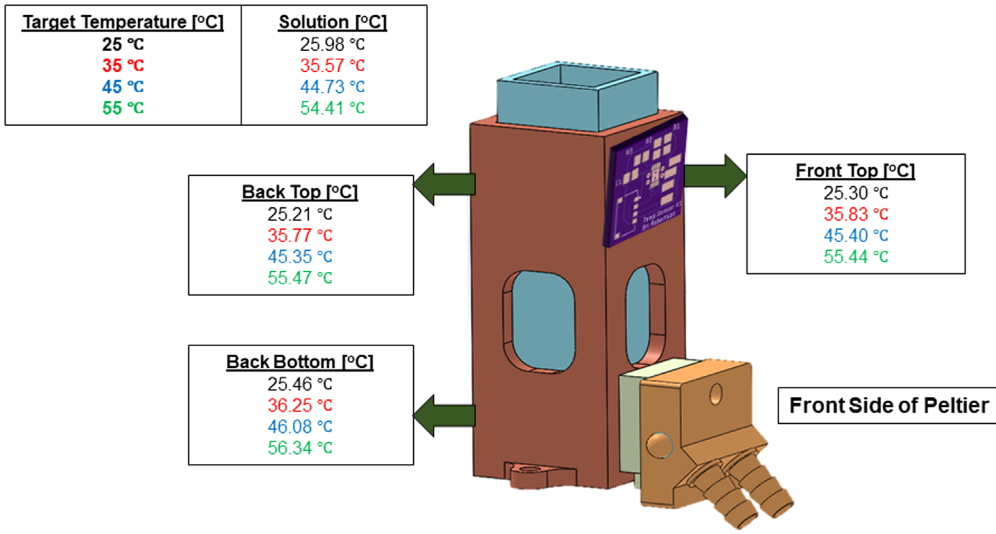

Figure 5. Copper cuvette illustrated with distribution of temperature in stabilized region.

Before a solution reaches stabilization, the copper cuvette does have a temperature disparity between the Back-Bottom sensor and the Back-Top sensor, which is utilized in the temperature algorithm to prevent overheating the solution. The disparity is caused from the amount of surface area that the Peltier device shares with the bottom sensor. There is a possibility of non-uniformity in the solution temperature; however, the module employs a magnetic stirrer, internal to the solution cuvette, to induce a convection current to equally disperse the temperature.

To demonstrate the controllability of the temperature stabilization module, the device's stabilization is assessed from 20 °C to 50 °C in 10 °C steps at room temperature. In the heating direction, the solution temperature changes at a rate of approximately 4 °C per minute. In the cooling direction, this is reduced to 3 °C per minute. In Fig. 6, the solution temperature response is illustrated, and the current applied to achieve stabilization is pictured below each experiment. After the user inputted T_d, the device determined the output current necessary to achieve the temperature, limiting overshoot of T_d. The region of stabilization is defined as the point when a second current push was initialized, with good stabilization defined as being within 1 °C of T_d. Furthermore, in Fig. 6, progressing from (a) to (d), the current fluctuations after the initial surge depict almost a "dampening" effect, which is indicative of the algorithm finding the correct current level to sustain stabilization. As the difference between T_d and ambient temperature increases, the current level at stabilization increases, which indicates that larger temperatures require more power for stabilization at long durations.

Another important factor of the module is the power consumption for each test case. For each of these tests in Fig. 6, the total power consumption in Watt-hours or Wh is indicated in Table I. The device will employ a battery with 26,800 mAh with an output voltage of 3.7 V, with a capacity of 96.48 Wh. This indicates that with a field-deployable setup, the device can perform a total of 311 temperature-controlled tests that average 0.241 Wh per test. This average was computed over the power consumption values in Table I. However, one note to mention is that cooling the solution is more difficult that heating the solution, which is seen in the 20 °C versus the 30 °C case. If the user plans to only cool a solution, the number of possible tests done in a field setting is expected to decrease. The power consumption during a test is dependent on the change of temperature required and the number of temperature changes required for a test to be complete. The power consumption can be minimized by applying a thermal insulation coating on the surface of the copper cuvette holder. Moreover, the surface coating will offer faster cooling and heating time with more stable temperature profile of the copper body.

High Ambient Temperature Performance

Figure 7 shows the device's ability to remain in the stabilized region of 25 °C despite an ambient temperature of 46 °C, selected as the sustained ambient temperature due to being the highest recorded temperature in the state of Louisiana at the time writing this article.[12] The ambient temperature sustained decreased by 1 °C prior to running the stabilization test due a change in setup, which released heat from the chamber which represented the environment. A change in the device's ability to stabilize temperature despite an increased environmental temperature was not observed. Although the ambient temperature was high, the region of stabilization still existed within ±1 °C.

Rhodamine B Fluorescence Test

For analyzing the temperature stabilization module's viability for fluorophore analysis, the temperature dependency of Rhodamine B at five different temperatures is analyzed, as seen in Fig. 8. The solution is dissolved in methanol with a 5 μg ml^{-1} concentration. One concern was the ability to sustain the temperature of a methanol solution despite the vapor pressure, but due to the device's ability to quickly reach T_d, a significant loss of solution from evaporation due to the increased temperature is not observed. The excitation of $\lambda_{ex} =$ 553 nm resulted in a $\lambda_{em,peak} =$ 577 nm emission. Fluorescence emission spectra show a linear degradation as the temperature increases (Fig. 8). With a 30 °C change, the fluorescence emission drops to ~0.6 of its original value. This degradation on par with what literature has reported, where a 30 °C change leaves ~0.5 of original fluorescence emission yield.[6] The linear response of Rhodamine B's fluorescence highlights the modules ability to maintain the temperature of a solution until the test is completed.

The performance of the temperature stabilization module is illustrated, indicating its viability for on-site analysis of florescent solutions. Although the Peltier device does yield uneven temperature distribution in the heating/cooling process, once the solution's temperature stabilized, the average temperature distribution across the copper cuvette holder is restricted to <2 °C. This indicates that the solution temperature is uniform, which is further illustrated in Fig. 6, where the current's response at stabilization suggests that the device can limit temperature fluctuations in the solution, even at high ambient temperatures.

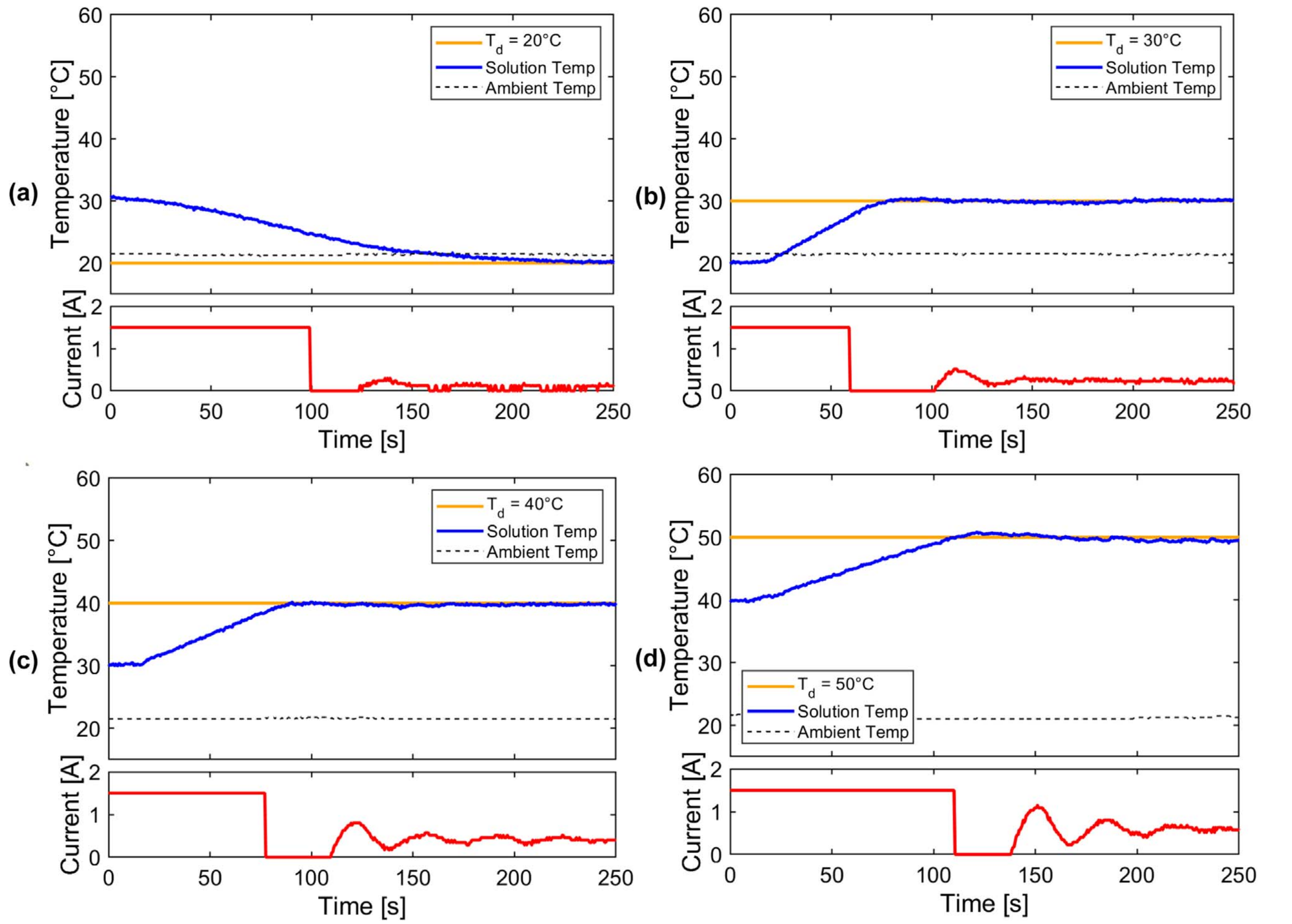

Figure 6. Temperature and current response to changing the target temperature such that (a) T_d = 20 °C achieving final stabilization of 20.98 ± 0.05 °C; (b) T_d = 30 °C achieving final stabilization of 29.96 ± 0.01 °C; (c) T_d = 40 °C achieving final stabilization of 39.74 ± 0.01 °C, and (d) T_d = 50 °C achieving final stabilization of 49.72 ± 0.02 °C. Note in (a) that initial solution temperature was heated to illustrate system's cooling control.

Table I. Power consumption in Wh for each trial case from Fig. 6. Each experiment ran for 250 s.

Temperature [°C]	Power Consumption [Wh]
20	0.26
30	0.22
40	0.32
50	0.42

Conclusions

The development of a temperature stabilization module for a portable fluorescent sensing platform was accomplished through a careful consideration of components, controllability, and power consumption. The implementation of the Peltier device, accompanied with a copper cuvette holder and several temperature sensors, achieved real-time temperature control with power considerations that are well within the capabilities of a portable battery. With the utilization of an in-house algorithm, we were able to achieve the temperature of a solution within ±1 °C of user-inputted temperature, with overshoot risk mitigated with examination of temperature distribution across the copper cuvette holder. Even in locations with high environmental temperatures, the experiment results show that temperature stabilization remains a viable option for solution testing. The effectiveness of the module at stabilization was also demonstrated through the fluorescence emission of Rhodamine B, which highlights both the controllability of solution temperature and

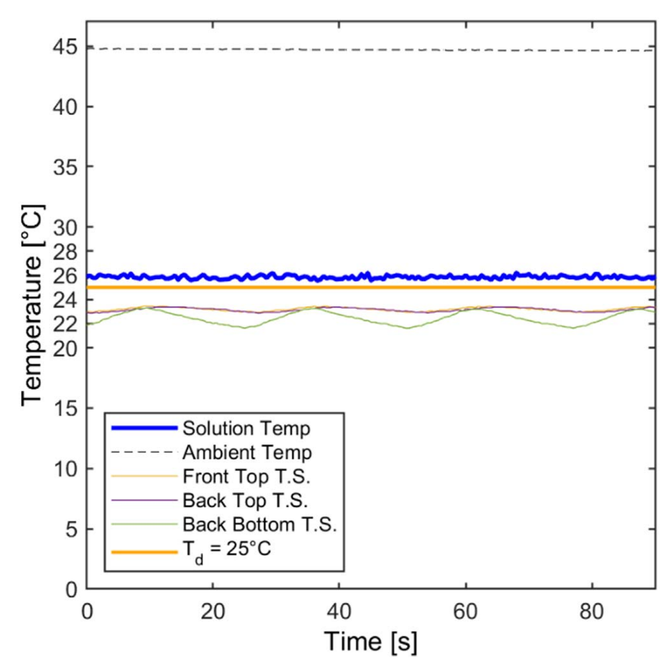

Figure 7. Stabilized Temperature at 25.85 ± 0.10 °C in high ambient environment. To keep the temperature sustained, the copper cuvette remains cooler than the solution temperature. The same effect occurs at higher targeted but lower ambient temperatures as well.

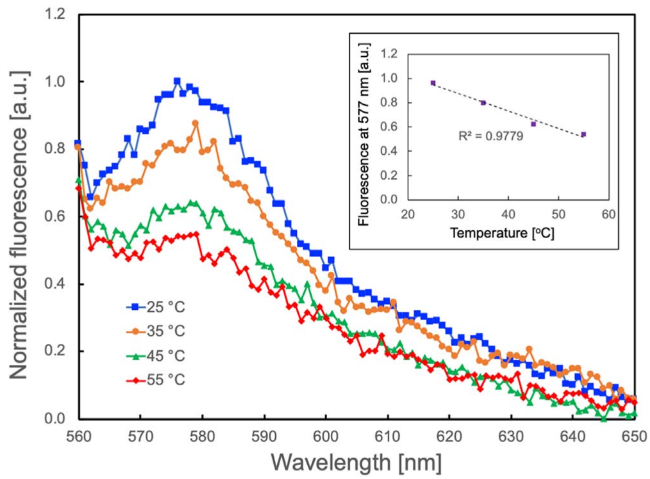

Figure 8. Fluorescent emission spectra of Rhodamine B showing normalized fluorescent emission spectra of Rhodamine B at varying temperatures (Inset: peak fluorescence emission as a function of temperature). The excitation wavelength used was 553 nm, and the resulting emission peak was observed at 577 nm. This experiment was performed at room temperature and operated under similar power consumption levels as those indicated in Table I. Stabilization for each of the four temperature cases were achieved in under 90 s.

the temperature dependence of a widely used fluorescent dye. This compact temperature controller system provides a viable option for temperature stabilization for portable fluorometers with a power-efficient approach. With the development of this module, temperature-sensitive fluorescent monitoring can be done accurately in real-time, without costly transportation delays or solution degradation that occurs when samples must go to another location for analysis. Future steps include moving forward with a full assembly of the system and further in-field analysis.

Acknowledgments

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