Graphical Rotation- “Boosting” the Interpretability of NIR Methods

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Outline

• Exploratory Modeling in NIR - Why?
• Special NIR Considerations
• “Effect” Spectra (vs. pure component spectra)
• Introduction to Rotation
  • Different types
  • Rotation for NIR
• 3 NIR Case Studies
• Conclusions/Summary
Exploratory Modeling in NIR- WHY?

• Compliments deployed models
  • Better-understand the basis of deployed models
  • FDA, others: “What is NIR *REALLY* monitoring?...”

• Can enable improved understanding of NIR spectroscopy itself
  • Band assignment based on quantum chemistry cumbersome and inaccurate (anharmonicity)

• NIR as a *RESEARCH* tool- WHY NOT?
  • Sampling versatility and non-destructiveness
    • Can study materials unaltered, in their “native” states!
Exploratory NIR - Considerations

- One “vibrating unit” can generate many bands!
- Bands from different analytes/phenomena typically not well-resolved!
- BUT... model spectra are easy to obtain!
  - More “direct” sampling options!

\[
\begin{align*}
\text{Cl} & \quad \text{Cl-C-H} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

*combinations and overtones*

**Table II: Vibrational Combination and Overtone Bands of Chloroform**

<table>
<thead>
<tr>
<th>Combination or Overtone Mode</th>
<th>Calculated Position (wavenumbers)</th>
<th>Calculated Position (nm)</th>
<th>Observed Position (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1 + v_4)</td>
<td>4.154</td>
<td>2.351</td>
<td>2.370</td>
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<tr>
<td>(v_1 + v_2 + v_4)</td>
<td>4.430</td>
<td>2.232</td>
<td>2.234</td>
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<tr>
<td>(v_1 + v_3 + v_4)</td>
<td>4.199</td>
<td>2.379</td>
<td>2.218</td>
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<tr>
<td>(4v_4)</td>
<td>4.931</td>
<td>2.047</td>
<td>2.049</td>
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<tr>
<td>(2v_1 + v_4)</td>
<td>4.974</td>
<td>2.010</td>
<td>2.058</td>
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<tr>
<td>(2v_1 + v_3 + v_4)</td>
<td>5.433</td>
<td>1.841</td>
<td>1.843</td>
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<tr>
<td>(2v_1 + v_2 + v_3 + v_4)</td>
<td>5.967</td>
<td>1.725</td>
<td>1.735</td>
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<td>(v_2 + v_4)</td>
<td>6.080</td>
<td>1.645</td>
<td>1.692</td>
</tr>
<tr>
<td>(v_2 + v_3 + v_4)</td>
<td>6.093</td>
<td>1.641</td>
<td>1.655</td>
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<td>(v_2 + v_1 + v_3 + v_4)</td>
<td>6.171</td>
<td>1.620</td>
<td>1.619</td>
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<tr>
<td>(2v_2 + v_4)</td>
<td>6.181</td>
<td>1.618</td>
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<td>(2v_2 + v_1 + v_2 + v_4)</td>
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<tr>
<td>(v_2 + v_1 + v_2 + v_3 + v_4)</td>
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<td>1.500</td>
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<tr>
<td>(2v_2 + v_1 + v_2 + v_3 + v_4)</td>
<td>7.124</td>
<td>1.404</td>
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<tr>
<td>(2v_2 + v_1 + v_2 + v_3 + v_4)</td>
<td>7.378</td>
<td>1.335</td>
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<tr>
<td>(2v_2 + v_1 + v_2 + v_3 + v_4)</td>
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<tr>
<td>(2v_2 + v_1 + v_2 + v_3 + v_4)</td>
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<tr>
<td>(2v_2 + v_1 + v_2 + v_3 + v_4)</td>
<td>8.351</td>
<td>1.200</td>
<td>1.210</td>
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<tr>
<td>(3v_1 + v_4)</td>
<td>8.841</td>
<td>1.118</td>
<td>1.120</td>
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<td>(3v_1 + v_2 + v_4)</td>
<td>9.050</td>
<td>1.105</td>
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<td>(3v_1 + v_3 + v_4)</td>
<td>9.247</td>
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<td>1.068</td>
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<tr>
<td>(3v_1 + v_3 + v_4)</td>
<td>9.435</td>
<td>1.050</td>
<td>1.059</td>
</tr>
<tr>
<td>(3v_1 + v_3 + v_4)</td>
<td>9.894</td>
<td>1.011</td>
<td>1.018</td>
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<tr>
<td>(4v_1 + v_4)</td>
<td>11.080</td>
<td>0.903</td>
<td>9.08</td>
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<tr>
<td>(4v_1 + v_2 + v_4)</td>
<td>11.950</td>
<td>0.834</td>
<td>8.30</td>
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<tr>
<td>(4v_1 + v_3 + v_4)</td>
<td>12.160</td>
<td>0.822</td>
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<tr>
<td>(4v_1 + v_2 + v_3 + v_4)</td>
<td>12.534</td>
<td>0.798</td>
<td>8.00</td>
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<tr>
<td>(4v_1 + v_2 + v_3 + v_4)</td>
<td>15.200</td>
<td>0.658</td>
<td>7.91</td>
</tr>
</tbody>
</table>

* * Band was not observed.*
“Effect” Spectrum Concept

• Instead of a pure component spectrum!
• Often- a simple subtraction of two spectra
• Reflects *differences* between two states
• Can be used to express *non-concentration* properties
• But, they require more thought: *Positive and Negative peaks* are meaningful!
• Allows effective interpretation of models built using *mean-centered* data!
• Derivative preprocessing-hinders interpretation, adds more peaks!

*Polyethylene before and after uniaxial stretching*

*PE uniaxial stretching effect spectrum*
NIR Exploratory Checklist

• Front End Loading (FEL1):
  • Experimental Design
    • The data (to be modeled..)
    • “Special Data”: Pure components, model compounds, data from special experiments, etc….
  • Background information: samples, instrument, sampling interface, process stream, etc…
    • Prior knowledge to guide interpretations
  • Software that allows tracking of class information

• Attitude: willingness to work with “effect spectra”

• Mathematical Tools:
  • Modeling Tools: PCA, CLS, MCR, PLS
  • Post-Modeling Tools
    • Rotation!
Introducing…Rotation!

• PCs from PCA constitute only one of infinitely many possible basis vector sets for your data!
  • Can be rotated to a more interpretable basis!
• However, must specify a target for this rotation!
• Thurstone (1947), later authors: “Rotate PCs to attain simple structure”
  • Each loadings vector has only a few non-zero elements
  • “exclusivity”
  • In sociology, psychology- allows grouping of variables into underlying phenomena!

\[
P = \begin{bmatrix}
.15 & .42 \\
.30 & .36 \\
.38 & .66 \\
.15 & -.07 \\
.38 & -.24 \\
.45 & -.12 \\
.61 & -.44
\end{bmatrix}
\]

\[
\Theta = \begin{bmatrix}
\cos \theta & -\sin \theta \\
\sin \theta & \cos \theta
\end{bmatrix}
= \begin{bmatrix}
.88 & .48 \\
-.48 & .88
\end{bmatrix}
(\Theta = -22.7^\circ)
\]

\[
P_{\text{rot}} = P\Theta = \begin{bmatrix}
-.07 & .44 \\
.09 & .46 \\
.02 & .76 \\
.16 & .01 \\
.45 & -.03 \\
.45 & .11 \\
.75 & -.09
\end{bmatrix}
\]
Rotation- Options

• Typically- two vectors (PCs) at a time
• *Orthogonal Rotation* \[ \Theta = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \]
  • Preserves orthogonality of vectors & explained variance structure
  • “*Graphical Rotation*” (Windig 1987, mass spectrometry)
    • Target based on preferred structure of loadings
• *Oblique Rotation*
  • Orthogonality *not* preserved, but more flexible
  • Lawton and Sylvestre (1971) \( \rightarrow \) curve resolution/MCR
    • Loadings all positive- more intuitive
  • *Simplimax*: Kiers (1994) Maximize “simplicity” of rotated pattern
Graphical Rotation with PCA - Math

Original PCA model:
\[ \mathbf{X} = \mathbf{T}\mathbf{P}^t \]

Choose 2 PCs to rotate

View loadings scatter plot

Determine optimal rotation angle \( \theta \), and rotation matrix \( \Theta \)

Rotate loadings to desired structure

\[ \mathbf{P}_{\text{rot,1}} = \mathbf{P}\Theta_1 \]

Counter-Rotate loadings

\[ \mathbf{T}_{\text{rot,1}} = \mathbf{T}\Theta_1^{-1} \]

View scores scatter plot

Determine optimal rotation angle \( \theta \), and rotation matrix \( \Theta \)

Normalize scores

Rotate scores to desired structure

\[ \mathbf{T}_{\text{rot,2}} = \mathbf{T}\Theta_2 \]

Counter-Rotate loadings

\[ \mathbf{P}_{\text{rot,2}} = \Theta_2^{-1}\mathbf{P}^t \]

Rotation is NOT just “forcing” what you want: must counter-rotate the other vector set in order to explain the original data!
Rotation in NIR Spectroscopy

- A rotation target based on structure in *loadings* can be problematic!
  - Pure components & effects often do *NOT* involve isolated, discrete bands!
- So- why not use a rotation target based on structure in *scores*?....
  - Can be done *WITH* sufficient prior knowledge of objects!
Case Study 1- Polyethylene blend films

- 7 different blends of low- and high-density polyethylene (Statoil A/S)
  - 0, 2.5, 5, 10, 25, 50 and 100% HDPE
- Extruded into thin films
  - 25-40 μm thick
- 5 replicates of each composition analyzed by NIR (Technicon 500)
  - Replicates taken from different parts of extruded film

Polyethylene- PC 1 & 2 scores

Scores on PC 1 (72.32%)
Scores on PC 2 (21.72%)

Variability in replicates!
100% HDPE discriminator

Class 0
Class 2.5
Class 5
Class 10
Class 25
Class 50
Class 100

x-axis zero
y-axis zero

Decluttered
Rotate PCs 1&2 +15°

Resultant (counter-rotated) loadings!
Effects, from counter-rotated loadings

Counter-rotated loading 1 (replicate effect)

Weighted subtraction (stretching effect)

PE film before and after uni-axial stretching

Counter-rotated loading 2 (100% HDPE discriminator)
Case Study 2- Polyurethanes

- Polyurethanes produced via reaction-injection-molding (RIM, ICI Polyurethanes)
- Sheets produced at 4 nominal compositions
  - 42.5, 46, 51 & 55 % hard block
- 3 sample strips cut out of each sheet
  - At different locations of sheet
- NIR diffuse reflectance analysis
  - Technicon I/A 500

"soft block"  "hard block"

**PCA scores 1 & 2**

**By hard block %**

**By sheet position**

Interestingly, these two pure effects appear to be orthogonal (in this 2 PC-space)
Rotate PCs 1&2 +37°

Resultant (counter-rotated) loadings!
Effects, from counter-rotated loadings

Counter-rotated loading 1 (sheet position effect)

Effect: as score on PC 1 increases; valleys deeper at shorter wavelengths, and peaks shorter at longer wavelengths (remember - MSC!)

Counter-rotated loading 2 (hard block % effect)
Case study 3- Nylon/EVOH/Nylon films

• Used as moisture barrier in food packaging
  • Nylon-6/EVOH/Nylon-6 “sandwich”
• 16 film samples cut from different regions of same extruded sheet
• NIR spectra obtained
• Subsequently analyzed by polarized light microscopy
  • EVOH content varies from 3-8%

PCA scores 1 & 2

Samples/Scores Plot of NENfilms_NIR

Scores on PC 1 (67.72%)
Scores on PC 2 (27.39%)

EVOH thickness effect

7-8
4-5
6-7
5-6
3-4
8-9
Rotate PCs 1&2 -38°

Resultant (counter-rotated) loadings!
Effects, from counter-rotated loadings

Counter-rotated loading 1 (*inverse* of EVOH thickness effect)

[Nylon6 – EVOH] (composition effect)

Nylon6 and EVOH pure component spectra

Counter-rotated loading 2 (unknown variation)

Annealing effect spectrum

Film before and after annealing
Summary

• Interpreting loadings from NIR is not hopeless!
  • But must accept “effect” spectra,
  • Get background information, auxiliary data!
  • Rotate to a more interpretable structure
• Rotation: a very simple, time-tested alternative for exploratory NIR
• In NIR, though, rotation is more useful when target is based on structure in scores, not loadings
• Can be extended to multi-block PCA, PLS
• Rotation concept is a good framework for development of “purity” methods (MCR….)

PLS Latent Variables can be considered a
_________________
_________________
of the PCA Principal Components generated from the same data set.

ORTHOGONAL ROTATION!