The Design and Construction of an Affordable Raman Spectrometer

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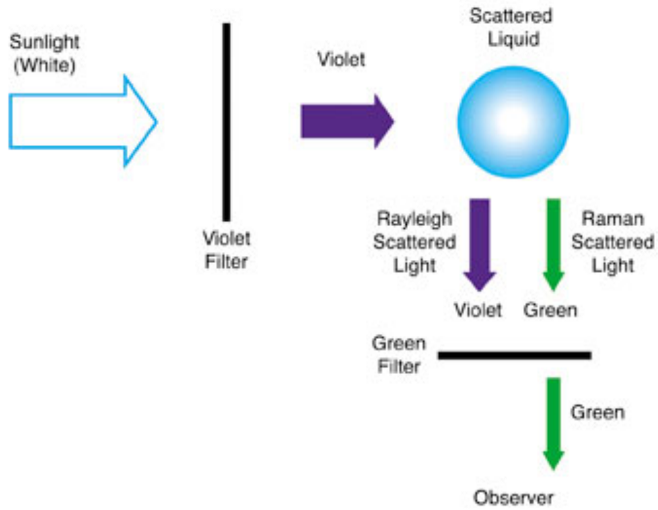
Abstract

Raman spectroscopy is capable of identifying unknown substances in a fast and non-destructive manner and has found a wide range of uses, such as identifying hydrogen peroxide-based explosives, characterizing chocolate, and verifying gemstone identity. Commercial Raman spectrometers can easily cost tens of thousands of dollars and building a low cost version would enable more widespread adoption of this technique and make additional analytical applications feasible. Undergrad chemistry courses leave out how an instrument works in favor of teaching how to interpret the results unless special topics classes are offered. In industry, chemists are expected to do general maintenance and troubleshooting on all instruments present in the lab. Giving students the opportunity to handle equipment prior to a business setting allows for increased confidence. The basic parts have been assembled with the aid of a 3D printer. Preliminary results will be discussed as well as possible future uses of the project.

Introduction

In 1921 C.V Raman met J.J. Thomson and Ernest Rutherford to discuss several new theories including the vibrations of sound and light scattering. At the time, Lord Rayleigh's prevailing idea was that the ocean was blue because it was reflecting the color of the sky. Rayleigh had proved that the sky was blue due to light scattering in the air. This explanation did not sit right with Raman who went on to prove that liquids and even solids can scatter light.[1] Raman spectroscopy works by shining a light with a known wavelength at a sample. The atoms in the sample then absorb a small amount of the energy from the light and then when the atoms relax they release incident light at a different wavelength. This difference is called a Raman shift. The change in wavelength is measured and can be used to create a unique fingerprint for the sample. This fingerprint is based on the crystal structure of the molecule. Raman spectroscopy offers a fast and non-destructive way of testing samples



Scheme 1: Raman shift

that has been in a multitude of fields with new applications being found everyday. Handheld Raman spectrometers have been used in the forensic field to identify hydrogen peroxide-based explosives through different kinds of containers.[2] In the environmental sector, Raman is being used to identify microplastics in marine soil to track polution.[3]

Instrumentation is often an abstract concept for the majority of people that use it. The best way to understand the mechanics behind the most used instruments is with hands-on learning. However with how expensive most instruments are it is hard to offer opportunities to undergraduate students. The majority of the pieces used for Raman are also used in other instruments, like IR and UV-Vis, which means that understanding the basics behind one of these helps gain insight into the others. UV-Vis tells little information about the structure of a sample and Raman's biggest advantage over IR is that samples can be analyzed in any state: solid, liquid, or gas. Giving students and future industry workers or researchers a better idea of what makes up the tools they use gives them the ability to do better on the job troubleshooting. The ultimate goal was to create a Raman Spectrometer with less than 200 dollars with every piece of hardware used in this project available to be purchased online with no need for academic or business affiliations.

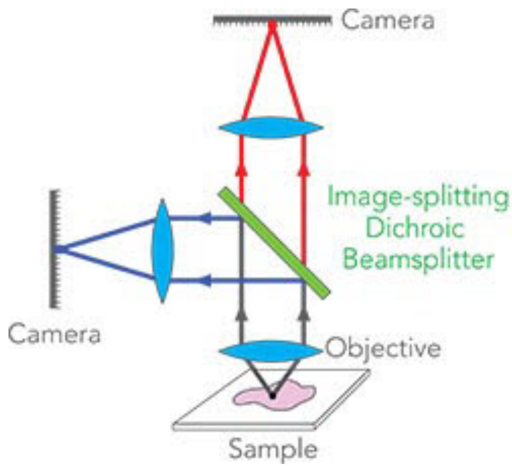
Design

In its most simple form a Raman spectrometer is composed of a few basic parts: the excitation light source, a sample holder, a filter or beam splitter, a detector, and a computer. Depending on the complexity and intended use of the spectrometer there are additional parts that can be added. The excitation light source is commonly a laser somewhere between 532 nm - 1064 nm. A laser offers a high intensity stable light source at a known wavelength. The range is large because it is based on the kind of samples that are going to be identified as well as the detector used. If the target samples are known to fluoresce, a higher wavelength laser will be chosen to mitigate that response. Fluorescence will overpower or damage most detectors made for measuring Raman shifted light and lead to inaccurate readings.Larger wavelengths have less energy which means samples will not reach a level of excitement capable of fluorescence.

There are two places to put filters: before and after the sample. The filter before the sample selects only the excitation wavelength to pass through. This is generally used if the excitation source has some variability to it and noise needs to be limited. The filter after the sample is used to remove the excitation light source from the incident light before it hits the detector. The excitation light source is several magnitudes more intense than the incident light. Detectors are very sensitive to measure the low levels of incident light and are very easily overwhelmed with excitation light hitting them. The two main kinds of filters are diffraction gratings and dichroic filters. Diffraction gratings have up to 3600 grooves per millimeter which split a light source into individual wavelengths so if there is any variation of wavelengths they are all separated.[4] When holding up a diffraction grating to a white light source, the result is a separation of all visible light resulting in a rainbow.

Figure 1: 500 lines/mm linear diffraction grating splitting white ambient light

The more grooves a diffraction grating has, the greater dispersion and more expensive it becomes. Diffraction gratings are normally placed after a sample so the different incident wavelengths can be separated and the detector can identify them without having to factor in overlap.



Scheme 2: Dichroic Beamsplitter[5]

There are a wide variety of dichroic filters but the most basic reflect a specific range of wavelengths and let another range pass through. Some dichroic filters are also built as beamsplitters. Dichroic beamsplitters let the excitation light pass through but angle the incident light towards the detector (Scheme 2).

Detectors for Raman spectrometers have to be pretty sensitive because the amount of incident light is normally miniscule compared to the excitation source. Molecules give off several different wavelengths of light all at once so a detector also has to be able to identify multiple wavelengths all at the same time. The easiest way to circumvent overlapping wavelengths is to use a diffraction grating to split them up.

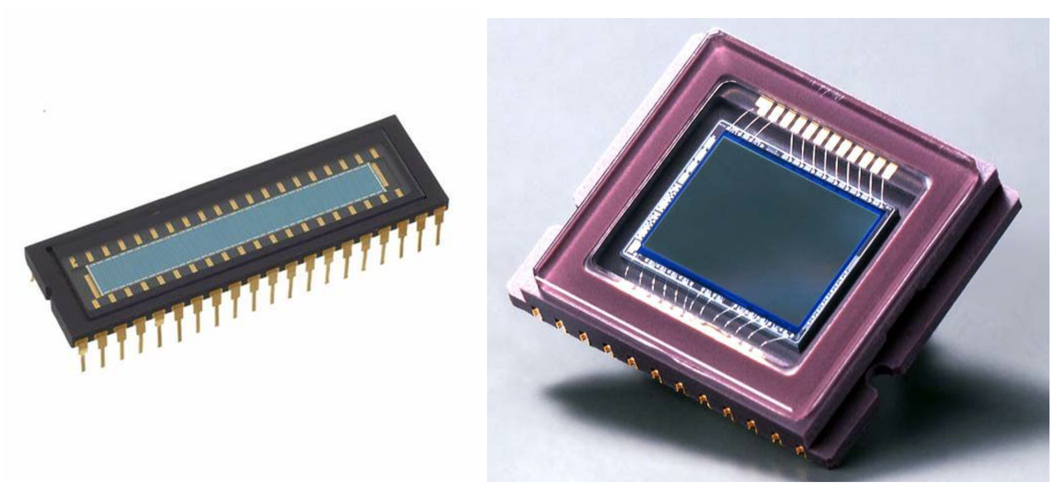


Figure 2: Photodiode Array and Charge Coupled Device

Older Raman spectrometers had photodiode arrays where each diode corresponded to a different wavelength (Figure 2). The most prevalent kind of detector today is called a charged coupled device (CCD) and is used quite often in cameras. When light hits a CCD detector, the detector builds up a charge that corresponds to the intensity and duration of light. Each pixel on a CCD detector can be assigned a wavelength so the intensity of each wavelength coming from the sample can be quantified.[6] CCD detectors allow for much more compact designs and are often cheaper due to their everyday use in cameras.

Methods and Materials

Construction began backwards beginning with the detector and ending with samples. The majority of cameras today have CCD detectors, so theoretically any camera can be used to collect Raman scatter light. Most cameras use IR filters over the lens because our eyes do not pick up infrared light. Raman shifted light, however, does show up often in the IR region which means the filter would either need to be removed or the camera would need to be made without one. In terms of affordability, the best option is the NoIR camera by Raspberry Pi which comes without the IR filter. It is often used as a security camera or for watching wildlife at night coupled with an IR light. The IR light bounces off everything within range, but only the camera will pick up the light because most eyes cannot observe the IR wavelengths. The camera is also extremely small, about the size of the head of a pencil.

Figure 3: NoIR CCD Camera

The NoIR camera is also compatible with the Raspberry Pi which is a small computer capable of running several programming languages and perfect for taking the images from the camera and converting them into spectra. The two main modes of using the Raspberry Pi have been coding a live stream of the camera view to troubleshoot angles and taking photos to create spectra.

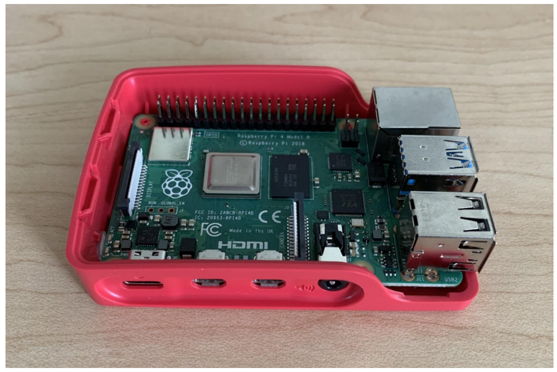


Figure 4: Raspberry Pi computer

According to the manufacturer specifications that came with the NoIR camera, the lowest wavelength that can be picked up by the camera is around 900 nm, so the incident light cannot be lower in energy because the camera will not register the charge. Therefore the excitation light was chosen to be a 5 Volt 650 nm diode with more than enough energy for Raman shifting to still be above 900 nm.

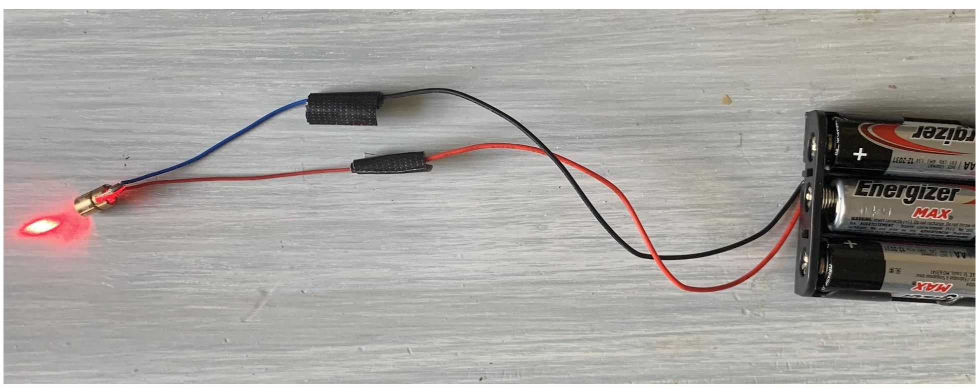


Figure 5: 5V 650 nm diode connected to a battery pack

The diode was connected to a battery pack to make a crude laser that could easily be swapped out if the sample needed a higher or lower energy source to avoid florences or generate more Raman scattered light.

Before the excitation source hits the sample it passes cleanly through a beamsplitter and then is concentrated using a microscope objective lens. The object lens makes up for using a less expensive laser diode and allows for more intense light to hit a smaller portion of the sample. Once the excitation light hits the sample and Raman shifted light is passed back through the microscope objective lens, the light is spread out again and hits the beamsplitter.

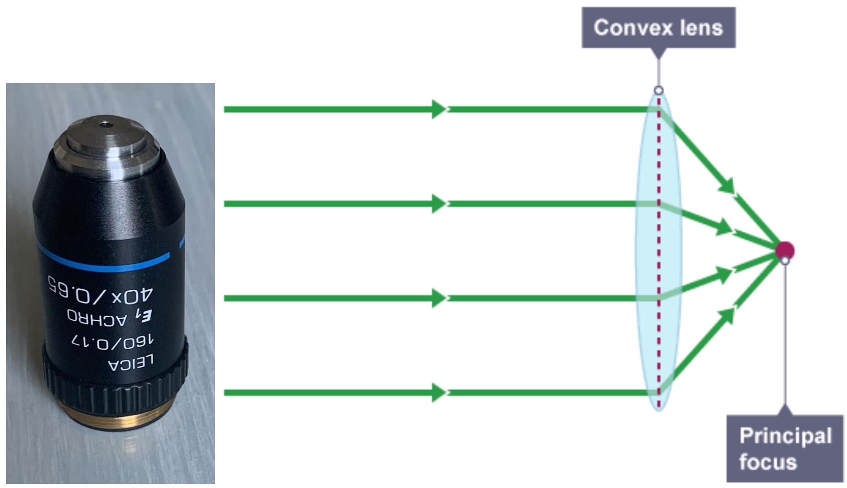


Figure 6: Microscope Objective Lens and Diagram of the focusing of excitation light[7]

The incident light is then bent 90 degrees towards the detector to remove the incident light from the path of the excitation light. Before light hits the detector, the individual wavelengths need to be separated so as to not drown each other out and the detector is not overwhelmed. A simple diffraction grating pulled from the general chemistry lab was sufficient to separate the wavelengths enough for the detector to differentiate them.

Once all the components were collected, housing had to be constructed to keep all the parts in place and remove all outside light sources. The first step was to create housing for the individual parts. TinkerCad is a free 3D printing software that allows users to model simple designs. The 3D printing process as a whole is very stop and go. The actual designing in TinkerCad only takes 30 minutes to an hour, but the print often took several. Also once a build was printed, it was incredibly difficult to make any changes as the structures are very rigid. Often a design had to be printed and then the design tweaked at least two or three times before it held the component perfectly. The best example of this was the first compartment constructed: the diffraction grating housing.

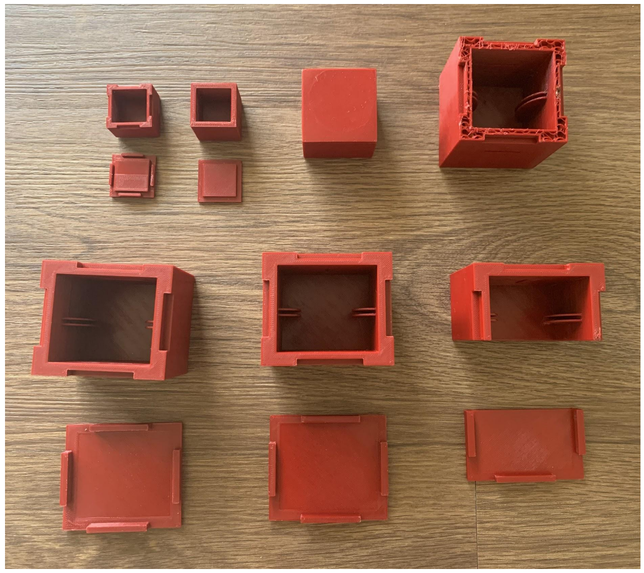


Figure 7: Seven iterations of the diffraction grating housing

Knowing that outside will drown out Raman scattered light completely, boxes with snug lids were designed first. In Figure 7, starting with the top left box, the lid was designed to snap on, however the lid did not fit. The next build was made with the idea of the lid just being able to rest on the box, but it easily fell off. The 3rd box had a lid that fit, but it fit so well it never came off. The 4th box was built with the intention of fitting the diffraction grating inside for the first time, but the lab was so cold, the build popped off the printing platform and never finished. The 5th box was the same build as the 4th, however when the diffraction grating could not fit inside without bending which was less than ideal. The build was widened by 1 mm for the 6th print which fit the diffraction grating perfectly, but due to the grating offsetting the incident light, the exit slit was in the wrong place, so the final build pictured has the back half of the box cut off to determine where and how wide the exit slit should be.

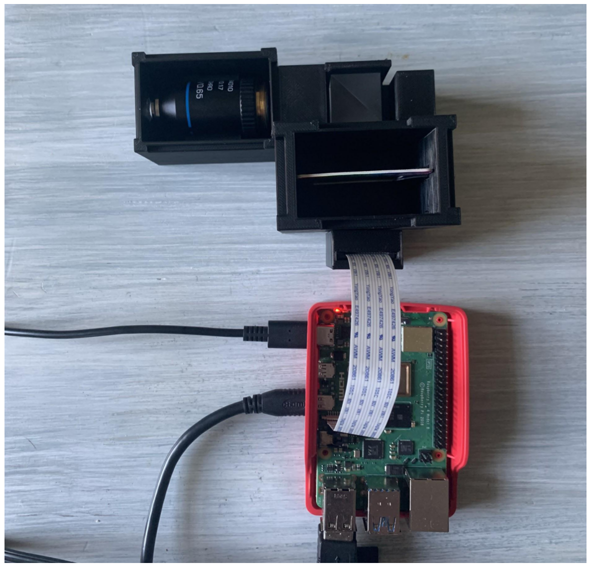


Figure 8: Final Raman build excluding lid

Once the designs were finalized for each component, they were all brought together. It is important for none of the pieces to move so the light always hits the detector in the same place and those pixels can be assigned specific wavelengths.

Image to Spectra Transformation

The final step in the project was to take the images from the detector and transform them into usable Raman Spectra. The diffraction grating evenly splits white light into all its individual wavelengths, so knowing this, it is possible to create a rainbow with every wavelength from the visible spectrum. A phone flashlight uses an LED bulb for which there are many examples of emission spectra available, so it is possible to compare the accuracy of the homemade spectrometer. In order to transform the image into a spectra, the free program ImageJ was employed. ImageJ allows the user to isolate specific pixels on an image and then creates a spectra based on intensity values. The second image in Figure 9 is the emission spectrum of a standard white LED light bulb[8]. The spectra both have two distinct peaks which line up with intensity spikes in the blue and green-yellow wavelength regions.

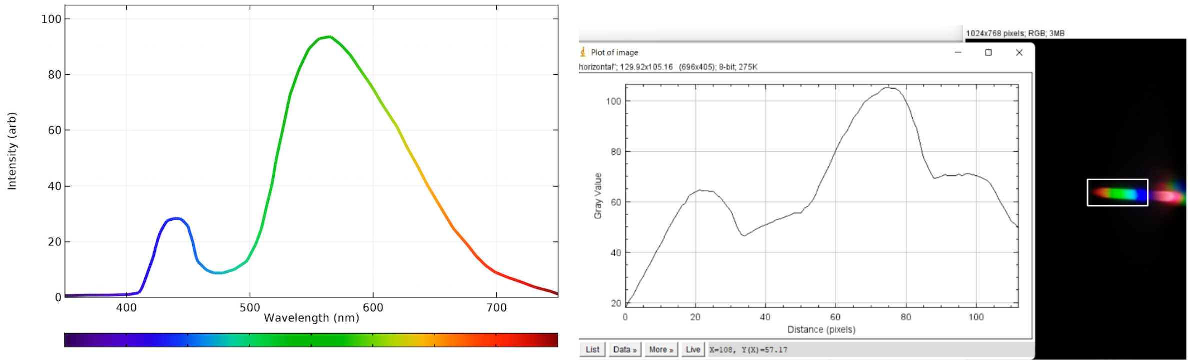


Figure 9: Standard and Homemade Raman Spectra

Even though good images were taken with a white light source, the full image has lots of stray light entering the diffraction grating housing. The stray light will be separated along with any incident light which ultimately overpowers any Raman scattered light. This is caused by misalignment of the components. This problem could be solved with changes to the 3D housing and adjusting the angles of the excitation source.

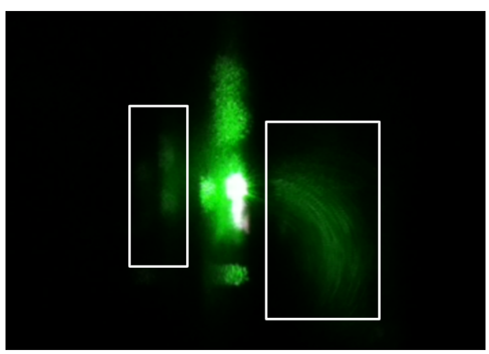


Figure 10: Example of stray light entering the diffraction grating housing

Cost

The goal of this project was to keep the costs under $200 using parts that could be found in undergraduate chemistry labs. Some components were taken directly from the lab, like the microscope objective lens and diffraction gratings, so the total cost was lower than this estimate.

Component	**Cost**
Raspberry Pi	34
NoIR camera	24
Beamsplitter	42
Diffraction Grating	.25
Laser Diode	1.25
Battery Packs + Batteries	12
3D filament	10
Total	183.50

Table 1: List of Expenses

The total cost was under $200, so future versions of this project could use higher quality components and still stay within budget.

Conclusion

The basic components of a Raman Spectrometer can be easily and cheaply acquired. Ultimately the biggest roadblock was time with the last few 3D builds taking a minimum of 12 hours to complete. This project is still incomplete because the stray light interferes too much for proper analysis. The next steps would be to clean up the build to remove more of the excitation source and use standard light, like a Hydrogen lamp, to better assign wavelengths to pixels. From there, solid and liquid samples could be tested. Design and construction are not the first thing most instrument users think about, but having an idea of the basics helps students not only with troubleshooting, but better understanding their results.

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