Raman Spectroscopy for Mineral Identification: A Practical Guide

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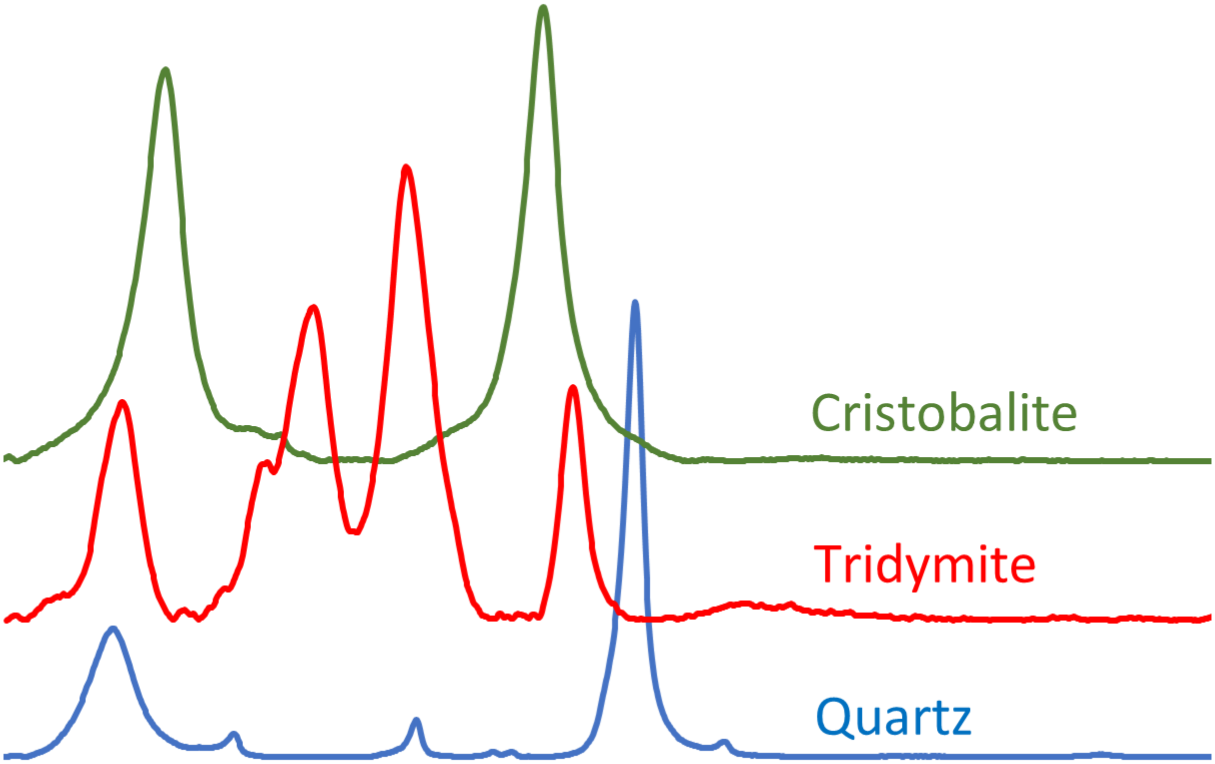

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Foreword

With the improvements to and proliferation of Raman instruments, of many sizes and formats, plus the ongoing population of reference Raman databases for minerals, Raman spectroscopy is increasingly being used as a routine analytical method in the geosciences. While there are many publications that describe what Raman technology has accomplished, or can accomplish, for geoscience research, there is a lack of instructional, "how to" information. It is the purpose of this document to fill this gap. While an introduction to the basic principles of Raman spectrometry is presented, the primary focus of this Guide is to present a practical level introduction to the method with emphasis on the use of Raman spectroscopy for identification of minerals.

Since technology is constantly advancing and experience with minerals in particular will accumulate, it is expected that this document will be updated with some regularity. Accordingly, we invite you to take note of the version number on the cover page and the publication date on the MSA website and switch to an updated version when one becomes available.

In order to collect the information that will contribute to future versions of this Guide we invite its readers and users to submit suggestions, corrections, requests, etc. to ramanformineralid@gmail.com .

A. Principles, Challenges and Solutions

A.1. Introduction

Mineral identification is essential to most geoscience investigations including research (field and experimental), industrial, and regulatory investigations in the fields of mineralogy, petrology, geochemistry, geochronology, petroleum exploration, mineral exploration, mining geology, gemology, mineral processing, building materials, environmental health, medical mineralogy, forensic mineralogy, planetary geology, and more. In addition to being geologically informative on its own, mineral identification is also necessary precursor to identify the targets for micro-geochemical techniques such as electron microprobe, secondary ion mass spectrometry, laser ablation mass spectrometry, etc. Both trace minerals and microscopic mineral inclusions can have an essential role in petrologic and geochemical interpretation.

While some individuals may have trained themselves to identify many minerals in hand specimen, the traditional first-line analytical technique is optical mineralogy with a polarizing (petrographic) microscope. The potential for mineral identification by optical techniques, however, is generally restricted to 200-300 rock forming minerals. In addition, it is common for optical petrography to ignore or make guesses regarding opaque minerals since the additional components and training required for reflected-light microscopy is not universally available. For many years the most widely used tool for mineral identification has been powder XRD (PXRD). However, PXRD has some scope-of-application limitations. Traditional laboratory-based PXRD requires that the target phase be extracted and ground to a powder – limiting the size-scale of its application as well as excluding it from being an in-situ technique. Advances in XRD instrumentation (e.g. large-detector systems) now allow for application to small grains (down to 10μm) without powdering and allow, for some sample configurations, in-situ application at a size scale down to 100μm (or smaller for synchrotron diffraction). However, the PXRD technique remains limited in its range of application scenarios, especially in-situ analysis. While SEM/EDS and EPMA provide in situ analyses down to ~1 μm areas, the resulting chemical information is not always sufficient for phase identification and the expense of these instruments prevents such techniques from becoming universal and routine for basic mineral identification.

Many geoscientists have recognized the potential for Raman spectroscopy to be used for mineral identification since the early 1960's (e.g. Frost et al., 1999; Griffith, 1969; Krishnamurti, 1960; Mao et al., 1987; Mernagh & Trudu, 1993; White, 1975). Mineral identification via Raman is a fingerprint-type technique very much like PXRD – a spectrum is collected from a mineral target and then compared with a database of spectra collected from known minerals. Like PXRD there are potential analytical difficulties resulting from factors like sample fluorescence and low crystallinity, and interpretation quickly becomes more difficult when more than one phase is excited in the process of producing a spectrum. Where Raman shines is in its range of application scenarios and, in some cases, its application convenience. Mineral ID via Raman can be applied:

- Non-destructively
- With little to no sample preparation
- Truly in-situ
- On a scale down to a few microns
- With bench-top, portable, or even hand-held instrumentation
- Through a transparent window such as a coverslip, a transparent mineral (i.e. for fluid inclusion minerals), or a diamond anvil cell
- Even at a distance up to several meters (albeit with a concomitant loss of resolution).

Some of these analytical conveniences, especially the fact that destructive sample prep may not be required and the Raman spectrum is collected non-destructively, have made Raman spectroscopy particularly popular in gemology (e.g. Raneri et al., 2020). When a Raman microscope is combined with a computer-controlled stage, mineral mapping/imaging can be performed (see Foucher et al., 2016).

While Raman offers a number of application conveniences and advantages, it is worth pointing out that PXRD has distinct analytical advantages of its own. For example, the position of PXRD peaks can be related directly (and numerically) to physical elements of the mineral structure (d-spacings). This can both be helpfully informative if reference-spectra matching is inconclusive, and it also enables secondary confirmation by comparing the structure of the "best match" phase to the peak positions in the PXRD spectrum. In contrast, relating specific Raman peaks to specific elements of a mineral's structure is both difficult and imprecise. In many situations, however, the application advantages of Raman make it an extremely valuable tool.

In recent years an increasing number of geoscience-oriented publications have expounded upon both the advantages of Raman technology and the wide range of potential geoscience applications (e.g. Dubessy et al., 2012; McMillan & Hofmeister, 1988; Neuville et al., 2014; Pasteris & Beyssac, 2020). These publications, however, give little attention to routine mineral identification as a basic application and they give the reader little assistance with the practical details required to choose a Raman instrument and learn how to use it. This is the reason for and the purpose of this document.

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A.2. The Raman Effect and Raman Spectroscopy

A.2.1. The Raman Effect

There are many publications available that can explain the Raman effect to any desired level of detail (e.g. Ferraro et al., 2003; Smith & Dent, 2019; Wilson et al., 1980). Below is a brief summary for the purposes of this guide, followed by some practical implications.

The Raman effect is a form of inelastic scattering of light that is controlled by the energy levels of molecular vibrations – the vibration of atoms that are bonded to other atoms within a compound. Figure A.2.1 shows the primary vibrational modes for the water molecule. As with electron energies in an atom, vibrational energies do not have arbitrary energies, but are restricted to quantum energy states.

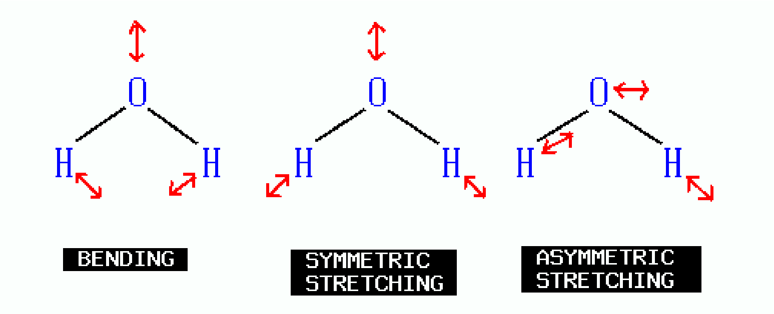

Figure A.2.1. Vibrational modes of the water molecule. Adapted from https://cimss.ssec.wisc.edu/goes/misc/wv/vibration_modes.gif

Incident photons (typically from a laser) that are absorbed by a molecular substance raise its vibrational modes to arbitrarily elevated energy states. This is quickly followed by energy-state decay accompanied by photon emission. If the energy state of a vibrational mode begins and ends in its ground state, the wavelength of the emitted photon is the same as the incident photon. This is elastic (Rayleigh) scattering. If the vibrational mode begins at its ground state, but returns to an elevated quantum state, the emitted photon is shifted to a longer wavelength – the magnitude of the shift being determined by the difference between these ground and elevated energy levels. This is the Raman effect. In particular, this is referred to as Stokes Raman. If the vibrational mode begins at an elevated energy level and ends at the ground state the wavelength of the emitted photon is again shifted, but this time to a shorter wavelength. This is referred to as Anti-Stokes Raman (Figure A.2.2).

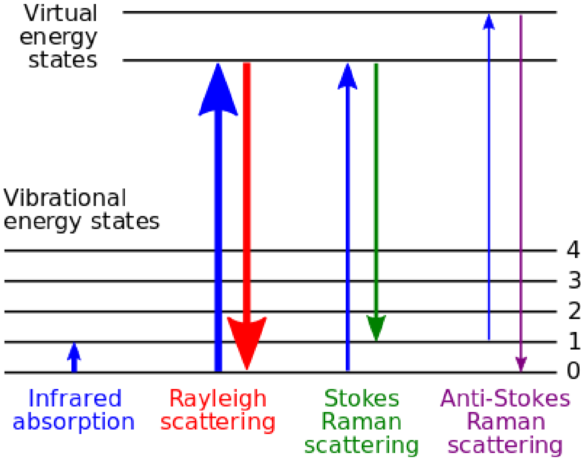

Figure A.2.2 Vibrational energy state transitions and the Raman effect. Downloaded from https://commons.wikimedia.org/wiki/File:Raman_energy_levels.svg

A.2.2 Raman Spectroscopy

Several practical spectroscopic details emerge from the nature of the Raman effect. Figure A.2.3 shows example Raman spectra of the SiO_2 polymorphs to help illustrate these details.

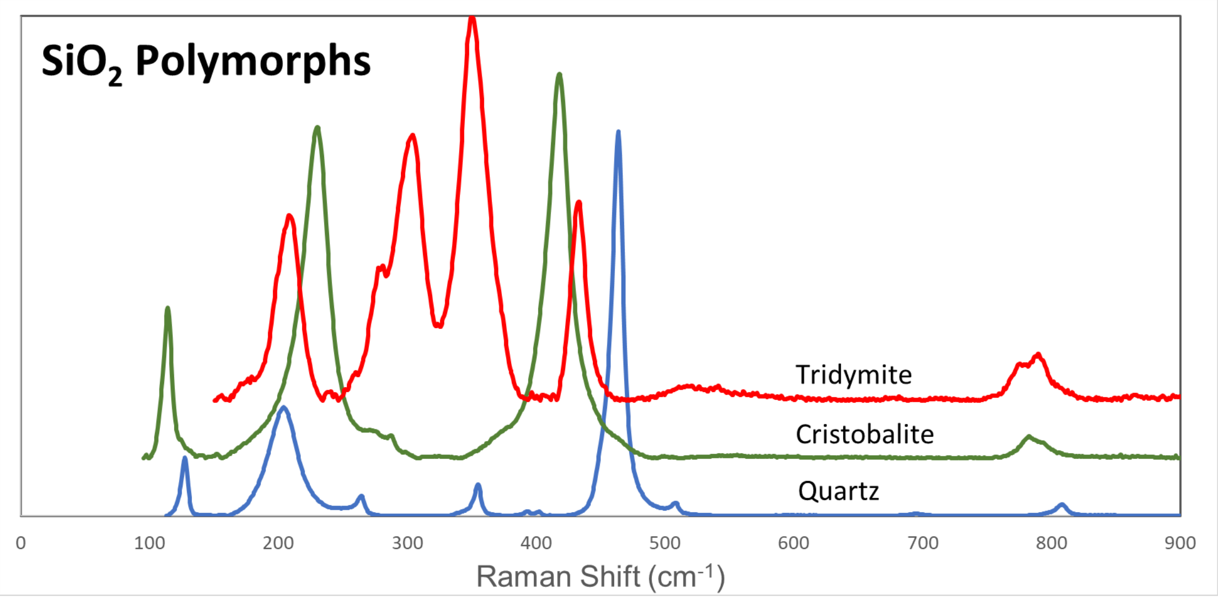

Figure A.2.3 Raman spectra from rruff.info of quartz and cristobalite and tridymite.

Note in Figure A.2.3 that the X-axis is labeled Raman Shift – a change in wavelength. The standard scale used is reciprocal wavelength in units of waves per cm (or cm^{-1}) which is also known as wavenumbers. For context yellow light measured on this scale has a wavenumber around 17000 cm^{-1} and green light around 19000 cm^{-1} making the difference between them about 2000 cm^{-1}.

Raman Peaks: In the most conceptual sense every vibrational mode of the target would be represented by a separate peak in its Raman spectrum. However, in reality, some modes result in peaks that are too weak to be detected, some modes have characteristic energies so close together that they may not be resolved, and for reasons out of the scope of this introduction, some modes are unable to exhibit the Raman effect (i.e. Raman inactive modes).

Peak Positions: The magnitude of the Raman shift for each vibrational mode is related to atomic masses, bond lengths, bond strengths, and structural geometry and symmetry. While Raman shift values do not translate directly into structural parameters - such as the d-spacings derived from 2θ values in XRD - the peak patterns of Raman spectra are characteristic of the structure. Figure A.2.3 shows how the Raman pattern changes for three polymorphs of SiO_2.

Excitation Source: In order to detect and accurately measure the characteristic wavelength shift of the Raman effect, the source of incident light must be as monochromatic as possible. Hence Raman excitation sources are generally lasers.

Source Independence: Since the spectroscopic quantity being measured is a shift in wavelength this means that 0 on this scale always represents the wavelength of the excitation source. The pattern of peak positions (on a scale of cm^{-1}), accordingly, is independent of the absolute wavelength of the source. Absolute and relative peak intensities, however, do vary with source wavelength (as well as other factors, see below).

Weak Signal: The probability of Raman scattering events is very small – about 10^6 less likely than Rayleigh scattering - making it advantageous to have an intense excitation source or a very sensitive spectrometer or both.

Source Filter: Note in Figure A.2.3 that the spectroscopic data does not begin until around 100 cm^{-1}. As mentioned above, 0 shift corresponds to the wavelength of the excitation source. One of the basic technological challenges of Raman spectroscopy is the source filter. This filter has to block transmission of un-shifted (Rayleigh scattered and reflected) laser light, which is around 10^6 times as intense as the Raman signal, while still passing light, with little intensity reduction, at wavelengths that are within 10's to low 100's of cm^{-1} from the laser wavelength.

A.2.3. Controls on Absolute and Relative Signal Intensity

As with any analytical technique the quality of the results is dependent upon obtaining a strong signal with adequate signal-to-noise ratio (SNR). In addition, phase identification via spectrum matching has some dependency on relative peak heights being similar to the reference spectrum for the same phase. Following are the factors governing absolute and relative intensity for Raman spectrometry with some emphasis given to the factors one may have some control over.

Sample Properties: A number of sample-level factors influence absolute and relative intensity:

- Molecular/Crystal Structure and Chemistry: For the mineral identification task, structure and chemistry are factors we don’t know in advance, however, we may know the geologic/geochemical environment of your sample well enough to restrict the possibilities. Some guidelines are listed in the following Raman Spectroscopy of Minerals section (A.3).
- Amount of Sample Excited: As with many analytical methods signal strength is dependent upon how much of the target material is reached by the excitation source and how much of the signal produced is able to reach the detection system. For gasses and solutes in a liquid this is primarily dependent upon concentration (per unit volume). For solids this is dependent upon color, density, and opacity. The more these factors impede penetration of the sample by the laser light, the lower the Raman signal strength.
- Physical Form/Habit: For crystalline solids with a grain/crystallite size smaller than the laser beam, high concentration of grain boundaries and defects can diffract and scatter both the laser light and the Raman scattered light resulting in less signal production and less signal reaching the detector (e.g. many clay mineral samples).
- Sample Surface Characteristics: It matters, to some degree, whether the sample surface is rough or polished flat. For a translucent sample surface roughness can reduce the amount of laser light penetrating the sample, however, for an opaque sample surface roughness can increase the amount of sample illuminated by the laser.

Instrumentation: This topic will be covered in some detail below; however, it is worth mentioning here that the intensity of the Raman signal collected by an instrument is dependent on technology factors such as solid angle of scattered light collected by objective optics, light losses on the optical path to the detector, and detector sensitivity.

Source Wavelength: Raman theory predicts that Raman scattering intensity will vary with the 4th power of the excitation laser wavelength, and that for photon counting, the proportionality is actually $v_0(v_0 - v_r)^3$ where v_0 is the reciprocal wavelength of the scattered light and v_r is the Raman shift of a particular Raman mode, both in cm^{-1} (McCreery, 2000). Figure A.2.4 shows what this proportionality looks like for the case where a Raman intensity for a 780 nm laser is set to 1 for a Raman mode with a 500 cm^{-1} Raman shift. For example, the Raman intensity in response to a 405 nm excitation laser can be expected to be about 15 times the Raman intensity from the same sample using a 780 nm laser. This increase in signal intensity, however, comes at a cost. Also illustrated in Figure A.2.4 is the spectroscopic range required to see a Raman shift of 1500 cm^{-1} for a number of common laser sources. While Raman shifts are independent of source wavelength when measured in reciprocal wavelength, in terms of wavelength (e.g. in nm) they become smaller and smaller as the source wavelength gets shorter. Raman spectrometers with shorter wavelength laser sources must use more advanced (and both physically larger and more expensive) technologies (e.g. optics, source cutoff filter, dispersion optics) to achieve the same spectroscopic results.

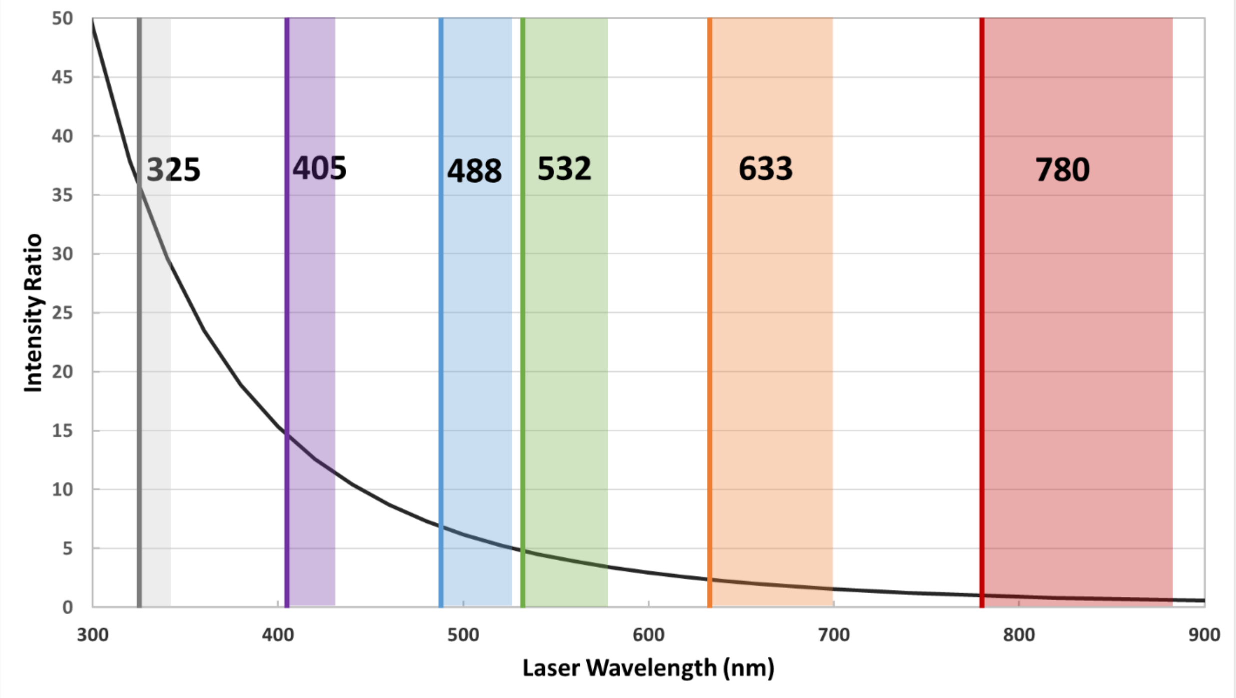

Figure A.2.4. The black line is the ratio of Raman signal intensity (for a vibrational mode with a 500 cm^{-1} Raman shift) to Raman signal intensity for the same sample/mode using a 780 nm laser. The colored boxes illustrate the spectroscopic range a Raman spectrometer must cover for it to see a Raman shift of 1500 cm^{-1} from the labeled excitation laser.

In addition to variations in absolute intensity, Raman spectra collected with different excitation lasers are also subject to intensity variations in individual Raman modes/peaks relative to each other. An example for montebrasite is shown in Figure A.2.5. While many phases show smaller variations in relative intensity than this example, it is relevant to be aware of this factor when using a spectrum matching technique for phase identification.

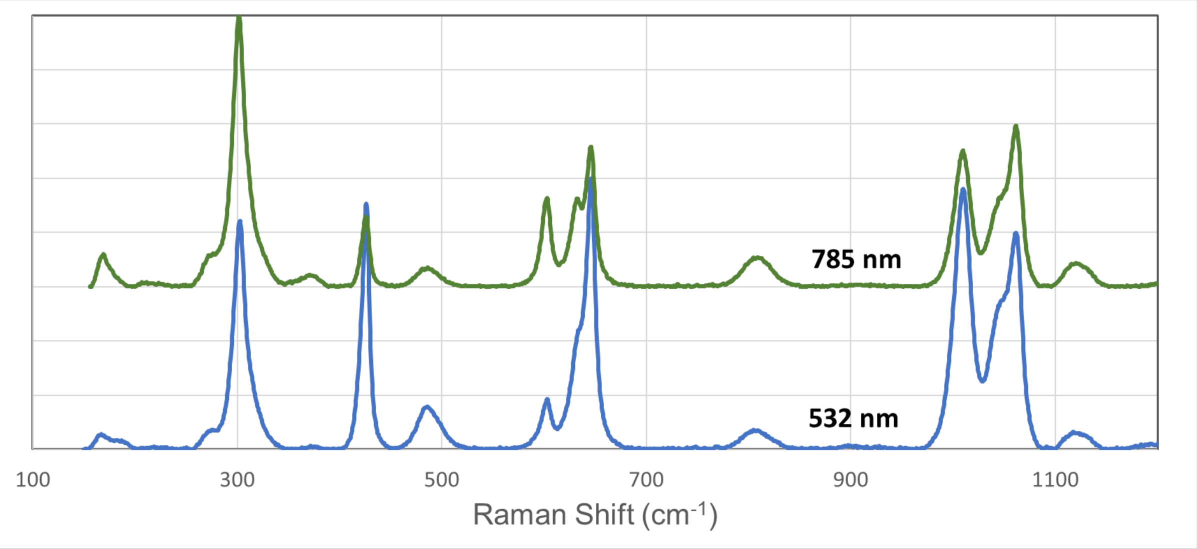

Figure A.2.5 Raman spectra of a montebrasite (RRUFF sample R060890) collected on the same instrument with a 532 nm laser and a 785 nm laser (rruff.info).

Crystallographic Orientation: Due to the wave nature of light and the inherent polarized nature of laser light, it makes a difference, in terms of Raman scattering intensity, what the geometric relationship is between the motion vector of a molecular vibration and the vibration vector of laser light. For gasses, liquids and solutes (in a liquid or gas) this is not generally a factor because the laser light intersects with a large number of molecules in random orientations. For single grains of crystalline solids, however, the geometric relationship between laser and crystal structure is fixed. As long as some vector component of the optical vibration is in the direction of the molecular vibration some Raman scattering will occur. However, as the geometric relation between the two vibrations is shifted towards parallel the intensity of Raman scattering increases towards a maximum. Conversely, if the two vectors are exactly perpendicular there will be no Raman scattering. Restrictions on interatomic vibrations forced by a crystal structure and its symmetry operations make it common for some vibration modes in a crystalline material to be parallel to the major crystallographic axes. This means that in the special case of the Raman laser being parallel to a crystallographic axis, the intensity of some vibrational modes will be at a maximum and the intensity of some modes will be at a minimum or even quenched. For example, note in Figure A.2.6 that there is a Raman peak at about 730 cm-1 that is very strong when the laser is parallel to the crystallographic c axis but undetected when the laser is parallel to the a-axis.

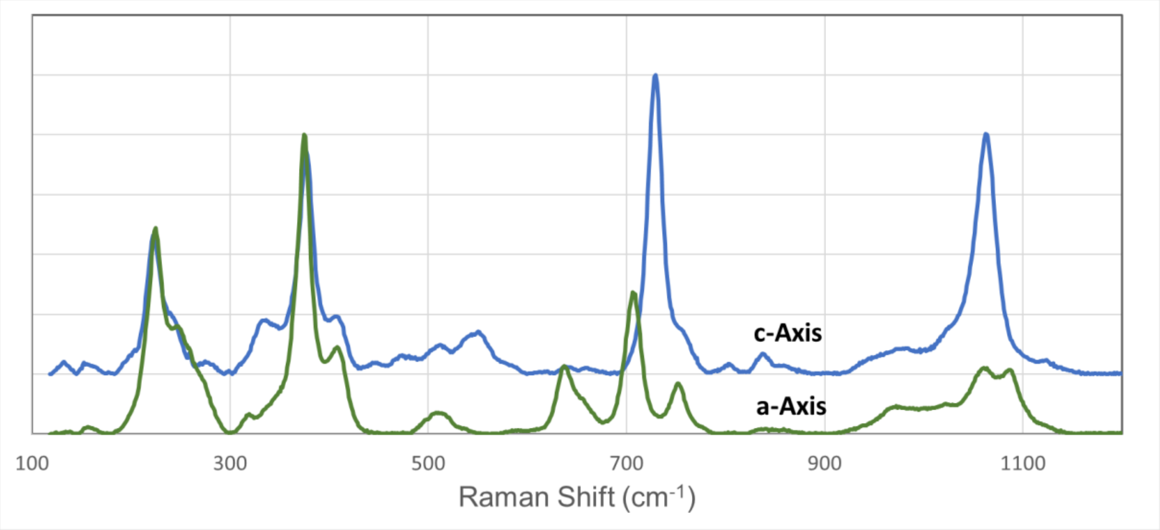

Figure A.2.6. Oriented Raman spectra of Elbaite R050260 from rruff.info. Both used an unpolarized 514 nm laser beam. As labeled, one spectrum was collected with the laser beam parallel to one of the crystallographic a axes and the other spectrum was collected with the laser beam parallel to the c axis.

Signal Enhancement Methods: A hand-full of methods and technologies have been discovered and developed which significantly increase the intensity of the Raman signal (see Smith & Dent, 2019). Examples include Resonance Raman, surface enhanced Raman (SERS) and tip enhanced Raman (TERS). These technologies, however, require advance knowledge of the target compound/phase and/or specialized equipment and sample preparation, and therefore, are not generally useful for basic mineral identification.

A.2.4. Analytical Challenges – Especially Fluorescence

As with any analytical method, Raman spectroscopy is subject to certain challenges. Many of these are reviewed in later sections, but undoubtedly the most common, and frustrating, difficulty encountered when using Raman spectroscopy on some minerals is sample fluorescence. Fluorescence emission following excitation by the Raman laser can be many times more intense than Raman scattering – effectively overwhelming some or all Raman peaks in the spectrum.

Fluorescence results when absorption of incident photons by the sample excite electrons to higher energy states. Given the relatively modest energy of light photons, the affected electrons are outer shell electrons – whose energy states are influenced by crystal field and other nearest-neighbor interactions. After excitation, such electrons quickly return to their ground state releasing energy via 2 different pathways – radiative decay (i.e. photon emission) and non-radiative decay. Non-radiative decay is primarily thermal – electron energy transferred to the vibration of surrounding atoms. As small amounts of energy are lost to structure relaxation and thermal vibration, when radiative decay occurs, the energy of the emitted photon is lower and therefore has a longer wavelength than that of the excitation source. Fluorescent photon emission occurs at characteristic wavelengths corresponding to transitions between specific electron energy levels, and it is typically related to a relatively short list of "activator" ions in the sample atomic structure. Some common activators are transition metals and lanthanides (REE). Typically in minerals fluorescence is extrinsic – meaning the activator is present as a small or trace impurity. For additional details, with a focus on minerals, see Gaft et al., 2015; Waychunas, 2014.

The fluorescence effect in Raman spectroscopy is similar to the neon-bright colors one sees when a UV light is shone on a fluorescent mineral in a darkened room, but in a Raman experiment, the excitation light source is not specifically UV light, but the particular laser used, even into the NIR. Fluorescence emission produced from the Raman laser is only a problem if its characteristic wavelength range intersects the spectral region that the Raman spectrometer is examining (see Figure A.2.4). In fact, Raman systems that employ a UV laser see very little fluorescence interference because most fluorescence emission occurs at much longer wavelengths. Also, as fluorescence always occurs at a longer wavelength than the excitation source, fluorescence from some activators will not be excited by some longer wavelength lasers.

Although, in principle, fluorescence from a given activator occurs at a characteristic wavelength, most fluorescence occurs over a wavelength range (see Figure A.2.7). As the fluorescence-producing electron transitions in transition metal activators are in outer shell *3d* orbitals, their emissions occur over a broad wavelength range. In contrast, many of the fluorescent electron transitions in REE activators involve *4f* orbitals, which are significantly shielded by *5s* and *5p* outer shell electrons, resulting in narrow-range fluorescence emission. Additionally, emissions from the same activator in different compounds/minerals, with different local (atomic/electronic) environments, occur over a range of wavelengths.

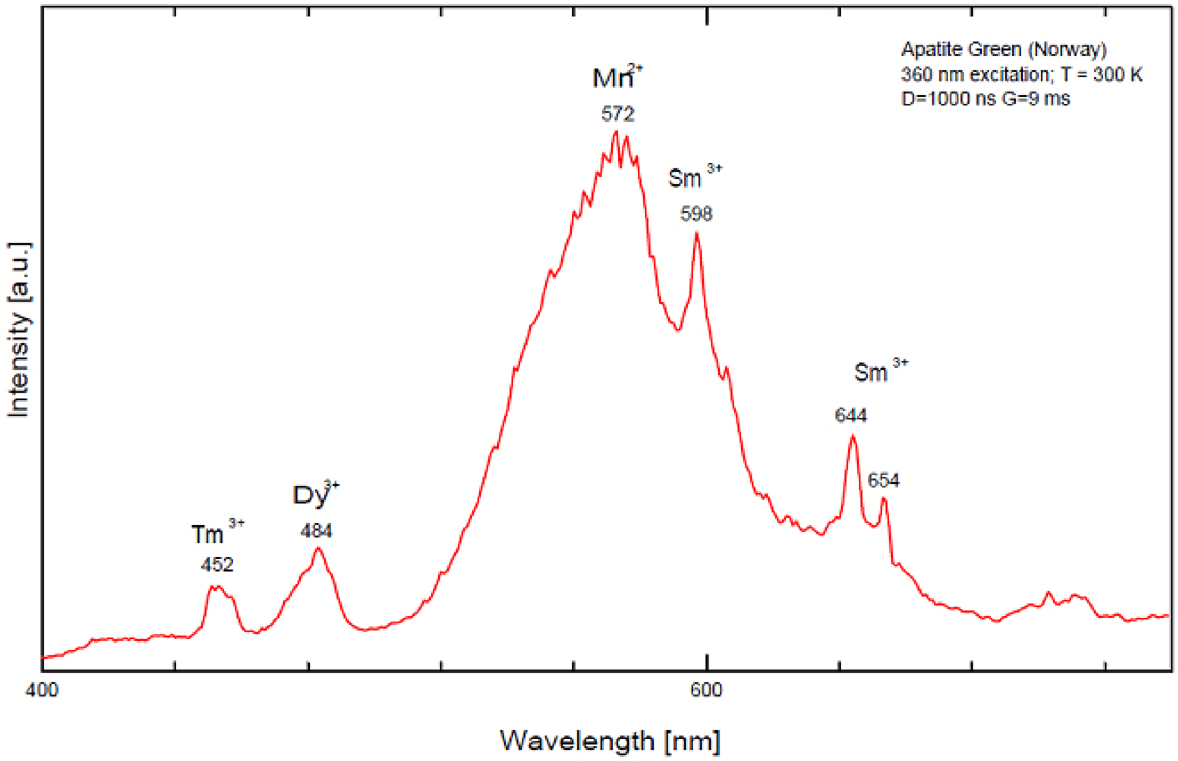

Figure A.2.7 Luminescent spectrum of an apatite showing a broad peak from Mn2+ and much narrower peaks from REE activators. Downloaded from fluomin.org.

Significantly, fluorescence occurs on a different time scale than Raman scattering. Raman scattering occurs within about 1 ps after excitation while fluorescence occurs from 100's of ps to 1 ms after excitation (Gaft et al., 2015; Gaft & Nagli, 2009). This time difference is the basis for a new generation of pulsed laser Raman systems that can effectively isolate Raman spectra from the slower emitted fluorescence.

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A.3. Raman Spectrometry of Minerals

When designing a data collection methodology for mineral identification, it is helpful to understand the nature of the Raman response from minerals. The expected signal intensity informs choice of dwell time, while knowing the likely (and unlikely) Raman shift of characteristic peaks informs choice of spectral range. A brief review below of Raman scattering principles and some spectra systematics by mineral type/group will help determine appropriate data collection parameters.

In the Raman spectrum for gypsum ($CaSO_4 \cdot 2H_2O$) (Figure A.3.1), the peaks with Raman shifts above about 200 cm^{-1} are referred to as internal modes, in that they typically involve vibrations among nearest neighbor atoms. The peaks below ~200 cm^{-1} are commonly external modes, or lattice modes, and represent vibrations among larger groups of atoms within the crystal structure. Assigning peaks to specific sets of atoms and types of vibrations (such as the labeled examples in Figure A.3.1) is not necessary for mineral identification, but we will need to use the associated terminology in order to discuss Raman spectrum systematics. Note the large spectral separation in Figure A.3.1 between the characteristic gypsum peaks (in the range ~200 to 1200 cm^{-1}) and the peaks attributed to H_2O stretching modes. The information provided by H_2O and/or OH peaks can be useful (e.g. for differentiating between hydrous and non-hydrous minerals), however, phase identification for most minerals can be accomplished using the characteristic peaks in the frequency range ~ 100 to 1400 cm^{-1}.

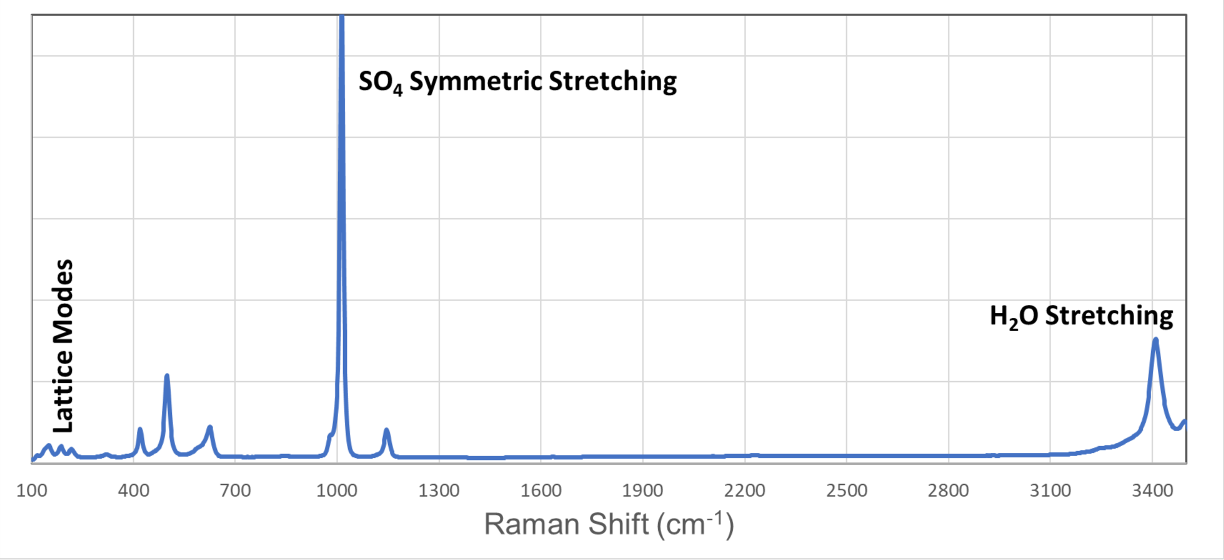


Figure A.3.1 Full range Raman spectrum of gypsum - see text for explanation. This is spectrum 24215 from sample R060509 from www.rruff.info.

Some principles of Raman scattering that are helpful for mineral identification are discussed below.

A.3.1 Number of Raman Peaks

In general, Raman spectra for high-symmetry crystal structures show fewer Raman peaks than do low symmetry structures. Also, some vibrational modes may not be "Raman active" and, as described in section A.2.3 above, some Raman modes can be extinguished for particular geometric relationships between the vibration direction of the laser beam and the crystallographic orientation of a mineral grain.

For certain mineral structures, all vibrational modes are Raman inactive. This happens when every atom in the structure is positioned at a point of inversion symmetry, and therefore, minerals with no Raman peaks tend to have higher symmetries and relatively simple chemical formulae. While some are relatively common, such as galena, pyrrhotite, and halite, most of the minerals expected to have no Raman peaks are rare. In fact, the absence of Raman peaks is uncommon enough that it sometimes provides a clue to a mineral's identification. It should be noted, however, that structural defects and chemical impurities can cause some modes to become Raman active in these minerals. A list of known and predicted examples of minerals with no Raman active modes is presented in Appendix 1.

A.3.2 Raman Peak Positions

Vibrations between light elements and between strongly bonded atoms tend to produce Raman peaks at higher Raman shifts. For example, vibrations between H and O in hydrous and hydrated minerals occur beyond 3000 cm^{-1}, as seen for gypsum in Figure A.3.1. The converse is true of vibrations between heavy elements and between less strongly bonded atoms. To illustrate this point, compare histograms b and h in Figure A.3.2 which show strongest-peak positions for oxides and silicates, with bonds involving oxygen anions, to histograms c and d for compounds of heavier sulfur and halide anions. Lattice modes occur at low Raman shifts (see Figure A.3.1) because groups of atoms that are vibrating as a unit have more mass than a single atom.

The shifts of Raman peaks related to solid-solution substitutions can sometimes be complex. Substitution of a lighter element for a heavier element, and/or substitutions that result in shorter/stronger bonds should shift Raman peaks to higher frequencies, and vice versa, but these effects can offset or overlap and the results can be difficult to anticipate.

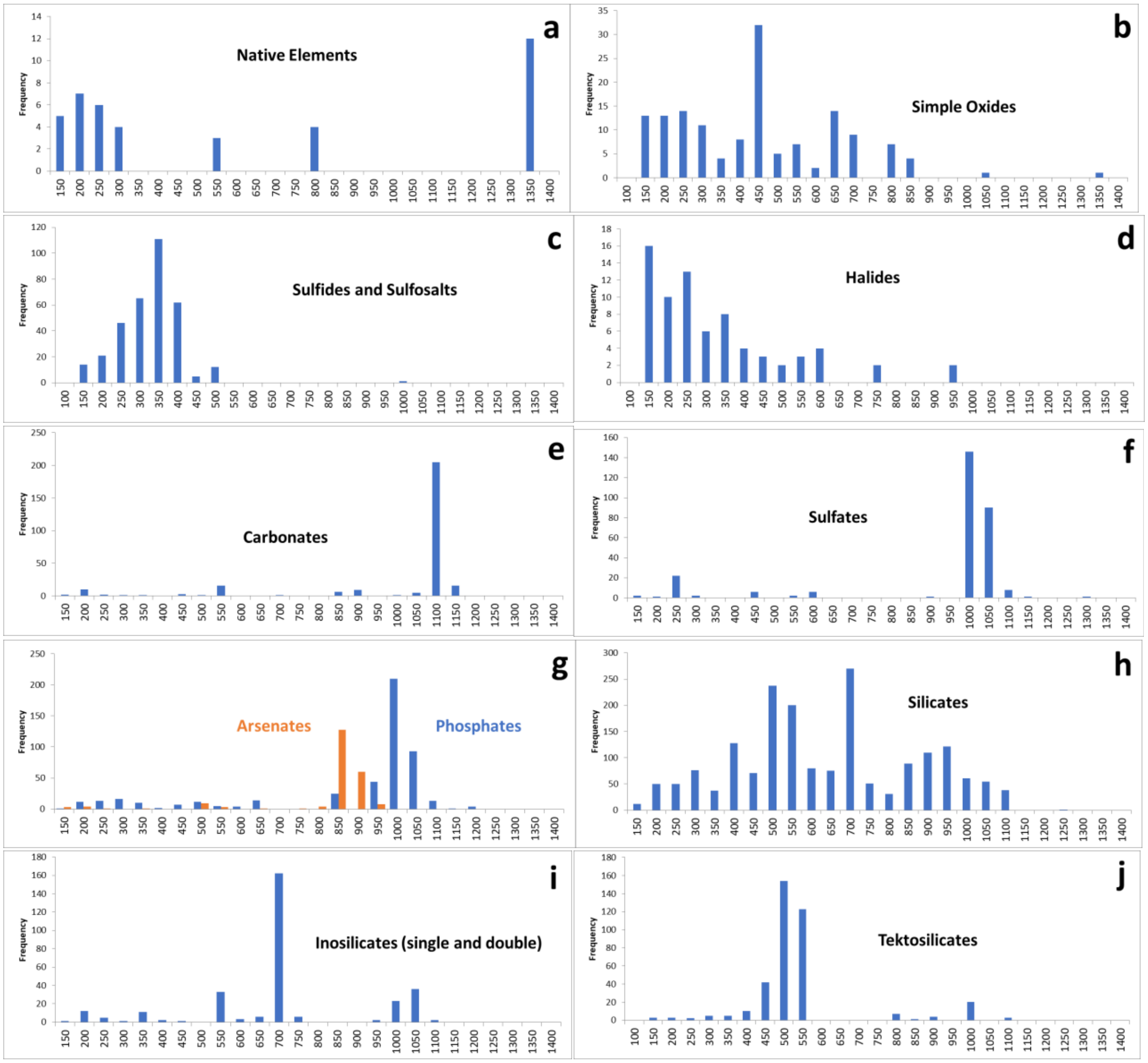


Figure A.3.2 Histograms showing frequency of position of the strongest peak for mineral species in each mineral class. The horizontal axis in all cases is Raman Shift in cm^{-1}. Strongest peak position data is derived from an extract from www.rruff.info that includes only independently verified mineral specimens and only "unoriented" spectra with a SNR > 40. The RRUFF database includes 2 or 3 spectra from each specimen and often includes more than one specimen of more common mineral species. Accordingly, the frequency values represent number of spectra and not necessarily number of distinct species.

A.3.3 Raman Peak Shapes

The Raman spectra of well crystallized minerals typically consist of sharp and narrow peaks (e.g. Figure A.3.1) however, they can also consist of a mixture of sharp and broad peaks (e.g. quartz) or only broad peaks (e.g. rutile) as shown in Figure A.3.3. Peak shapes tend to broaden as crystallinity decreases (including radiation damage), as grain size becomes very small, and to some extent, as the temperature of the sample increases under heating by the Raman laser. In addition, solid solution can broaden Raman peaks. For example, in Mg-Fe olivines, the M2 octahedra is edge-shared with 4 other M1 and M2 octahedra. While internal vibrational modes are primarily about nearest neighbor interactions, changes in occupancies of these second-nearest neighbors also have an effect. In pure forsterite (Fo_{100}), all M2 sites will have identical vibrational modes. In an intermediate olivine, the M2 sites will be occupied by Mg or Fe and each will be surrounded by 0, 1, 2, 3 or 4 of the opposite metal ion. Peaks in the Raman spectrum are broadened because they actually consist of the sum of very closely spaced peaks. Figure A.3.4 shows that, not only are the peaks for the Fo_{44} intermediate olivine displaced to lower cm^{-1} as expected (because of substitution of the heavier Fe for Mg, see above), but they also are significantly broader than the peaks for the Fo_{100} end-member.

Figure A.3.4 also illustrates that various sample-related broadening factors, and limits to spectrometer resolution, can result in Raman peaks that are partially, or completely, overlapped. For this reason, strategies that use whole-spectrum comparisons rather than individual peak positions are typically more effective for phase identification. If precise peak positions need to be determined (e.g. for solid solution composition estimation) decomposition methods involving peak-shape fitting are required. In general, the theoretical shape of Raman intensity about a vibrational mode is a Lorentzian curve but thermal broadening adds a Gaussian component. Accordingly, efforts to decompose overlapping peaks via peak-shape modeling generally use Voigt or Pseudo-Voigt peak shape formulae, since these incorporate an adjustable mixture of Lorentzian and Gaussian forms.

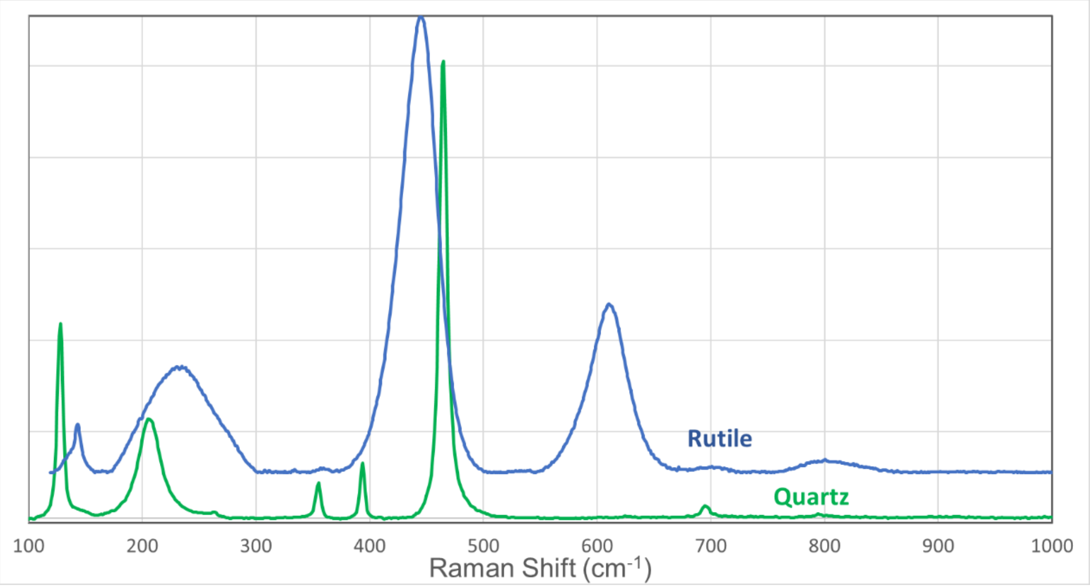


Figure A.3.3 Raman spectrum of rutile showing inherently broad peaks and a Raman spectrum of quartz showing a mixture of sharp peaks and one broader peak.

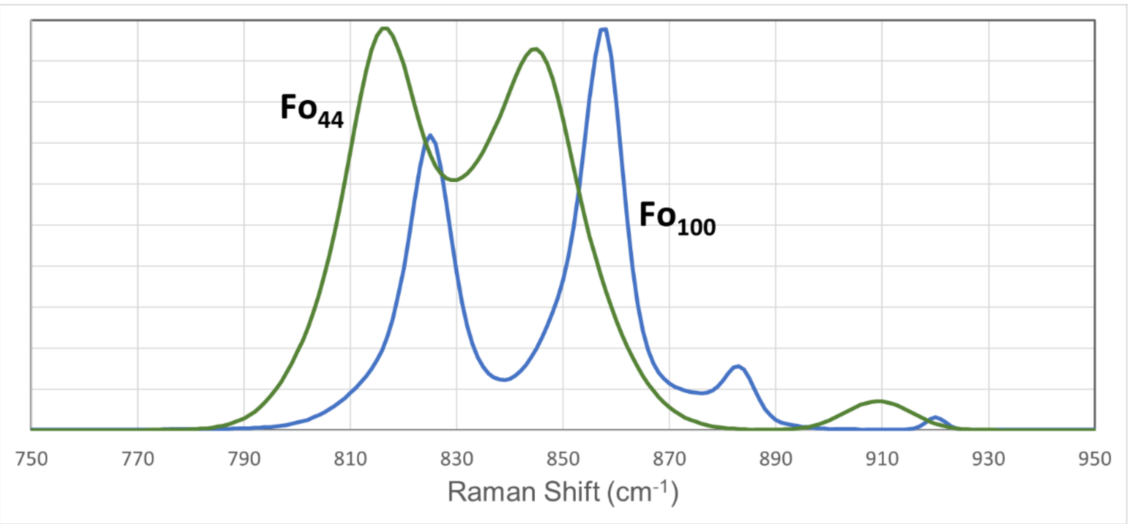


Figure A.3.4 Raman spectra of 2 olivine phases zoomed in to show the major peaks between 750 and 950 cm^{-1}. Both spectra are from www.rruff.info and both were collected with the same instrument using the same laser. The Fo$_{100}$ composition is RRUFF specimen R100099 and the Fo$_{44}$ specimen is R100102. The raw spectra have been smoothed and normalized to facilitate direct comparison of peak positions and shapes.

A.3.4 Raman Peak Intensities

As introduced in section A.2.3, intensities of individual peaks as well as overall signal intensity are influenced by various sample-level factors, including atomic structure and composition, crystallographic orientation, physical form (e.g. grain size, surface roughness), and optical density. Some of these can be controlled by the analyst but others need to be considered when setting up data collection methodology.

Crystal Chemistry and Structure

While chemistry and structure are generally unknowns for the mineral identification task, understanding their effects on Raman signal intensity can be helpful in interpreting Raman spectra.

Figure A.2.1 showed that there are different types of vibrational modes, which have different probabilities of Raman response (i.e. Raman cross sections) and therefore different Raman peak intensities. Stretching vibrations typically produce stronger Raman peaks than bending modes, and symmetric stretching vibrations produce the strongest Raman peaks. For example, minerals that are compounds of anionic functional groups such as carbonates, sulfates, phosphates, arsenates, etc., tend to have multiple/degenerate symmetric stretching vibrations within the anionic group, and as a result, their Raman spectra commonly consist of one strong peak, produced by the sum of the symmetric stretching vibrations, and an array of weaker peaks, e.g. as for the Raman spectrum of gypsum (Figure A.3.1). Likewise, simple high-symmetry structures typically show only one strong peak and a few weaker ones, e.g. simple oxides and halides.

Crystallographic orientation

In cases of single mineral grains, as previously described in section A.2.3, significant variations in relative intensities for certain peaks can result when the laser beam vibration direction is parallel or perpendicular to a crystallographic axis. For many geological samples this may not be a problem as mineral grains will often be present in random orientations with a low probability of being close to a special crystallographic orientation. However, preferred orientation will be a factor to consider for rocks having a distinct mineral-orientation fabric and for separated mineral grains that tend to sit flat on cleavage surfaces. In such cases, it might be helpful to collect multiple spectra from mineral grains in a variety of orientations in order to assess variations in relative peak intensities.

Physical Form "Sample texture"

Sample grain size can also influence Raman signal intensities. When mineral grains are smaller than the laser spot, grain boundaries scatter both the laser light and the Raman light resulting in a lower overall signal entering the spectrometer as well as broadening of the Raman peaks.

Optical Density

Optical density of the sample directly affects Raman signal intensity. The Raman signal is a function of the volume of the sample that is excited by the laser, as well as the volume and depth from which Raman scattered light can escape to the spectrometer. For transparent minerals, this volume is limited primarily by the cross-section of the laser spot, and depth for which the spectrometer apertures (especially confocal hole) define the space from which light can enter the spectrograph. For highly opaque minerals this volume can be limited to little more than the area defined by the intersection of the laser beam and surface of the sample. Accordingly, signal intensity varies with optical density between these extremes. Figure A.3.5 compares the Raman signal intensity from a highly transparent forsterite to that of increasingly densely colored fayalites.

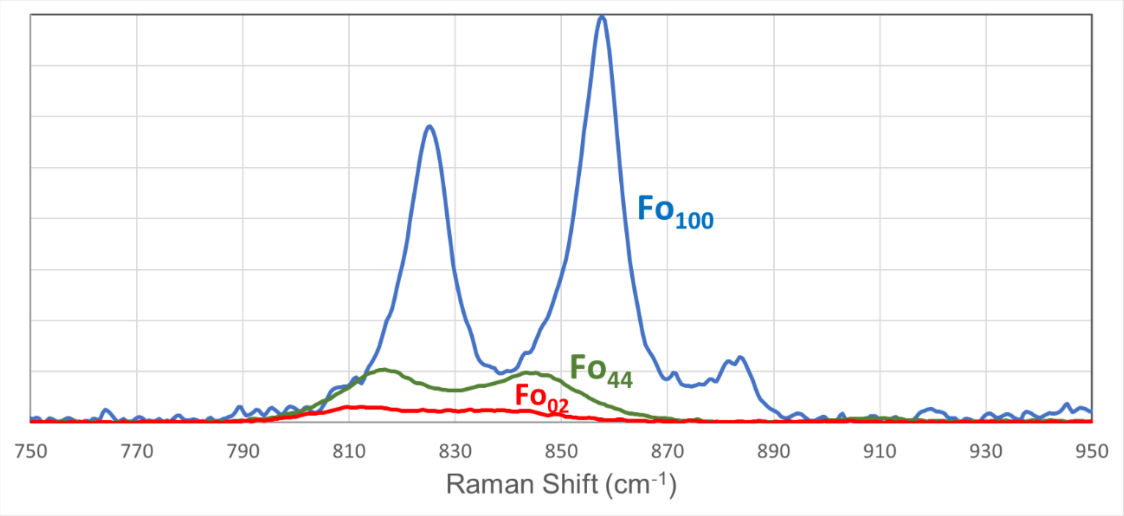


Figure A.3.5. Instrumental intensity comparison for 3 olivine composition of increasing color density. All 3 spectra were collected on the same instrument under the same operating conditions using a 780 nm laser. All 3 spectra are from www.rruff.info. The Fo_{100} and Fo_{44} compositions are the same spectra shown in figure A.3.3 except the raw instrumental spectra are shown here.

One consideration with highly transparent minerals is that the laser light might intersect mineral grains below or adjacent to the target mineral grain, resulting in a mixed-phase spectrum. In such cases, adjustment of the confocal optics on the Raman system can limit the volume sampled by the spectrometer.

A.4. The Raman Spectrometer

In practice, there is considerable variation among custom and commercial Raman instruments. Here we will review the basic components, functions, and configurations with emphasis on the practical implications for mineral identification.

A.4.1 Raman Spectrometer Components and Functions

Figure A.4.1 shows the basic components of a Raman spectrometer which include:

- Monochromatic Light Source. This is typically a laser. Since lasers generally emit more than one characteristic wavelength a "cleanup" filter is required which passes only the desired laser wavelength.
- The Sample. Note that the sample and optical pathways are not under vacuum so the sample can simply sit on a holder, or even be inside a container (including under a coverslip or inside a diamond anvil cell), as long as the container has an optically transparent window.
- The Laser-Wavelength Cutoff Filter. This filter absorbs the scattered or reflected light having the wavelength of the excitation laser while passing other light wavelengths, starting as close as possible to the laser wavelength. Most Raman instruments examine the Stokes Raman scattering (see A.2.1), which means the cutoff filter only needs to pass wavelengths longer than the laser wavelength.
- The Spectrograph: This component consists of an optical path and grating for dispersing light, and a sensitive detector to measure light intensities over a range of (dispersed) wavelengths.
- The Computer: Whether on-board or external or some combination, a computer is employed to both control instrument components and to store the resulting spectrum as digital intensities.

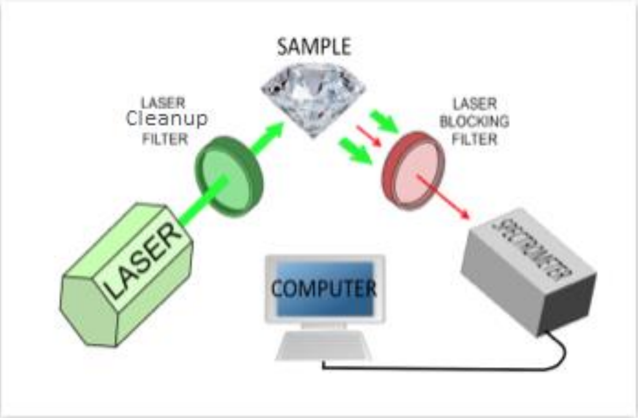


Figure A.4.1 Core components of a Raman Spectrometer. From https://agta.org/advantages-and-disadvantages-of-raman-fourier-transform-infrared-spectroscopy-ftir-in-the-gemological-field/

Figure A.4.1 shows an optical path with a 90° angle between the laser beam and the scattered light path to the spectrograph. While configurations similar to this are common for custom-made optical-table Raman systems, most commercial Raman spectrometers engineer an optical path where the excitation laser and the path to the spectrograph are coaxial, and the excitation/signal angle is 180° as schematically shown in Figure A.4.2.

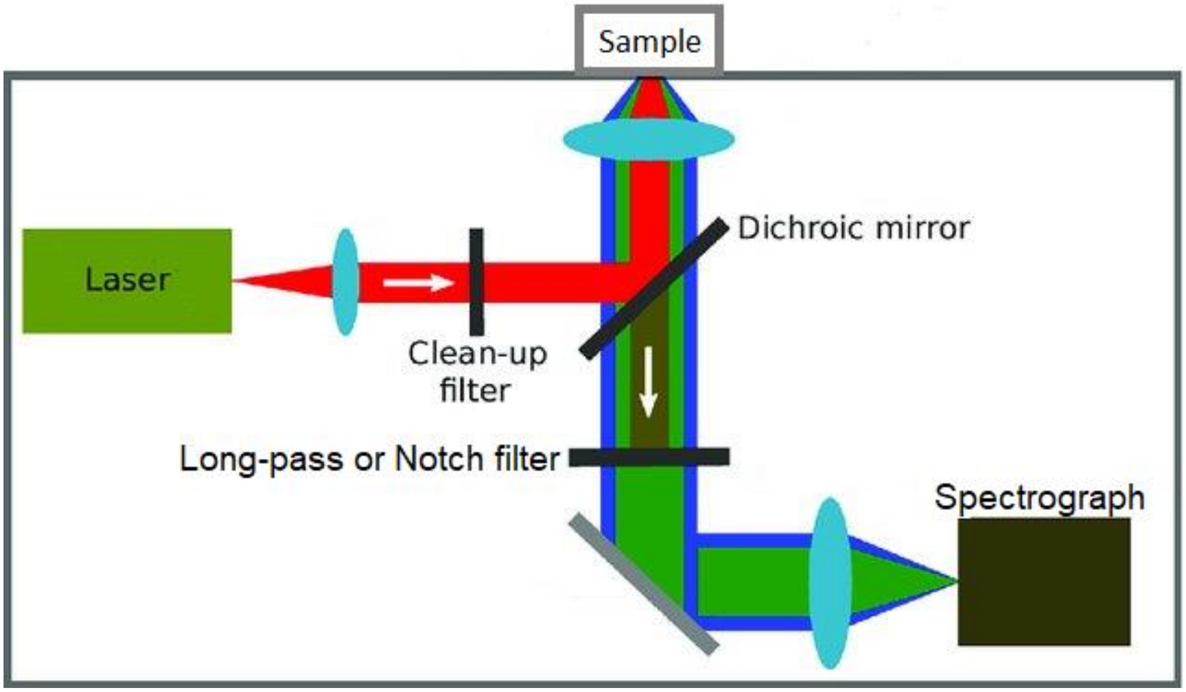


Figure A.4.2 Optical path schematic for a Raman spectrometer with coaxial laser insertion. Adapted from https://www.researchgate.net/figure/Schematic-presentation-of-portable-Raman-spectrometer-The-output-from-the-diode-laser_fig1_325097383

<u>A.4.2 Raman Spectrometer Engineering</u>

- The Laser: The laser may be a gas laser, a solid-state, or a semiconductor laser. Due to their physical size, gas lasers and many solid-state lasers are mounted externally and smaller, self-contained Raman systems generally use semiconductor lasers. Most Raman systems employ continuous wave (CW) lasers, having a continuous output while gated Raman systems (see Configurations below) employ pulsed lasers. Since the laser-line cleanup filter must be specific to the laser wavelength, this component is often integrated into the laser. As one of the strategies for avoiding fluorescence interference is switching laser wavelengths (see section A.6 below), many Raman systems are configured with more than one laser.

  Many Raman spectroscopy applications, including mineral identification, require the ability to control the laser intensity at the sample. Most laser systems allow for some electronic control of their output intensity, or alternatively, use a series of neutral-density filters. In some cases, both types of intensity control are combined in order to vary laser intensity over a wider range. Laser intensity is generally reported in terms of milliwatts (mW) and intensities typically employed for mineral identification ranges from a fraction of 1 mW to several 10's of mW. Raman systems may report to the user the raw laser output, which is generally greater than the amount that reaches the sample, and some systems will only report laser output in percent (of the raw laser output). The use of an external laser intensity meter is required to measure actual laser intensity on the sample.

- Signal Collection Optics: Many Raman systems, including most Raman microscopes, employ signal collection optics similar to Figure A.4.2 where the optical path is open and directed only by lenses and mirrors. A common variation is the employment of fiber optics. Here a distinction must be made between fiber optic bundles being employed to carry light between modular instrument components and a single fiber optic bundle being employed to combine both laser delivery and signal collection. The latter is employed primarily in the form of a fiber optic probe. Figure A.4.8 illustrates how the internal optics of such a fiber-optic probe contains both the laser cleanup filter and the laser-wavelength cutoff filter. As such, each of these probes is specific to a single laser wavelength.

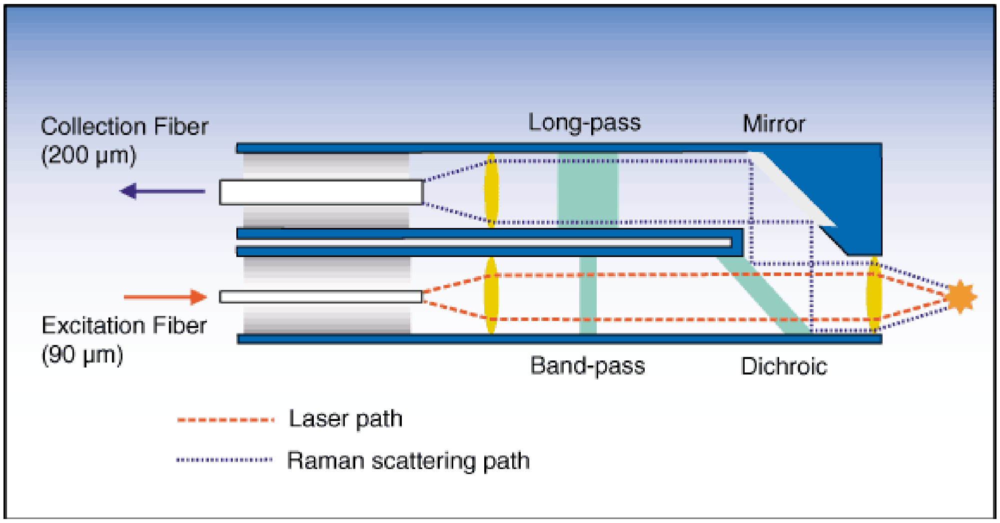


Figure A.4.8 Schematic of the components and optical pathways contained in a Raman fiber-optic probe. Downloaded from https://www.inphotonics.com/opticallayout.htm

- Relationship Between Signal Collection Optics and Signal Intensity: As explained in section A.3.4 above, various minerals produce Raman intensities that range from weak to strong. This makes it important to understand the relationship between Raman optical engineering and the amount of Raman signal from the sample that is transmitted to the spectrograph.
  - Open Optics versus Fiber Optics: When separate fiber optic bundles are employed for laser light delivery and transmission of scattered light to the spectrometer the transmission effectiveness may be nearly as good as open optics. However, when these light paths are combined into a single bundle in a fiber optic probe, the signal light transmission is reduced.
  - Objective Lens Selection: It is common in Raman studies to use a high

magnification objective (40X to 100X). Not only do they deliver smaller laser spots, which carries a spatial resolution advantage, but they also provide greater signal intensities. Higher magnification objectives require a smaller working distance and consequently collect a wider cone of light (Figure A.4.9). The common measure of the relative size of this cone is numerical aperture (NA), which is generally reported as one of the performance characteristics of a lens. Note, however, that in cases where your sample does not present a flat surface the sub-millimeter working distance of a high NA lens may be impractical. Here a long working distance objective will be more practical without sacrificing spatial resolution, but the tradeoff is the lower intensity that goes with a lower NA.

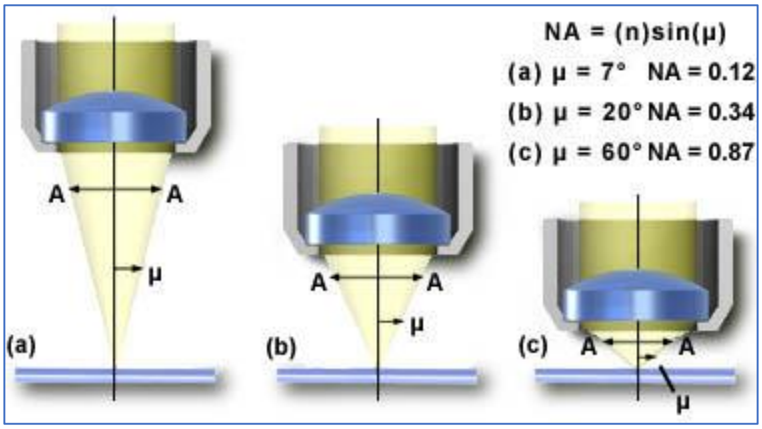


Figure A.4.9 Illustration of the relationship between working distance and numerical aperture for microscope objective lenses. Adapted from https://www.olympus-lifescience.com/en/microscope-resource/primer/anatomy/numaperture/

- The Laser-Line Cutoff Filter: There are two primary types of laser line cutoff filters: edge filters and notch filters.
  - Edge filters are characterized by an edge wavelength – passing light wavelengths on one side of this edge wavelength and blocking wavelengths on the other side. Edge filters that pass longer wavelengths and block shorter wavelengths are called long-pass filters. Since most Raman systems look only at Stokes Raman scattering, they require a long-pass filter. The steepness of the edge on such a filter refers to how quickly, as wavelength changes, the filter transitions from blocking to passing, and this determines the lowest Raman shift that can be observed by a Raman system using the filter.
  - Notch filters block light over a very small range of wavelengths and pass all other wavelengths. As such, notch filters can enable a Raman system to see on both sides of the laser wavelength – to see both Stokes and Anti-Stokes Raman scattering. Notch filters can have very steep filtering edges – so steep that some allow a Raman system to see Raman shifts as low as 10’s of cm^{-1}. The notch filters with the steepest edges are the so-called holographic notch filters (also known as Bragg filters).

- The ability of an edge or notch filter to remove the unwanted (laser wavelength) light is measured as optical density or OD. This is a logarithmic scale so that, for example, a filter with OD=2 reduces light transmission to 1/100th of the incident. Since Raman scattering has a probability about 10^6 lower than Rayleigh scattering, a Raman spectrometer requires an edge/notch filter rated at OD of 6 or greater at the laser wavelength.

➢ Light Path Apertures: Two types of pinhole or slit apertures are commonly employed in Raman spectrometers to improve spectral and/or spatial resolution.

- A spectrograph-entrance aperture is commonly employed to improve spectral (Raman shift) resolution. A smaller aperture will result in greater spectral resolution, but it will also reduce the amount of Raman scattered light that enters the spectrograph. As such, there is a trade-off between spectral resolution and signal intensity when selecting the entrance aperture. It is also true that an entrance aperture improves lateral spatial resolution at the sample – rejecting light that is scattering from locations away from the laser spot on the sample. This is especially important when the analytical target is translucent to transparent.

- A confocal aperture can be employed to improve spatial resolution at the sample. A confocal aperture is located midway along the optical path between the sample and the spectrograph. In addition to rejecting scattered light from locations laterally away from the laser spot, a confocal aperture will reject scattered light from locations above and below the plane of focus on the sample (Figure A.4.5).

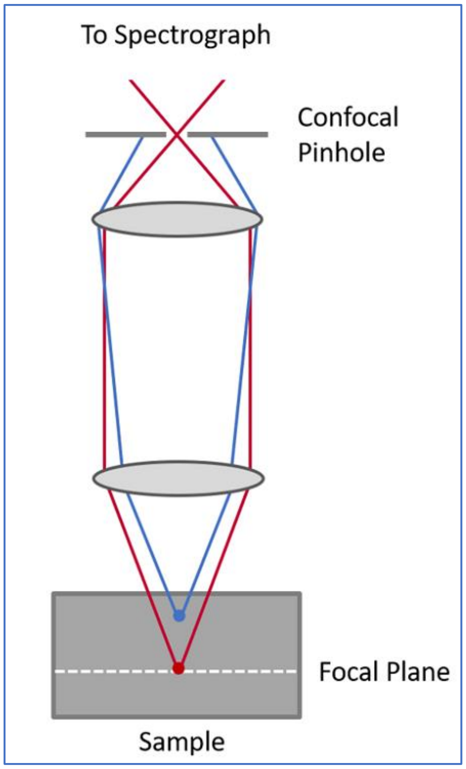


Figure A.4.10 Diagram showing how a confocal aperture controls vertical resolution. Adapted from Figure 2 of https://www.edinst.com/blog/what-is-confocal-raman-microscopy/

➢ Polarizers and Depolarizers: Neither of these components is standard in Raman systems, but each can be helpful for analysis of minerals.

- Lasers tend to naturally deliver plane-polarized light which produces variations in Raman intensities with crystallographic orientation (see sections A.2.3 and A.3.4). Accordingly, a depolarizer configured between the laser and the sample can greatly reduce such variations and improve spectrum matching for phase identification.

- A rotatable polarizer can be configured between the sample and the spectrograph to establish polarization/orientation dependency of specific Raman modes. While this information can be used to establish the orientation of each mineral grain or elucidate the symmetry of each Raman mode, it is not relevant to phase identification.

- Spectrograph Components: The essential components of a spectrograph are a light-dispersion device and a detector. Most of the commercial Raman instruments will employ a diffraction grating for light dispersion and a semiconductor-array detector.
  - Diffraction Grating: A diffraction grating has a series of parallel grooves etched into its surface. The more closely spaced these grooves are, the greater the degree of wavelength dispersion they produce. Diffraction gratings are rated by this spacing in lines per mm or grooves per mm (gr/mm). The gratings used in Raman spectrographs range from 300 gr/mm to 3600 gr/mm. Some instruments will have multiple gratings on a turret affording user selection. Some performance tradeoff comes with grating selection. A higher groove density grating will produce narrower peaks spaced farther apart, but the intensity of the peaks will also be lower.
  - Array Detector: Semiconductor array detectors come in different pixel widths (e.g. 512 or 1024 or 2048 pixels). The pixel width determines the spectral width (range of Raman shift) that the detector can capture at once and the pixel resolution – the degree of separation of the spectrum into digital channels. Different semiconductor types are chosen for their sensitivity to different wavelengths (e.g. visible versus IR). For gated Raman spectroscopy (see below) a gated detector is employed. A gated detector can be turned on and off on a very short time scale (e.g. picoseconds).
  - Detector Cooling: Semiconductor detectors are subject to a background signal caused by internal thermal interactions. A cooled detector will be characterized by a higher signal-to-noise ratio for a standard signal and by a lower detection limit. While a high-end laboratory Raman system may use LN_2 cooling, most commercial instruments employ thermoelectric (Peltier) cooling.
  - Fixed versus Scanning Spectrographs: A fixed spectrograph has a constant internal geometry in terms of grating position and detector position. A fixed spectrograph can only see one specific range of Raman shifts. A scanning spectrograph has electronically controlled moving parts that can shift the position of the grating and/or the detector (or mirrors that accomplish the equivalent change in geometry). Scanning detectors can achieve a higher spectral resolution by using a higher groove density grating and then collecting multiple portions of the resulting spectrum via grating/detector motion and then digitally splicing these spectrum fragments together.
  - Spectrograph Resolution: Practical spectral resolution of a Raman spectrograph is the result of a combination of laser wavelength, optical resolution, and pixel resolution. Optical resolution is governed by both the grating groove density and the spectrograph focal length. It is common to employ mirrors to fold the internal light path - to lengthen the spectrograph focal length without making the spectrograph physically longer. As illustrated in Figure A.2.4 the same spectral range in terms of Raman Shift translates into smaller and smaller spectral ranges in terms of absolute wavelength as the excitation laser wavelength becomes shorter. This means that a

Raman system using a shorter wavelength laser requires a higher groove-density grating and/or a longer focal length spectrograph to achieve the same Raman shift range and the same spectral resolution as a Raman system using a longer wavelength laser.

- The Computer and Software: The computing capacity resident within the Raman spectrometer case can range from onboard electronics only for controlling internal components and collecting digital data to a complete on-board computer that handles the data collection methodology and provides for partial or complete data processing. If an external computer is required for managing data collection and data processing, commercial instrument makers will provide software for this purpose. *Whether on-board or external, the software must be critically evaluated. As is too often the case, the analytical potential of excellent hardware features can be severely limited by poorly designed/written software*.

A.4.3 Raman Spectrometer Configurations

There is a wide variety of Raman instruments that can be grouped into a few classes based upon commonality of features and functions. Only Raman instruments available as commercial models are described here. The order of listing is from small units with limited features to large and fully featured systems. Accordingly, the order of listing also is from least to most expensive.

- The Handheld: Handheld Raman spectrometers are small, battery-powered, self-contained units with one optical port that coaxially delivers laser light and accepts scattered light. These units are fixed configurations with no moving parts. Only functional adjustments that can be administered electronically are available. All, or at least most software-driven data collection and analysis functions are performed with a touch-screen graphic interface. Software functions, including an onboard spectrum-comparison database, tend to be aimed at specific applications such as identifying pharmaceutical compounds. These small handheld units are only functional with longer wavelength lasers. While most examples employ just one semiconductor laser, some models employ 2 lasers for the purpose of shifted-excitation fluorescence interference rejection (see section A.6.4 below).
- The Bench Portable: These are compact units that are meant for benchtop use but can be transported from one location to another without loss of optical alignment. They are designed to be plugged in, but some may have a battery power option as well. Some require external computer connection and software to achieve data collection and data analysis functions, and some have extensive onboard software and a touch-screen graphic interface. One essential feature of this class of Raman systems is that their case contains the laser and spectrograph, but they interface to a fiber optic cable and some form of fiber probe for interaction with the target sample. Some manufacturers offer a type of microscope that can be interfaced with the fiber optics, but these are not classed with the Raman Microscope group since

they have the same signal-intensity limitation as any other fiber optic probe. Most units contain only one laser.

- The Bench Macro-analyzer: These are benchtop models that are configured with an internal sample holder that is designed to hold cuvettes or vials. They may offer a solid-sample holder option, but they are difficult to employ for mineral identification, since they do not offer a mechanism for aiming/locating the analytical focal point on the sample. The do, however, offer better spectral resolution and may even have a scanning spectrograph. Some are outfitted with two lasers.
- The Benchtop Raman Microscope: This class of Raman microscope is self-contained. It employs primarily semiconductor lasers and, if more than one laser is offered, it is either manually switched with a modular component system or internally switched with electromechanical controls. These units have the greater signal throughput offered by open optics and may (or may not) have a confocal aperture. Some units offer multiple user-selectable gratings, and some have a scanning spectrograph. As a result, considerable control is offered over data collection conditions. An external computer is required to administer data collection methodology and for analysis of collected spectra.
- The Research Raman Microscope: This is the largest, most flexible, and most powerful class of Raman instrument. The instrument typically is installed on an optical table unless any/all lasers employed are small and internally mounted. When gas and/or solid-state lasers are included, they are also mounted on the optical table so their optical interface with the Raman microscope is stable and maintains installed alignment. Multiple gratings and multiple laser line cutoff filters are commonly available and confocal apertures and scanning spectrographs are generally employed. Resolution and signal-throughput can be expected to be greater, and considerable control over data collection conditions is available. An external computer is required to manage data collection and for analysis of collected spectra.
- The Gated Raman Spectrometer: This class of Raman instrument employs a pulsed laser and a gated detector. Electronic timing circuits coordinate firing of the laser and gating of the detector so that the detector collects data for only a short period of time after each laser pulse. The duration of laser pulses and detector gating is measured in 10’s to 100’s of picoseconds. This analytical technology is designed to take advantage of the fact that Raman scattering takes place on a shorter time scale than generation of fluorescence. For some time after its invention, gated Raman systems only existed as custom-made optical-table instruments, but commercial instruments employing this technology have begun to appear on the market.

A.4.4 Performance Parameters

When purchasing or using a Raman system it is important to understand its performance parameters, or specifications. They might be available from the manufacturer’s website or representative. Performance characteristics should be evaluated via instrument demonstration on samples that are known and relevant to you.

- Laser Wavelength: Typically, manufacturers offer more than one laser wavelength. One might be “standard”, with custom wavelengths provided if requested. As certain performance parameters such as spectral range and spectral resolution are a function of laser wavelength, it is important to determine which lasers will be most useful for your applications.
- Spectral Range: This is listed as the lowest and the highest Raman shift the instrument can measure, in terms of wavenumbers or cm^{-1} (e.g. 100-3000 cm^{-1}). As shown in section A.3, some minerals have all of their major Raman peaks below 300 cm^{-1}. Accordingly, for mineral identification, the low Raman shift cutoff should be no higher than 150 cm^{-1}, and 100 cm^{-1} (or even lower) is ideal. For the high Raman-shift limit it is worth noting that most minerals have characteristic Raman peaks below 1600 cm^{-1}, and currently many of the reference spectra databases for pattern-match identification do not include data past 1200-1300 cm^{-1}. However, to observe OH stretching peaks, indicating a hydrous (or hydrated) mineral, you will need to be able to see Raman shifts up to 3500 cm^{-1}. Finally, it will be important to determine if the specified spectral range is accessed by the spectrometer as a single spectrum or via two or more scanned spectra spliced together. The former limits spectral resolution to the detector pixel resolution, and the latter increases the data collection time for a full-range spectrum.
- Spectral Resolution: In concept, spectral resolution is a measure of a spectrometer’s ability to separate 2 closely spaced peaks. Almost certainly, the value reported by the instrument maker will be the best resolution the spectrometer can achieve, which was measured under optimal conditions which might not be the same as those used for routine mineral analysis. Ideally, one should measure resolution for your normal data collection conditions, but this can be difficult because the natural/actual width of Raman peaks can be affected by the nature of the sample, temperature, and other factors. One approach is to collect a Raman spectrum from a flat surface of a clear (spar) calcite crystal and measure the width (full width at half maximum or FWHM) of the strongest peak (about 1086 cm^{-1}). Subtract from this the theoretical width of this peak which has been found to be about 0.7 cm^{-1}.

  Instruments with long focal length spectrographs have better (smaller in cm^{-1}) resolution, and tend to be physically larger, and not surprisingly, tend to cost more. So, how much resolution is enough? For mineral identification, the ideal is to match the resolution of the spectra in the reference database, and most reference spectra are collected with a resolution of 3 to 4 cm^{-1}. However, one can commonly achieve successful matches with significantly different experimental resolutions with the right search/match software (see section B.5).

- Detector Width: This is the number of pixels in the semiconductor detector imager. Expressed as a power of 2 like many other digital quantities (e.g. 512, 1024, 2048), the value determines the effective spectral resolution – more pixels gives a higher resolution.
- Sensitivity: This parameter is important especially if working with weak Raman scatterers (e.g. deeply colored or opaque minerals). If provided, sensitivity is typically reported as the signal to noise ratio for the primary Raman peak of a standard material such as pure crystalline silicon. Of course, the value reported is based upon specific ideal conditions for signal gathering and throughput, such as for the highest NA objective and the largest diameter apertures, for a particular laser. Ultimately, the best way to evaluate and compare instrument sensitivity is through testing on a standard sample under identical operating conditions.
- Spatial resolution: Many manufacturers/models will not list the laser spot size on the sample in their instrument specifications – partially because this varies with both laser and objective lens, but many models that offer confocal optics will specify achievable vertical (depth) resolution as well as horizontal (in-plane) resolution.

A.4.5 Software

The functionality of instrument software significantly affects the usability and performance of the instrument hardware. Hands-on testing is the best way to assess the functionality and ease of use of manufacturer-supplied software. The major software functions needed for mineral identification, including data collection, data processing and phase identification, are described below.

A.5. Analytical Challenges of Raman Mineral Identification

In this section, we introduce some analytical challenges that are specific to Raman spectroscopy, and to its application on minerals.

In order to perform basic Raman mineral identification:

- A spectrum is collected using a Raman spectrometer.
- Continuum background, from the instrument and the sample, is removed.
- The result is compared to a database of reference spectra, and the best match is determined based on similarity of both peak positions and their relative intensities.

Analytical scenarios that interfere with collecting a quality representative Raman spectrum of the intended target include:

1. Some (or all) of the spectral peaks are not Raman peaks representative of the targeted sample.
2. The intensities of some (or all) of the sample's Raman peaks are too weak to be discernable from background noise.

A.5.1 Noise and Signal to Noise Ratio

Every analytical method has sources of random signal variability referred to as noise. A common measure of signal definition (or spectrum quality) is the ratio of the height of the strongest characteristic peak to the average magnitude of the random signal variability – signal to noise ratio (SNR).

Some amount of noise is generated by the spectrometer itself. However, there is also unavoidable variability that is inherently associated with counting signal photons from the sample – known as shot noise. Since the magnitude of shot noise is the square root of the sample signal (as total counts) the relative contribution of shot noise to SNR decreases as the total number of counts collected increases. The SNR of a sample spectrum can generally be improved by taking steps to increase the signal intensity from the sample, e.g. by increasing laser intensity. However, when this isn't possible, the impact of shot noise alone on the SNR can be reduced simply by collecting data (counting) for a longer period of time.

The role of shot noise becomes much greater, however, when there is a high continuum background signal from the sample. Consider a scenario where the height of a Raman peak above the continuum background is 100 counts. If the continuum background is low, say an average of 10 counts, the background shot noise is sqrt(10) and the SNR is 32. If the continuum background is high, say 5000 counts on average, the background shot noise is sqrt(5000) and the SNR is 1.4. Since it is generally accepted that a signal peak is not discernable from noise unless its SNR is at least 3, this shows that a high background can bury peaks in shot noise. In addition, since this background is coming from the sample, any analytical reconfiguration that results in greater signal intensity from the sample will increase the background from the sample just as much. As a result, when the continuum background is high a reasonable strategy is to increase counting time or average a number of spectra to improve SNR.

A.5.2 Analytical Challenges for Minerals

The typical sample-based causes of analytical scenarios #1 and/or #2 that are common for Raman spectroscopy of minerals include:

- Photoluminescent Interference (see section A.3): For minerals, fluorescence interference can take the form of either non-Raman peaks (scenario #1) or a very high continuum background (scenario #2) or both!
- Modifications by Laser Heating: In this case, conversion of laser energy to heat in a mineral can: a) break down the crystal structure, b) cause chemical reactions, or c) trigger phase transformations. In all cases, the results are loss of Raman peaks characteristic of the (original) target and/or introduction of new peaks that are characteristic of some other phase.
- Weak Raman Scatterers: Many minerals inherently produce very weak Raman signals. While one might be tempted to increase the intensity of the excitation laser to boost signal intensity, one must be aware that consequent laser heating might cause sample modifications.

A.5.3 Mineral Mixtures and Quantitative Mineralogy

The analytical techniques detailed in section B below give considerable stress to the methodology required to sample a single phase. This is because the interpretation of Raman spectra that sample more than one phase can be challenging. In principle one can employ a least-squares type of computational methodology to determine which combination of reference (mineral) spectra produces the best fit to the experimental spectrum – and the required intensity scaling factors are used to quantify the amount of each phase in the mixed-phase spectrum. This approach is problematic with Raman spectra primarily for two reasons.

1. As mentioned above, some minerals produce very weak Raman signals. Conversely, some minerals produce very strong Raman signals. Consequently, the Raman laser could sample equal volumes of two intergrown minerals and yet the peaks from one phase in the resulting Raman spectrum could be, for example, 1/10th or 1/100th (or less) the intensity of the Raman peaks from the second phase.
2. As described in section A.2.3 the relative intensities of peaks in a Raman spectrum can vary substantially with variations in laser wavelength and crystallographic orientation. This can be a considerable hindrance to the success of a computational operation that is attempting to reproduce all of the intensity variations in an experimental spectrum from the combined intensities contained in reference spectra.

The scenario where least-squares fitting of a mixed phase spectrum could be informative about what phases are mixed and provide some sense of their relative amounts is when a) the list of potential phases is both known and relatively short, b) the potential phases have at least broadly similar Raman signal strengths, and c) reference spectra were collected under similar conditions as the sample spectrum.

Quantitative mineralogy – the quantification of modal amounts of each phase in a sample – is clearly impractical to achieve from individual Raman spectra that sample multiple phases. Raman spectroscopy, however, can accomplish quantitative mineralogy via analysis of a large number of spectra from spatially separate points – in effect, a point-counting methodology – as long as the grain size is significantly greater than the laser spot size. While not covered by this edition of the Practical Guide, Raman mapping and Raman imaging can accomplish modal analysis even though typically the primary objective of these operations is a visual image of phase relationships.

A.6. Fluorescence

Fluorescence interference is arguably the most problematic analytical challenge in Raman spectroscopy. For routine mineral identification, it is important to have some understanding of:

- Which analytical scenarios are, or are not, likely to involve fluorescence interference.
- How to recognize fluorescence interference.
- How to avoid fluorescence interference as much as possible.
- Scenarios where fluorescence is analytical data.

A.6.1 General Concepts via Illustrating Examples

Recall from section A.2.:

- Fluorescent light emission occurs at specific wavelengths in contrast to Raman scattering which occurs at specific shifts away from the excitation wavelength.
- Fluorescent light emission from specific luminescent centers may occur over a very narrow range of wavelengths or over a broad range of wavelengths.
- The wavelength of fluorescence emission is at a longer wavelength than the excitation light source.

Figure A.6.11 shows the fluorescence emission spectrum resulting from minor substitution of Mn for Zn in a sample of willemite. The curve labeled *Emission* shows the range of wavelengths of emitted light when the wavelength of the excitation light source is 405 nm. Note that the emission maximum is at 520 nm, but some amount of fluorescence emission intensity exists from about 470 nm to about 670 nm. Note also that while the entire fluorescence emission curve shown will be produced by a significantly shorter wavelength excitation source (e.g. 405 nm) some amount of fluorescence emission will be produced from an excitation wavelength anywhere within this curve.

Figure A.6.11 also illustrates the overlap of Mn fluorescence emission with Raman spectral ranges for various lasers. The shaded rectangles in the figure show the range of light wavelengths seen by a Raman spectrometer using a source laser whose wavelength corresponds to the left (short wavelength) vertical edge of the rectangle, and the right edge corresponds to the wavelength for a maximum Raman shift of 1500 cm^{-1}. Due to overlap with the Mn fluorescence emission curve, a Raman system with a 532 nm laser will see a considerable amount of fluorescence interference and a 633 nm Raman system will see a small amount of fluorescence interference. A 780 nm Raman system will not see Mn fluorescence because the 780 nm laser cannot excite Mn fluorescence. On the other hand, a 405 nm Raman system will not see Mn Pl – not because it does not excite Mn fluorescence, but because the spectral range it is examining does not include any of the Mn fluorescence curve.

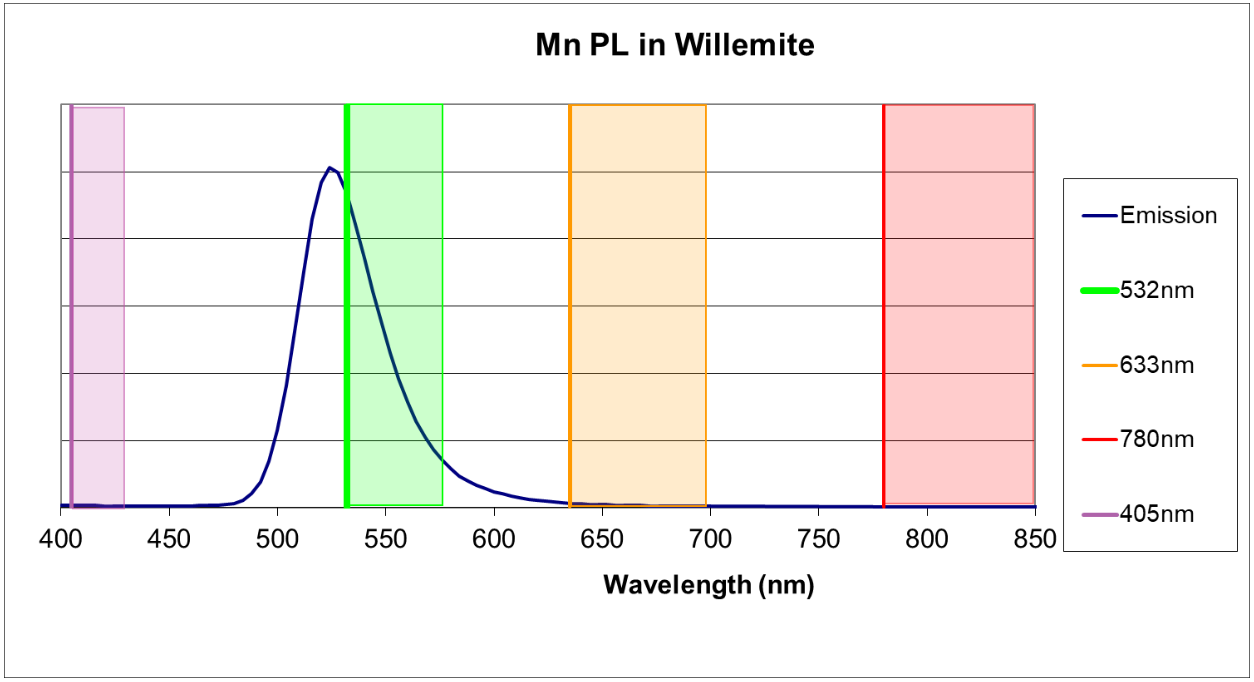


Figure A.6.11. Emission spectrum of Mn^{2+} fluorescence from a sample of willemite compared to a spectral range up to 1500 cm^{-1} examined by Raman spectrometers employing the listed excitation lasers.

Figure A.6.2 shows the Raman spectra of willemite collected using two different lasers. The spectrum from a 780 nm Raman system shows several distinct Raman peaks, including several weaker peaks that could be important for phase identification. The spectrum from a 532 nm Raman system includes fluorescence as a high, continuous and sloping background. The strongest willemite Raman peaks are still evident, but the weaker peaks are lost in the shot noise of the high background caused by fluorescence. In some analytical scenarios (other minerals and/or other Raman systems) with strong fluorescence, all Raman peaks may be indistinguishable from signal noise.

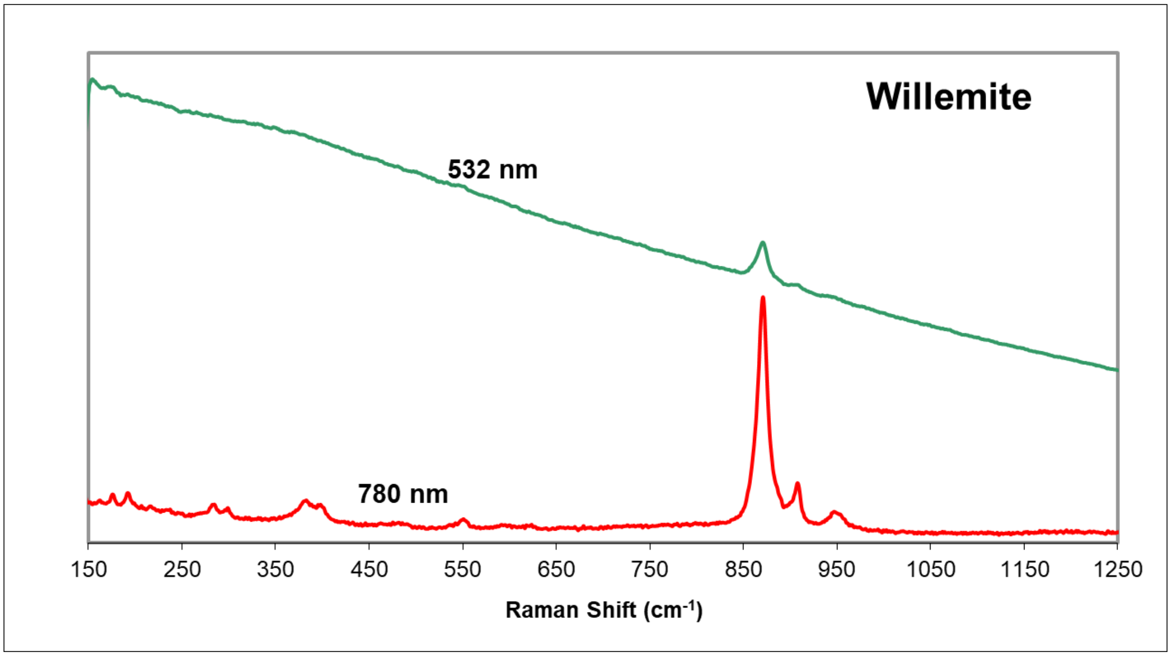


Figure A.6.12. Raman spectra of the same sample of willemite employing a 780 nm laser and then a 532 nm laser. Note that the intensity values of the 532 nm spectrum have been reduced by a factor of 30 to show both of these spectra together.

Figure A.6.13 shows Raman spectra for fluorite in which a variety of REE are substituted for Ca at trace element levels. Only the one strong peak at about 320 cm^{-1}, common to the spectra collected using 514 and 532 nm lasers, is a Raman peak. The strong and weak peaks in only one or the other spectra are narrow-band fluorescence emission from the REE. Since fluorescence emission occurs at specific wavelengths, the REE fluorescence peaks only appear in Raman spectra that sample those light wavelengths.

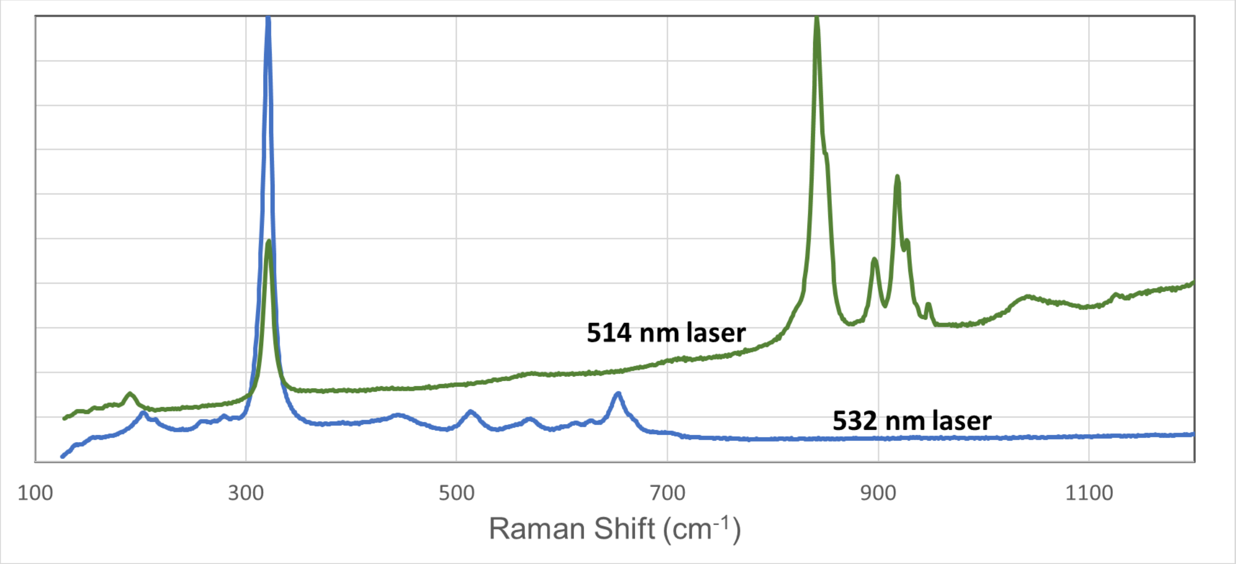


Figure A.6.13. Raman spectra of a fluorite employing the labeled excitation lasers. Only peaks common to both spectra are Raman peaks. Both spectra are RRUFF spectra from RRUFF sample R050045.

A.6.2 Anticipating Fluorescence in Mineral Systems

Understanding the causes of fluorescence in minerals might help anticipate which minerals are likely to produce fluorescence interference in particular Raman configurations. Even in the case of an unknown mineral, some knowledge of the chemistry of the rock system you are working with can help anticipate fluorescence interference. Conversely, encountering fluorescence using a particular Raman configuration (e.g. a particular source laser wavelength) can sometimes provide clues to the chemistry of the unknown mineral.

Structural sources of fluorescence, or luminescent centers, typically involve the interaction between an activator ion and its surrounding structural/chemical environment. Different valence states of the activator ion (including zero) might yield different fluorescence intensities and at different wavelengths. Fluorescence from an activator in a particular structure occurs at a specific wavelength, but fluorescence from the same activator in other mineral structures might be shifted to different wavelengths.

Luminescent centers in minerals can be intrinsic or extrinsic. An intrinsic luminescent center is characteristic of the essential elements and normal structure of a mineral. Examples include the tungstate (WO_4^{2-}) ion in scheelite and the uranyl (UO_2^{2-}) ion in many uranium minerals. An extrinsic luminescent center is formed when major elements are replaced by trace to minor level elements or by structural defects. Extrinsic fluorescence, also known as impurity fluorescence, is the most common source of fluorescence in minerals. For an overview of the variety of luminescent centers in minerals go to Gaft et al., 2015. For exhaustive coverage of which minerals are prone to fluorescence and the wavelength of the resulting fluorescence consult Gaft et al., 2015; Gorobets & Rogozhin, 2001; and MacRae & Wilson, 2008. Here we will review the most common sources of fluorescence in minerals and the impacts on their Raman spectra.

In addition to the experiences of the authors of this guide, the overview of what sources of fluorescence in minerals are the most common is based upon both published works and crustal abundance of activator elements. Table 2 of Gorobets & Rogozhin (2001) quantifies how common each type of luminescent center is based upon fluorescence spectrometry of some 320 mineral species. They found that the most common source of fluorescence was Mn^{2+}, followed by Cr^{3+} and Fe^{3+}. While all of the REE are known to produce luminescent centers, many have low crustal abundances and therefore are less likely to cause fluorescence. Fluorescence induced by Ce^{3+} and Nd^{3+} are included here because their crustal abundances are the highest of the REE. Despite it's lower crustal abundance, Eu^{3+} is also considered here since it preferencially partitions into some Ca minerals, especially plagioclase. Note that the following review of common luminescent centers illustrates the class of minerals affected, but is not intended as an exhaustive list of minerals likely to exhibit fluorescence from each center.

Mn^{2+}: One of the most common sources of fluorescence in minerals is minor to trace substitution of Mn^{2+} for other divalent cations (especially Mg), other divalent transition metals, and Ca. While some manganese minerals are photoluminescent, the luminescent center is understood to be structural defects. It may seem that any geologic environment somewhat rich in Mn is likely to present fluorescence interference challenges, but it is also known that the presence of Fe^{2+} tends to quench the Mn^{2+} fluorescence. In addition to Zn minerals like willemite, Mn^{2+} fluorescence is common in many nominally magnesian minerals including forsterite, enstatite, pyrope, talc, and magnesite. Mn^{2+} fluorescence is also common in many Ca minerals including apatite, calcite, clinozoisite, anhydrite, wollastonite, pectolite, and plagioclase.

Cr^{3+} and Fe^{3+}: These two ions tend to substitute for Al^{3+} and sometimes Si^{4+}. As such examples of minerals with these luminescent centers include corundum, the aluminosilicates, garnets, beryl, topaz and wollastonite.

Nd^{3+}, Ce^{3+}, and Eu^{3+}: The REE commonly substitute for Ca. Some of the minerals known for their REE fluorescence include apatite, calcite, aragonite, fluorite, titanite, anhydrite, apophyllite, plagioclase, tremolite, scheelite, datolite, danburite and some of the Ca tourmalines.

While it is helpful to anticipate which minerals are likely to produce fluorescence, analytical fluorescence interference depends upon whether the fluorescence wavelength(s) overlaps the range sampled during the Raman experiment. As mentioned above, the characteristic fluorescence wavelength of an activator ion can vary from one mineral structure to another, but within limits. Figure A.6.14 shows both the range of fluorescence wavelengths for some common luminescent centers and how they intersect with the wavelength ranges sampled (up to 1500 cm^{-1} Raman shift) by Raman systems for a variety of lasers. The figure illustrates analytical scenarios (i.e. laser wavelengths) where fluorescence interference can be expected, or avoided.

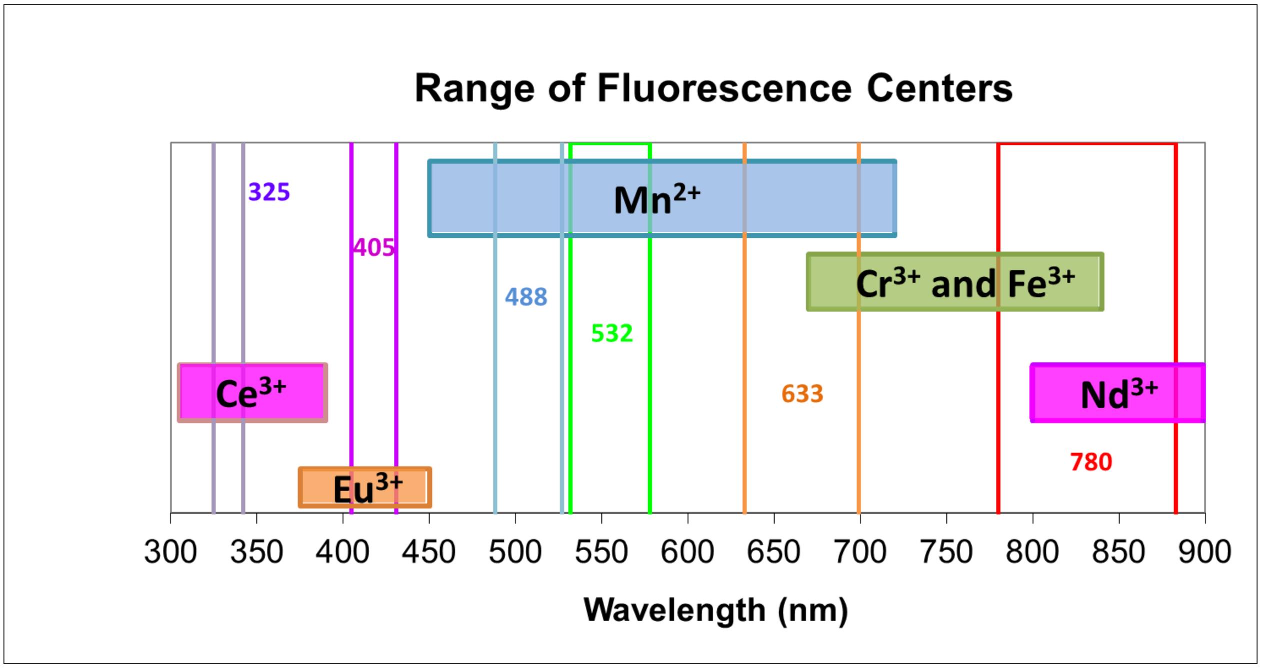


Figure A.6.14. The range of wavelength each of the more common luminescent centers produces fluorescence within compared with the range of wavelengths sampled by Raman systems employing the labeled laser wavelengths (in nm).

A.6.3 Recognizing Fluorescence Interference.

Figures A.6.2 and A.6.3 illustrate common types of fluorescence interference. Additional variations and challenges are discussed below.

- Figure A.6.12 shows one type of broad-spectrum fluorescence, but fluorescence interference in the form of continuously high background may also be sloped upward with increasing Raman shift, be flat, or form a broad mound.
- Graphical interfaces used to display Raman spectra typically automatically adjust the Y-axis range to display the highest data value near the top of the graph. This sometimes makes it difficult to tell the difference between a) a strong Raman signal on top of high-intensity broad-spectrum fluorescence, and b) a weak Raman signal on top of a relatively modest amount of broad-spectrum fluorescence.
- There are other potential explanations for a continuously high background, most commonly inelastic scattering of the laser light at structural defects and grain boundaries, for example, when the sample is a composite of fine grains. (e.g. many clay minerals)
- Comparison of Raman spectra collected with different lasers clearly identifies the peaks that are due to fluorescence and not Raman scattering. If working with a single spectrum it is important to be aware of the possibility of narrow-peak fluorescence features that might result in database-search identification failures or erroneous results.

A.6.4 Strategies for Working with Fluorescence Interference

The following list includes some common strategies for avoiding or removing fluorescence interference.

Background Removal: For fluorescence interference observed as continuously high background (Figure A.6.12), it might be possible to remove it using a simple background-removal algorithm, but there are a couple of challenges to consider.

- The high-count rate of the fluorescence background means that there is commensurately large shot noise (see section A.5.1). Consequently, when the high intensity background is removed, the resulting spectrum is likely to have a poor SNR. A potential remedy is to collect the spectrum many times, and average them to improve counting statistics and improve the resulting SNR.
- Raman spectra containing high levels of broad-spectrum fluorescence commonly exhibit regular repeating hill/valley features that are caused by etaloning in the detector or optical interference/edge effects generated by the spectrometer. Most background-removal algorithms will not remove these features.

Figure A.6.11 illustrates both of these spectrum challenges. Note that some sharp Raman peaks are clearly discernable in the raw spectrum. Background removal greatly strengthens their definition, but the height of the periodic waves in the spectrum is also strengthened, and the resulting processed spectrum is markedly noisy.

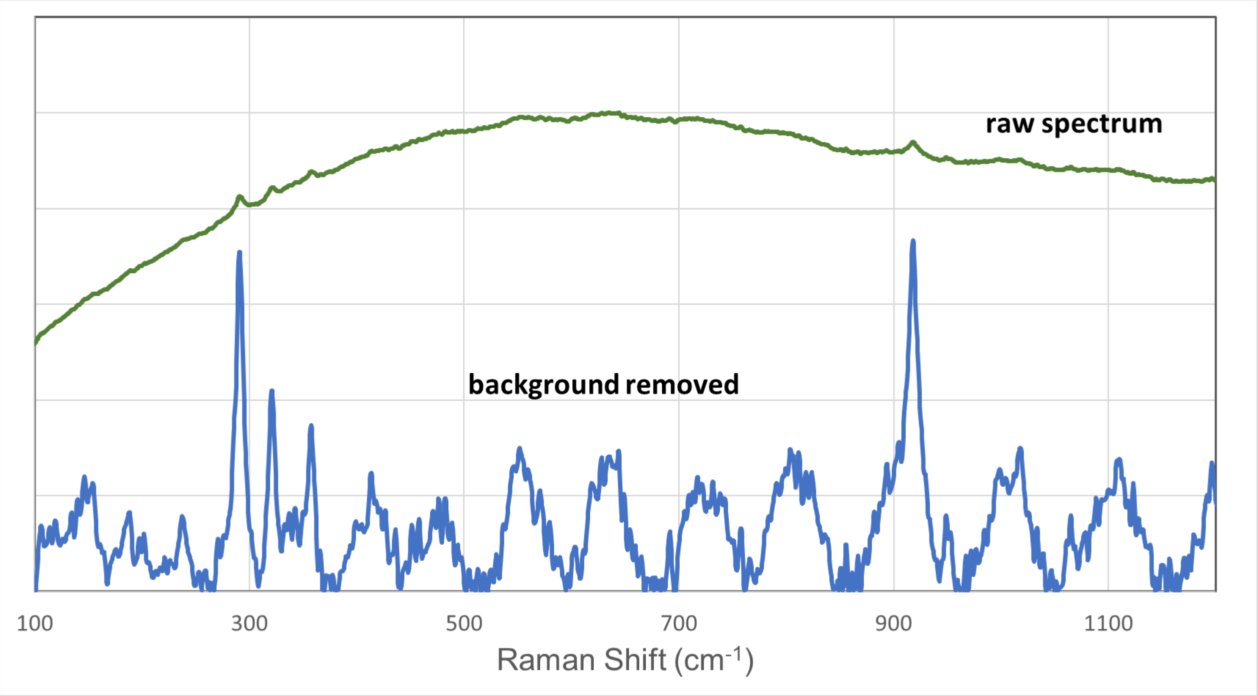


Figure A.6.15. Raman spectrum of a sample of andalusite affected by broad-spectrum fluorescence and the same spectrum after processing with a background removal algorithm. Note both the poor SNR of the processed spectrum and the regular repeating waviness of the baseline of the processed spectrum. The intensity values of the raw spectrum were reduced by a factor of 20 in order to show these spectra together in this way.

Multiple laser systems: If serious fluorescence-interference exists for a sample, one possible solution is to use a Raman spectrometer with multiple lasers. As discussed above, fluorescence occurs over a specific range of wavelengths, and it might be possible to select a laser wavelength that does not excite that fluorescence. Considering the example in Figure A.6.11 of a mineral containing more than one luminescent center, it might require more than 2 lasers to avoid fluorescence interference. Unfortunately, for some samples, even multiple lasers do not circumvent the fluorescence problem.

IR Lasers: As discussed above (A.6.1) one basic requirement for fluorescence to occur is that the incident light excites electrons to higher energy states, and infra-red radiation (e.g. 1064 nm IR laser) has insufficient energy to cause such transitions. While this has applications in the pharmaceutical field, IR laser sources have limited use for mineral identification because many minerals are weak Raman scatterers, and, as illustrated in Figure A.2.4, the probability of Raman scattering steadily decreases as the wavelength of the excitation laser gets longer. Consequently, the Raman signal from many minerals when excited by an IR laser is so low as to be analytically impractical. IR Raman systems, however, can be helpful in cases where minerals generate strong Raman signals but exhibit strong fluorescence with other lasers.

UV lasers: As Figure A.2.4 illustrates, the Raman signal intensity from a 325 nm UV laser is ~35 times that from a 780 nm laser. In addition, Figure A.6.14 shows that while UV light easily excites fluorescence, the wavelength of most forms of fluorescence is outside the range of the working wavelengths of a UV Raman spectrometer. Despite these conceptual advantages, UV Raman systems are not routinely used for mineral identification due to the optical technology challenges. The wavelength range a UV Raman system must cover is rather narrow, and therefore to achieve adequate resolution in Raman shift, the spectrograph has to be large with long focal-length optics. Even more important for mineral systems, the laser line cutoff filters engineered for UV Raman systems are unable to achieve a low Raman-shift limit below 350 cm^{-1}. Since many minerals have important Raman peaks below 350 cm^{-1} and some minerals have all of their Raman peaks in this range, UV Raman systems are limited in their applicability to mineral identification.

Shifted Excitation or Dual Laser Fluorescence Rejection: As the title implies, this is a method of removing fluorescence interference instead of avoiding it. Two Raman spectra are collected using two laser sources that are typically close together in wavelength. The two spectra are processed with the assumption that Raman features occur in the same position in each spectrum, and fluorescence features shift an amount equal to the difference between the source wavelengths. Figure A.6.13 can be used to illustrate this technique. If the two spectra are processed in a way that rejects peaks that occur in only one spectrum and keep the peaks that occur in the same place in both spectra, you are left with one peak at about 320 cm^{-1} – which is what the Raman spectrum of fluorite looks like. Unfortunately, this technique is not effective when there is high intensity broad-spectrum fluorescence. If the two laser wavelengths are close to each other, both spectra may contain similar amounts of fluorescence-based high background. Not only does the spectrum-comparison algorithm have trouble recognizing what to exclude (as fluorescence), but the result still has the problem with shot noise from counting the fluorescence background, resulting in a Raman spectrum with very poor SNR. The forte of a dual-laser fluorescence rejection system is therefore primarily the rejection of narrow- peak fluorescence, especially REE fluorescence.

Gated Raman: This technology takes advantage of the difference in time scales within which Raman scattering and fluorescence occur. Employing a high-speed pulsed laser and a high-speed gated detector, such a Raman system is carefully timed so that the detector is open and counting when the laser pulse hits the sample and closes within a few hundred ps – which is before most or sometimes all fluorescent light can be generated. The laser and detector are controlled to wait until all or most fluorescence emission is likely to have decayed and then repeat this excitation/detection pattern – generally thousands of times per second. The result is a high degree of exclusion of fluorescence interference. The one limitation of gated Raman technology is similar to the limitation with IR Raman systems – the ability to get useful Raman intensity from minerals that are weak Raman scatterers. In this case, the technical issue is the effective data collection time. Even if a gated Raman system is operated at a excitation/detection cycle frequency of 100 kHz, it spends only 5% of every second with the detector open and collecting data. Such a system may have to collect data for an extended period of time for the many minerals that are weak Raman scatterers.

A.6.5 Scenarios Where Fluorescence is Analytical Data

While fluorescence is not characteristic of a mineral phase, it is characteristic of a particular sample of a mineral and its minor/trace element chemistry. Different samples of the same mineral with different trace element chemistry will have different fluorescence signatures and, accordingly, samples of the same mineral from the same locality with similar trace element chemistry will have similar fluorescence signatures. Spectral comparison and matching against a reference library containing many spectra of the same mineral from different localities can facilitate provenance identification. This is particularly important in the fields of gemology and archeology.

A.6.6 Thermoluminescence

Thermoluminescence is unique to crystalline materials and both less common and less predictable than fluorescence. This form of luminescence is the result of excited electrons being trapped or arrested in a crystalline structure until heating of the sample triggers them to be released via radiative decay. These electrons may have been excited by radiation from radioactive elements in a rock over time or by exposure to sunlight or even forms of light and other radiation encountered during sample preparation. Thermoluminescent light is then a response to heating by the Raman laser. The good news is that this luminescence dissipates over a relatively short time and its impact can be minimized by, in effect, pre-heating the sample (see section B.3 below).

References

Gaft, M., Reisfeld, R., & Panczer, G. (2015). *Modern luminescence spectroscopy of minerals and materials*. Springer.

Gorobets, B. S., & Rogozhin, A. A. (2001). Luminescence spectra of minerals. Handbook. *RITS VIMS, Moscow*.

MacRae, C. M., & Wilson, N. C. (2008). Microscopy Microanalysis Luminescence Database I — Minerals and Materials. *Microscopy and Microanalysis*, *14*, 184–204.

A.7. Laser Damage

Laser light impinging on the sample that is not reflected or scattered is absorbed as heat. The resulting elevated sample temperature can have a variety of effects including Raman peak shifts, phase transformations, changes in chemistry (e.g. de-volatilization), chemical reactions (especially oxidation), and amorphization, which can produce changes in the Raman spectrum and affect analytical success. It is therefore important to know how to detect laser damage and manage laser heating, and to be aware of mineral types and groups that are more vulnerable to laser damage.

A.7.1 Controls on Laser Heating

Factors that might affect damage caused by laser heating are the structure, chemistry and color of the sample, laser wavelength, laser intensity, and the laser spot size.

Of course, a higher intensity laser will produce more sample heating, but the impact on the sample is also dependent on the spot size. The energy impinging on the sample under the laser beam is the power density – the laser power per unit area. A simple calculation shows that a 1 mW laser beam focused to a 5 µm diameter results in a power density of just over 5000 watts per cm^2. The same laser beam focused down to a 1 µm diameter results in a power density of over 125,000 watts per cm^2.

Dark materials absorb more light than light-colored or transparent materials. In colored samples excitation of specific electron transitions cause preferred absorption of certain wavelengths. The color of the sample results from light wavelengths that are not being absorbed – which implies that a Raman laser similar in color to the sample will be absorbed the least. Single-laser Raman systems don’t give you the option of switching lasers, and, in any case, switching lasers to match the color of the sample might not always be practical.

The potential of sample damage from laser heating also can be a function of structure and chemistry of a mineral sample. Just as an electron microprobe operator learns what types/groups of minerals require lower beam currents, a Raman operator must do the same. Some guidelines for which mineral types/groups are susceptible to sample damage during Raman analysis are detailed in section A.7.5.

A.7.2 The Consequences of Laser Heating.

- Raman Peak Shifts: The frequencies of Raman modes are determined by atomic masses, bond strengths and bond lengths. As a mineral is heated under the laser, thermal expansion increases bond lengths, resulting in small changes in Raman shift position of peaks to lower frequencies (lower Raman shift).
- Phase Transformations: If the subject phase has relatively low temperature polymorphic transitions, the laser heating could result in a structure change. If the polymorphic transition is non-displacive, such a structure change could be reversible. For example, Figure A.7.16 shows three Raman spectra collected on the

same spot on a grain of pyrrhotite. The first (before) spectrum, collected with the laser set to 2 mW, shows no Raman peaks – which is exactly what group theory predicts for Raman scattering from pyrrhotite. The second spectrum collected 3 minutes after the laser power was increased to 10 mW shows 2 distinct Raman peaks. The third (after) spectrum was collected at laser power of 2mW, after allowing the pyrrhotite to cool off (with no laser exposure) for 10 minutes.

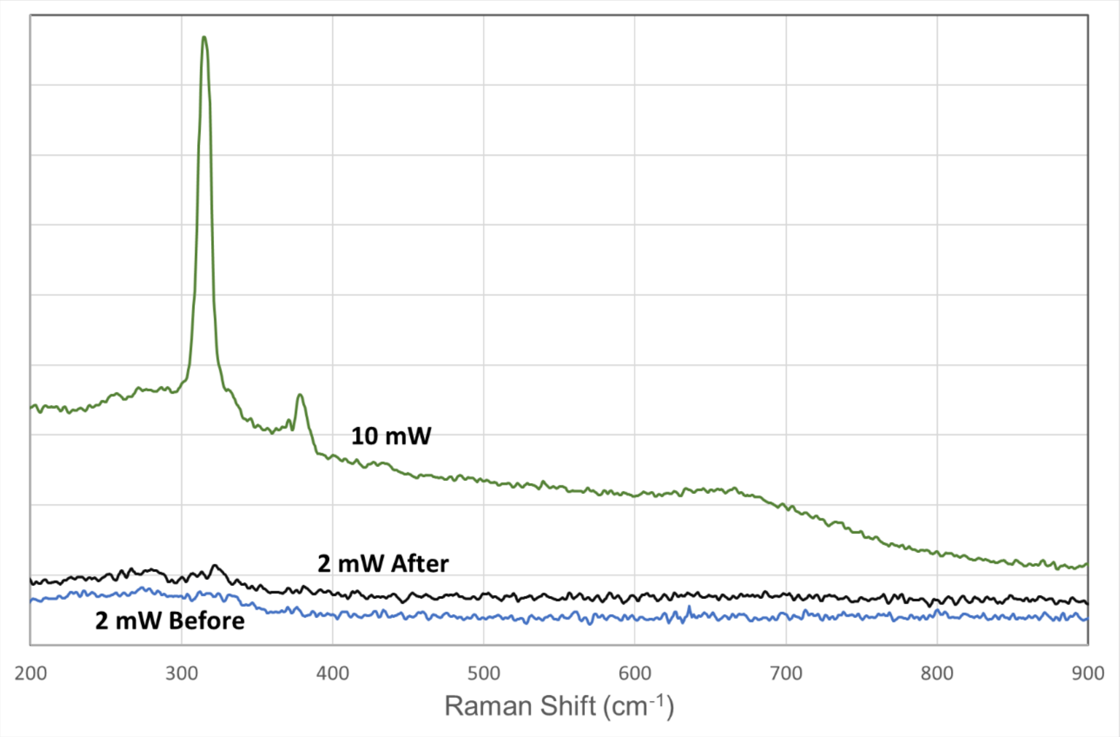


Figure A.7.16. Raman spectra from the same spot on a grain of pyrrhotite using a 532 nm laser. See text for explanation.

- Devolatilization: Similar to heating under an electron beam, some chemical components such as volatiles (e.g. H_2O) can be driven away.
- Chemical Reactions: Under laser heating a mineral sample may react with the available external reactants such as oxygen in the air over the sample. For example, subjecting the pyrrhotite of the above example to even higher laser intensity results in a Raman spectrum of hematite. Mn oxides, on the other hand, tend to be reduced by laser damage e.g. pyrolusite (Mn4+) is altered to hausmannite (Mn3+ and Mn2+).
- Amorphization: In some cases, laser heating of a sample catastrophically breaks down the mineral structure and/or drives away chemical components– leaving a darkened spot or crater behind.

A.7.3. Detecting Laser Damage.

The classic indication of sample damage is a visible burn at, or a halo around, the laser spot. However, some types of laser-induced alterations (including the example illustrated in Figure A.7.16 above) do not leave a visible burn spot.

Another method for detecting sample damage is to collect multiple spectra on the same spot and check whether the Raman spectrum is changing over time. If your data collection software actively displays the results after each of a series of accumulations, you can monitor spectra for changes. Spectra changes to look for include:

- Loss of Intensity: When sample heating is progressively breaking down the mineral structure, Raman peaks likely get weaker and broader. Since graphical spectrum displays typically auto-scale, you may see a reduction in Raman peak intensity as a reduction in apparent SNR.
- Appearance of new Raman peaks. Both chemical reactions and polymorphic transitions form new phases which have characteristic Raman spectra. Concurrently, Raman peaks from the original phase progressively become weaker.

A.7.4 Solutions for Preventing Laser Damage.

As described above, one solution to minimize damage from laser heating is simply to reduce the laser intensity, but of course this lowers signal intensity as well. When assessing the possibility of laser damage for a sample, one practical approach is to start with a low laser intensity and collect spectra with gradually increasing intensity steps, watching for changes in the spectra. Then, use a laser intensity for data collection that was below threshold that caused changes.

Other solutions involve reducing laser power density on the sample or progressively moving the laser beam to fresh, unheated areas, e.g.:

- Defocusing the laser beam to a wider spot. While this can be accomplished by switching to a lower magnification objective (on a Raman microscope) this will lower the signal at the detector as well. As a result, an optical system that can defocus the beam independent of the objective lens selection can have advantages.
- Some instruments employ systems to scan the laser beam over a small area rather than keep it static on a single point.

A.7.5 Mineral Groups/Types Known to be Sensitive to Laser Heating.

The following list is based upon the experience of the authors, but some overall trends are observed.

- Many sulfides and sulfosalts.
- Many hydrated minerals including hydrated carbonates, phosphates, sulfates and arsenates, but also some hydrated silicates as well.
- Many Mn-oxide minerals, especially those with large tunnel structures or hydrated layers.

A.8. Weak Raman Scatterers

As described in sections A.2. and A.3, the Raman signal intensity is influenced by a combination of instrumental and sample factors, and many minerals inherently produce weak Raman signals. If your experimental setup is unable to adequately work with weak intensities, phase identification will be challenging or not possible in these cases. The intent of this section is to provide guidance on anticipating weak Raman scatterers and how to adjust the instrumental factors to ensure successful mineral identification.

A.8.1 Anticipating Weak Raman Signals

Bartholomew et al., 2015 evaluated the large number of mineral Raman spectra collected from the same instrument that are posted on www.rruff.info to demonstrate how Raman signal intensities vary among mineral species. Figure A.8.17, taken directly from their paper, illustrates two observations about Raman spectroscopy of minerals:
1) the range of expected signal intensities can vary over 4 orders of magnitude and
2) there is a distinct contrast between the signal intensities of opaque and non-opaque minerals.

The large range of signal intensities requires a rather adaptable data-collection methodology. This will be discussed in detail in Part B of this Guide.

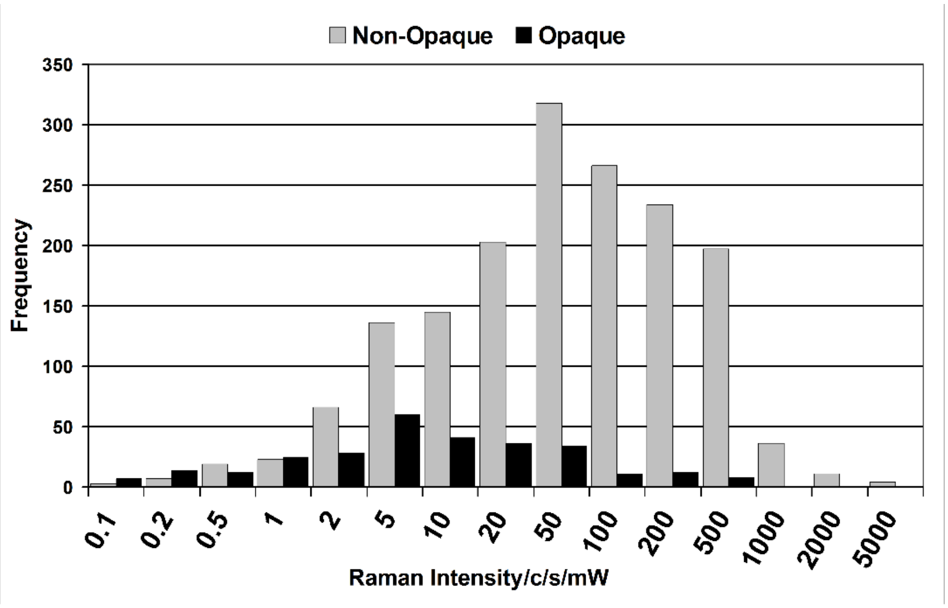


Figure A.8.17. Pseudo-logarithmic histogram illustrating the distribution and range of Raman intensities for opaque and non-opaque minerals obtained from the 532-nm RRUFF instrument. The intensities used in the diagram are the intensity of the strongest peak in each Raman spectrum normalized to counts per second per milliwatt of laser power. Each bin label on the x-axis corresponds to the high magnitude limit of the corresponding bin and the low magnitude limit of the next higher bin. Adapted from Figure 2 Bartholomew et al. 2015.

The contrast between opaque and non-opaque minerals is intuitive since the volume of the mineral sample that is excited by the Raman laser is smaller for an optically opaque mineral. At the same time Figure A.8.17 shows a considerable overlap between these two optical classes of minerals. There are two primary reasons for this overlap:

1) Many minerals that are not classified as opaque are only partially translucent or are deeply colored, once again, leading to a restricted volume of the mineral that the Raman laser can see and excite.

2) As introduced in sections A.2 and A.3, different types of vibrational modes can produce inherently stronger or weaker Raman intensities. Consequently, depending upon the type of dominant mode, some transparent minerals have weak Raman intensities, and some opaque minerals have surprisingly strong Raman intensities. For example, zeolites are often transparent, but their Raman intensities are modest, at best, and stibnite, an opaque sulfide, produces a rather strong Raman signal.

Some general guidelines therefore are:

- light-colored and especially transparent minerals typically produce a strong Raman signal – although there are exceptions.
- for dark colored and opaque minerals, analytical methods should be optimized for weak Raman intensities.

A.8.2 Analytical Methods for Weak Raman Scatterers

Instrument Selection Considerations

- Instruments employing open optics have higher signal throughput than instruments employing fiber optic probes.
- Raman microscopes with high magnification objectives, that generally have the highest numerical aperture (NA), capture a large solid-angle of scattered light from the sample. Long working-distance lenses, although easier to use, or necessary for some types of samples, have lower NA's and lower signal collection than standard working distance lenses.

A variety of other spectrometer components can affect Raman intensity; *sensitivity* is the corresponding instrument performance parameter. As instrument makers don't use the same method/scale to measure sensitivity, or do not provide this at all, it is helpful to collect spectra from known samples to assess signal sensitivity performance.

Instrument Configuration

If using a Raman microscope fitted with multiple objectives, select the lens with the highest NA, typically the highest magnification objective. Larger apertures and lower line-density diffraction gratings also yield higher signal intensities at the detector, although at a cost of lower spatial and spectral resolution.

Data Collection Parameters and Methods

In principle, one can improve signal strength simply by increasing the intensity of the laser, but that also increases the risk of sample damage (see section A.7). Alternatively, when working with weak Raman signals, it might be possible to use data collection methods that reduce or remove noise and other artifacts introduced in the data collection process.

One obvious strategy for samples with weak signals is to use longer counting times. Commonly, Raman spectra are collected using an accumulation (counting) time and some number of accumulations, which are averaged (for reasons that will be explained in section B.3). Statistical “averaging” noise is introduced when a large number of accumulations is averaged. Therefore, it is better to achieve a total counting time via 2 to 4 long accumulations rather than 10 or more short accumulations.

Every Raman instrument introduces spectral artifacts from spectrometer components, from the air along the optical path, and as a result of slight variations in detector sensitivity from one pixel to the next. When the Raman signal is reasonably strong, these variations in the instrumental background are generally inconsequential. Also, high-end research instruments commonly use components and designs that minimize these effects. However, when the Raman signal is weak, such instrumental artifacts might be significant and should be subtracted out.

Most Raman spectrometer software systems provide for removal of the detector “dark” signal and the pixel-by-pixel variations in detector sensitivity. The software will generally refer to this as “background” and will offer options for how often to collect it and whether to subtract it. Figure A.8.18 shows how subtracting detector background removes signal variations that would otherwise be seen as noise or small spectral features. If your spectrometer software does not offer automated removal of detector background, you can collect and subtract an instrument blank (see below).

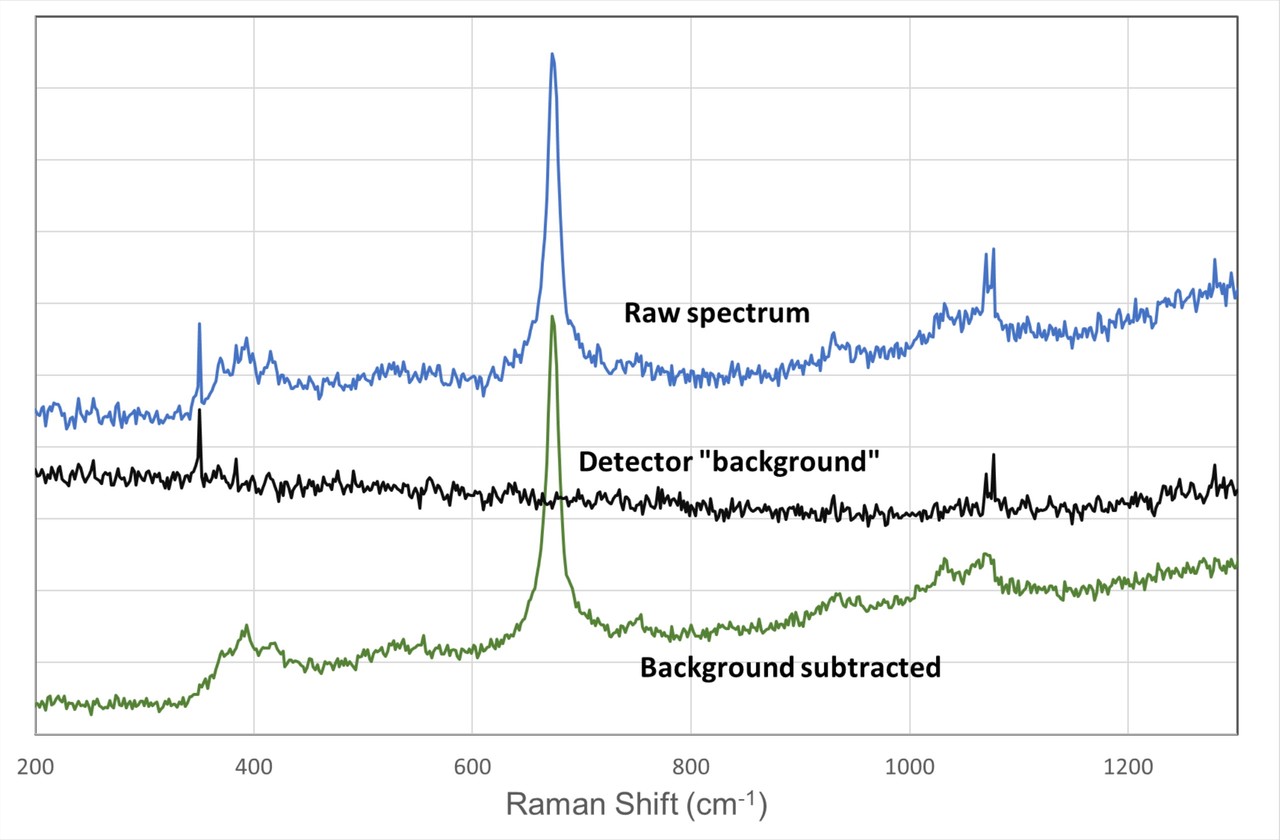


Figure A.8.18. Illustration of the character of detector background and the benefits of background subtraction.

Some Raman spectrometer systems produce low intensity artifacts that can complicate interpretation of low-intensity Raman spectra. Such spectrometer artifacts can be identified and subsequently removed by collecting a spectrometer blank and the subtracting this from the sample spectrum. A spectrometer blank is collected by removing the sample (and any other material near the focal point of the spectrometer) and collecting a spectrum using the identical instrument parameters as will be used on your sample. The result is illustrated in Figure A.8.19.

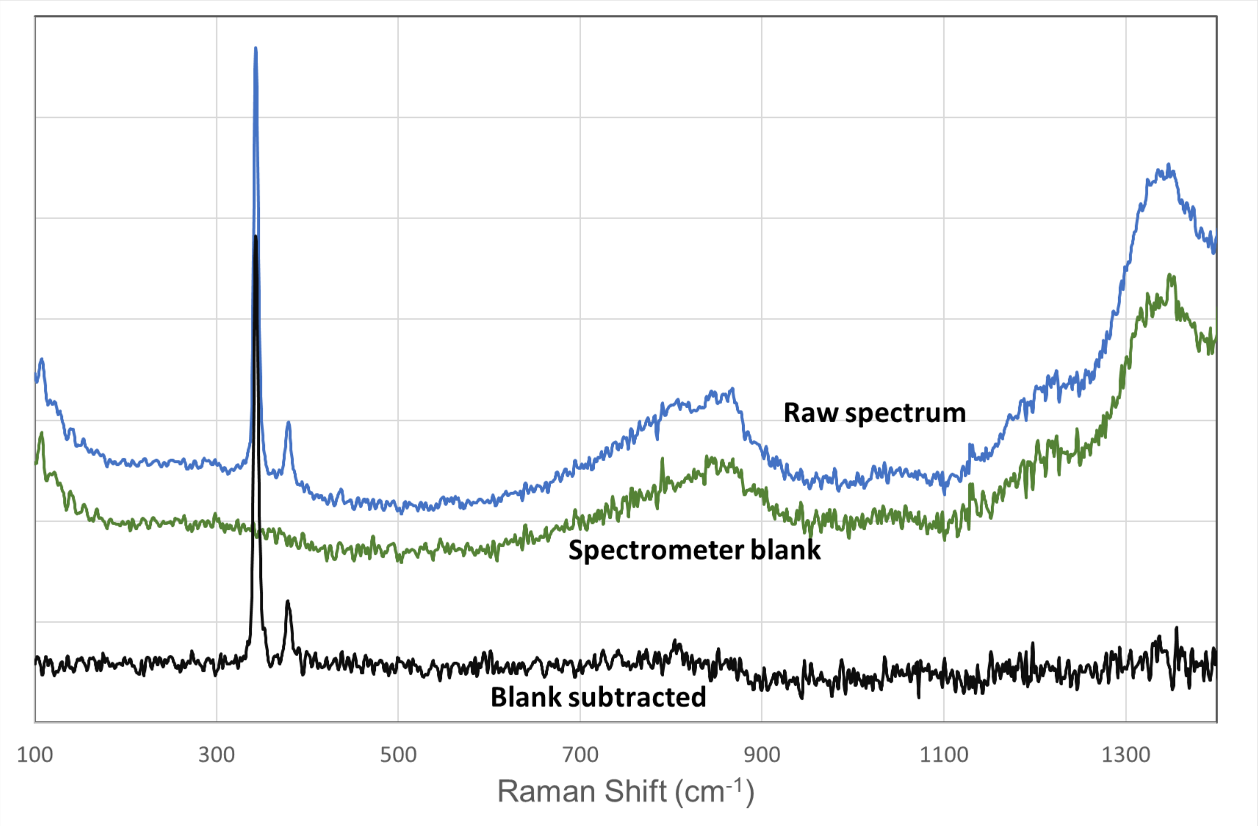


Figure A.8.19. Illustration of the benefits of collecting and removing a spectrometer blank for samples with weak Raman signals.

One more spectroscopic artifact that can be encountered when working with weak Raman scatterers is rotational Raman modes from O_2 and N_2 in the air. These all occur at Raman shifts below about 125 cm^{-1} so the come into play when the Raman range you are examining goes below this. It is common to be including Raman shifts down to 100 cm^{-1} or below when working with ore minerals since many have all of their Raman peaks below 300 or 400 cm^{-1} and some (notably heavy metal tellurides) have their primary Raman peak right at about 100 cm^{-1}. Figure A.8.4 illustrates what this looks like in practice – note the spectral range being shown. Here the Raman spectrum of brass is included because this alloy is Raman inactive and has no characteristic Raman peaks. The 4 peaks below 125 cm^{-1} that are common to all 3 spectra are the air peaks. The primary solution for this scenario is simply to truncate off the portion of the Raman spectrum containing only these air peaks before comparing spectra for identification purposes.

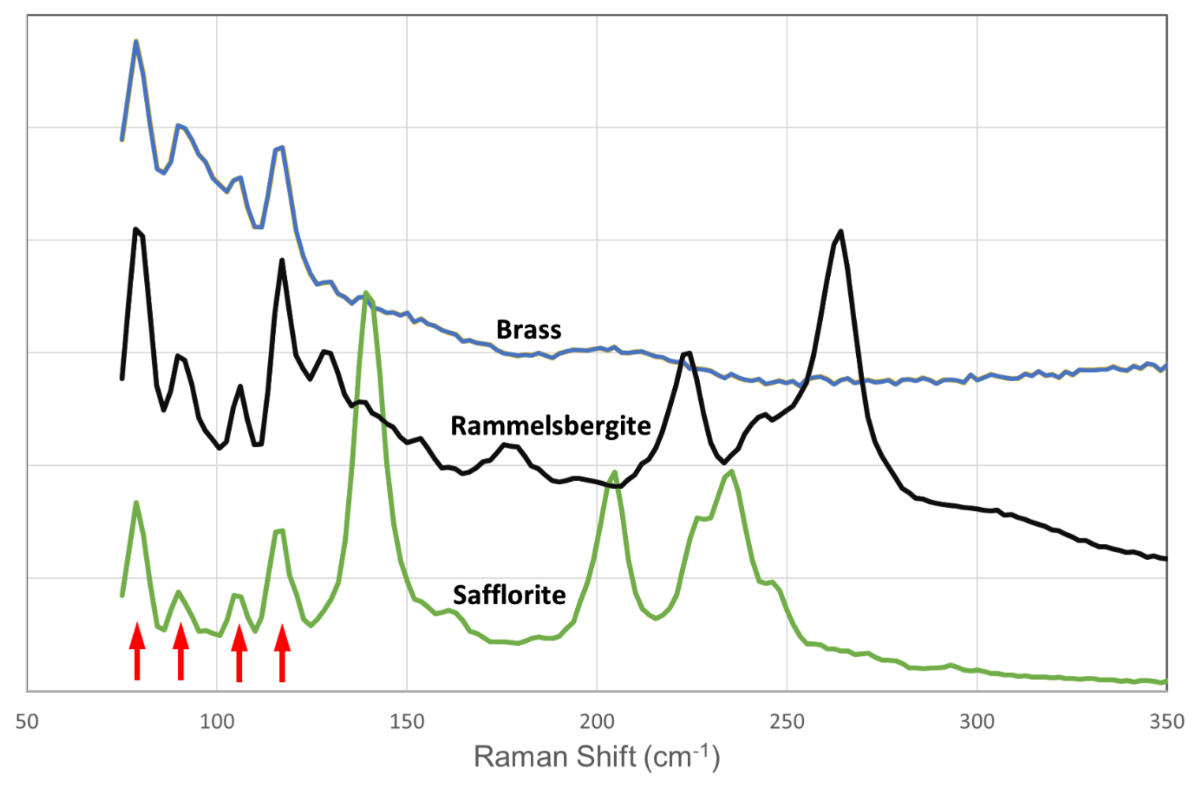


Figure A.8.4. The impact of rotational Raman modes from air gasses (red arrows) on the Raman spectra of some ore minerals. See text for details.

References

Bartholomew, P. R., Dyar, M. D., & Brady, J. B. (2015). The role of intensity and instrument sensitivity in Raman mineral identification. *Journal of Raman Spectroscopy*, *46*(10), 889–893. https://doi.org/10.1002/jrs.4707

B. Practical Mineral Identification with Raman Spectroscopy

B.1. The Basic Operational Methodology

The elements of Raman methodology for mineral identification include the following:

- Sample preparation. As discussed below, this could be anything from nothing at all to polished thin sections.
- Sample presentation and target aiming.
- Instrument configuration. While the details are instrument dependent, this may include selection of laser, objective lens, pre-spectrometer aperture, spectrometer grating, and spectral range.
- Calibration. Regular calibration against a Raman-shift standard.
- Collection of instrumental background. This step allows for subtraction of any amount of instrumental signal that is NOT produced by laser interaction with the sample. This may amount to a data collection with a laser/spectrometer shutter closed or a true "blank" with the laser on but no sample in the instrument.
- Selection of data collection time. Data collection typically consists of integration of a series of replicate counts with a specific dwell time. The replicate counts can be used to provide for detection and removal of cosmic ray events (CRE) and for detection of sample damage.
- Data collection.
- Spectrum processing. This will always include background modeling and removal but may also include range clipping, normalizing and/or some form of noise reduction.
- Database comparison searching. Since the Raman spectra of minerals often contain overlapping peaks and sometimes rather broad peaks, whole-spectrum matching is the preferred method. Match quality is scored and some number of the top matches are presented to the user.

Note that some instruments may not give you control over all of these steps. In addition, many of these steps only need to be carried out once for a series of Raman data collections.

B.2. Sample Preparation and Target Aiming

B.2.1 Sample Preparation

The level and type of sample preparation required for Raman spectroscopy depends upon both the nature of the rock/mineral sample and the style of sample presentation incorporated by the Raman instrument. We will consider the range of sample preparation types and sample presentation styles and then summarize the intersection of these two factors.

The range of sample preparation types include:

- None – While this does mean "as-is", only hand-held Raman systems can work with random sample sizes (including outcrops). Other Raman systems that are capable of working with as-is samples will generally require fabrication of a "hand" sample or smaller (e.g. micromounts).
- Saw Cut – Liquid lubricants must be cleaned off. Water may not interfere with the most important portion of the Raman spectrum for mineral ID, but oils and other surface contaminants might. The ideal is a dry and clean surface.
- Flat Grind – This covers a range of surface preparation between Saw Cut and a polished surface.
- Polished Thick Section – This covers a variety of thicknesses with one target surface polished.
- Polished Thin Section
- Standard Thin Section – with coverslip
- Grain Mount – mineral grains picked out of a sample or from soil, sediment, heavy mineral separate, etc. dispersed on a flat substrate (ideally a Raman-inactive substrate such as aluminum metal/foil).

Sample presentation is typically determined by the style of Raman instrument, although some models offer an optional secondary presentation system.

- Direct Contact Snout: This presentation style is used with most portable Raman systems and many fiber-optic probe systems. The end of the snout corresponds to the ideal distance between the sample and the spectrometer optics for maximum signal strength into the instrument's spectrograph. Accordingly, the portion of the sample presented to the snout should be flat enough to ensure that the portion of the sample hit by the Raman laser is positioned at this ideal distance. Unfortunately, this approach does not permit the user to see an image of the sample area being analyzed. Accordingly, even if the actual laser spot is sub-millimeter, the grain size of the sample must approach the inner diameter of the snout (typically several mm to 1 cm) in order to ensure that the intended target is being interrogated.
- Fiber-Optic Probe: Many fiber optic probes are not fixed with an ideal-distance snout (or offer a removable snout). Such probes offer working distances of 2 to 10

mm (or more) which means they can be used on samples that have uneven surfaces on this scale. Hand-holding the probe is not possible and some kind of adjustable stand to hold the probe is required. Again, imaging of the sample area viewed by the probe is not generally possible, making it difficult to work with grain sizes smaller than a few mm. Direct observation of the analysis spot may be possible if the laser wavelength is in the visible light range AND appropriate eye-protection filters are employed.

- Direct Contact Window: This style of presentation can be found on some benchtop instruments that are designed to examine solutions in cuvettes or samples such as pharmaceutical tablets. Using this style of presentation for geological samples requires a sample that is at least saw-cut flat and small enough to fit to the window. Sample imaging is not possible and the mineral grain size must be on the same size scale as the window to ensure accurate aiming.
- Raman Microscope: Raman microscopes are able to work with small mineral grain sizes, and they offer the benefit of direct coaxial observation of the analytical target. Decisions about the amount/style of sample preparation required depend upon several factors:
  1. For optimum signal transmission into the spectrograph the sample must be in focus under the microscope in reflected light. This can be difficult to accomplish if the sample isn't reasonably flat and smooth. Loose grains showing cleavage surfaces will also work, but, even rough surfaces, or grains, at high magnification typically have areas that are "flat" for a ~1 micron beam.
  2. While some microscope objectives can focus at a working distance up to a few mm, as explained in section A.4 above, the best signal collection is accomplished with high NA, high magnification objective lenses which typically have working distances significantly less than 1 mm.
  3. While Raman data collection from standard thin sections is possible there will be interference from the coverslip and it's adhesive unless confocal optics are available and employed.
  4. When attempting to sample isolated grains/crystals in a small hand sample or micromount, the ideal is to present a natural crystal face or cleavage surface perpendicular to the objective to facilitate optical focusing. Methods for managing sample orientation in this way include a putty or plasticine clay or a "rice bowl" (which may be filled with synthetic beads rather than uncooked rice).

Table B.2.1. Summary of sample preparation styles that can be employed with each type of sample presentation.

	Snout	FO Probe	Window	Microscope
None	1	1,3	1,3	3,4
Saw Cut	1	1	1,3	3,5
Flat Grind	1	1	1,3	3,5
Polished Thick	1	1	1,3	Yes
Polished Thin	1,2	1,2	1	Yes
Standard Thin	1,2	1,2	1	Yes
Grain Mount	No	1	1	Yes

Notes:

1. Aiming challenges require multi-mm grain size.
2. While thin section sample types may be presentable, their shallow (30um) thickness may result in a low signal strength.
3. Overall size of the sample must be reduced to a size conformable with the presentation style.
4. Potential application exists if sample can be freely positioned to bring the surface of any point of interest perpendicular to the objective lens.
5. Surface roughness makes it difficult to focus on the surface and a long working-distance objective may be required.

B.2.2 Target Aiming

It is assumed here that the goal is to both unambiguously sample the target phase and also to avoid sampling a second (or more) phase at the same time. Accordingly, one has to be aware of the spatial resolution of the instrument. Also, to ensure that you obtain a representative spectrum, one has to consider the effect of crystallographic orientation.

Spatial Resolution

The volume of the target that is sampled depends upon beam diameter, depth of penetration, volume of beam scattering, and volume of space from which the spectrometer can receive the generated signal. Following are the factors that must be considered.

- Transparency: When the target is opaque the depth of (laser) light penetration is minimal. As degree of translucency and transparency increases, there is both an increase in depth of light penetration and an increase in light scattering, which can result in generating Raman signal from a region much larger than the diameter of the laser beam – especially in the direction axial to the laser beam. Without limiting apertures (see below), millimeter-sized regions might be sampled from a laser beam only microns in diameter.

- Interfering phases: For transparent minerals with weak Raman intensities, adjacent phases with strong Raman intensities that have even minor interaction with the laser light can substantially contaminate the Raman spectrum.
- Spectrograph apertures and confocal apertures: Spectrometer apertures are the primary tools for managing spatial resolution in translucent and transparent samples. The spectrograph aperture is positioned at the entrance into the spectrograph and selecting a smaller aperture will improve spatial resolution in the direction perpendicular to the Raman light path (the horizontal in a Raman microscope). A confocal aperture, which is positioned at a crossover point in the Raman light path (see section A.4), can be effective for limiting the depth into the target from which signal is received.

Selecting Apertures and Quantifying Resolution

Options for selecting apertures depend upon the type of Raman instrument and the options installed on that instrument. For example, if you are using a handheld or fiber-optic probe instrument, it is likely that the entrance aperture is fixed, and confocal optics are not offered. In these cases, an estimation of the spatial resolution can be obtained by experimenting with known samples with various grain sizes.

Selectable apertures and confocal optics are primarily offered on Raman microscope instruments. Quantifying depth resolution is difficult unless you have a sample with a sequence of thin layers of known substances. Since depth resolution is an important feature of an instrument equipped with confocal optics, the manufacturer likely performed a resolution quantification and reported it as a performance parameter.

Quantifying lateral resolution can be accomplished with a polished section having known mineralogy. Collecting spectra at a series of measured distances from a grain boundary provide the lateral resolution for various entrance or confocal apertures, keeping in mind that the results will be different for transparent versus opaque minerals.

Crystallographic Orientation

As introduced in sections A.2 and A.3, variations in the orientation of crystallographic axes with respect to the vibrational axis of the laser beam can affect relative intensities of certain Raman peaks. At orientations where the vibration direction of the laser beam is parallel to a primary crystallographic axis some Raman peaks can have uniquely high intensities, and some Raman peaks are quenched. As a result, for routine mineral identification, the ideal is to collect a Raman spectrum from a target mineral orientation somewhere between its crystallographic axes. While one does not generally have direct knowledge of and control of crystallographic orientation of the target, there are a couple of guidelines that can be helpful.

1. If possible, collect spectra from more than one grain of the same phase. You can compare them to see if they are consistent in relative intensity or average them.

2. Be aware when using grain mounts –minerals with a strong cleavage will preferentially orient parallel to that cleavage plane when deposited on a substrate. Since cleavage planes are often special orientations with respect to crystallographic axes, you may not get a general/representative Raman spectrum from such a grain. One can try to tilt the substrate off of perpendicular to the laser beam or one can use a substrate with surface irregularities (such as aluminum foil that has be crumpled and semi-flattened) so that individual grains are unlikely to lie perpendicular to the laser.

Critical Aiming

If your sample target size is near the limit of the instrument's spatial resolution, it is critical to know precisely, in the microscope field of view, the laser beam position and diameter. Determining these can be complicated by the following:

- some laser wavelengths, i.e. NIR, IR and UV, are not visible
- direct observation of the sample is not available during data collection.

The beam position and diameter can be accurately determined using a material that reacts to the laser beam (e.g. changes color or vaporizes). This beam-sensitive material, e.g. a polished grain of proustite, should be mounted under the Raman microscope in the same way as a target sample.

Note also that small mineral grains dispersed on a substrate without an adhesive sometimes respond to laser heating by "jumping". Since direct observation of the sample is not available during data collection, make sure to verify that your target grain has not moved after data collection has completed!

B.3. Collecting the Raman Spectrum

Data collection parameters and strategies will vary with type of instrument (and its software, and type of sample. The coverage of this topic, below, addresses instruments that have the most options and the most controls. Simpler instruments will have some options fixed.

B.3.1. Operator and Instrument Preparation

Operator preparation consists primarily of reading instrument/software documentation and availing oneself of demonstrations and training offered by the instrument maker, or, for an established Raman facility, training offered by a facility manager or "superuser". Typically, operator preparation is iterative. The operator may need to read the remainder of this section before he/she knows which instrument/software features they need to be familiar with. However, should they switch to a different class of target materials, they may need to go back to documentation and training as well as re-read this section.

Instrument preparation covers actions that need to be taken regularly that are independent of the specific analytical task. The most basic of these preparations is simply ensuring that you know how to turn the instrument on and, in most cases, how long the instrument must be on (warming up components and cooling down the detector) before the instrument is ready for meaningful data collection. In addition, the instrument must be calibrated.

Physical vibrations, temperature changes, and aging of components can affect spectroscopic accuracy, the position where the beam impacts the sample, and the instrument working distance. Accordingly, calibration of beam position, spectrometer focus, and spectrographic position and scale are required. Beam position and working distance calibrations may be performed only by an instrument service technician or the lab manager. Spectrographic calibration, however, is generally part of the operator's protocol.

Beam Position Calibration

As mentioned in the previous section, laser safety controls and non-visible laser wavelengths may prevent simultaneous observation of the sample and the laser beam. Anytime mineral grain size makes critical aiming essential, it is worthwhile having some kind of laser-sensitive material on hand to verify beam position.

For portable and fiber-optic probe instruments there generally are no controls to adjust beam position. Some of the Raman microscope makers consider beam positioning so robust that only a service engineer is equipped to make adjustments. If an instrument comes with physical tools and software features for beam position calibration, it is up to the instrument manager to establish who will have the training to perform this calibration and how often it is prudent to do so.

Working Distance Calibration

The working distance of a Raman instrument is the physical distance between the objective lens and the sample for which the maximum amount of signal is focused into the spectrograph. For portable and fiber-optic probe instruments a front-end snout (which is often removable) is generally provided to key sample positioning to the optimum working distance. The operator may also be free to remove the snout to achieve an optimum working distance.

For Raman microscopes, the optimum working distance is ideally exactly the same as the optical focus point for sample imaging. Again, some instrument makers consider this positioning robust and only a service engineer is equipped to test and make adjustments. If an instrument comes with physical tools and software features for working distance calibration it is up to the instrument manager to establish who will have the training to perform this calibration and how often it is prudent to do so.

Spectroscopic Calibration

Spectroscopic calibration establishes the accuracy of the relationship between detector pixels/positions and quantitative Raman-shift. The criticality of this calibration along with the impact of relatively small temperature shifts and physical vibrations makes this calibration something that should be performed as part of each data-collection session.

Spectroscopic calibration is conducted with reference to some standard. Some instruments employ an internal standard such as the emission lines of a noble gas lamp. Many instruments use an external standard, typically crystalline Si, and assume a nominal position for a reference peak. Other instruments allow the operator to specify a reference material and expected position(s) of one or more reference peaks.

In general, spectroscopic calibration consists of 2 components:

1) Zero-point calibration – calibration against a single Raman peak with known Raman shift establishes the position of zero Raman shift in the spectrometer system. Some instruments measure the position of the laser source independently making this a two-point calibration
2) Detector linearity calibration – establishing the actual position on the detector system of 2 or more Raman peaks (or noble gas lamp emission lines) covering the range of Raman shift of interest provides corrections for any deviations in linearity in the detector system.

The ideal is a calibration system that provides for both of these. If your instrument provides only for single-peak (zero point) calibration it is worth collecting a spectrum on some standard material after calibration to validate spectral accuracy over the range of Raman shift you are interested in. One example that is generally available to geoscientists is clear (spar) calcite which can be depended upon to be virtually free of lattice defects and chemical impurities. Sharp peaks with significant intensities have well established positions at 154.9, 281.2, 712.4, 1086.2, and 1435.8 cm^{-1}.

Instruments with internal standards may not offer you the opportunity to use an external standard as well, but they should give you some control over how often calibration is performed. Instrument makers will often provide recommendations for frequency of spectroscopic calibration, but it is prudent for a Raman facility to perform frequent calibrations (multiple times per day), monitoring the amount of adjustment required by the instrument for each calibration, until a recommended calibration schedule can be established.

Every time you change the instrument configuration (see below) the spectral calibration should be repeated. Even if your instrument configuration is static, the minimum spectroscopic calibration frequency should be no fewer than twice during a data-collection session with the first calibration after the recommended instrument warm-up period. Instruments with internal spectroscopic standards may take advantage of the independence from user intervention and offer calibration frequency as often as every time a sample spectrum is collected. Even if spectroscopic calibration is entirely automated, it is worthwhile for the operator to be aware of how and how often calibration is being performed.

B.3.2 Data Collection Controls

For a full-featured instrument there are 2 groups of data collection controls: 1) instrument configuration controls, and 2) spectrum collection controls. Compact instruments typically have fixed configurations and only spectrum collection controls are adjustable.

Instrument Configuration Controls

A full-featured instrument might offer multiple apertures, lasers, and diffraction gratings, and might offer cutoff filter selections. In addition, a Raman microscope generally is fitted with a selection of objective lenses. These components were described in section A.4 but are reviewed here as they apply to configuring the instrument for specific experiments.

Apertures: Smaller apertures improve spectral and/or spatial resolution but also reduce observed signal strength. A spectrometer entrance aperture will improve spectral resolution and lateral (across the sample) spatial resolution. A confocal aperture, if present, will improve depth (into the sample) spatial resolution. Aperture selection is determined by sample type and analytical goals. Some typical analytical configurations are provided below, but in general, if spatial resolution on the sample is not a critical need, select the largest aperture (which may be a slit rather than a pinhole).

Lasers: As explained in section A.2, shorter wavelength lasers inherently yield stronger Raman signals, but any particular laser wavelength might also produce fluorescence interference in a given sample. Section A.6 provides guidance for anticipating and managing fluorescence interference. Also, the higher energies of the short wavelength lasers might be more likely to damage some samples. Unless such problems are observed or expected, shorter wavelength lasers are commonly the first choice because of their signal-strength advantage.

Gratings: Diffraction gratings are generally rated in grooves per millimeter (g/mm). A higher number of g/mm has higher dispersion power resulting in greater spectral resolution, but also yields lower signal strength at the detector. In addition, for imaging detectors, the spectral range (in Raman shift) that can be captured by the detector decreases as the dispersion power of the grating increases. As a result, if you select a high g/mm grating and want a wide-range spectrum (e.g. up to 3000 or 4000 cm^{-1}), the spectrum will be collected as a series of smaller segments, which are then digitally spliced together. This process can significantly increase the total data collection time.

Cutoff Filters: The laser-line cutoff filter must match the laser selected. For instruments with software-controlled selection of laser wavelength, the cutoff filters are typically selected automatically.

Objective Lens: For Raman microscopes, higher power objectives focus the incident laser to a smaller diameter, thereby improving the analytical spatial resolution. Additionally, a high magnification objective has a greater NA, and therefore, collects a larger solid angle of scattered light from the sample, resulting in a higher Raman signal intensity. Consequently, even for coarse-grained samples it might still be advantageous to use a 100x objective to maximize the Raman intensity. That said, the smaller spot size, and greater power density, for a high magnification objective might more likely produce sample damage. Finally, if multiple objectives are available, it might be helpful to use lower magnification options for navigating the sample and analytical targeting, and then switch to the higher magnification objective for data collection.

Spectrum Collection Controls

Spectral Range: The selection of spectral range depends on sample type and analysis objectives. For routine mineral identification, set the low end of the range to the minimum Raman-shift limit for the instrument, but avoid including the spectral region where the intensity drops due to the laser-line cutoff filter, as this will complicate the background/baseline removal (see section B.4 below). Also, as discussed in section A.3, as most minerals have their characteristic Raman peaks below 1400 cm-1, the upper end of the spectral range should be at least that high.

Laser Intensity: As discussed in section A.7, although a higher intensity laser yields greater Raman intensity, it also increases risk of sample damage. Although not essential for basic data collection, it is sometimes helpful, or necessary (for publications or when documenting experimental procedures), to know the laser power at the sample. Software controlled attenuators might reduce incident laser power to some percent of maximum, but the actual laser power on the sample typically can only be determined by using a laser power meter.

Acquisition Time and Accumulations: Acquisition time refers to a single continuous detector data collection time, and accumulations is the number of times this data acquisition will be repeated, and either added together or averaged. There are several advantages to using multiple accumulations for most data collections including:

a) Detector intensity spikes from cosmic ray events (CRE) can be detected and eliminated by mathematically comparing one accumulation to the next,

b) Changes in spectral features from one accumulation to the next reveal sample damage, and

c) The likelihood of detector saturation can be reduced.

While some instrument-control programs have auto-exposure features, the process of selecting acquisition time and accumulations generally requires one or more short acquisitions on examples of your target(s) to establish the range of signal strength you can expect to encounter. Some practical guidelines include:

1) Choose at least 2 accumulations so that CRE can be detected and removed.

2) When working with medium to high signal materials, a large number of short accumulations will reduce the chances of detector saturation,

3) When working consistently with minerals having weak Raman signals a small number of long acquisitions will generally result in a higher SNR spectrum than a large number of short acquisitions.

Acquisition Delay Time: This is a period of time during which the laser is on your sample, but data collection is not started. If you have reason to believe that your sample will produce thermoluminescence (see section B.3.3 below) it is appropriate to use a delay time of, typically 10 to 60 seconds during which thermoluminescence will dissipate.

Instrument Background Collection: This is not continuum from the sample (which also is referred to as “background”), but detector signal generated by the instrument, primarily by thermal electrons in the detector. For instruments with deep-cooled (e.g. -70 C) detectors, this contribution is generally insignificant, and can be ignored. On many instruments, however, it is standard to measure instrumental/detector background by performing an acquisition with the laser shuttered, thereby preventing any signal from the sample. This instrumental background spectrum is subtracted from each sample spectrum. In some cases, a background collection frequency can be set in the instrument software, which can range from “every time I acquire a spectrum” to “only when needed”. Typically, “only when needed” includes any time a change is made to the instrument configuration or data collection parameters.

B.3.3 Selecting Experimental Parameters

The general principles detailed above, including principles communicated in sections A.2 through A.8, can be used to guide your selection of instrument configuration options and data collection parameters, however, it is difficult in most cases to predict the Raman response of your sample. Accordingly, it is often helpful to take an iterative approach to selecting your data collection parameters and even, at times, your configuration options. This is accomplished via a very common instrumental software option – Live Mode.

Different software applications may use a different term/label for this function, but Live Mode amounts to repeatedly collecting Raman spectra under all of your chosen experimental parameters except acquisition time. The default may be to collect a spectrum every second, but this is generally configurable (e.g. every 2 seconds or every 0.5 seconds). While you are watching the graphic display look for the following:

- Look at the intensity of the highest peak. Once you know the saturation point of your detector (commonly around 70,000 counts) you can calculate a suitable acquisition time that avoids saturation.
- If you are seeing a very high background, watch to see if that high background is decreasing with every new spectrum. This would be an indicator that your sample is generating some thermal luminescence under laser heating. Consider setting an Acquisition Delay time.
- As you watch the sequence of spectra look for a progressive reduction in peak intensities, a progressive decrease in the apparent SNR, peak broadening, or even the appearance of new peaks. Any or all of these are signs that the laser is damaging your sample. In response it is appropriate to visually check your sample (after exiting Live Mode) for a burn spot and follow the guidelines in section A.7.4 to avoid sample damage.

B.3.4 Collecting the Raman Spectrum

Once all of the experimental parameters have been set, the next steps are selecting the sample target spot and collecting the Raman spectrum. Raman systems (e.g. Raman microscopes) that allow for direct imaging of your sample are configured so that the target is in the optimum laser focus position when its image is in focus. For some laser wavelengths, however, the optical focus and laser focus are not coincident, and in such cases, the laser should be focused visually onto the sample, or by adjusting the sample height to maximize the Raman signal intensity. Most software systems have a data field for recording identifying information about the sample and analytical target. Typically, Raman systems will not provide an image of the analytical target during data collection, but most will graphically display the spectrum as each accumulation is completed.

During data collection, presuming you have selected more than one accumulation, you can observe the cumulative Raman spectrum as each accumulation completes. Ideally, spectral features will be consistent, and the SNR will improve. In addition, be on the lookout for changes to the spectrum that would be indicative of sample damage that is happening on a slower time scale than Live Mode (see above). Also, if the first accumulation shows signs of detector saturation (see Figure B.3.1 below), data collection should be aborted followed by lowering the acquisition time.

Once data collection is completed, the spectrum data should be stored. Most instrument software systems have proprietary data formats, and saving data only in this format works fine if you are going to do all of your post-processing in the same software application. Some 3rd party spectroscopic data processing software systems are equipped to read a wide variety of proprietary file formats, but also saving a copy of each spectrum in text format provides maximum flexibility in choice of post-processing software. Text file options might be referred to as ascii format; the most transportable text-file formats are comma delimited (CSV) or tab delimited (TSV).

B.3.5 General Analytical Scenarios

While the above provides basic guidelines for acquiring Raman spectra for mineral identification, some amount of trial-and-error is commonly required to design an analytical methodology that is most advantageous for your samples. Following are example strategies for some common analytical scenarios.

Mineralogical Surveying

Collecting spectra from a variety of minerals in a sample or a series of samples might be complicated by the fact that Raman signal strength can vary up to 4 orders of magnitude from one mineral to the next (section A.3). Consequently, data acquisition parameters that are adequate for strong-signal minerals might yield spectra with no obvious peaks for weak-signal minerals. Conversely, data acquisition parameters suitable for weak-signal minerals might produce detector saturated spectra for strong-signal minerals. Therefore, it is useful to have separate data-collection protocols for strong-signal minerals and for weak-signal minerals.

For example, acquisition times between 1 and 5 seconds might be adequate for strong-signal minerals, but for weak-signal minerals, acquisition times between 30 and 100 seconds are required. Most instrument-control software systems include provisions for saving a specific data-collection protocol and recalling such (by file name) as needed. As summarized in Section A.3.4, in general, dark colored and opaque minerals tend to yield weak Raman intensities, and light colored to transparent minerals are more likely to produce strong spectra.

Ore Minerals

Since the laser-sample interaction for opaque minerals is essentially restricted to the surface, many ore minerals yield weak Raman signals. The advantages of increasing signal strength by using maximum laser power, are reduced by the potential for laser damage to the sample (see section A.7). Consequently, ore minerals, and other opaque samples, require special data collection strategies.

In addition to increasing signal strength by upping the laser power, it is also possible to improve Raman intensities by optimizing the selection of objectives and apertures.

- In general, objectives with a higher NA gather more scattered light and give higher signal strength at the detector. Typically, higher magnification objectives have greater NA values, but this is not always the case, for example, long working distance objectives generally have a lower NA than standard objectives with the same magnification. It is standard for magnification and NA to be stamped on the objective barrel.
- Apertures with larger openings allow more light into the spectrograph and slit-type apertures pass more light than circular (pinhole) apertures. A tradeoff, however, is that larger apertures result in lower spectral resolution and a larger analytical spot size on the sample. It might be helpful to collect spectra from a known sample using a range of apertures to assess this tradeoff.

Likewise, in order to recognize and minimize laser damage to the sample, test data collections might be carried out on standard minerals that are known to be prone to laser damage in order to determine optimal data-collection parameters consistent with minimal laser-damage. Some strategies to consider:

- Start data collections with a low laser power and increase stepwise until laser damage is observed, and then back off to the highest laser power that did not produce noticeable laser damage.
- During data acquisition, note changes in peaks and apparent SNR between accumulations. If the software does not display individual accumulations, collect a second spectrum on the same sample spot immediately after the first and compare.
- Note changes in the optical image of the sample after data collection, e.g. discoloration or crater, for indications of sample damage.
- Laser power density on the sample can be reduced by spreading out the laser beam, e.g. on Raman microscopes by switching to a lower power objective, or slightly defocusing the laser (e.g. moving the sample slightly from the laser focus height).

B.3.6 Evaluating Data Quality

Some common challenges that can affect mineral identification success for a given Raman spectrum include detector saturation, inadequate SNR, fluorescence interference, and mixed-phase spectra.

Detector saturation is easy to detect and to correct for. Figure B.3.20 shows typical examples of spectra affected by detector saturation, 1) high-intensity peaks have truncated/flat tops, and 2) sections of the spectrum (at the highest intensity) are flat and horizontal. The simple remedies are reducing the total acquisition time or decreasing the laser intensity.

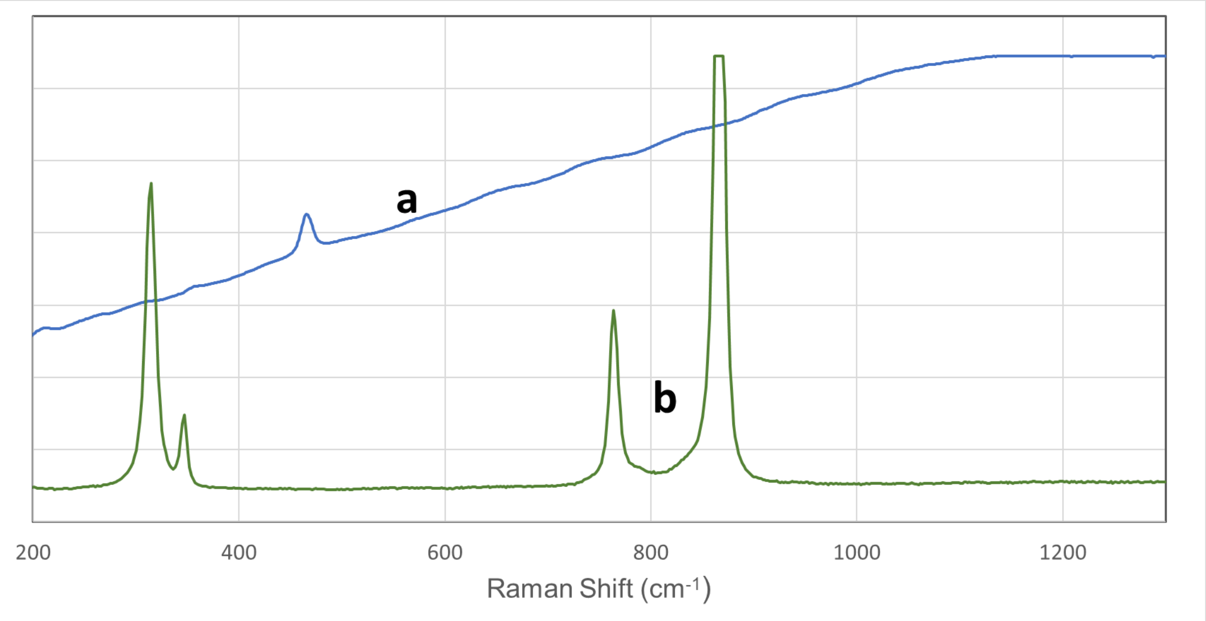


Figure B.3.20 Raman spectra truncated by detector saturation: a) broad-spectrum fluorescence leads to data loss beyond ~1100 cm-1, due to detector saturation and b) spectrum with high-intensity peak truncated by saturation.

Inadequate SNR can be a consequence of the experimental conditions or result from inherent low Raman scattering from the sample. Consider also that your sample may be Raman inactive, although this is uncommon (see Appendix 1). As reviewed above, adjustments to data collection procedures that might improve SNR include: selecting a higher NA objective, using larger diameter apertures, and increasing acquisition time. Also, a small number of accumulations (2 minimum to detect and remove CREs) of a long acquisition time will often yield better noise statistics than a large number of short accumulations.

As described in sections A.2 and A.6, fluorescence interference can manifest as narrow peaks similar to other peaks in your spectrum, or more commonly as broad-wavelength features, including extremely wide peaks, a pronounced slope to a portion or all of the spectrum or a continuously high baseline/background across the entire spectrum (See figures A.6.2 and A.6.3).

If fluorescence interference is obvious, one remedy might be to switch to another laser wavelength (if available). Section A.6 provides some guidance as to what wavelength to choose, but in practice, some trial-and-error might be required.

Assuming Raman peaks are evident, a useable spectrum might be extracted by background/baseline removal of the broad spectrum fluorescence interference (see section B.4 below). Averaging multiple accumulations will improve the SNR and likewise the quality of the extracted Raman spectrum.

B.4. Spectrum Processing

Spectrum processing, including background subtraction, CRE removal, smoothing, and range trimming, optimizes spectra for whole-spectrum matching against a reference Raman database for phase identification.

B.4.1 Removing CRE

Cosmic Ray Events (CRE) are the result of high speed atomic particles (a.k.a. cosmic rays) impacting the detector during spectrum acquisition. CRE appear in spectra as uniquely narrow peaks – often affecting only one detector pixel (Figure B.4.21). Most spectrometer software systems can mathematically identify and remove CRE by comparing two spectra acquired sequentially.

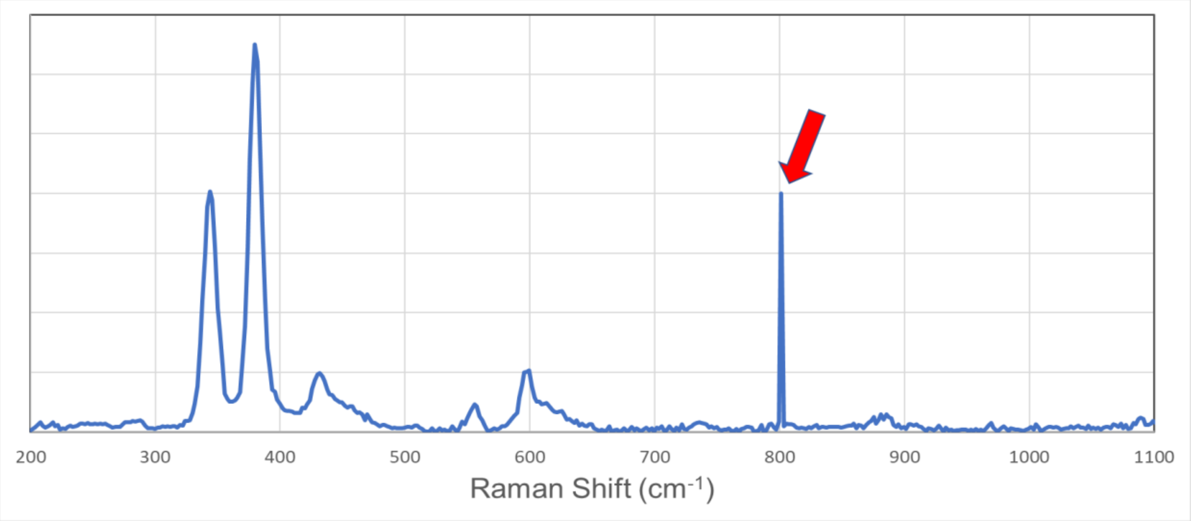


Figure B.4.21. Raman spectrum including a CRE event (arrow). CRE peaks are considerably narrower than typical Raman peaks.

B.4.2 Range trimming

If your chosen data collection range includes the region affected by the laser line cutoff filter, the resulting steep drop in the baseline at the low Raman-shift end of the spectrum will be problematic for the baseline-removal process. Figure B.4.22 shows an example where this filter-related baseline drop results in a false spectral feature in the background-subtracted spectrum. This problem can be avoided by determining, on a standard sample without low Raman-shift peaks, where this baseline drop begins and setting the lower end of the spectral range to this value. Spectra that show such a baseline-drop can also be trimmed after data collection using spectrum-processing software or manual data-file editing.

If your data collection range goes below 125 cm^{-1} and you are employing the long counting times necessary for minerals with weak Raman signals such as ore minerals you may need to trim off the portion of the spectrum that is registering Raman peaks from gasses in the air (see section A.8.2).

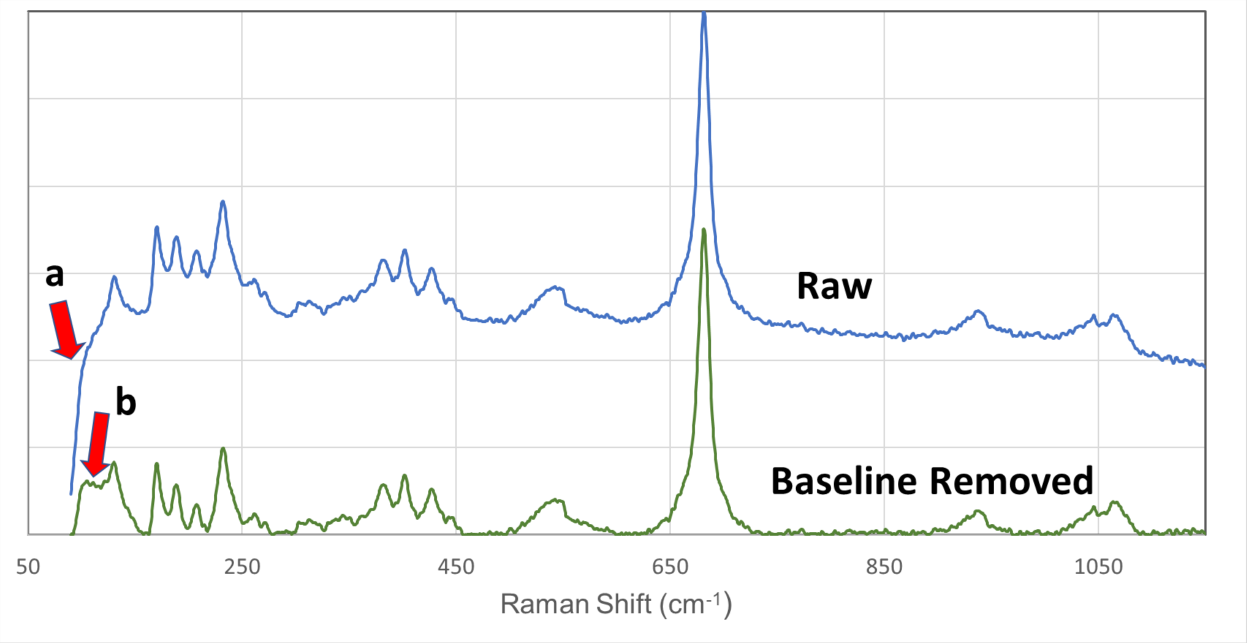


Figure B.4.22. False spectral feature (b) resulting when a baseline-removal algorithm is applied against a raw spectrum containing a filter-related baseline drop (a).

B.4.3 Noise Reduction

Noise reduction is a mathematical process to smooth out random variations in spectral intensities ideally without removing spectroscopic peaks. If your spectrum has a low SNR noise reduction might improve the potential for pattern-match identification. At the same time noise reduction should be used carefully since it also has the potential to obliterate minor peaks. A variety of noise reduction algorithms are available, and if your software offers more than one, or control over adjustable parameters, experiment with these, but avoid over-smoothing. Since smoothing modifies the range of variation in the baseline and the shape of peaks, it should be done before baseline removal or curve fitting (section B.6.1).

B.4.4 Baseline Removal

A necessary processing step for most Raman spectra before performing a search-match mineral ID is removal of the background continuum (a.k.a. baseline). The challenge is to apply a mathematical/logical process that accurately models the baseline without being deflected by the peaks. The fitted baseline intensity at every spectral channel is subtracted from the raw spectrum (Figure B.4.23). Many mathematical models and computer algorithms have been applied to this task – helpful reviews of the topic include Carey et al., 2015 and Schulze et al., 2005. The goal here is to provide guidance on evaluating the results of a particular baseline removal methodology whether provided by the instrument software or from 3rd party software.

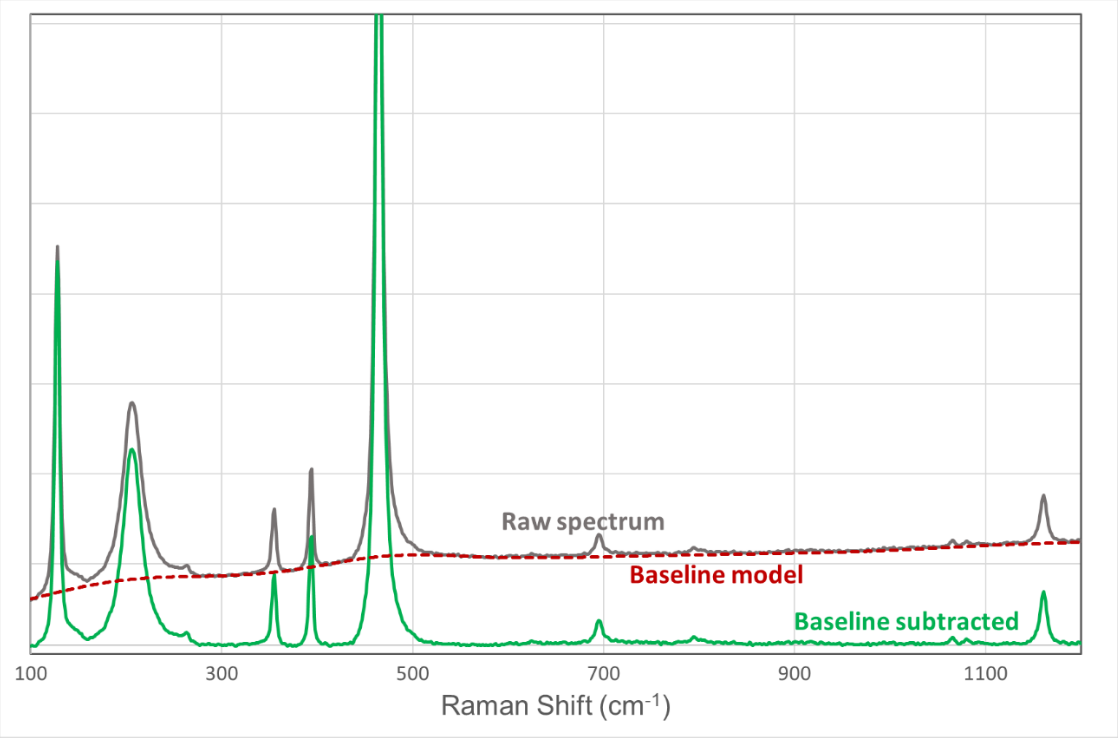


Figure B.4.23. Raman spectrum of quartz showing an example of a baseline model and the result after the baseline model is subtracted.

Types of Baseline Shapes and Magnitudes.

The success of baseline removal algorithms is influenced by both baseline shape and peak shape, and also by the presence broad-spectrum fluorescence. The baseline might be flat, linear but gently or steeply sloped, curving up at one end of the spectrum, curving up at both ends of the spectrum (concave), curving down at both ends of the spectrum (convex) or even linear over some portion but containing a broad hump (Figure B.4.24). In addition, the intensity of the baseline may be low, or high, compared to peak intensities, and when Raman peaks are weak, and/or data-collection time is low, the baseline can be noisy. Instrumental effects on the baseline can include the filter-produced baseline drop illustrated above as well as a regular, repeating, low-intensity waviness often seen when fluorescence interference intensity is high (see Figure A.6.5).

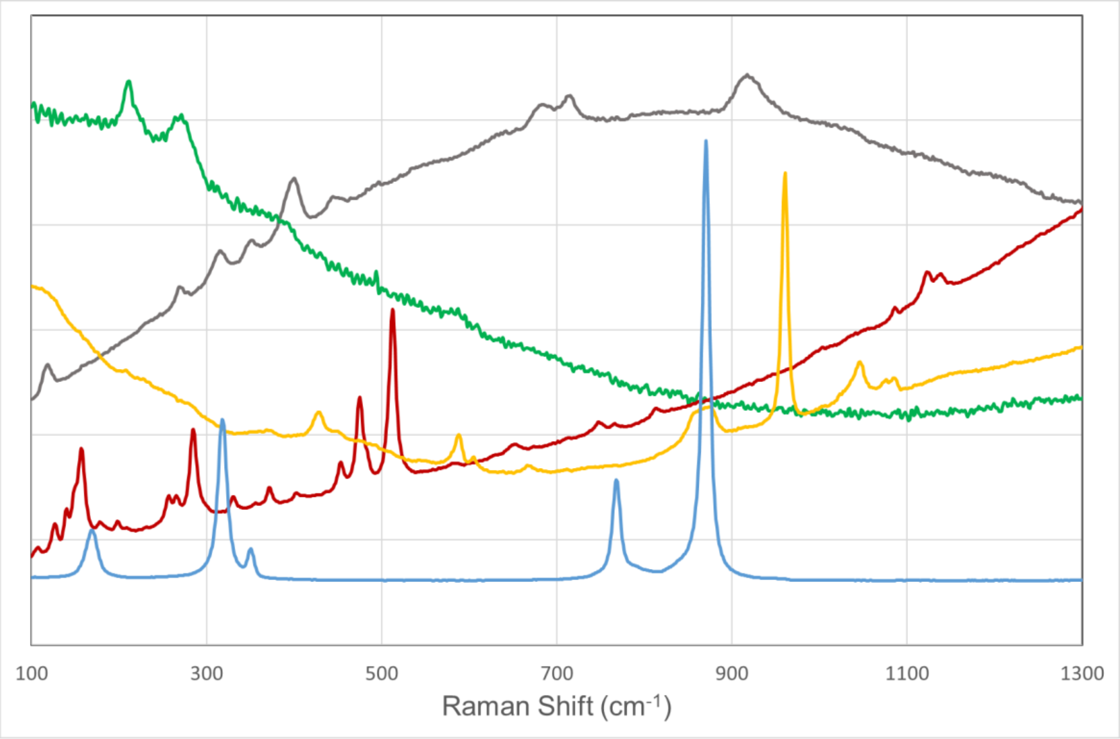


Figure B.4.24. Examples of the variety of Raman spectra baseline shapes.

Additionally, Raman peaks may be narrow or broad because of crystallinity, solid solution, grain size, etc., and some mineral spectra exhibit a mixture of peak shapes. Baseline removal algorithms that are able to model a strongly curved baseline might also fit all or portions of broad spectral peaks as part of the baseline, thereby removing or modifying them (Figure B.4.25).

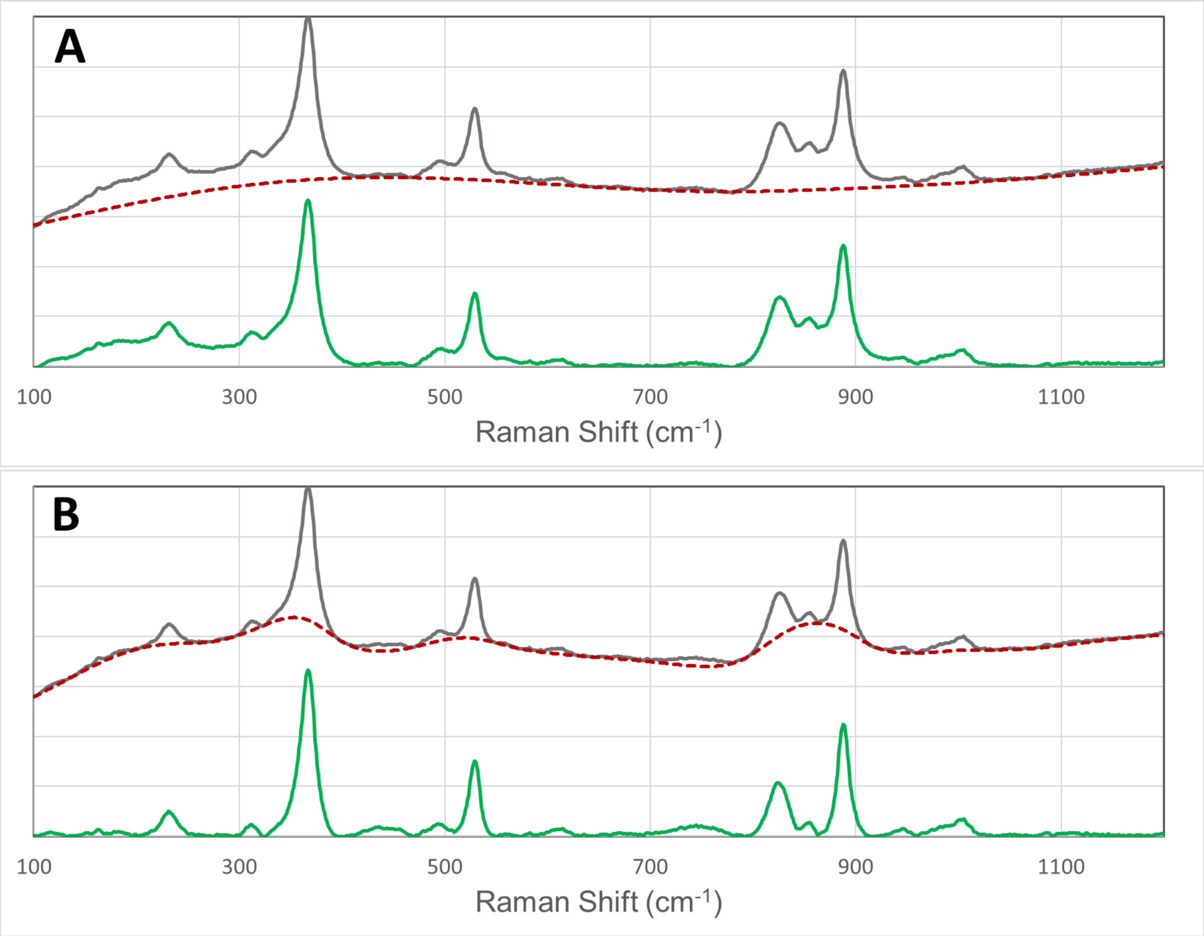


Figure B.4.25. Illustration of baseline modeling errors. A. This baseline model sweeps smoothly under peaks above 400 cm^{-1} but fails to fit the curvature in the baseline at lower Raman shifts, resulting in an artificially elevated spectrum intensity below 400 cm^{-1} when the baseline model is subtracted. B. This baseline model fits the curvature of the baseline below 400 cm^{-1}, but incorporates portions of some Raman peaks, reducing the intensities of the major peaks in the subtracted spectrum, and introducing small positive intensity artifacts at about 450 cm^{-1} and about 750 cm^{-1}.

In general, baseline-removal algorithms work best when characteristic peaks are narrow and the baseline is linear, but they can be challenged by broad peaks and strongly curved baselines.

Baseline Removal Recommendations.

- The primary lesson from the above examples is to be aware of the limitations and potential for error in your baseline removal process. Compare the spectrum before and after baseline removal to determine the most effective applications and strategies for your software.
- Watch out for spectral artifacts produced by the baseline removal process (e.g. Figure B.4.22 and Figure B.4.25)
- Spectrum trimming can prevent certain baseline-removal-induced artifacts, as illustrated in Figure B.4.22. Baseline removal algorithms generally have adjustable parameters. If the software provides control over adjustable parameters (or even a

selection of baseline algorithms), some trial-and-error experimentation will reveal the best strategies for baseline removal.

References

Carey, C. J., Dyar, M. D., Boucher, T., Giguere, S., Hoff, C. M., Breitenfeld, L. B., Parente, M., Tague, T. J., Wang, P., & Mahadevan, S. (2015). Baseline removal in Raman spectroscopy: optimization techniques. *46th Lunar and Planetary Science Conference*, 2464.

Schulze, G., Jirasek, A., Marcia, M. L., Lim, A., Turner, R. F. B., & Blades, M. W. (2005). Investigation of selected baseline removal techniques as candidates for automated implementation. *Applied Spectroscopy*, *59*(5), 545–574.

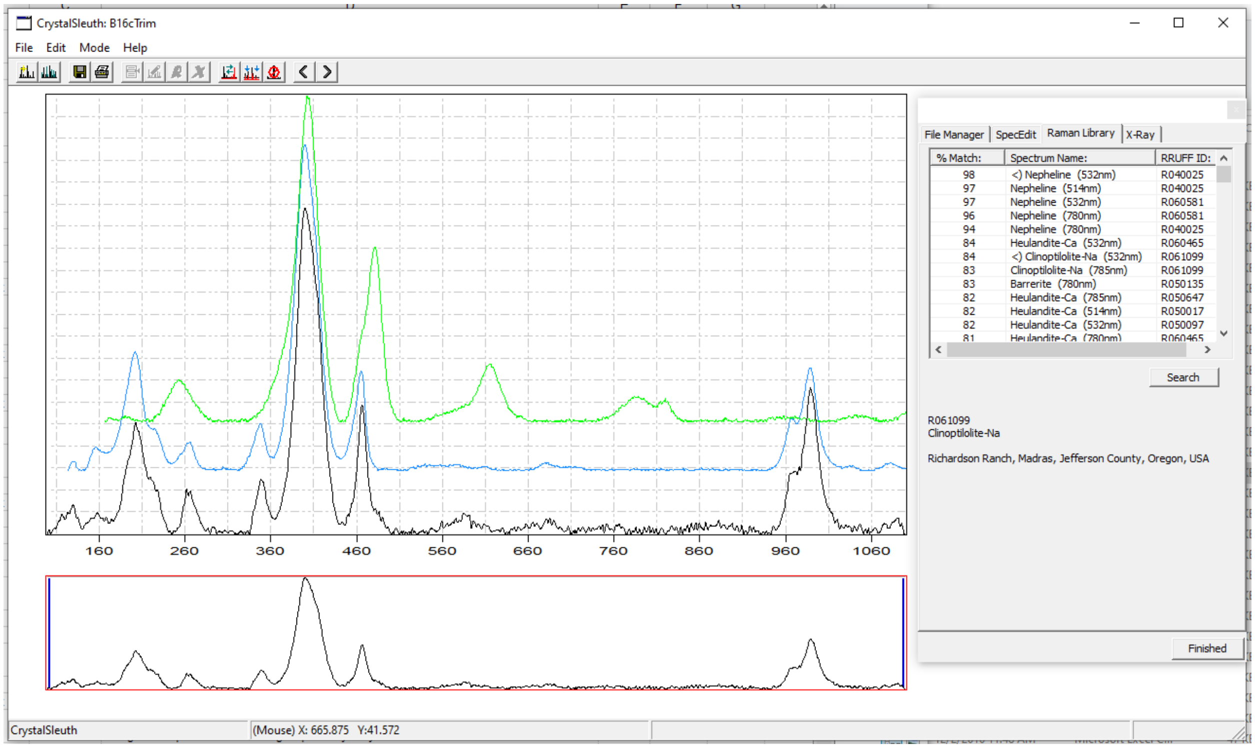
B.5. Mineral Species Identification

Species identification via Raman spectroscopy is referred to as fingerprint-style identification because, like forensic fingerprint analysis, the features of the Raman spectrum are compared to a database (a.k.a. library) of reference spectra (from known mineral species), and a match-scoring system is used to identify which reference spectrum is the best match to the unknown. While this system is generally effective, it is important to evaluate the match results based upon some understanding of its limitations.

The previous section described and recommended spectrum processing practices to remove instrumental artifacts and spectral features that do not represent Raman scattering. Typically, such processing has been applied to spectra in the reference database.

B.5.1 Basic Mineral Identification Procedure

The database/library search function may be integrated into the instrument manufacturer’s data-collection software, or it may be a separate program. To perform a search/match for an unknown spectrum, the software might ask to choose a reference library, if more than one is available. The search result lists the top matches, ideally with a match score value next to each. Most programs also permit graphical comparison of your unknown spectrum to each of the potential matches. Figure B.5.26 shows an example of a successful match from the public-domain software CrystalSleuth that is available from rruff.info. The success of the search-match process depends upon a) a match scoring system that is suitable for Raman spectra, b) an accurate and representative spectrum from your unknown, and c) a comprehensive reference database that includes the species that matches your unknown.



% Match:	Spectrum Name:	RRUFF ID:
98	<) Nepheline (532nm)	R040025
97	Nepheline (514nm)	R040025
97	Nepheline (532nm)	R060581
96	Nepheline (780nm)	R060581
94	Nepheline (780nm)	R040025
84	Heulandite-Ca (532nm)	R060465
84	<) Clinoptilolite-Na (532nm)	R061099
83	Clinoptilolite-Na (785nm)	R061099
83	Barrerite (780nm)	R050135
82	Heulandite-Ca (785nm)	R050647
82	Heulandite-Ca (514nm)	R050017
82	Heulandite-Ca (532nm)	R050097
81	Heulandite-Ca (780nm)	R060465

R061099
Clinoptilolite-Na

Richardson Ranch, Madras, Jefferson County, Oregon, USA

Figure B.5.26. Screen shot from CrystalSleuth (available from RRUFF.info) showing database match results. The black line is the experimental spectrum from a grain of nepheline, the blue line is the library spectrum of nepheline and the green line is the library spectrum of Clinoptilolite-Na.

B.5.2 Evaluating Match Results

The mineral species at the top of the match-results list might not always be the correct match for your unknown phase. In evaluating the accuracy of search results, one should:

a) Examine the top-match results list. Multiple entries for the same species might occur if the database contains: spectra from multiple examples of the species (which may have minor compositional differences); spectra from the same sample using different laser wavelengths, and/or spectra from the same sample with different crystallographic orientations. When top matches are mostly species in the same mineralogical group (e.g. amphiboles or garnets) it is a strong indication that the unknown belongs to that group.

b) Graphically compare matched spectra with the unknown. In Figure B.5.26, the nepheline library spectrum matches every peak in the unknown spectrum. Keep in mind that it is more meaningful that peaks appear in the same position (in Raman shift) than whether the relative peak heights match, as many instrumental factors and sample properties (e.g. crystallite orientation) can lead to variations in relative intensities. In Figure B.5.26, note that the library clinoptilolite-Na spectrum produces a lower match score because it is missing some peaks in the unknown spectrum and contains extra peaks.

c) Consider if the chemical formula or measured chemistry of the matching library spectra is realistic for your unknown.
d) Consider the possibility that your Raman spectrum has sampled more than one mineral. In some cases, this can be evident if your spectrum contains both broad and narrow peaks, however, there are also some minerals whose Raman spectra inherently include a mixture of peak shapes. One option that could be helpful is, if your search/match software allows, to search on only a portion of your Raman spectrum – typically the region of the strongest peak. Then evaluate the results using a), b) and c) above.

If none of the mineral species on the search-match results list are a convincing match to the unknown, then your phase is not in the reference database (including a new mineral!), or the unknown spectrum is of too poor quality to match, or the unknown spectrum is a mixture from more than one phase.

B.5.3 Factors Affecting Match Success

Assuming your target mineral is in the reference database, the success of the search/match process can depend upon data collection parameters (e.g. calibration, resolution, etc.) and the proficiency of the match scoring algorithm employed by the software. Since Raman spectra can have a wide variety of peak shapes and peak overlaps are common, the match scoring algorithms employed generally use whole pattern matching - comparing intensity fluctuations across the entire spectrum.

Due to the whole-pattern matching approach any instrumental/sample factor that makes the Raman spectrum of a mineral look different from its reference spectrum can impact match success. This includes:

- Calibration error – results in systematic shifts in peak positions.
- Resolution Contrast – reference spectra are generally collected with instruments having spectral resolution in the range of 2 to 4 cm^{-1} so instruments having significantly lower resolution produce broader peaks.
- Instrumental noise – many peaks can be indistinguishable from noise in a low SNR spectrum.
- Crystallographic orientation – as previously described, orientation variations can result in major variations in relative peak intensities.

Only the last of these is exclusively sample dependent and strategies for reducing the impact of preferred orientation were described in section B.2.2. The remaining factors, calibration, resolution and noise, can all be remedied via a high-performance instrument and extra care in the data-collection process, however, these remedies come at a cost – high monetary expense, high level of training, and extended time investment. Users with limitations on these resources are going to want to know how much instrument performance is enough ? Towards this end the authors have conducted a Match Success Impact Factors study designed to quantify the impact of these factors as follows.

Match Success Impact Factors

The Test Set: A set of 77 Raman spectra was assembled representing 59 mineral species. About 50% of these were silicates but sulfides, oxides, carbonates, phosphates, halides, sulfates and tungstates were included as well. All species were independently verified and all of the spectra were from 2 instruments that are distinct from the instruments used to produce the reference spectra.

Reference Database: The reference library employed for match testing was a subset of the RRUFF database (see below) curated for data quality.

Spectrum Modeling: All spectra in the test set were modeled as the sum of pseudo-Voigt curves (one for each peak) thus both removing instrumental noise and reducing each spectrum to a mathematical formula.

Spectrum Simulations: All modeled spectra were mathematically modified to simulate the match-success factors as follows:

- Calibration Error: A constant was added or subtracted from the Raman-shift values.
- Resolution: The parameter controlling peak-width in the pseudo-Voigt formulas was increased to simulate specific levels of spectral resolution.
- Noise: A random-number generator was used and then the range of random values was fixed in order to simulate specific values of spectrum SNR.

Figure B.5.2 shows an example of the results. Here spectrum A is the original instrumental spectrum (from a talc), B is the modeled version, C simulates a calibration error of +4 cm^{-1}, D simulates a spectral resolution of 22 cm^{-1}, and E simulates a spectrum having an SNR of 20.

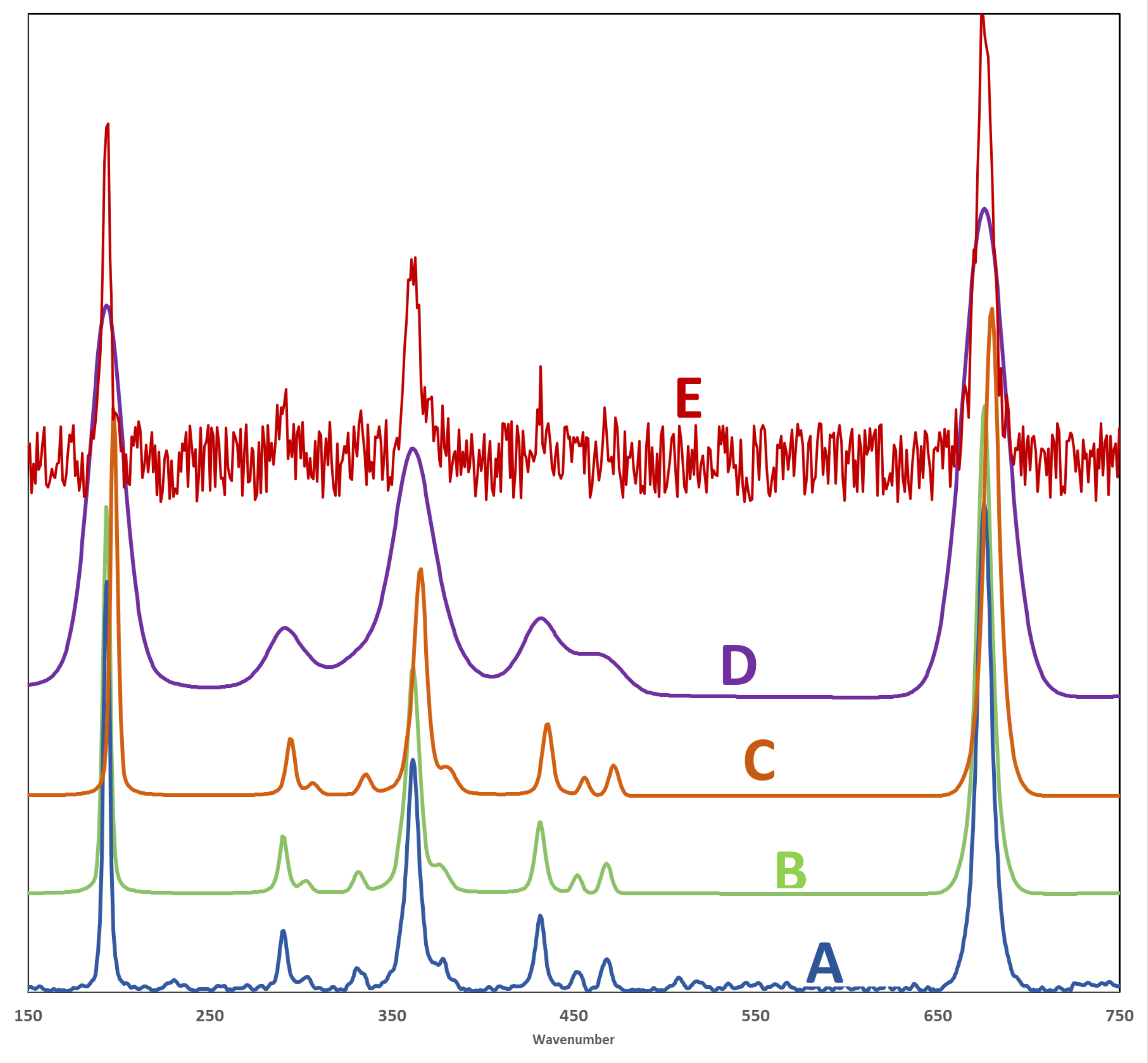


Figure B.5.2 Examples of modeled and simulated spectra for a Raman spectrum of a talc. See text for explanation.

Match Scoring: There are a wide variety of algorithms in use for the purpose of whole-spectrum match scoring and there is ongoing research on how to optimize match scoring for minerals in particular. Your instrument software and/or 3rd party spectroscopic software may or may not tell you which whole-spectrum matching algorithm they are employing so match proficiency becomes identified with the software product. It was not possible for this Match Success Impact Factors study to test a wide variety of software products so the authors chose 2 examples to test as follows:

- Program A: This is the free software available from the rruff.info website
- Program B: This is the software extension of JADE prepared by ICDD and MDI to accompany their own Raman reference library (see below).

Match Success Grading: The process of quantifying match success took into account that a) automated identification systems and many users may only look at the top/first match; b) the wrong end-member of a binary solid solution is very near identification success, and c) even another member of a mineral group (e.g. garnets, amphiboles, etc.) is useful information. Accordingly, for each member of the test set, and considering only the top match, success grades were assigned as follows:

exact match = 100
same series = 80
same group = 50
any other = 0

For each simulated impact factor (i.e. calibration error of +1) these grades were averaged for the entire test set to produce a success grade for that factor, and for each software program.

Study Results: In Figure B.5.3 the dashed line represents what we expect many users to consider the dividing line between acceptable and unacceptable match success performance at 90%. Each graph shows how match success falls off as the 3 impact factors vary away from the ideal. Of course, for SNR the ideal is a high number so deviation from the ideal progresses to the left on this graph. Note that Program B is significantly more tolerant of increases in all three impact factors.

Recommendations: This Match Success Impact Factors study shows that the right search/match software can accommodate a large range of instrumental and data collection performance. However, without knowing how tolerant of the impact factors your software is, you would be advised to:

- Employ an instrument/configuration that has a spectral resolution of 8 cm^{-1} or less.
- Recalibrate often to keep your calibration error at or less than 1 cm^{-1}.
- Employ configuration and data-collection parameters that will produce spectra whose SNR is at least 50.

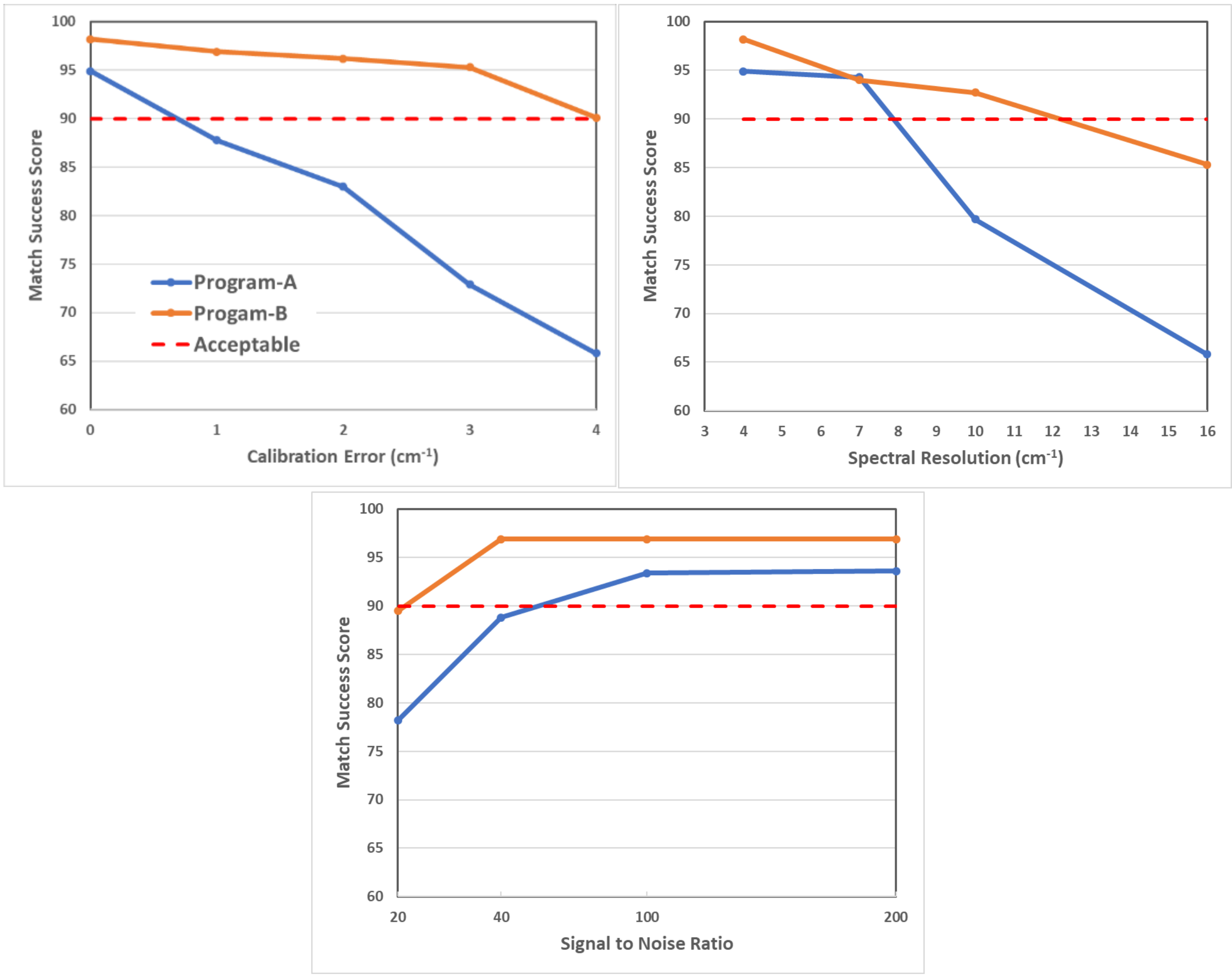


Figure B.5.3 Results of the Match Success Factors Study – see text for explanation.

B.5.4 The Reference Database

Of course, successful mineral identification via spectrum matching requires that the unknown is represented with a high-quality spectrum in the reference database. There is currently no Raman reference database that includes all known minerals, but, as is discussed below, there are several publicly and commercially available databases that have various strengths and shortcomings. It is obviously important to select a reference database(s) that includes the minerals of interest for a particular investigation.

Assessing Data Quality

A reference database should include information about each sample and spectrum, for example, sample locality, chemical composition, information about species validation, and spectrum data collection parameters. Additionally, it is important to know how the reference database was compiled. Were spectra evaluated/curated according to specified quality standards, or simply crowd-sourced without independent data-quality evaluation? Also, accurate search-match identification is facilitated if a database includes multiple spectra for the same species - from different compositions (for solid solution minerals), different orientations, and/or collected with multiple Raman laser wavelengths.

Available Databases

Existing commercial databases typically contain proprietary data, and/or publicly-available data that are formatted exclusively for their software, and accessible through a licensing agreement. Public databases might be the product of a specific analytical lab or program, or they may be "wiki" systems that allow anyone to post data, with or without editing or other quality controls. Some databases are specific to minerals, but others might include inorganic and organic compounds in various states (gas, liquid, etc.). Several examples of public databases are posted at:

http://www.irug.org/resources/spectral-databases-for-raman

Some of the databases listed on this page are reviewed below. Many of the available databases are static, and some are expanding slowly, or sporadically.

- Commercial databases: many Raman instrument manufacturers offer their own reference databases, and commercial databases offered by 3rd parties are available as well. Some are offered as part of the instrument purchase, and others must be purchased/licensed separately. The authors of this guide are, in fact, involved in the design, data standards and data collection of a Raman database that will be hosted and maintained by a non-profit company. Here a subscription fee will be used to ensure continuous growth, quality control, and longevity (see below).
- The RRUFF Project (https://rruff.info): This is the largest public database currently available for minerals. It was created by the University of Arizona under the direction of Bob Downs, and the original goal was to include powder X-ray diffraction data, electron microprobe analyses, Raman spectra, and powder ATR infrared spectra for every mineral species. While considerable progress was made, the database is not complete, and its use for Raman species identification has limitations due to the following:
  1) many spectra were collected from samples whose species identifications were not fully confirmed,
  2) spectra containing non-Raman features like REE luminescent peaks are not excluded or flagged,
  3) many spectra have SNR too low to be effective reference spectra,
  4) many species that are important for applied mineralogy are missing and many entries represent truly rare minerals that few geoscientists will ever encounter.
- Raman Open Database (ROD) (https://solsa.crystallography.net/rod/index.php): This is a wiki-style database allowing anyone to upload data. While it contains some mineral spectra, it also contains data for other types of crystalline solids, and its search criteria do not allow one to restrict results to minerals-only. The intended design of this database is to include crystallographic and chemistry

characterization of the sample by requiring cross-linking to a sample in the Crystallography Open Database (COD). In practice, however, some Raman spectra are being posted by linking to a COD record that is for a sample different than the one used to acquire the Raman data. This is particularly problematic for solid solution minerals.

- Other Public Databases: There are additional public databases, but most have limited mineral entries, or they focus on compounds that have limited overlap with minerals.

Towards the Future

The shortcoming of free/public databases is lack of longevity for both data quality management and data availability. Most of the commercial databases lack any drive to continue their growth in species representation. The authors have partnered with ICDD (International Center for Diffraction Data) to produce a Raman reference database that is designed specifically to enable and support routine mineral identification.

The backbone of the database design is a quantified scale of "likelihood of encountering" that is based upon a) a published list of "rock forming minerals", b) locality counts from mindat.org that take into account man's incentive to seek out some minerals, c) a USGS list of critical minerals, and d) requests from academic geoscientists. Accordingly, both the initial contents and the growth progress for this spectral database are prioritized by how common or how commercially or academically important each mineral is (focusing on the truly rare minerals last).

While access to this database requires a subscription fee, ICDD is a non-profit company so this fee will go entirely to support longevity of availability, continuous data quality control, and continuing drive to grow the database towards the "all known minerals" objective.

B.6. Estimating Solid Solution Composition

Section A.3 introduced the concept that variation in chemistry of solid-solution minerals can result in shifts in the position of Raman peaks. These peak-shifts can be used for estimation of composition within a solid solution once the magnitude and direction of Raman peaks shifts have been calibrated. In a process very similar to PXRD solid-solution calibrations, Raman spectra are gathered on a series of samples of known composition, peak positions are measured, and then mathematical calibration curves are fit to this data. Estimating the composition of your unknown then requires determining accurate peak positions in your own Raman spectrum and applying these to the published calibration curves.

It is reasonable to ask whether it would work just as well to place the Raman spectra from solid-solution minerals of known composition into the reference database and count on the match scoring algorithm to identify the reference spectrum with the right composition. The weakness of this approach is due to the fact that the Raman peaks that most strongly shift with composition are often minor peaks in the spectrum and match-scoring algorithms always place the most weight on the strongest peaks in the spectrum.

B.6.1 Quantifying Peak Positions

While most spectroscopic software packages include some version of a peak-finder function, these are not generally adequate for accurately determining Raman peak positions. Typically, peak-finder routines depend upon reversals in the slope of the spectrum, and as a result they commonly miss shoulders on larger peaks. In order to accurately quantify peak positions in situations where there are severe peak overlaps, it is necessary to model the spectrum as a series of mathematical peak curves. The best peak shape to use is a Voight (or pseudo-Voight) function, since the shape of Raman peaks is a mixture of Lorentzian and Gaussian curves.

Figure B.6.27 shows the Raman spectrum of an andradite that has been analyzed with both a peak finder function (using Spectragryph) and a curve-fitting system (using Fityk), and Table B.6.1 lists the peak positions determined by each method. Notice that the peak-finder missed the major overlapping peaks and confused some background noise with peaks. Also, even in cases where both routines found the same peaks, the peak positions differ by up to 3 cm^{-1}.

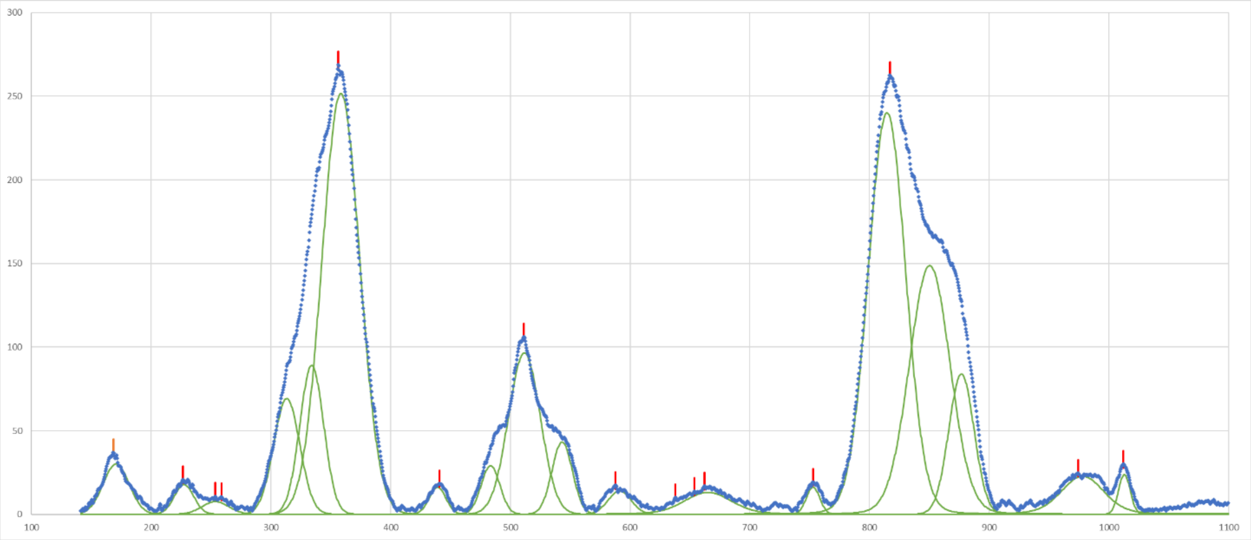


Figure B.6.27. Raman spectrum of an andradite that has been analyzed for peak positions. Short red lines mark peak positions identified by a peak-finder routine and green curves are Voight-shaped peak-curves determined by a peak-fitting routine.

Table B.6.1 Peak positions (in cm^{-1}) determined by a curve-fitting system and a peak-finding function. See text for discussion.

Curve Fitting	Peak Finding	Difference
170.7	168.5	2.2
227.4	226.7	0.7
253.7	253.6	0.0
	258.8	
313.2		
334.1		
358.4	356.5	2.0
439.2	440.7	-1.5
483.4		
511.7	511.3	0.4
543.2		
591.3	587.7	3.6
	637.9	
	653.9	
665.0	662.1	2.9
752.8	753.0	-0.2
814.5	817.2	-2.7
850.3		
876.7		
977.9	974.3	3.6
1012.8	1012.1	0.7

The process of employing a curve-fitting/spectrum modeling software routine generally is interactive. Modeling and removing baseline intensity must be completed first and there is often a tool for manually adding peaks that the software doesn't find on its own. Look to see if your instrument software includes a peak fitting option before looking for a 3rd party software that offers this functionality.

B.6.2 Raman calibrations of Mineral Solid Solutions

Typically, solid solution composition estimates require referencing publications that present Raman calibrations. Following is a listing and brief description of several Raman calibrations that have been published to date.

- Mg-Fe Olivines: Kuebler et al., 2006, present a calibration of Mg-Fe olivine composition based upon the 2 strongest peaks in the olivine spectrum. Mouri & Enami, 2008 explore the effects of adding Mn, Co, and Ca to the olivine structure, but their calibration is still only for Mg-Fe olivines.
- Quadrilateral Pyroxenes: Huang et al., 2000, investigate the Raman peak positions within the so-called quadrilateral pyroxenes. They graphically present the trends in peak position and discuss the potential for estimating composition but don't offer specific formulas to apply to Raman peak positions for this purpose.
- Plagioclase Feldspars: Bersani et al., 2018, present a calibration of the plagioclase feldspars that takes into account the impact of variations in structure/point-group. The calibration is based upon both peak positions and peak widths. The authors recognize that peak-width is going to be instrument-dependent and present a method of calibrating the peak-broadening of the instrument.
- Garnets: Smith, 2005, presents a generalized method called RAMANITA for producing Raman calibrations of solid solution minerals and then applies this method to the pyrope-almandine-spessartine-grossular-andradite garnets. Bersani et al., 2009, present their own calibration of the same range of garnet compositions with the objective of achieving composition estimation with a less complex procedure and with Raman data alone. Their system is dubbed MIRAGEM.
- Zn-Fe Sphalerites: Osadchii & Gorbaty, 2010, studied the Raman spectra and lattice parameters (via XRD) of a series of synthetic sphalerites of varying Fe contents. They propose that their data could be used as a calibration for sphalerite composition estimation, but their calibration is based on a ratio of Raman peak intensities. While they have minimized the role of crystallographic orientation on their data collection by averaging spectra from several randomly oriented grains, it is unlikely that their intensity-ratio calibration will be applicable on another Raman instrument or another laser wavelength.
- Carbonates: Rividi et al., 2010, studied the Raman spectra of Ca-Mg-Fe carbonates of known composition and produced, and tested, Raman peak-position calibrations of the siderite-magnesite solid solution and the dolomite-ankerite solution.

- Titanomagnetites: Zinin et al., 2011, studied the Raman spectra of a series of titanomagnetites and propose a calibration for determining the Fe-Ti composition. However, this is another calibration that is based upon intensity ratios and it is unclear the extent to which this calibration can be applied with a different instrument or a different Raman laser due to variations in relative peak intensity that can be expected to accompany such experimental variations.
- Mg-Fe Calcic Amphiboles: Bersani et al., 2014, studied the Raman spectra of a series of amphiboles along the tremolite-ferro-actinolite join and develop 2 calibrations for estimating X_{Mg} within this solid solution. Their intent is to have a calibration for estimating the composition of nephrites.

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Appendices

Appendix 1: Minerals Known or Predicted to have No Raman Peaks.

The following table lists those minerals which are expected to have zero Raman active modes. Note that solid solution, impurities and structural defects may result in one or more Raman modes becoming active in these minerals.

This list was produced by downloading 14736 crystal structures in CIF format from the American Mineralogist Crystal Structure Database (http://rruff.geo.arizona.edu/AMS/amcsd.php) and then using the Vibrate! Computer program by Michael Glazer (https://www.amg122.com/programs) to calculate the number of IR and Raman active vibrations predicted for each structure.

Note that there may be minerals that should be included in this list but are missing because their crystal structure is not represented in the American Mineralogist Crystal Structure Database. However, these omissions generally are rare minerals.

Mineral	Formula	Mineral	Formula
Alabandite	MnS	Monteponite	CdO
Altaite	PbTe	Nantokite	CuCl
Aluminium	Al	Nickel	Ni
Atokite	$(Pd,Pt)_3Sn$	Nickeline	NiAs
Atokite	Pd_3Sn	Niningerite	MgS
Auricupride	$AuCu_3$	Niobocarbide	NbC
Awaruite	$FeNi_3$	Nisnite	Ni_3Sn
Awaruite	Ni_3Fe	Oldhamite	CaS
Bogdanovite	Au_3Cu	Osbornite	TiN
Bromargyrite	AgBr	Osmiridium	(Ir,Os,Ru)
Bunsenite	NiO	Palladium	Pd
Carlsbergite	CrN	Periclase	MgO
Carobbiite	KF	Platinum	Pt
Chengdeite	Ir_3Fe	Potarite	HgPd
Chlorargyrite	AgCl	Pyrrhotite	Fe_7S_8
Chromium	Cr	Rhodium	Rh
Clausthalite	PbSe	Rustenburgite	$(Pt,Pd)_3Sn$
Cobalt	Co	Schreibersite	$(Fe,Ni,Cr)_3P$
Copper	Cu	Silver	Ag
Cuboargyrite	$AgSbS_2$	Skaergaardite	CuPd
Ferronickelplatinum	Pt2FeNi	Steinhardtite	Al
Galena	PbS	Suessite	$(Fe,Ni)_3Si$
Gold	Au	Sylvite	KCl
Griceite	LiF	Tantalcarbide	TaC
Halite	NaCl	Tantalum	Ta

Hapkeite	Fe_2Si	Tetraauricupride	AuCu
Indium	In	Tetraferroplatinum	FePt
Iridium	Ir	Tetrataenite	FeNi
Iron	Fe	Tin	Sn
Isoferroplatinum	$FePt_3$	Titanium	Ti
Keilite	(Fe,Mg)S	Tulameenite	Pt_2CuFe
Khamrabaevite	TiC	Tungsten	W
Kitagohaite	Pt_7Cu	Uakitite	VN
Lafossaite	TlCl	Vanadium	V
Lead	Pb	Villiaumite	NaF
Lime	CaO	Wairauite	CoFe
Miersite	AgI	Wustite	FeO
Molybdenum	Mo	Yixunite	Pt_3In
		Zvyagintsevite	Pd_3Pb