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User-Friendly 3D Printed Colorimeter Models for Student Exploration of Instrument Design and Performance

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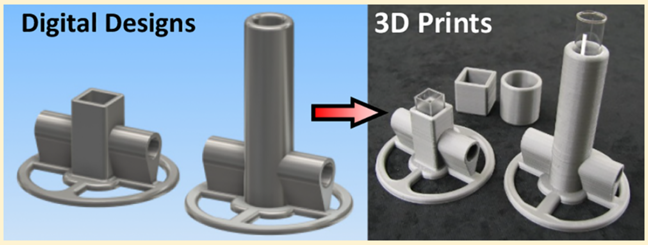
Ⓢ *Supporting Information*

ABSTRACT: A user-friendly set of computer-aided design (CAD) models and stereolithography (STL) files is reported for the production of simple and inexpensive 3D printed colorimeters. The designs shared here allow educators to provide active learners with tools for constructing instruments in activities aimed at exploring the technology and fundamental principles related to quantitative analysis. While previous efforts focused on fabricating inexpensive instruments from building blocks and other household items, 3D printing transcends the limitations of conventional tooling. The digital models described here are flexible in design, printed quickly, and each requires less than a dollar's worth of plastic filament. These designs are compatible with simple CAD software, such as Inventor Professional and Tinkercad, commonly available to educators and students. With the use of programs of this type, CAD files are easily modified in order to produce customized models for exploring a variety of concepts inaccessible to more conventional instruments. Developed with novice 3D printer users in mind, comprehensive slicer settings are provided to assist educators in obtaining reliable results. Once printed, the resulting colorimeter instruments perform very well when compared to commercially available spectrophotometers.



KEYWORDS: *High School/Introductory Chemistry, First-Year Undergraduate/General, Second-Year Undergraduate, Analytical Chemistry, Public Understanding/Outreach, Hands-On Learning/Manipulatives, Instrumental Methods, Laboratory Equipment/Apparatus, Quantitative Analysis, Spectroscopy, UV-Vis Spectroscopy*

■ INTRODUCTION

While several recent efforts report using 3D printers to produce models for visualizing molecular structures[1] and energy surfaces,[2] few focus on the development of 3D printed analytical tools for student use in laboratory learning.[3] The recent and accelerating advances in computer-aided design (CAD) and 3D printing methods provide access to a fundamentally unique means of instrument design and customization. Recent examples from the primary research literature demonstrate the versatility and innovation made possible by applying 3D printing to the design of analytical instrumentation.[4] With adequate expertise and support infrastructure, virtual designs can be created, processed, and fabricated cheaply via consumer-grade 3D printers. While this evolving technology offers great potential for educators, the barrier to entry is often intimidating for those unfamiliar with CAD software and fabrication equipment. In an added layer of complexity, CAD models must be exported to stereolithography (STL) mesh files and ultimately converted into G-code files, which contain the numeric control instructions required by current 3D printers. Without experience, the myriad parameters for generating files that produce reliable 3D prints can be daunting. In an effort to assist educators and students, a user-friendly set of CAD models and STL files is reported for the production of simple and inexpensive 3D printed colorimeters. In addition, introductory CAD tutorials, design notes, and comprehensive slicer settings for the production of G-code files are also provided in the Supporting Information.

While much has been accomplished in developing low-cost instruments using children's building blocks,[5] household items,[6] and other materials at hand, greater access to 3D printing via community makerspaces and university fabrication centers will transcend the limitations of conventional tooling. Creative digital design of instrumentation, coupled with inexpensive new desktop fabrication methods, provides access to unique and exciting approaches in the development of innovative new educational tools. Increased accessibility to this technology will grant teachers and students the ability to produce customized analytical tools for exploring a variety of concepts inaccessible to more conventional instruments. Low-cost 3D printing now offers the ability to rapidly customize, prototype, and revise designs to meet individual user specifications for nearly any given application.

While few, earlier efforts have produced more complex 3D printed colorimeters, requiring multipart assemblies and case-styled enclosures.[7,8] Given the limitations of current consumer-grade 3D printers, these instrument designs often require over

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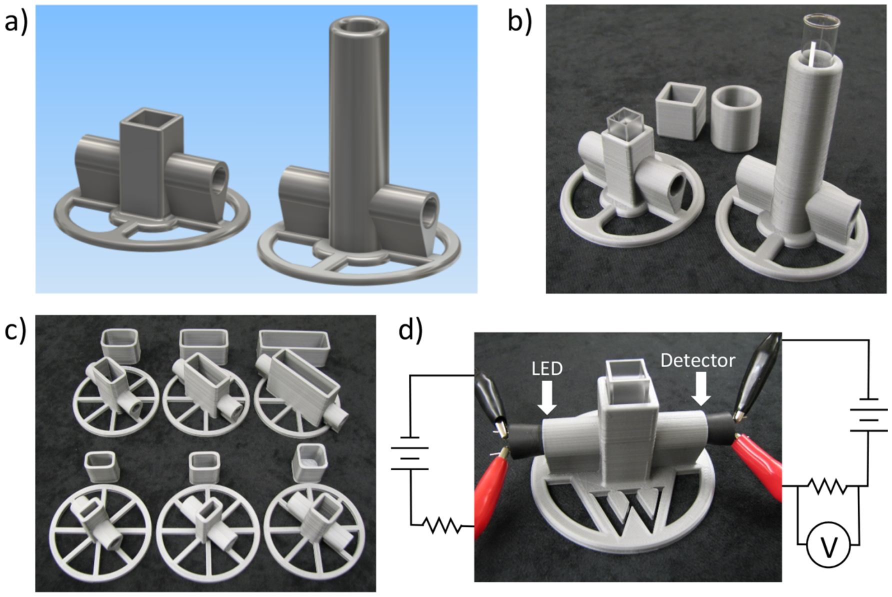

Figure 1. (a) Example cuvette and test tube colorimeter CAD models. (b) Colorimeter designs, with optional caps, fabricated with a 3D printer using polylactic acid (PLA) plastic. (c) Modified colorimeters designs produced to accommodate cuvettes of various path length (2, 3, 10, 20, 30, and 50 mm). (d) Simplified wiring diagram shown alongside a fully assembled colorimeter.

12 h of printing time for a single device.[7] Colorimeters of this type are self-contained, near-commercial in appearance, and may require programming and microcontroller expertise. In a departure from previous work, the simple designs presented here are reliably printed in 1−3 h (Figure 1). These user-friendly models are aimed to assist educators in fabricating inexpensive and customizable 3D printed tools for engaging students in the exploration of instrument design, operation, and performance. To provide the greatest utility to educators and students, the colorimeter designs are compatible with a wide range of LED source and solid-state detector configurations. Digital design affords a great deal of flexibility for quick and simple alterations to accommodate any variety of cell geometries (Figure 1a). For example, colorimeters compatible with either cuvette or test tube sample containers were produced (Figure 1b). In addition, the sample cell compartment design was customized in several models to explore instrument performance using cuvettes of various path length (Figure 1c). These instrument files provide educators with a simple starting point for developing purpose-built devices for use in laboratory activities and outreach projects.

■ ASSEMBLY AND OPERATION

At Wabash College, these models have been printed and used in both majors and nonmajors courses and are appropriate for high school and outreach activities. When used in laboratory activities, the colorimeter units are provided to students in kit form, consisting of the 3D printed piece, circuit components (e.g. batteries, resistors, LED source, phototransistor detector, and alligator clip leads), and an inexpensive digital multimeter. The entire kit, including digital multimeter and batteries, can be obtained for less than $25 from commercial sources and a full list of materials and assembly instructions are included in the Supporting Information. Active learning, via student construction of functional instrumentation, is an effective way to assist learners in discovering the technology and fundamental principles of analysis.[9] This method of avoiding the “black box” perception of instrumentation has long been a goal of chemical educators. The various experiments that make use of the 3D printed colorimeter all include supplemental instructions and wiring diagrams required for instrument assembly and operation. This design, by intention, leaves every component of the instrument exposed in an effort to help students isolate and explore the LED source and solid-state detector choices separately during assembly.

Two separate voltage divider circuits are used (Figure 1d); however, essential circuitry is kept simple and components are reduced to the minimum. Each circuit is powered by a separate 9 V battery and contains a simple fixed resistor, wired in series with the appropriate LED or silicon phototransistor. As an alternative to batteries, AC to DC power supply wall adapters also work well. The light source and detector are secured in place on opposite arms of the instrument with a rubber stopper dock or 3D printed end-cap for careful alignment. These colorimeter models are compatible with commercially available LEDs that offer low-voltage, long-lived, and inexpensive light sources. The same degree of customization applies to detector choice as well. Silicon phototransistors, cadmium sulfide photocells, and silicon photodiodes may be used with the 3D printed colorimeter. The docking apertures may be enlarged or reshaped in order to accommodate larger CdS photocells and other detector configurations. With CAD use, instrument designs are easily modified for use in more advanced courses, where the colorimeter may be adapted to accommodate additional optical elements, such as lenses and filters. More complex circuitry may be explored as well, incorporating filters, rectifiers, and amplifiers, as appropriate.[10]

Once the 3D printed colorimeter is assembled, taking measurements is quick and simple. An inexpensive digital multimeter is employed to make all voltage measurements. Voltage readings are first recorded for the background signal (V_{dark}) after inserting a cuvette filled with black clay. A sample cell housing cap may be 3D printed, but is not required. The 100% transmittance value ($V_{\mathrm{reference}}$) is obtained with a cuvette filled with solvent. In this way, transmittance is accessed directly through sample voltage measurements (V_{sample}) and allows students to calculate sample absorbance through use of eq 1. Data collected in this way presents an opportunity for students to explore the mathematical power of linear and directly proportional relationships, as well as the important distinctions between percent transmittance and absorbance.

$$A = -\log\left(\frac{V_{\text{sample}} - V_{\text{dark}}}{V_{\text{reference}} - V_{\text{dark}}}\right) \qquad (1)$$

■ PERFORMANCE

Access to an absorption spectrum provides the opportunity to engage students in a discussion of appropriate LED source selection for a particular analyte of interest. While a great variety of LEDs are commercially available, it is important to recognize that these light sources are not tunable. Therefore, proper selection of an LED source with greatest emission intensity near the analyte absorption maximum is important. The emission spectra for several LED sources are superimposed onto the visible absorption spectrum for aqueous copper complexed with cuprizone (CPZ, oxalic acid bis(cyclohexylidene hydrazide)) (Figure 2a). Here, it is clear that the yellow (591 nm) LED best matches the $\lambda_{\max}$ = 600 nm for the copper−CPZ complex. This source results in maximum instrument sensitivity, the greatest change in absorbance per unit of concentration. Sensitivity variation arising from various LED sources is displayed in Figure 2b via the slopes of several calibration curves generated from data obtained using the cuvette cell model of 3D printed colorimeter (Figure 1d). These plots yield linear fits over the concentration ranges investigated. Linear regression data also allows for simple identification of molar absorptivity (ε) values for the copper−CPZ complex at various source wavelengths. The greatest ε (15 500 M^{-1} cm^{-1}), determined by the slope of the calibration curve, is obtained using the yellow LED. Although more appropriate for advanced courses, the 3D printed colorimeter provides an excellent opportunity for students to explore calculations related to figures of merit.[8] Example values for sensitivity, detection limit, and dynamic range are available in the Supporting Information.

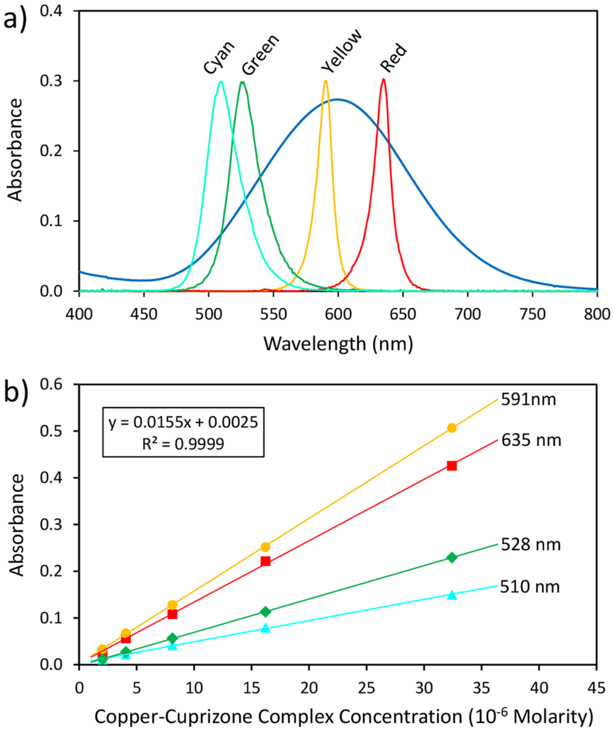

Figure 2. (a) Absorption spectrum of aqueous copper−CPZ (1.61 × 10^{-5} M) with an overlay of the normalized emission spectra for cyan (510 nm), green (528 nm), yellow (591 nm), and red (635 nm) LEDs. Absorbance data was acquired using a PerkinElmer Lambda 40 UV/vis spectrophotometer, and emission spectra were obtained using an Ocean Optics USB-650 spectrometer. (b) Calibration curves obtained from a 3D printed colorimeter for copper−CPZ using (●) yellow, (■) red, (◆) green, and (▲) cyan LEDs with a photoresistor detector. Linear regression data is displayed for the plot collected using the yellow LED source.

It is important to recognize that LEDs are incoherent light sources, which introduce deviations from the Beer−Lambert Law.[11] In many cases, this error can be minimized by selecting LED sources that emit bands corresponding to analyte absorption maximum or spectra regions that exhibit minimal deviations in molar absorptivity. However, this is not always possible due to LED emission or intensity limitations at given wavelengths. Analysis of polychromatic deviations provides an excellent opportunity for additional investigation and discussion in advanced coursework.[12]

Given the simple and inexpensive nature of the 3D printed colorimeter, it was surprising to discover how well it performed when compared to more sophisticated UV/vis spectrophotometers. Figure 3 displays calibration curves for the copper−CPZ complex obtained using a Thermo Scientific Spectronic 20D+ spectrophotometer, Agilent 8452 photodiode array spectrophotometer, and the 3D printed colorimeter at 591 nm. For this concentration range, the silicon phototransistor equipped 3D printed colorimeter produced a linear calibration curve, similar to those of the spectrophotometers. The linear regression data displayed in Figure 3 demonstrates that while the sensitivity of the two commercial spectrophotometers was greater, the 3D printed colorimeter offers excellent performance for its cost. Although CdS photocells are commonly employed in previously reported colorimeters, we elected to use a silicon NPN epitaxial planar phototransistor. This inexpensive and simple detector offers enhanced sensitivity over CdS photocells for a large region of the visible spectrum. Figure 3 shows that the phototransistor was about 6 times as sensitive as the photocell detector.

Figure 4a displays calibration curves obtained for FD&C Red 40 (Allura Red AC) using a cyan (510 nm) LED. The cyan LED was chosen to maximize instrument sensitivity owing to the $\lambda_{\max}$ = 504 nm of Red 40. The calibration curves presented in Figure 4 were obtained using three customized models of the 3D printed colorimeter, each designed to accommodate a glass sample cell with a different path length (l = 10, 20, and 30 mm). The flexibility of CAD modeling makes colorimeter customization simple, offering routes to activities that prove challenging or inaccessible to more static instrument designs. The linear regression data demonstrate that all three colorimeters yield linear performance over the concentration range explored in this activity. Minimal deviation from the Beer−Lambert Law was observed upon comparison of the Red 40 molar absorptivity ratios for the three instruments. A ratio of 2.9:1.0 was measured when comparing the calibration curve slopes for the 30 mm path length colorimeter to the 10 mm sample cell instrument. Similarly, a ratio of 2.0:1.0 was obtained when comparing the 20 mm path length model to the 10 mm colorimeter variant. In a related activity, all of the 3D printed

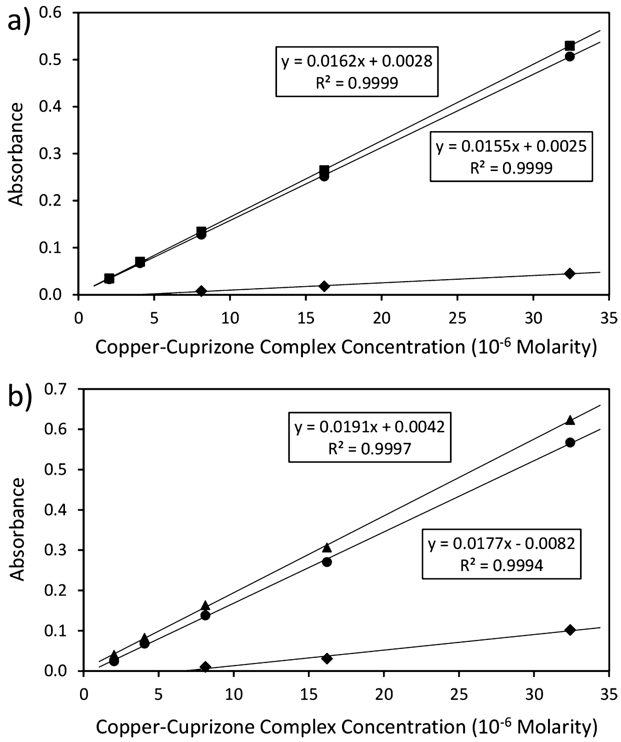

Figure 3. Calibration curves obtained for aqueous copper−CPZ complex at 591 nm. (a) Data obtained using an (■) Agilent 8452 photodiode array spectrophotometer is compared to a 3D printed colorimeter employing (●) a phototransistor detector and (◆) CdS photocell detector. (b) Data acquired using a (▲) Thermo Scientific Spectronic 20D+ spectrophotometer is compared to a 3D printed colorimeter employing (●) a phototransistor detector and (◆) CdS photocell detector. For consistency, instruments that shared the same sample cell configuration were compared in each of the plots above; 10 mm cuvette in (a) and 1/2 in. test tube in (b).

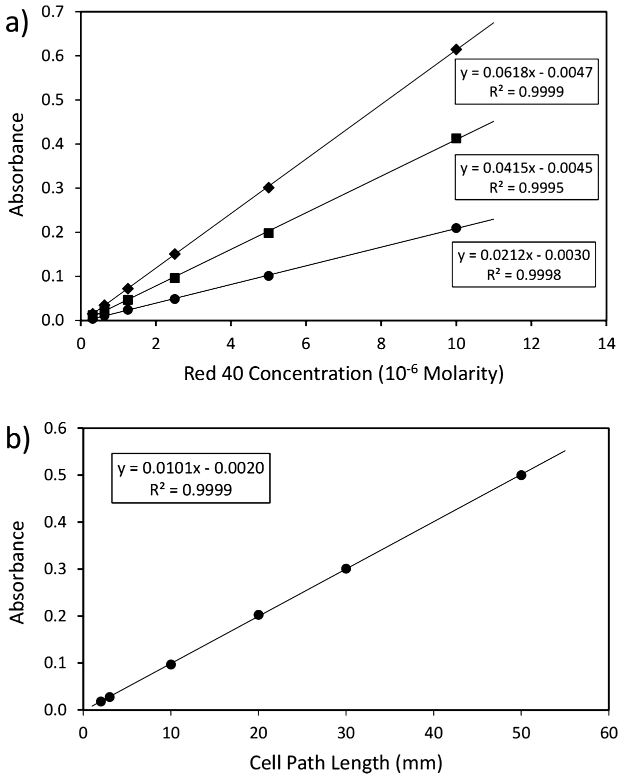

Figure 4. (a) Calibration curves obtained for Red 40 using a 3D printed colorimeter. Data was obtained using cell path lengths of (●) 10 mm, (■) 20 mm, and (◆) 30 mm. (b) Calibration curve of absorbance vs path length for Red 40 using a solution concentration of 4.80×10^{-6} M. Data shown in this plot was obtained using the various path length colorimeters displayed in Figure 1c. All data were obtained using a cyan LED (510 nm) source and phototransistor detector.

colorimeters shown in Figure 1c were employed to generate the single path length calibration curve for a 4.80×10^{-6} M solution of Red 40 (Figure 4b). This data produced a linear plot with strong adherence to the expected Beer−Lambert Law relationship. Simple measurements such as these allow students to explore instrument performance with respect to concepts and mathematical relationships derived in the classroom.

■ CONCLUSION

A versatile set of tools was reported for engaging students at all levels in the exploration of quantitative analysis. The 3D printed colorimeter kit confronts the "black box" notion of instrument design by empowering students to assemble their own device. Operation of the colorimeter is straightforward, and the performance reported is impressive considering its simplicity and cost. Introductory students may employ the kit in simple concentration determination activities, while more advanced courses may use it to explore deviations from the Beer−Lambert Law, advanced electronics, and calculations involving figures of merit. These instrument designs also present an exciting opportunity for preparing activities appropriate for high school students, science outreach programs, and service learning field work experiences.

This work demonstrates that accessible computer-aided design provides a fundamentally different means of instrument design and customization. Examples of this new approach to fabrication and modification are becoming more prevalent in the research literature. Flexible designs that can be printed quickly and cheaply via consumer-level 3D printers offer great potential for students and educators. Digital modeling, coupled with 3D fabrication, will continue to provide access to unique and exciting approaches in the development of innovative new educational tools.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00041.

> Slicer settings; material lists; wiring diagrams; assembly and operation instructions; calibration plots; detector comparisons; figures of merit; photographs; introductory laboratory activity (PDF)
> CAD tutorials (PDF)
> Colorimeter design photos (PDF)
> Downloadable CAD and STL files (ZIP)

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Notes

The authors declare no competing financial interest.

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