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

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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!

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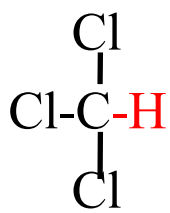
Exploratory NIR- Considerations

- 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!

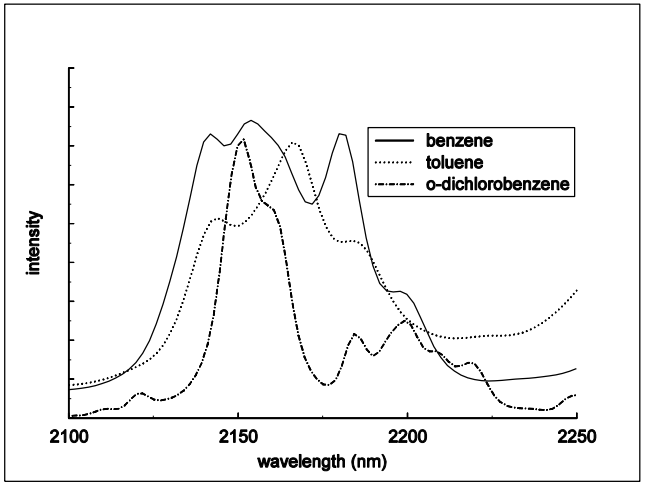


combinations and overtones

TABLE II
Vibrational Combination and Overtone Bands of Chloroform

Combination or Overtone Mode	Calculated Position (wavenumbers)	Calculated Position (nm)	Observed Position (nm)
$\nu_1 + \nu_4$	4,254	2,351	2,370
$\nu_1 + \nu_4 + \nu_6$	4,480	2,232	2,234
$\nu_1 + \nu_4 + \nu_3$	4,589	2,179	2,181
$4\nu_4$	4,856	2,059	2,107
$\nu_1 + \nu_4 + \nu_2$	4,886	2,047	2,049
$\nu_1 + \nu_4 + \nu_5$	4,974	2,010	2,008
$\nu_1 + 2\nu_4$	5,433	1,841	1,843
$\nu_1 + 2\nu_4 + \nu_6$	5,687	1,758	1,757
$\nu_1 + 2\nu_4 + \nu_3$	5,796	1,725	1,735
$2\nu_1$	6,080	1,645	1,692
$\nu_1 + 2\nu_4 + \nu_2$	6,093	1,641	1,655
$2\nu_1 + \nu_6$	6,171	1,620	1,619
$\nu_1 + 2\nu_4 + \nu_5$	6,181	1,618	1,618
$2\nu_1 + \nu_3$	6,280	1,592	1,590
$2\nu_1 + \nu_2$	6,577	1,520	1,525
$\nu_1 + 3\nu_4$	6,640	1,506	1,517
$2\nu_1 + \nu_5$	6,665	1,500	1,494
$2\nu_1 + \nu_4$	7,124	1,404	1,405
$2\nu_1 + \nu_4 + \nu_6$	7,378	1,355	1,357
$2\nu_1 + \nu_4 + \nu_3$	7,487	1,336	1,341
$2\nu_1 + \nu_4 + \nu_2$	7,784	1,285	1,290
$2\nu_1 + \nu_4 + \nu_5$	7,872	1,270	1,270
$2\nu_1 + 2\nu_4$	8,331	1,200	1,210
$3\nu_1 + \nu_6$	8,941	1,118	?[a]
$3\nu_1 + \nu_3$	9,050	1,105	1,109
$3\nu_1$	9,120	1,097	1,152
$3\nu_1 + \nu_2$	9,347	1,070	1,068
$3\nu_1 + \nu_5$	9,435	1,060	1,059
$3\nu_1 + \nu_4$	9,894	1,011	1,018
$3\nu_1 + 2\nu_4$	11,080	903	908
$4\nu_1 + \nu_2$	11,990	834	830
$4\nu_1$	12,160	822	883
$4\nu_1 + \nu_4$	12,534	798	800
$5\nu_1$	15,200	658	721

[a] ? = Band was not observed.



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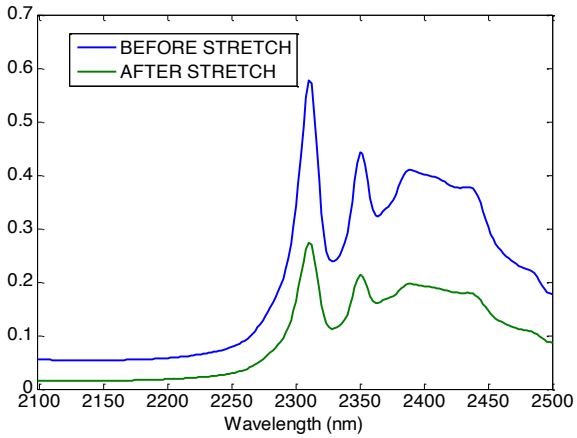
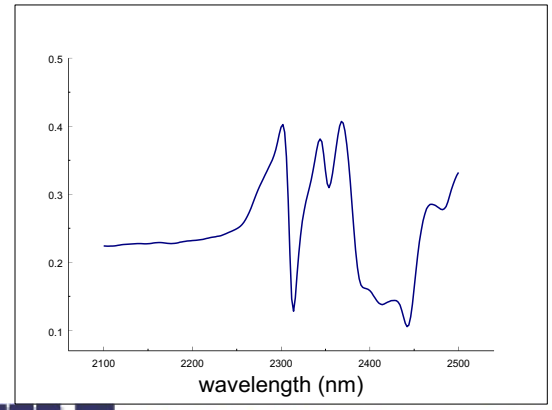
"Effect" Spectrum Concept

- 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***



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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!***

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Introducing…Rotation!

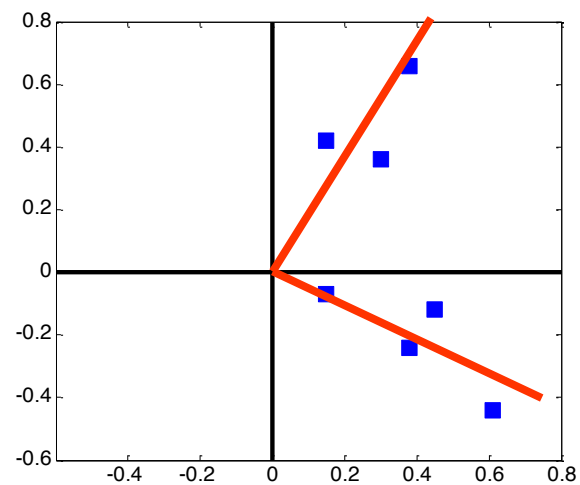
- PCs from PCA constitute only one of ***infinitely many*** possible basis vector sets for your data!
  - Can be ***rotated*** to a more interpretable basis!
- However, must specify a ***target*** for this rotation!
- Thurstone (1947), later authors: "Rotate PCs to attain ***simple structure***"
  -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

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

$$\mathbf{\Theta} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} = \begin{bmatrix} .88 & .48 \\ -.48 & .88 \end{bmatrix}$$

$$(\Theta = -22.7^{o})$$

$$\mathbf{P_{rot}} = \mathbf{P\Theta} = \begin{bmatrix} -.07 & .44 \\ .09 & .46 \\ .02 & .76 \\ .16 & .01 \\ .45 & -.03 \\ .45 & .11 \\ .75 & -.09 \end{bmatrix}$$



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Rotation- Options

- **Typically- two vectors (PCs) at a time**
- ***Orthogonal* Rotation** $\mathbf{\Theta} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$
  - Preserves orthogonality of vectors & explained variance structure
  - ***Varimax*** (Kaiser, 1958): specific target : ***max***imize ***vari***ance 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) →curve resolution/MCR
    - Loadings all positive- more intuitive
  - ***Simplimax:*** Kiers (1994) Maximize "simplicity" of rotated pattern

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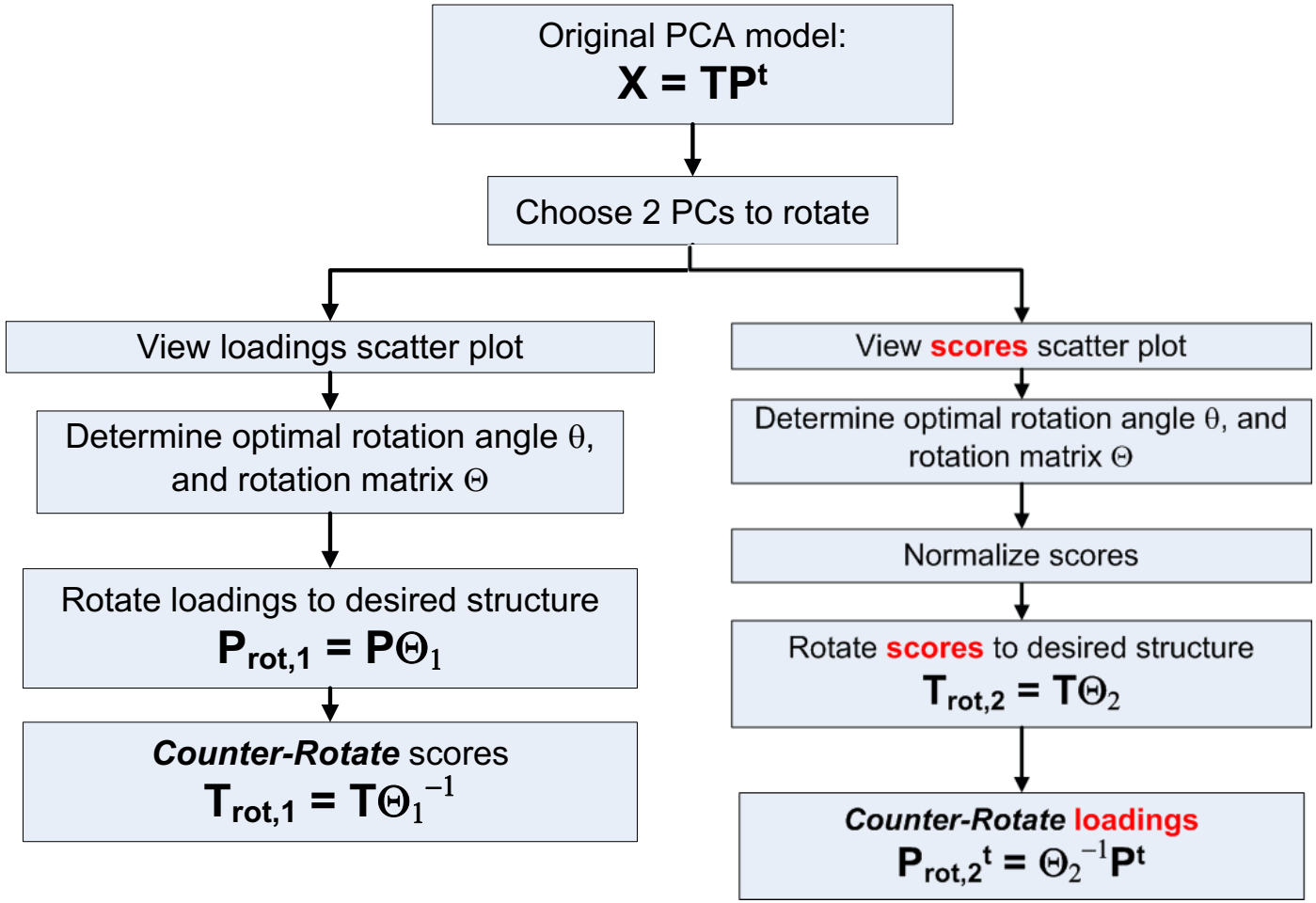
Graphical Rotation with PCA- Math



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

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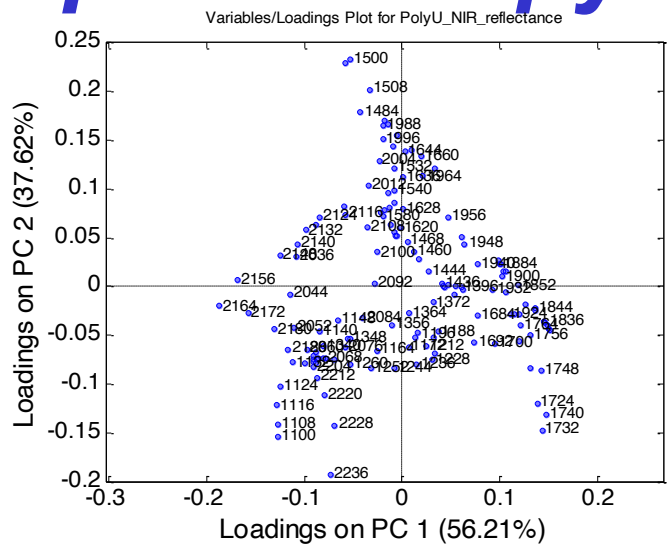
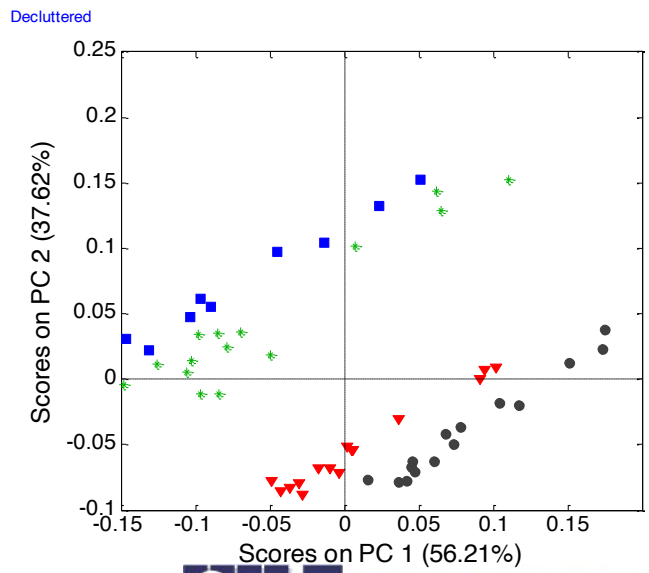
Rotation in NIR Spectroscopy

- 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!***





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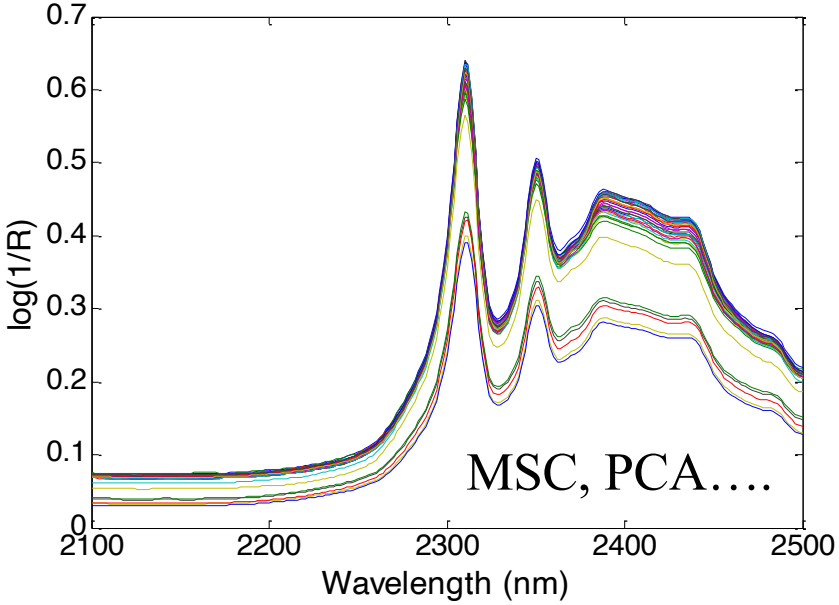
Case Study 1- Polyethylene blend films

- 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



Ref: C. Miller, Appl. Spectrosc., 47(2), 222 (1993).

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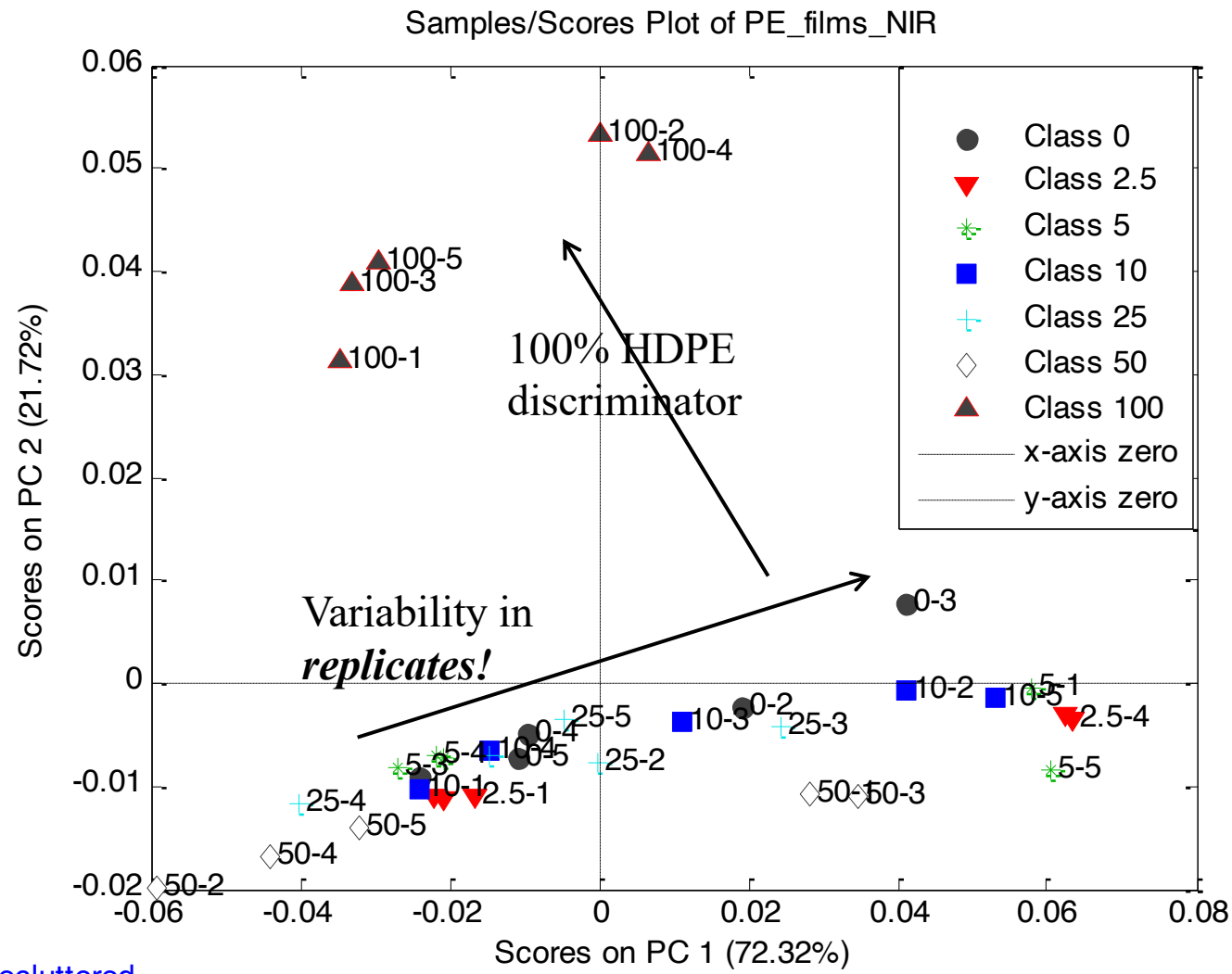
Polyethylene- PC 1 & 2 scores



Decluttered

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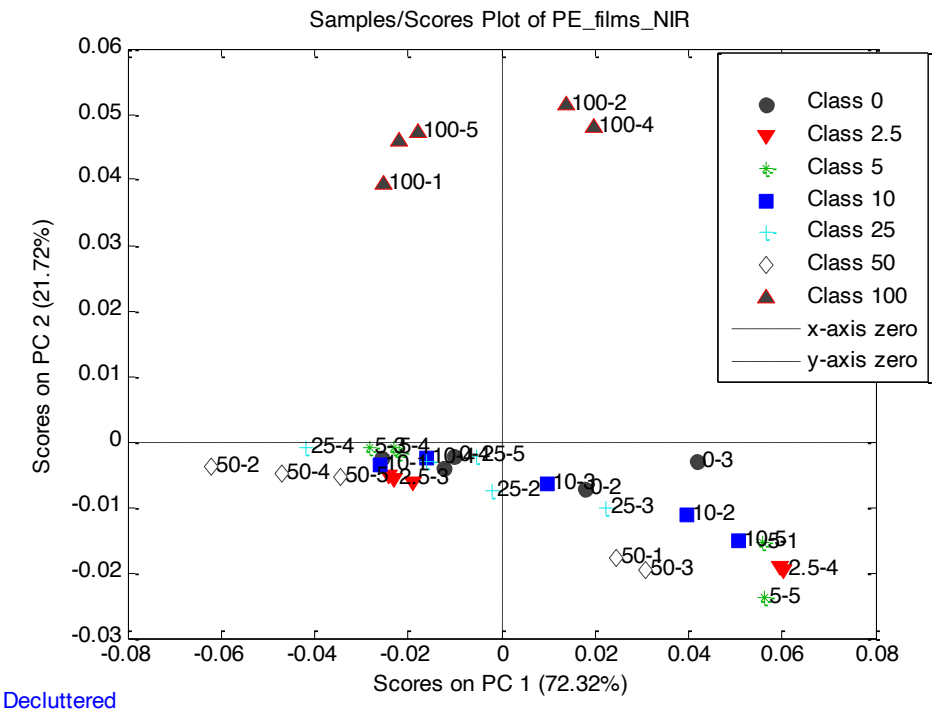
Rotate PCs 1&2 +15°

Resultant (counter-rotated) loadings!



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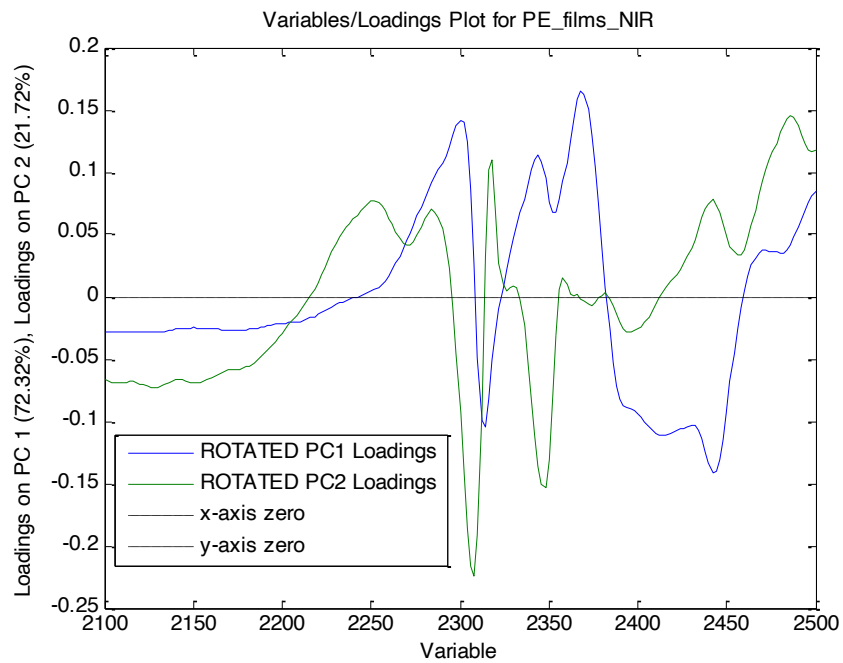

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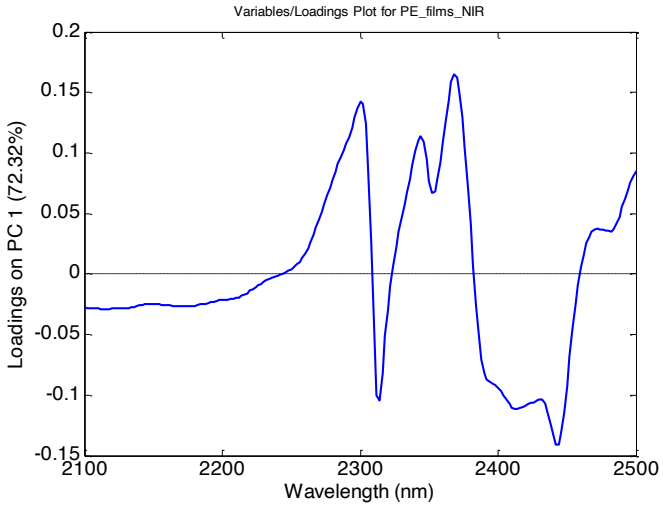
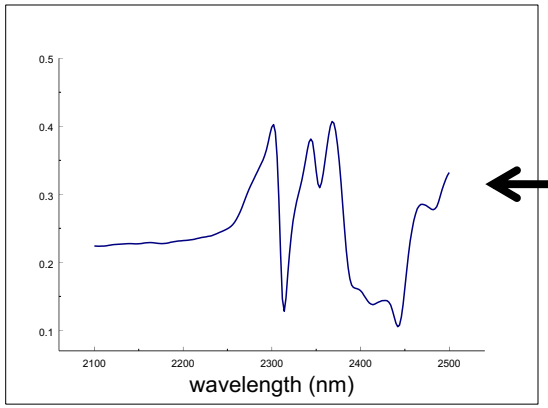
Effects, from counter-rotated loadings

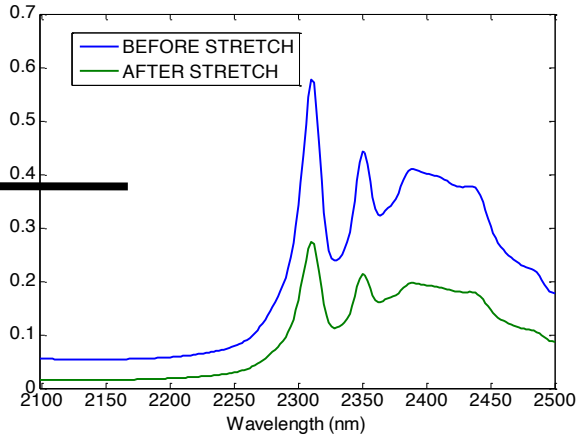
Counter-rotated loading 1 (replicate effect)



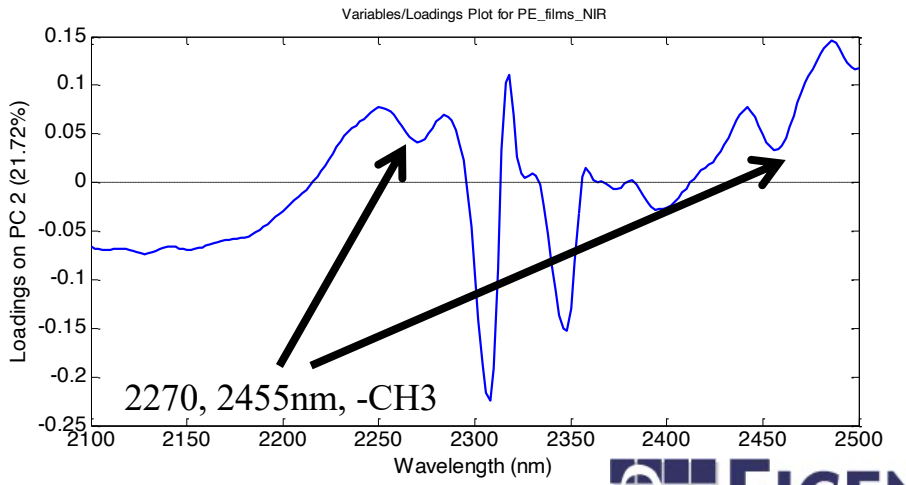
Weighted subtraction (stretching effect)



PE film before and after uni-axial stretching



Counter-rotated loading 2 (100% HDPE discriminator)



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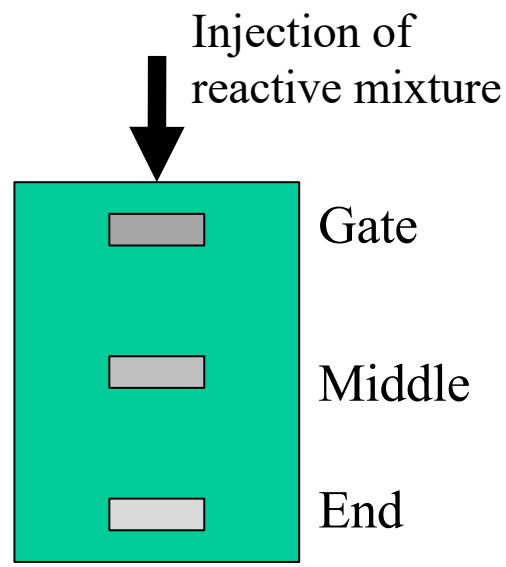
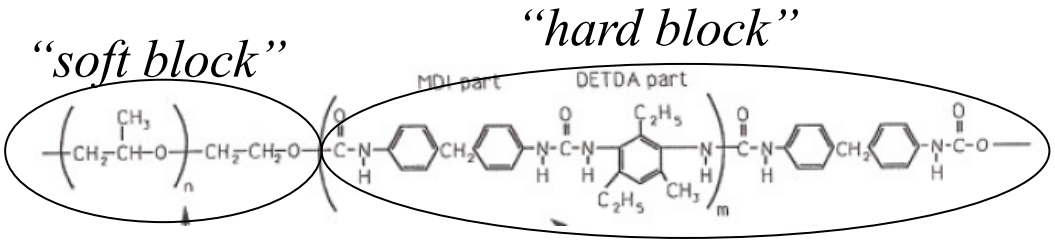
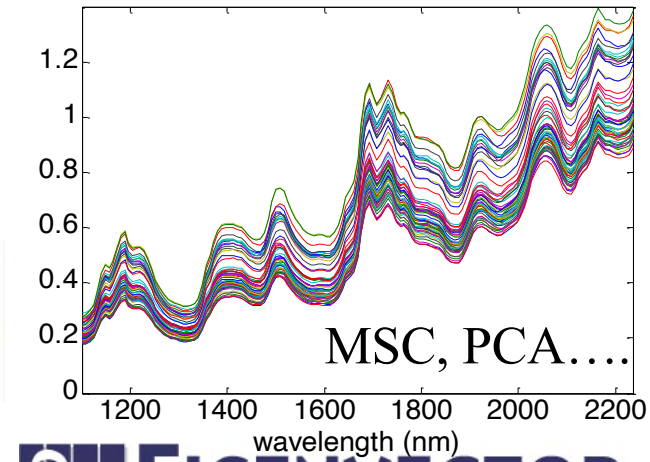
Case Study 2- Polyurethanes

- 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







Ref: C. Miller, B. Eichinger, J. Appl. Poly Sci., 42, 2169 (1991).

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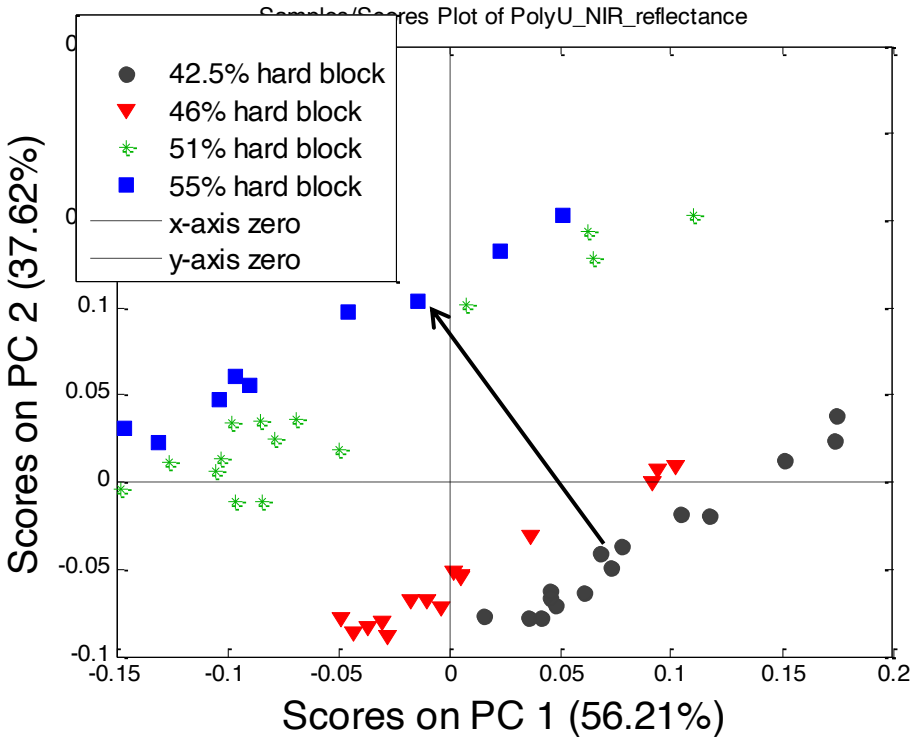
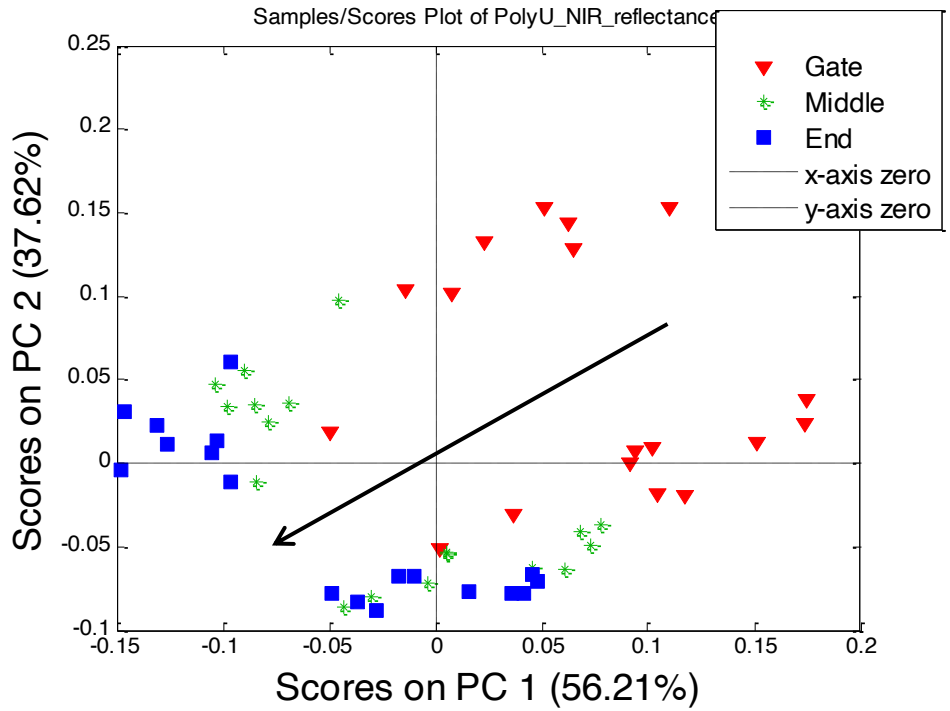
PCA scores 1 & 2

By hard block %



By sheet position



Interestingly, these two pure effects appear to be orthogonal (in this 2 PC-space)

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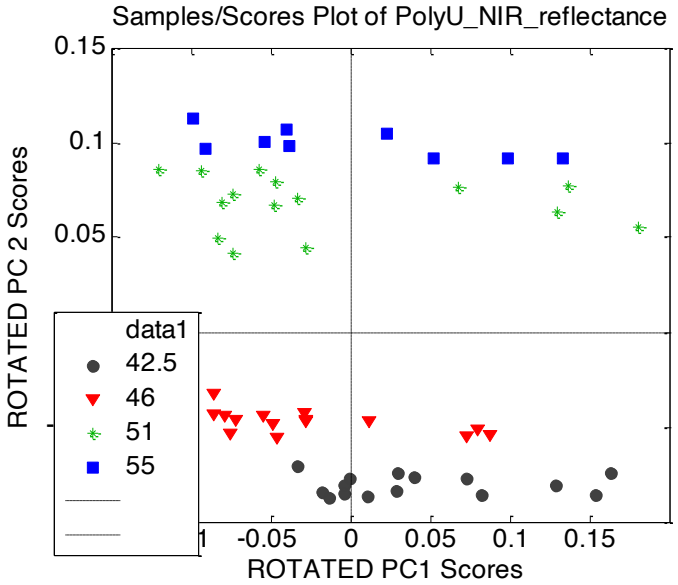
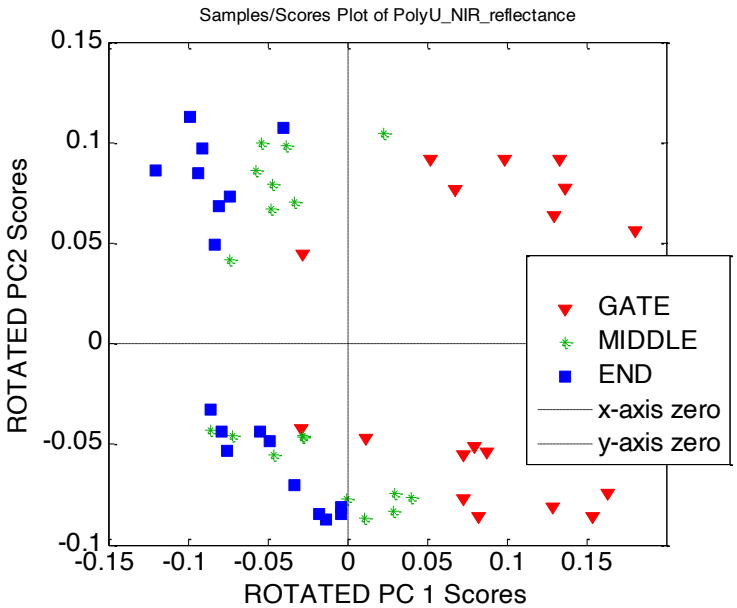
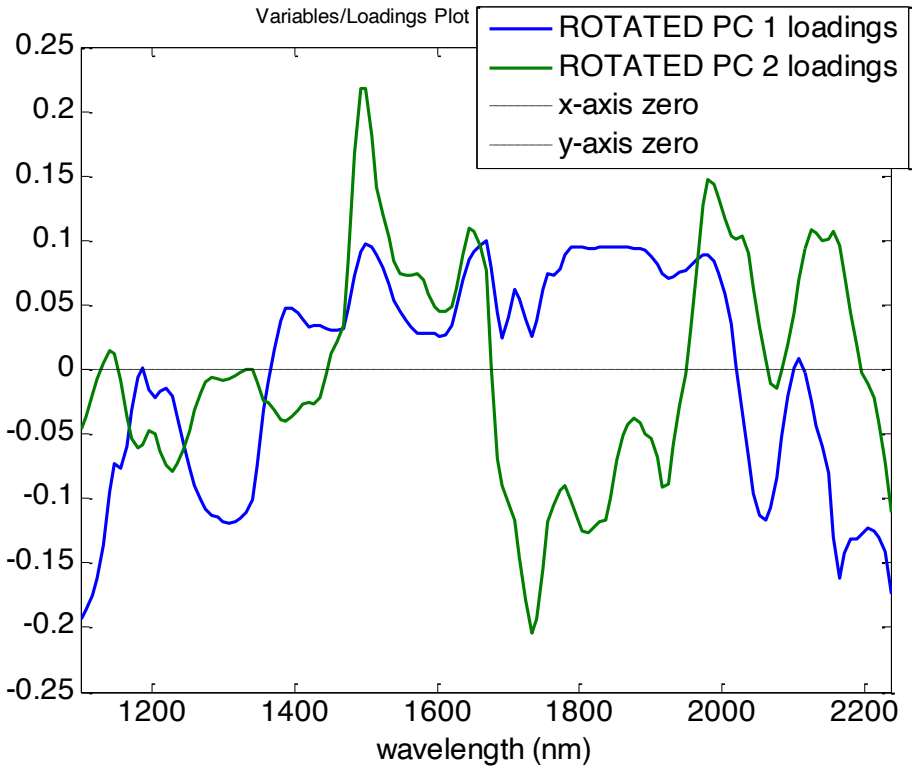
Rotate PCs 1&2 +37°





Resultant (counter-rotated) loadings!



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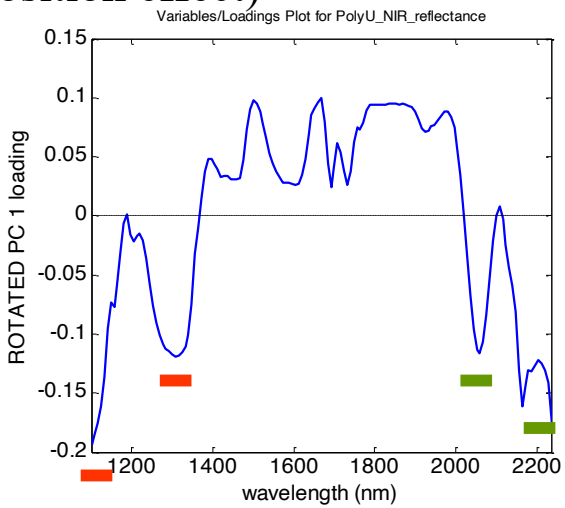
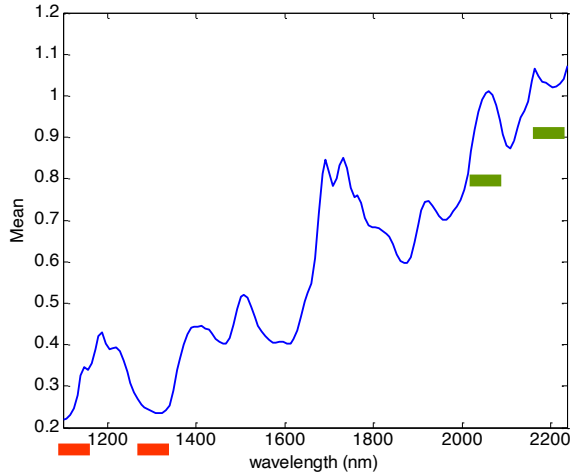
Effects, from counter-rotated loadings

Counter-rotated loading 1 (sheet position effect)

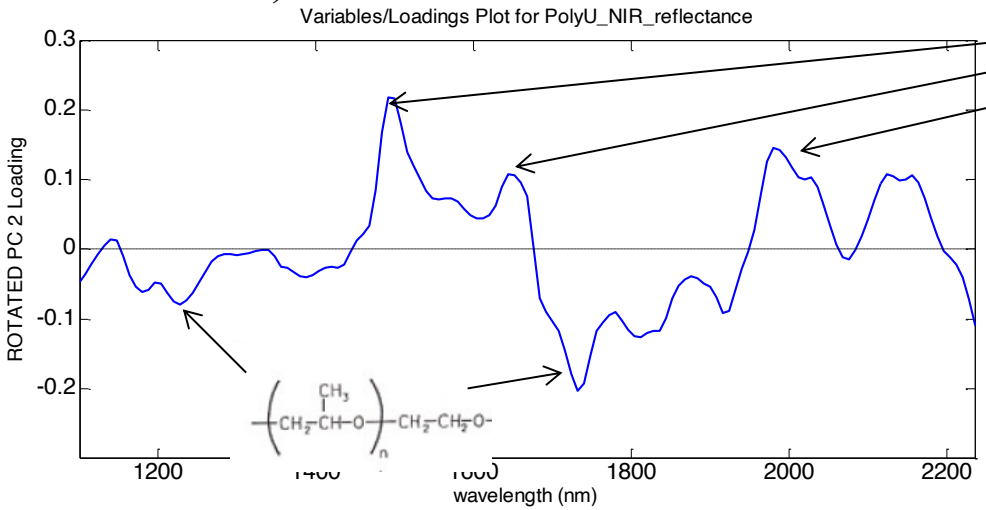


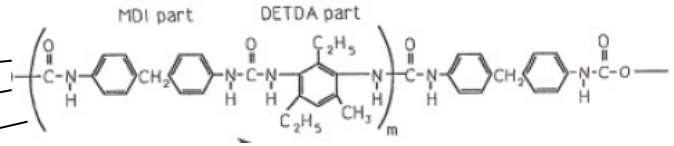
MEAN SPECTRUM



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)





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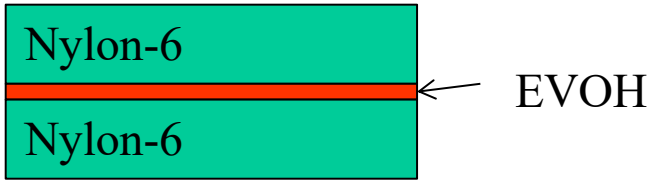
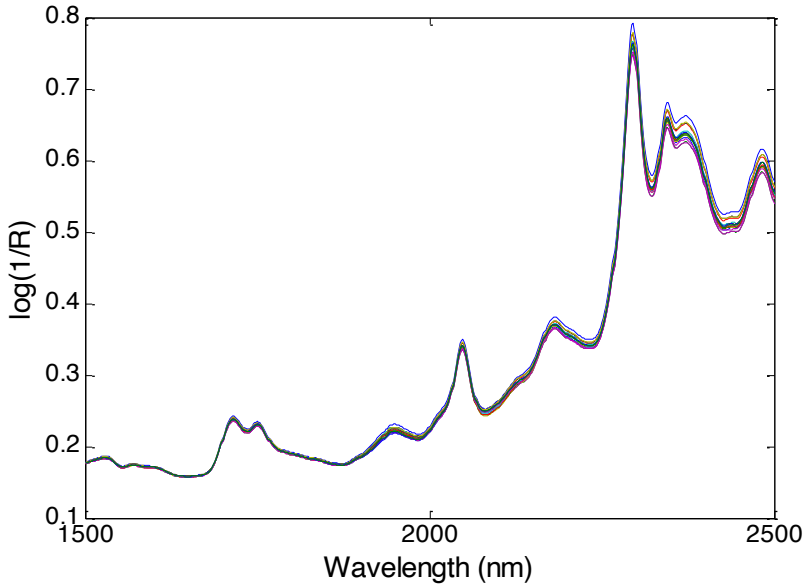
Case study 3- Nylon/EVOH/Nylon films

- 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%





Ref: C. Miller S. Svendsen, T. Næs, Appl. Spectrosc., 47(3), 346 (1993).

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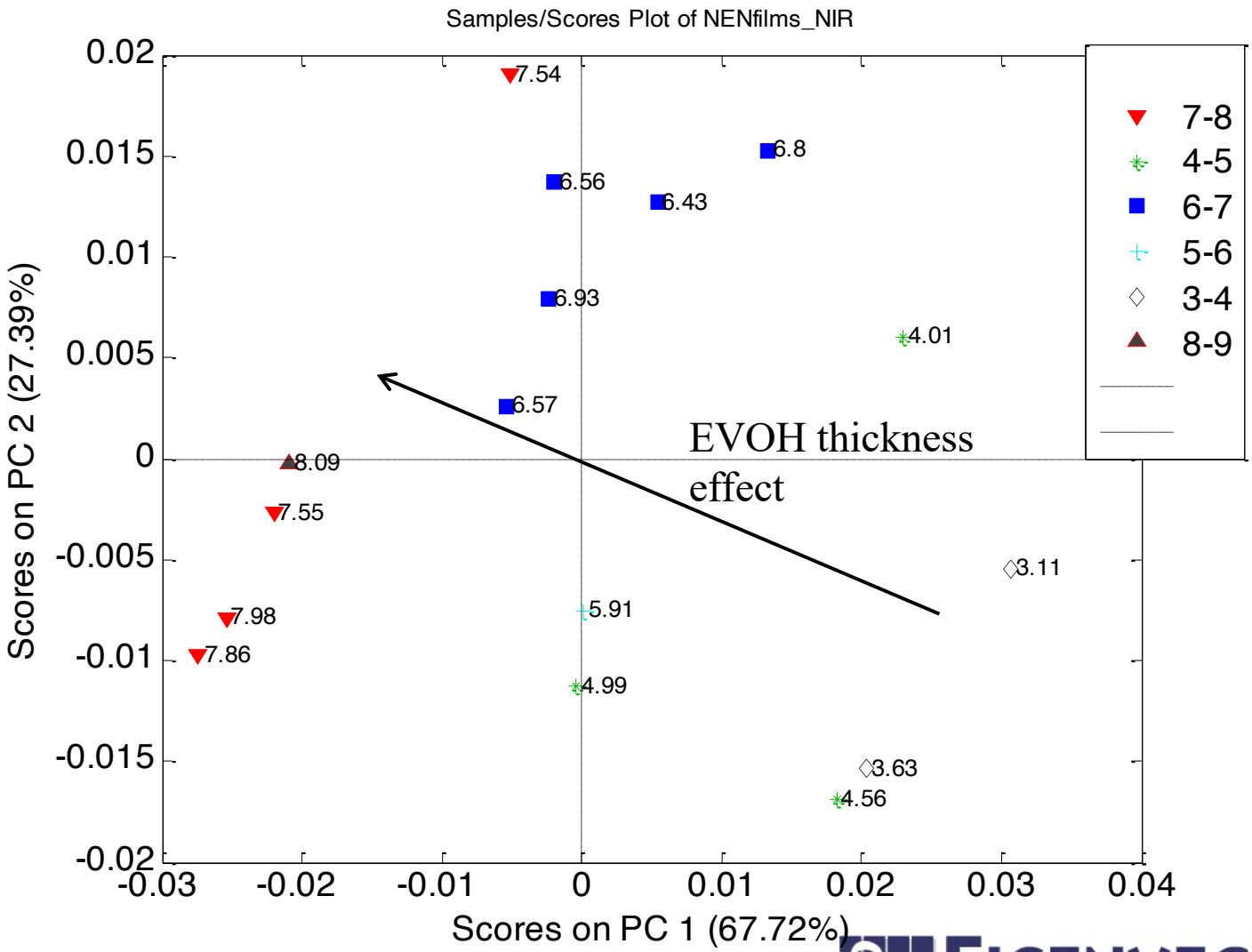
PCA scores 1 & 2



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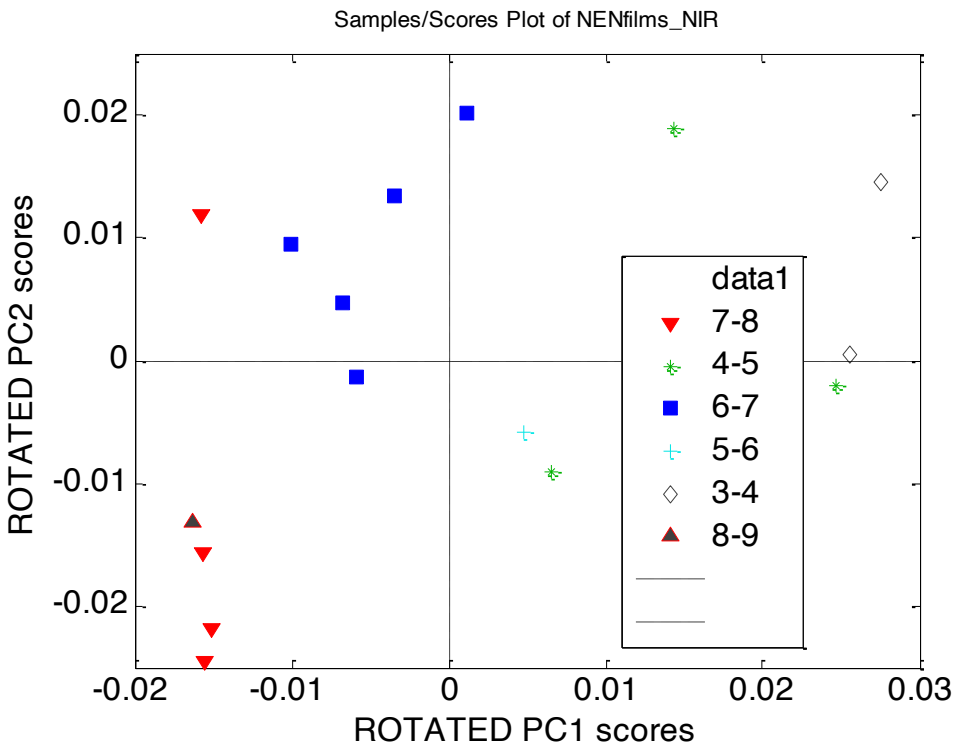
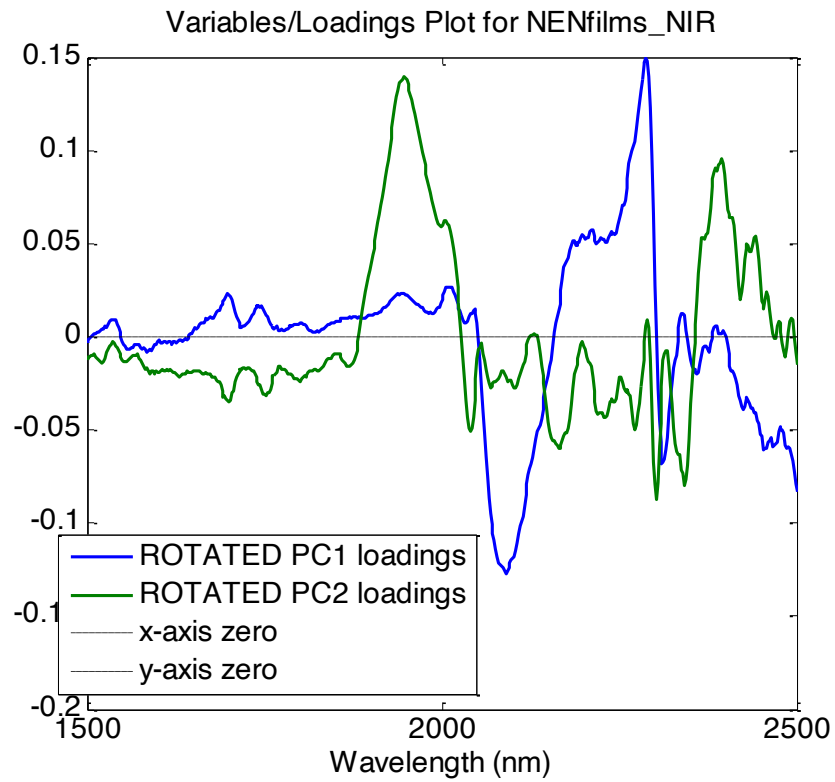
Rotate PCs 1&2 -38º

Resultant (counter-rotated) loadings!





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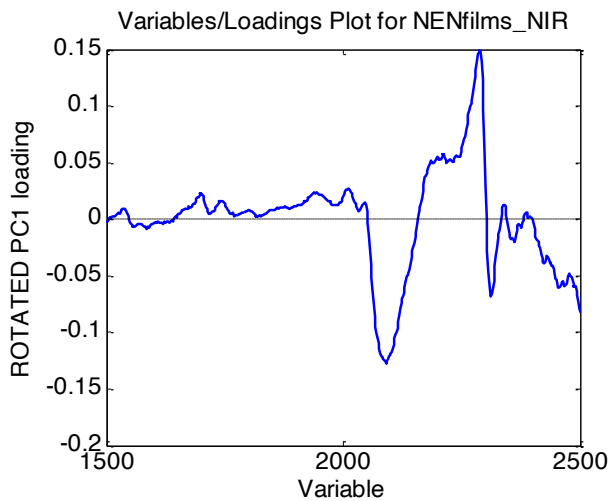
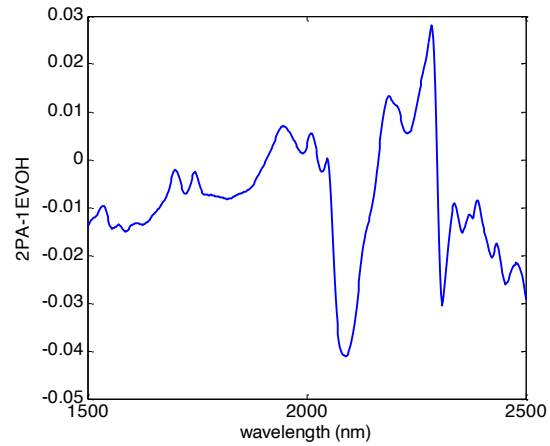
Effects, from counter-rotated loadings

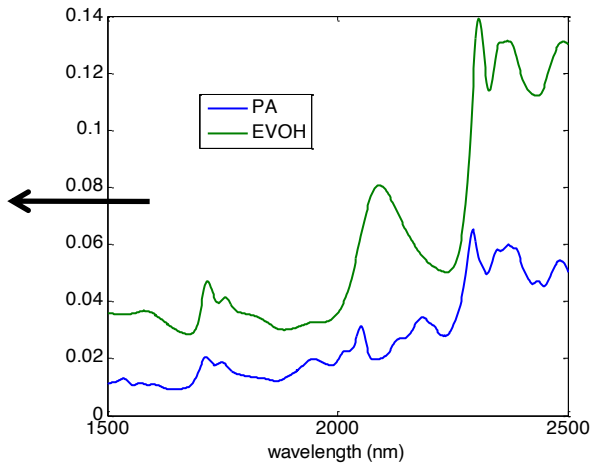
Counter-rotated loading 1 (***inverse*** of EVOH thickness effect)



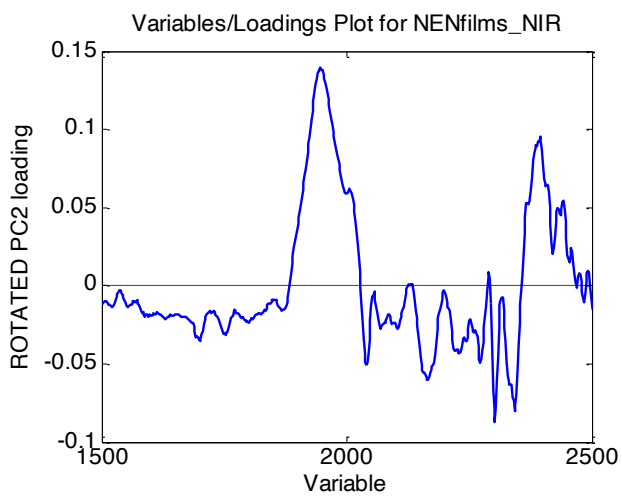
[Nylon6 – EVOH] (composition effect)



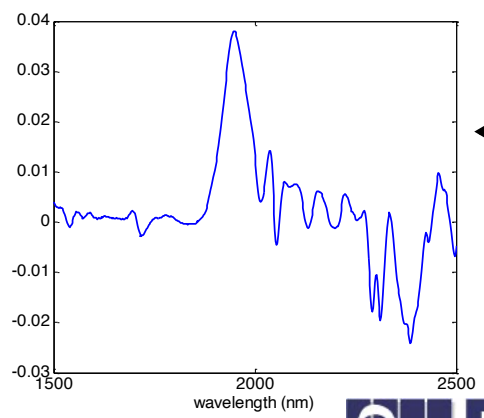
Nylon6 and EVOH pure component spectra



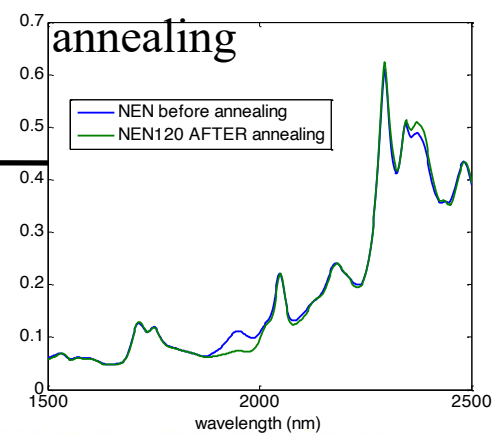
Counter-rotated loading 2 (unknown variation)



Annealing effect spectrum



Film before and after annealing



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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….)

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TEST

PLS Latent Variables can be considered a

_____

_____

of the PCA Principal Components generated from the same data set.

ORTHOGONAL ROTATION!

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