

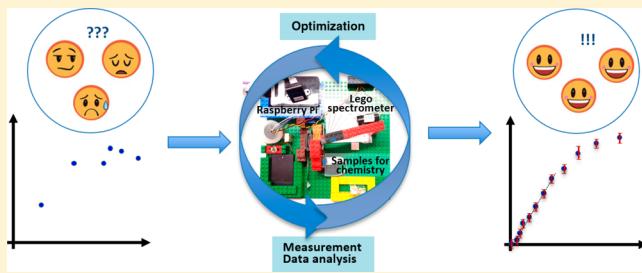
# Optimization and Design of an Absorbance Spectrometer Controlled Using a Raspberry Pi To Improve Analytical Skills

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 Supporting Information

**ABSTRACT:** It is not uncommon for students to view laboratory instruments as black boxes. Unfortunately, this can often result in poor experimental results and interpretation. To tackle this issue, a laboratory course was designed to enable students not only to critically think about operating principles of the instrument but also to improve interpretation skills. Students were required to build their own visible spectrometer using interlocking building bricks with simple optical elements and a Raspberry Pi computer. Experiments were then conducted to explore the instrumental capabilities while, at the same time, using Python programming to plot data, perform linear least-squares fitting, and calculate errors. Instrument response and spectral measurements were followed by kinetic studies, enabling the students to tackle a “real” problem by extracting rate constants. The main learning outcomes were that the students would gain a better understanding of instrumental components and at the same time learn valuable analytical techniques such as calibration, determination of the limits of linearity, and dynamic range. These outcomes were achieved by applying a problem based learning approach.



**KEYWORDS:** First-Year Undergraduate/General, Physical Chemistry, Analytical Chemistry, Problem Solving/Decision Making, Instrumental Methods, Interdisciplinary/Multidisciplinary, Quantitative Analysis, Laboratory Computing/Interfacing, Kinetics, UV-Vis Spectroscopy

One of the most commonly used measurement tools in the physical and chemical sciences is a UV-vis spectrometer. This instrument is a simple and versatile tool that allows a sample to be probed by analysis of its optical properties. It is a key piece of equipment in many laboratories allowing researchers and students alike to measure concentrations, characterize samples, and study reaction kinetics.<sup>1</sup> UV-vis spectrometers are popular and relatively low priced, but tend to exist as “black boxes”, especially in a teaching environment where students seldom question the inner workings of these instruments. This ultimately limits critical thinking, which has a direct consequence on the end-users’ ability to optimize parameters to minimize errors while, at the same time, maximize the signal-to-noise ratio and resolution of a measurement. There is no better way to solve this problem than to open the black box and probe the end-users’ understanding of the operational principles.<sup>2</sup>

As part of a new first year undergraduate laboratory within the Department of Chemistry at Imperial College London, we attempted to tackle these challenges by developing a synoptic experiment which covers physical chemistry, analytical chemistry, and computer programming. This diverges from more conventional practice whereby labs are often broken down into distinct fields, and can be well implemented through absorbance spectrometry. In this context, groups of students were asked to

- (1) design and build their own visible spectrometers integrating a Raspberry Pi computer
- (2) determine limits of detection
- (3) determine the “unknown” concentration of a provided sample
- (4) measure an absorption spectrum
- (5) perform kinetic studies for the reduction of methylene blue (3,7-bis(dimethylamino)-phenothiazin-5-iium chloride) in the presence of ascorbic acid ((5R)-[(1S)-1,2-dihydroxyethyl]-3,4-dihydroxyfuran-2(5H)-one)
- (6) use Python programming to interpret and analyze the data whereby student explored the value of repeating experiments and performing statistical processes such as averaging and error determination.

The general ethos of the laboratory was for students to problem solve and think about each component to obtain reasonable results. To achieve this goal, it was important to step away from the conventional, recipe like, experimental script where students follow a set of instructions. Instead, students were issued with a laboratory manual that provided all relevant information but stopped short of step by step instructions. Acquisition and data analysis were performed using a Raspberry Pi computer and Python programming. For reference, the

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Session 1	Session 2	Session 3	Session 4
Part 1: Design and build the spectrometer	Part 1: Design and build spectrometer followed by integration of Pi	Part 2: Determine detectable concentration range	Part 2: Optimization of signal and quantification of detection limits
Session 5	Session 6	Session 7	Session 8
Part 3/Part 4: Determination of unknown concentration / full absorbance spectra	Part 4: Absorbance spectra and comparison with commercial instrument	Part 5: Kinetics of Methylene Blue and Ascorbic acid	Part 5: Kinetics of Methylene Blue and Ascorbic acid / Disassembly of Spectrometer

Figure 1. Suggested breakdown of lab, 8 sessions.

Session 1	Session 2	Session 3	Session 4	Session 5
Part 1: Design and build the spectrometer	Part 1: Design and build spectrometer followed by integration of Pi and Absorbance spectra by commercial instrument	Part 2: Determine detectable concentration range and quantify detection limits	Part 2-3: Determine detectable concentration range and quantify detection limits / Kinetics of Methylene Blue and Ascorbic acid	Part 3: Kinetics of Methylene Blue and Ascorbic acid / Disassembly of Spectrometer

Figure 2. Suggested breakdown of lab, 5 sessions.

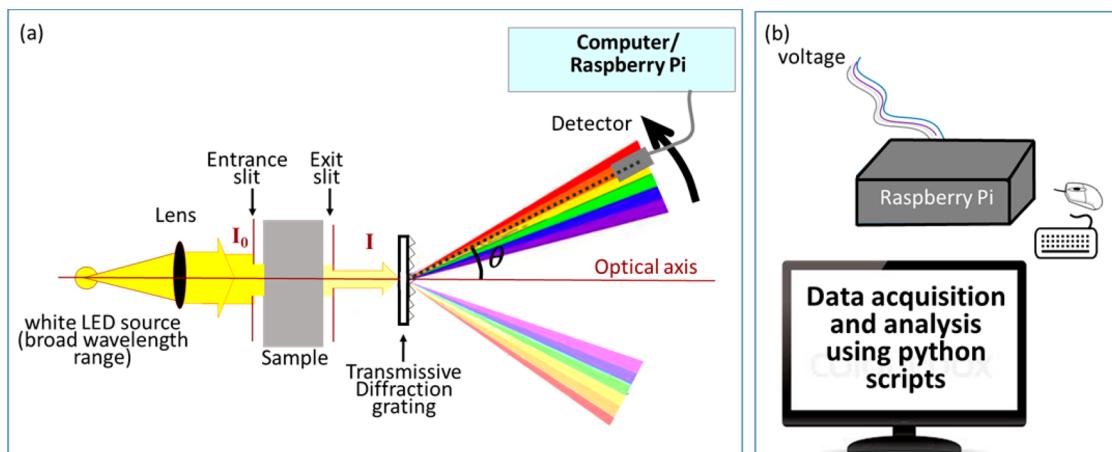


Figure 3. (a) Schematic of a visible spectrometer instrument consisting of a white light LED, collimation optics, entrance and exit slits, sample, transmissive diffraction grating, detector. (b) Raspberry Pi control and readout of the photodetector voltage.

laboratory manual, instructions for the Raspberry Pi, and example of Python scripts are provided as Supporting Information S1, S2, and S3.

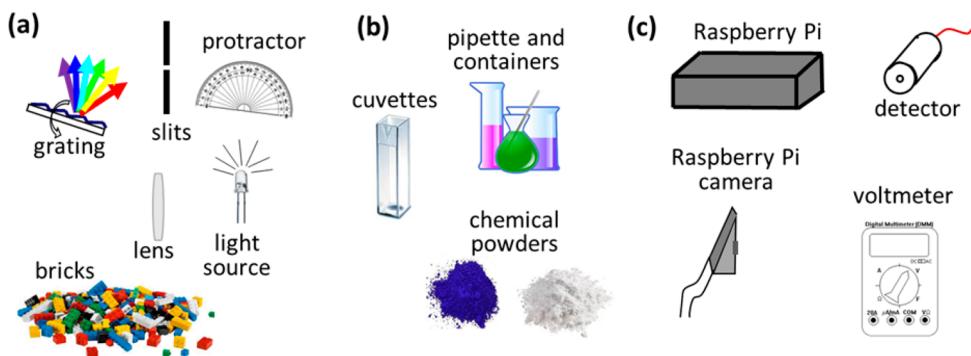
Due to the synoptic nature of the lab, the experiment was run over 8, 3 h sessions. However, this can be easily truncated as necessary if one wants to alter the focus on a particular component. For example, Figure 1 highlights material covered during the 8 sessions and is broken down into 5 distinct parts. Would time be more limited, we suggest in Figure 2 a 5 sessions breakdown, with instrumental response study and kinetic study, the spectrum being measured by a commercial instrument only.

Data acquisition requires some skills which are best taught through practice. Our approach was therefore to design

experiments for students, in which they would have to optimize their instrument to obtain the best performances and a good understanding of errors.

Throughout the course, the importance of quality rather than quantity of data was emphasized. Students were instructed that if time was limited, it was more important to obtain meaningful data rather than to cover all the tasks of the lab. Ultimately, this lab was an opportunity for students to work in teams and tackle an iterative process through problem based learning and group work. As such, the timetable was only a suggestion and teams were asked to judge and time manage their respective progress.

Students were divided into groups of 3–4. At all times, one coordinator and 3 demonstrators were present to ensure efficient progress. Each demonstrator was in charge of



**Figure 4.** Materials provided to students (a) to build their spectrometer (b) to perform accurate chemistry preparation and experiments (c) to measure, analyze, and interpret data.

approximately 10 groups. Within this template of independent thinking, the role of the demonstrator was to guide the students and help them solve technical problems rather than to supply answers. This leaves the students with the ability to innovate and develop ideas which can be tested.

In term of data acquisition and analysis, the Raspberry Pi computer was chosen. It is a low-cost, credit-card sized computer that plugs into a computer monitor and uses standard mouse and keyboard. It runs Linux in a graphical environment and provide GPIO (general purpose I/O) for controlling sensors and recording signals. The simplicity and cost of the Raspberry Pi make it highly advantageous in teaching environments, yet it still remains relatively new in this context.<sup>3</sup> An additional advantage of using such a platform is that it allows the user to gain a working knowledge in Linux terminal environment, shell scripting, and computing in a practical setting. It is thus perfectly suited for the implementation with a large group of students, doing data acquisition and further analysis.

## SPECTROMETER OPERATING PRINCIPLES

The absorbance spectrometer was chosen due to its broad use in chemistry together with simple operating principles, thus perfectly suited to teach “measurement science”. A schematic of a visible spectrometer implementing a transmissive grating as the dispersion element and details of the data acquisition elements are shown in Figure 3. White light is emitted by a source and passes through a lens to create a collimated beam. This beam then goes through an entrance slit, a sample, and an exit slit before being diffracted and detected. Entrance slits and exit slits are used to optimize the spectral resolution. The absorbance of light,  $A$  is defined by the Beer–Lambert law in eq 1, where  $c$  is the concentration,  $\epsilon(\lambda)$  is the extinction coefficient at the wavelength  $\lambda$ , and  $l$  is the sample path length. The extinction coefficient is an empirical coefficient unique for each substance with units of concentration per length.<sup>4</sup>

$$A(\lambda) = \epsilon(\lambda)cl \quad (1)$$

The absorbance can also be calculated by measuring the intensity of the collimated beam of light by eq 2:

$$A(\lambda) = \log \frac{I_0(\lambda)}{I(\lambda)} \quad (2)$$

where  $I_0(\lambda)$  is the intensity of the light passing through the reference cell (a cuvette filled with solvent but zero concentration of the chromophore is used as the blank) and  $I(\lambda)$  is the intensity of the light passing through the sample

cell.<sup>5</sup> As the absorbance is wavelength-dependent, a diffraction grating is used to separate the wavelengths. The wavelength is related to the angle of incidence in a simple relationship given as eq 3:

$$d \sin \theta_m = m\lambda \quad (3)$$

where  $\theta$  is the angle relative to the grating (defined from the grating normal, as sketched in Figure 3a),  $d$  is the period of the grating, and  $m$  is the diffracted order, here  $\pm 1$ .

The signal is measured by a photodiode, which converts photons into a current proportional to the voltage  $V$ . Therefore, in eq 2,  $I$  can be replaced with the voltage  $V$ . This gives eq 4:

$$A(\lambda) = \log \frac{V_{\text{blank}}(\lambda) - V_d}{V_{\text{sample}}(\lambda) - V_d} = \epsilon(\lambda)cl \quad (4)$$

where  $V_{\text{blank}}(\lambda)$  is the voltage measured for the blank,  $V_d$  is the dark voltage or voltage when the light source is switched off, and  $V_{\text{sample}}(\lambda)$  is the voltage measured for the sample.

## MATERIALS AND METHODS

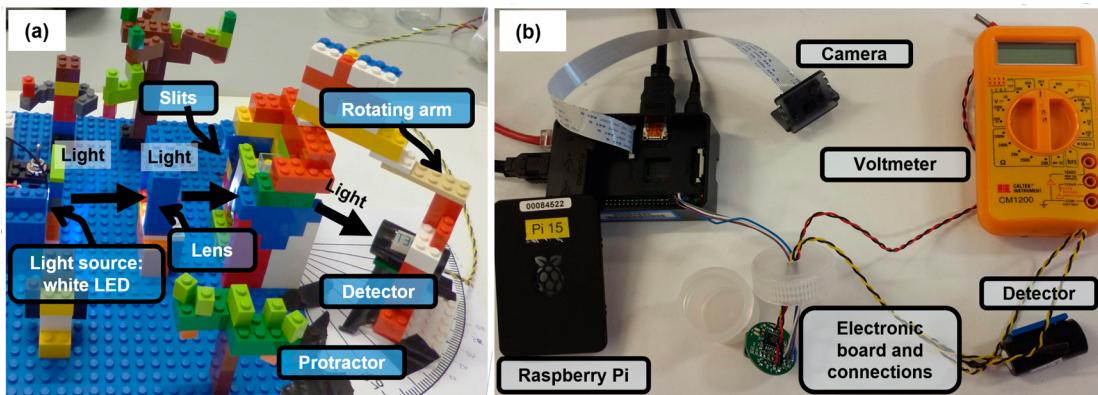
### Materials

The components provided to the students to build their instrument as well as perform and analyze experimental data are shown in Figure 4. Briefly, to create the spectrometer the students were supplied with a black cloth, an LED light source, a power source, a lens, slits, a diffraction grating, and a protractor (Figure 4a). Additionally, for sample preparation, the students were given pipettes, containers, and 2 glass cuvettes. Methylene blue and ascorbic acid were provided in powder form (Figure 4b). To measure the absorbance, students were provided with a photodiode detector, connected to a voltmeter and a Raspberry Pi for signal optimization (Figure 4c). The list and cost of each component are given in Supporting Information S4.

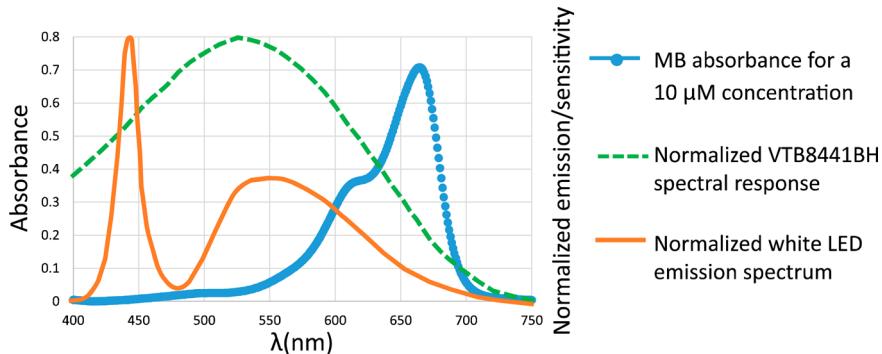
### Building and Optimization of the Spectrometer

The basic building of a low-cost spectrometer has been previously described in detail.<sup>6,7</sup> Here, detailed instructions for building a spectrometer were not provided, aside from Figure 3a, to encourage the students to take initiatives in their designs. This resulted in many different configurations, many of which had equally good performance.

At the heart of building a successful spectrometer, it was important for students to work as a team to design an optimal configuration. An accurate spectrometer relies on proper horizontal and vertical alignment of the optical path, as well as sensible distance choices, in term of source, lens, cuvette,



**Figure 5.** (a) Typical spectrometer with all key components highlighted. (b) Instrumentation for measurements: the detector is connected to an electronic board with an operational amplifier and then output to a voltmeter and an ADC converter chip. The digital signal is recorded using the Raspberry Pi interfacing.



**Figure 6.** Emission spectrum of the LED and responsivity spectrum of the detector, superposed to the absorption spectrum of methylene blue using a 10  $\mu\text{M}$  concentration in water.

grating, protractor, slits, and detector position. The spectrometer is designed and optimized to obtain an optimal signal-to-noise ratio, together with good resolution for spectral measurements accuracy.

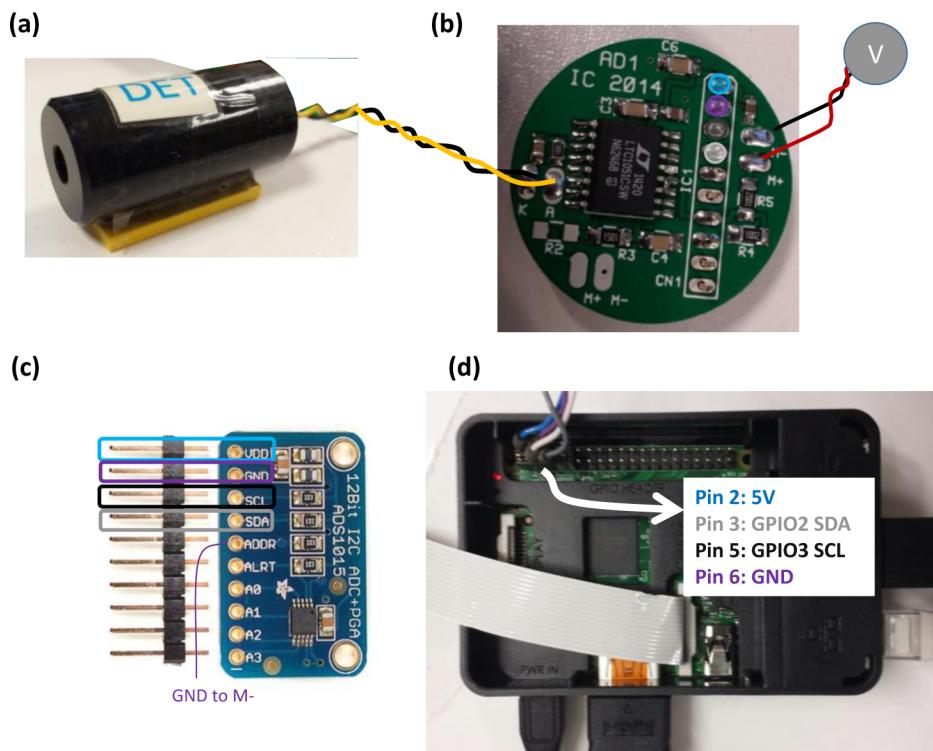
Slits were provided on printed paper, and their sizes had to be optimized, as there is a compromise between spectral resolution and signal intensity. The grating was a holographic transmission grating from Edmund Optics, with 1000 lines/mm. Optimizing the detector angle and position was critical in ensuring that the correct wavelength is probed. Resources such as the Internet, text books, and manuals were available to the teams in order to facilitate in deciding on the ideal configuration. An example of a successful instrument is shown in Figure 5a, and more examples are provided in Supporting Information S5.

Unlike other UV-vis spectrometers previously reported based on similar principles,<sup>7</sup> the students incorporated a simple and cheap Raspberry Pi computer to enable efficient recording and data processing, as shown in Figure 5b. Thanks to an electronic board, the voltage from the detector photodiode could be read by connecting and using the voltmeter, and at the same time the Raspberry Pi could be used to perform data acquisition. The Raspberry Pi has a camera module; this was installed and used by the students to take photographs of their spectrometer's evolution. By doing so, they were able to build a spectrometer that closely mimics a commercially available instrument and obtain measurements with similar levels of accuracy. Details on the Raspberry Pi integration and electronic will be given in a following section.

### Light Source and Detector

We now turn our attention to the signal and measurement aspects of the spectrometer. The light source was a white light LED (RL5-W18015, Superbright LEDs). The choice of photodiode is critical in ensuring low detection limits. Therefore, a balance between robustness and sensitivity must be achieved for the students to succeed. A silicon photodiode on an 8 mm ceramic plate with an IR blocking filter was used (VTB8441BH, Excelitas Technology). This photodiode is blue enhanced, and benefits from a very low dark current. The LED emission spectrum<sup>8</sup> and detector spectral response<sup>9</sup> are provided in Figure 6.

To improve the signal-to-noise ratio, the photodiode was fitted in a black detector housing, with an aperture diameter of 6 mm and an acceptance angle of  $\sim 30^\circ$ . The amplification was performed using a LTC1051 dual operational amplifier.<sup>10</sup> Specifically, the signal from the detector photodiode (Figure 7a) was fed into an LTC1051(1/2) operational amplifier in a transimpedance configuration (Figure 7b), with a gain of  $10^7$ . The amplified signal was then passed through a low pass filter before finally being buffered with an LTC1051(1/2) operational amplifier and then output to a Digital Voltmeter (DVM) and a 12-bit Analogue to Digital Convertor (ADC) board (Figure 7b,c). Design of the electronics and connections was realized for the students prior to the lab. We provide details of the integrated circuit and electronic components of the photodiode amplifier in Supporting Information S6 for reference. The detector saturated at 4 V, and finding the optimal dynamic range of the detector was an aspect students



**Figure 7.** (a) Photodiode in its black detector housing. (b) Electronic board with LTC1051 operational amplifier with detector connection, voltmeter connection, and soldered pins to the ADC chip surrounded. (c) ADC converter board with colored connections to the Raspberry Pi's GPIO pins. (d) Raspberry Pi B+ picture with connected GPIO pins.

had to consider when quantifying sensitivity and limits of linearity.

#### Raspberry Pi Integration

The voltage from the photodiode detector could be read simultaneously on a multimeter and a Raspberry Pi via an ADC board (Figure 7b). The ADC chip was an Adafruit 4 Channel I2C 12-bit (Figure 7c);<sup>11</sup> it was chosen due to its low price, ready availability and as it is well supported by a Python library. The ADC converts the analogue voltage reading to a digital signal that can be read by a Raspberry Pi through the onboard General Purpose Input Output (GPIO). The GPIO pins allow the Raspberry Pi to interface with the ADC chip. Figure 7c,d gives the details of the connections between the ADC chip and the GPIO pins. The Raspberry Pi B+ model was chosen as it had adequate RAM and processor speed (700 MHz ARM Processor; 512 MB RAM). At the time of the experiment, it was the highest specification Raspberry Pi available.

The Raspberry Pi supports Python language programming, giving a concrete opportunity for students to control measurements and perform data analysis. Python is a high level language supporting multiple programming paradigms. Moreover, CPython, the reference implementation of Python is a free and open-source software. These aspects make it an excellent teaching tool bridging the gap between desktop programs such as Excel and lower level languages.

The Raspberry Pi root partition was mounted as an NFS (Network File System); this required modifying the Raspberry Pi boot script but allowed easy control of 30 Raspberry Pi's from one server.

#### Sample Preparation

Even the best spectrometer is of little use if samples are poorly prepared and the experiments poorly planned. For their

experiments to answer the problem posed to them, the students had to first determine a suitable range of sample concentrations for testing. Having chosen their range to ensure accurate results, the students had to carefully make up the samples from chemicals provided in powder form.

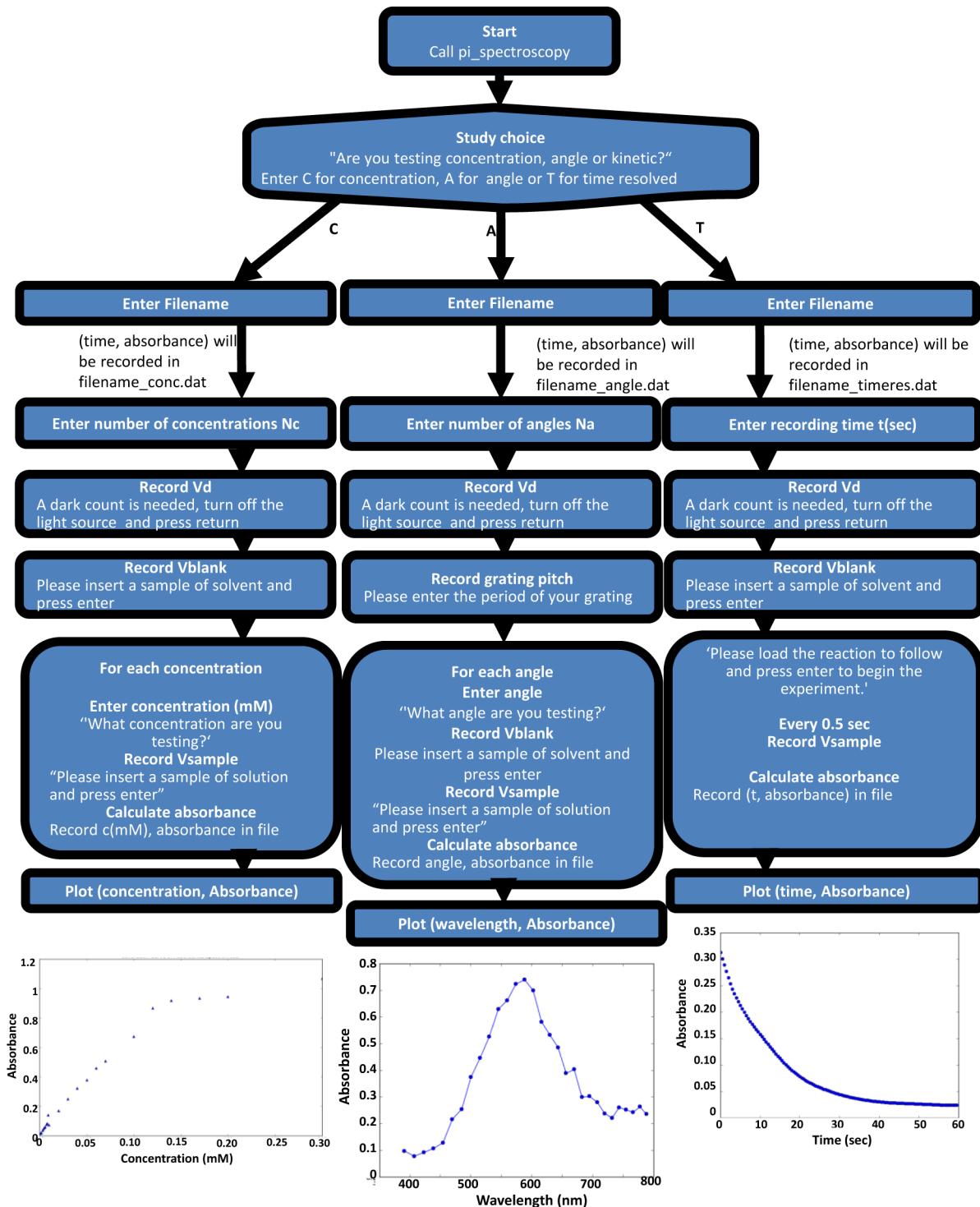
The principal chemical used for all parts was methylene blue which is a heterocyclic aromatic compound, and common and readily available dye. Its absorption spectrum given in Figure 6 has been measured with a commercial spectrometer. We used a solution of 10  $\mu$ M concentration, diluted down from a stock solution of 1 mM with water as solvent.

Students also used ascorbic acid in kinetic studies. Typically, the students first made a stock solution and then performed further dilutions to obtain the desired concentrations. They were encouraged to think about how to reduce their errors with many determining for themselves that errors related to the preparation of stock solution can be reduced by increasing the quantity of material used. It was found that stock solutions of 1 mM methylene blue and 50 mM for ascorbic acid were a good starting point.

The students were not provided with any assistance when making solutions and determining ideal concentrations. The key to success for the students was to prepare solutions accurately within a range of concentrations that gave sufficient data to draw conclusions yet also not so much data that they had insufficient time to complete the experiment.

#### Signal Acquisition

Within the department of Chemistry at Imperial College London, students are introduced to Python programming prior to commencing lab work. To ensure a deeper understanding, it is better for students to have basic introductory knowledge of computing (e.g., importing, plotting, and fitting data). Never-



theless, more scripts could be provided if the students have more limited computing knowledge or less allocated time.

To highlight the versatility of the spectrometer, the laboratory course included three distinct parts relating to data acquisition and analysis: a concentration study, an angle dependent study, and a time dependent study. The students were provided with acquisition scripts, and basic data analysis scripts. Flowchart of the acquisition scripts is provided in Figure 8, and scripts provided to students are given in Supporting

Information S3. For reference, the program output is also shown in Figure 8.

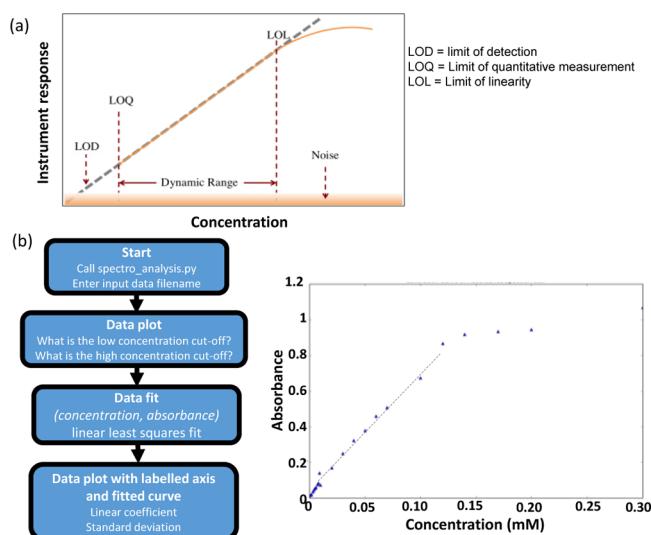
In practice, students had to call the script 'pi\_spectroscopy' and choose the study that they want to perform, through the "concentration", "angle", or "kinetic" options. It recorded the dark voltage  $V_d$ , the voltage  $V_{\text{blank}}(\lambda)$ , and the voltage  $V_{\text{sample}}(\lambda)$ . The script used the voltage values to calculate the absorbance  $A(\lambda)$  using eq 4.

For concentration or kinetic studies, the wavelength  $\lambda_0$  is chosen prior to the measurement, and  $V_{\text{blank}}(\lambda_0)$  can be

recorded once. The voltage  $V_{\text{sample}}(\lambda_0)$  is then recorded for each sample or each time step depending on the study. For angular dependent study, a sample is chosen, with accurate concentration. A reference value  $V_{\text{blank}}(\lambda)$  needs to be recorded for each angle (or equivalently wavelength), as well as a voltage  $V_{\text{sample}}(\lambda)$ . The wavelength is calculated from the incident angle, using eq 3.

On the basis of this integration, students could perform measurements, record data and further optimize them exploiting the Raspberry Pi interface.

The students were also provided with an initial data analysis program (see flowchart in Figure 9, and `spectro_analysis.py` script provided in Supporting Information S3). They were expected to optimize and modify it for their various data analysis needs.



**Figure 9.** (a) Instrumental response, with dynamic range corresponding to the range of concentration of interest. (b) Flowchart of the initial data analysis program and example of fitted data.

## MEASUREMENTS AND DATA ANALYSIS

The students had to assess the limits of linearity and calibrate their instrument and measure absorption spectra, as well as carry out kinetic studies. The elements were designed to test specific aspects of the instrument and allowed the students to collect meaningful data.

### Instrument Calibration

Understanding the instrumental response is an exceptionally important task in analytical science. This is something that both new and seasoned scientists alike tend to overlook. Ultimately, this has a direct consequence on parameters such as sensitivity, working concentration range, and errors. With this in mind, students were asked to assess the dynamic range of their instrument by measuring the signal as a function of concentrations. As part of assessing such parameters, students had to determine the limit of detection LOD (lowest concentration of a substance which can be distinguished from the noise), the limit of quantification LOQ (lowest concentration of a substance which can be reliably determined), and the limit of linearity (LOL) (concentration from which the measurement is no longer proportional to the concentration), Figure 9a.

The obtained calibration curve depends on the instrument characteristics (components, optical adjustment and wavelength). The characterization and optimization of the instrumental response was a fundamental step for the accuracy and reliability of measurements in all subsequent parts of the lab. To obtain a dynamic range within a reasonable concentration window, students had to first determine an appropriate wavelength to probe. It should take into account the chemical compound spectral properties, while at the same time ensure compatibility with the components. The most important elements in the present case are the source and detector spectral characteristics. The LED emission spectrum and detector spectral response have been provided in Figure 6. Other contributions are grating efficiency, lens transmission, optical adjustments, and wavelength choice. The absorption spectrum of methylene blue (Figure 6) was not provided, although students could easily look this up or alternatively use a color wheel. The relationship between the angle and wavelength is given by eq 3. Taking into account both extinction coefficient and instrument components spectral characteristics, a position around  $\lambda_0 \sim 580$  nm was found to be good.

The acquisition script could be used to perform the concentration dependent study (see Figure 8 and Supporting Information S3). To facilitate data analysis, an initial Python script was provided which enabled plotting of the acquired data and performing a linear least-squares fit to determine the dynamic range (see Figure 9b and Supporting Information S3).

After finding the useful concentration range, students had to determine their sources of errors, as well as improve on their measurements if possible. This is an iterative process where the experimental setup had to be optimized to minimize random and determinate errors. With a fully optimized instrument, errors on the order of  $1 \mu\text{M}$  could be obtained. A concentration of  $1 \mu\text{M}$  of methylene blue corresponds to an absorbance of  $A = 0.014$  at  $\lambda_0 = 580$  nm, using  $\epsilon(\lambda) = 14\,399 \text{ M}^{-1}\cdot\text{cm}^{-1}$ . This compares well to the sensitivity that can be obtained with commercial spectrometers. Such sensitivity was challenging to obtain but yet possible. After the instrument has been fully calibrated, a sample of methylene blue with "unknown" concentration was supplied and students had to determine the concentration. To challenge the students, samples were made up at concentrations close from the limit of quantitative measurement.

### Absorption Spectrum

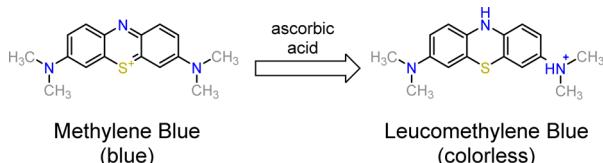
Students had to measure the absorption spectrum of methylene blue. This measurement was a good "calibration test". To obtain accurate results, proper spectrometer alignment and protractor positioning, as well as a good detector arm design, were vital. A bidimensional detector measuring RGB images of the diffracted spectrum would be an alternative to a rotational arm.<sup>12</sup> Nevertheless, spectrum calculation from RGB images is not straightforward. Angle nonlinearity and detector cost are additional reasons supporting our choice.

For this measurement, the acquisition script supplied was used (see Figure 8 and Supporting Information S3). The detector angle could be varied such that the absorbance could be measured at different angles  $\theta$ . At the beginning of the program, the dark voltage  $V_d$  was measured. Then, for each wavelength  $\lambda$  (or equivalently angle  $\theta$ , as described by Equation 3), the absorbance was calculated (eq 4), by recording the voltage of the reference  $V_{\text{blank}}(\lambda)$  and of the sample  $V_{\text{sample}}(\lambda)$ . Accurate measurement of the angle (meaning accurate

positioning and alignment of the pieces of the spectrometer) was necessary to obtain a high quality spectrum. An important parameter to consider was the number of angles measured and the step size as it has direct consequences on the quality of the spectrum obtained. The step could be varied through the measurement if necessary. Students were asked to compare their results with a spectrum taken with a commercial spectrometer (USB4000 from Ocean Optics). Aspects that need to be taken into consideration are the differences in absorbance levels between the instruments and differences in the noise.

### Kinetic Studies

Once the home-built spectrometers have been fully calibrated and optimized by performing measurements as described above, there is no better way to test the use of the instrument than by performing a chemical reaction and characterizing the kinetics. UV-vis spectroscopy is a common method to monitor such reactions and at the same time acts as a good introduction to kinetic experiments.<sup>13</sup> We chose the reduction of methylene blue ( $\text{MB}^+$ ) by ascorbic acid (A) to its colorless conjugate leucomethylene blue (LB). The reaction is illustrated in Figure 10.



**Figure 10.** Reduction reaction of methylene blue ( $\text{MB}^+$ ) with ascorbic acid (A).

In all cases, the  $[\text{MB}^+]$  concentration was less than 1% of the ascorbic acid concentration [A], ensuring pseudo first-order conditions,<sup>14,15</sup> as given by eq 5:

$$-\frac{d[\text{MB}^+]}{dt} = k_0[\text{A}][\text{MB}^+] = k_{\text{exp}}[\text{MB}^+] \quad (5)$$

Students had to confirm the reaction order and compare the results obtained to literature values.

A Python script was provided which could be used to record the dark voltage  $V_d$ , the reference voltage  $V_{\text{blank}}(\lambda_0)$ , and subsequently  $V_{\text{sample}}(\lambda_0)$  as a function of time (see Figure 8 and Supporting Information S3).

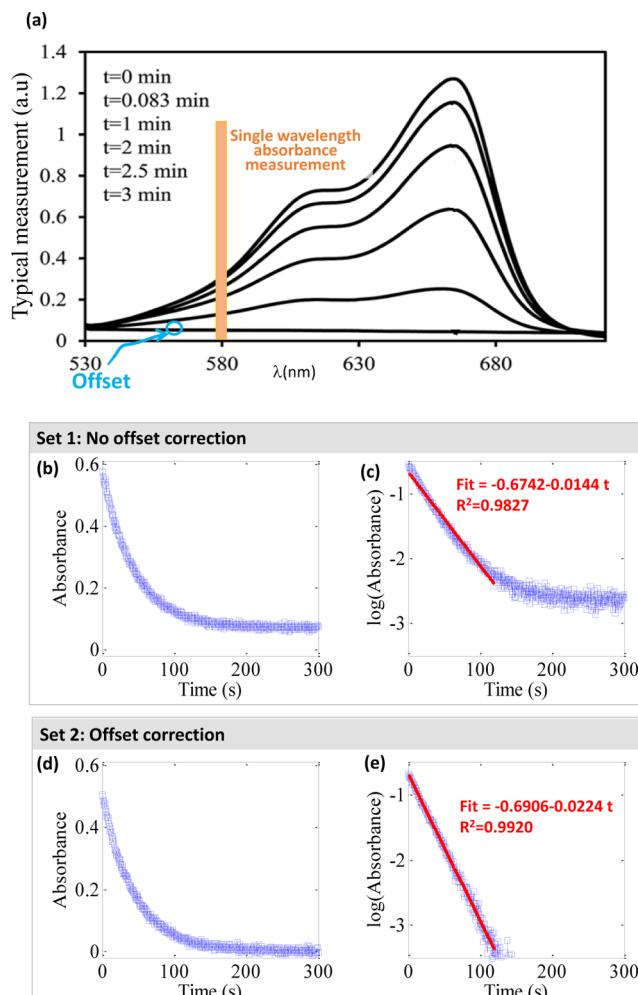
As this is a pseudo first-order reaction, it is expected to follow an exponential decay (see eq 6) of which the rate constant  $k_{\text{rate}}$  had to be determined.

$$A(t) = A_0 \exp(-k_{\text{rate}}t) \quad (6)$$

Initially, it was suggested to use varying concentrations of methylene blue  $[\text{MB}^+]$  in order to rationalize the change or lack of change in absorbance and constant rate. This was followed by varying the concentration of ascorbic acid [A] to validate how the rate of reaction changes. The rate constants could easily be determined by plotting the data linearly using the logarithm of the absorbance. To extract and determine fitting parameters, students had to modify the analysis script provided. This increased their learning outcomes to include practical Python scripting. It also improved the students' understanding on data fitting.

### Typical Errors

Perhaps one of the biggest issues with obtaining the rate constants was the lack of baseline calibration. For example, if the absorbance does not tend toward zero, significant error will be introduced when trying to fit an exponential decay. This is illustrated in Figure 11 using simulated data. The model data



**Figure 11.** Typical measurement trend outlining the effect of a wrong offset correction with (a) spectrum with offset; the orange area indicates single wavelength configuration of the kinetic measurement, (b and c) absorbance through time from (set 1) values (no offset correction) in linear scale, and its logarithm (d and e) absorbance through time using (set 2) values (offset correction) and its logarithm.

has an initial absorbance  $A_0 = 0.5$  without offset, and a rate constant of  $K_{\text{rate}} = 0.0222$ . This is an arbitrary choice, not fully representative of the reaction between methylene blue and ascorbic acid but is useful to highlight the cause of error.

We use simulated data to illustrate noise and offset contribution. In the first data set (set 1), there is a baseline offset of 0.07 and a random noise of amplitude 0.007. This is illustrated in Figure 11a. The corresponding absorbance decrease is illustrated in Figure 11b,c with (b) absorbance and (c) logarithm of the absorbance used for further fitting. In the second data set (set 2), this offset is corrected. Figure 11d,e gives the corresponding absorbance plot, with (d) absorbance and (e) logarithm of the absorbance.

By fitting the data, we can extract the rate constant from a fit of the absorbance measurement. We choose the beginning of the measurement, as the sample signal tends to the blank signal during the reaction, the solution becoming colorless. Here we fit over the range [0–120 s]. For our specific simulated data sets, we obtain  $K_{\text{rate,sel1}} = 0.0144$ , with  $R^2 = 0.9827$  and  $K_{\text{rate,sel2}} = 0.0224$ , with  $R^2 = 0.9920$ . By fitting the values considering only the offset of 0.07 (no random noise), we obtain a constant rate  $K_{\text{rate,offset}} = 0.0143$ , with  $R^2 = 0.9865$ , while our reference model corresponds to  $K_{\text{rate}} = 0.0222$  ( $R^2 = 1$ ). This illustrates how a bias in the measurement can affect the constant rate determination.

## CONCLUSION

This project provided the opportunities for students to accomplish a number of learning objectives. The common place task of building an instrument was extended to include the workings of commercial instruments, experimental design and the iterative nature of scientific research. Throughout the experiment, the students appeared to be enjoying their work and often took ownership of their instruments. They also learned how to troubleshoot, tackle errors and need for realistic expectations given the limits of optimization.

The various designs from each group varied from simple but yet effective to scale replicas of the Hanging Gardens of Babylon masquerading as a spectrometer. It demonstrates the initiative taken by students and the enthusiasm they had for the project.

The final outcome was an ~2 page report. It was written on the Raspberry Pi using the LyX document processor. The students were suggested to write the report during the sessions. This report was an additional motivation to get nice and interpretable data, with error analysis. In that sense, it provided an additional opportunity for the students to apply their critical thinking skills. This report also outlined the iterative process of scientific approach; from this synthesis, they could strengthen their ideas around minimizing errors, an essential skill for all their future projects.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: [10.1021/acs.jchemed.5b01006](https://doi.org/10.1021/acs.jchemed.5b01006).

S1: Lab manual ([PDF](#))

S2: Raspberry Pi manual ([PDF](#))

S3: Python scripts ([PDF](#))

S4: Material costs ([PDF](#))

S5: Spectrometer pictures ([PDF](#))

S6: Circuit diagram and electronic board ([PDF](#))

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### Notes

The authors declare no competing financial interest.

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