

## THE ROLE OF INTENSITY AND INSTRUMENT SENSITIVITY IN RAMAN MINERAL

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**Introduction:** Raman spectroscopy (RS) has proven to be a powerful tool for geoscience research applications that would have been impossible otherwise. The very features that make RS a powerful cutting-edge research tool also give it the potential to be a powerful and widely accessible tool for applied mineralogy and petrology in industrial, educational, and traditional research applications. While RS will not replace XRD for characterizing crystal structures, its non-destructive nature, ability to work in-situ and potential to be both smaller and less costly than XRD give RS the potential to provide the same brand of fingerprint-style routine mineral identification as XRD yet be faster, cheaper and utilizable in the field and in thin section. This translates into expanded availability and use of this brand of geoscience investigation in both industry and smaller geoscience departments.

Despite its potential, RS has not been widely adopted by geoscience industry professionals, educators and researchers. The resistance to universal adoption likely stems from a number of factors including lack of confidence, lack of guidance, and lack of geoscience-customized instrumentation. The latter should naturally follow if the first 2 sources of resistance are resolved. In order to improve confidence in the RS option for routine mineral identification it must be established, as quantitatively as possible, just how accurate and dependable the technology/methodology is. A recent study [1] showed, quantitatively, that the accuracy of RS for fingerprint-style mineral identification can be comparable to powder XRD – if the impact/incidence of photoluminescent (PL) interference can be reduced or resolved.

While ongoing research seeks to reduce the impact of PL interference, there are other challenges of employing RS for mineral identification that require specific methodology and guidance. Such guidance needs to be as detailed/quantitative as possible and formally published rather than communicated by word-of-mouth or existing only in unpublished form. The additional challenges include working with minerals that are weak Raman scatterers, addressing the role of crystallographic orientation, working with minerals vulnerable to laser damage, and choosing a suitable instrument. The purpose of the current study is to a) provide some concrete guidance as to the range of Raman intensity that can be expected from minerals, and b) pro-

vide some guidance for the instrument sensitivity required for mineral identification. In order to develop this guidance this study investigates a) ranges of Raman intensity that can be expected from minerals, b) the impact of random spectral noise (e.g “shot noise” and random electronic noise) on mineral identification, and c) the impact of instrument sensitivity on mineral identification.

### Methods:

*Raman Intensities of Minerals:* A subset of the Raman spectra stored in the RRUFF database ([www.ruff.info](http://www.ruff.info)) consisting of those spectra taken from randomly oriented samples and processed to remove background and edge and instrument artifacts was downloaded (8629 spectra). A combination of Python and Windows scripts was employed to extract the maximum peak height and RMS background noise level for each spectra. The resulting table of spectral data was joined to a table of RRUFF database data associated with each spectrum including mineral name, instrument, laser wavelength, exposure time, and spectrum-quality. Also joined to this table, by mineral name were additional mineral data items downloaded from [www.webmineral.com](http://www.webmineral.com) including Strunz Class, Group and Family, point group, crystal system, luster, color, and diaphaneity. Derived spectral characteristics were produced such as normalized peak intensity (counts per second per mW) and S/N ratio (for the highest peak in each spectrum). Since the significance of peaks above the continuum is of concern here the “noise” level used to calculate S/N was 2 x RMS. RRUFF spectrum-quality data combined with derived spectral characteristics and visual inspection were employed to remove from the data table spectra that were dominated by PL interference or had very weak peak expression. For the purposes of comparing typical Raman (strongest peak) intensity for each mineral, average normalized intensities were derived for each instance where spectra were taken from multiple samples of the same mineral. Since each instrument has its own unique performance characteristics, only multiple spectra taken from the same instrument (and the same excitation laser) were averaged together.

*Impact of Random Noise:* The impact of random noise was investigated by mathematically adding simulated random noise to a few spectra representing some of the challenges of RS mineral identification and ex-

aming the impact on search/match identification using the RRUFF distributed CrystalSleuth software. Examples included: aragonite – distinguishable from calcite primarily upon minor peaks, magnetite – a relatively weak Raman scatterer, and spessartine - structurally similar to a number of other garnet species. In each case one representative spectrum was taken from the RRUFF spectra, simulated noise was added to reduce the S/N of the spectra to 100, 20, and 10, and these simulated spectra were put through the CrystalSleuth search/match algorithm (ignoring any matches to itself). For magnetite a simulated spectra with a S/N of 5 was included.

**Impact of Instrument Sensitivity:** Additional spectra on common mineral species (e.g. quartz and pyrite) were gathered on 2 representative (product line, non-customized) Raman instruments available locally. One instrument was a Raman microscope with a 14mW 780nm laser and the second instrument was a semi-portable fiber-optic-probe style instrument with a 50mW 532nm laser. The fiber-optic machine was found to have a lower sensitivity so longer counting times were required, especially in order to achieve clear peak definition on the pyrite. The spectra were processed and normalized highest-peak intensities and S/N ratios were calculated.

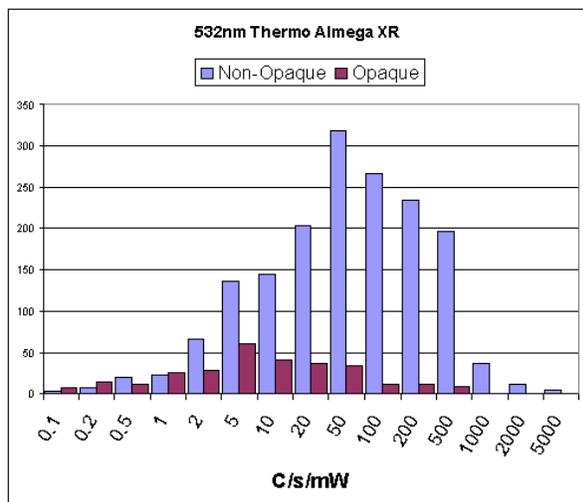


Figure 1. Histogram showing range of normalized Raman intensities for primarily opaque and nominally non-opaque minerals.

**Results:**

**Raman Intensities of Minerals:** Since every instrument has its own spectroscopic performance, comparison of mineral intensities with each other can only be accomplished by comparing spectra from a single instrument. Figure 1 is a histogram of normalized Raman intensities of 1957 spectra from the spectral collection described above that are all from the 532nm Almega

XR at the RRUFF lab at the University of Arizona. Primarily opaque and nominally non-opaque minerals are displayed separately. Note the pseudo-logarithmic scaling of the X axis. While specific intensities will be somewhat different on different Raman instruments, the user guidance contained in this graph includes: a) the data-gathering methodology must be able to adapt to intensity variations from mineral to mineral that could span 4 orders of magnitude, and b) for opaque minerals Raman intensities are generally going to be 1 order of magnitude lower than non-opaques. Many of the weakest Raman scatterers are opaques yet a number of opaques actually produce strong Raman intensities.

**Impact of Random Noise:** Random noise had minimal impact on the results of search/match mineral identification.

**Impact of Instrument Sensitivity:** For a Raman instrument signal sensitivity stems from the combination of the solid angle of light collection above the sample, light losses on the way into the spectrometer, grating efficiency and detector sensitivity. For the spectra gathered for this study the Raman microscope was found to have over 100 times the sensitivity of the fiber-optic instrument. For the latter, although distinct Raman peaks were produced from the pyrite by extending counting time, spectral features left behind after background removal (minor variations in detector behavior not normally visible) prevented the whole-spectrum matching algorithm that CrystalSleuth uses from succeeding for this pyrite spectrum. As much as more expensive instruments devote more technology to reducing electronic noise, instrumental sensitivity appears to be a more important factor for mineral identification, especially if routine identification of opaque minerals is essential. Unfortunately it is currently very difficult to turn this experience into guidance for the prospective RS user since instrument manufacturers currently use a variety of standards and practices for reporting spectrometer sensitivity. It would help the geoscience community if a geoscience-relevant sensitivity standard could be agreed upon and offered to instrument manufacturers for voluntary measurement.

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**References:** [1] Bartholomew, P.R. (2013) *Geostand. & Geoanal. Res.*, 37, 353-359.