Quantifying Mineral Abundances in Mixtures Using Raman Spectroscopy: Toward a Method for Spectral Unmixing

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Spectral Unmixing

The process of separating out pure phases from a spectrum acquired from a heterogeneous sample.

Existing Approaches

Several unmixing techniques exist for reflectance and thermal emission spectroscopy:

- Radiative transfer (RT) theory can be applied to nonlinear spectral mixing and extracting quantitative mineral abundances in the VNIR.
- Multiple scattering models can provide approximate numerical or analytical solutions to the RT in a particulate medium.

Raman Spectral Unmixing

No analogous methods exist for unmixing Raman spectra.

- Most development work has focused on micro-Raman techniques that probe pure minerals, so unmixing isn't an issue.
- Impending use of cm-scale Raman spectroscopy on Mars by SuperCam will require new techniques for unmixing.

Data

The following experiments used two sets of Raman spectra.

Mineral Mixtures

- 322 Raman spectra of binary mineral mixtures in varying proportions, plus 46 spectra of pure samples.
- 24 unique endmembers of common mineral species.
- All samples were crushed, handpicked for purity, and sieved to grain sizes <64 mm, then verified X-ray diffraction.
- All spectra were averaged over three 10-second scans , collected with a BRAVO spectrometer from Bruker Optics, Inc.
- 80 mixtures included diamond as one of the endmembers, as diamond's Raman spectrum is relatively simple to distinguish.

The 24 pure mixture components used were: alunite, anhydrite, augite (clinopyroxene), bytownite (feldspar), calcite, clinochlore (chlorite), diamond, diopside (clinopyroxene), enstatite (orthopyroxene), forsterite (olivine), gypsum, hematite, ilmenite, jarosite, rozenite, labradorite (feldspar), magnesite, magnetite, montmorillonite, nontronite, saponite, siderite, tremolite, and chabazite (zeolite).

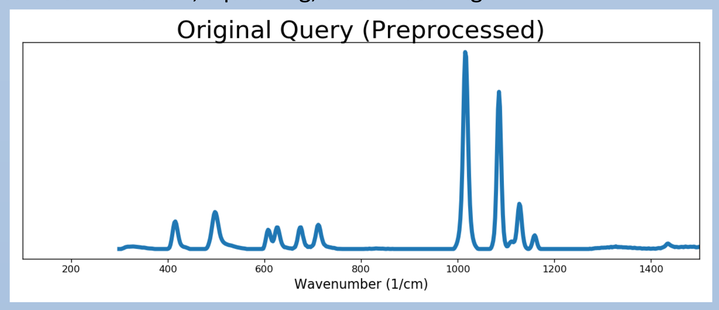
RRUFF Subset

- 4019 Raman spectra of pure minerals, each confirmed by X-ray diffraction, downloaded from the RRUFF database.
- 1231 mineral species are represented, including each of the 24 species present in the mixtures dataset.
- Each spectrum was baseline corrected and preprocessed by the RRUFF team, prior to download.

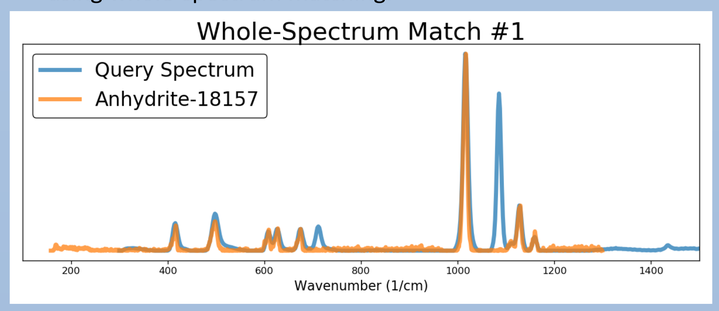
Method

Given a query spectrum of an unknown binary mixture:

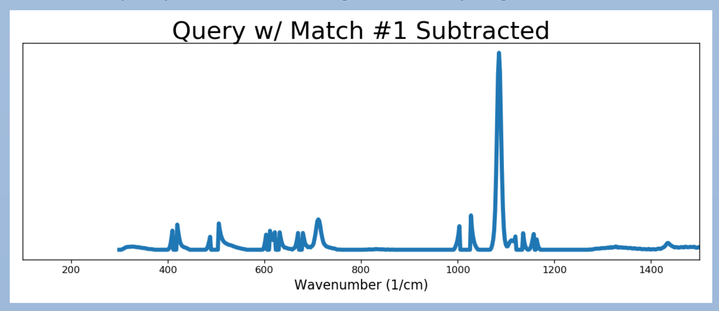
1. Preprocess the query: perform baseline correction, normalization, squashing, and smoothing.



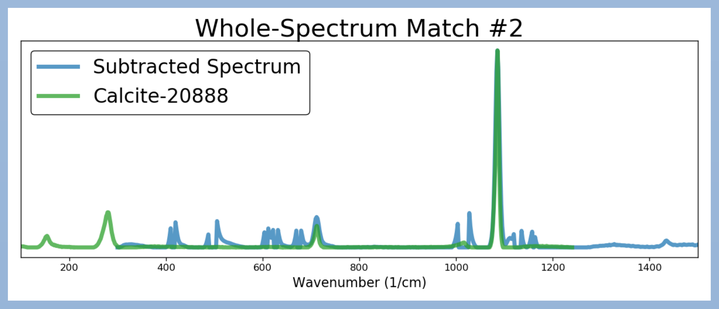
2. Search for the top k matching spectra in the target library using whole-spectrum matching.



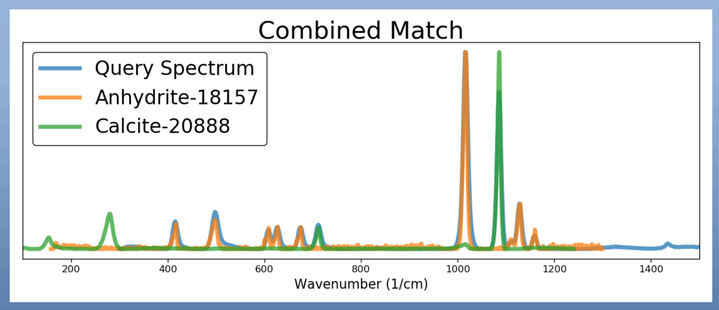
3. For each potential match, M:
   a. Compute regions of wavenumbers with high similarity between the query and M.
   b. Set query intensities in high-similarity regions to zero.



   c. Search again for the top k matching spectra in the target library, this time using the modified query spectrum.



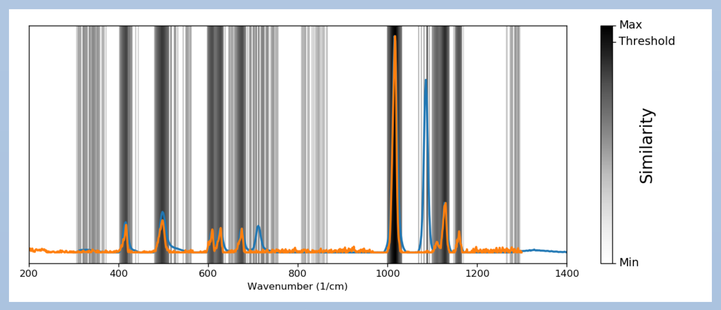
4. Rank the resulting k^2 pairs of matches by the product of their constituent matches' similarity scores.



Finding High-Similarity Regions

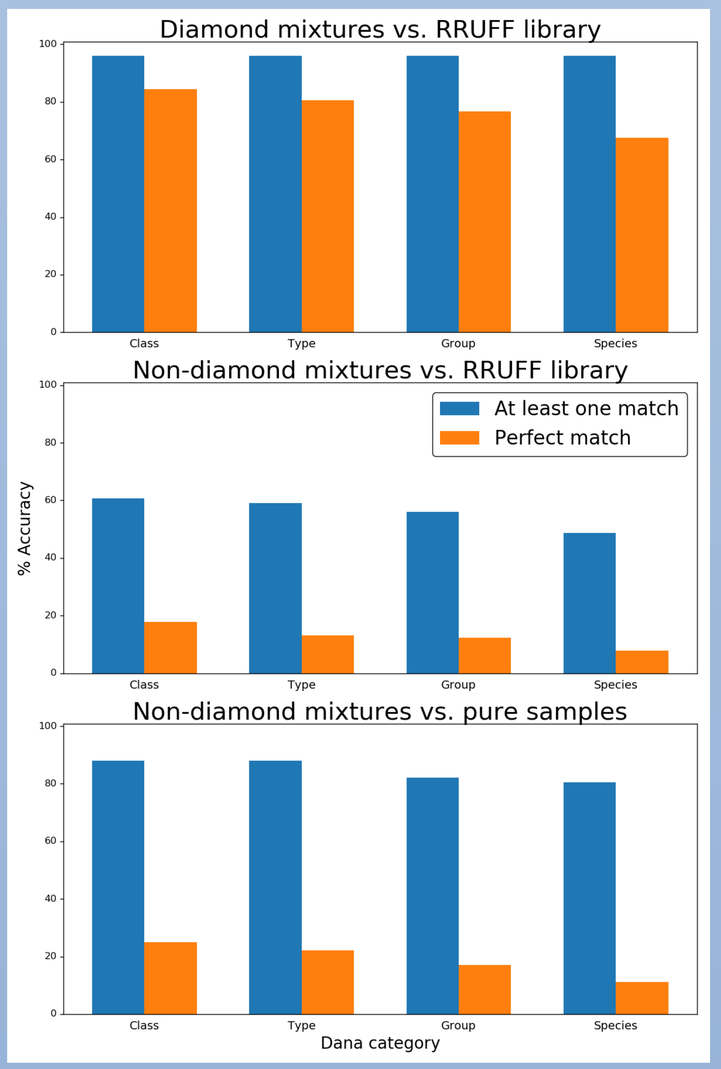
For a given pair of spectra (A, B), compute a local similarity score for each wavenumber in A:

$$\mathrm{Sim}(y_A, y_B) = (1-w)y_A y_B - w|y_A - y_B|$$



A simple threshold (e.g., 95th percentile) can be used to define the boundaries of the high-similarity regions.

Results: % Accuracy in Top 5 Pairs



Conclusion

Our method produces the correct pair of endmember species in the top 5 results for 67.5% of diamond mixtures. It struggles with the harder case of non-diamond binary mixtures, though using a more selective search library does improve performance.

Acknowledgements

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