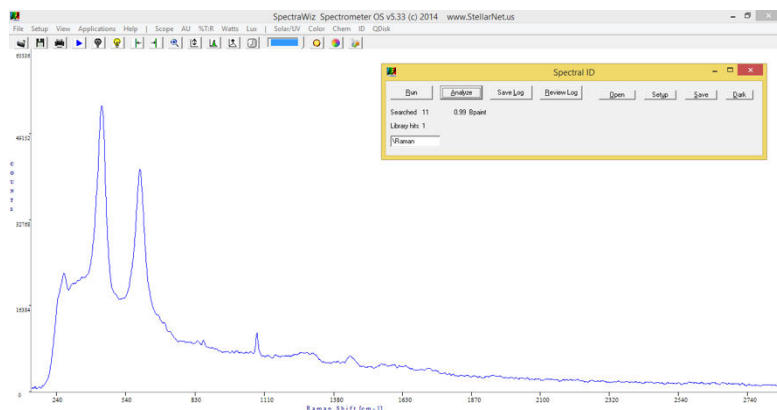


Spectroscopy Application: Using Raman Spectroscopy to Detect Art Forgeries

5



Detecting art forgeries using Raman spectroscopy

In the previous experiment, you were introduced to Raman spectroscopy. This week you will explore how Raman spectroscopy can be used to solve real-world problems. You will use Raman spectroscopy to determine the validity of two paintings – one painting is a forgery and one is genuine. This analysis will allow you to gain experience in Raman spectroscopy and apply these principles to a real-world problem. You will have to make decisions to optimize the spectra and explain the reasoning behind these decisions. You will create a library of Raman spectra from known materials and use it to identify the presence or absence of those materials in other samples.

INTRODUCTION

Learning Goals¹

In this experiment, you will use Raman spectroscopy to analyze two paintings from a museum. One of the paintings is a forgery and one is genuine and the museum curator wants your help in determining which painting should be displayed in the museum. The museum curator wants you to use Raman spectroscopy to examine the two paintings and determine which one is a forgery. You are allowed access to the paintings, as well as reference samples of paints that the curator suspects were used in the paintings.

This analysis will allow you to gain experience in Raman spectroscopy and apply these principles to a real-world problem. You will have to make decisions to optimize the spectra and explain the reasoning behind these decisions. You will create a library of Raman spectra from known materials and use it to identify the presence or absence of those materials in other samples.

Art and Spectroscopy

Paintings often have a *provenance* – a record of the history and ownership of a painting. This provenance is often critical to authenticating a painting. If a painting does not have a provenance then it can be difficult or impossible to determine the authenticity of the painting – at least before modern scientific methods. Museums often turn to scientific tests to determine the composition of the paints used in the artwork. This provides evidence for when a painting may have been created and who may have created it.

Paints

The type and composition of paints used in artwork has changed over time. Paints used before the 20th century often contain metal compounds, as most of the colored pigments available at the time were metal salts. Synthetic organic compounds became widely available in the 20th century and eventually replaced many of the metal salt pigments. Some pigments that were historically favored are no longer used due to their toxicity (e.g. lead, arsenic, and mercury containing pigments) and cost of metal salts (e.g. cobalt, cadmium, and chromium containing pigments). Table 1 shows some common pigments and the timeline for their usage.

¹ **This experiment was adapted from:** Nielsen, S. E., Scaffidi, J. P., & Yezierski, E. J. (2014). Detecting Art Forgeries: A Problem-Based Raman Spectroscopy Lab. *Journal of Chemical Education*, 91(3), 446–450. <https://doi.org/10.1021/ed400319k>

Table 1: Timeline for paint color usage

Paint Color	Timeline
Phthalocyanine Green	Used since 1938
Viridian	Used since 1859
Phthalocyanine Blue	Used since 1938
Ultramarine (synthetic)	Used since 1928
Cobalt Blue	Used since 1804
Dioxazine Purple	Used since 1952
Cobalt Violet	Used since 1859
Cadmium Yellow Light	Used since 1851
King's Yellow	Used since 1816
Mars Black	Used since the early 20th century
Ivory Black	Used since prehistory
Titanium White	Used since 1921
Lead White	Used since antiquity

Mixtures in artwork

Paintings are seldom comprised of only type of paint or clearly delimited paint types. Most paintings are composed of a mixture of paints to achieve the widest range of colors. Additionally, black and white paints are often used to adjust the color and brightness of other pigments. *How will you account for paint mixtures when determining the authenticity of the paintings in this experiment?*

Additional resources:

<http://www.webexhibits.org/pigments/index.html>

<http://coolcolors.lbl.gov/LBNL-Pigment-Database/database.html>

<http://www.jcsparks.com/painted/pigment-chem.html>

Raman Spectroscopy

Raman spectroscopy is based on scattering of light; scattering occurs when light interacts with particles. When the size of the particle is smaller than the wavelength of light, *elastic* scattering is known as Rayleigh scattering. Elastic scattering means that the particle has the same energy after it interacts with a photon. If the particle does not have the same energy after interacting with light it has undergone inelastic scattering. Additionally, particles can undergo Stokes Raman scattering (particle absorbs energy and the scattered photon has less energy than the incident photon) and anti-

Stokes Raman scattering (particle loses energy and the scattered photon has more energy than the incident photon). Rayleigh scattering is much more efficient than Raman scattering because most scattering that occurs is elastic.

Raman and infrared (IR) spectroscopy are often seen as complementary techniques. Both excite vibrational transitions in molecules, which means that the locations of the peaks in IR and Raman spectra are similar. One of the main advantages that Raman spectroscopy is that water and glass, which absorb strongly in the IR region, only weakly scatter photons. This means that aqueous samples and samples in glass containers can be analyzed with Raman spectroscopy. However, unlike with IR, there is the possibility of fluorescence with Raman spectroscopy is the possibility. Fluorescence results from an electronic transition in molecules. IR photons cannot excite electronic transitions but the excitation source in Raman spectroscopy can. Many organic molecules, like pigments and dyes found in paintings, undergo electronic transitions and fluoresce. Fluorescence is more efficient than Raman scattering allowing it to overwhelm the Raman signal.

There are many factors that affect the Raman signal including the power of the laser, the concentration of the sample, the path length of the sample, the area of the sample illuminated by the laser, the exposure time, the efficiency of the detector, and the amount of light collected by the detector. In this experiment, you will optimize several of these parameters to increase the Raman signal relative to noise and/or fluorescence.

EXPERIMENT PREPARATION

Before you come to lab

In preparation for this experiment, you should read the **StellarNet Raman spectroscopy operation manual** as directed by your instructor. Safety when working with a laser is of the utmost importance.

- Caution – use of controls or adjustments or performance of procedures other than those specified in the StellarNet manual may result in hazardous radiation exposure.
- Do not point laser or allow laser light to be directed or reflected toward other people or reflective objects.
- Always wear appropriate protective eyewear.

- Do not modify unit or remove protective covers or housings.
- Laser light emitted from this equipment may be sufficient to ignite some materials and initiate fire.
- Never operate laser if unit is defective or if safety covers, locks, and labels are damaged or missing.

Collaboration

You will work with a partner to complete this laboratory experiment. You and your partner should work on developing a procedure for this experiment together. It may be helpful to first write-up individual procedures and then discuss as a pair. You can then develop one unified procedure to use Raman spectroscopy to determine the validity of a painting.

Safety

In preparation for this experiment, you should look up hazard information on the chemicals and equipment used in this laboratory. This might include looking at the Material Safety Data Sheets (MSDS) or Safety Data Sheets (SDS) for the chemicals used in this experiment. Additionally, the Pharos Project's Chemical and Materials database (<https://www.pharosproject.net>) provides a wealth of hazard and safety information on thousands of chemicals. You should identify the hazards associated with each chemical used in this experiment, the necessary personal protective equipment (e.g. lab coats, goggles) you should use, and any toxicology and ecological information. After completing this search, you should understand both how to handle chemicals safely in lab and how these chemicals effect the environment outside of your laboratory. Remember, the chemicals you use and the waste you generate don't stay in lab – they have to be disposed of after you complete your experiment.

PRELAB QUESTIONS

1. Familiarize yourself with the spectrometer system you will use for this experiment. Using Figure 1 as a guide, explain what is different from the setup you used in the last experiment.
2. What pigments do you expect to see in the authentic painting? What pigments do you not expect to see? Why?
3. Why are some paints so strongly fluorescent?
4. Why is the fluorescence so much stronger than the Raman signal?
5. What techniques could you use to limit fluorescence?
6. For this experiment, you will not be given step by step instructions. In your lab notebook, describe the procedure you will use to determine the validity of a painting using Raman spectroscopy. Make sure to include:
 - a. the information you need to collect,
 - b. the important parameters you need to document, and
 - c. how you will use the data you collect to determine the authenticity of the paintings.
7. In order to obtain quality spectra, you may need to adjust the integration/exposure time and laser power. What effect does the laser power and integration time have on a spectrum?
8. Describe all the hazards associated with the spectroscopy system for this experiment. What precautions should you take when working with this system?
9. Describe the hazards associated with the chemicals for this experiment. What precautions should you take when working with these chemicals?

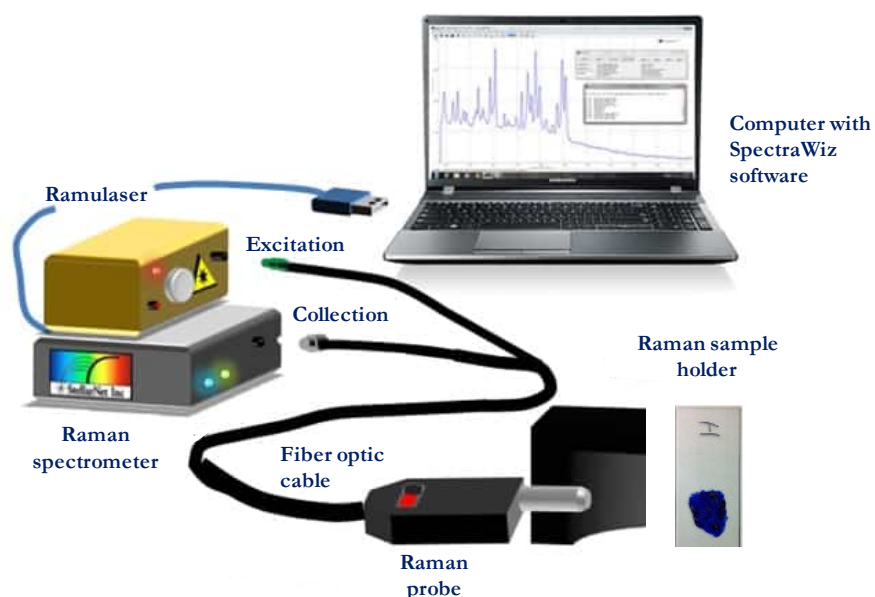


Figure 1: StellarNet Raman spectroscopy system

PROCEDURE

Material and Equipment

Chemicals

- ✓ Paint samples (lead white, titanium white, dioxazine purple, cadmium yellow light, phthalo green, cadmium red medium, phthalo blue, ultramarine blue, ivory black, king's yellow, cobalt violet, cobalt blue light, viridian, alizarin crimson, mars black)
- ✓ Art samples

Equipment

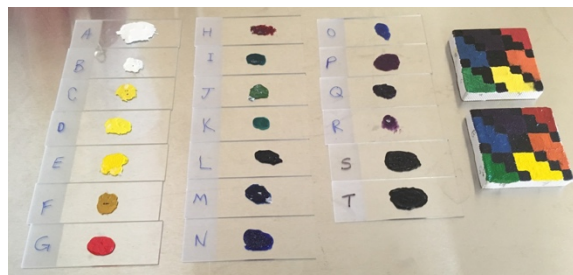
- ✓ Spectrometer (Raman-HR-TEC)
- ✓ Raman sample holder
- ✓ Ramulaser and Raman probe
- ✓ Computer or tablet
- ✓ Fiber optic cable
- ✓ USB cable

For this experiment, you will need to come up with a plan for determining if a painting is a forgery or genuine. You will have access to multiple paint samples as well as two paintings. Before you begin this experiment make sure to read the following instructions on operating a Raman spectrometer safely. You will use this information to gather spectra for each paint sample and painting.

CAUTION

The Raman spectroscopy system uses a laser source. Visible and/or invisible laser radiation can be emitted from the Raman probe. Appropriate laser safety procedures should be observed when operating the probe with a laser source, including the use of protective eyewear. Read StellarNet laser manual for precautions before operating this system.

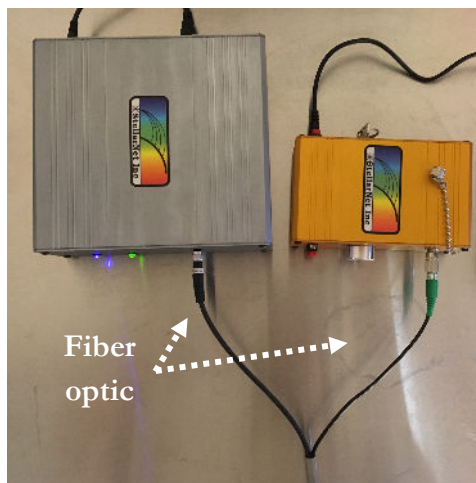
1. Your instructor will demonstrate how to properly use the Raman spectroscopy system and discuss proper safety precautions you should take while working with this system. During this experiment, make sure to ask your instructor any questions you have about using the Raman spectrometer – don't guess!
2. Obtain several paint samples. Don't take all the paint samples at once – there is a limited number of samples for your lab section. Once you have obtained spectra for the paint samples switch with another group or return the samples to your instructor.



Spectrometer Setup

1. Review the spectrometer system setup and make sure that the spectrometer system resembles the setup below. Make sure that you can identify all the components of the spectrometer system.

Top view



Front view



Make sure the Raman probe fiber optic is securely connected to the laser. While working with this spectrometer never remove Raman probe from the sample holder. **The laser is powerful enough to cause serious eye injury.**

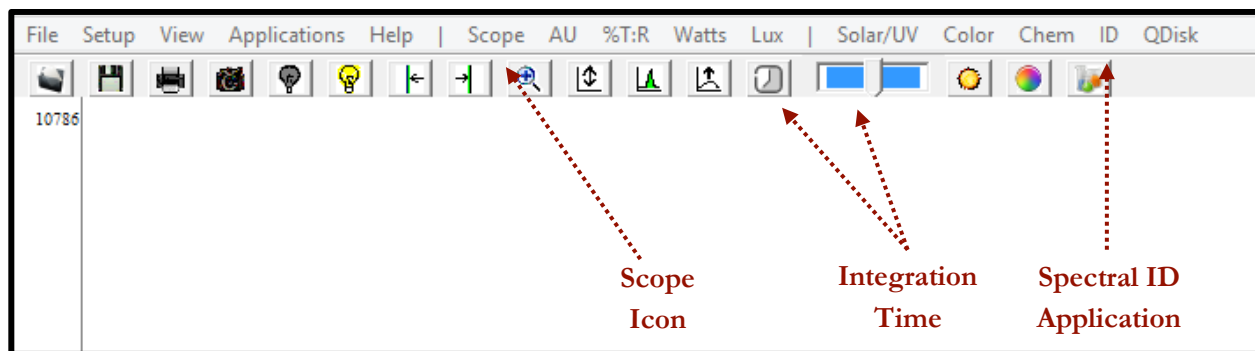
2. Look at the back of the laser. First, make sure the key is not in the laser yet. If you are running the laser **on battery power** push the red button on the back of the laser in. If you are **NOT running the laser on batter power** first make sure the red button on the back of the laser is not pressed in. Then make sure the power adaptor is connected to the outlet on the back of the laser.



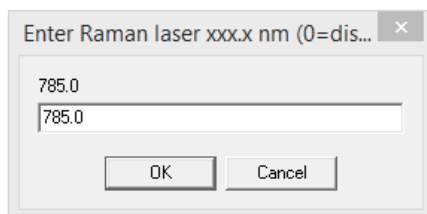
3. Make sure the interlock jack is placed in the remote interlock on the rear panel of the laser.
4. You may now insert key into OFF (vertical) position.
5. You may now enable the laser power by turning the key to the ON (horizontal) position.

Taking Raman Measurements

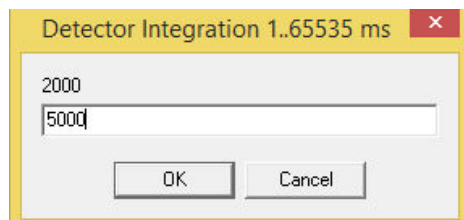
1. Align the Raman probe with your paint sample.
2. Turn on the computer. Open the StellarNet software by double clicking on the desktop icon *SpectraWiz* to open the application
3. When you first open the software, you should see a screen that looks like:



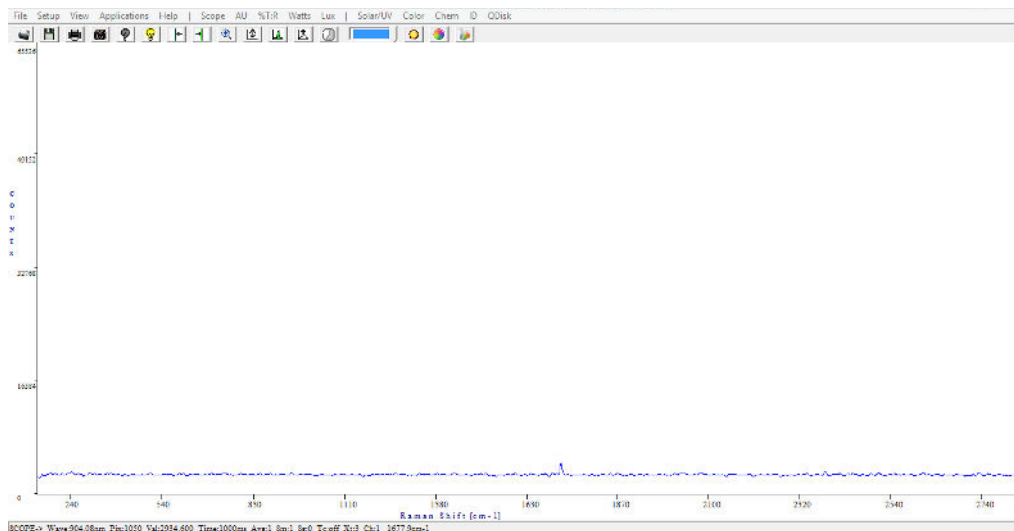
4. Click on the **Setup** dropdown menu and then select the **Raman laser wavelength** and enter the wavelength for the laser (785 nm).



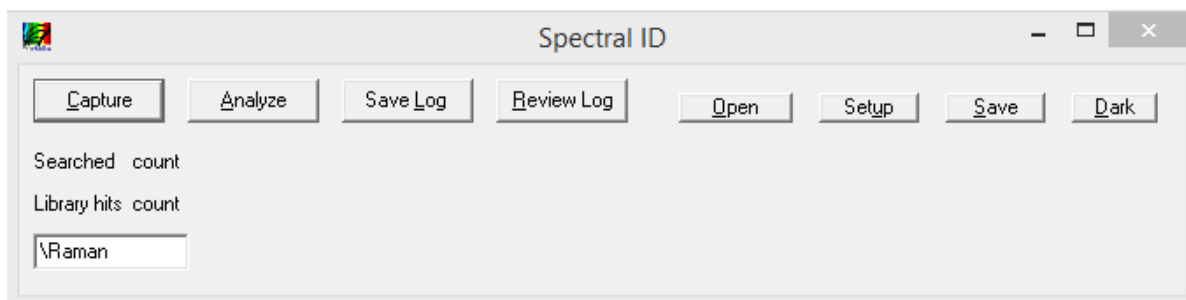
5. Click on the **integration time** icon  and increase the exposure time to 5000 ms (5 seconds). You may need to increase the integration time depending on what sample you're analyzing.



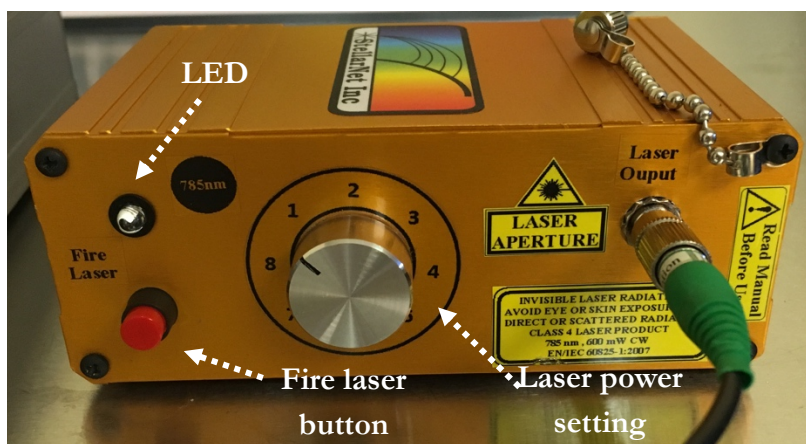
6. Click on the **Scope** icon (highlighted above). This will show you the number of counts (photons) the detector receives. You should see a spectrum of counts versus Raman shifts [cm^{-1}].



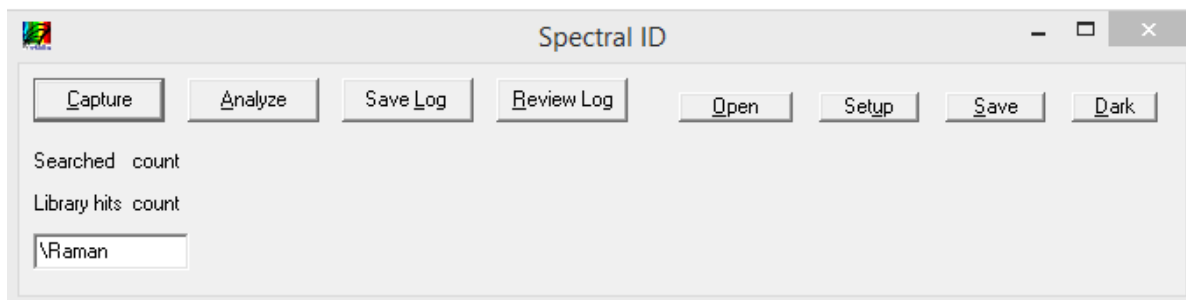
7. Click on the **ID** icon to open the Spectral ID application. You should see a panel like:



8. Turn the **laser power** to the lowest setting for your first trial spectrum. You should always start with the laser power as low as possible and then slowly increase it.
9. Press and hold left front panel button (marked **Fire Laser**) to fire the laser. The LED bulb next to this button will light up red indicating that the laser is in operation. You should see a spectrum appear on the computer screen in the SpectraWiz software.



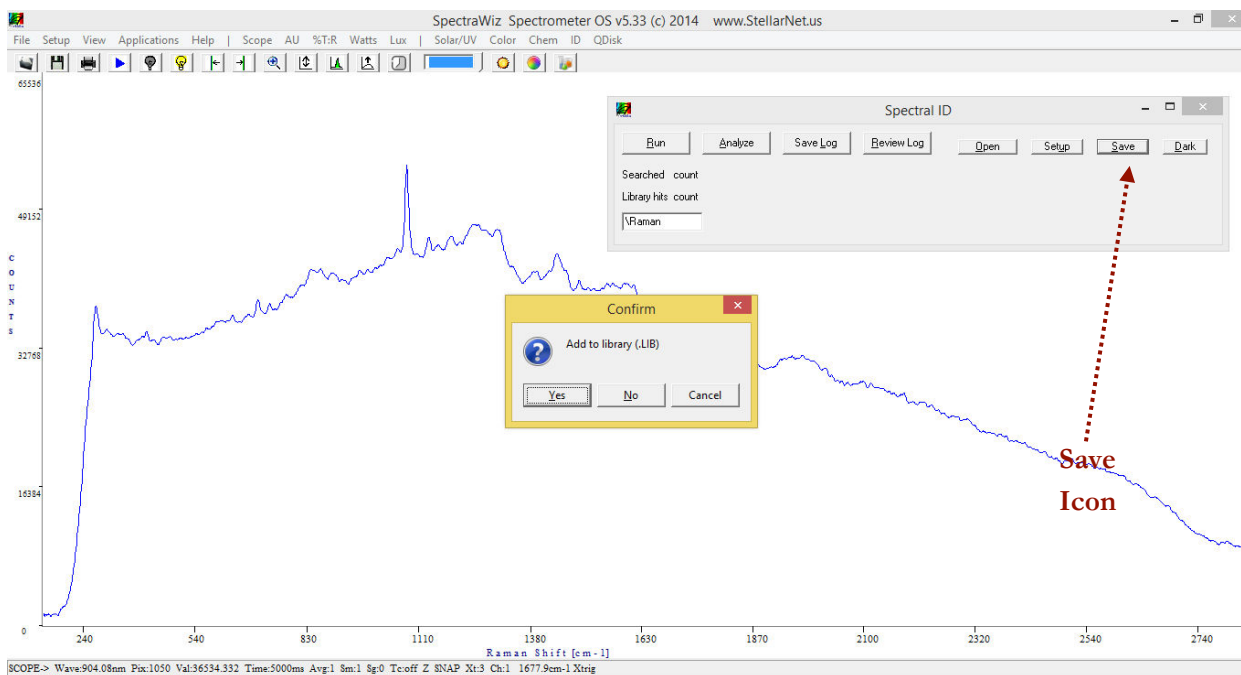
- While still holding the **Fire Laser** button, click on the **Capture** button on the Spectral ID application to collect the displayed Raman spectrum. You can then release the **Fire Laser** button.



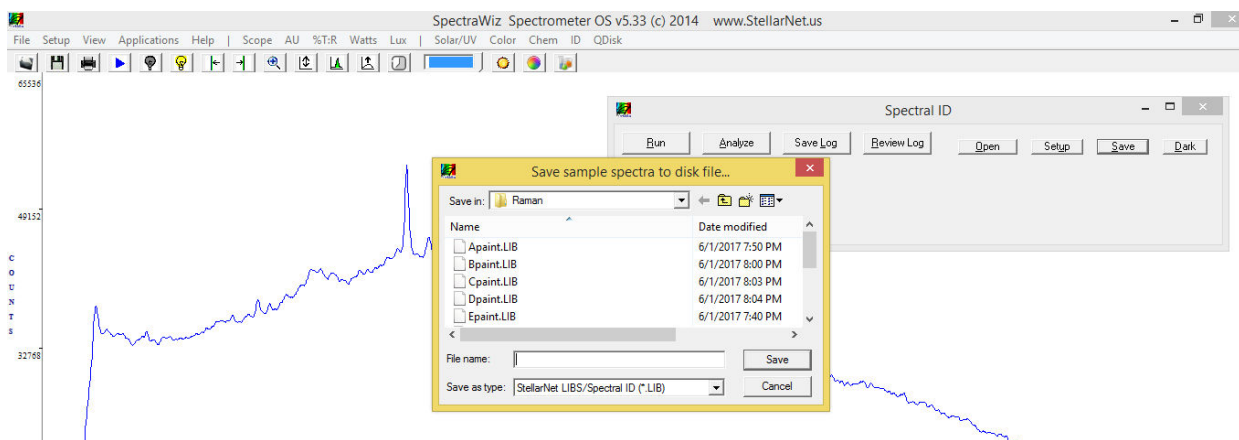
- Adjust your integration time and laser power setting until you achieve the highest count spectrum without burning the sample.

Building a Spectral Library

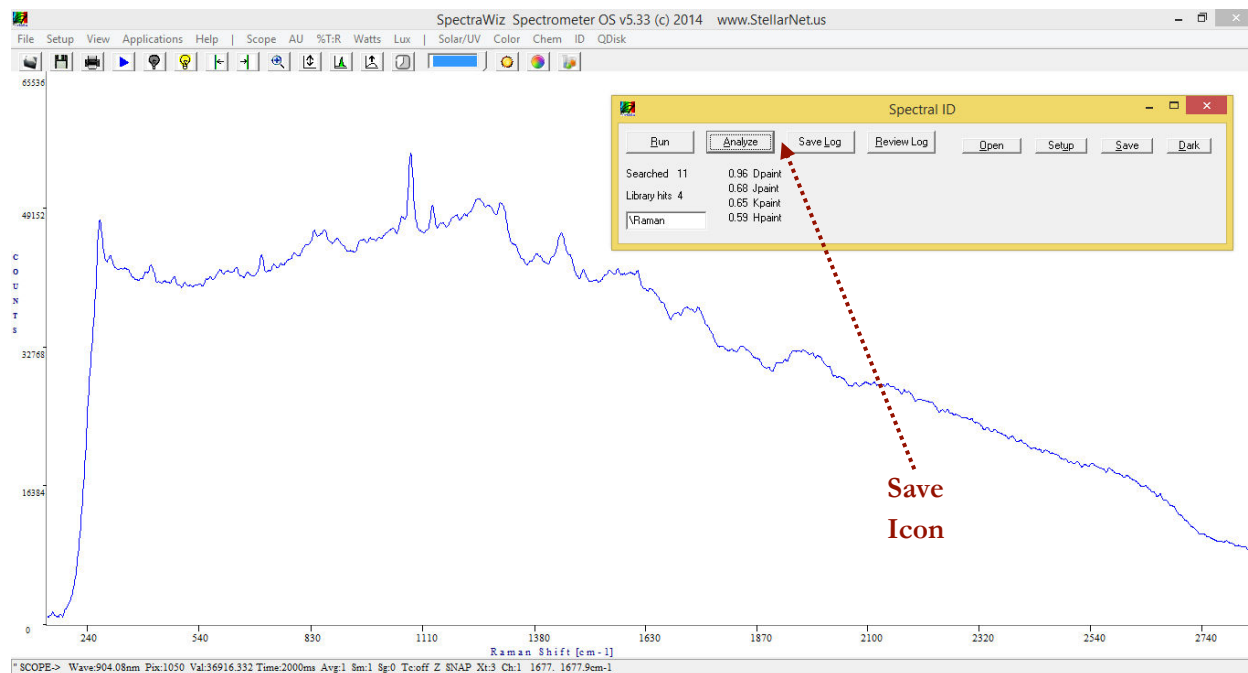
- After you have collected a spectrum you can save it to a spectral library. Click on **Save** to add a spectrum to the library. This spectrum can then be used as a reference to identify unknown compounds in other samples.



- Choose a logical name for your sample and save.



- After you have added samples to your library you can then use it to identify unknown components in a sample. Obtain a spectrum of your unknown sample (i.e. a painting) and click on the **Analyze** button. This will match the unknown spectrum to spectra in your library. The number next to each match indicates how closely the spectrum in the library matches the unknown spectrum (i.e. 1 indicates a perfect match).



Laser Shutdown

1. Once you have collected all of your spectra you can shut the laser down.
2. Make sure to release the **Fire Laser** button and observe that the red LED turns off, which indicates the laser is no longer active.
3. For complete shutdown, turn the key switch on the rear panel to the OFF (vertical) position. This allows key removal and disables ALL power.

DATA ANALYSIS

1. What materials were analyzed?
2. How were the samples prepared?
3. For each sample:
 - a. What integration time did you use? Why?
 - b. What laser power setting did you use? Why?
 - c. What other variables may have affected your data collection?
4. What laser was used?
5. What wavelength of light was used?
6. What type of detector was used?
7. What effect does the laser excitation wavelength have on the samples?

DISCUSSION QUESTIONS

1. What information did you record about the environment? What other information might a scientist need to understand and/or replicate your work?
2. Some of the pigments were extremely fluorescent. What techniques did you have to use to obtain spectra of these sample?
3. What paints were used in the paintings? How do you know what paints were used in the paintings? What spectral features did you use to make your determination?
4. Determine the validity of the paintings.
 - a. What is the oldest painting A could be? Give evidence for your assessment of painting A's age.
 - b. What is the oldest painting B could be? Give evidence for your assessment of painting B's age.
 - c. Which painting is the original and which is the forgery?
5. What other explanations could there be for the presence of newer pigments on a painting? Is it always the case that a painting with newer pigments is a forgery?
6. If you had to choose 1 or 2 paints to make your determination, which would you choose? Why would you choose those paints?
7. What implications does this analysis have for working with potentially priceless artwork? How would that impact your analysis?
8. What other techniques could be used to analyze these paintings? Why would you choose to use these techniques?