Cell Phone Spectrometer: Learning Spectrophotometry by Building and Characterizing an Instrument

Alexander Scheeline (scheelin@illinois.edu) and Kathleen Kelley (kathleen.kelley@yahoo.com)
Department of Chemistry
University of Illinois at Urbana-Champaign
600 S. Mathews Ave.
Urbana, IL 61801 USA

Version of November 18, 2009

I. Abstract

The wide availability of cellular telephones equipped with CMOS cameras (and of digital cameras directly exporting JPG files) opens many opportunities for inexpensive, portable photometric measurements. Spectrophotometry makes more sense to students when they can see light change intensity when passed through a sample than when they can only see equations, sketches, or the output of a computer screen or meter. Better yet, they can learn the concepts of dynamic range, stray light, saturation, digitization error, order overlap, and dispersion more easily by seeing the phenomena than by only hearing of them. In this paper, we report the construction and give the hardware, software, and laboratory instructions for a diffraction spectrograph/cell phone (or digital camera) array detector suitable for high school and college students.

II. Introduction

Spectrophotometry is covered in every introductory text on quantitative analysis or instrumental analysis. Beer's Law can be quoted by nearly every student who has taken chemistry in the last half century. Yet it is our experience that students have only a weak understanding of the relationship between light intensity, transmittance, and absorbance, that they report absurd numbers of significant figures, and that they fail to grasp topics such as stray light, noise, dynamic range, linearity, saturation, and order overlap. Until recently, having students dissect photometric instrumentation was prohibitively time consuming and expensive. In the days of photographic photometry, film calibration and quantification of emission (let alone absorption) took endless hours of experimentation, dark room work, densitometry, and interpretation. Photomultiplier tubes were delicate, required high voltage power supplies, and could only measure one wavelength at a time. Although semiconductor photodiodes were not so delicate and required only low voltage power, they required a current-to-voltage converting amplifier and readout electronics, and were difficult for students to understand. In recent years, diode array or CCD array spectrometers have provided full spectral coverage, but all of the optics and electronics are buried behind a computer screen. Student interaction with the measurement was reduced to a press of a (virtual) button, and the instrumentation for everything from computer-controlled chromatographs to cybernetic potentiostats became indistinguishable from a parametrically-intensive computer game. Direct sensing of measured quantities has effectively ceased.

Sometime during 2008, it occurred to the corresponding author that cell phone cameras had become common among students. "They're only 8 bit CMOS chips," was the initial thought. "The signal-to-noise ratio will be terrible. Dark current is likely to be a problem. No one in their right mind would use such a poor detector for doing quality spectrophotometry." In November, 2008, the author had a double-take. If all these measurement problems were so blatant, wouldn't that make the concepts behind the problems easier to sense and learn than if one used a high quality detector and system? The result is reported in this paper: an inexpensive array detector spectrometer useful for teaching the basics of visible absorption spectrophotometry and the concepts general to spectroscopy at all wavelengths. The students supply the detector, while the instructor provides all other parts, costing no more than $3 per group (2009 prices). After watching individuals, pairs, and triples of students use the parts, the authors believe that a team size of 3 is optimal, being big enough to have discussions, but small enough that all students get a turn to influence the engineering. This paper reports work in progress. Comparative, statistically-validated student evaluation has not yet occurred. Bugs continue to appear in the software. And yet, the enthusiasm with which the cell phone spectrometer has been met by nearly everyone who has heard of it suggests that an early "roll-out" of the concept is warranted. As an Open Access/Creative Commons publication, the author solicits participation by the community in implementation, debugging, and evaluation of this pedagogical instrument.

The use of cameras in cellular telephones for optical spectroscopy has been previously patented.[1]

III. Educational Goals and Methods

If successful, the student will be able to:

- List the components of a spectrophotometer and the order in which light traverses those components.
- Explain what a diffraction grating does, specifically including the concepts of dispersion and diffraction order.
- Explain what stray light is and explain how stray light decreases the quality of spectrophotometric measurement.
- Describe how a quality spectrophotometer would differ from the hand-made device.

The approach taken is, in essence, POGIL.[2] Students are given open-ended guidance as to how they might build the spectrometer. Typically, after a few minutes, the stimuli from the components cue the students as to what may be interesting or productive. To date, no student has reported an accurate, quantitative measurement. Yet, in discussion, it appears that they understand gratings, stray light, and dispersion more clearly than do students who have only heard of or seen pictures of the instrument components.

IV. Scientific Background

Any text on analytical chemistry (e.g. Harris,[3] Harvey,[4, 5] Skoog,[6]) covers the basics of absorption and fluorescence spectrophotometry. The central relationship is Beer's Law (or, for purists, the Beer-Lambert Law),

$$A = \varepsilon bC = \log_{10} T = -\log_{10} \frac{I}{I_0} \tag{1}$$

Where

A	Absorbance
T	Transmittance
ε	Molar absorptivity, L mol^{-1} cm^{-1}
b	Light path length through specimen, cm
C	Absorber concentration, mol L^{-1}
I	Intensity detected in the presence of sample
I_0	Intensity detected absent sample but with solvent present

Greater detail is contained in a vast literature, including discussion of spectrometer design,[7] detectors,[8] and measurement non-idealities.[9, 10] A review of spectrometer instrument design is thus omitted here, though simplified discussions do appear in the "High School Teacher Module" and "Student Module" accompanying this paper. Critical ideas include how diffraction gratings function:

$$n\lambda = d(\sin \alpha - \sin \beta) \tag{2}$$

with

n	diffraction order (integer)
λ	wavelength (nm)
d	grating groove space (nm)
α	incidence angle of light on grating, measured counter-clockwise from grating normal
β	exit angle of observed, constructively-interfering light, measured counter-clockwise from grating normal

Low-granularity optical detectors (8-10 bit intensity digitization per pixel or channel) for chemical analysis have previously been employed by, e.g., Suslick,[11, 12] Whitesides,[13-16] and others.[17-21] Accepted practice is that charge-coupled arrays are employed for low-light-level applications (fluorescence, Raman, atomic emission), while diode arrays are used for absorbance measurements (including commercial instruments by Agilent, Ocean Optics, Stellarnet, and others). In the limiting case that readout granularity is the limiting noise source, the signal-to-noise ratio for concentration measurement is given by:

$$\frac{C}{\delta C}=\frac{-I_0 T\ln T}{\delta I\left(1+T^2\right)^{1/2}} \qquad (3)$$

For an 8 bit digitizer, $I_0/\delta I$ = 255 or less. A plot appears in Figure 1.

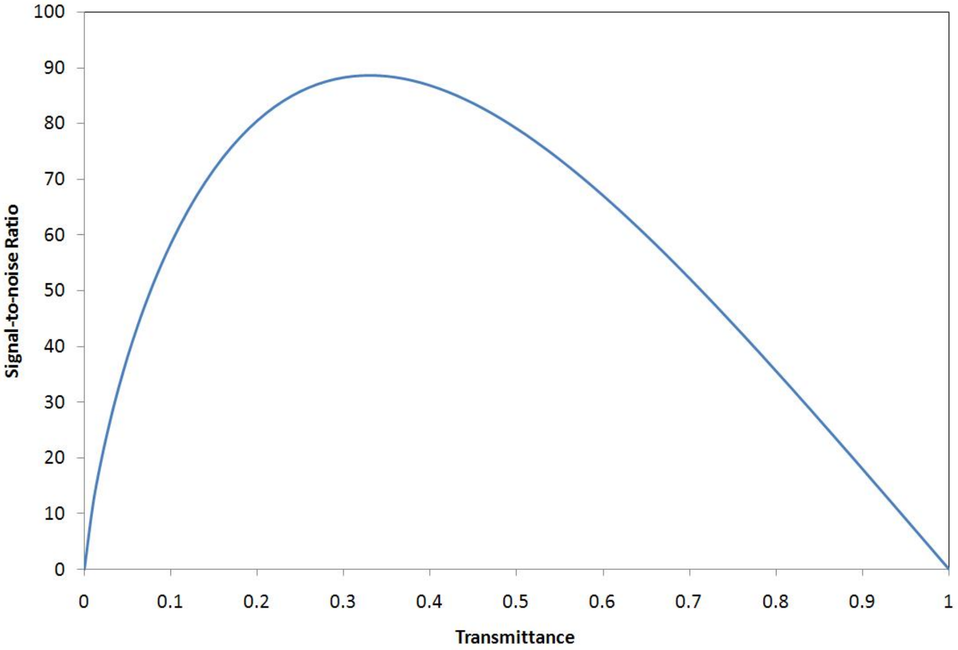


Figure 1. Signal-to-noise Ratio for an 8 Bit Digitized Photosignal. Assumptions include: I_0 is full-scale exactly, at $A=\infty$, I = 0 (no stray light), and intensity is high enough and stable enough that no noise source other than digitizer resolution contributes to measurement uncertainty.

What is not obvious is that instrument alignment, actual use of digitizer range, and positional stability of the detector all overwhelm the influence of digitizer resolution for the open geometry employed here. One may thus ignore all the usual theory and mathematics prior to having students build instruments; they will discover measurement flaws without the burden of algebra in advance.

V. Components

Any camera that outputs a 24 bit JPEG file is adequate as a detector. Let the students bring whatever they have to lab. Their familiarity with their own cameras and cell phones obviates the need for instructors to document anything about the detectors, or even to know how to use them. When, in prior practice, has it been feasible to use instruments where the students were presumed to be technically more proficient than the instructors?

Every spectrometer needs a baseplate. A PDF file of a simple design is included in this paper. What it lacks in rigidity and sophistication is made up for by low cost. Any photocopier or printer can provide adequate replicas. Using heavy paper or thin cardstock has a slight advantage. The original drawing was made in *Autocad 2004*, and is linked to this paper.

The light source is a blue-LED-pumped fluorescent light source, dubbed a white LED (not to be confused with LEDs that are three independent emitters, one red, one green, and one blue). We have used an RL-5-W5020 device, the specifications for which can be found at http://www.superbrightleds.com/specs/w2_specs.htm. The output divergence angle, ±9°, is narrow enough to provide high intensity, while being narrow enough to confine most light to the area of the grating. Approximate output as claimed by the vendor is replotted in Figure 2. Output power is specified for a current of 20 mA which requires a drive voltage of 3.8 V. For simplicity, we instead use a CR2032 3V battery, commonly employed in remote keyless entry transmitters. The LED/battery combination results in a current of barely 2 mA, so output is only about 1/10 of the full power rating (see Figure 3). While the batteries are available off-the-shelf world-wide, we have found Digikey (www.Digikey.com) is a particularly inexpensive vendor.

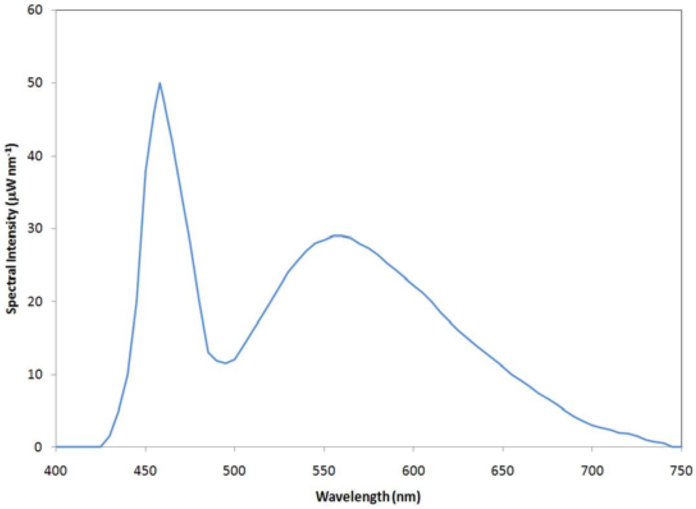


Figure 2. LED Emission Spectrum for 20 mA drive current. (replotted from Superbright LED website)

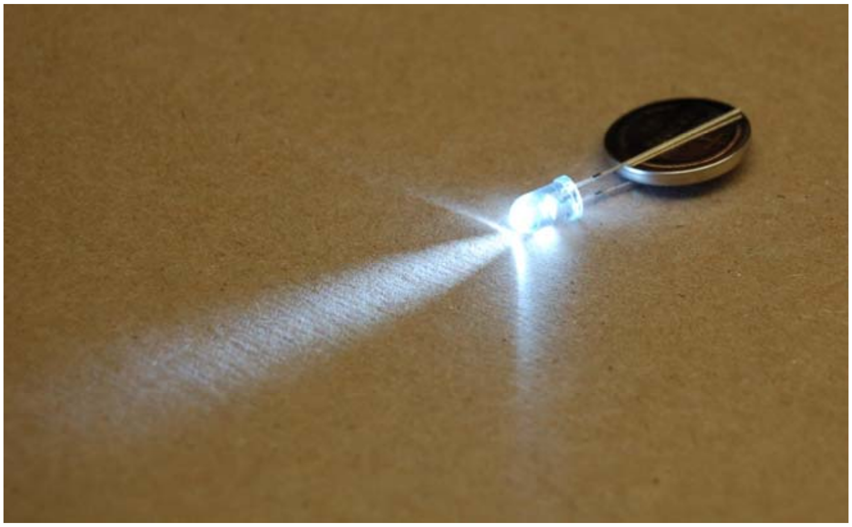


Figure 3. LED and Battery. LED diameter is 5 mm.

Plastic 1 cm square, 3.5 mL cuvettes are entirely adequate; they are opaque below 300 nm, but the light source only emits above 425 nm. Commonly available from most lab supply houses, 100 unit quantities are available at approximately $0.15 each from Vernier Software and Technology (http://www.vernier.com/accessories/access.html?cuv&template=basic.html).

Finally, one must obtain transmission diffraction gratings. Edmund Scientific Optics http://www.edmundoptics.com/onlinecatalog/displayproduct.cfm?productID=1490 is a convenient reseller. Edmund's stock number NT54-512 is a 500 line/mm grating available for $0.78 each in quantities of 80. Apparently, Edmund purchases the gratings from Rainbow Symphony http://www.rainbowsymphonystore.com/scienanded1.html. Rainbow's price for 500 line per mm gratings starts at $0.40 in quantities of 50. An important reason that the spectrometer design and software are being shared through a Creative Commons license is in the hope that without the possibility of license fees or aggregator's markup, costs will remain low, allowing wide use. The assembled spectrometer (sans detector) is shown in Figure 4.

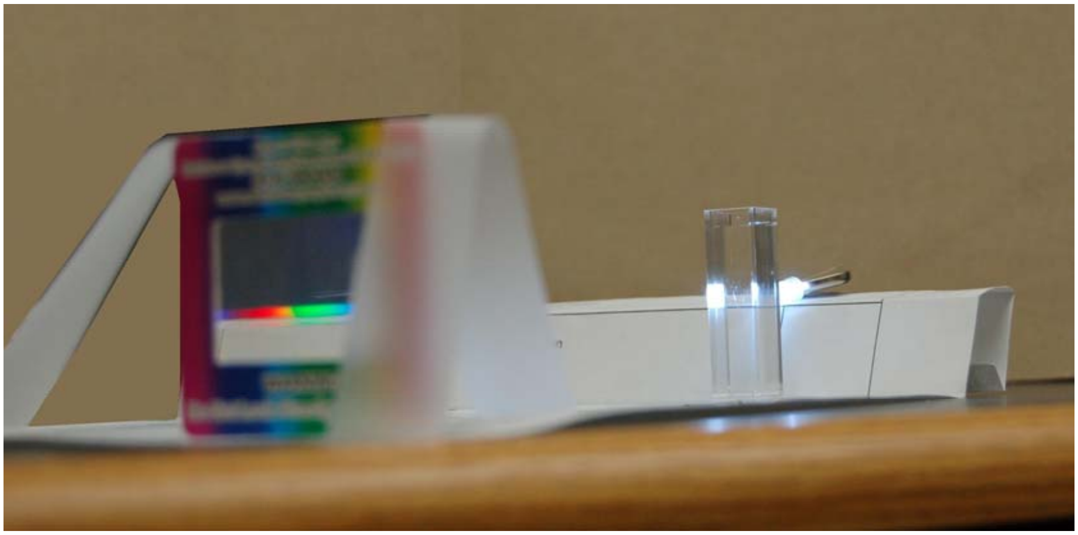


Figure 4. Assembled Spectrometer. LED, perched 1" above desk, shines through cuvette, aimed directly at grating, which in turn is braced with transparent tape. Spectrum and LED glare are unretouched (laboratory background removed for clarity). Picture obtained with Nikon D50 camera.

VI. Software

Cameras typically output JPEG files. Spectral measurement thus proceeds most easily if software can directly import such files, extract spectra, and manipulate the spectra into intensity, transmittance, and absorbance data. Data export to other software, such as spreadsheets, is also critical, as students will want to adjust for stray light or saturation once they realize the problems exist. One could, of course, use commercial graphics software to pre-process the images and commercial mathematical packages such as *Matlab* or *Mathematica* to do the manipulations, but this would subvert one of the goals, making data manipulation accessible to all students. We have thus made available both the source code and executable file for software to carry out the necessary processing. CodeGear RadStudio Delphi 2007 was employed, using IOComp's ixyPlot and related components. A version of the software that will run in a web browser (Java code) is being planned. It is obvious that a native cell phone application would be highly desirable. It is likely that a reader of this paper can write such an application sooner than the current authors can! An impediment to native cell phone coding is the range of common operating systems (Windows CE Mobile, Symbian, Palm, Google/Android, iPhone/Linux, RIM/Blackberry, …).

The software loads reference and sample spectra (I_0 and I respectively) from a directory of the user's choice; picture preview is not available inside the program, so the Windows "Thumbnail" function in *Windows Explorer* is helpful for selecting data. If files are too big to conveniently navigate in the image displays, *Windows Paint* is entirely adequate for making smaller JPG files, either by cutting out the desired data and making a new, smaller inset file or by "stretching" the file to some smaller footprint. Resolution must suffer from compression, but since we have not yet characterized system resolution we do not yet have data on this aspect of performance. If some user has a mercury penlamp or other line source, students could easily "play with" the parametric dependence of dispersion, resolution, and throughput. In any event, once spectra are loaded, one can use either typed-in pixel coordinates or a point and click mouse interface to tell the software where the useful spectral data appear, how many pixels high the integration area should be, and the range of wavelengths putatively covered by the extracted spectrum. Once the desired area is defined, plots of I, I_0, both on the same axes, T, and A can be rendered. Because one must assume that no two frames are taken with the same hand-held camera orientation, an algorithm to linearly interpolate $I(\lambda)$ applicable to the wavelengths of $I_0(\lambda)$ is included in the transmittance computations. Comma-delimited lists of all extracted and computed data are available once any have been plotted. One can then transfer the data to a spreadsheet, allowing improved data processing. For example, an average stray light level could be subtracted.

VII. Audiences and Initial Experience

The cell phone spectrometer has been used three times as of this writing. First, a group of instrumental analysis students at the Faculty of Chemistry, Hanoi University of Science worked with the components. By fluke, two-dimensional "double axis" diffraction gratings (diffraction/dispersion in two directions simultaneously, see http://www.rainbowsymphonystore.com/scienanded1.html accessed 6/30/09) were obtained, giving more complicated visual patterns that could be used easily since the software had no predetermined, assumed diffraction pattern to fit. Second, a group of high school teachers from Illinois were given the components and allowed to explore how a spectrometer so designed might fit into their classrooms. Finally, 26 high school students (mostly seniors, but at least 2 sophomores) in groups of three, attending a summer outreach program at Clark Atlanta University were given the components and some guidance in their use. In all cases, while there was a sequence of questions that could be followed, the students/participants were encouraged to ignore the writeup and proceed until they could obtain reproducible exposures at controlled dispersions so that absorbance experiments could be performed. At that point, "primary color" samples (Kool Aid for the high school teachers, $CuSO_4$ for students) were provided.

In all three cases, the classroom dynamics were the same. After a few minutes of confusion and intense questioning of the instructor, the idea of "playing in the sandbox" to optimize throughput, dispersion, exposure, alignment, stability, and so on "clicked." In place of a frenzied instructor, there was intense student-student interaction, with an occasional, "look at this!" as the photographic spectra started rolling forth. A few students never tried to engage the project for reasons unclear; those who stayed focused for at least 5 minutes generally completed assembly and were able to obtain pedagogically-significant data i.e. data that led them to understand one or more of the ideas previously listed.

For illustrative purposes, here are data obtained by this paper's authors. A Nikon D50 camera, operating without flash, set for closeup focus, and aimed at the spectrum transmitted by water or 20 µM Methylene Blue, obtained f/4, 1/30 s exposures as shown:

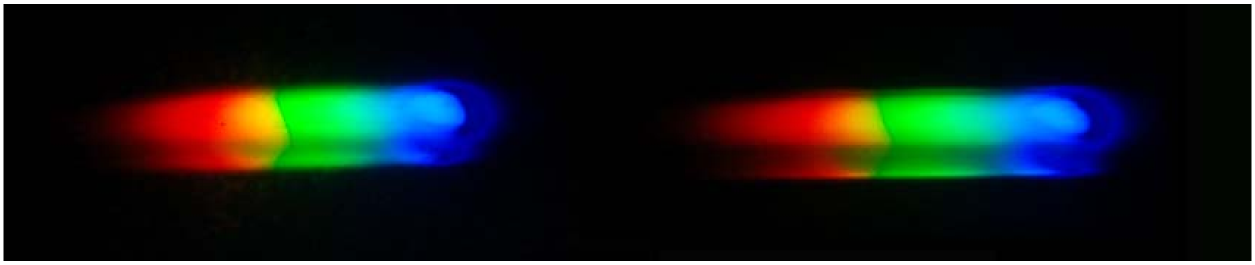
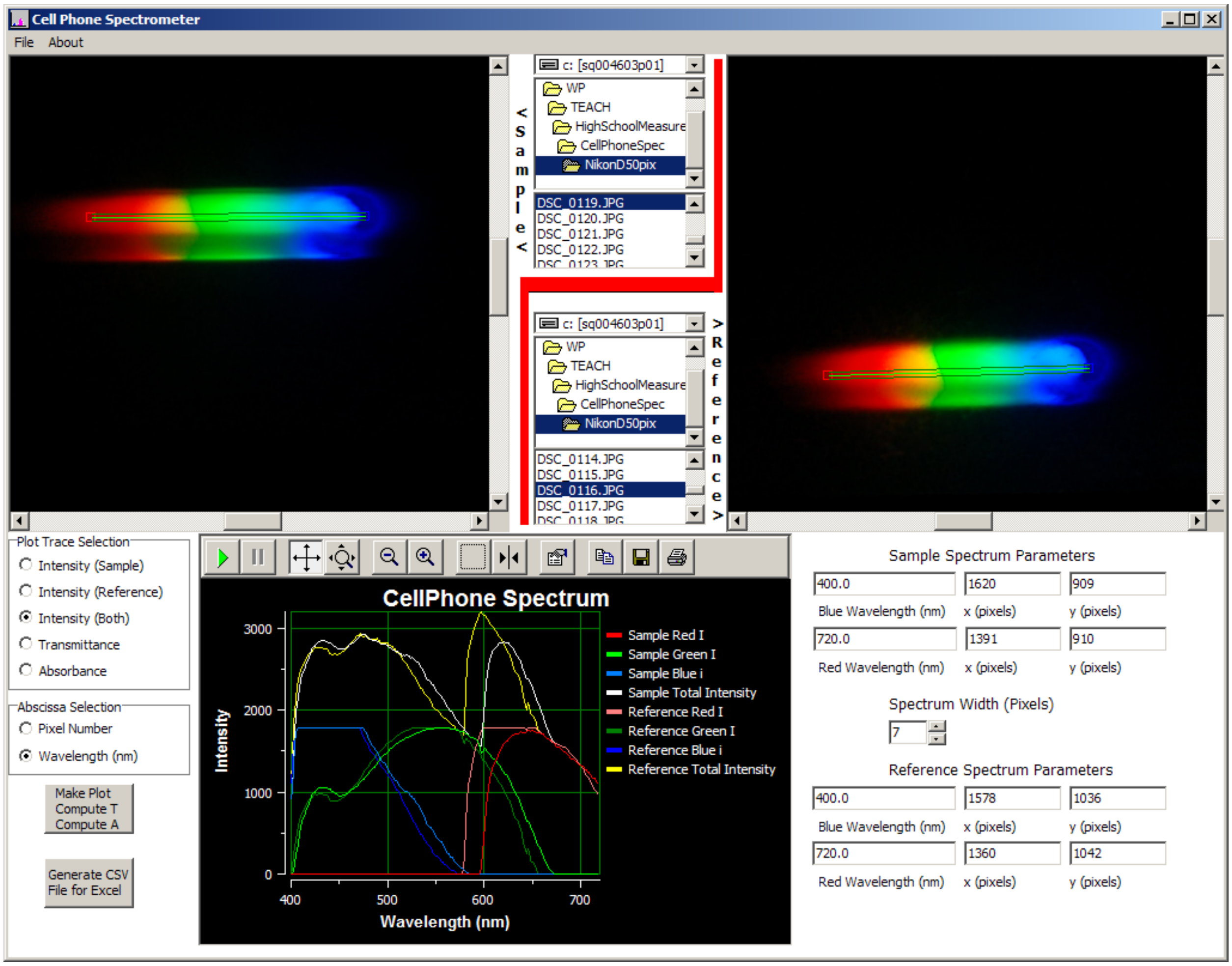


Figure 5. Spectral Data for 20 µM Methylene Blue. Left spectrum: I_0. Right spectrum: I. Insets combined using Windows *Paint*. Line near the left end of the green part of the spectrum due to dirt on the grating. Note change in yellow part of spectrum due to MB absorption.

A screen grab of the spectra as processed by the software, showing raw intensity data, is in Figure 6. The green line across the spectra shows the region plotted, and the dimmer lines above and below the green central line show the range of pixels summed. Note that near reported wavelengths of 450 nm and 625 nm, the I_0 spectrum can be seen to saturate. Wavelength calibration can be seen to be terrible; methylene blue absorption is centered at 655 nm in a well-calibrated measurement, but turns up here at 590 nm (Figure 7). The reason for non-calibration is clear from the way the wavelength calibration is set; the user simply guesses which pixels correspond to the extreme wavelengths emitted by the LED and detected by the camera, with no knowledge of the red or blue cutoff of the sensor. If this were a "real" measurement, such arbitrariness would be unacceptable. Here, it helps make the case for careful calibration, for showing the effect of the spatial extent of the light source on dispersion and resolution. Saturation at blue wavelengths in both spectra and in red wavelengths for the reference spectrum illustrates dynamic range limitations. Because these spectra were taken in a darkened room, stray light is minimal. In a brightly-lit room as shown in Figure 4, stray light is also obvious.



Cell Phone Spectrometer

File About

c: [sq004603p01]
WP
TEACH
HighSchoolMeasure
CellPhoneSpec
NikonD50pix
DSC_0119.JPG
DSC_0120.JPG
DSC_0121.JPG
DSC_0122.JPG

c: [sq004603p01]
WP
TEACH
HighSchoolMeasure
CellPhoneSpec
NikonD50pix
DSC_0114.JPG
DSC_0115.JPG
DSC_0116.JPG
DSC_0117.JPG

Plot Trace Selection
○ Intensity (Sample)
○ Intensity (Reference)
● Intensity (Both)
○ Transmittance
○ Absorbance

Abscissa Selection
○ Pixel Number
● Wavelength (nm)

Sample Spectrum Parameters

Blue Wavelength (nm)	x (pixels)	y (pixels)
400.0	1620	909

Red Wavelength (nm)	x (pixels)	y (pixels)
720.0	1391	910

Spectrum Width (Pixels): 7

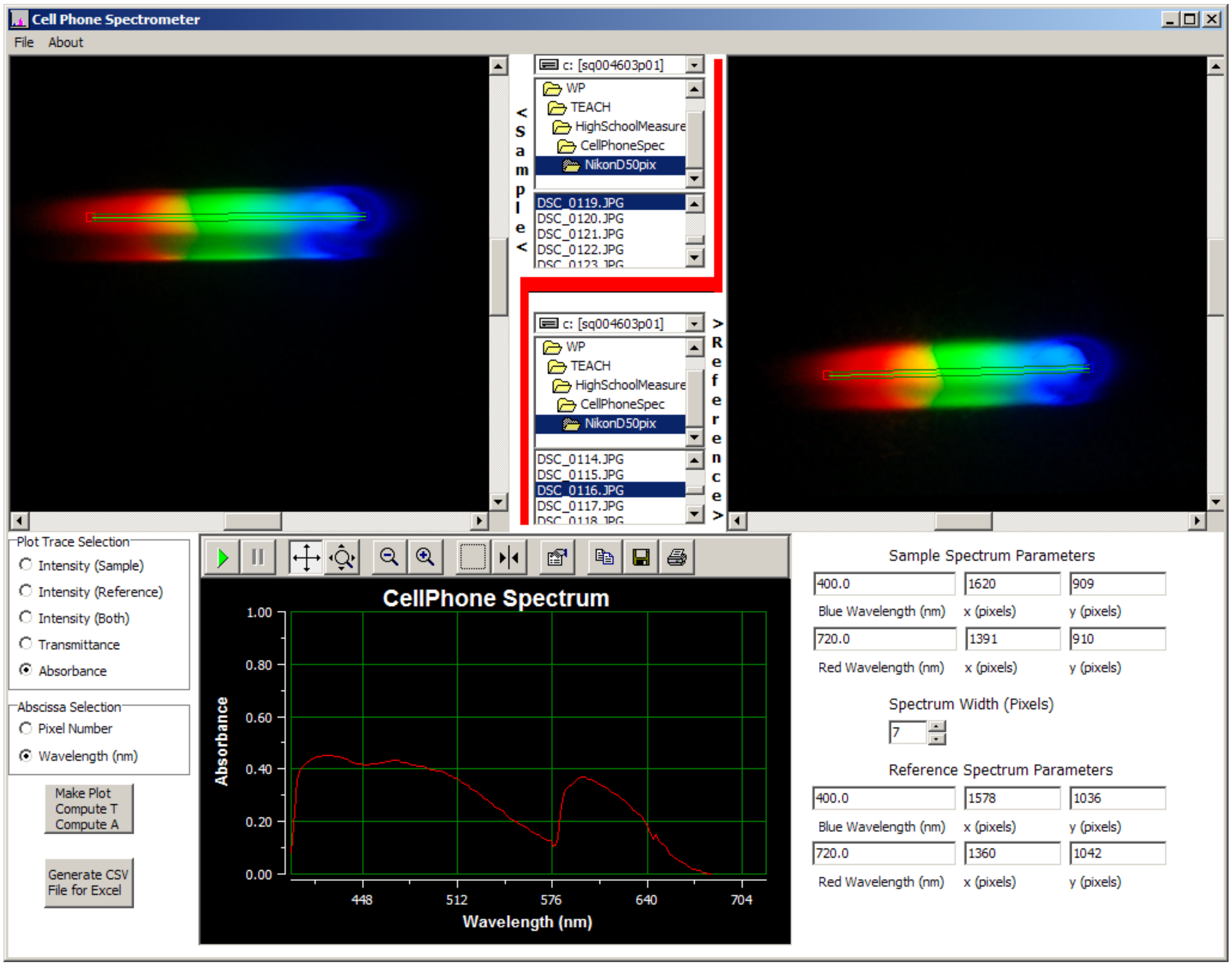
Reference Spectrum Parameters

Blue Wavelength (nm)	x (pixels)	y (pixels)
400.0	1578	1036

Red Wavelength (nm)	x (pixels)	y (pixels)
720.0	1360	1042

Figure 6. Screen Grab of Raw Intensity Data for 20 μM Methylene Blue.

The artifactual "absorbance" at blue wavelengths (<512 nm on the graph abscissa in Figure 7) makes the students question when Beer's Law fails due to the instrument as well as when chemistry may be involved. Is there a way to distinguish the two? Inexpensive cameras adjust exposure to avoid detector saturation; getting reproducible exposure is easiest when there is much stray light to fool the camera electronics, but of course this generates dynamic range and background subtraction difficulties. Students can explore the noise reduction due to signal averaging by varying the number of rows of pixels average to produce the raw spectrum. The lack of correspondence between $I(\lambda)$ for any color sensor and the purported output of the LED naturally leads to discussion of quantum efficiency, throughput, and the fraction of generated light that actually reaches the detector. A mercury penlamp could be used to show wavelength range, resolution, and wavelength calibration (warning: such lamps typically produce substantial ultraviolet light; while brief exposure is unlikely to cause sunburn, eye protection is essential). The range of discussion that may come from this instrument is yet to be fully explored; in no case as yet have all students had convenient ways to offload their spectra to their laptops in real time. Emailing spectra to the instructor served as a proxy for full, real-time participation.



Plot Trace Selection
○ Intensity (Sample)
○ Intensity (Reference)
○ Intensity (Both)
○ Transmittance
● Absorbance

Abscissa Selection
○ Pixel Number
● Wavelength (nm)

Sample Spectrum Parameters

Blue Wavelength (nm)	x (pixels)	y (pixels)
400.0	1620	909

Red Wavelength (nm)	x (pixels)	y (pixels)
720.0	1391	910

Spectrum Width (Pixels): 7

Reference Spectrum Parameters

Blue Wavelength (nm)	x (pixels)	y (pixels)
400.0	1578	1036

Red Wavelength (nm)	x (pixels)	y (pixels)
720.0	1360	1042

Figure 7. Absorbance Spectrum Corresponding to Figure 6.

VIII. Conclusion

While there has been no controlled testing of student learning with the home-made spectrometer compared to other approaches, decades of watching students and reading misguided exam answers, when contrasted with discussion during construction and use of the cell phone spectrometer, suggests that this highly visual, intentionally crude approach to teaching about spectroscopic instruments is more effective than any other approach the author has tried.

References Cited

1. S. X. Wang, and X. J. Zhou, "Spectroscopic Sensor on Mobile Phone," Patent 7,420,663 (US, 2008).
2. *Process Oriented Guided Inquiry Learning*, http://new.pogil.org/ (Accessed 07/10/2009).
3. D. C. Harris, *Quantitative Chemical Analysis* (W. H. Freeman, New York, 2007).
4. D. Harvey, *Modern Analytical Chemistry* (McGraw Hill, New York, 2000).
5. D. Harvey, *Analytical Chemistry 2.0: An Electronic Textbook for Introductory Courses in Analytical Chemistry* (Greencastle, IN, 2009) http://fs6.depauw.edu:50080/~harvey/eText%20Project/AnalyticalChemistry2.0.html.
6. D. A. Skoog, F. J. Holler, and S. R. Crouch, *Principles of Instrumental Analysis* (Thomson Higher Education, Belmont, CA, 2007).
7. J. James, *Spectrograph Design Fundamentals* (Cambridge University Press, Cambridge, 2007).
8. G. Rieke, *Detection of Light: From the Ultraviolet to the Submillimeter* (Cambridge University Press, Cambridge, 2003).
9. L. D. Rothman, S. R. Crouch, and J. D. Ingle, "Theoretical and Experimental Investigation of Factors Affecting Precision in Molecular Absorption Spectrophotometry," *Anal. Chem.* **47,** 1226-1233 (1975).
10. J. D. Ingle, and S. R. Crouch, *Spectrochemical Analysis* (Benjamin Press, New York, 1988).
11. N. A. Rakow, and K. S. Suslick, "A Colorimetric Sensor Array for Odor Visualization," *Nature* **406,** 710-713 (2000).
12. K. S. Suslick, and N. A. Rakow, "A Colorimetric Nose: 'Smell – Seeing'," *Proc. Electrochem. Soc.* **2001-15 (Artificial Chemical Sensing: Olfaction and the Electronic Nose),** 8-13 (2001).
13. G. M. Whitesides, "Paper Diagnostics - Using First World Science in Developing Economies," in *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy*, (Chicago, IL, 2009).
14. A. W. Martinez, S. T. Phillips, E. Carrilho, S. W. Thomas III, H. Sindi, and G. M. Whitesides, "Simple Telemedicine for Developing Regions: Camera Phones and Paper-based Microfluidic Devices for Real-time, Off-site Diagnosis," *Anal. Chem.* **80,** 3699-3707 (2008).
15. E. Carrilho, S. T. Phillips, S. J. Vella, A. W. Martinez, and G. M. Whitesides, "Paper Microzone Plates," *Anal. Chem.* **81,** 5990-5998 (2009).
16. A. K. Ellerbee, S. T. Phillips, A. C. Siegel, K. A. Mirica, A. W. Martinez, P. Striehl, N. Jain, M. Prentiss, and G. M. Whitesides, "Quantifying Colorimetric Assays in Paper-based Microfluidic Devcies by Measuring the Transmission of Light through Paper," *Anal. Chem.* **81,** 8447-7452 (2009).
17. J. Gordon, and S. Harman, "A Graduated Cylinder Colorimeter: An Investigation of Path Length and the Beer-Lambert Law," *J. Chem. Ed.* **79,** 611-612 (2002).
18. J. Gordon, A. James, S. Harman, and K. Weiss, "A Film Canister Colorimeter," *J. Chem. Ed.* **79,** 1005-1006 (2002).
19. J. Castillo, H. Gutierrez, Y. Vitta, M. Martinez, and A. Fernandez, "Development and Testing of Multi-well Plates Absorbance Reader for Clnical Analysis Using Inexpensive Web-Cam," *Proc. SPIE Int'l. Soc. Opt. Eng.* **6755,** 67550W-67551 - 67550W-67559 (2007).
20. P. R. Teasdale, S. Hayward, and W. Davidson, "In situ, High-Resolution Measurement of Dissolved Sulfide Using Diffusive Gradients in Thin Films with Computer-Imaging Densitometry," *Anal. Chem.* **71,** 2186-2191 (1999).
21. D. N. Breslauer, R. N. Maamari, N. A. Switz, W. A. Lam, and D. A. Fletcher, "Mobile Phone Based Clinical Microscopy for Global Health Applications," *PLoS ONE* **4,** e6320 (2009).