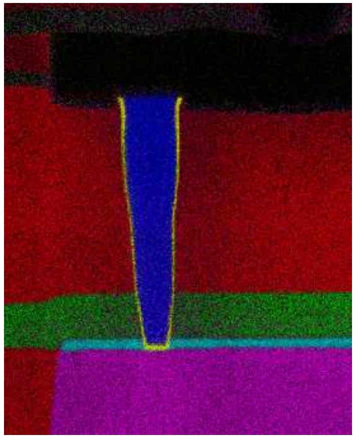
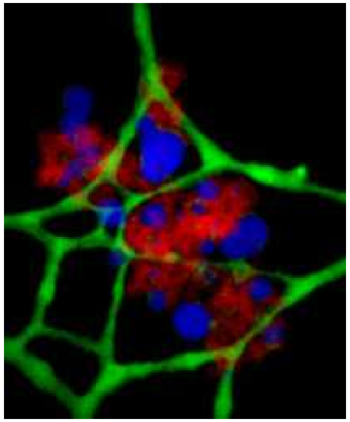
SAND2011-3539C

Multivariate Statistical Analysis Strategies for Hyperspectral Data: EDS and EFTEM/EELS





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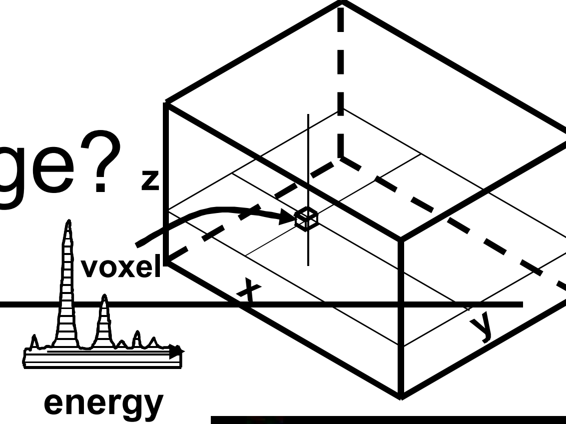
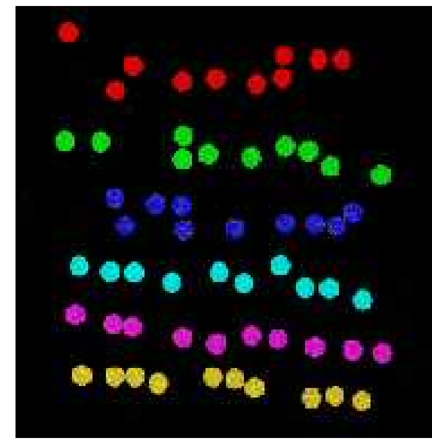
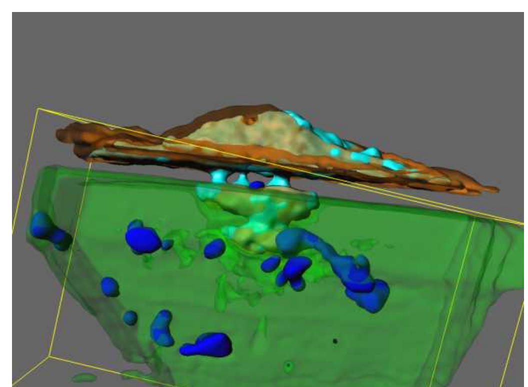
What is a spectral image?

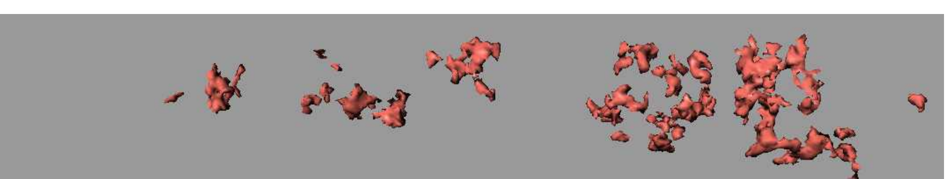


- A series of complete spectra resolved in 2- or higher dimensions
  - Conventional spectral images-2D
  - Tomographic spectral images-3D
    - Direct-FIB, Metallography
    - Computed-Tilt series of spectral images
    - Confocal
  - Resolved in other dimensions
    - Time, process condition, projection, etc.



- As far as MSA is concerned these can all be treated equivalently
  - Non-image-resolved data work the same





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Data types discussed today

- STEM-EDS from the Tecnai Osiris (0.9sr)
  - CMOS specimen
  - 200,000 pixels acquired in 4 minutes
  - Acquired in frames
- GIF Spectrum Line
  - Oxide interface
  - Acquired as a single ‘image’
  - Distance by energy-loss
- EFTEM spectrum image
  - Catalyst specimen
  - Acquired image-plane by image plane
  - Image alignment critical to a successful analysis

What is Multivariate Statistical Analysis?

- MSA comprises many techniques for factoring spectral image data into other hopefully more useful forms
- Makes use of high-degree of redundancy in data
  - Many observations of similar, noisy spectral or image features, tens of thousands to billions
  - Noisy data can be used to advantage
  - Large number of spectral channels, 50-100000
- Typically used to reduce dimensionality of the data and filter noise of known structure
- A 128x128 pixel by 1024 channel data set has 1024 dimensions, of which only a handful will represent chemical information…MSA helps find the correlations
- Should be fast
  - Seconds for small data sets to at most tens of minutes for the largest data sets.

What are the basic steps of MSA?

- Keenan, M.R., *Multivariate analysis of spectral images composed of count data*, in *Techniques and applications of hyperspectral image analysis*, H. Grahn and P. Geladi, Editors. 2007, John Wiley & Sons: Chinchester.
- Scale data for non-uniform noise*
  - Assumption here-we know the noise structure in these counting experiments
  - Down-weights large variations in intense spectral or image features which are due to noise
  - Rank 1 approximation to the noise
    - In the image domain divide by the square-root of the mean image
    - In the spectral domain divide by the square-root of the mean spectrum
    - Essentially the same answer as maximum likelihood methods with but far less computational complexity**

*M.R. Keenan and P.G. Kotula, *Surf. Int. Anal.* **36** (2004) 203-212

M.R. Keenan, J. Vac. Sci. Tech. A **23 [4] (2005) 746-750

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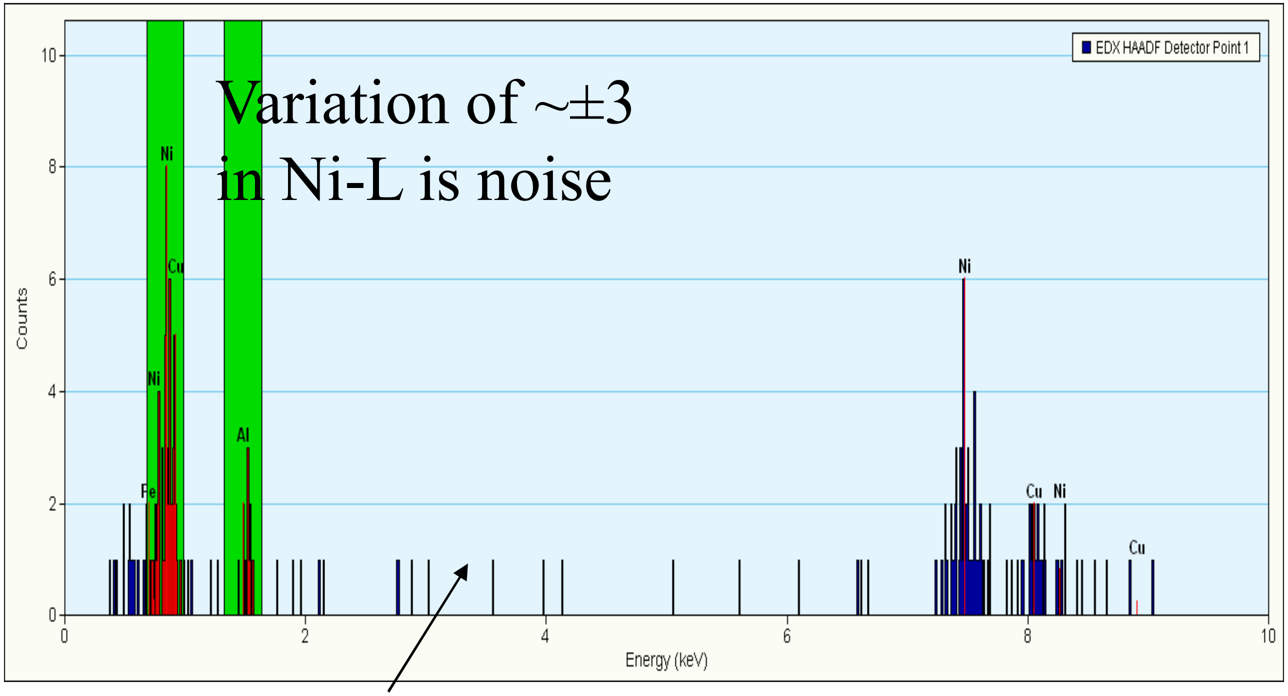
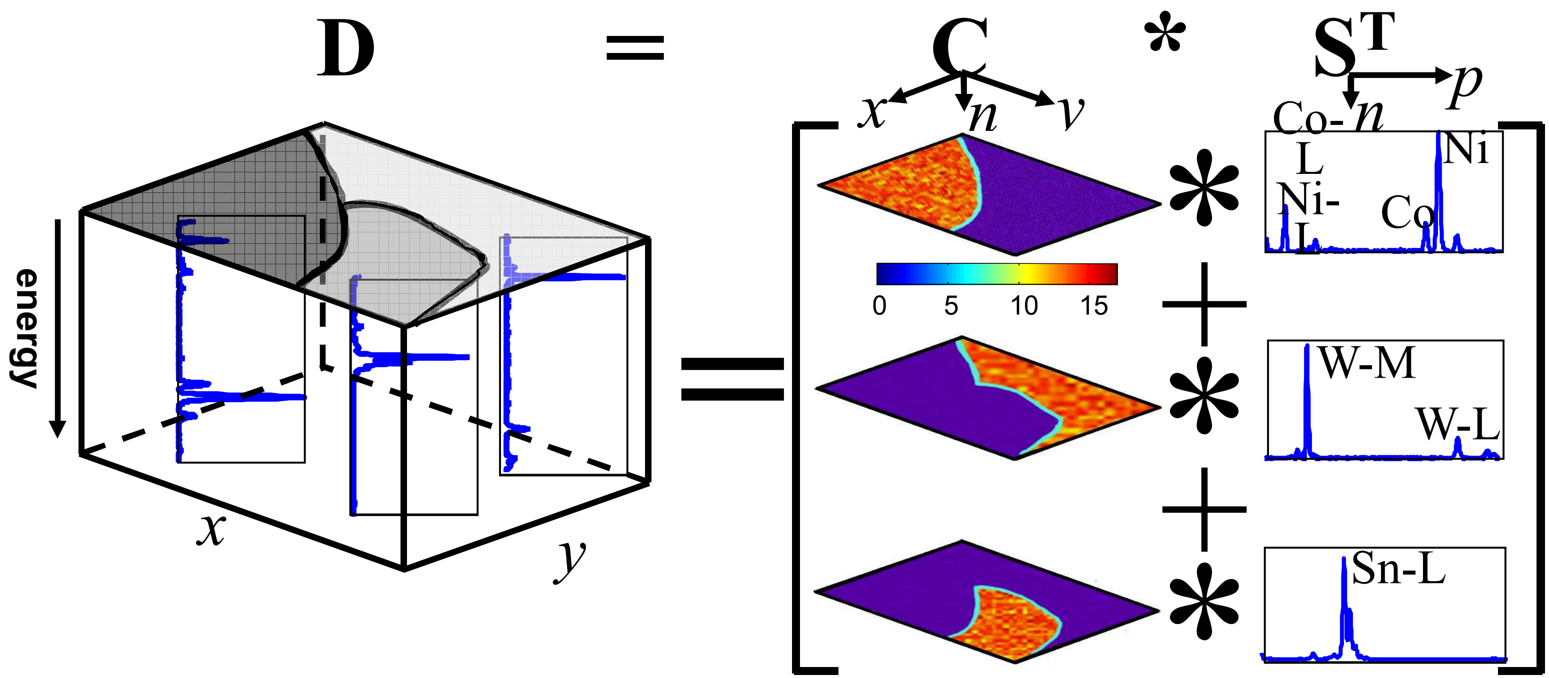
Normalizing for noise

Typical x-ray spectrum from STEM-EDS



3 counts in this part of the spectrum would be significant

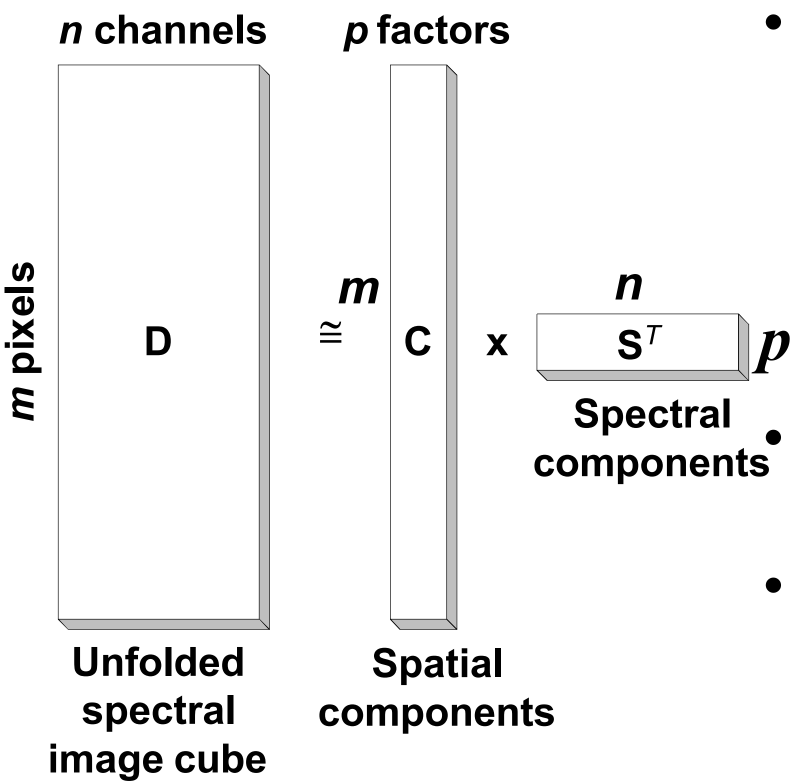
Multivariate Analysis: All Methods Assume a Linear Additive Model



Multivariate Processing:

- **Scale data for Poisson counting statistics**
- **Determine the number of components to keep**
- **Factor the data matrix (D) into C and S**
- **Inverse scale the components**

We have several options in our multivariate "Toolbox"



Analysis goal: Obtain an easily interpretable representation of the data

- Principal Component Analysis (PCA)
  - Factors are orthogonal
  - Factors serially maximize variance
  - Provides best LS fit to data
  - Non-physical constraints
  - Factors are abstract
- PCA + factor rotation (Varimax)
  - Rotate factors to "simple structure"
- MCR-ALS
  - A refinement of Rotated PCA
  - Non-negativity of C and/or S
  - Equality, closure and others
  - Constraints may not be effective

Spectral- vs. Spatial-Domain Simplicity: Analysis of CMOS

- Planarized CMOS in-situ lift out specimen on a Mo grid
- Data acquired on a FEI Tecnai Osiris, 200kV FEG with SuperX (0.9sr)
- The data are 400 x 500 pixels by 4096+channels
- >99% sparse (~811M elements = 0, ~7.7M elements >0)
  - But it's important to note the data are randomly distributed
- Data acquisition 249 seconds @ 1.5nA or 1.245msec/pixel
- ~10.6M total counts
  - 43kcps summed or 11kcounts/second/spectrometer
  - Average of 53 counts per spectrum
- Data analysis took 144 seconds on a decent lab workstation (XP-x64)

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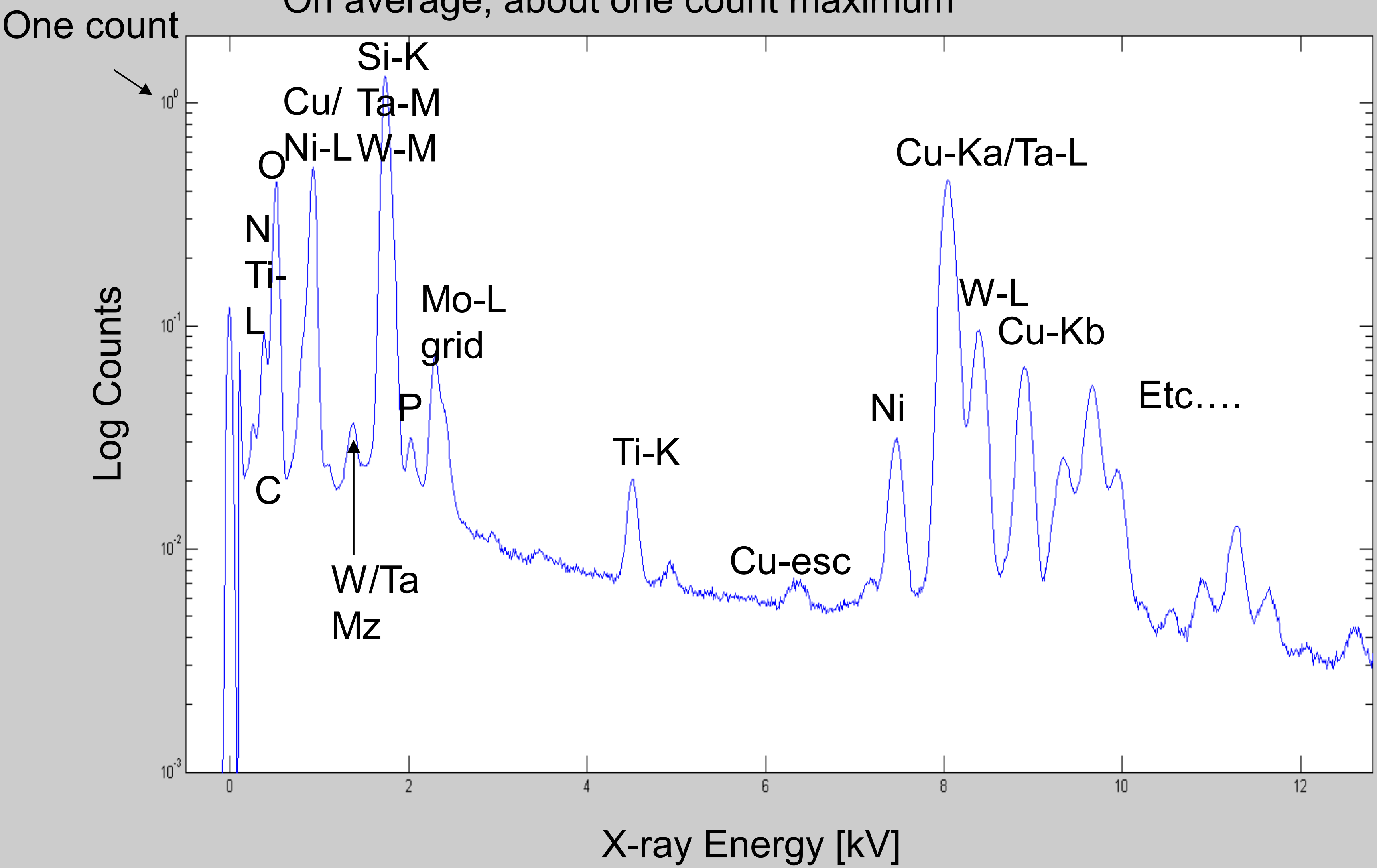
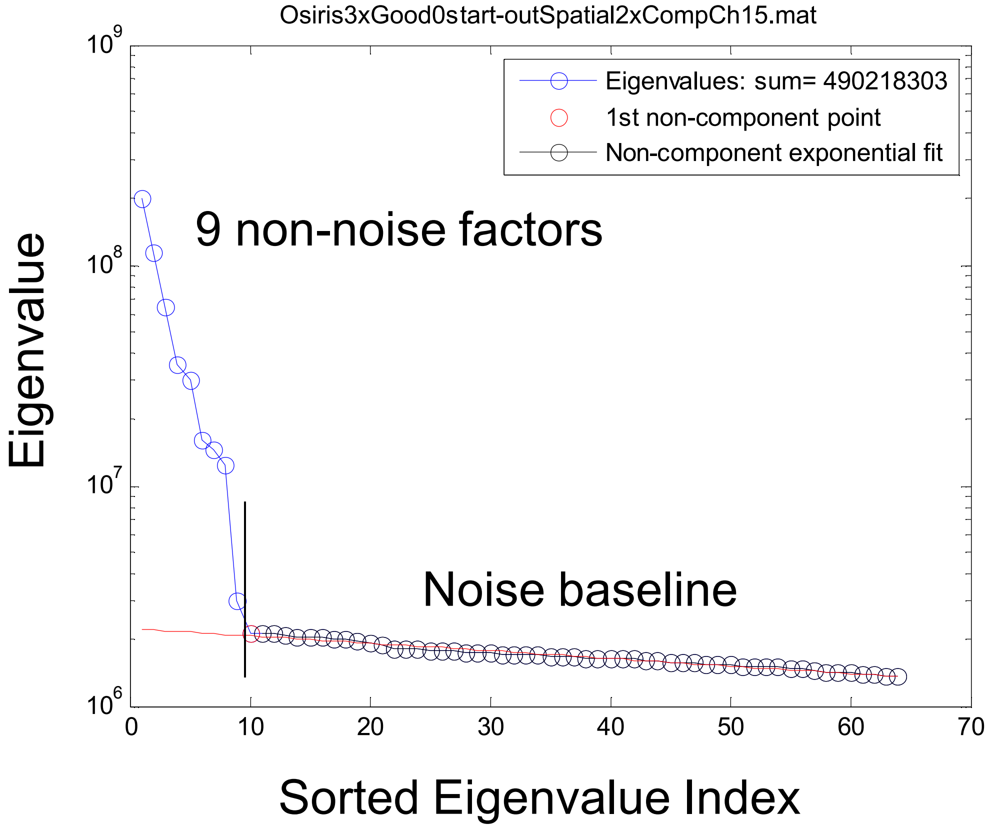
Mean Spectrum from the CMOS spectral image

On average, about one count maximum



Eigenanalysis of the CMOS SI data



Clearly 9 factors automatically resolved above the noise

Spatial Domain Simplicity*

Often the elemental viewpoint

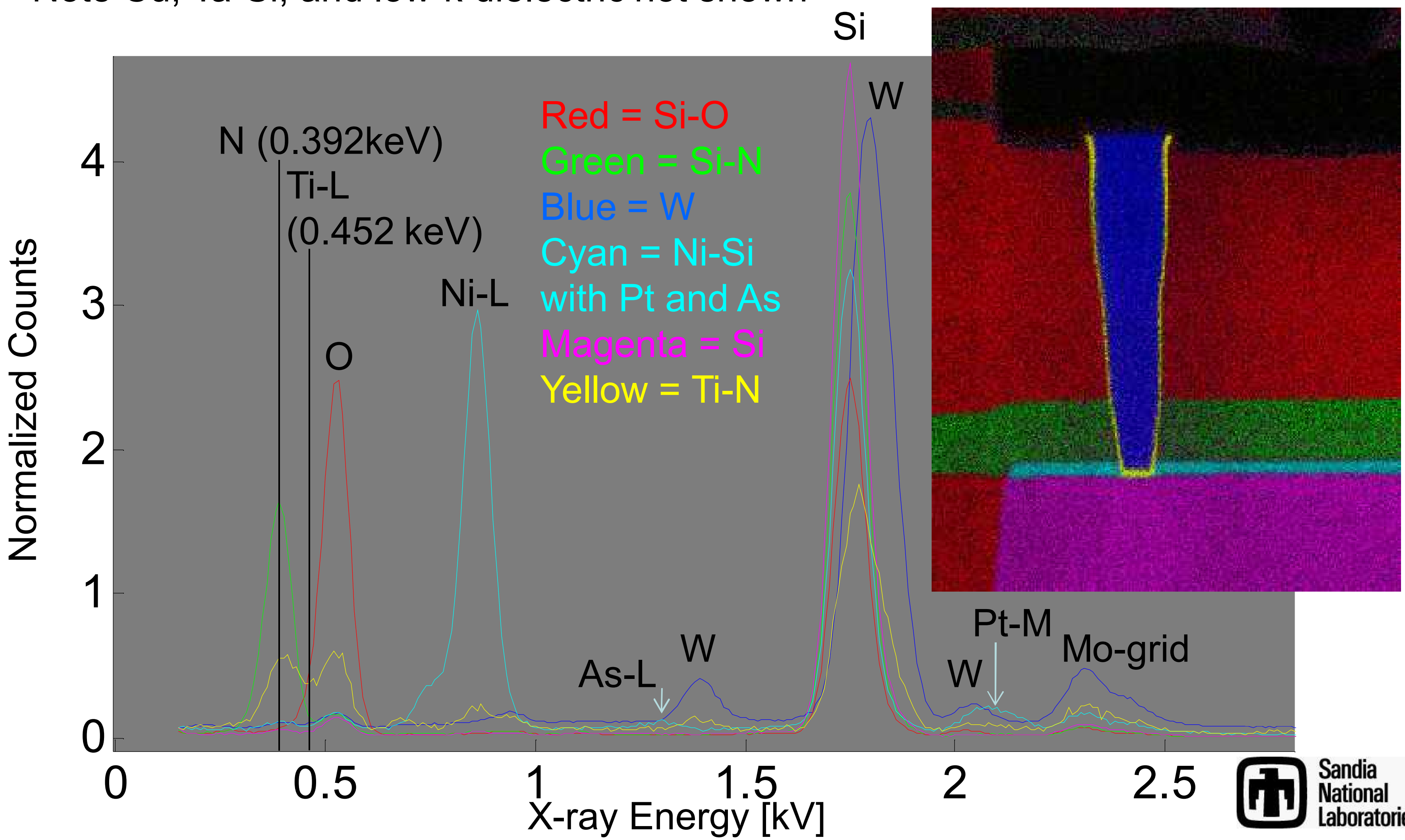
- $D = CS^T$ (Goal: Factor raw data into C and S…linear model)
  - D is an m-pixel × n-channel raw spectral-data matrix
  - S is an $n \times p$ matrix containing the p pure-component spectra shapes
  - C is an $m \times p$ matrix containing their spatial distributions/abundances
- Data is scaled to account for non-uniform (Poisson) noise**
- Number of factors to retain is chosen (Eigenanalysis)
- PCA is performed on the scaled data such the spectral components are orthogonal and the spatial components are orthonormal
- Rotate the orthonormal spatial components to maximize their mutual simplicity with the VARIMAX procedure
- Apply the inverse rotation to the spectral components which relaxes orthogonally in this domain
- Optionally: Impose non-negativity (e.g., via CLS etc.)
- Inversely scale the components for Poisson noise

* M.R. Keenan, *Surf. Int. Anal.* **41** (2009) 79-87.

M.R. Keenan and P.G. Kotula, *Surf. Int. Anal.* **36 (2004) 203-212.

Spatial-Domain Simplicity
Best Spatial 'Contrast'

Note Cu, Ta-Si, and low-k dielectric not shown



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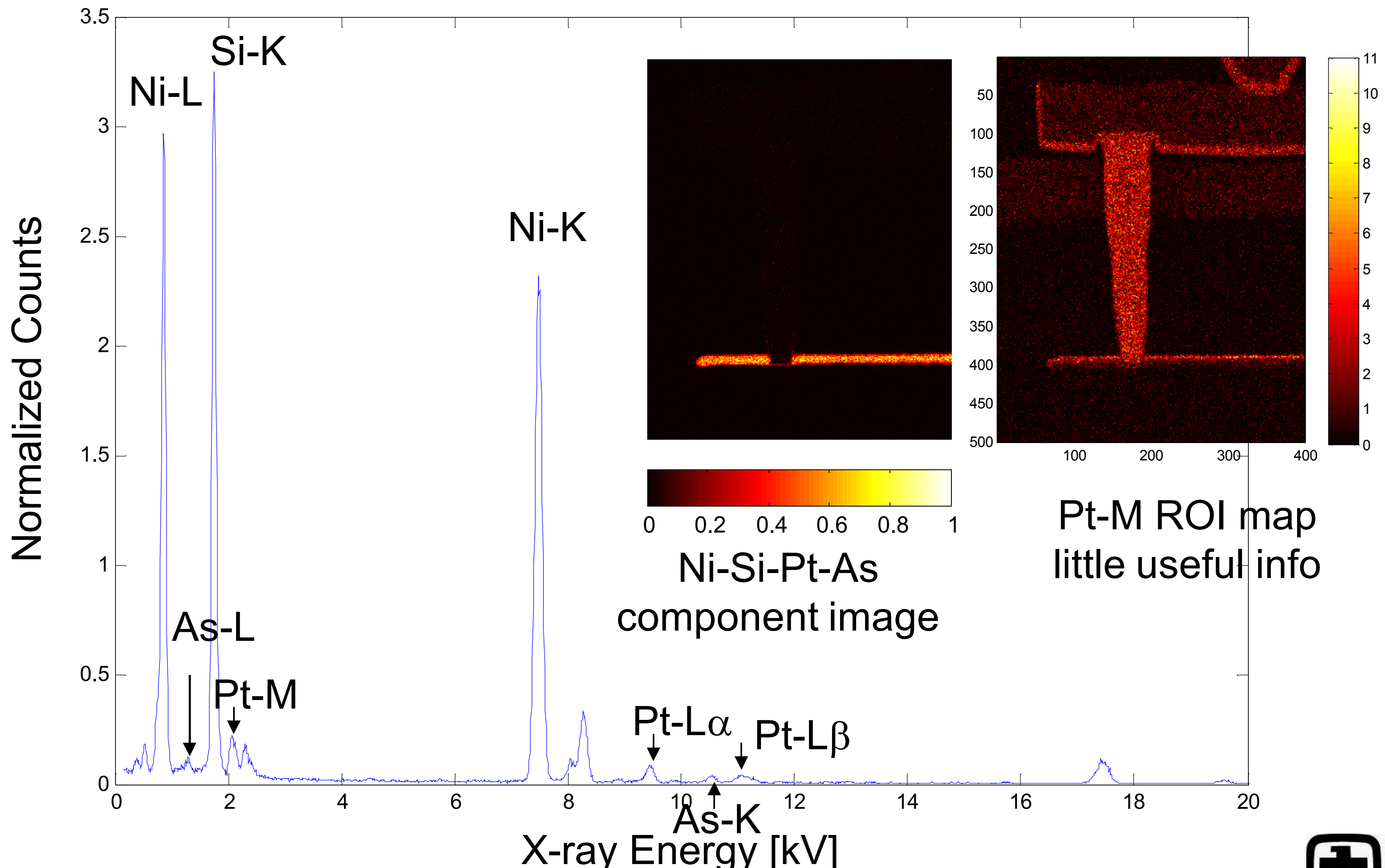
Spatial-Domain Simplicity
Ni-silicide contact, MSA shows minor elements



Spectral Domain Simplicity*

Often the phase viewpoint

- $D = CS^T$ (Goal: Factor raw data into C and S…linear model)
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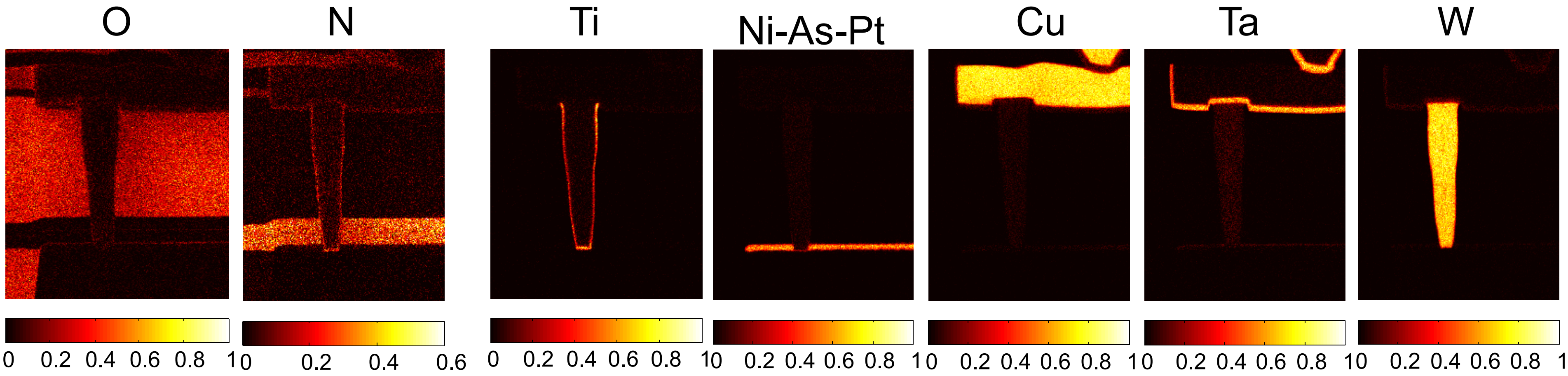
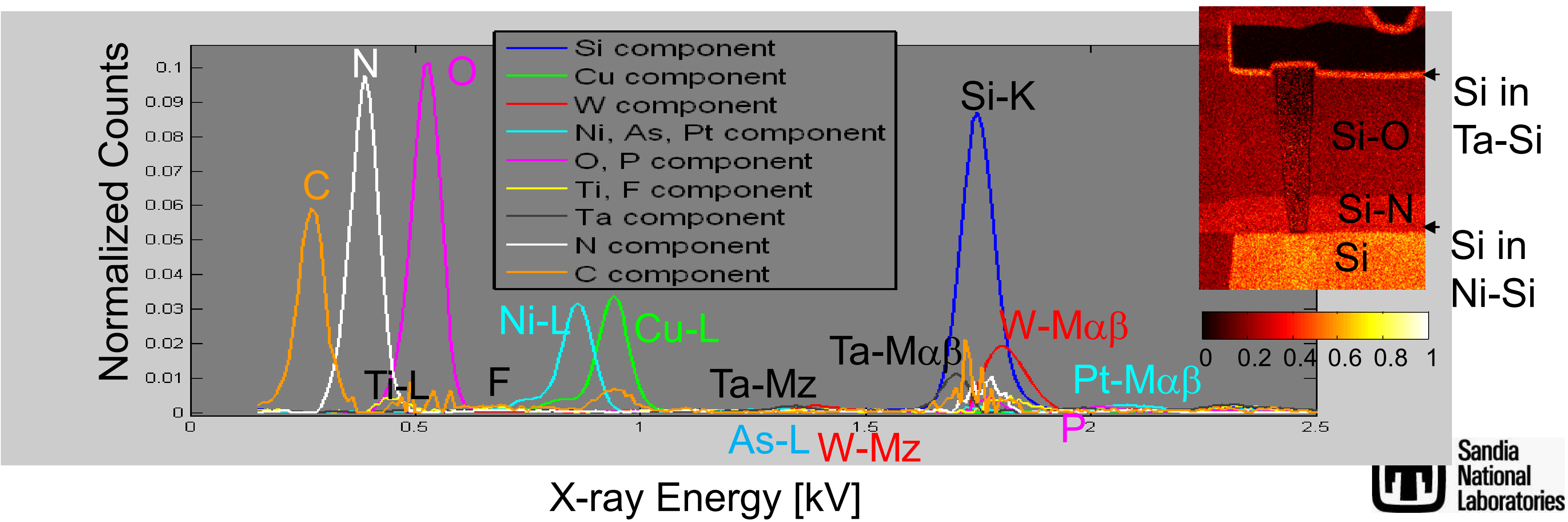
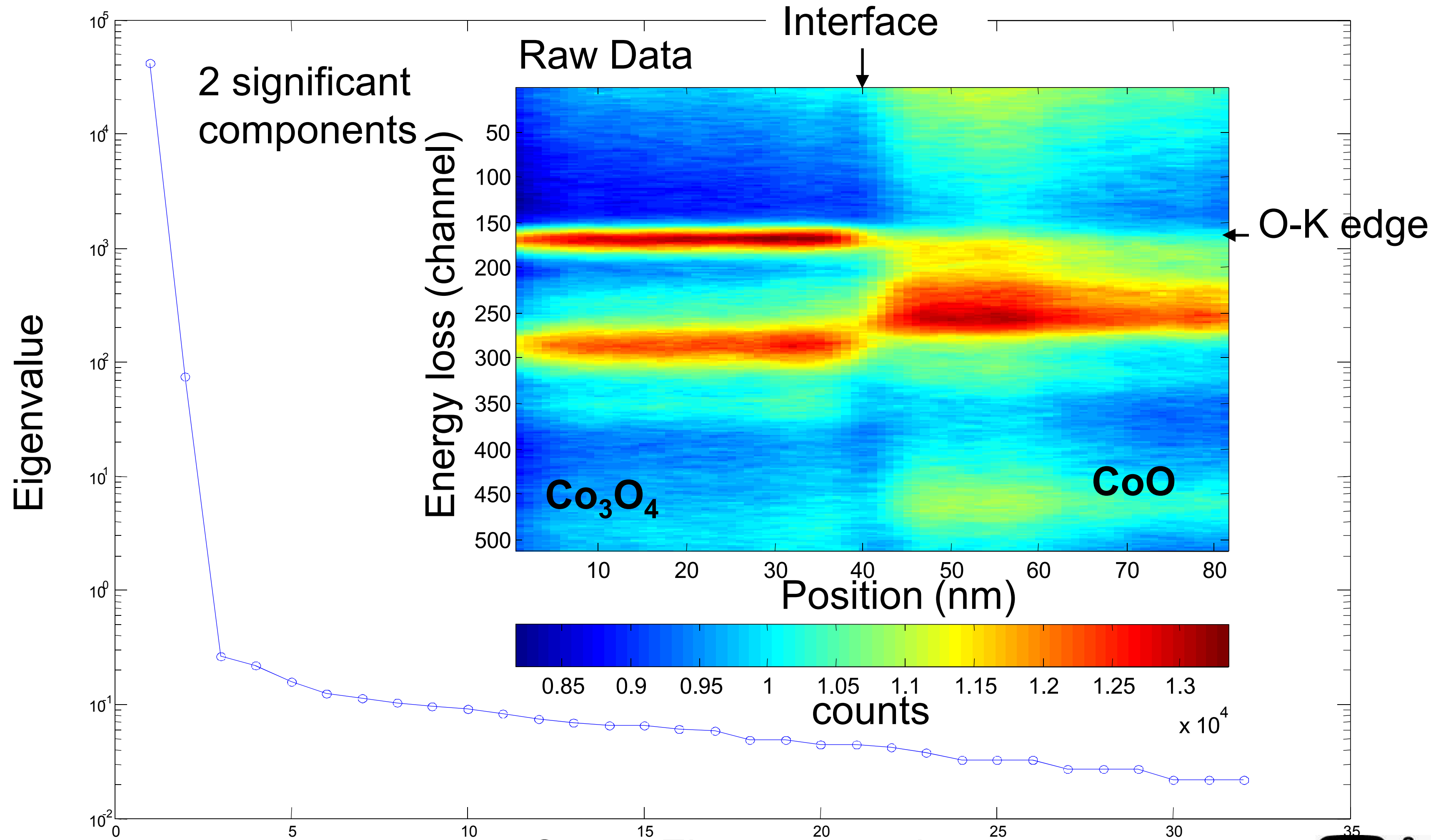
Spectral-Domain Simplicity
Best Spectral or Elemental 'Contrast'





Spatial-domain simplicity of GIF Spectrum-Line, O-K Edge, CoO/Co_3O_4

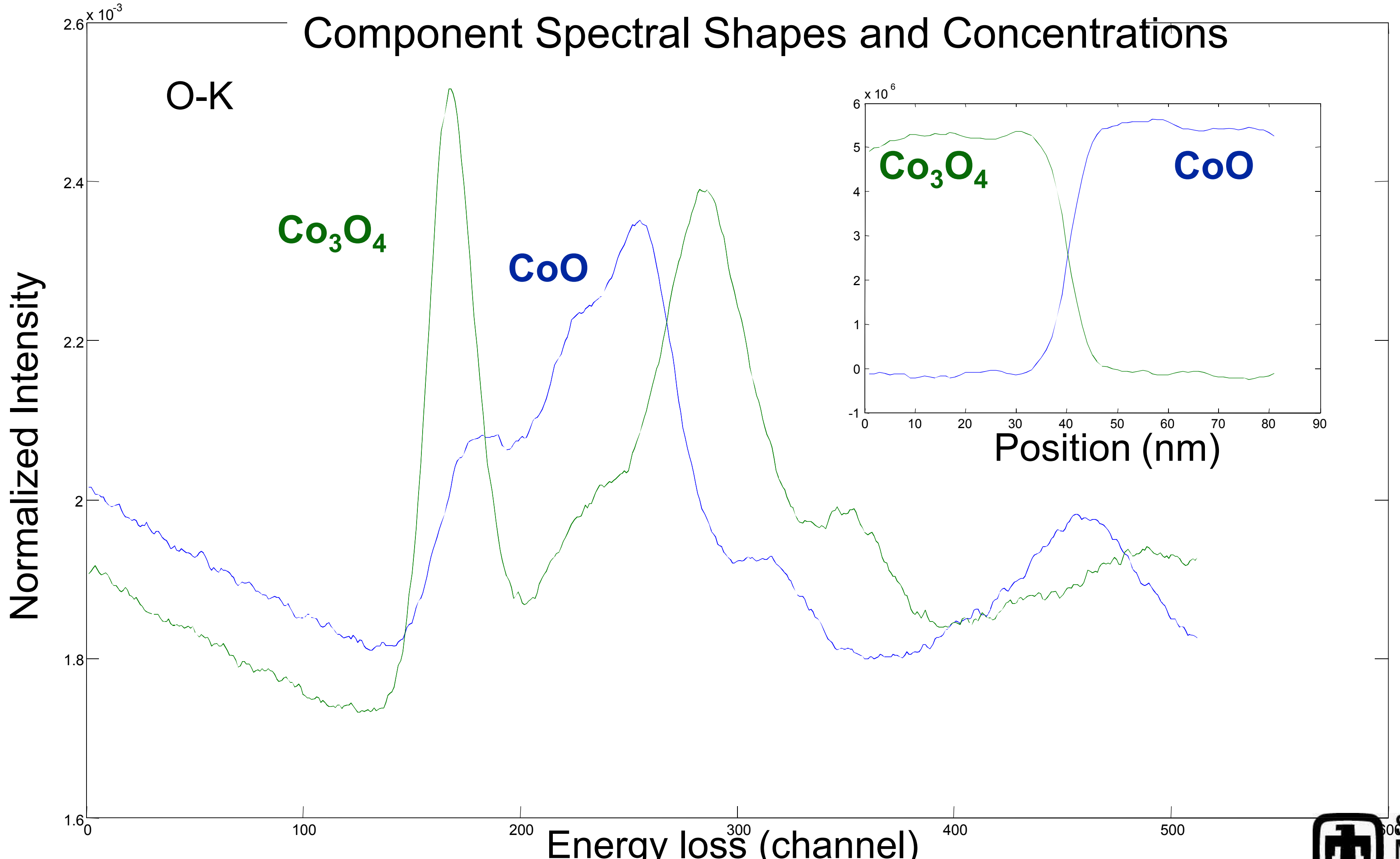
Drift spatially, HT, etc. distort everything so no pre-processing necessary



0.1eV/channel, 512 channels, 82 spectra, ~1nm/spectrum

Spatial-domain simplicity of GIF Spectrum-Line, O-K Edge, CoO/Co_3O_4

Solution captures significant near-edge fine structure changes with no *a priori* knowledge



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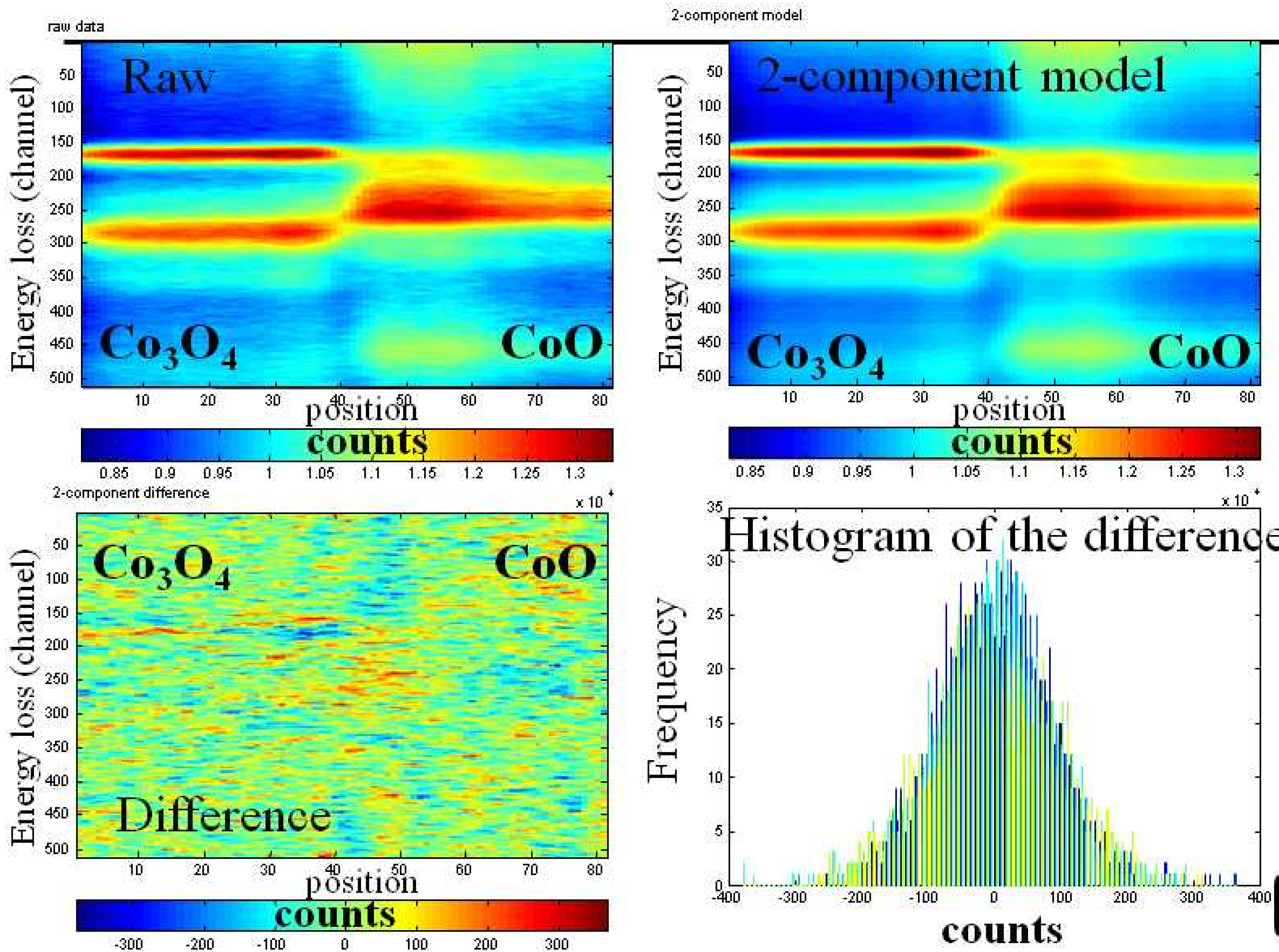
Spatial-domain simplicity of GIF Spectrum-Line, O-K Edge, CoO/Co_3O_4



Spatial-Domain Simplicity of and EFTEM-SI of a catalyst

- 79 EFTEM images, 256x256 pixels were acquired at 5eV intervals from 225-620eV
  - JEOL 2010F with Gatan GIF-2001
  - 32 nm/pixel
- Images were aligned with the FELMI-Graz DM-script "SDSD" (Schaffer et al., *Ultramicroscopy* **102/1** (2004) pp.27-36)
  - Critical step prior to MSA
  - 254x209 pixels after alignment (8.1 x 6.7 μm)
  - Also x-rays filtered prior to image alignment
- Data set not perfect as sample distorted slightly during acquisition

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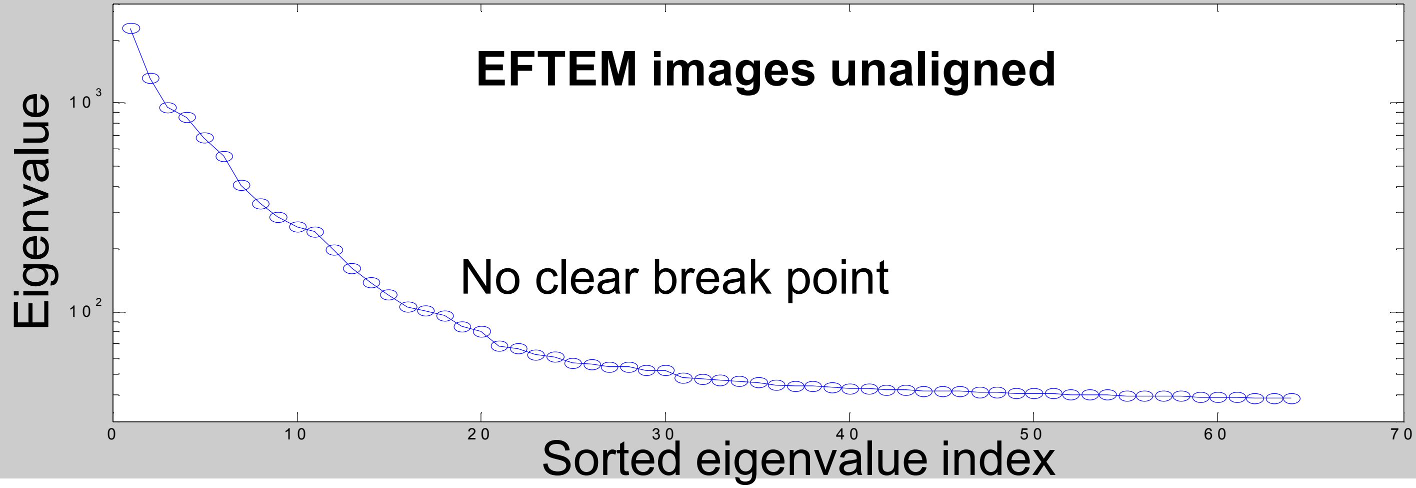
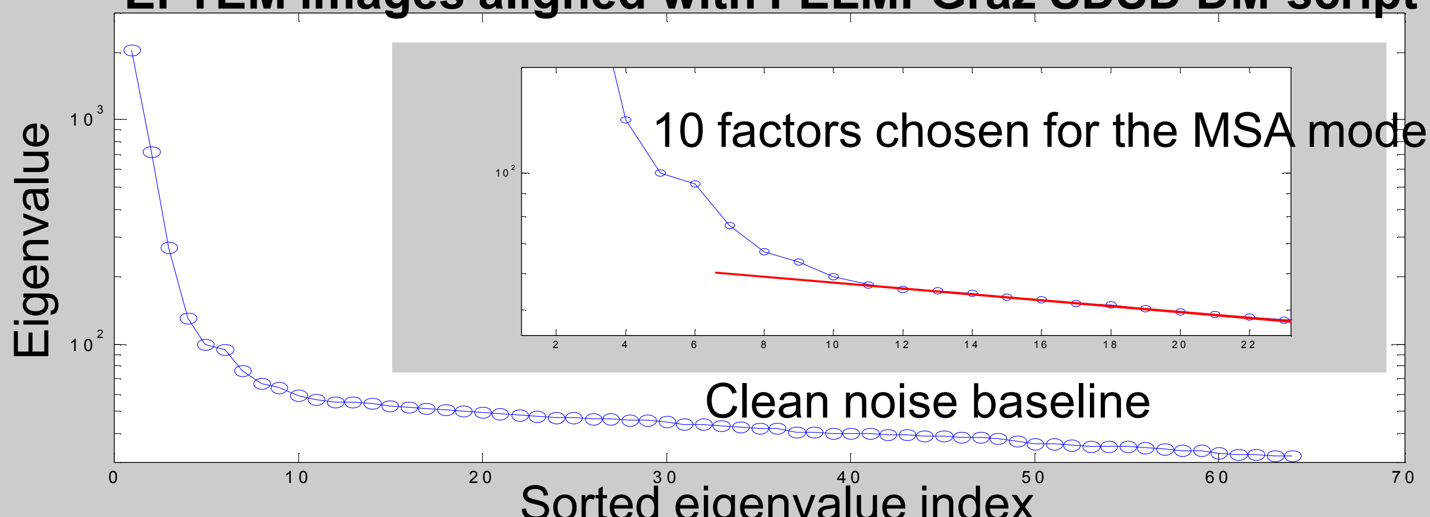
Spatial-Domain Simplicity of and EFTEM-SI of a catalyst

Image alignment prior to MSA is critical

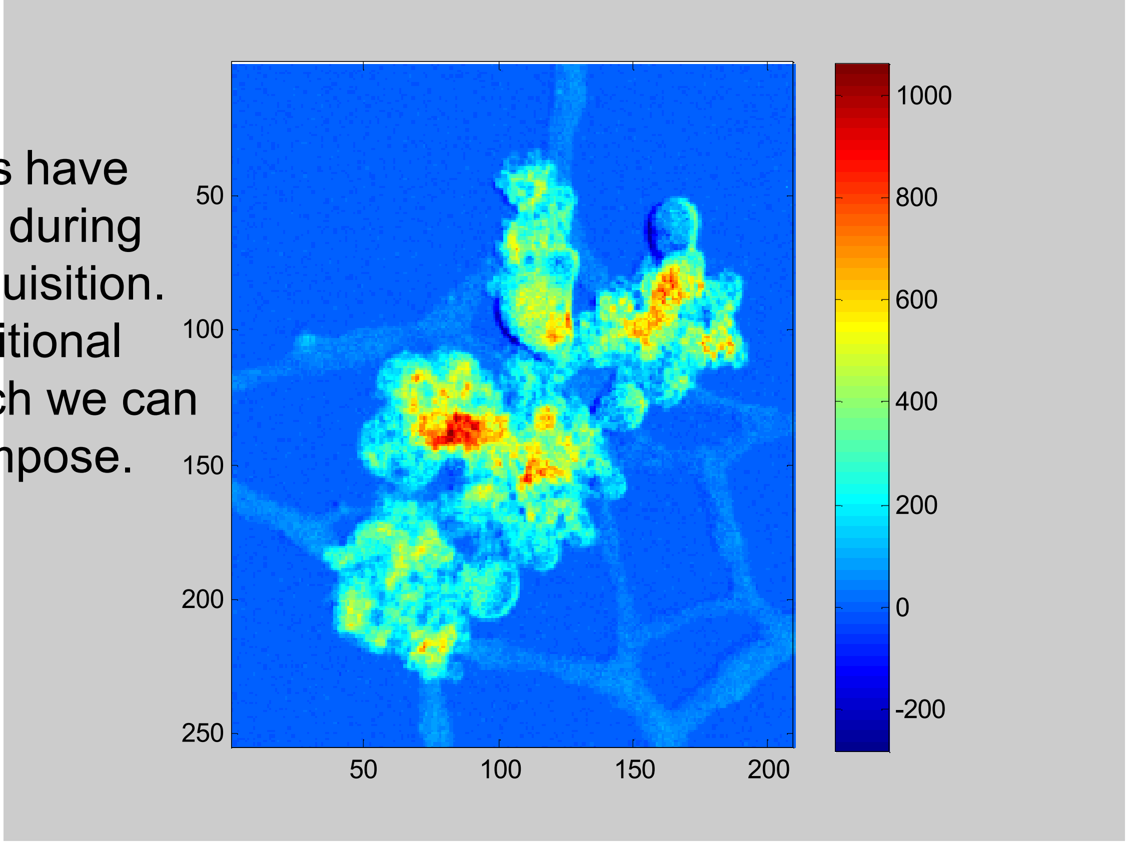




Spatial-Domain Simplicity of and EFTEM-SI of a catalyst

Some extra components are due to sample distortion during acquisition

Note the particles have moved/damaged during image series acquisition. This will add additional MSA factors which we can manually superimpose.



Difference image of Channel 1 and Channel 79

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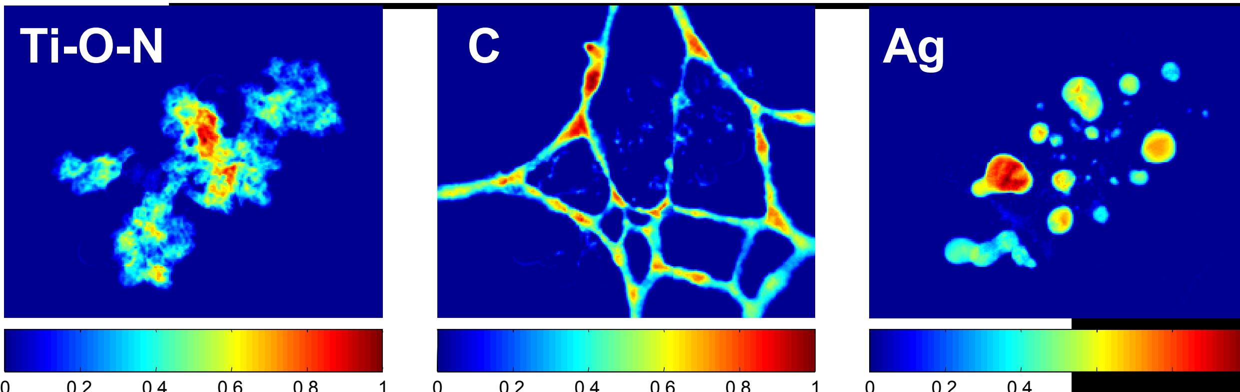
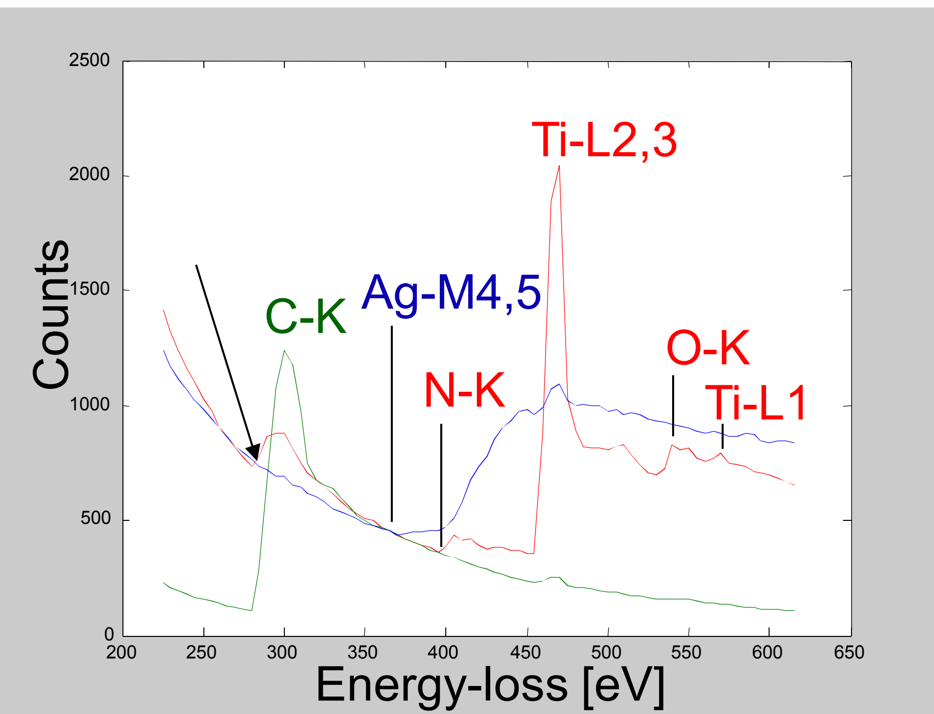
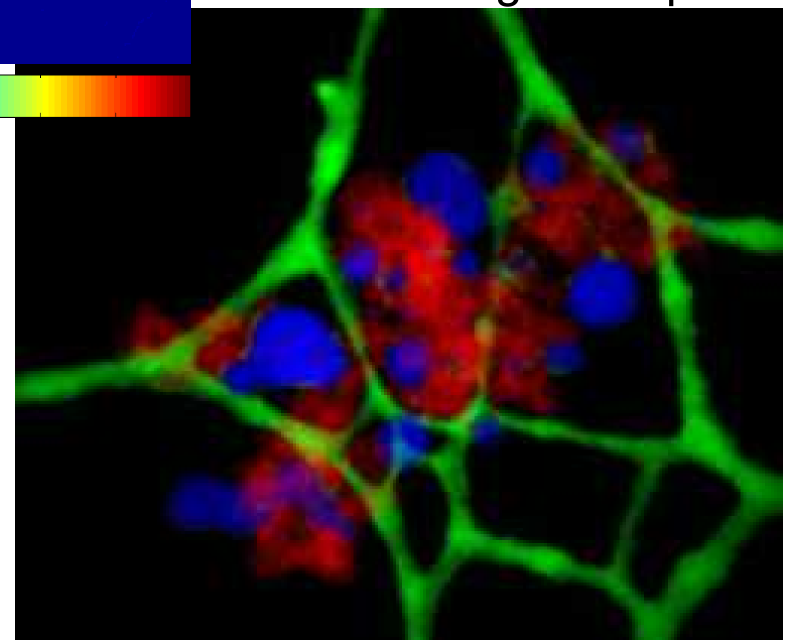
Spatial-Domain Simplicity of and EFTEM-SI of a catalyst

Inspection of the 10 MSA factors reveals 3 underlying relevant ones



Extra factors arise due to:
Imperfect image alignment
Sample distortion
Non-linear signal response





Red = Ti-O (N)
Green = C
Blue = Ag

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Conclusions

- MSA methods are every useful for simplifying the analysis of large, complex data sets
  - Importance of Poisson normalization
  - Factor rotation, MCR, etc. give different viewpoints
- Unbiased analysis powerful for forensics, materials science, etc. Needle in the haystack….
- Annular x-ray detector geometry makes STEM in SEM microanalysis practical
- High count rates (>100kcps typically) from thin samples, >1Mcps of bulk samples
- High throughput bio-forensics application