Objective of the Study

Proof-of-principle: Can Mid-IR diffuse reflectance spectroscopy be used to separate/differentiate minerals of interest (MOI)?
- Can it also do so in the presence of ubiquitous interferences?
- Potentially fast, non-invasive tool for monitoring raw materials in mining applications
Model Calibration & Test

A Classical Least Squares (CLS) model was calibrated on 22 mixtures of known composition:
- spectra measured at 7490 to 650 cm\(^{-1}\) @ 1.4 cm\(^{-1}\) increments
- range of interest: 5500 to 2996, 2829 to 1121 cm\(^{-1}\)
- \(\log_{10}(R)\), 1\(^{st}\) derivative [SavGol(25,2,1)], 1-Norm
- XRD (vol %) first guess of contributions
- Multivariate Curve Resolution (MCR) tuned up the model

Additional 28 samples available for testing:
- known interferences (no MOI / composition unknown)
- possible minerals of interest
  - mixtures with low or ~unknown composition

CLS (& ELS)

Classical least squares (CLS) is a linear mixture model.
The Extended Mixture Model (Extended Least Squares) can be used to account for interferences.

Model:

\[ x = Sc + e \]

\[ x = Sc + Pt + e \]

**contributions**
- spectra of constituent minerals
- a single measured spectrum of a mixture

**spectra or basis for interferences**
### Interferences and Minerals of Interest (MOI)

<table>
<thead>
<tr>
<th>Number</th>
<th>Mineral Name</th>
<th>Formula/Description</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Calcite</td>
<td>CaCO$_3$</td>
<td>ubiquitous interference</td>
</tr>
<tr>
<td>2</td>
<td>Silica</td>
<td>SiO$_2$</td>
<td>ubiquitous interference</td>
</tr>
<tr>
<td>3</td>
<td>Gypsum</td>
<td>CaSO$_4$·2(H$_2$O)</td>
<td>ubiquitous interference</td>
</tr>
<tr>
<td>4</td>
<td>Malachite</td>
<td>Cu$_2$(CO$_3$)(OH)$_2$</td>
<td>mineral of interest</td>
</tr>
<tr>
<td>5</td>
<td>Na-boltwoodite, Boltwoodite</td>
<td>(K,Na)(UO$_2$)(SiO$_2$OH)·1.5(H$_2$O)</td>
<td>mineral of interest</td>
</tr>
<tr>
<td>6</td>
<td>Autunite</td>
<td>Ca(UO$_2$)$_2$(PO$_4$)$_2$·6(H$_2$O)</td>
<td>mineral of interest</td>
</tr>
<tr>
<td>7</td>
<td>Cuprosklodowskite</td>
<td>Cu[(UO$_2$)(SiO$_2$OH)]·6(H$_2$O)</td>
<td>mineral of interest</td>
</tr>
<tr>
<td>8</td>
<td>Metatorbernite</td>
<td>Cu(UO$_2$)$_2$(PO$_4$)$_2$·8(H$_2$O)</td>
<td>mineral of interest</td>
</tr>
<tr>
<td>9</td>
<td>Uranophane</td>
<td>Ca(UO$_2$)$_2$SiO$_3$(OH)$_2$·5(H$_2$O)</td>
<td>mineral of interest</td>
</tr>
<tr>
<td>10</td>
<td>Meatauanocircite</td>
<td>Ba(UO$_2$)$_2$(PO$_4$)$_2$·10(H$_2$O)</td>
<td>mineral of interest</td>
</tr>
<tr>
<td>11</td>
<td>Metazuenerite</td>
<td>Cu(UO$_2$)$_2$(AsO$_4$)$_2$·8(H$_2$O)</td>
<td>mineral of interest</td>
</tr>
<tr>
<td>12</td>
<td>Na-Zippeite</td>
<td>Na$_4$(UO$_2$)$_6$(SO$_4$)$<em>3$(OH)$</em>{16}$·4(H$_2$O)</td>
<td>mineral of interest</td>
</tr>
<tr>
<td>13</td>
<td>Tyuyamunite</td>
<td>Ca(UO$_2$)$_2$(VO$_4$)$_2$·5·8(H$_2$O)</td>
<td>mineral of interest</td>
</tr>
<tr>
<td>14</td>
<td>UO2</td>
<td>UO$_2$</td>
<td>mineral of interest</td>
</tr>
<tr>
<td>15</td>
<td>U$_3$O$_8$</td>
<td>U$_3$O$_8$</td>
<td>mineral of interest</td>
</tr>
</tbody>
</table>

**Example mixture:** Cuprosklodowskite-Powdered-2-100208

Measured minerals are mixtures of constituent minerals that can be treated as individual chromophores.

The composition was initially estimated by XRD and 15 major constituents were included in the analysis.
Advantages of CLS

- Contributions and spectra are interpretable
  - signal on interferences and minerals of interest are easily separable
    - statistics can be applied to each source individually
- Can apply non-negativity
  - contributions must all be $\geq 0$
  - $1^{\text{st}}$ derivative of the spectra are unconstrained during model identification

Example Spectra used in ELS

1$^{\text{st}}$ derivative used in the model
Residuals Analysis

Two interferences had low residuals:
- 3) Nv Sand
- 34) Sand125mesh lane mt

Six potential MOI had low residuals e.g.,
- 37) Tyuyamunite-Powdered-100282
- 39) Uranium-Mineral-Carnotite-Powdered-100280

CLS Contributions for Interferences

'Nv Sand' is high in SiO$_2$ and MOI indicating a possible detection/false alarm

'Sand 125 mesh' is high in SiO$_2$ and is not a false alarm
- low residual but no contributions on MOI
**CLS Contributions for Potential MOI**

37) Tyuyamunite-Powdered-100282

‘Tyuyamunite’ is high in Calcite and possible detection of MOI/false alarm

39) Uranium-Mineral-Carnotite-Powdered-100280

‘Carnotite’ is high in SiO$_2$ and possible detection of MOI/false alarm

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**Questions / Future**

- The proof-of-principal was a global model that included 15 factors
- Can sensitivity be improved with local models?
  - hierarchical for models with many analytes and/or
  - specific to task of interest
Conclusions

Laboratory study showed that it is possible to use Mid-IR diffuse reflectance spectroscopy to separate/differentiate minerals of interest.

- 1st derivative was more sensitive and selective than w/o
- however, preprocessing can be targeted to task of interest
- Augmenting the analysis with NIR may help