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Communication

An Inexpensive 3D Printed Periscope-Type Smartphone-Based Spectrophotometer for Emission, Absorption, and Fluorescence Spectrometry

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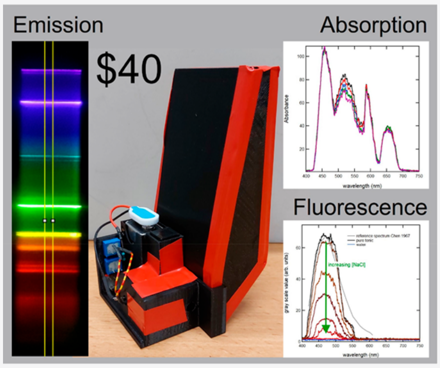
ABSTRACT: We present the design of a periscope-type VIS spectrometer for educational purposes that combines strong features from various earlier designs and adds new ones. Three 3D-printed pieces that hold a small thin mirror sheet, a 1/8th wedge of a DVD, and two razor blades are easily assembled and facilitate insight into its construction. A new feature is the permanent attachment of the flexible back cover of any smartphone, allowing for repeated removal and insertion of the smartphone with precision alignment for recording spectra. An optional fourth 3D-printed piece acting as a container for a PMMA UV semimicrocuvette, a white LED and a UV LED, and a 9 V battery attaches to the front. Beyond commonly applied absorption spectroscopy with similar devices, our design also allows for fluorescence spectroscopy. We report results of straightforward experiments illustrating the various uses of this less than \$40 MiniSpectroscope.



KEYWORDS: *High School/Introductory Chemistry, First-Year Undergraduate/General, Analytical Chemistry, Absorption, Hands-On Learning/Manipulatives, Spectroscopy*

INTRODUCTION

The importance of spectroscopy to chemical education, the widespread availability of smartphones and digital cameras that facilitate easy collection and handling of images, and simple solutions to convert images of visible spectra into graphic representations have spurred the design of affordable spectrometers for use in high schools and undergraduate education. A recent review of student-built spectroscopy instruments shows that several educators across the globe have developed such instruments.[1]

In this Communication, we report on a new design that combines several strong features from earlier designs and adds two new ones. In particular, our design allows students to repeatedly use their own smartphone for taking images of diffraction patterns while requiring only a single calibration. It also uniquely combines qualitative and quantitative emission and absorption spectroscopy with fluorescence spectroscopy. Our design also makes it easy to perform experiments. It stands straight up on any benchtop while the electronics controlling light from LEDs and the mobile phone's screen are easily accessed. Our MiniSpectroscope has been developed through multiple successive student projects at Leiden University's Chemistry Department since 2015. Some intermediate designs are illustrated in Figure S1 of the Supporting Information. The current level of design is simple and versatile enough that we feel it is opportune to make it freely available.

Our MiniSpectroscope is primarily based on the intuitive periscope-design by Wakabayashi.[2,3] It consisted of no more than some card stock, a 1/8th section of a DVD, and a piece of a thin mirror sheet. With a standard digital camera and a calibration based on Hg lines from a fluorescent lamp, it proved capable of resolving, a.o., Fraunhofer lines in the solar spectrum. With a cuvette attached to the front of the spectrometer and a fluorescent lamp as the illumination source, absorption spectra of permanganate solutions were obtained. While the ease of construction make it extremely valuable, the use of card stock as the main construction material makes it vulnerable, especially in the hands of inexperienced students. The design was also not particularly intended to be combined with use of a smartphone.

To introduce rigidity, we use a 3D printed housing for the spectrometer, as many schools and other educational institutions have or have access to 3D printers. This makes our design similar to the SpectroBox by Pap,[4] the DualSpec[5] and SpecPhone[6] by Smith and co-workers, and the G-Fresnel smartphone spectrometer by Zhang et al.[7] As we intended to

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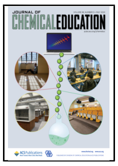

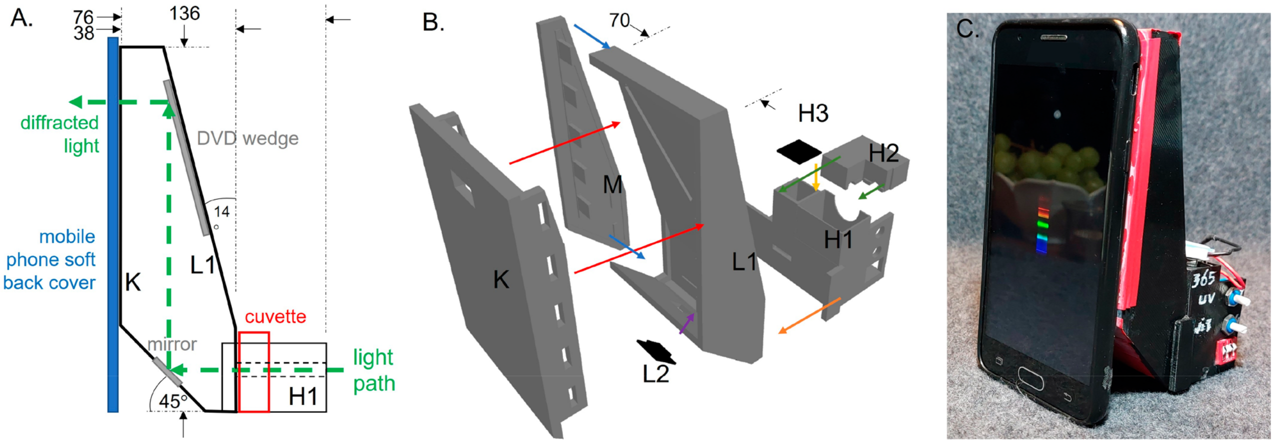

Figure 1. (A) Schematic of several crucial parts of the assembled MiniSpectroscope with the light path through the device indicated. Values indicate main dimensions in mm. The schematic is not to scale. (B) Exploded view of the main components of the body of the spectrometer. The letters are used to indicate the parts identically to the assembly description in the Supporting Information and in part A of this figure. (C) Photograph of a Samsung Galaxy S4 attached via a silicone soft back cover to the MiniSpectroscope.

have students construct the spectrometer, use their own smartphone to record images, and carry it in between home and school, we stayed away from bulkier designs[8−10] and other materials, e.g., MDF.[11] We also intended to expand its use to include fluorescence spectroscopy, as previously applied in noneducationally intended designs of smartphone fluorimeters.[12−14] Several other types using fluorescence (smartphone-based) spectrometers are listed in a recent review on smartphone sensing in resource-limited settings.[15] Finally, we decided not to try and incorporate a dual beam type design[5,16] or include optical components[17] for reasons of size, simplicity, and costs. Instead, we use the combination of a single cuvette and illumination by LEDs[18] for absorption and fluorescence spectroscopy.

■ DESIGN

Figure 1A shows a schematic of the main components and dimensions. The light path is indicated by a green dashed line through the device. The angles of the mirror and DVD wedge are chosen to have green light (~540 nm) exit parallel to the incoming light. Figure 1B shows an exploded view of the 3D-printed components. Parts K, L1, and M make up the body of the spectrometer. They easily click together and strongly reduce stray light. The edges may be covered with tape, as shown in the photograph in Figure 1C, to reduce stray light even more and to slightly increase rigidity. Here, red tape was used for contrast in the photographs.

A complete assembly description is provided in the Supporting Information. Briefly, a ~6 mm × 6 mm square of a self-adhesive bathroom mirror foil purchased at a local hardware store is glued to the separate mirror holder (Figure 1B, part L2) that subsequently inserts into the front plate (L1) of the MiniSpectroscope. Two razor blades (Derby Professionals single edge blade) are glued to form a narrow entrance slit on the opposite side of the front plate. An approximate 1/8th cut of a standard DVD is attached with hobby glue to the indicated area on the upper inside of the front plate. Subsequently, the front plate (L1), back plate (K), and side plate (M) are assembled. It takes anywhere between 5 min and 1 h depending mostly on the assembler's experience and the rate of hardening of the used glue. At this point a line spectrum from a fluorescent bulb is already easily observed by the eye through the opening on the back plate while pointing the slit in the appropriate direction.

The smartphone may be attached and removed repeatedly without losing alignment of a smart phone's camera with the emission spectrum through the use of a flexible smartphone back cover, as illustrated in Figures 1A and 1C. We generally use black silicone back covers and align the camera's view port with the opening in the MiniSpectroscope. With the camera in place, we check whether we see a complete spectrum on the smartphone in Camera mode, using an incandescent or fluorescent bulb, or a Hg lamp as a light source in front of the razor blade-defined slit. The smartphone's back cover is glued to the MiniSpectroscope. Double-sided adhesive tape also works well and makes it easier to correct misalignment at a later stage. When the glue has hardened, the smartphone can safely be removed and reinstalled repeatedly without loss of alignment.

A fourth major 3D-printed component (Figure 1, H1) connects to the front of the spectrometer housing. It holds a cuvette, two LEDs at orthogonal angles with the white LED being placed in the green light path shown in Figure 1A, a 9 V battery (opposite of the UV LED) and some simple electronics to switch and control the current running through the white (Mouser Electronics, OVLEW1CB9) and UV (OSA Opto light, EOLD-355-525 and EOLD-365-525) LEDs. Figure S6B provides a detailed view. It consists of a base (H1), an LED cover (H2), and a cuvette cover (H3). The complete H component may be considered optional as the basic housing with the smartphone acts very well as an accurate emission spectrophotometer. This additional component H extends the MiniSpectroscope's capabilities to include qualitative and quantitative absorption and fluorescence spectroscopy. This part may be glued to the front of the spectrometer housing, but generally attaches well enough through a tight fit. It also ensures stability and allows for the entire assembly to stand straight on a students' working table, as illustrated in the photographs in Figure 1C. For smartphones that extend below the housing or do not reach it, we simply fill the difference with a stack of cut cardboard or a piece of styrofoam to regain stability and a horizontal alignment of the MiniSpectrometer with the table's surface.

All 3D-printed components are printed in our lab using an Ultimaker 3 (Layertec, Zaltbommel, The Netherlands) with black poly(lactic acid) (PLA). The design of the parts and the layout on the print table are such that it does not rely on our printer's capability to use a water-soluble filler. We also used the largest print head orifice (the AA extruder, 0.4 mm) and lowest resolution settings in the machine's controls to show that the design works for much simpler 3D printers. The design files are freely available.[19] In the Supporting Information, we show several detailed photographs, drawings, and schematics of the components, the layout of the additional component holding the LEDs, and an electrical circuit. The soldering of the electronic components required for absorption and fluorescence spectrometry may be considered part of the experience for students to build the spectrometer. However, it is time-consuming and is likely out of reach for many high school students.

For the experiments described below, we used a commercial Hg lamp (HPLN 50W E27 SG, Philips) to calibrate several MiniSpectroscopes and various (monochromatic) light sources for verification. Emission spectra may be obtained either without the 3D-printed piece with electronics and LEDs in place or with the white LED removed from this part. For chemicals, we used $KMnO_4$ (Sigma-Aldrich, ≥99%) and table salt in absorbance and fluorescence experiments without further purification. We used standard glassware and standard procedures to produce solutions. We used PMMA semi-microcuvettes that allow for UV experiments in the range of 300−400 nm. Cuvettes were in some experiments filled and emptied while in the MiniSpectrometer using standard syringes. In other experiments, the cuvette was removed, cleaned, and replaced. To convert JPEG images from smartphones to actual spectra, we use ImageJ.[20] In case multiple images are taken in sequence for quantitative comparison, we ensure to select the exact same section of each image. The rectangular cut is between 5 and 50 pixels in height and the full length of the image. The number of pixels along the length depends on the smartphone's camera and is generally between 4000 and 5000 pixels. This section of the photograph is turned into a graphic representation of intensity vs pixel number using ImageJ's "Plot Profile" function with the standard RGB-to-gray scale conversion of ImageJ. The data are exported and treated further with MS Excel or Igor PRO (vs 8). We use a background spectrum and standard equations to turn transmission into absorption spectra.

■ HAZARDS AND SAFETY

Using a 3D printer brings minor hazards because of the hot print cores. The 3D printer should be handled according to its safety sheets. $KMnO_4$ used in the experiment needs to be treated according to the safety measurements given by the safety data sheet. Cutting a DVD brings minor hazards associated with the sharpness of the scissors. Razor blades used to define a entrance slit are very sharp and should be handled carefully. Glue may be hazardous, in particular when using a type that hardens extremely fast. One should avoid looking at the source of light in laser pointers, e.g., if they are used as described here for reference measurements.

■ RESULTS AND DISCUSSION

Spectral Calibration and Emission Spectra

We calibrate the spectroscope using emission lines from a Hg lamp. The process is illustrated in Figure 2. Here, an Samsung Galaxy S4 is used with a silicon back cover glued to a MiniSpectroscope with a 0.3 mm slit as its entrance. Three photographs were taken from spectra obtained from commercial Hg lamp at varying angles and intensities. Figure 2A shows a cut of one of the three photographs. Therein, the yellow rectangle encompasses the area used to create the gray value plot with ImageJ in the center section for the spectrum shown in green. The area is 4128 pixels broad and 42 pixels high. The two additional photos taken at different angles have lower exposures and their spectra appear in blue and red in Figure 2B. We identify several peaks in the spectrum and compare the pixel position to the wavelength's from the NIST database.[21] Figure 2C shows the comparison as data (crosses) for the three data sets with the same color as used for the spectra. The best linear fit to the complete data set is represented by the solid black line. Its slope yields us the sampling interval. It is the inverse of the slope and 0.218 nm/pixel.

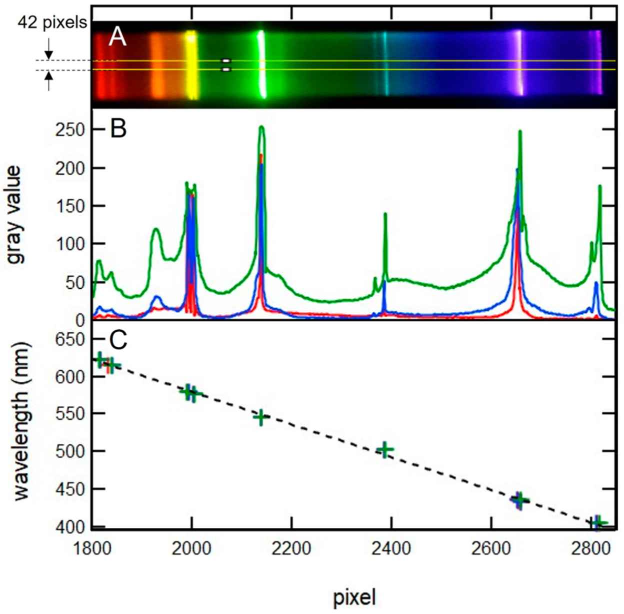

Figure 2. Illustration of the method used to calibrate the MiniSpectroscope once a smartphone's flexible back cover is attached. Here, a Samsung Galaxy S4 was used to collect three images of a commercial Hg lamp spectrum from different angles and distances. (A) A cut of a photograph showing the emission with a yellow box highlighting the area used to integrate data. (B) Three ImageJ created spectra as gray value vs pixel number. The green spectrum corresponds to the image in the top. The others were taken with lower light intensity. (C) Data showing the conversion of the observed peaks to known Hg emission lines, color coded to the spectra. The dashed solid line represents the best linear fit through all data.

We test the quality of the calibration using a Na lamp. The obtained spectrum is shown twice in Figure 3. Figure 3A shows a wider spectrum (490−710 nm) for a section of 29 pixels height taken at the upper part of the image's yellow diffraction line (indicated by the yellow box in the inset). In the zoomed

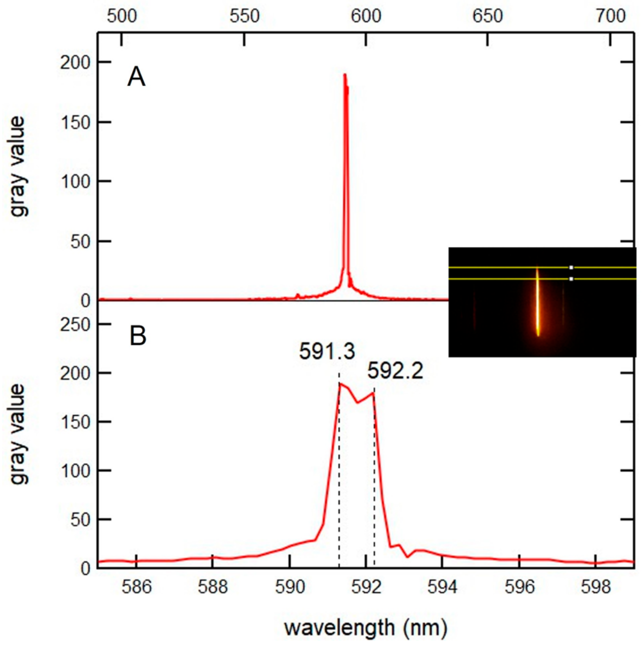

Figure 3. (A) Spectrum of a sodium lamp taken by the MiniSpectroscope with a Samsung Galaxy S4 with wavelength scale on the top axis. (B) The identical spectrum plotted versus the bottom wavelength axis. The ImageJ created gray values were obtained from the section indicated in the yellow box in the inset.

spectrum (Figure 3B), the sodium D-lines are nearly resolved without spectral magnification. The two highest gray values appear at ∼1.5 nm red-shifted from the tabulated values (588.995 and 589.59 nm). Taking a similar section of the image more centered on the yellow diffraction line observed in the photo results in loss of the distinction between the two maxima as a result of approaching saturation of the camera.

Improvements to the calibration are possible. Ensuring that light from various emitting objects always enters the spectrometer at the same angle improves results. We have used a spirit level app on the mobile phone for reference with light sources at fixed positions. Also, the subset of used reference lines may be re-evaluated. In our calibration data, the blue-green line assigned to 502.5 nm from the NIST database consistently appears significantly above the best fit calibration for multiple spectrometers and smartphone combinations. It suggests that this wavelength does not match the line appearing in the spectrum of our particular Hg lamp. The position of Hg lines is somewhat pressure dependent and we are unsure of the pressure in our lamp. Alternatively, the linear fit may be modified to a higher-order polynomial to correct for nonlinearities in the created image. With an improved alignment procedure and leaving the 502.5 nm reference line out of the calibration, the center of the Na D-lines appeared within 0.4 nm from the tabulated values for a Samsung Galaxy A52 attached to a MiniSpectroscope. The same accuracy has been obtained regularly over the past years with previous designs of our MiniSpectrometer.

To acquire a sense of obtainable resolution, we use a green laser pointer emission line at 532 nm as indicated by the manufacturer (EMAX, #0009878). Spectra of two sections are shown in Figure 4A and Figure 4B with insets showing the sections over which we integrate with ImageJ. Also, Gaussian fits are shown as black lines. Clearly, by taking a section on the side of the spectrum as observed in the photograph, the line width reduces nearly by a factor of 2. The resolving power of the MiniSpectroscope, $R = \lambda/\Delta\lambda$, is here on the order of 532 nm/0.6 nm = 900.

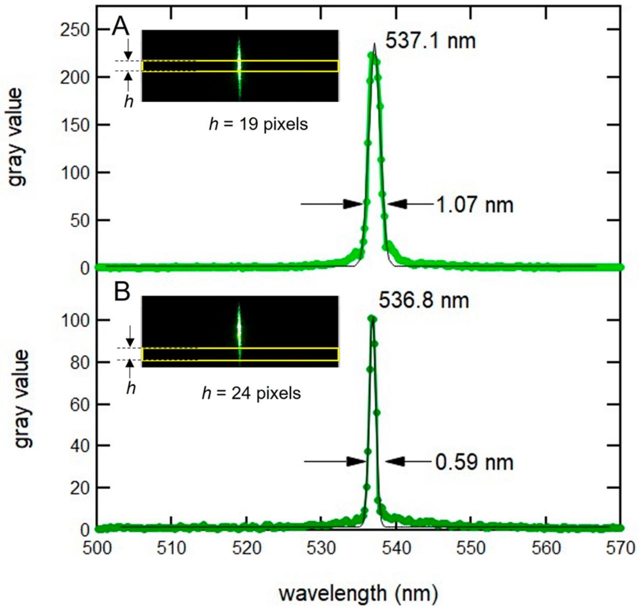

Figure 4. (A) Spectrum of a green laser pointer taken by the MiniSpectroscope with a Samsung Galaxy S4. Data are shown in green. The inset shows the photograph of the diffraction spectrum with a yellow box indicating the integrated area to produce the gray values of the spectrum. The solid black line is a Gaussian line shape fit to the data. (B) Identical to (A) with only a different section of the image selected to produce the spectrum.

Absorption by $KMnO_4$

With the additional part of the MiniSpectroscope, quantitative absorption spectroscopy can be performed. Here, we illustrate this using the absorption by MnO_4^-(aq) which peaks around 525 nm. We have taken a series of transmission spectra based upon a stock solution of 0.198 mM $KMnO_4$ by replacing the solution in the cuvette repeatedly. The transmission spectra, including a reference spectrum of deionized water, are shown in Figure 5A. From these, we obtain the absorbance spectra shown in Figure 5B. Figure 5C shows a Lambert−Beer analysis on these absorbances at 525 nm. In this particular case with a spectrophotometer using a Samsung Galaxy A52, a minor oscillation in intensity is observed across the entire spectrum. A photograph of the diffraction pattern, shown as an inset in Figure 5, shows this intensity variation. It is also observed in Figure S7 without the cuvette in place. The oscillation in transmission leads to oscillations in the absorbance and lowers the accuracy of determined absorbance-dependence on concentration in Figure 5C. To minimize its effect on the calculated absorbance at 525 nm, we have analyzed the data using averaged absorptions across 1, 2, 4, 6, and 10 nm ($\Delta\lambda$) centered at 525 nm, and find—as expected—a drop in the determined slope. This is only a minor effect of 1−2% though, while the R^2 value improves to 0.995. The slope of the best fit is shown in Figure 5C. Note that the determined slope disagrees rather strongly from the known extinction coefficient at 525 nm, i.e., 2.4×10^3 M^{-1} cm^{-1}. It also varies for different mobile phones. We found 1.2×10^3 M^{-1} cm^{-1} with an Galaxy S4 (see Figure S8), 6.2×10^2 M^{-1} cm^{-1} with a Galaxy A52 (Figure 5), and 5.6×10^2 M^{-1} cm^{-1} with the Galaxy S9. JPEG

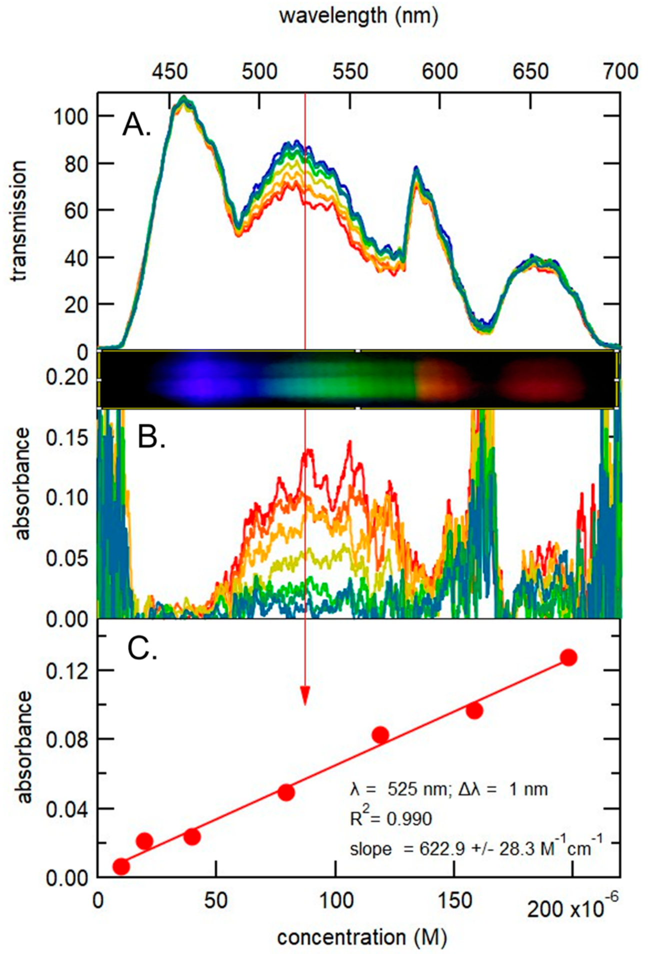

Figure 5. (A) Transmission spectra of water (blue line) and MnO_4^- solutions with increasing concentration (green to red). (B) Absorbance spectra from the MnO_4^- solutions. (C) Lambert−Beer analysis at $\lambda = 525$ nm with data averaged over $\Delta\lambda = 1$ nm. The best linear fit is shown as a red solid line. The inset between (A) and (B) shows a photograph of the spectrum taken with deionized water. Data were taken with a Samsung Galaxy A52.

images produced by mobile phones are not *a priori* suitable for absolute measurements of this type. Varying doping values in CCD sensing elements creates varying responses for identical changes in light intensity at a fixed wavelength. In combination with subsequent software filters that are applied by the phone to create the actual color images as JPEG files, this makes the determination of the correct extinction coefficient reliant on an additional type of calibration of the absorption spectrometer.[25] The extinction coefficient probed at 591 nm, as described in more detail in the Supporting Information and derived from Figure S8, also does not match earlier experimentally determined extinction coefficients.[26]

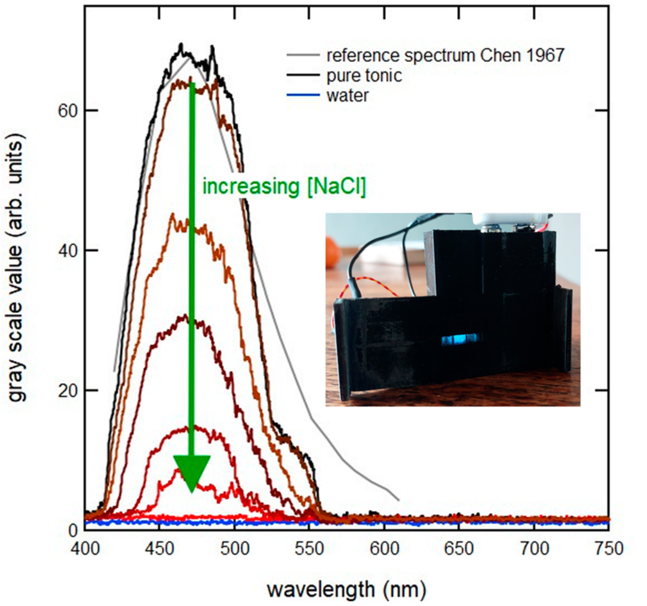

Figure 6. Fluorescence spectra of quinine as present in Royal Club Tonic Classic. The fluorescence of the original spectrum of 0.7 mL tonic (black) is quenched by random increases in NaCl concentration until the spectrum shows no more fluorescence (red) and is identical with that of 1 mL deionized water (blue). For reference, a digitized version of a spectrum published by Chen[22] is shown (gray). The inset shows the fluorescence observable by the naked eye from pure tonic water in the PMMA semimicrocuvette when illuminated with the 355 nm UV LED from the inside of the cuvette holder without the MiniSpectroscope attached. The camera's software was set to manual control with ISO 3200 and 4 s exposure time to collect photographs of the spectra. To convert the images to graphs, we summed the identical set of 48 lines of pixels.

Fluorescence and Extinction

Figure 6 shows that the MiniSpectrometer can easily collect fluorescence spectra. Here, we used the 1.2 mW 355 nm UV LED, a single-use PMMA UV semimicrocuvette, and a Samsung Galaxy A52 attached to a MiniSpectroscope. The wavelength calibration was done as described before without the cuvette holder attached. The resulting fluorescence spectrum of quinine present in Royal Club Tonic Classic (shown in black) matches that of a reference spectrum for quinine in an acidic solution.[22] For reference, we also show the spectrum collected under identical UV illumination conditions for deionized water (blue). Also, we show several spectra after adding random amounts of table salt and letting it dissolve. Chloride ions quench the fluorescence of quinine and various types of student experiments on this phenomenon have been described in this Journal.[23,24] The inset in Figure 6 shows the inside of the cuvette holder with the spectrophotometer not attached. The blue hue from the fluorescence is clearly visible in the center of the PMMA UV semimicrocuvette.

Out-of-Pocket Expenses of the MiniSpectrometer

We estimate the out-of-pocket expenses for producing a MiniSpectroscope in Table 1. The costs are approximated by taking the costs for items as purchased. For example, the $45 cost for one 750 g role of PLA and the printer software

Table 1. Cost for MiniSpectroscope

Item	Approximate Cost Per MiniSpectroscope ($)
PLA	∼5
Mirror sheet	<0.10
Razor blades	<0.20
1/8th DVD	<0.25
Silicone back cover	5−10
Electronic components	5−10
White LED	<1
PMMA semimicrocuvette	<0.30
UV LED	15−35

estimate of 8 complete sets of 3D-printed items necessary for a single spectroscope yields a cost per item of nearly $6. We find that the number of items printed from one role in reality is significantly larger and we estimate the cost to be at most $5 for PLA per spectrophotometer. Several other items come in larger quantities and those costs are combined less than $1 per MiniSpectroscope. The cost for the back cover varies per type and make of the mobile phone. The costs for the basic MiniSpectrometer used for emission spectroscopy only amounts to $11−16 and primarily depends on the cost of the silicone back cover.

The more expensive components are part of the extension to the MiniSpectrometer that allows for absorption and fluorescence spectroscopy. We purchased most of the electronic components (e.g., the 9 V battery, the switches, and variable resistors) in larger quantities (50−100) and estimate the cost based on total costs and the number of spectrometers we can construct from these purchased items. While white light LEDs required for absorption spectroscopy are cheap, the more powerful 365 nm (6 mW output) UV LED costs ∼ $35. The less powerful 355 nm (1.2 mW output) costs ∼ $15 but also yielded fluorescence spectra of quinine with little effort. Commonly used quart cuvettes for fluorescence spectrometry can be purchased for as little as $10, but much cheaper disposable single-use PMMA UV (semimicro)cuvettes work well in the range above 300 nm. Hence, for an additional approximate $25 (and a total of $35−40) the complete MiniSpectroscope can be made in any school setting if multiple copies are made.

■ CONCLUSION

We have shown that it is possible to manufacture for less than approximately $40 a rugged and accurate spectrophotometer that students can assemble, transport between home and school, and use in combination with their own smartphone. It stands straight up, facilitating various types of experiments, and uses a glued-on soft back cover of the student's mobile phone so that it requires only a single calibration procedure. A second unique feature is that it allows for emission, absorption, and fluorescence spectroscopy, hence supporting a large range of potential topics from chemistry, physics, and even biology curricula.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.2c00060.

Development, construction details, and absorption example (PDF) (DOCX)

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Notes

The authors declare no competing financial interest.

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