Graphical Rotation-
“Boosting” the Interpretability of NIR Methods

Neal B. Gallagher
Eigenvector Research, Inc.
nealg@eigenvector.com

Charles E. (Chuck) Miller, N.B. Gallagher, J.M. Shaver
R. Bro (University of Copenhagen)
Outline

- Exploratory Analysis of NIR - Why?
- Special NIR Considerations
- “Effect” Spectra vs. pure component spectra
- Introduction to Rotation
  - Different types
  - Rotation for NIR
- NIR Case Studies
- Conclusions/Summary
Exploratory Analysis in NIR

- Compliments deployed models
  - better understanding of system
    - physics and chemistry
    - i.e., 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 advantages
  - Sampling versatility and non-destructiveness
    - Can study materials unaltered, in their “native” states!
NIR Exploratory Considerations

- One “vibrating unit” can generate many bands!
- Bands from different analytes/phenomena typically **not** well-resolved!

However... model spectra are easy to obtain!
Instead of a pure component spectrum
- often due to physics instead of chemistry
- temperature shifts, polymer alignment

Often, a simple subtraction of two spectra can provide good insight
- Reflects differences between two states
- But, they require more thought: *Positive and Negative peaks are meaningful*

Similar to interpretation of models built using *mean-centered data*
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
Simple Orthogonal Rotation

PCs from PCA constitute only one of infinitely many possible basis sets for a data set
- 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!

\[ \Theta = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \]

\[ P_{\text{rot}} = P \Theta \]
Rotation- Options

- **Graphical rotation**
  - typical to use two vectors (PCs) at a time

- **Orthogonal Rotation**
  - Preserves orthogonality of vectors & explained variance structure
  - **Varimax** (Kaiser, 1958): specific target: maximize variance of loadings; **Quartimax** (1954), **Equimax** (1961)
  - **“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: \( X = TP^t \)

Choose 2 PCs to rotate

View loadings scatter plot

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

Rotate loadings to desired structure \( P_{rot,1} = P\Theta_1 \)

Counter-Rotate scores \( T_{rot,1} = T\Theta_1^{-1} \)

View scores scatter plot

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

Normalize scores

Rotate scores to desired structure \( T_{rot,2} = T\Theta_2 \)

Counter-Rotate loadings \( P_{rot,2}^t = \Theta_2^{-1} P^t \)

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**?....
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)


MSC, PCA....
Polyethylene- PC 1 & 2 scores

Samples/Scores Plot of PE_films_NIR

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

100% HDPE discriminator
Variability in replicates!

Decluttered

Class 0
Class 2.5
Class 5
Class 10
Class 25
Class 50
Class 100
x-axis zero
y-axis zero

Variability in replicates!
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 - Polyurethanes

Polyurethanes produced via reaction-injection-molding

- Sheets produced at 4 nominal compositions
  - 42.5, 46, 51 & 55 % hard block
- 3 sample strips cut from each sheet at different locations
- NIR diffuse reflectance
  - Technicon I/A 500

Injection of reactive mixture

Gate
Middle
End

“soft block”

“hard block”

PCA scores 1 & 2

By hard block %

scores on PC 1 (56.21%)
scores on PC 2 (37.62%)

By sheet position

scores on PC 1 (56.21%)
scores on PC 2 (37.62%)

"% hard block" and "sheet position" effects appear to be orthogonal (in this 2 PC-space)
Rotate Scores 1&2 +37°

Rotated loadings

Variables/Loadings Plot
- ROTATED PC 1 loadings
- ROTATED PC 2 loadings
- x-axis zero
- y-axis zero

GATE
MIDDLE
END
Effects: Rotated Loadings

Rotated Loading 1 (sheet position effect)

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

Rotated loading 2 (hard block % effect)
Loadings 1: Multiplicative

MSC Multiplicative Factor

EMSC Multiplicative Factor

EMSC 2nd Order Polynomial Coefficient

Sheet Position
Case Study – 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

Measured with NIR and polarized light microscopy
- EVOH content varies from 3-8%

PCA scores 1 & 2

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

MSC
Mean-center

EVOH thickness effect

MSC
Mean-center

MSC
Mean-center

EVOH thickness effect
Rotate PCs 1 & 2: 45°

Rotated loadings

EVOH (%)

Wavelength (nm)
Effects: Rotated Loadings

[Nylon6 – EVOH]  
(composition effect)

Rotated Loading 1  
\textit{decrease} of EVOH thickness effect

PC 1 (rotated)  
CLS fit to pure spectra

EVOH  
Nylon6

c = [6.61 -2.97]
Effects: Rotated Loadings

Rotated Loading 2
(unknown)

difference:
heating effect spectrum

Film before and after heating

NEN before heating
NEN AFTER heating

1500 2000 2500
1500 2000 2500

wavelength (nm)
wavelength (nm)
Interpreting loadings from NIR is useful
- can rotate to more interpretable spectra
- can interpret chemical and physical “effect” spectra

Rotation
- some forms are very simple
- useful alternative for exploratory NIR

In NIR
- it is expected that rotation is more useful when target is based on structure in scores, not loadings
Can be extended to other factor based analysis

Rotation concept is a good framework for development of “purity” methods

- Oblique geometrical methods for self-modeling mixture analysis
  - e.g., SIMPLSMA, DISTSLCT
- Good initial guess for least-squares based multivariate curve resolution