Multivariate Curve Resolution (MCR) and PARAFAC Analysis of Infrared Specular Reflection Spectra of Quartz Particles: Strategies for Optimal Surface Sensing

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Session 17IR04: Practical Implementation of Diffuse Reflectance Spectroscopy
Location: Carson 1
Time: 3:50 pm

Infrared reflectance measurements have been used extensively to characterize soil samples, and the ability to acquire measurements at multiple angles promises to improve measurement selectivity, and separate physical (e.g., particle size, shape, packing density, etc.) and chemical information. It also provides the potential to enhance detection and characterization of anomalies and targets of interest. This study made infrared reflectance measurements of quartz samples with five narrow particle size ranges, three soil samples, and a piece of sandpaper using an FTIR and specular reflectance accessory. The measurements were made at twelve different angles of incidence. Light from the spectrometer was partially polarized.
Although classification approaches can be based on a large number of available algorithms (e.g., PLS-DA), multivariate curve resolution (MCR) and parallel factor analysis (PARAFAC) have the unique ability to provide highly interpretable results. Interpretability is afforded because MCR is based on the classical least squares (CLS) model while PARAFAC can be considered a multi-linear CLS model and is a distinct advantage because it provides confidence in the underlying model and can be used to tune the model using a priori information (e.g., library measurements). This talk with show the results for a set of measurements on quartz and soil samples and compare MCR and PARAFAC results.
The analysis shows optimal angle of incidence ranges for different particle sizes where contrast between volume scattering and Reststrahlen regions can be increased, thus improving detection of chemicals that may be on those materials.

Introduction

- Measure laboratory specular infrared reflectance spectra of sands and soils
- Use MCR and PARAFAC to analyze spectra
- Determine component spectra of materials with respect to particle size and light incident angle
- Use results to inform strategies for active sensing of soils and chemical spills on soils in field

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Experiment

- Laboratory measurements made with specular reflectance accessory and FTIR
- Mid-infrared spectral measurements 5500 to 600 cm^{-1}
- Sand and soil samples packed into small troughs
- Spectra recorded at specular angles 15° to 70° in 5° steps
- Monodispersed quartz sands, quartz-dominant soils (NV clay and Quincy) and clay-dominant soil (League)
- Multiple replicate measurements for each material

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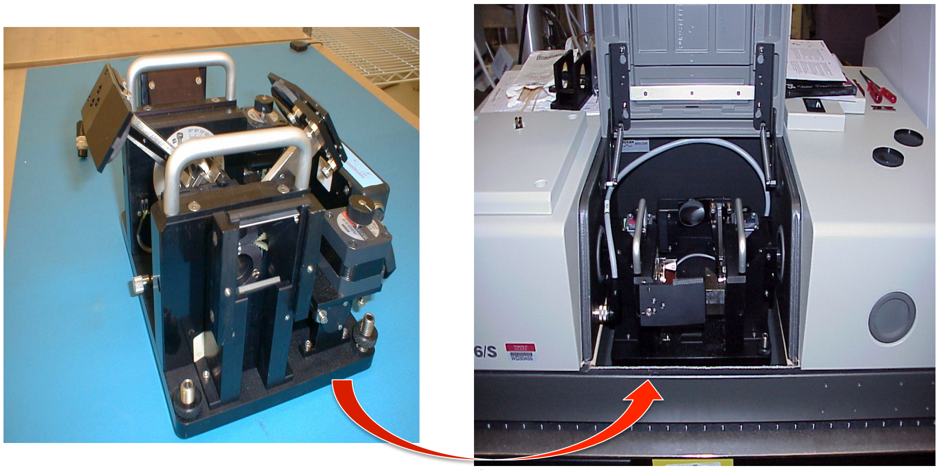
Specular Reflectance Accessory and FTIR



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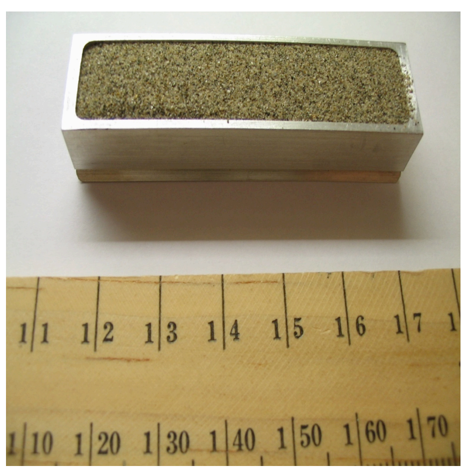
Sample Trough



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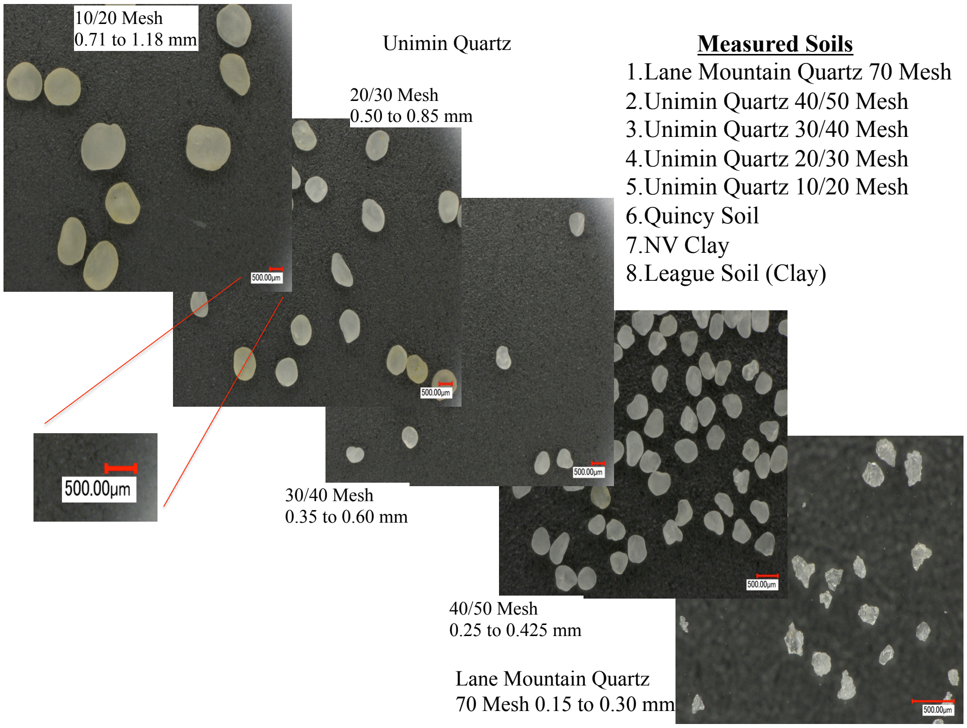
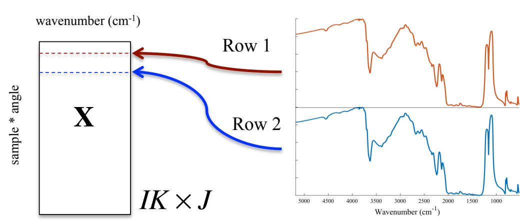
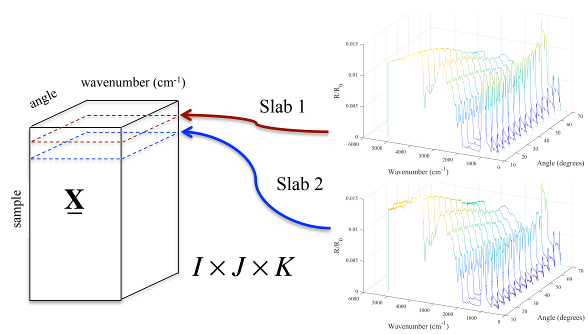


Measured Soils

1. Lane Mountain Quartz 70 Mesh
2. Unimin Quartz 40/50 Mesh
3. Unimin Quartz 30/40 Mesh
4. Unimin Quartz 20/30 Mesh
5. Unimin Quartz 10/20 Mesh
6. Quincy Soil
7. NV Clay
8. League Soil (Clay)



The two-way matrix is M by J where $M=IK$ is the (number of total spectra) = (number of samples) * (number of measured angles per sample) and J is the (number of wavenumbers).



The three-way matrix is I by J by K where I is the (number of samples), J is the (number of wavenumbers) and K = (number of measured angles per sample).

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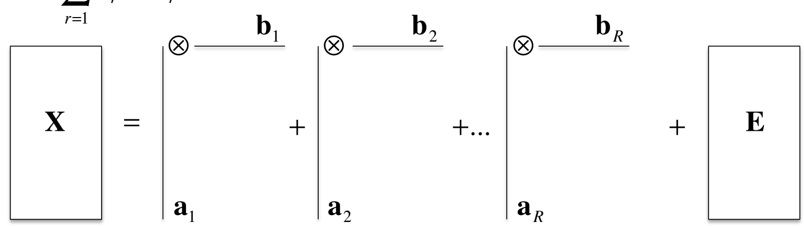
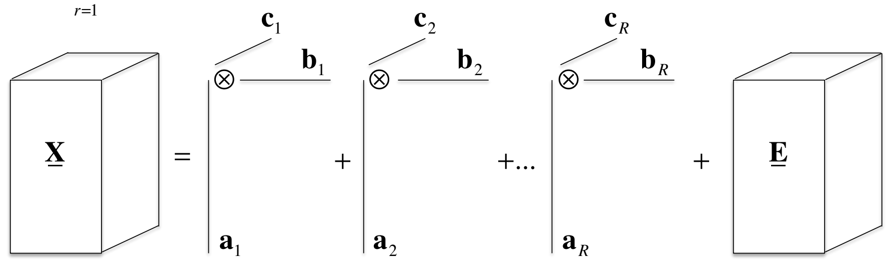
$$\mathbf{X} = \sum_{r=1}^{R} \mathbf{a}_r \otimes \mathbf{b}_r + \mathbf{E}$$



$$\underline{\mathbf{X}} = \sum_{r=1}^{R} \mathbf{a}_r \otimes \mathbf{b}_r \otimes \mathbf{c}_r + \underline{\mathbf{E}}$$



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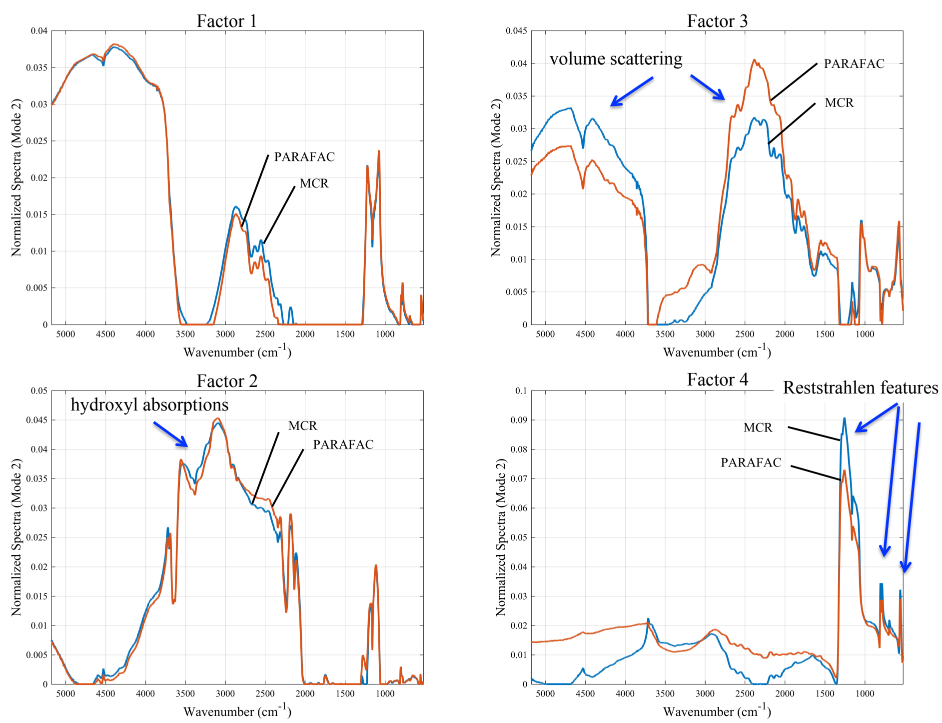
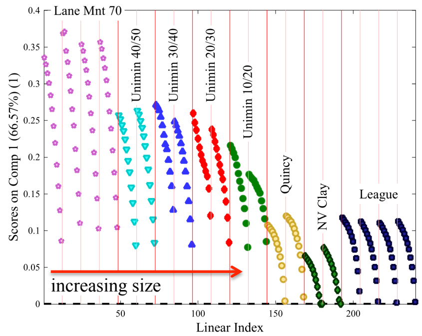
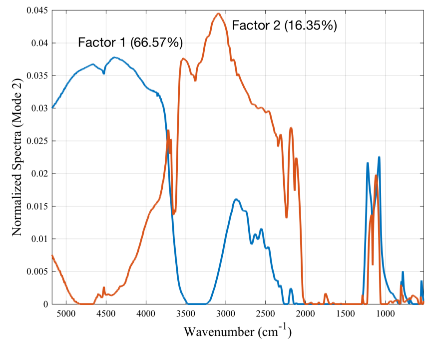
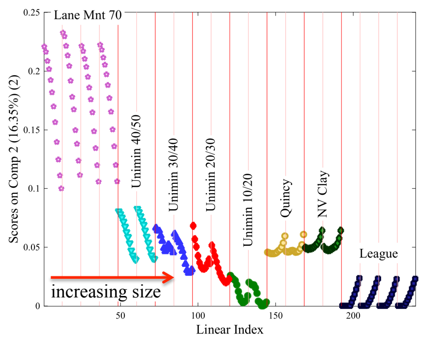


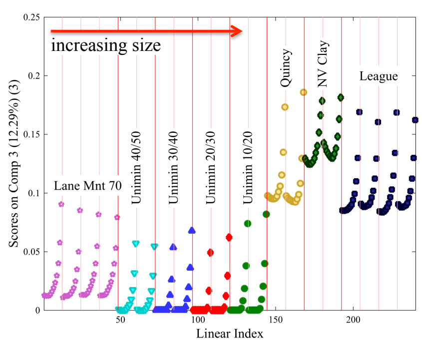


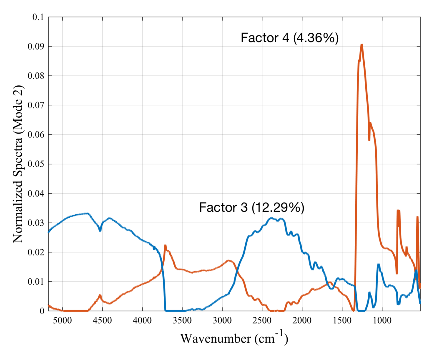


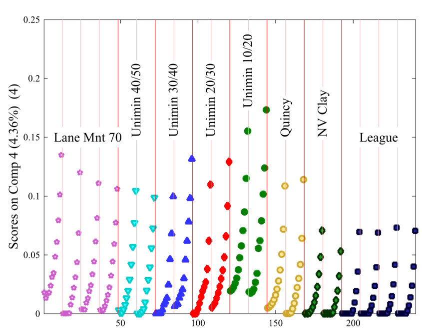


MCR results for Factors 1 & 2.

- Factor 1 decreases with angle for all soils.
- Factor 2 decreases with angle for the small Unimin, shows a minima for larger Unimin and increases with angle for other soils.
- The mean for Factor 1 & 2 tend s to decrease with size.

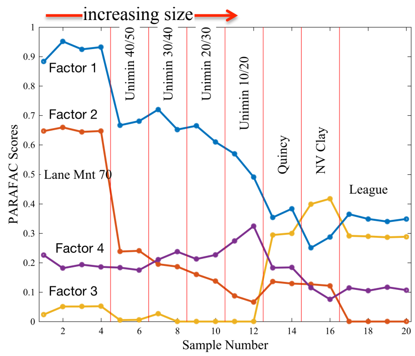


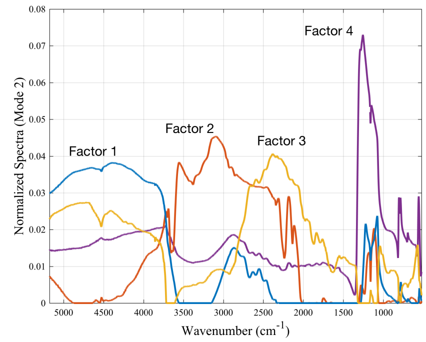


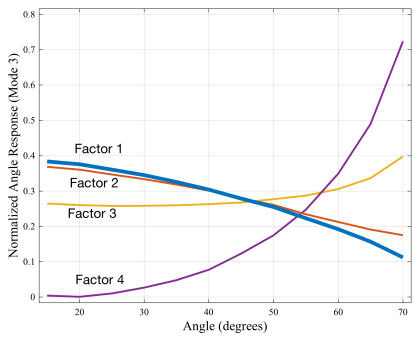


MCR results for Factors 3 & 4.

- Factor 3 & 4 tend to increase with angle for all soils but Quincy, NV Clay and League show a shallow minima.
- The mean for Factor 3 is higher for Quincy, NV Clay and League but no apparent trend for Unimin size (70 is a little higher, the smallest size).
- The mean for Factor 4 shows no apparent trend but is a little higher for Unimin 10/20 (the largest size).







PARAFAC results for Factors 1 to 4.

- Factor 1 decreases with size and decreases with angle.
- Factor 2 high for smallest size (Unimin 70) and not present for League. It decreases with angle, similar to Factor 1.
- Factor 3 is not significant in Unimin and is present at a similar level for Quincy, NV Clay and League. It increases slightly with angle.
- Factor 4 is about the same level for all soils (slightly higher for Unimin). It increases significantly with angle.

Model Comparison

Model Property	MCR	PARAFAC	Comment
Multiplicative Ambiguity	yes	yes	Resolvable with constraints or standards
Permutation Ambiguity	yes	yes	(trivial problem)
Rotational Ambiguity	yes	no	data dependent: MCR requires selective data PARAFAC requires tri-linearity

- MCR has more parameters = {(I samples)*(J angles)+(K wavenumbers)}*(R Factors) and is therefore more flexible.
  However, interpretation can be more difficult because the samples and angles are "convolved."

- PARAFAC has fewer parameters = {(I samples)+(J angles)+(K wavenumbers)}*(R Factors) and is therefore more restrictive.
  Interpretation can be easier because the samples and angles are "not convolved."

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Conclusions

- MCR and PARAFAC methods were used to analyze infrared reflectance spectra of soils and the estimated spectra (Mode 2) were similar for both methods
  - MCR more flexible and potentially prone to rotational ambiguity
  - PARAFAC results are easier to interpret
- Estimated spectra show separation into volume scattering and Reststrahlen features
- The Reststrahlen spectrum is largely independent of particle size and increases significantly with angle of incidence
- Liquid films on soils with absorptions coincident with Reststrahlen features may show significant contrast than at other wavenumbers and better detectivity at near grazing angles.