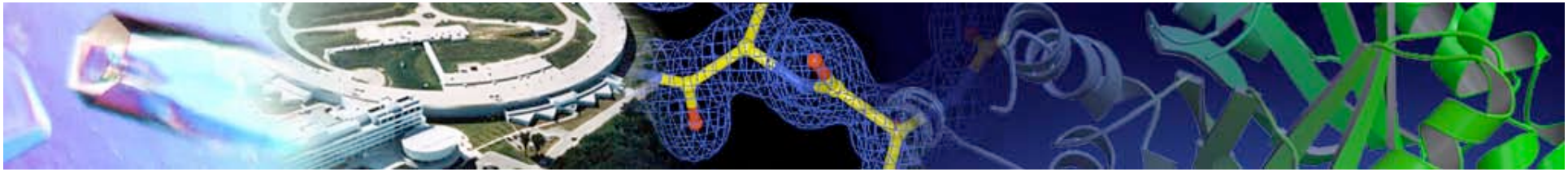


Principal Component Analysis in X-ray Absorption Spectroscopy

Stephen R. Wasserman

SGX Pharmaceuticals, Inc.

XAFS Studies of Nanocatalysis and Chemical Transformations

National Synchrotron Light Source

October 19, 2006

SGX Pharmaceuticals

Acknowledgments

- INE-FZK
  - Melissa Denecke
  - Kathy Dardenne
  - Jorg Röthe
- Simon Bare UOP
- BP
  - Gerry Zajac
  - David Sinclair
- FZ-Rossendorf
  - Andre Rossberg
- Spectra obtained at HASYLAB, NSLS, and APS

Mixtures

- Series of XAS spectra: may or may not be pure

- Traditional approach to analysis:

  - 1) Choose pure model compounds or simulate with *ab initio* calculations

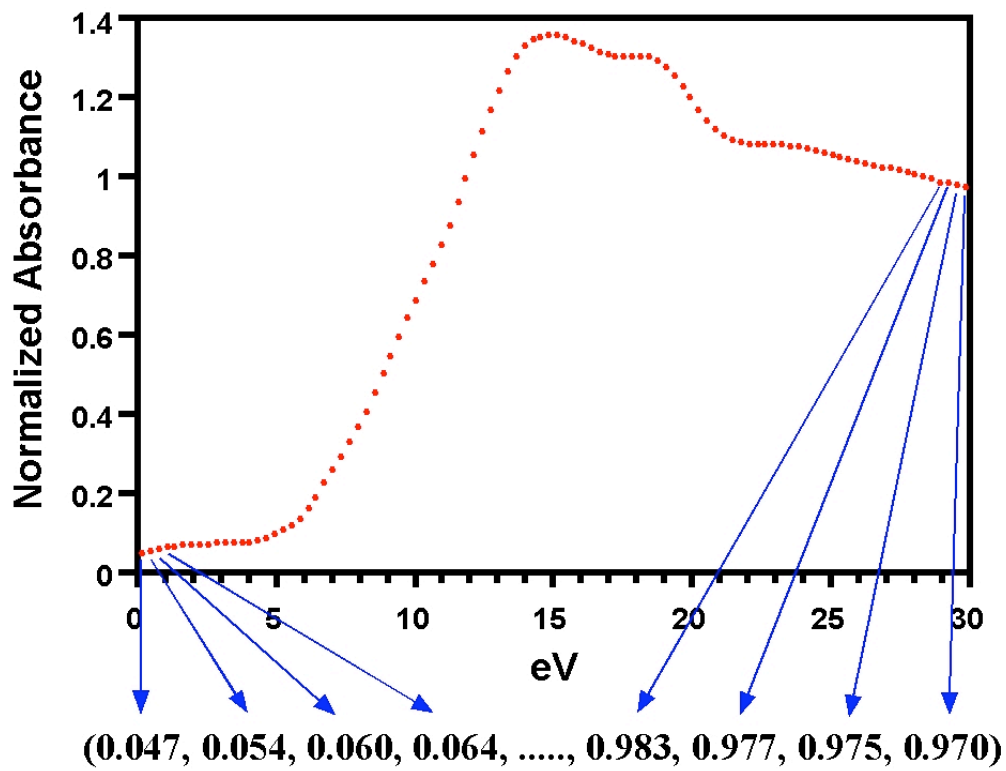
  - 2) Fit to these standards

The Problem

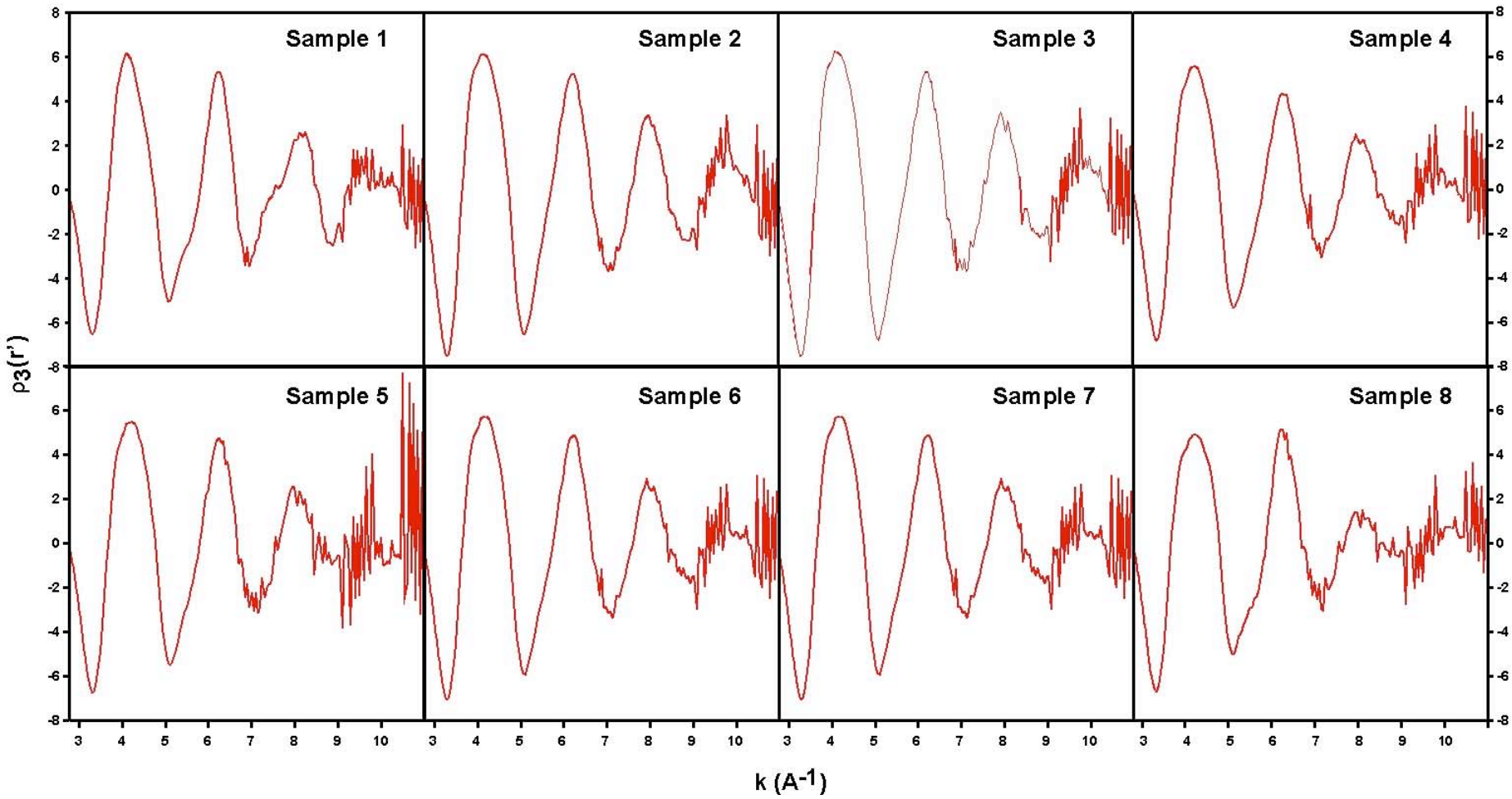
- How many standards are needed?
- How do we know the models are reasonable?
- "If you have the wrong group of standards..., there is no way you can get the right answer"

Vectors

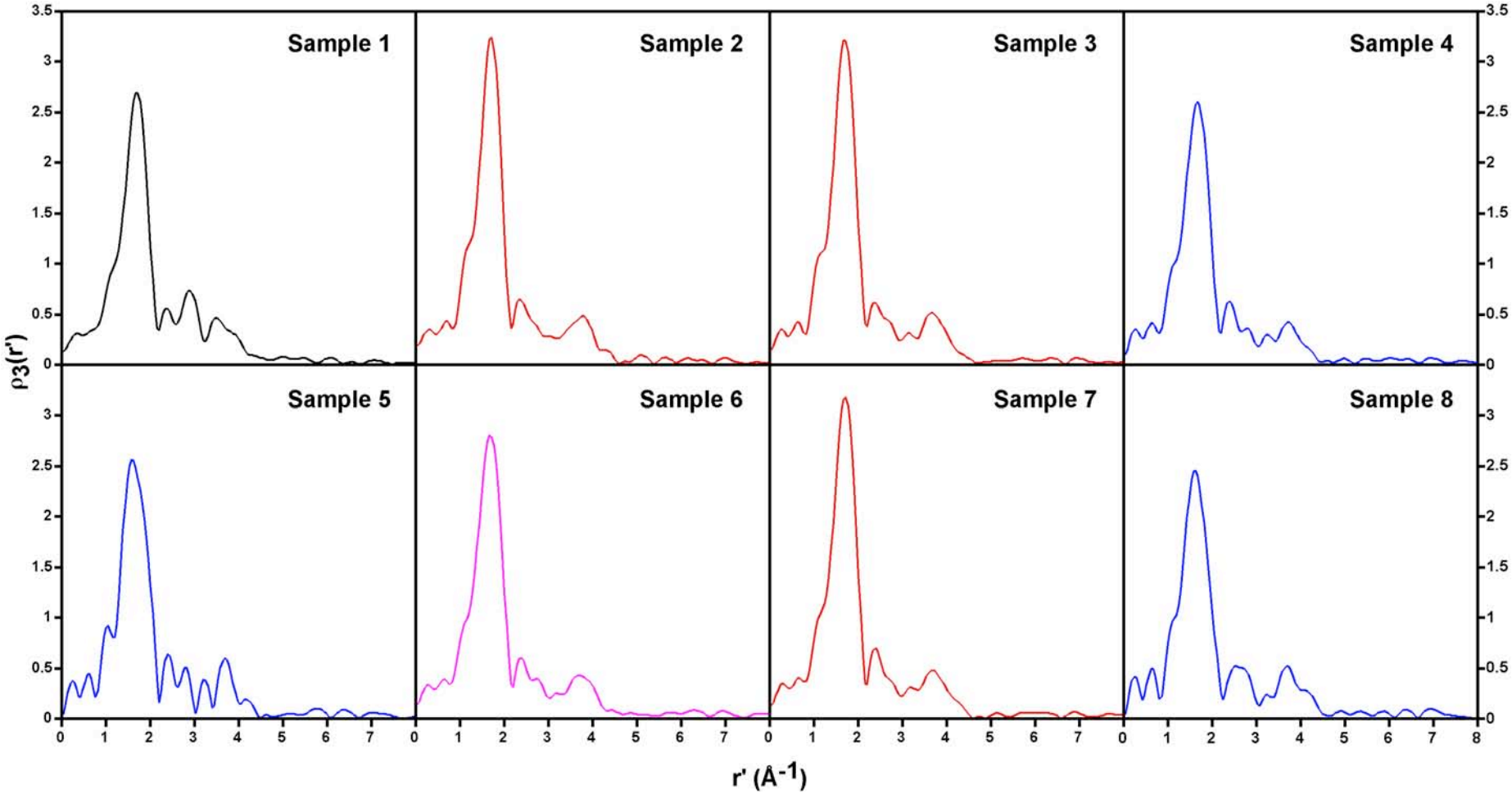
- Each spectrum can be represented as a vector
- Interpolated to same abscissa
  - Energy
  - Wave vector



Catalyst


Sample 1
Sample 2
Sample 3
Sample 4
Sample 5
Sample 6
Sample 7
Sample 8
ρ3(r')
k (A-1)

Catalyst


Sample 1
Sample 2
Sample 3
Sample 4
Sample 5
Sample 6
Sample 7
Sample 8
ρ3(r')
r' (Å-1)

Artificial Standards

- Mathematical constructs
- Derive from the original spectra (not separate standards)
- No two standards reproduce the same features
- Weighting factor to measure how important each artificial standard is in reproducing the entire series
- Unique

Linear Algebra

- Vector space
- Orthogonal
- Eigenvalue
- Normalized eigenvector

- PCA terminology: components

Components

- Number of derived components equals number of original spectra
  - Not equally important (weighting factor)
- Use of all the components will reproduce the original spectra EXACTLY (including experimental noise)
- Most important components (large weighting factor) contain real spectral features
- Least important components (small weighting factor) represent noise and other errors
- Each experimental spectrum contains both physically meaningful data and noise

Singular Value Decomposition

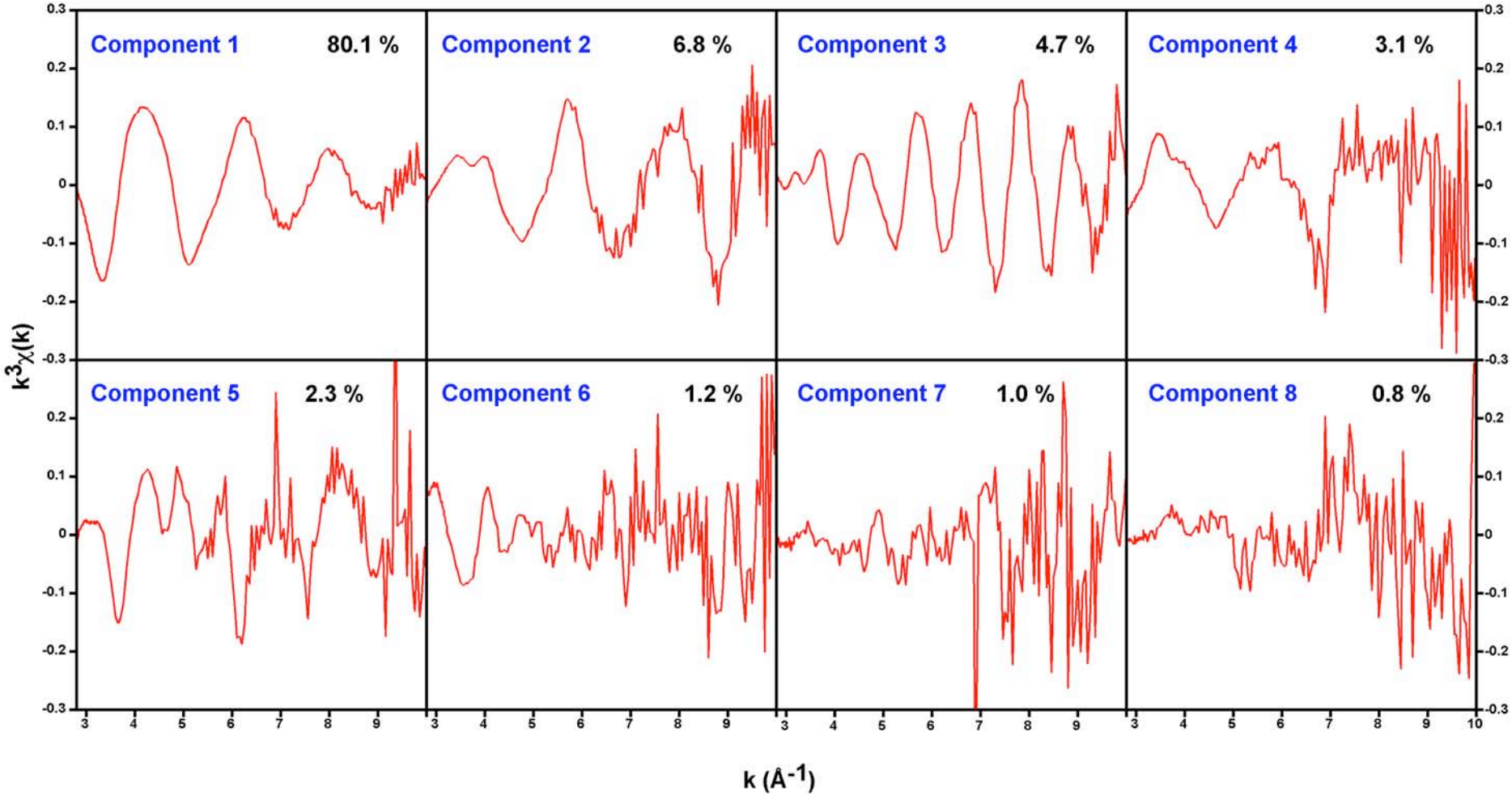
Matrix with M rows and N columns

$$\begin{bmatrix} \\ A \\ \\ \end{bmatrix} = \begin{bmatrix} \\ U \\ \\ \end{bmatrix} \cdot \begin{bmatrix} w_1 & & & \\ & w_2 & & \\ & & \ddots & \\ & & & w_n \end{bmatrix} \cdot \begin{bmatrix} \\ V^T \\ \\ \end{bmatrix}$$

M x N	M x N	N x N	N x N
	Columns orthogonal	Diagonal (positive or zero)	Orthogonal (square matrix)
Data	Components	Eigenvalues	Weights
		(importance for entire series)	(importance for an individual spectrum)

- PCA assumes data matrix is “effectively” singular

Components: Catalyst



Heart of PCA

- Goal: Find number of components that can reproduce the spectra to within experimental error

- Number of used components equals the number of pure species in the spectra

- Theorem: If a vector space has one basis with a finite number of elements, then all other bases are finite and have the same number of elements.

Primary Components

- Correspond to meaningful data
- Determination:

1) Error analysis
2) Reproduce the experimental data with components
3) For EXAFS, examine the Fourier transform
4) Amplitude of component times weighting factor

Secondary Components

- Not used in reproduction of data
- Weighting factors describe the contribution of a component to ENTIRE series
- Sum of weighting factors from secondary components represents errors
- Examine this sum as a function of number of primary components

Error Analysis

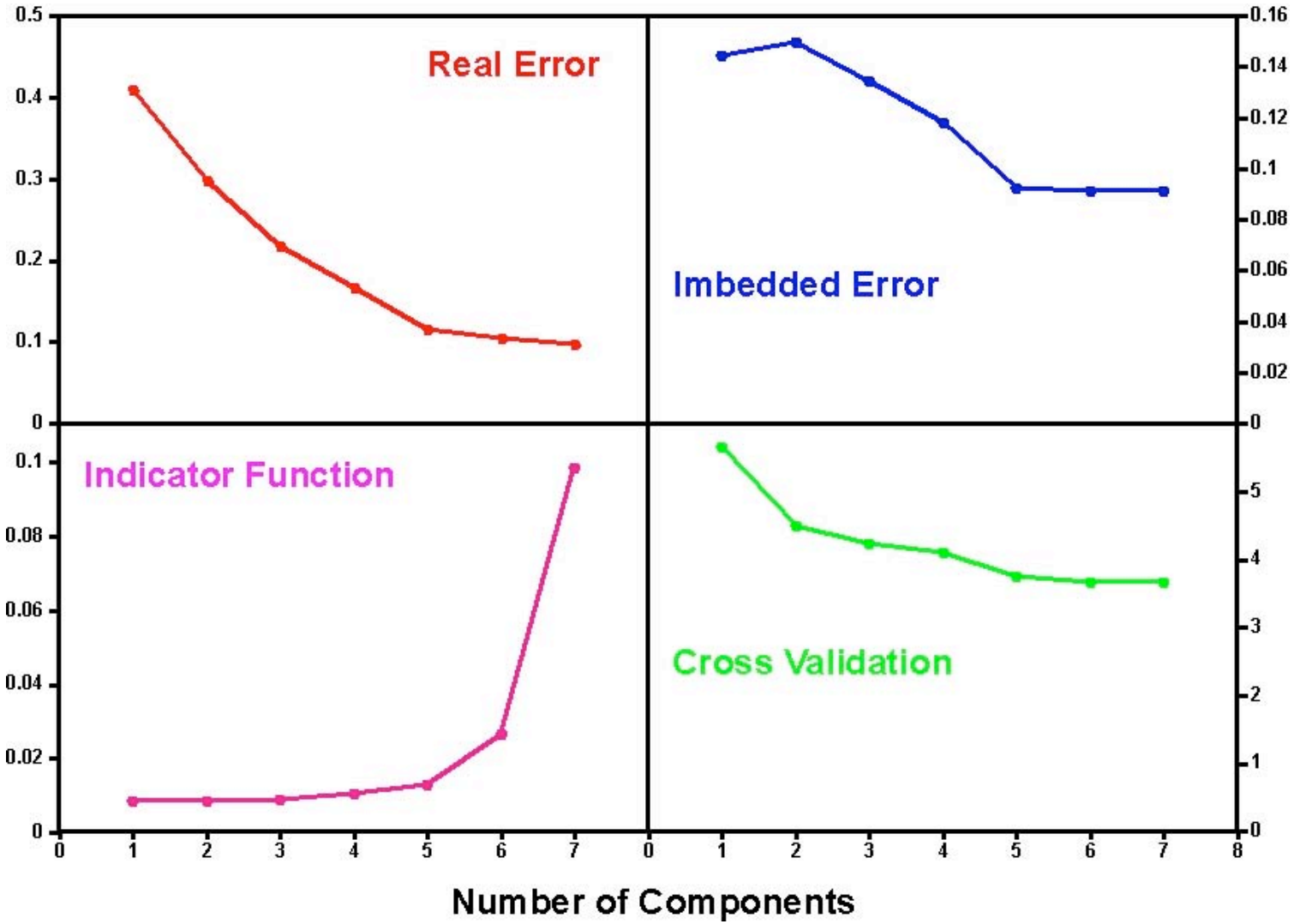
- Real Error (RE)
  - Difference between pure data and experimental data
  - Discontinuity as a function of number of primary components: change in type of information in components from data to noise
- Extracted error (XE)
  - Error separated from data by PCA
- Imbedded Error (IE)
  - Error present in primary components
  - Discontinuity

Error Analysis

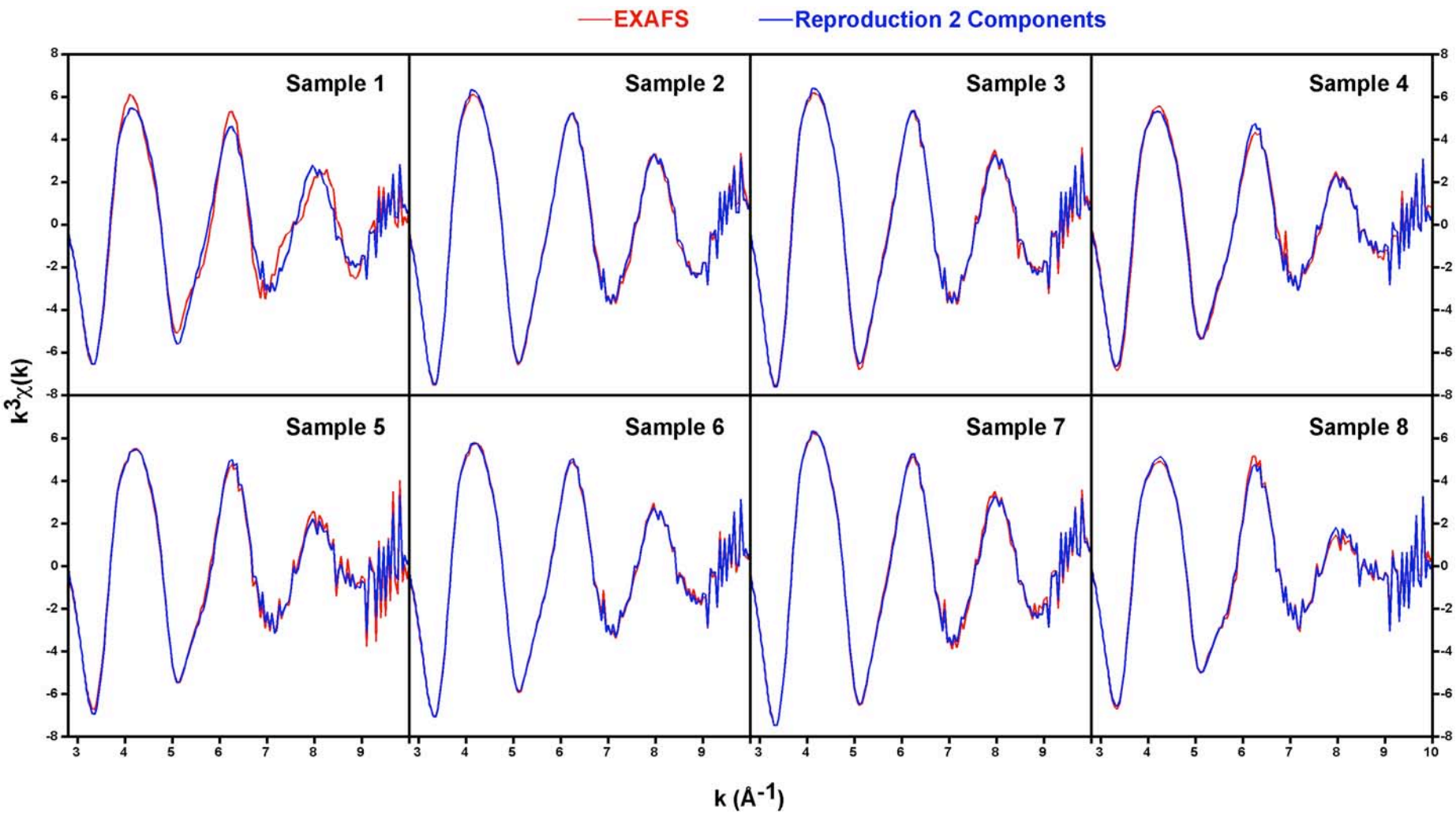
- Indicator Function
  - Penalty for inclusion of more primary components
  - Minimum

- Cross-Validation
  - Leave one out
  - Less sensitive to noise
  - Discontinuity

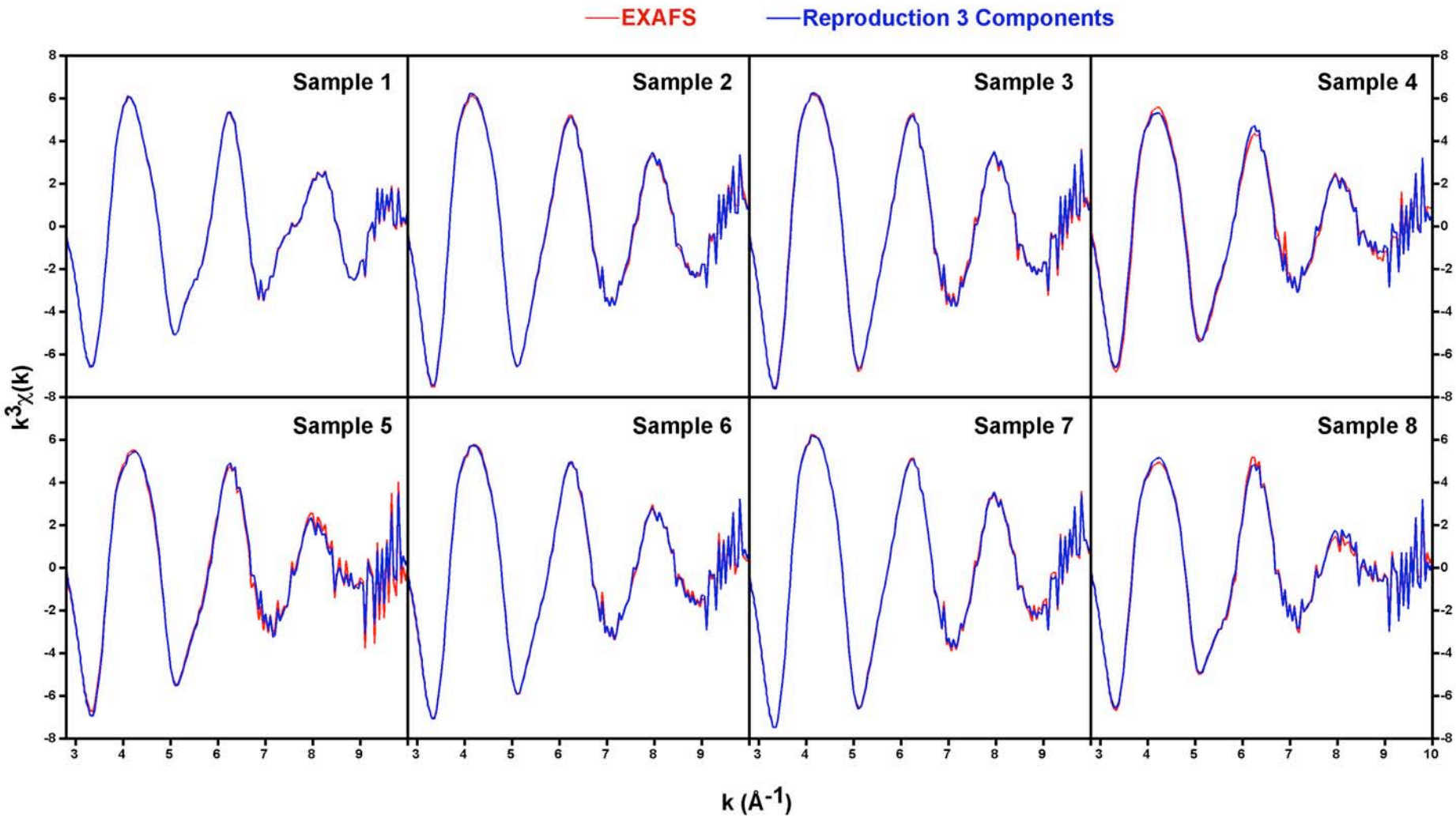
Errors


Real Error
Imbedded Error
Indicator Function
Cross Validation
Number of Components

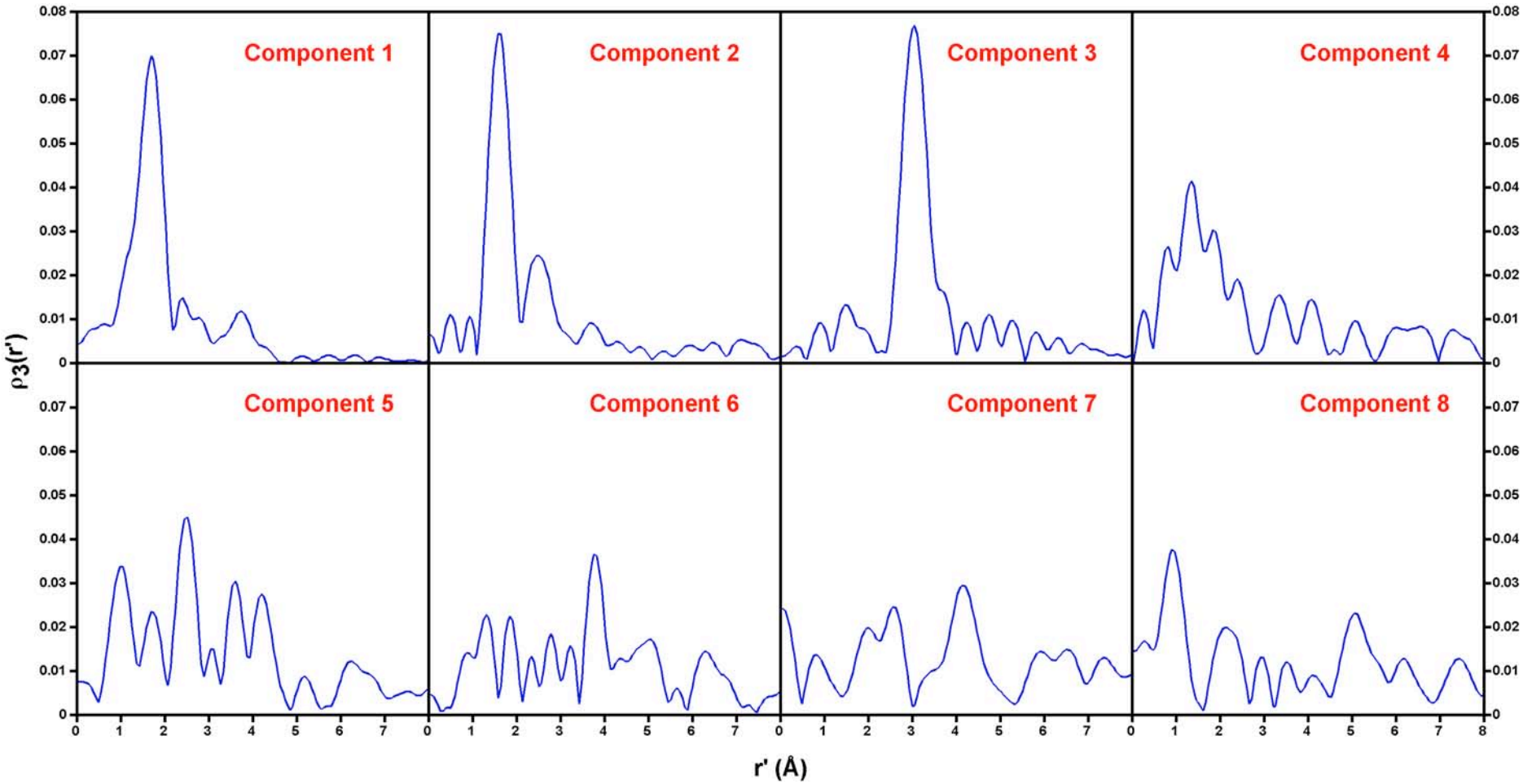
Reproduction: 2 Components



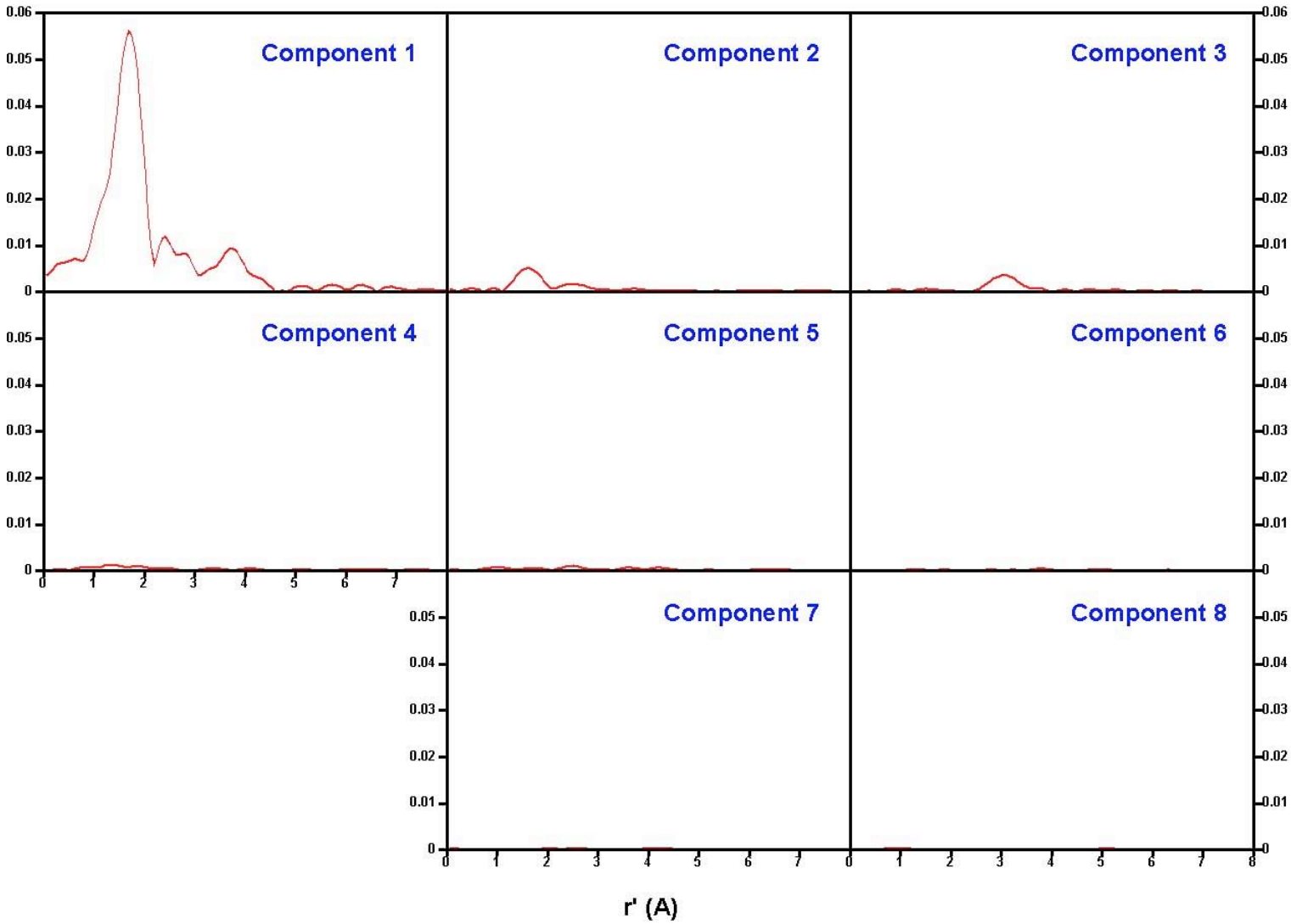
Reproduction: 3 Components



Components: Fourier Transform



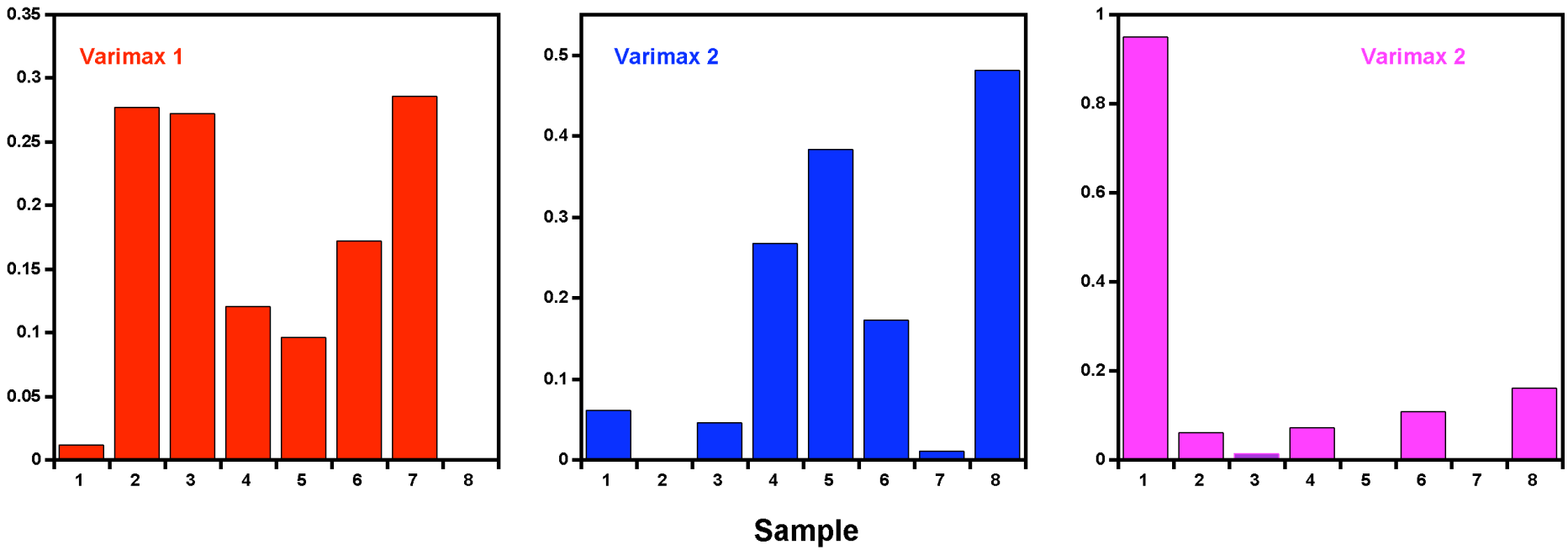
Weighted Components



Finding the Underlying Spectra

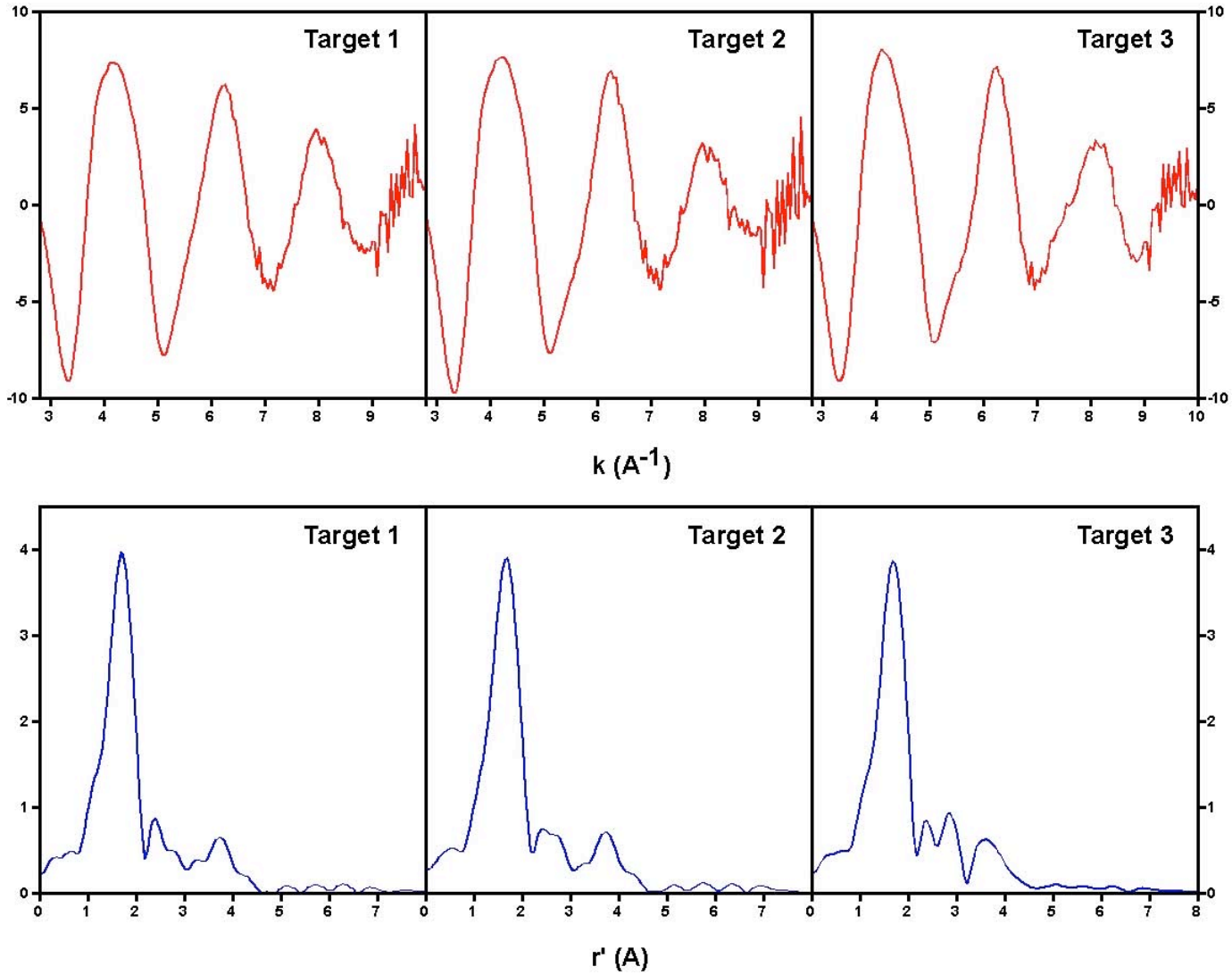
- Rotation
  - Orthogonal
    - Varimax
  - Oblique
    - Target Transformation
    - Next Example

Varimax Rotation



- Predictor of which spectrum has the greatest concentration of a particular species

Iterative Target Factor Analysis (ITFA)



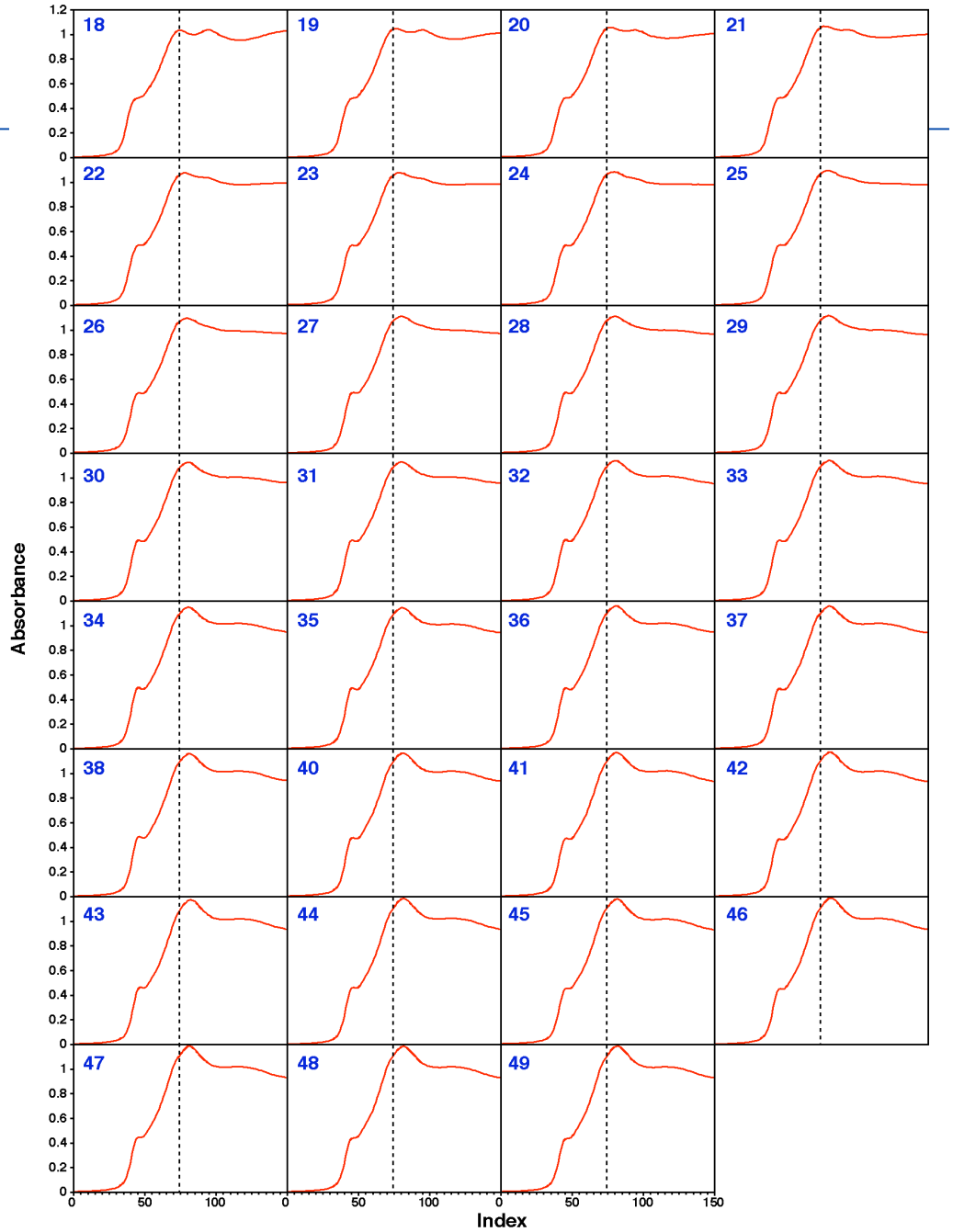
Cu Oxidation

7.8 μm

1) Ar / H_2

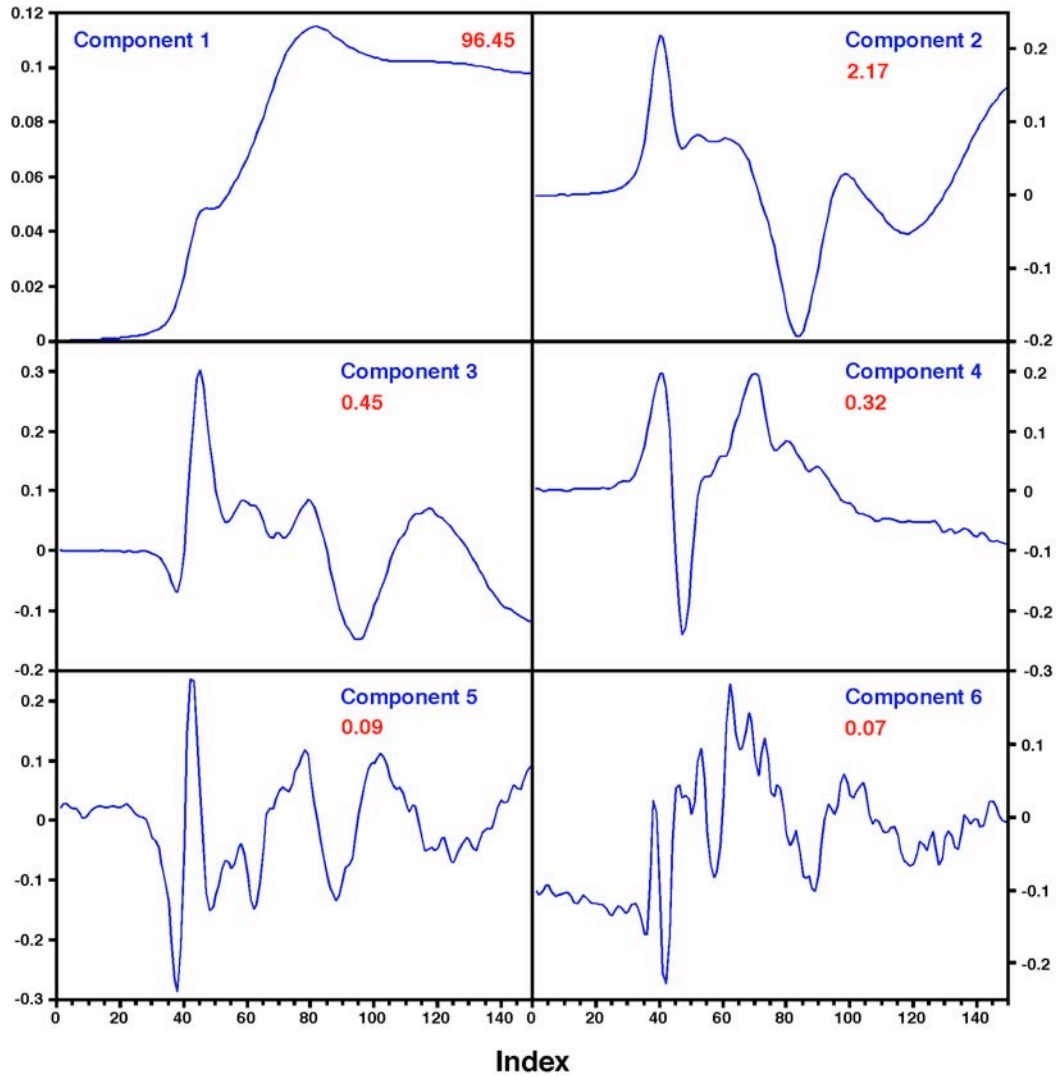
2) CO / CO_2

598 ˚C

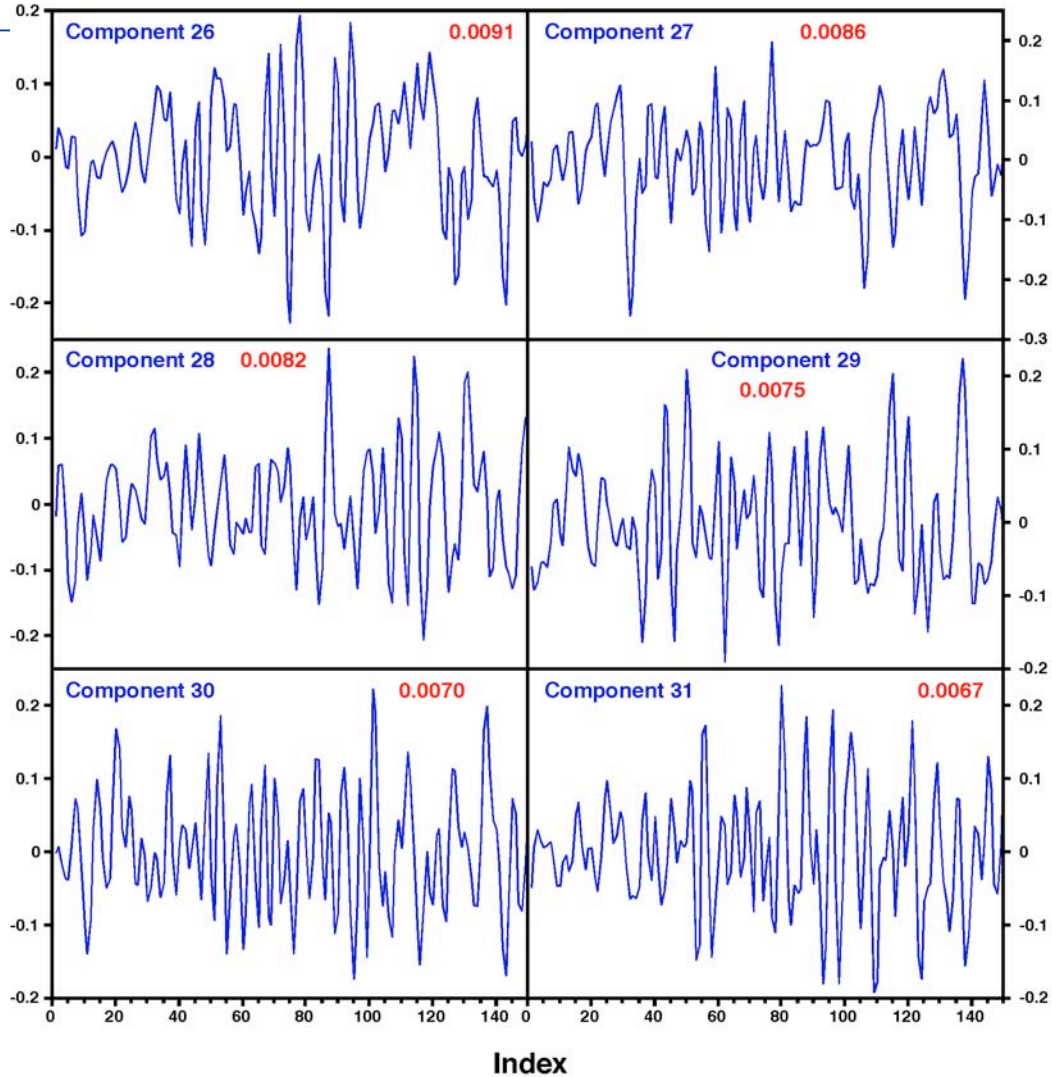


N. Hilbrandt, Th. Buhrmester, G. Schimanke, M. Martin

Components: Cu Oxidation

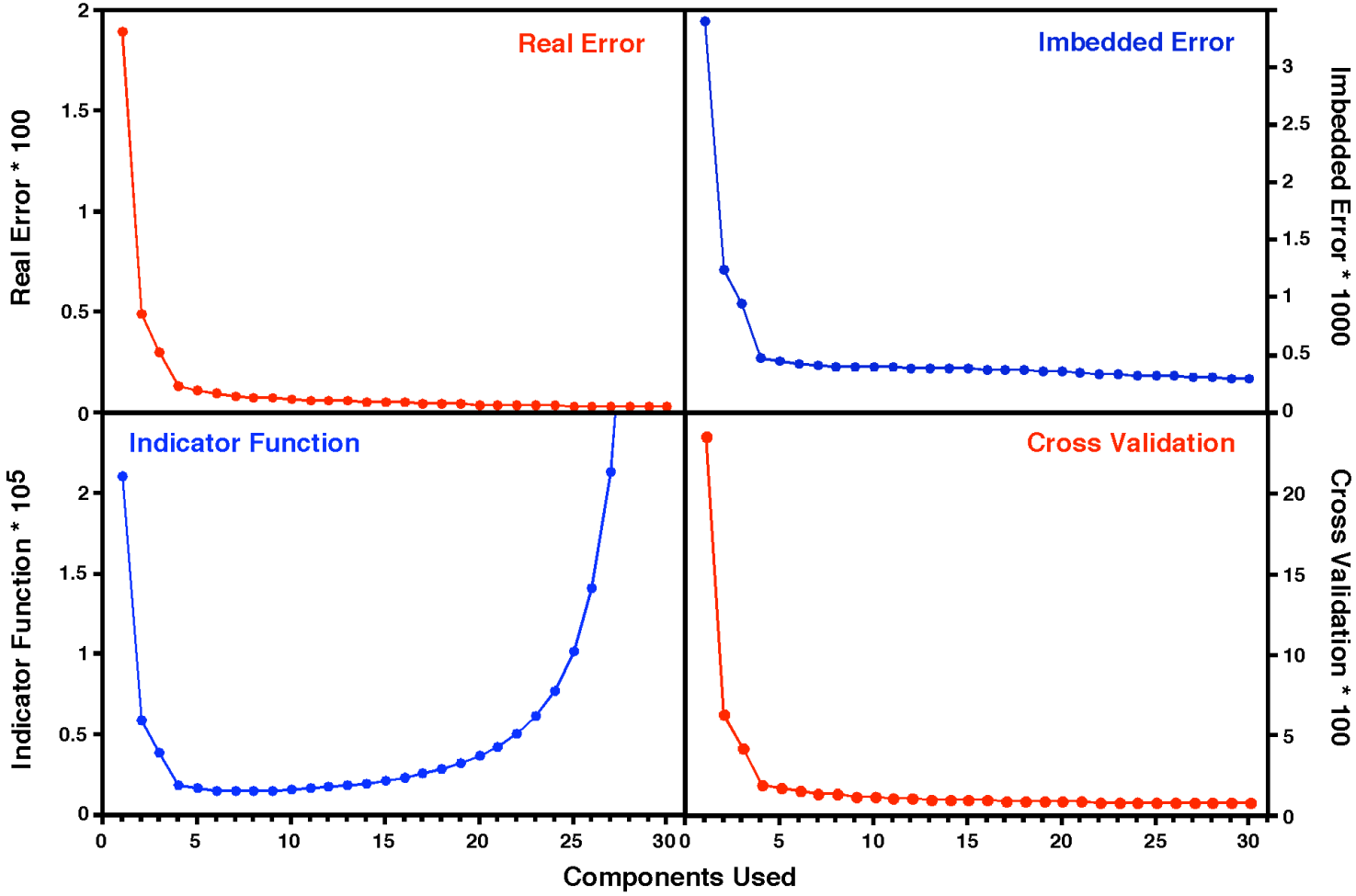


Components: Cu Oxidation

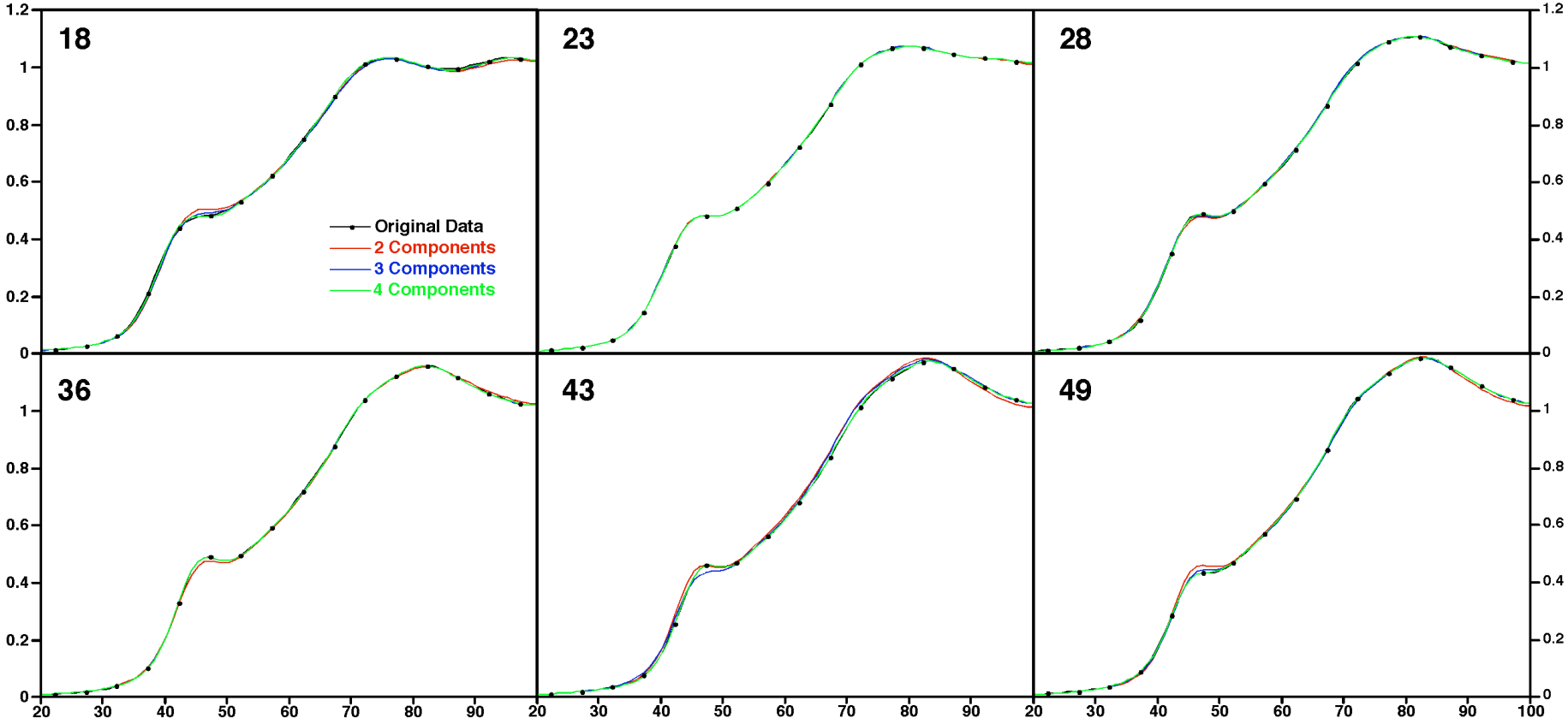


In the worst case, each component can represent only 0.03% of a single spectrum

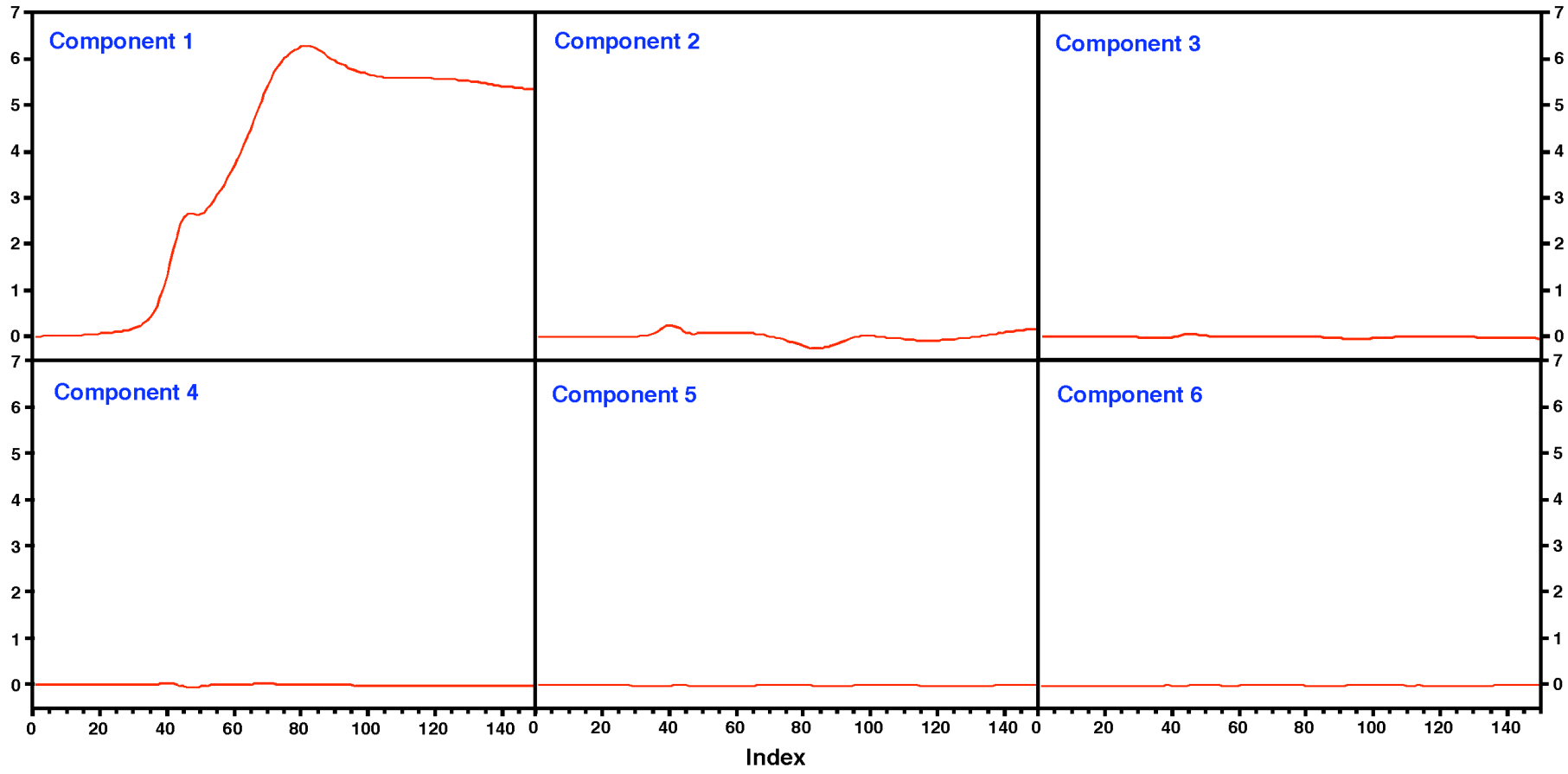
Cu Oxidation: Error Analysis



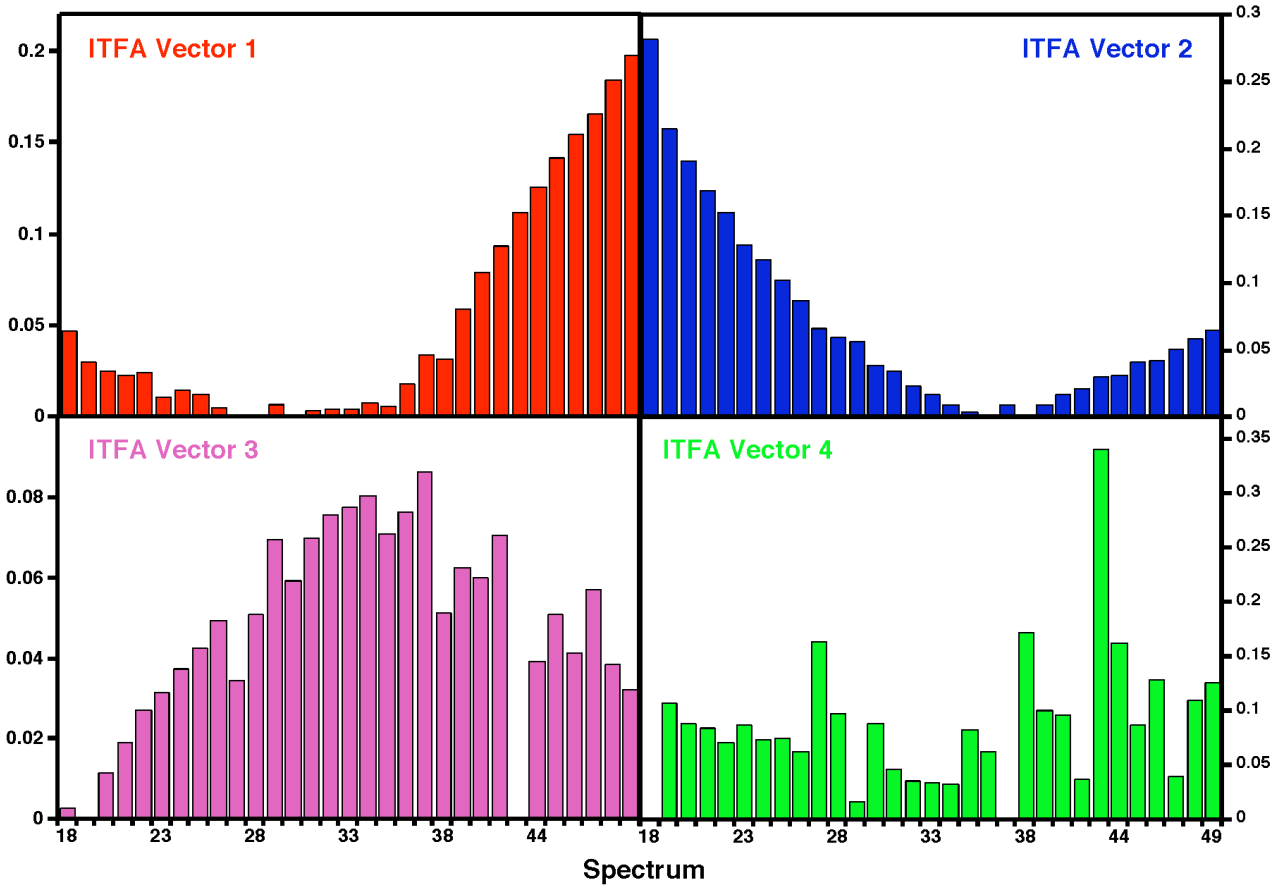
Reproduction: Cu Oxidation



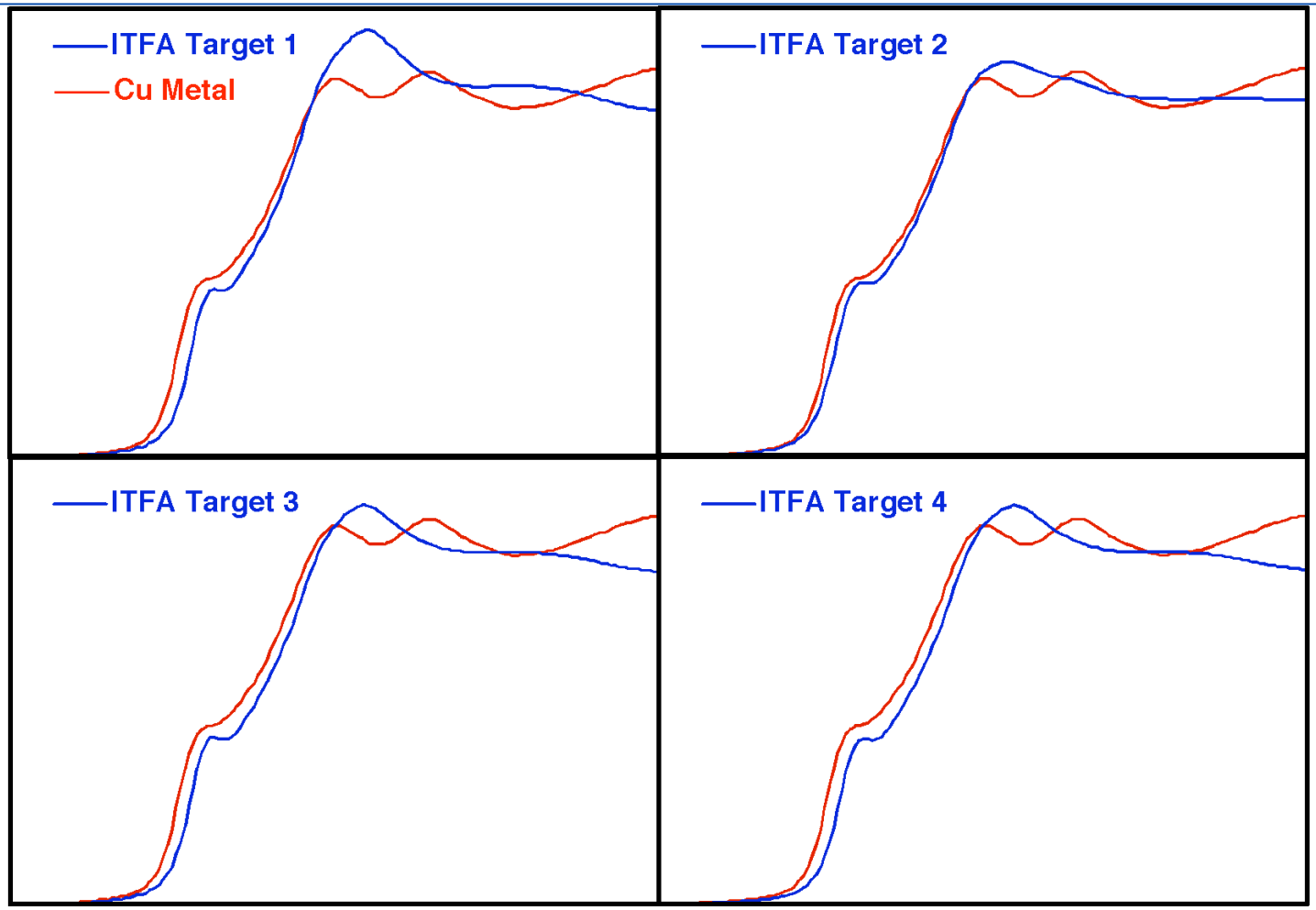
Weighted Components: Cu Oxidation



Varimax Rotation



Ab initio standards: Iterative Target Factor Analysis

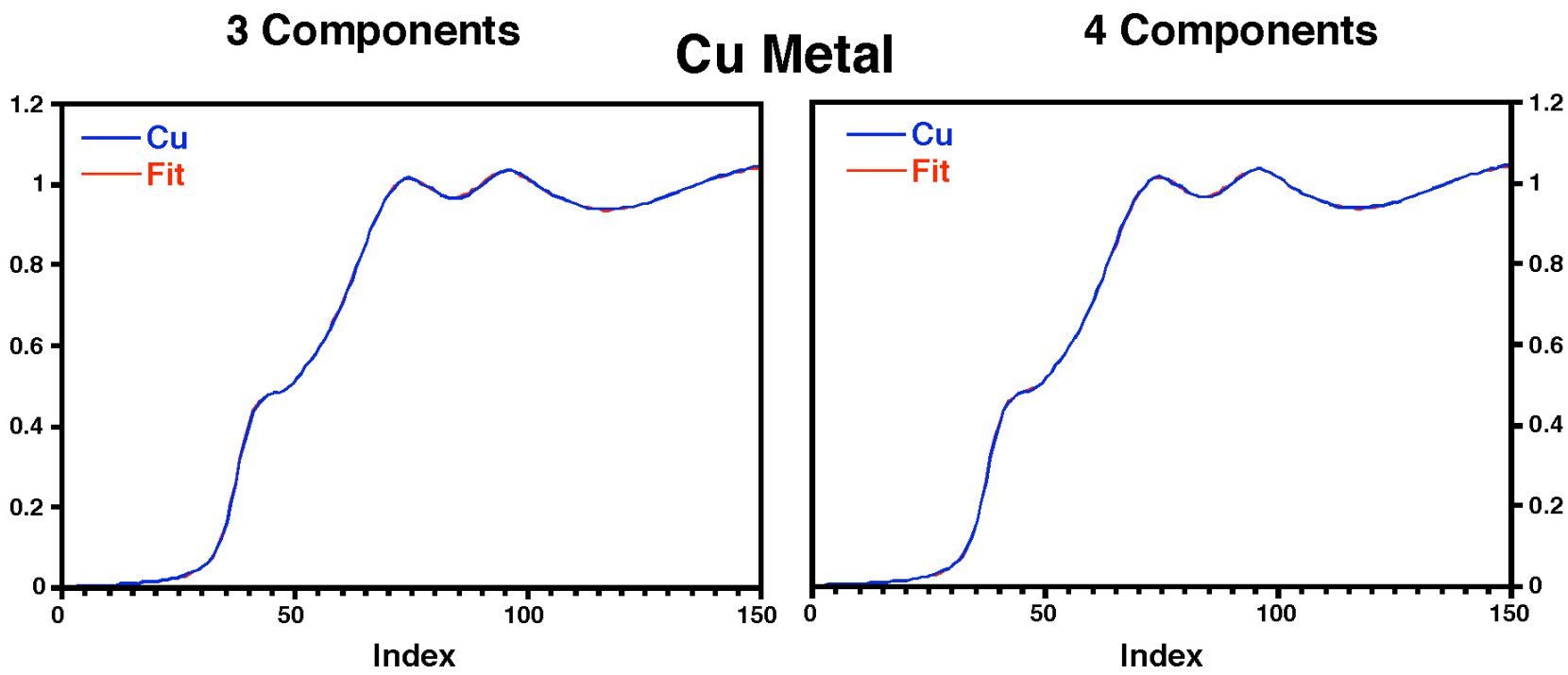


- The spectra predicted by ITFA generally cannot be trusted in XAS

Real Standards

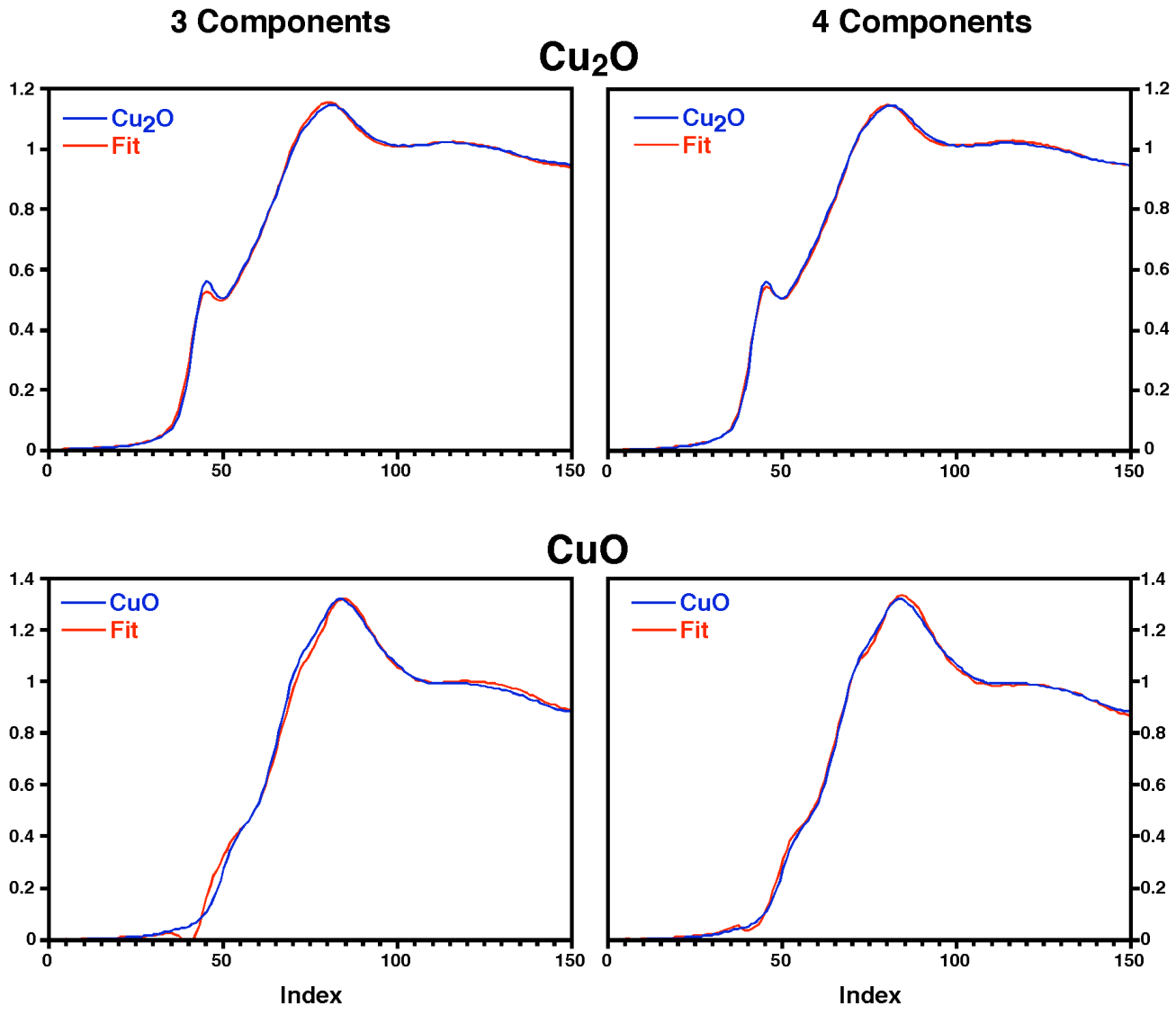
- A real standard must be fit by the primary components
- Examine a standard compound WITHOUT knowing which other compounds are present
  - Invert traditional method of fitting edges to standards
  - Mathematically, primary components are equivalent to the original spectra (except for error)
- PCA can eliminate potential standards
- Only determine if a standard is reasonable

Target Transformation

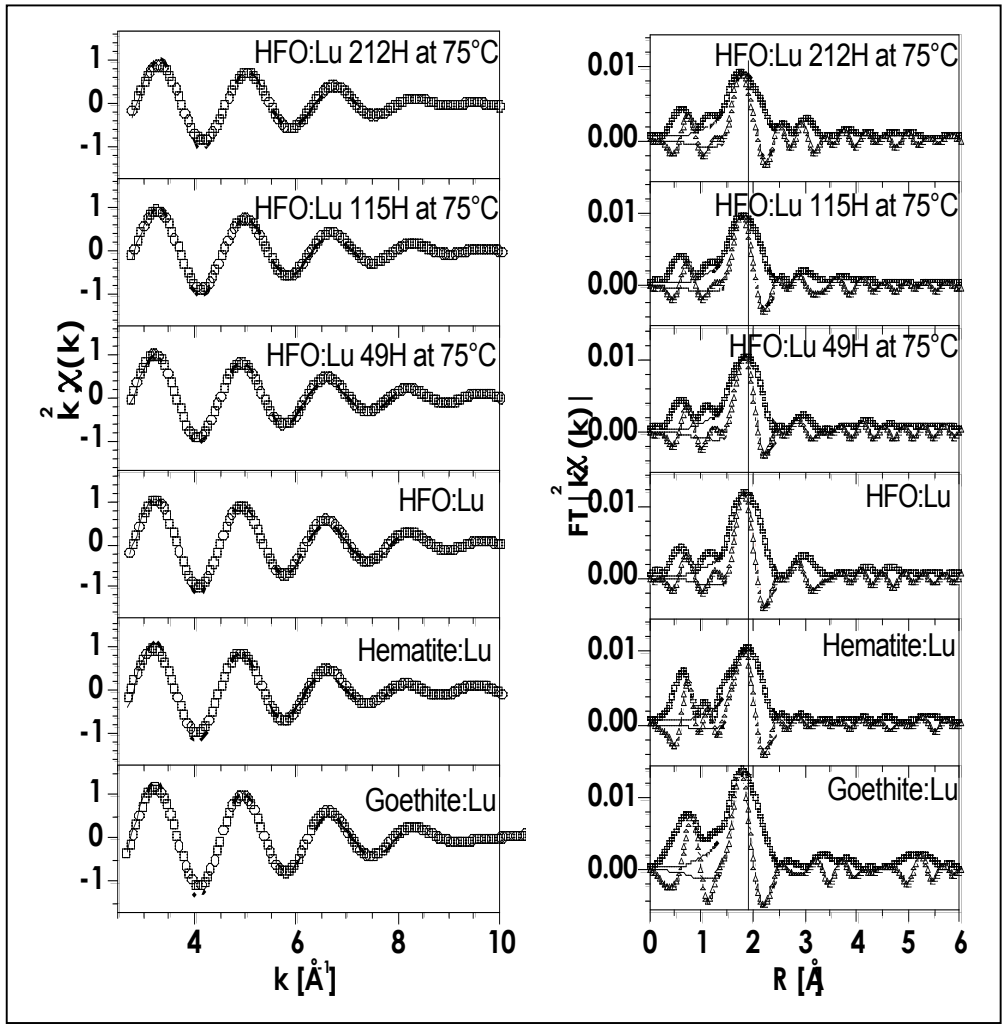


- A spectrum in the series is a valid standard by target transformation

Standards: Target Transformation



Sorption of Lu(III) on Hydrous Ferric Oxide



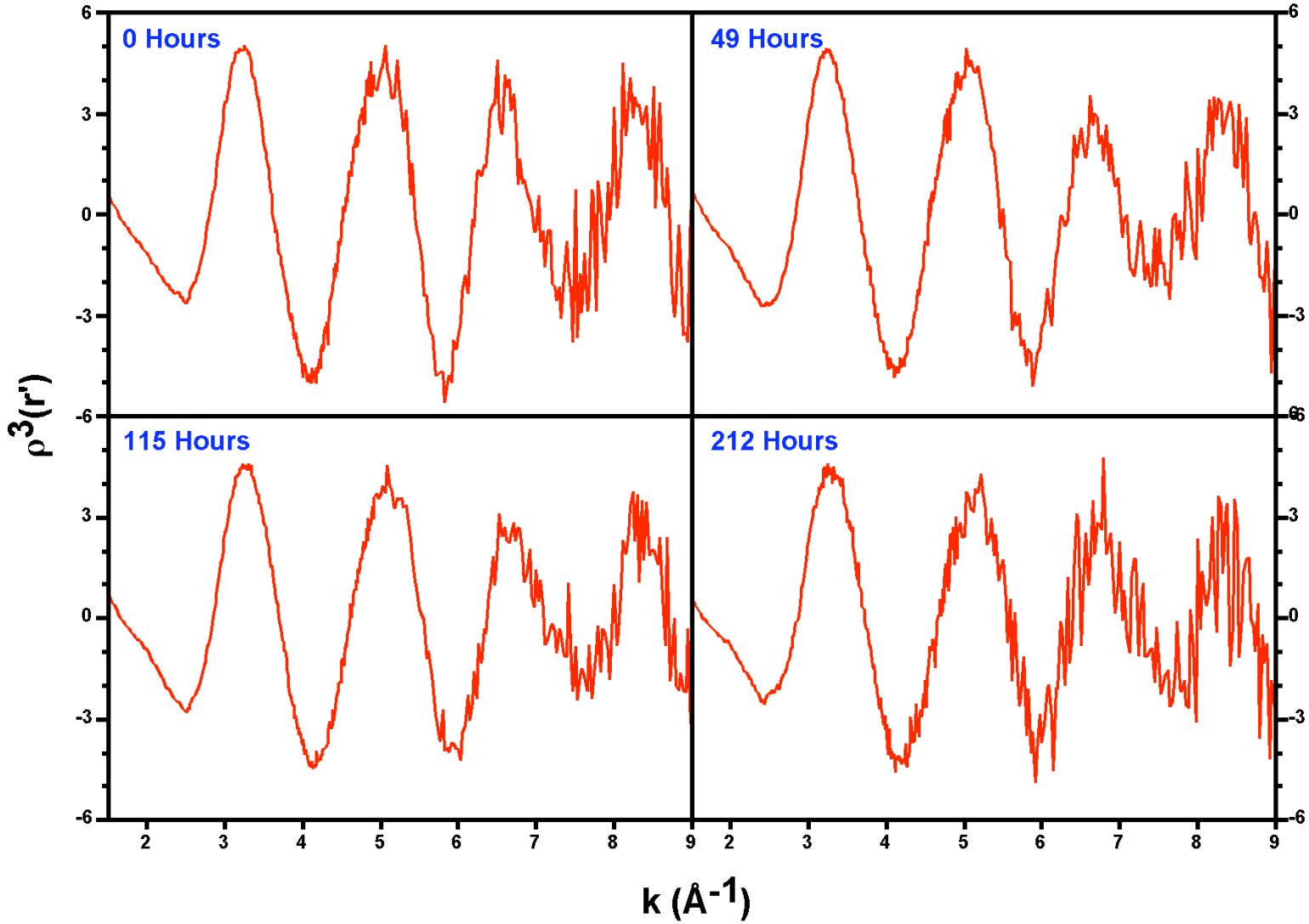
2.25 A

2.26 A

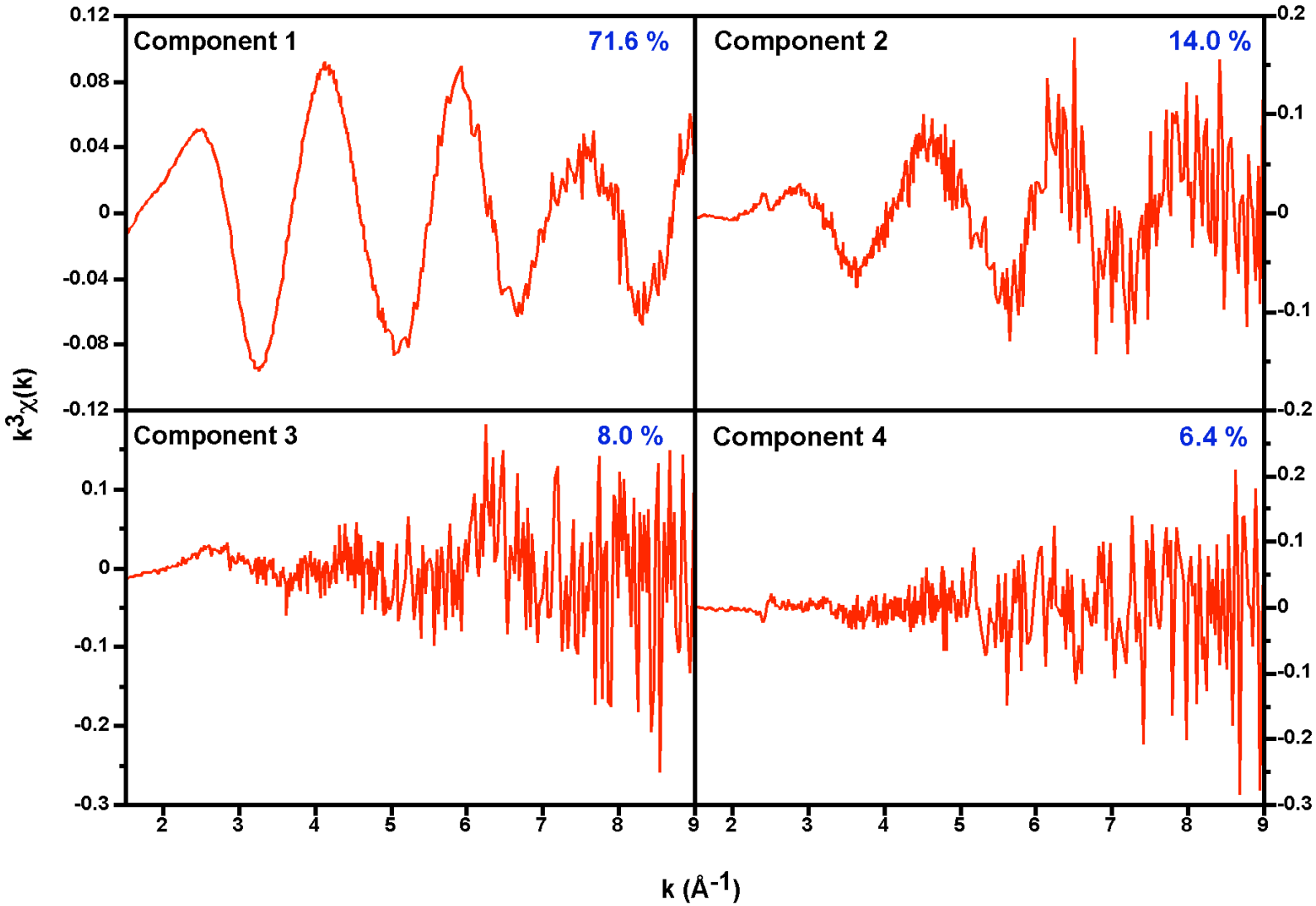
2.29 A

2.30 A

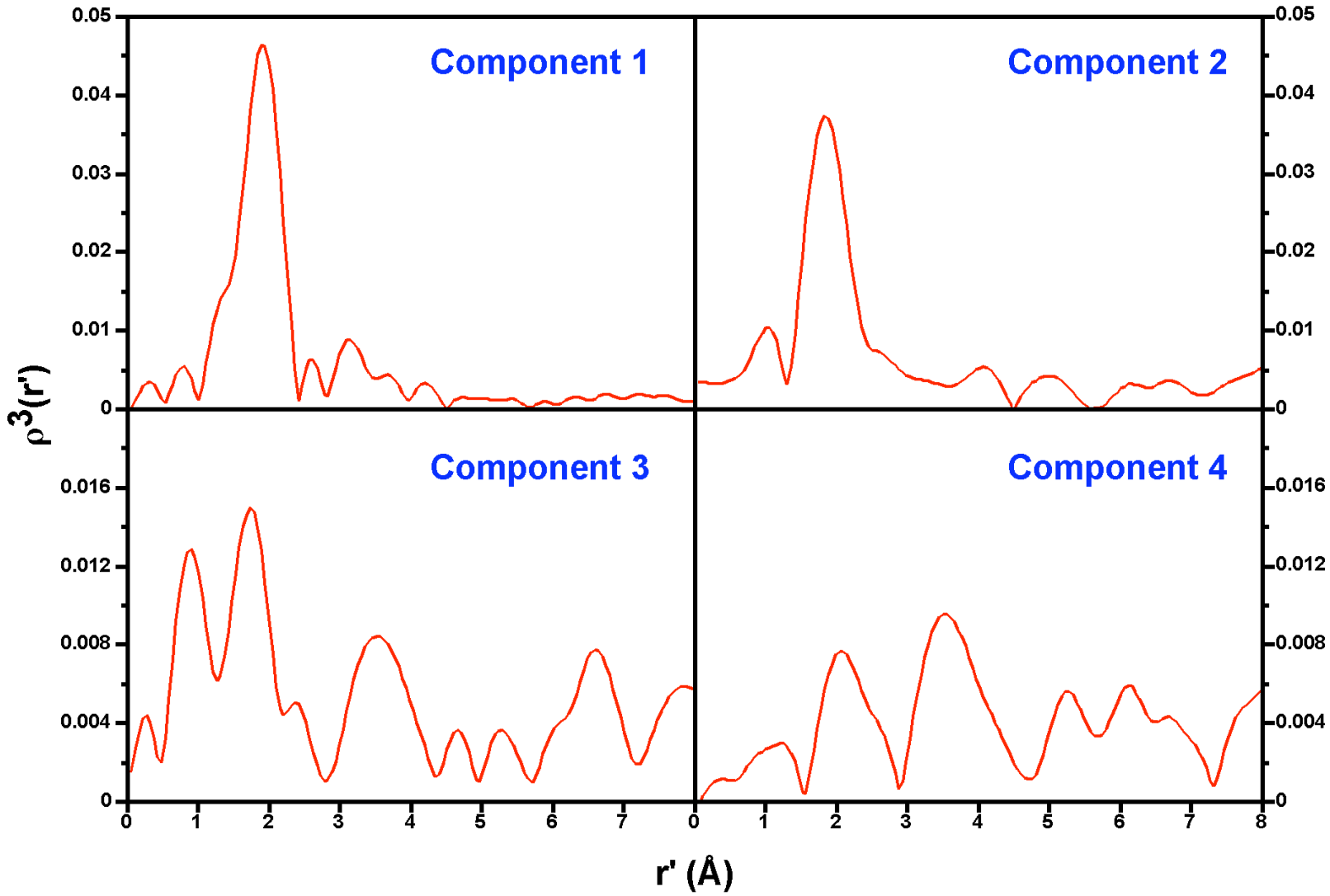
Sorption of Lu(III) on HFO



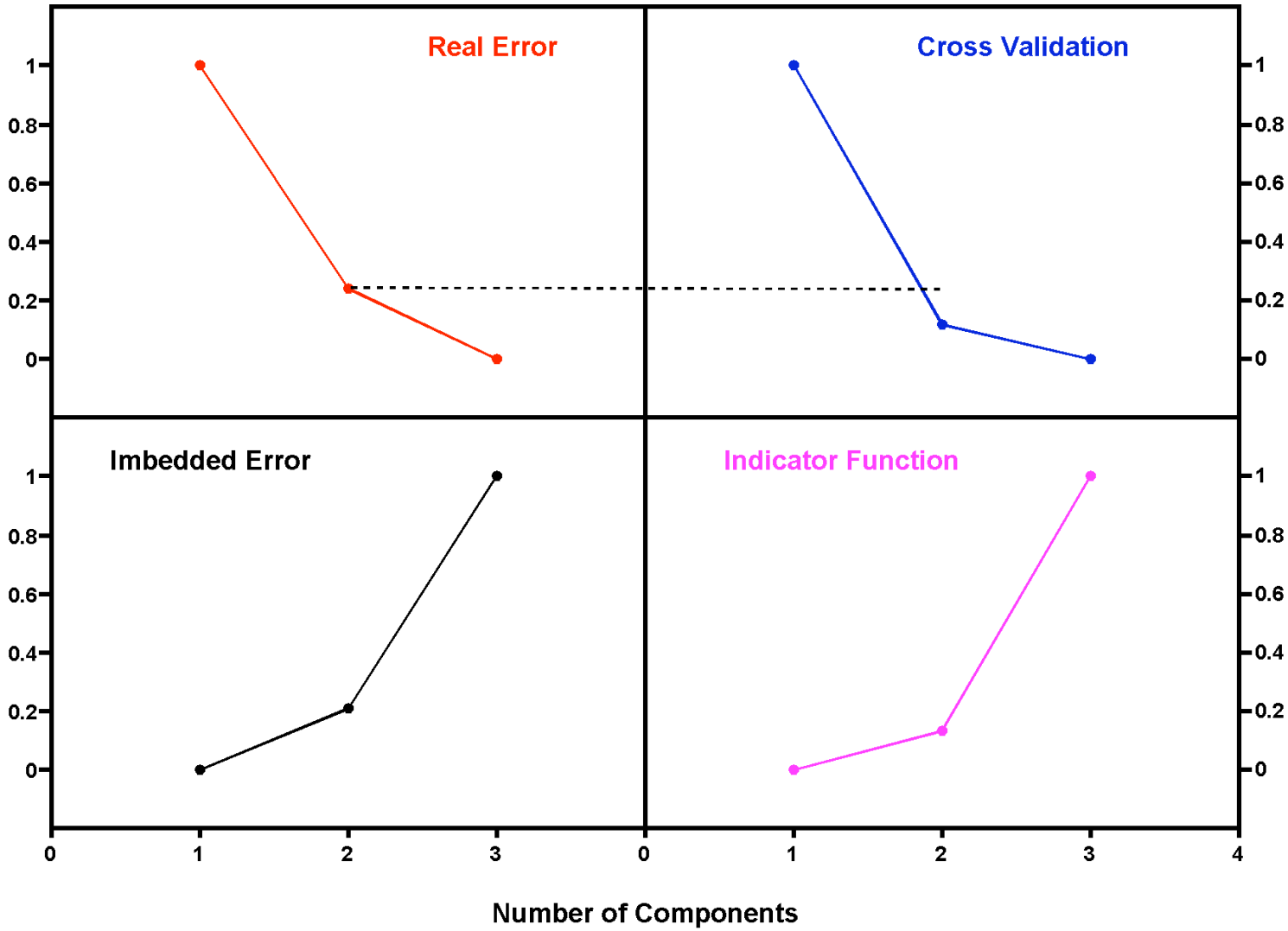
Lu(III) on HFO: Components



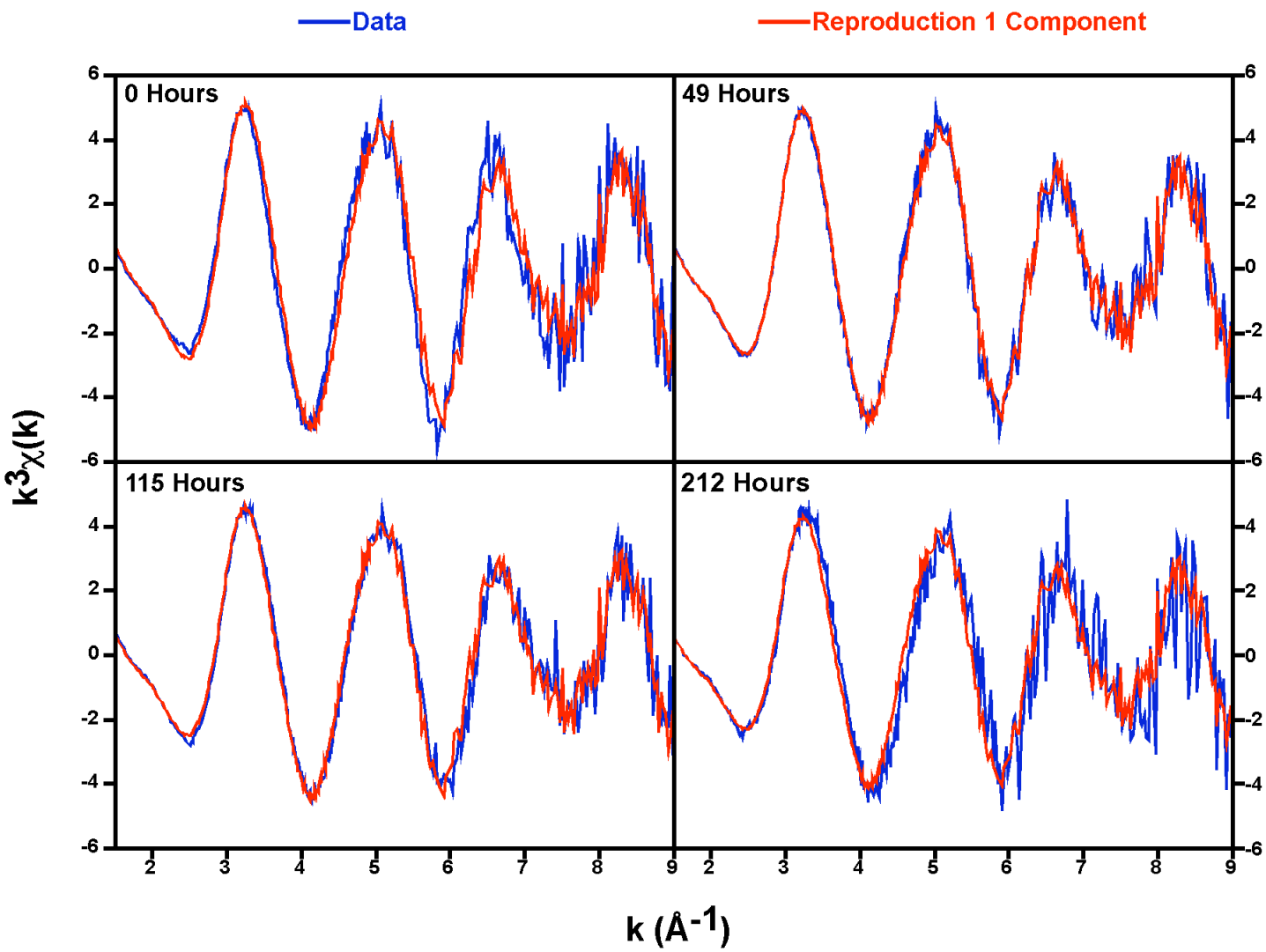
Lu(III) on HFO: Components



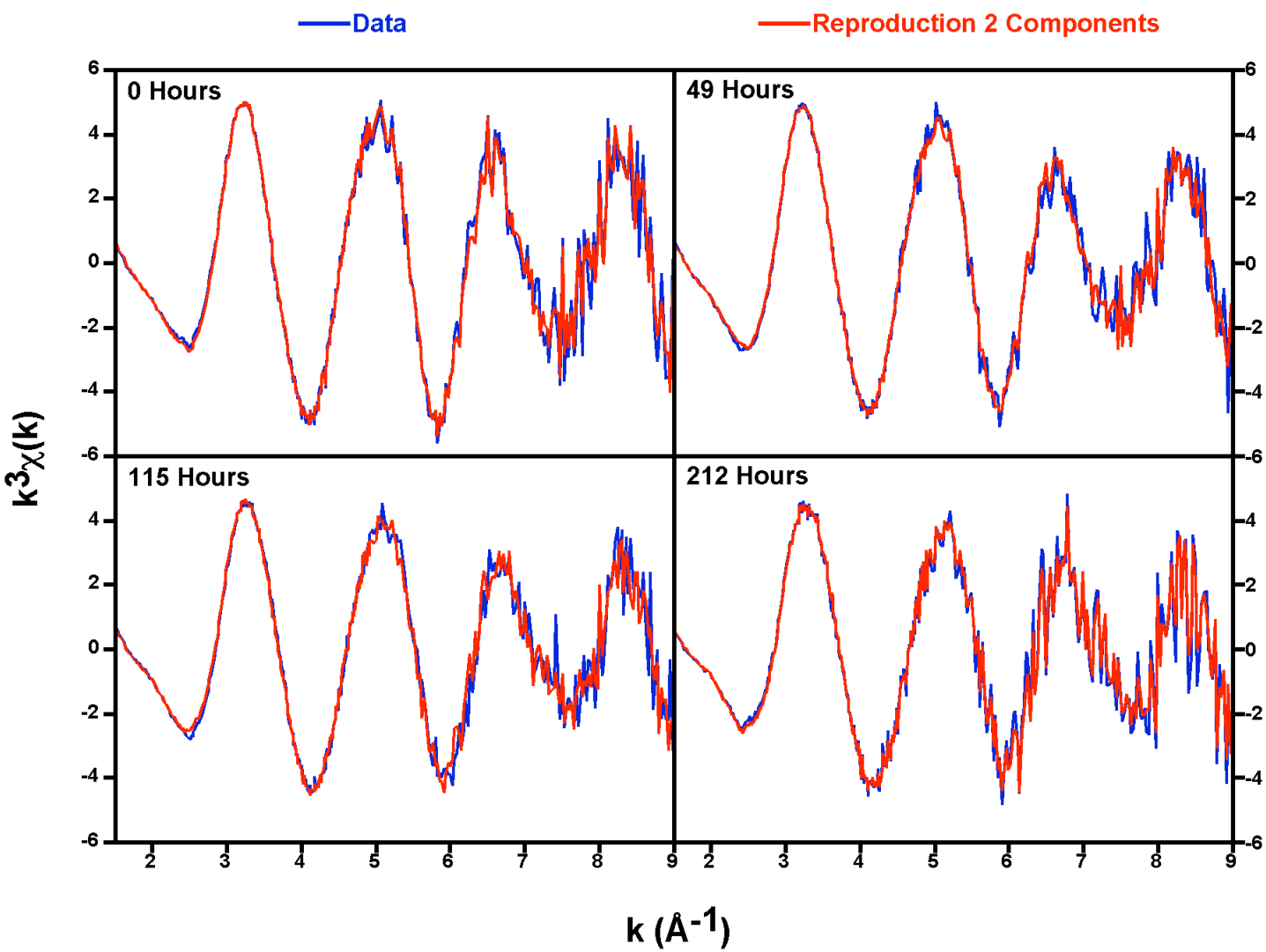
Errors: Lu(III) on HFO



Reproduction: 1 Component



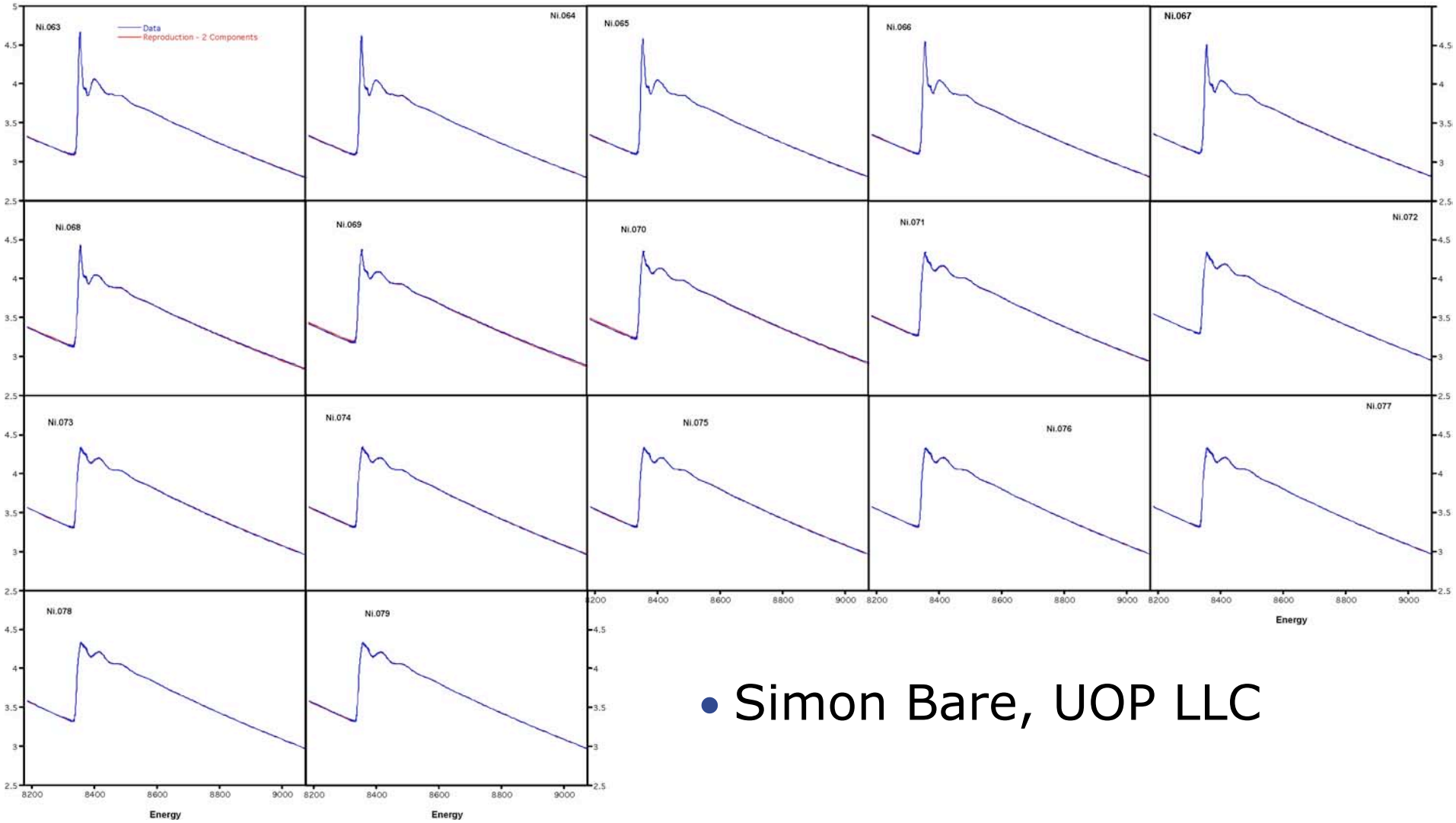
Reproduction: 2 Components



Degrees of Freedom: Lu(III) on HFO

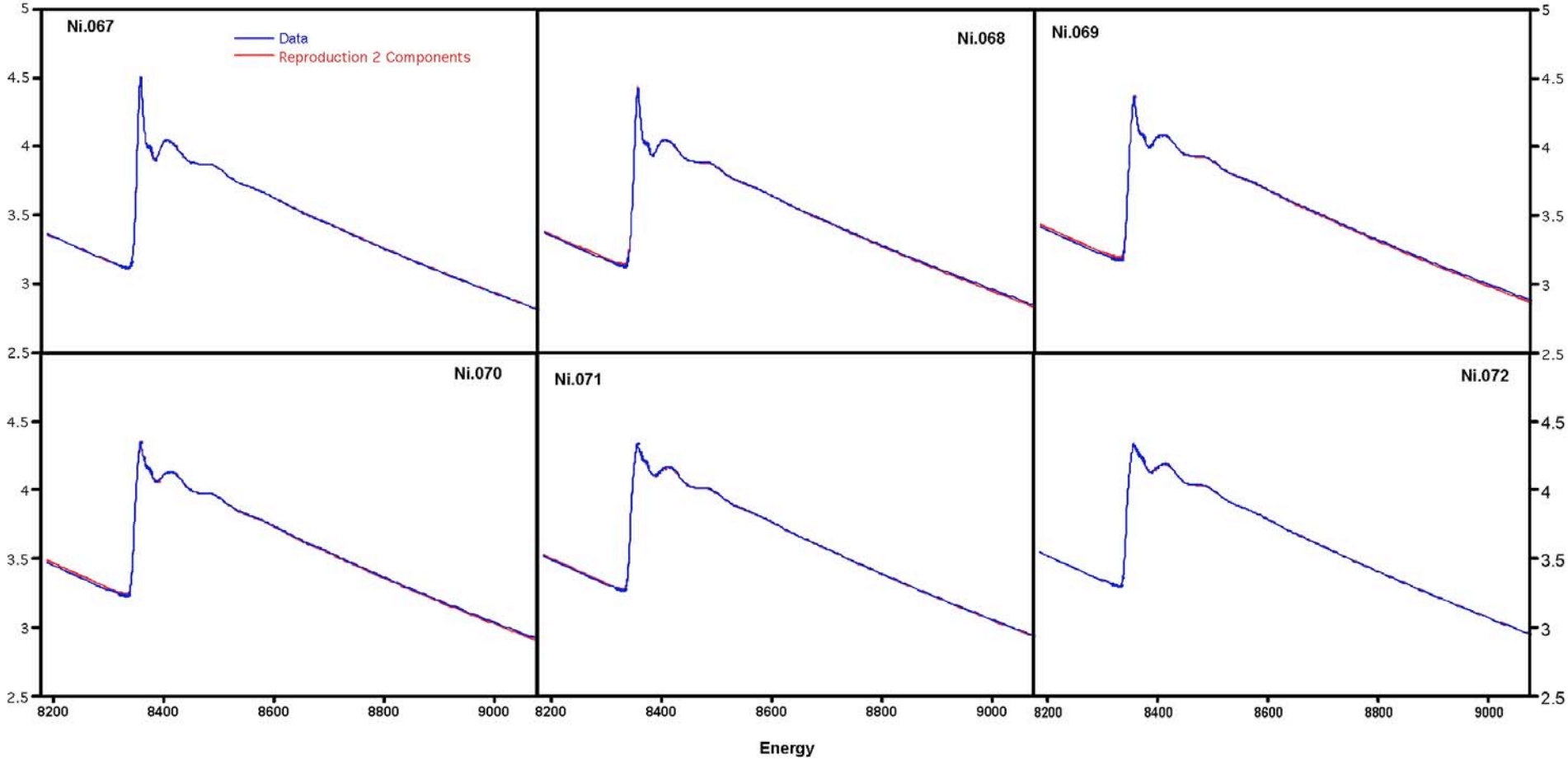
- $\delta k = 7.5$
- $\delta r \sim 1.5$
- d.o.f ~ 7
- Restricted to 1 shell (unless fix parameters)
- Increase d.o.f. using series of samples

Sulfidation of Ni Oxide

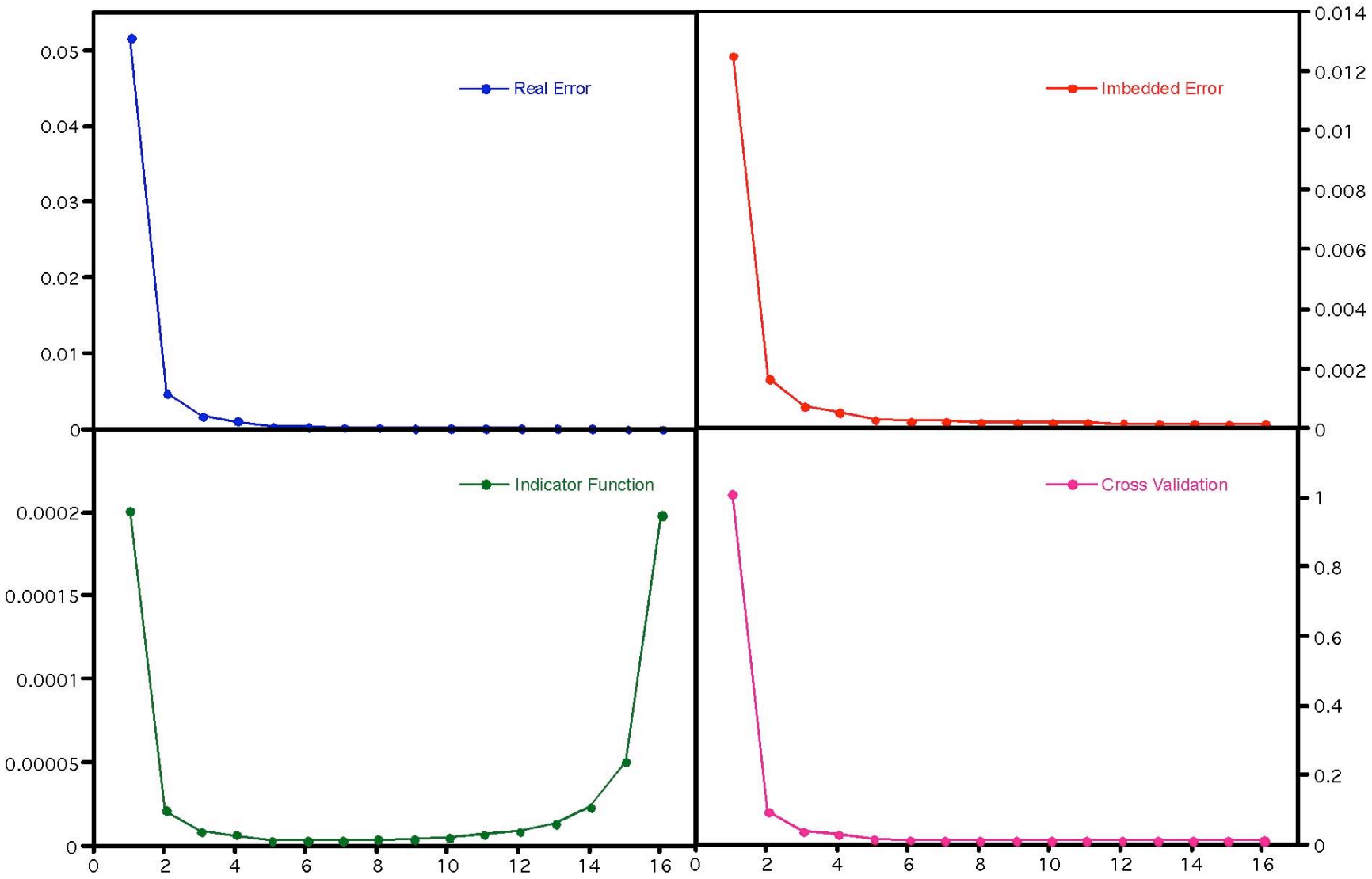


- Simon Bare, UOP LLC

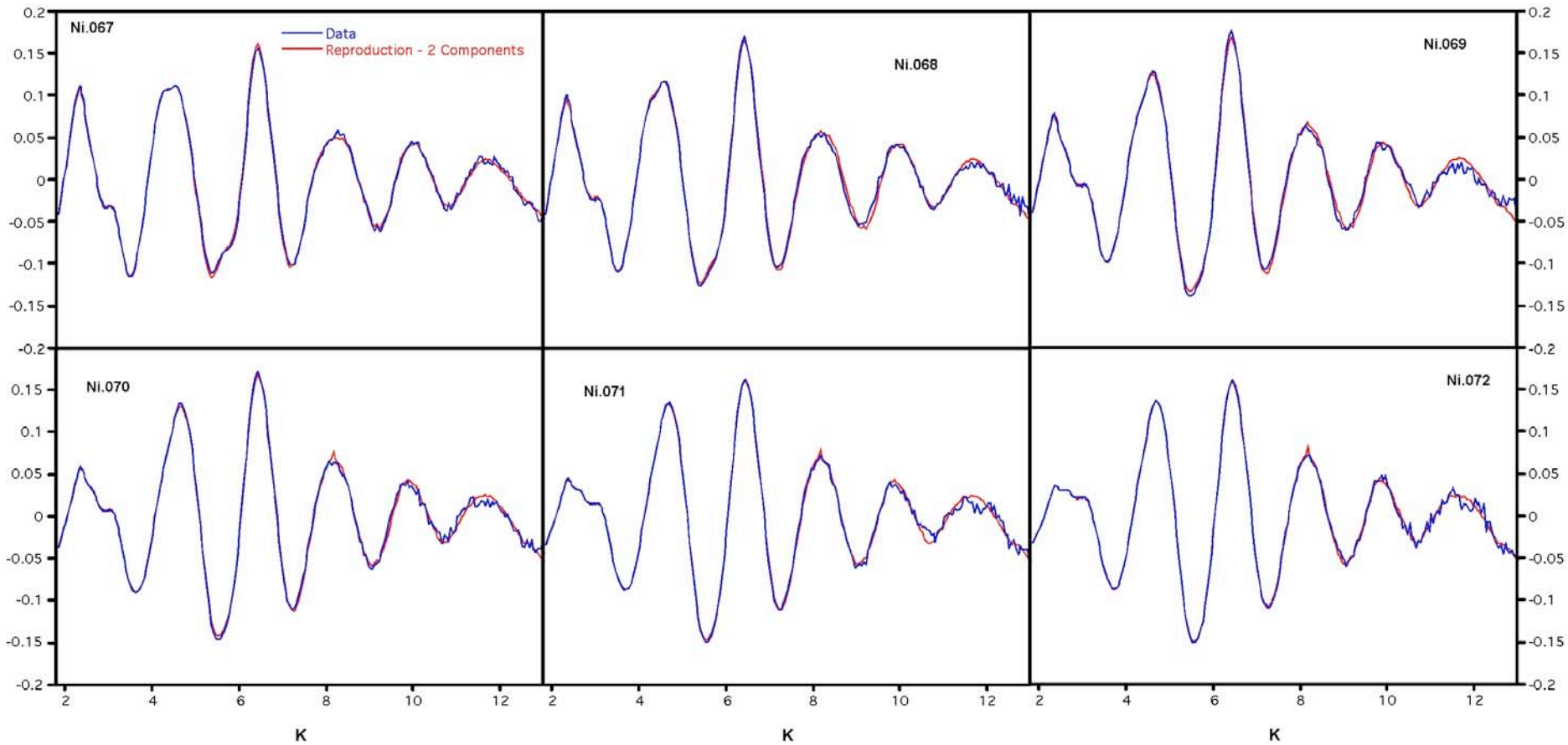
The Interesting Spectra



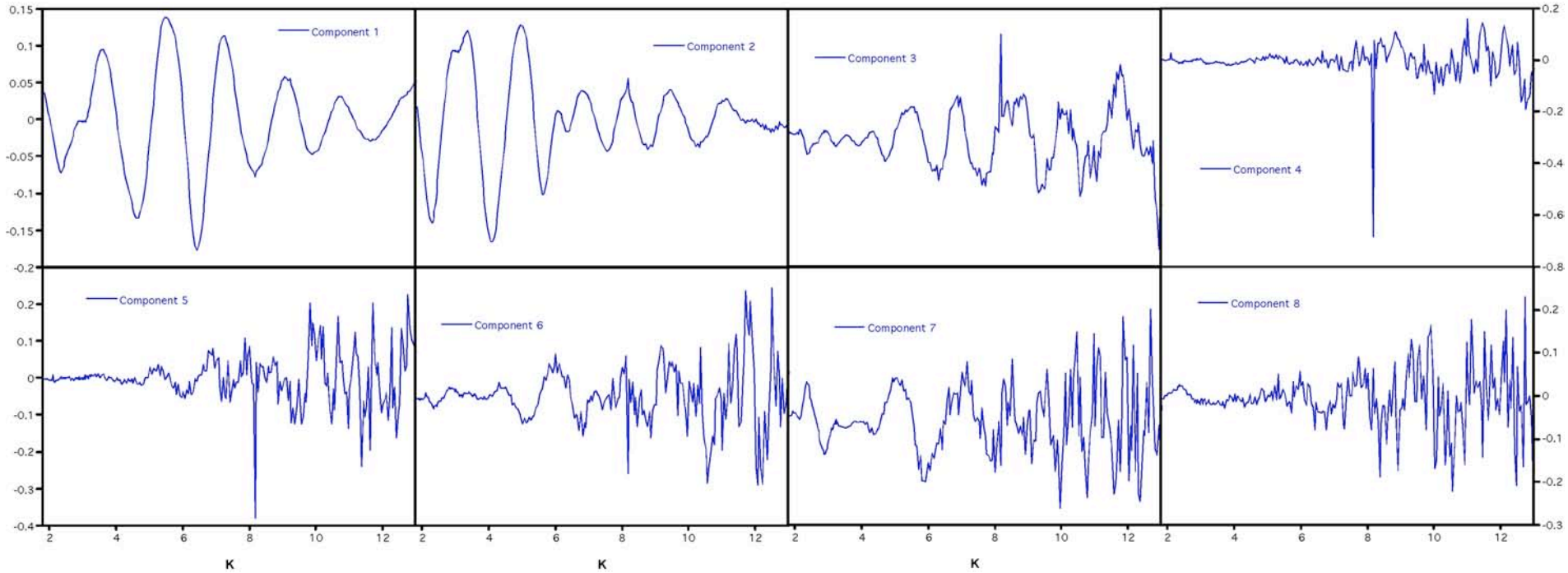
Ni Sulfidation - Error Analysis



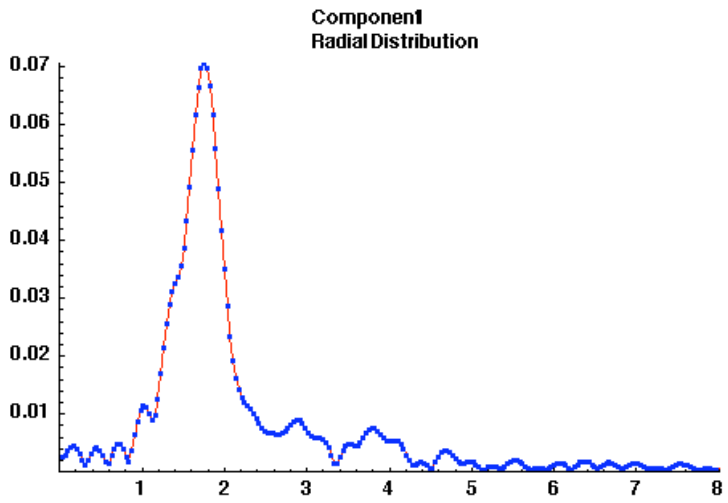
Ni Sulfidation - EXAFS Reproduction

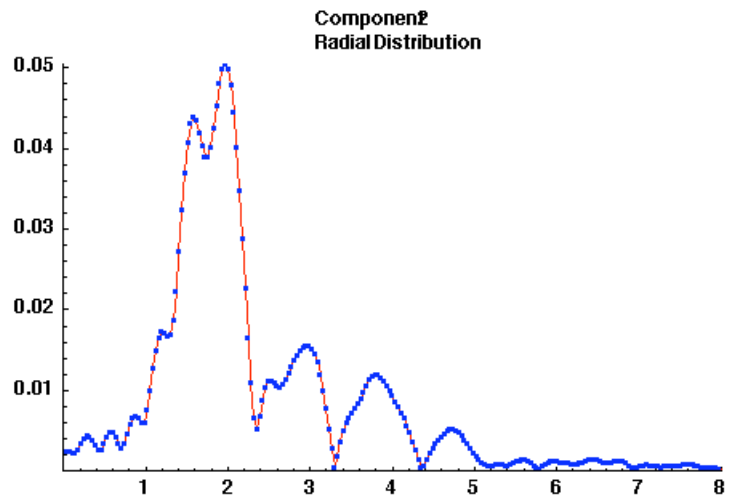


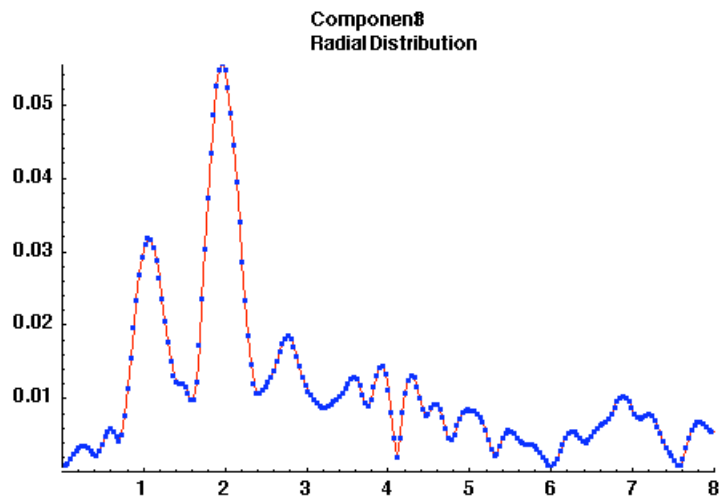
Ni Sulfidation - EXAFS Components

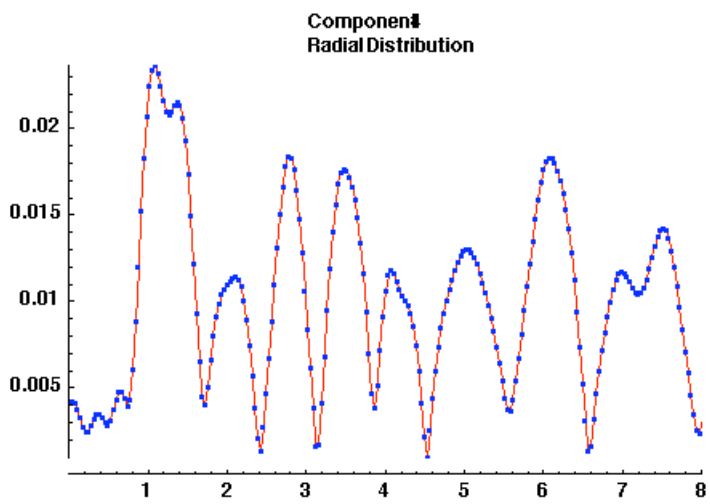


EXAFS Components









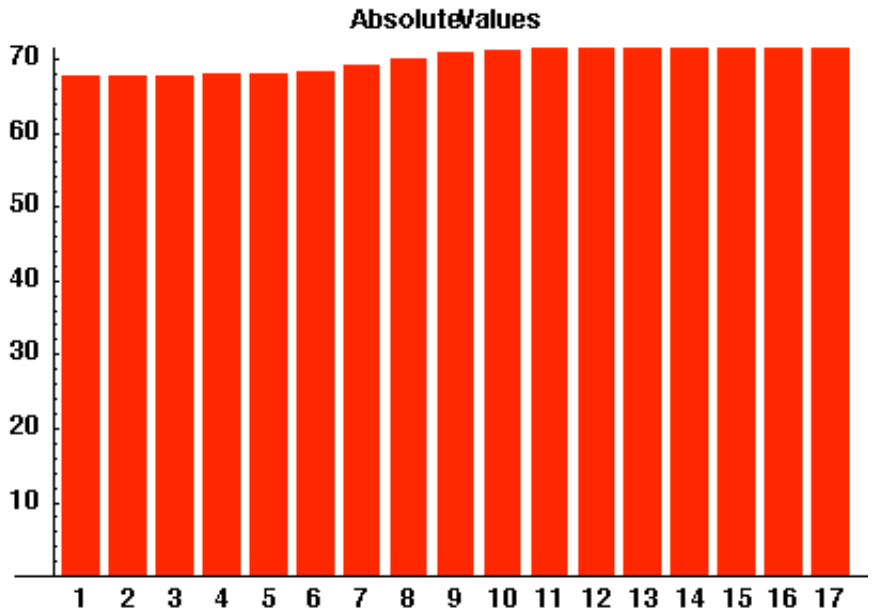
Is the Third Component Real?

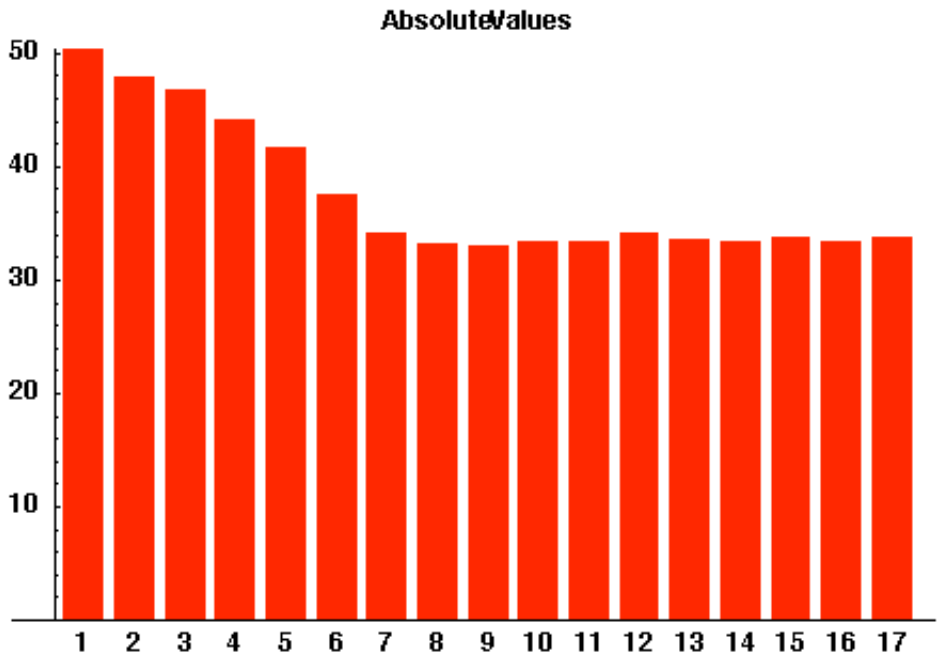
- Is it a primary component?
- Firm conclusion: the spectra are detectably different
  - Chemical
  - Experimental
- Data are well calibrated
  - relative range: -0.066 to 0.030 eV
  - less than ΔeV/2 ~ 0.25 eV
  - (do edge fits for more accurate calibrations)
- Seen in raw data and in EXAFS
- Less than 7.5 % of absorption in any spectrum

Absolute Value

- XANES

EXAFS





- XANES: Integrated intensity

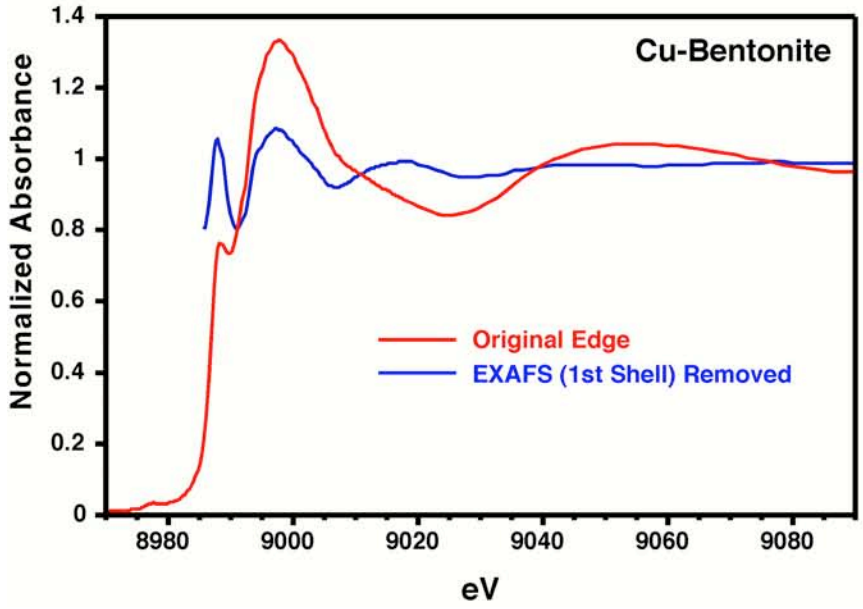
PCA vs. FT

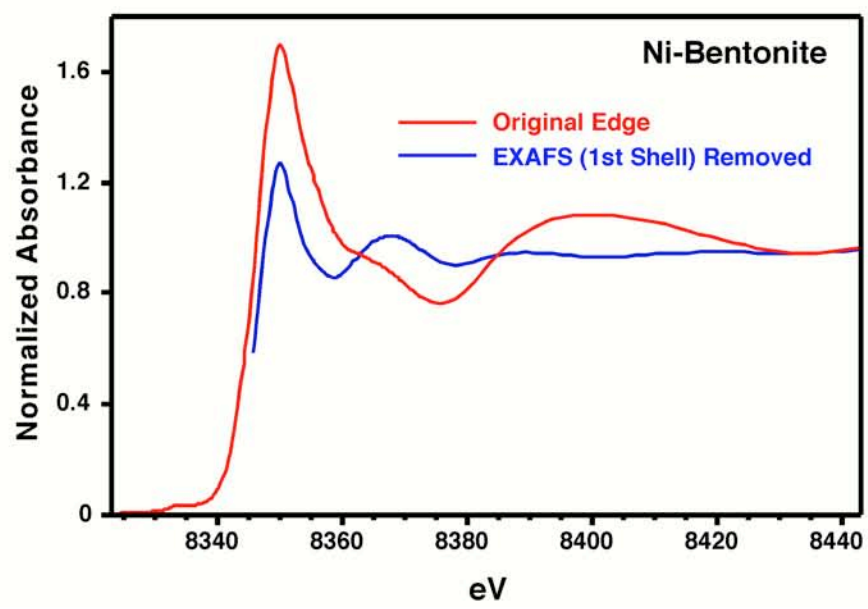
- PCA creates an alternative representation in vector space
- FT creates a representation in conjugate space
- For both, underlying data are unchanged

Limitations

- Experimental artifacts can be interpreted as components
  - Energy calibration
  - Mode of detection
    - Transmission
    - Fluorescence
    - Electron yield
  - Resolution
    - Monochromator crystals
    - Divergence
  - Thickness effects
  - Harmonic rejection

XANES vs. EXAFS





- Experimental equivalent of standard theoretical approach

PCA in EXAFS

- Advantages
  - Few spectra must be analyzed
  - EXAFS shells to fit are generally intense
- Difference from traditional methods
  - A single coordination shell will often appear in two or more components
  - Fit parameters apply to several spectra
- Disadvantages
  - Negative coordination numbers
  - Simultaneous fitting of two or more components may be necessary

PCA

- A change in perspective on XAS analysis.
- Global view of spectral series
- Delays, but does not eliminate, personal judgment
- More information in spectra than is used