SAND2011-6990C

Atomic-resolution X-ray microanalysis: Efficient X-ray collection and data analysis

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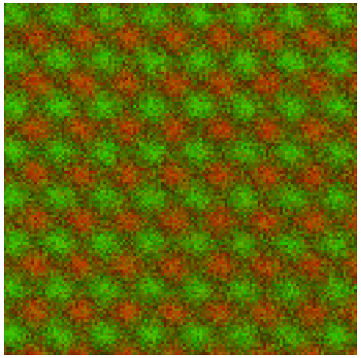
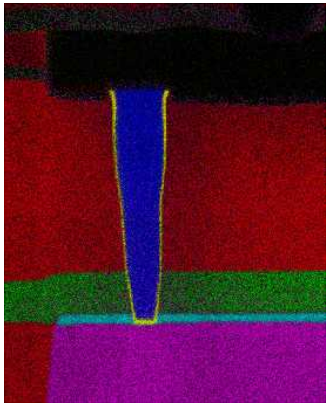


- Spectral imaging
- Multivariate statistical analysis
- Atomic-resolution x-ray microanalysis
  - Brighter sources
  - Probe correction
  - Efficient x-ray detectors
- Future applications



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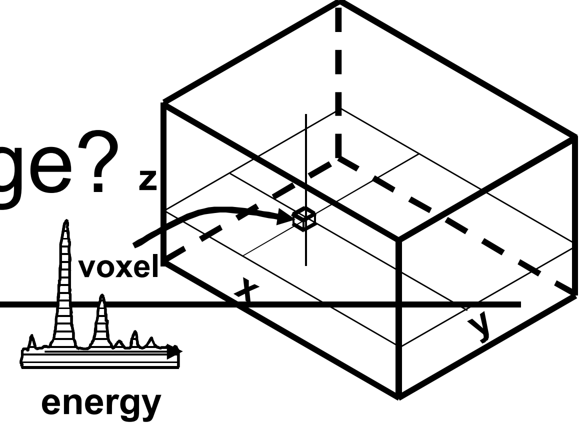
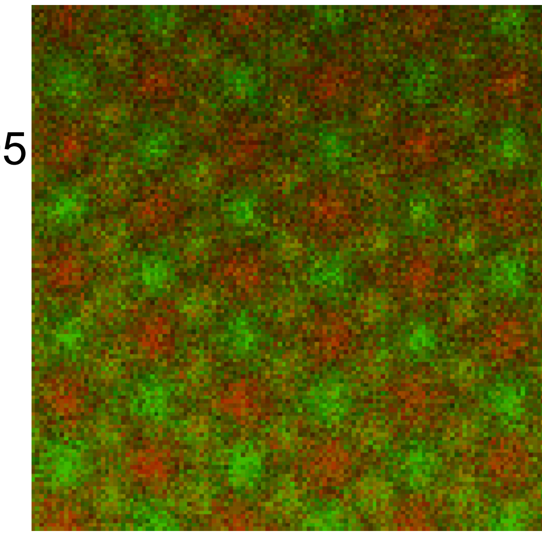
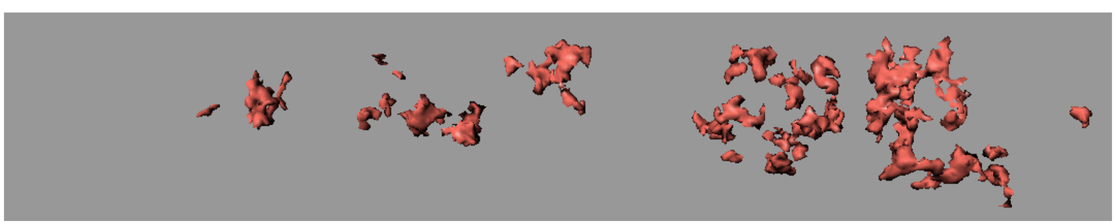
What is a spectral image?



- A series of complete spectra resolved in 2- or higher dimensions
  - Conventional spectral images-2D*
    - Demonstrated in 1979 and first product by PGT in 1995
  - 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 the same



*e.g., P.G. Kotula et al. *Microsc. Microanal.* 9 (2003) 1-17.
**e.g., P.G. Kotula et al. *Microsc. Microanal.* 12 (2006) 36-48.

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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 or variables, which can be transformed so as to represent chemical information…MSA helps find the correlations
- Results should be fast and readily interpretable
  - 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.

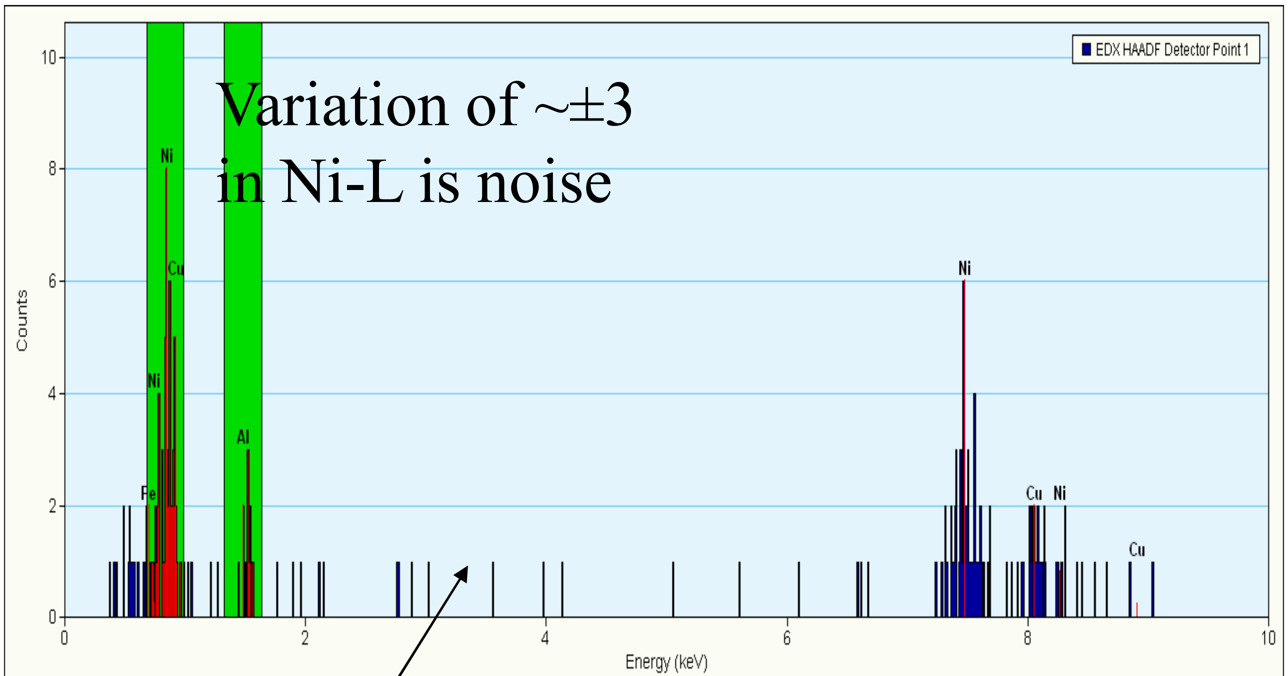
- Scale data for non-uniform noise*
  - Assumption here-we know the noise structure in these counting experiments
  - Down-weights large variations in intense spectral or image features which are due to noise
  - Rank 1 approximation to the noise
    - In the image domain divide by the square-root of 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**
- Factor analysis
- Inverse noise scaling

*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

Normalizing for noise

Typical x-ray spectrum from STEM-EDS



3 counts in this part of the spectrum would be significant

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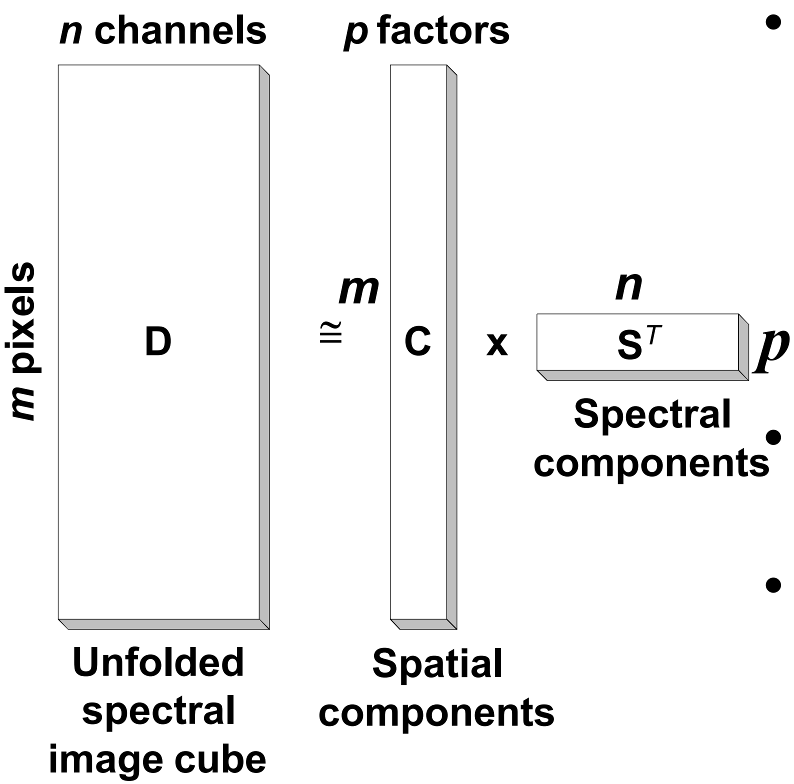
We have several options in our multivariate "Toolbox"



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
  - Bias due to error in variables

*M.R. Keenan, *Surf. Int. Anal.* **41** (2009) 79-87.
**P.G. Kotula, et al. *Microsc. Microanal.* 9 (2003) 1-17.

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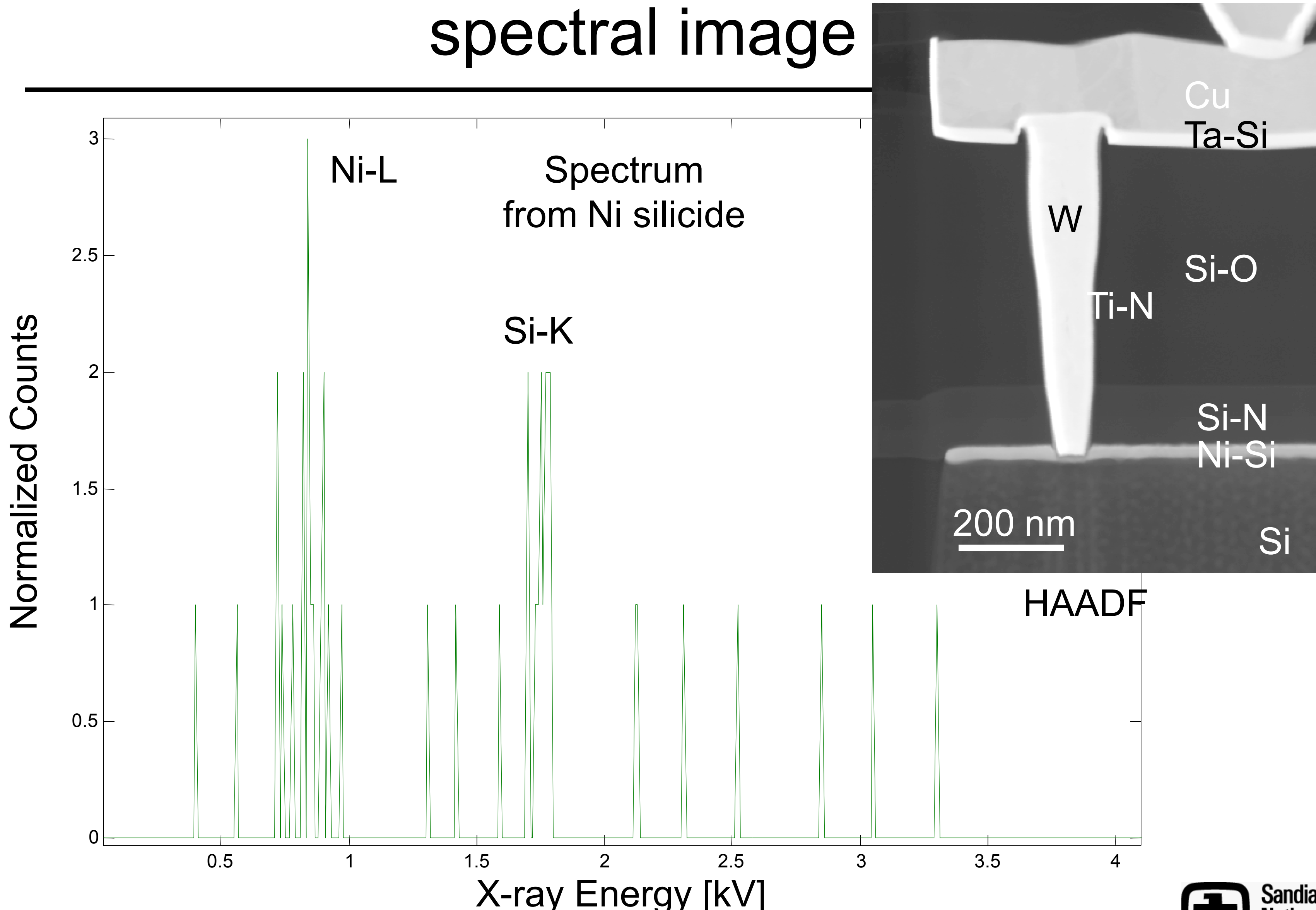
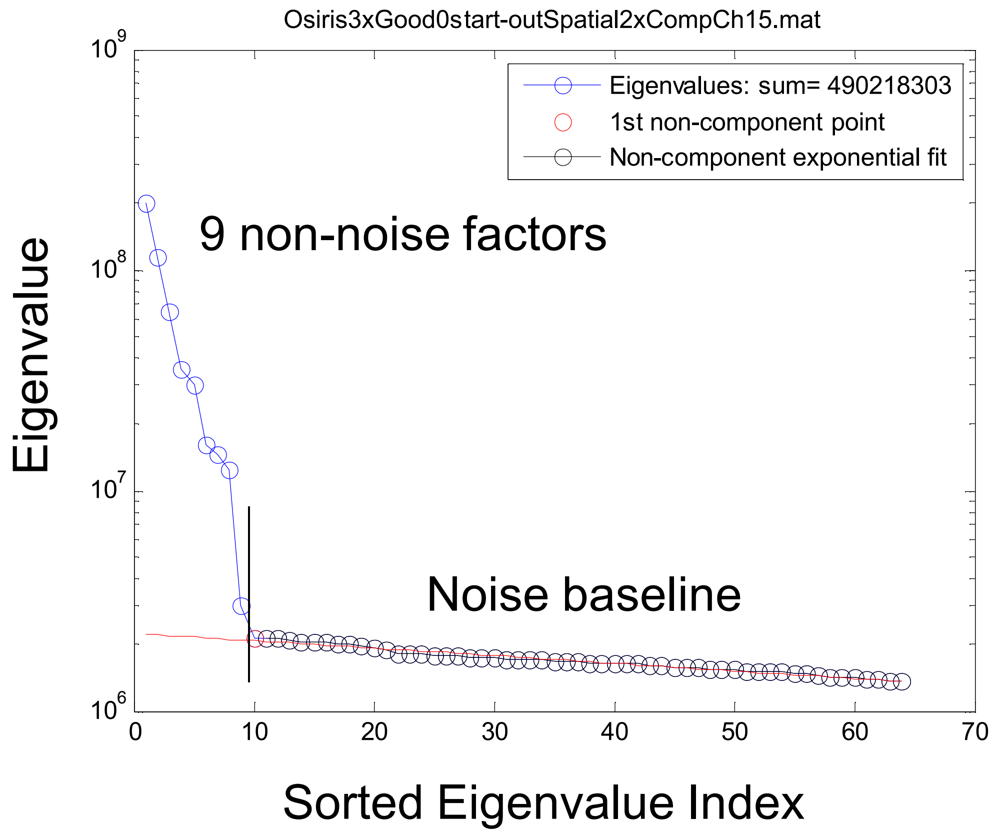
Spectral- vs. Spatial-Domain Simplicity: Analysis of CMOS

- Planarized CMOS *in-situ* lift out specimen on a Mo grid
- FEI Tecnai Osiris, 200kV FEG with SuperX (0.9sr)
- 400 x 500 pixels by 4096+channels, 2nm/pixel
- >99% sparse (~811M elements = 0, ~7.7M elements >0)
  - But it's important to note the non-zeros are for the most part randomly distributed
- Data acquisition 249 seconds @ 1.5nA or 1.245msec/pixel
- ~10.6 M total counts
  - 43 kcps summed or 11 kcounts/second/spectrometer
  - Average of 53 counts per spectrum
- Data analysis took 144 seconds on a decent lab workstation (XP-x64)

Raw spectrum from the CMOS spectral image



Eigenanalysis of the CMOS SI data



Clearly 9 factors automatically resolved above the noise

Spatial Domain Simplicity*

Often the phase 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* × *p* matrix containing the *p* pure-component spectra shapes
  - C is an *m* × *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 MCR, 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.

***P.G. Kotula et al. *Microsc. Microanal.* 9 (2003) 1-17.

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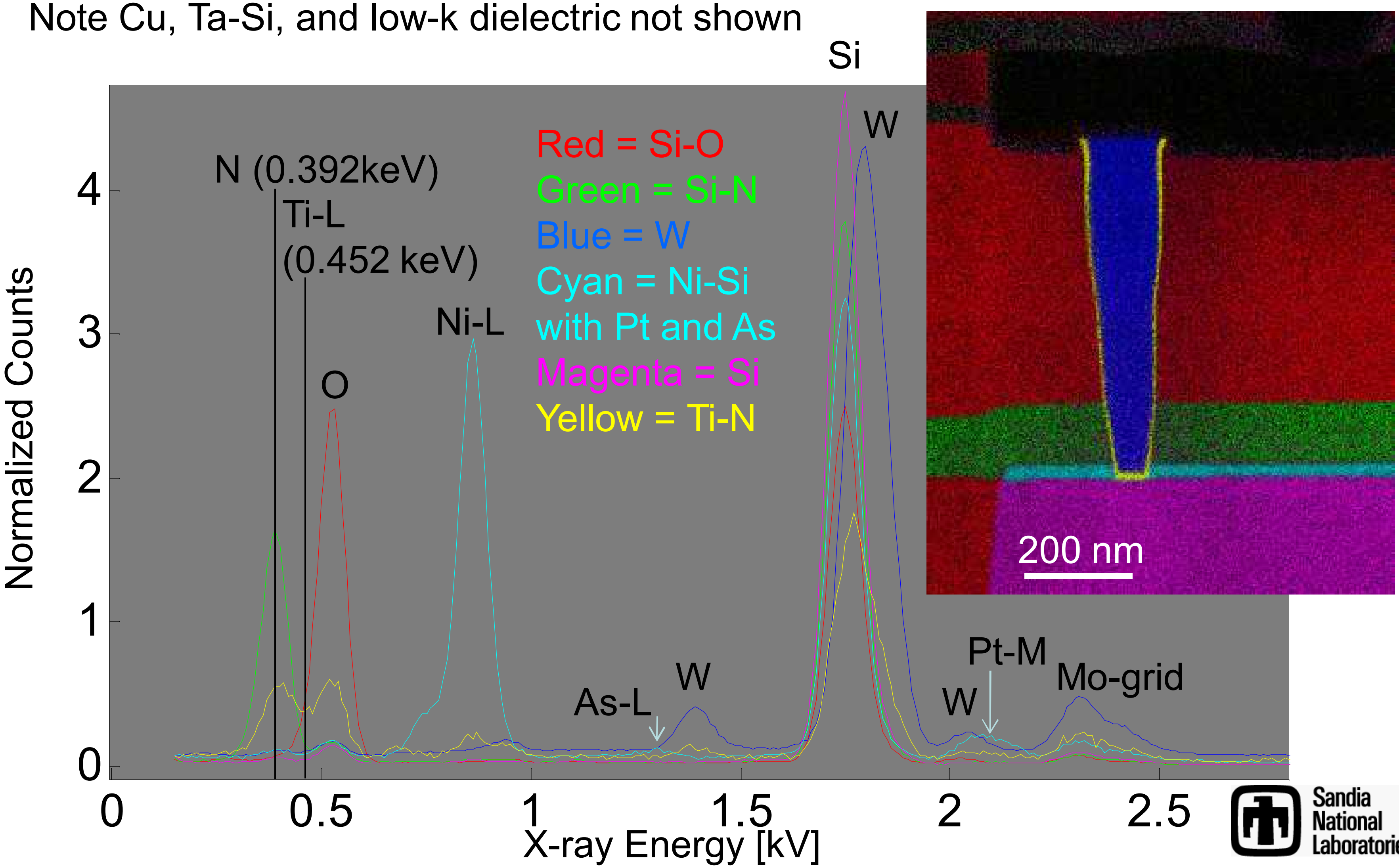
Spatial-Domain Simplicity
Best Spatial 'Contrast' (Phases)

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



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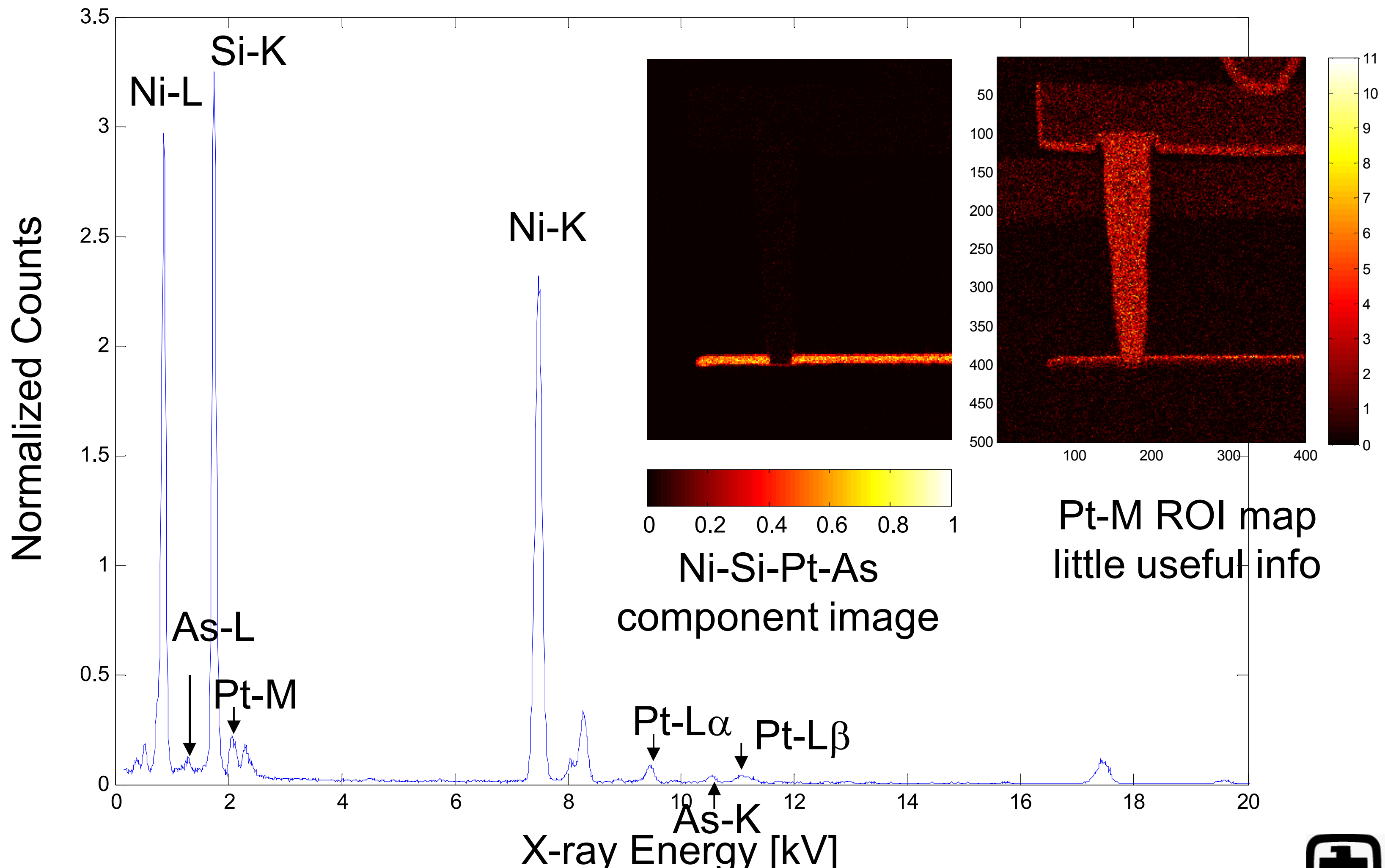
Spatial-Domain Simplicity
Ni-silicide contact, MSA shows minor elements



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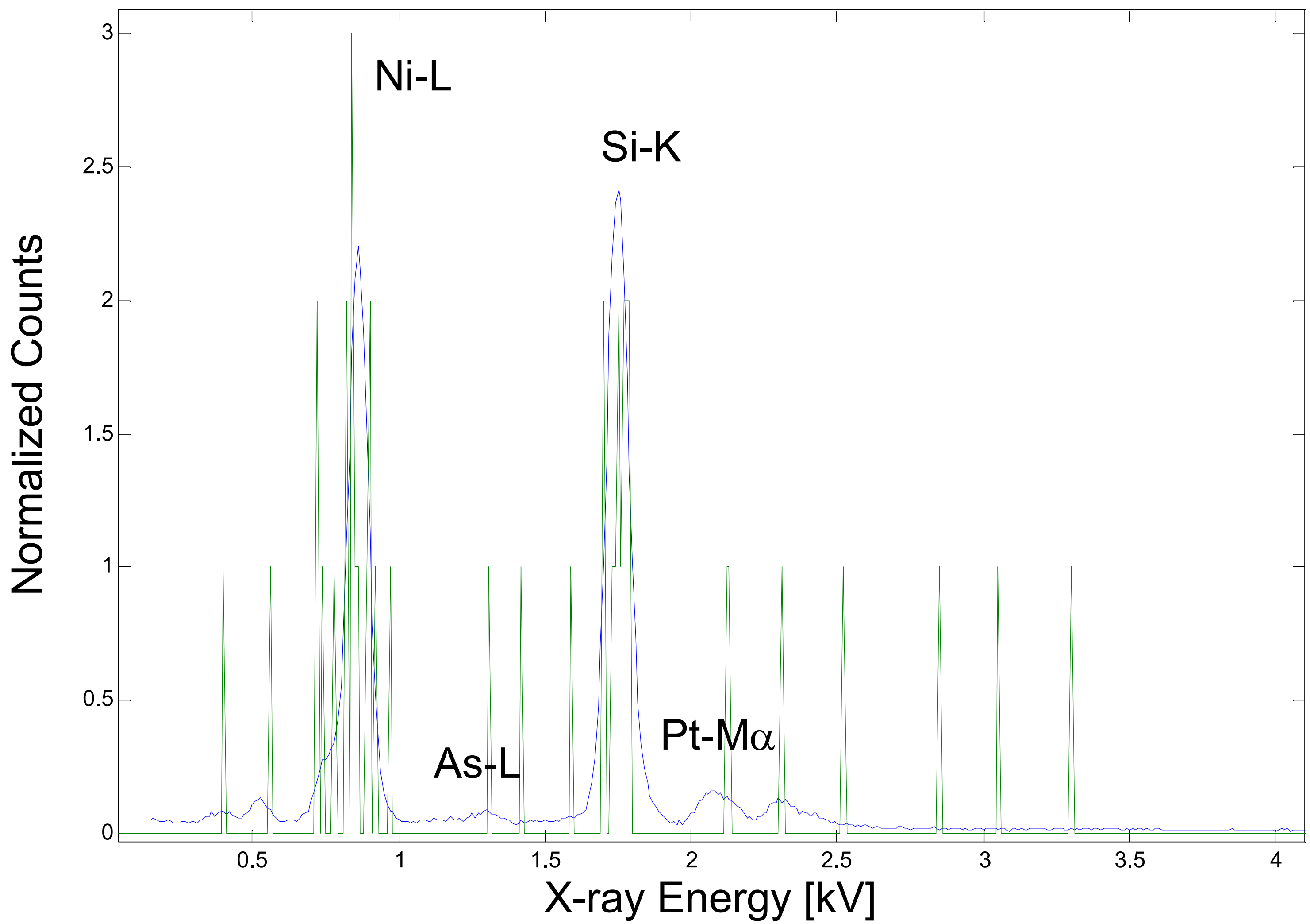
Spatial-Domain Simplicity
Ni-silicide contact, MSA shows minor elements

Raw versus MSA-processed



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Spectral Domain Simplicity*

Often the elemental/correlated 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
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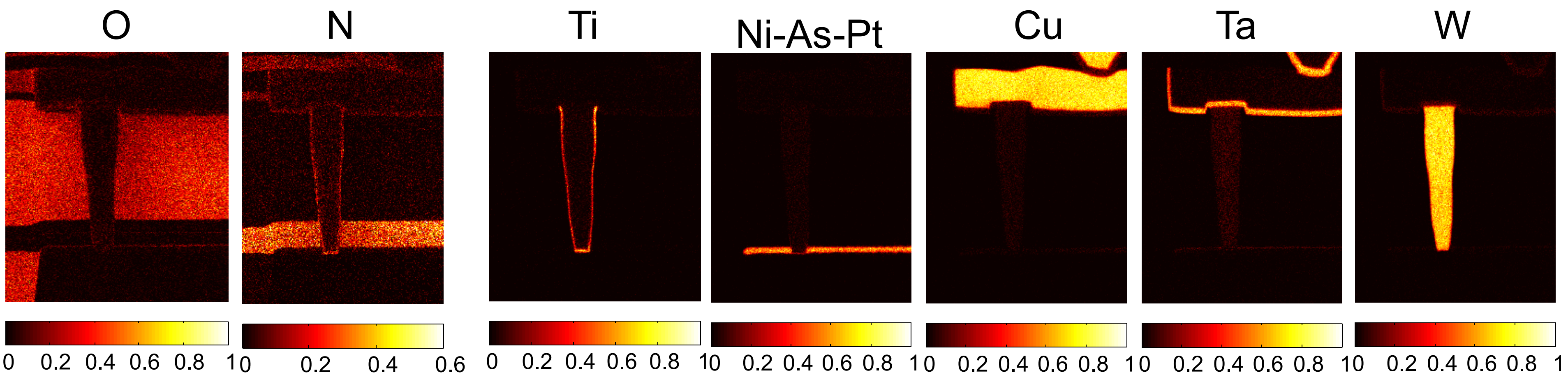
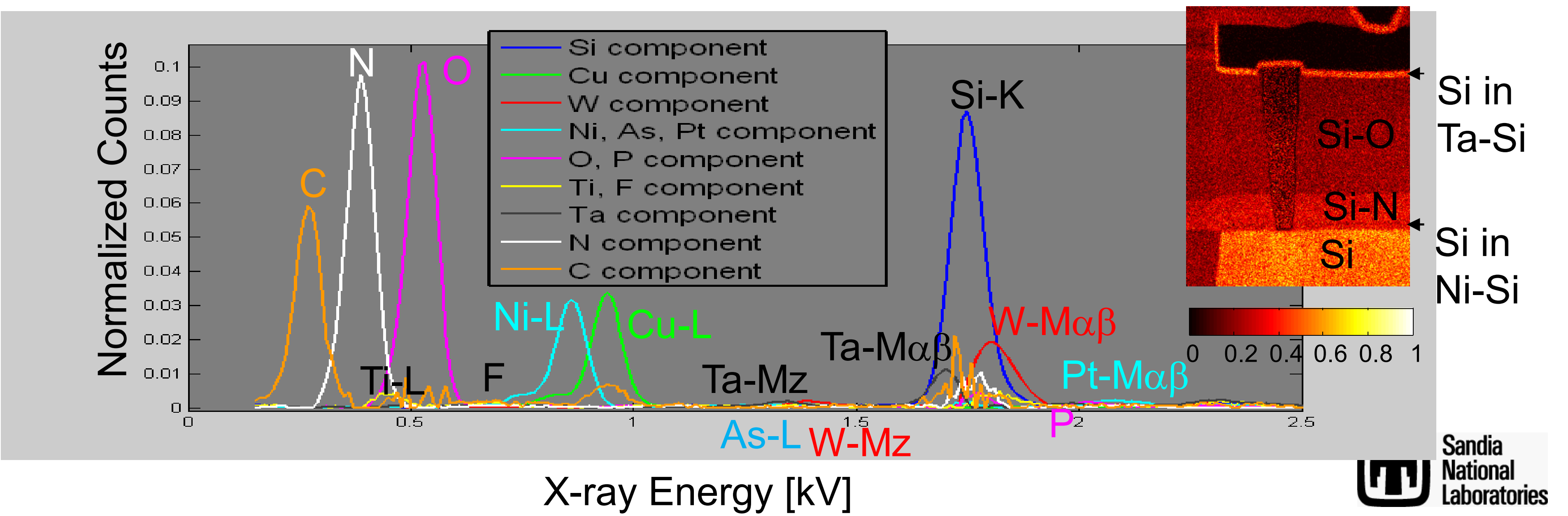
*M.R. Keenan, *Surf. Int. Anal.* **41** (2009) 79-87.
M.R. Keenan and P.G. Kotula, *Surf. Int. Anal.* **36 (2004) 203-212.
***P.G. Kotula et al. *Microsc. Microanal.* 9 (2003) 1-17.

Spectral-Domain Simplicity
Best Spectral or Elemental 'Contrast'



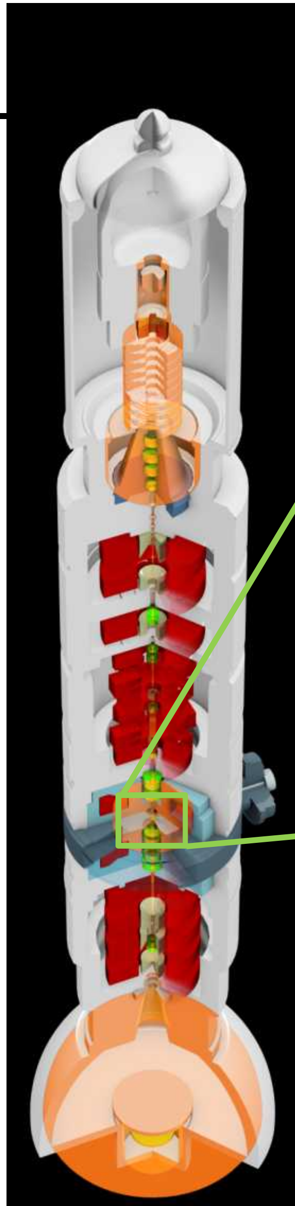


Atomic resolution x-ray microanalysis

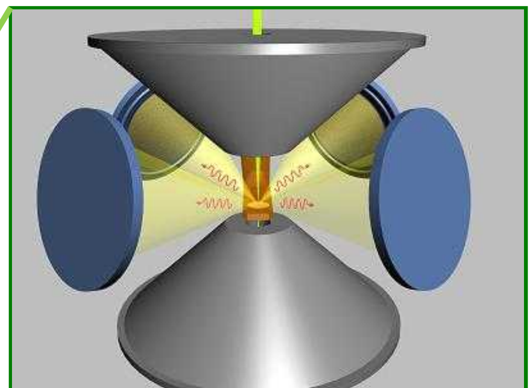
X-FEG

DCOR

Super-X



Critical elements for atomic resolution x-ray microanalysis



High brightness gun

Probe corrector

Efficient x-ray detector(s)

All of these elements have been integrated on the FEI Titan ChemiSTEM-P (200kV)

New Shottky emitter technology

- New Shottky emitter with the brightness of a cold FEG
- FEI X-FEG brightness increased to ~ 10^8 A/sr/m^2/ V
  - ~2 x 10^9 A/cm^2/sr @ 200 kV
- Probe current (w/o corrector)
  - 0.5 nA in 0.3 nm diameter
  - **Increased by 5x** relative to regular Schottky FEG
- Probe current (with DCOR probe corrector)
  - 200 kV, 1.3 nA in 0.2 nm diameter probe
  - 80 kV, 0.5 nA in 0.2 nm diameter probe
- Energy-spread = 0.9 eV

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Detector Efficiency: Arrays

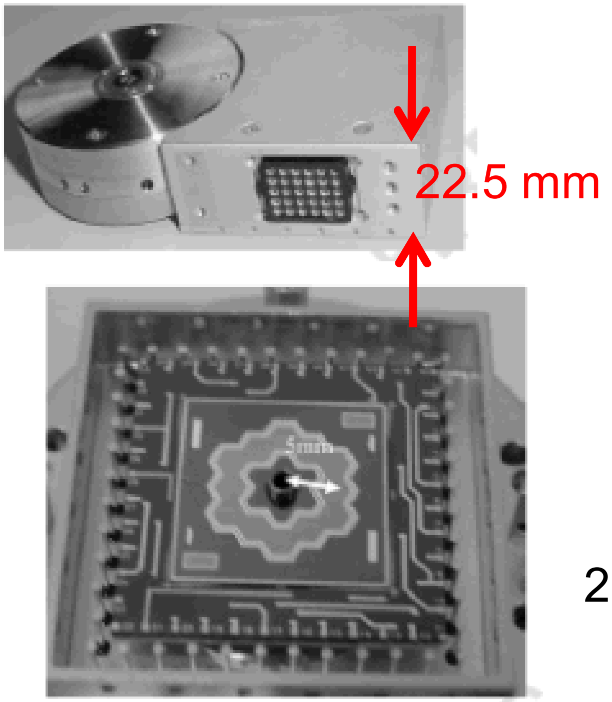
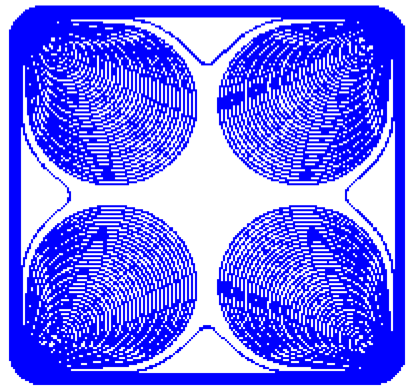
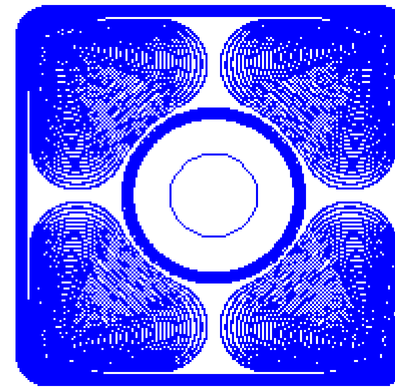


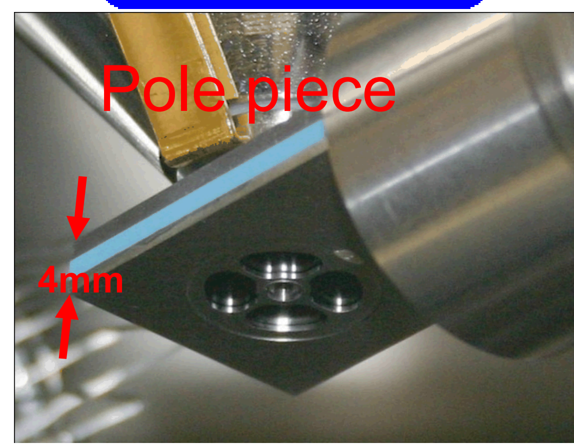
Figure 2. The Ketek 12-element annular SDD chip mounted in its package. The tantalum ion collimator that protects the SDD from scattered protons can be seen protruding through a hole in the center of the chip.

2005 Ketech/Custom imp.
2nd-3rd generation annular
(1.1 sr)



2005 pnSensor/Roentec
4-5th generation
conventional
(40 mm^2, 0.06 sr)





2007 pnSensor/Bruker
5th generation annular at
SNL(60 mm^2, 1.1 sr)

B. L. Doyle, D. S. Walsh, P. G. Kotula, P. Rossi, T. Schülein and M. Rohde, “An annular Si drift detector μPIXE system using AXSIA analysis,” *X-Ray Spectrom.* (2005) 34

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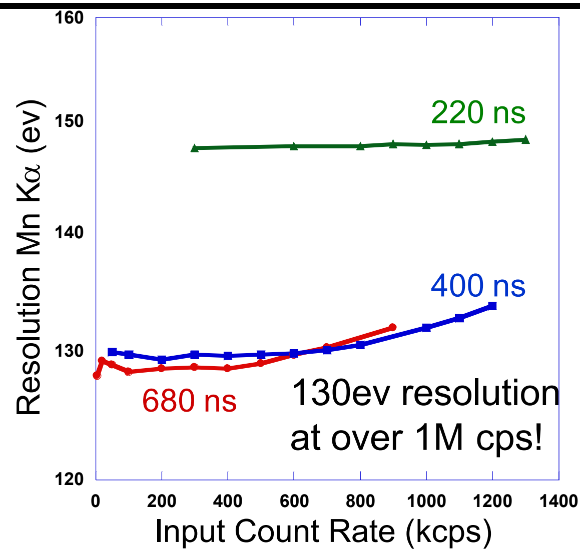
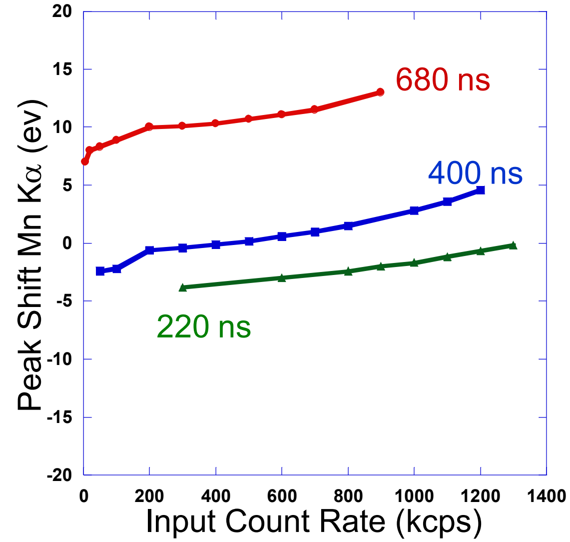
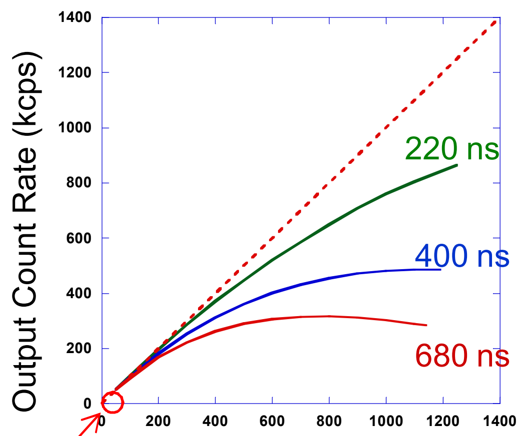
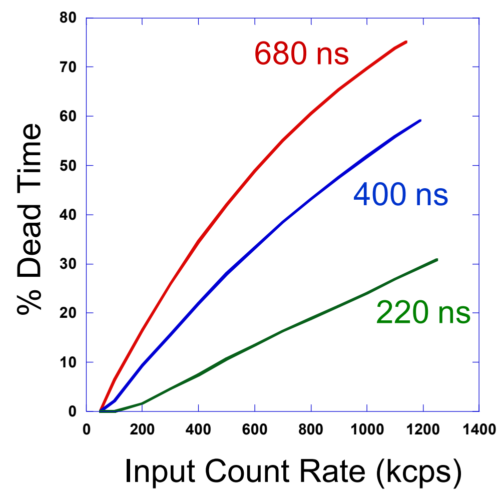
5th generation SDD performance

SEM data from 4-detectors summed









Si(Li) performance area at
180eV FWHM Mn-Kα

Performance superior in every way to Si(Li)

Silicon drift detector in AEM provides more flexible integration FEI/Bruker/pnSensor…SuperX™

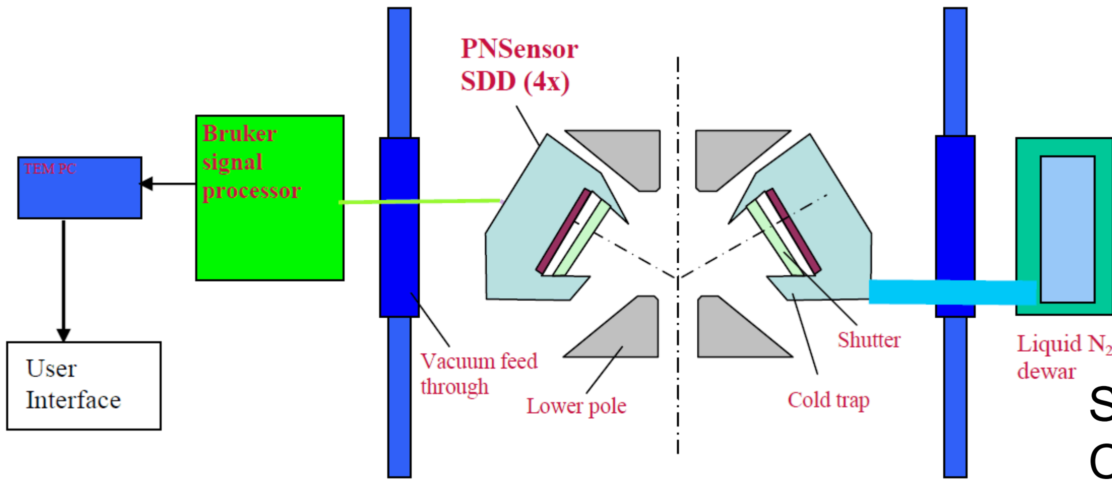


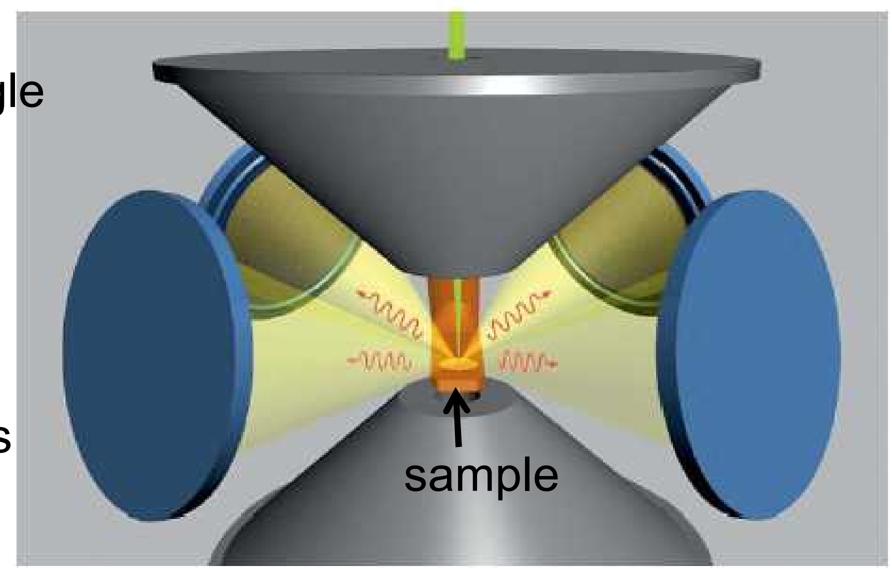
Figure 1. Schematic of Super-X detector

Field of the objective lens keeps electrons from hitting sensors

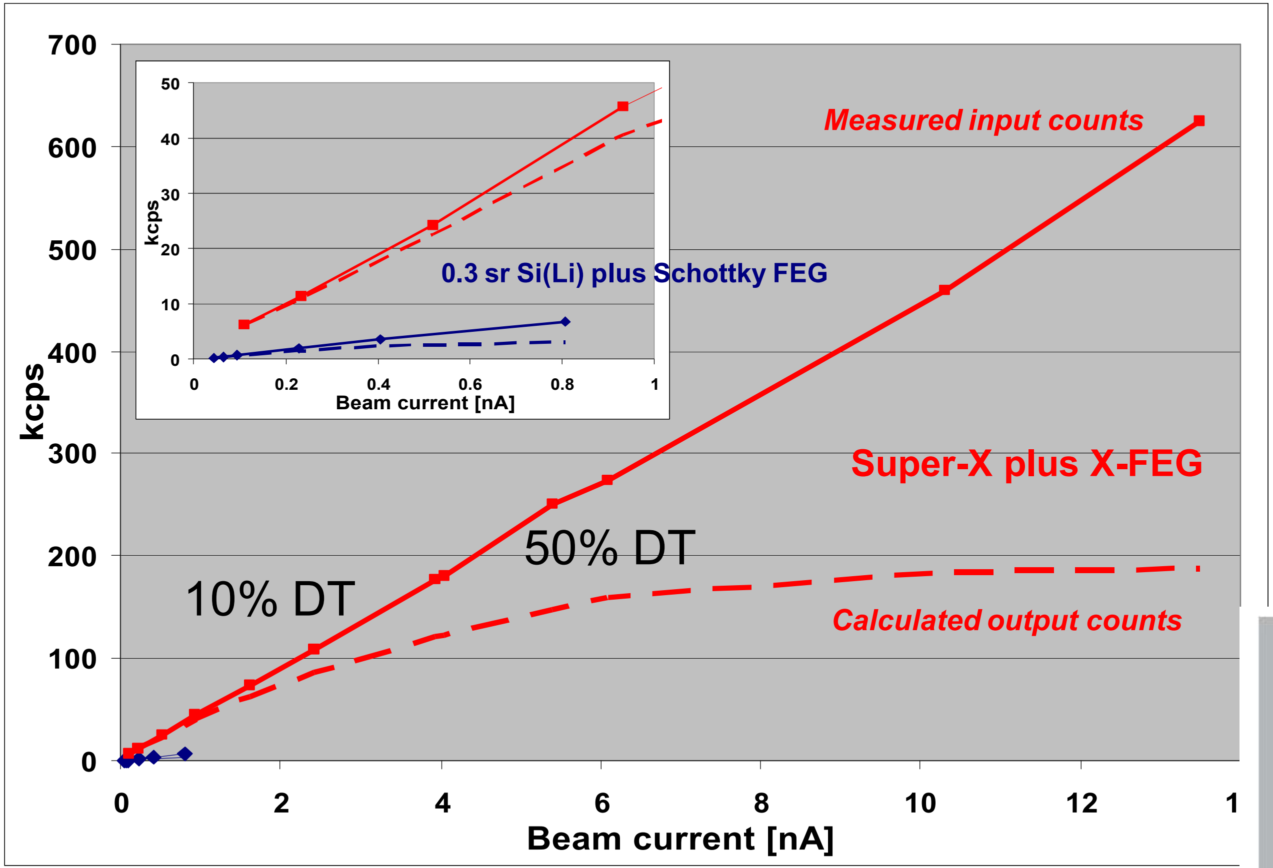
Revolutionary changes in AEM-EDS

SDDs cooled by the cold finger. Cooler than needed but no Peltier.

- 4-30mm^2 (120mm^2) SDDs with large solid angle
  - 0.9 sr (Osiris-uncorrected)
  - 0.7 sr (Titan-probe corrected)
  - State-of-the-art SDDs
  - Windowless & pnWindow…good light-element performance (C, N, O previously)
  - High-throughput…10 μsec instantaneous dwell times, multiple pass, drift correction

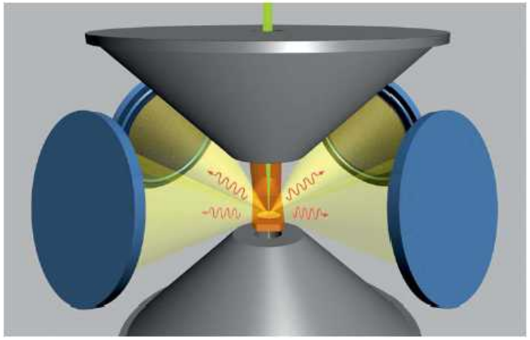


FEI/Bruker/pnSensor…SuperX™ Detector Performance



In both experiments the same FIB-cut InP sample was used with a thickness of about 200 nm.

Note: 1000 nsec shaping time
136 eV FWHM Mn-Kα



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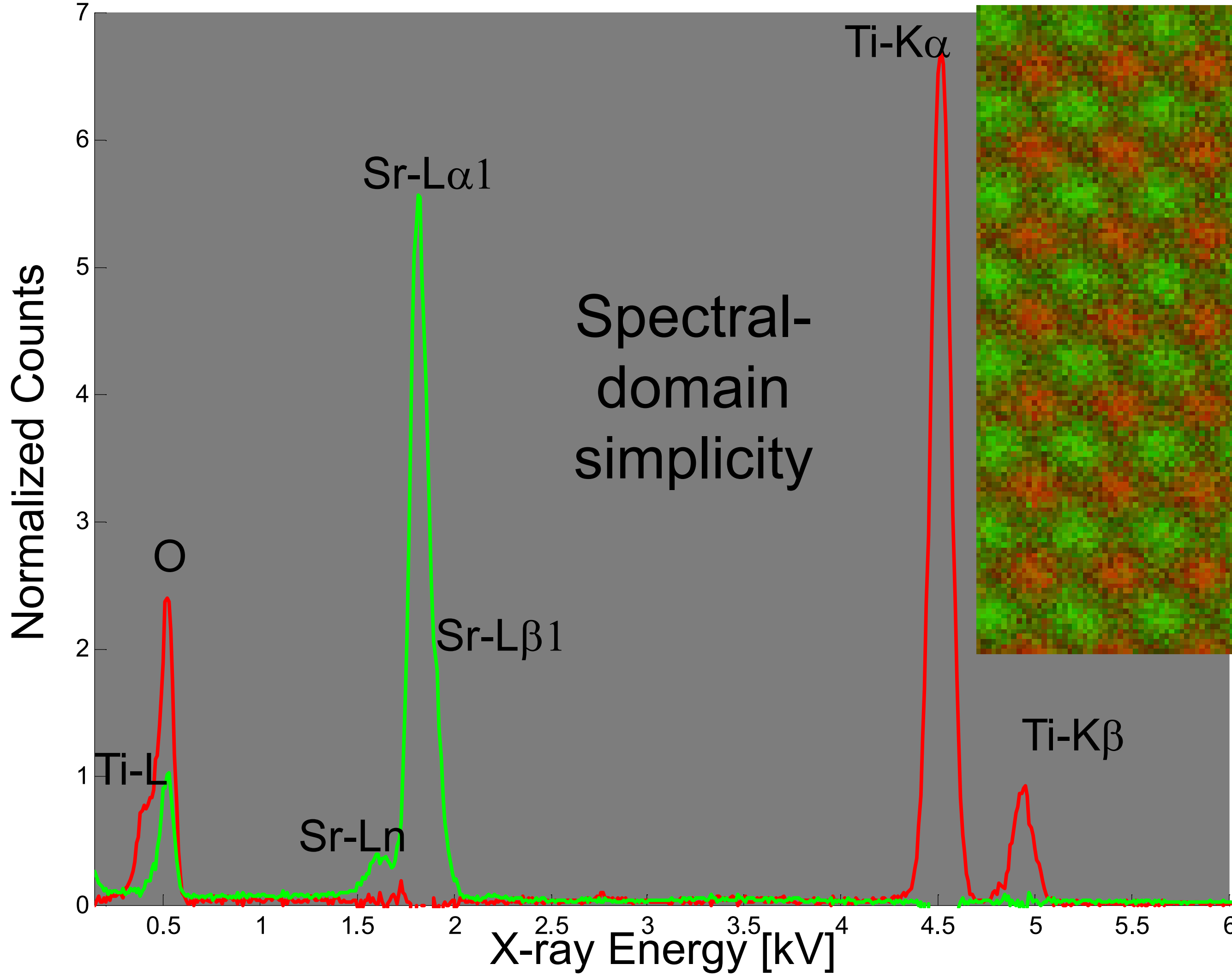
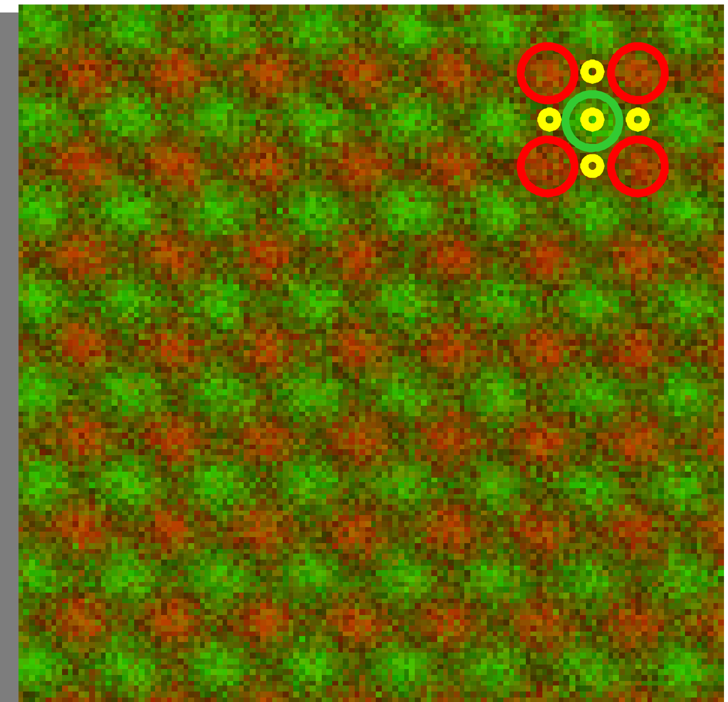
Example: SrTiO3 [100]

MSA-processed spectral image of $SrTiO_3$ with no *a priori* information



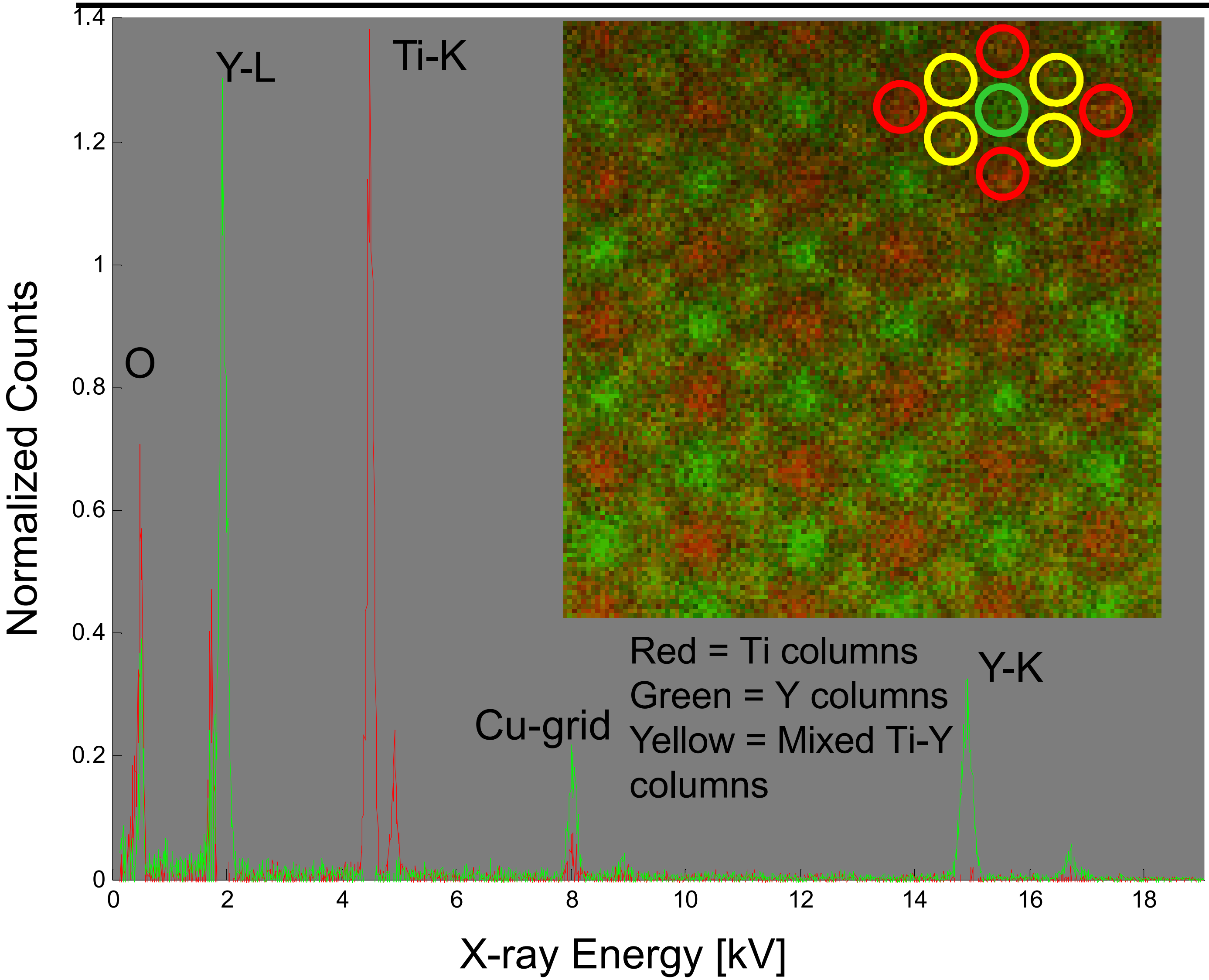


Red = Ti columns
Green = Sr columns

Sr-K lines not shown but correlate with Sr-L

Example: Y_2Ti_2O7 Pyrochlore [011]

128x128 Spectral image, 4x compression, Spectral domain simplicity



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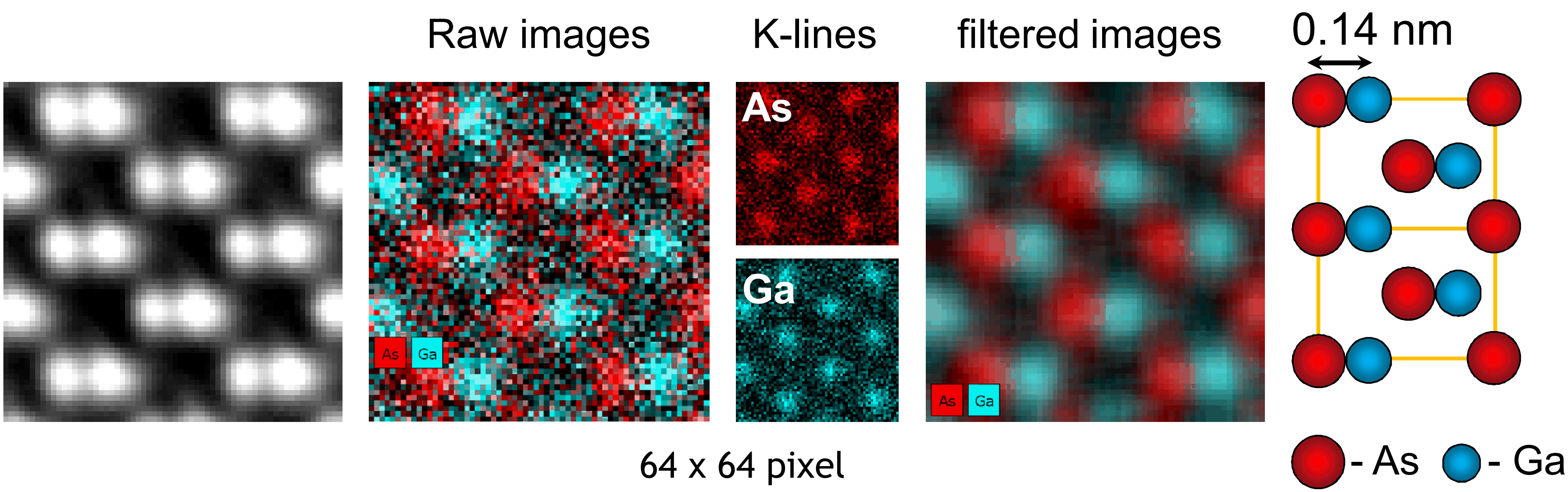
Example: GaAs [110]

No MSA applied here



64 x 64 pixel
200 pA beam current
917 sec total time
220 msec/pixel

Titan G2 @200 kV
probe-corrected (DCOR)
X-FEG, SuperX

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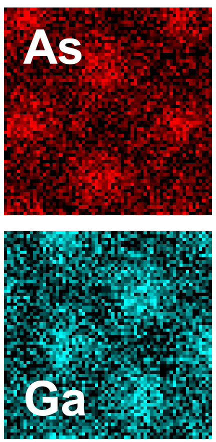
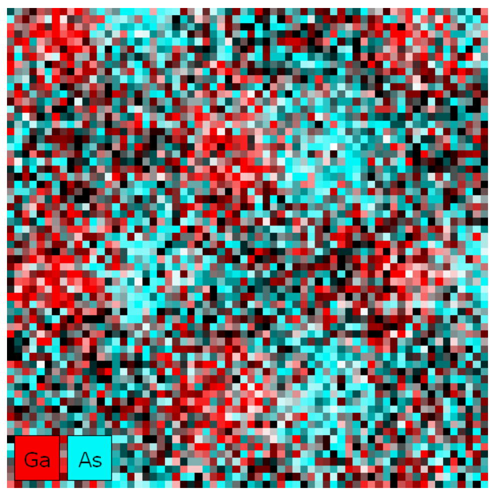
Example: GaAs [110]

MSA applied here with no *a priori* information

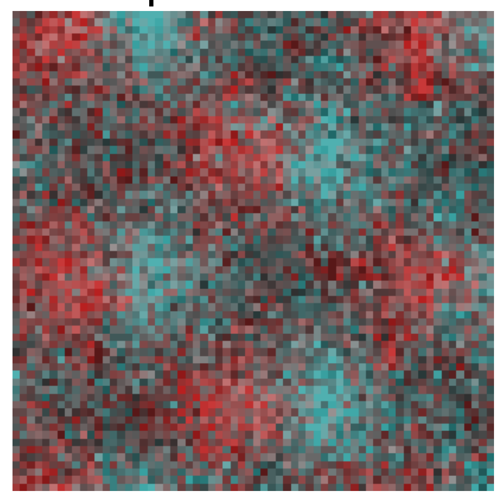
Raw maps



Raw K-lines ROI overlay

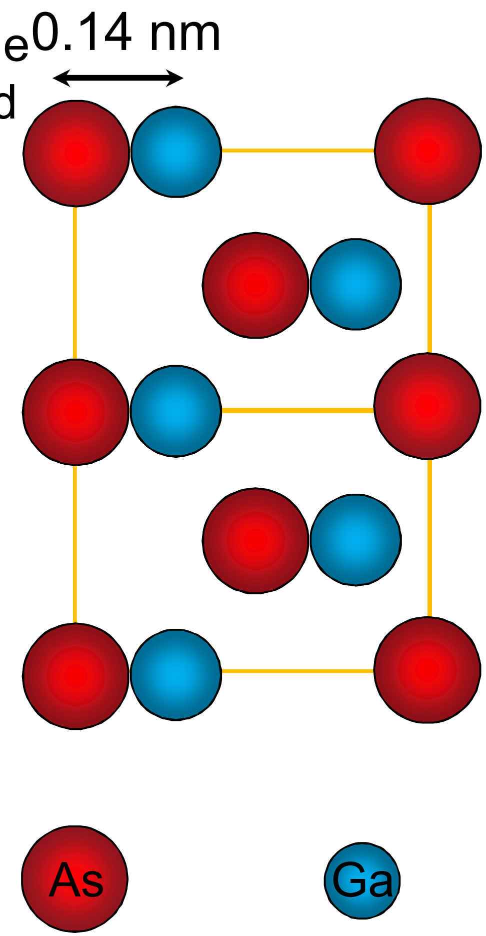


MSA results, K and L line overlaps ~deconvoluted



64 x 64 pixel
247 pA beam current
68 sec total time
17 msec/ pixel

Titan G2 @200 kV
probe-corrected (DCOR)
X-FEG, SuperX



~413k counts in the spectral image
Max counts in any channel is 10
Average of 100 counts per spectrum
MSA analysis took 300 msec with AXSIA

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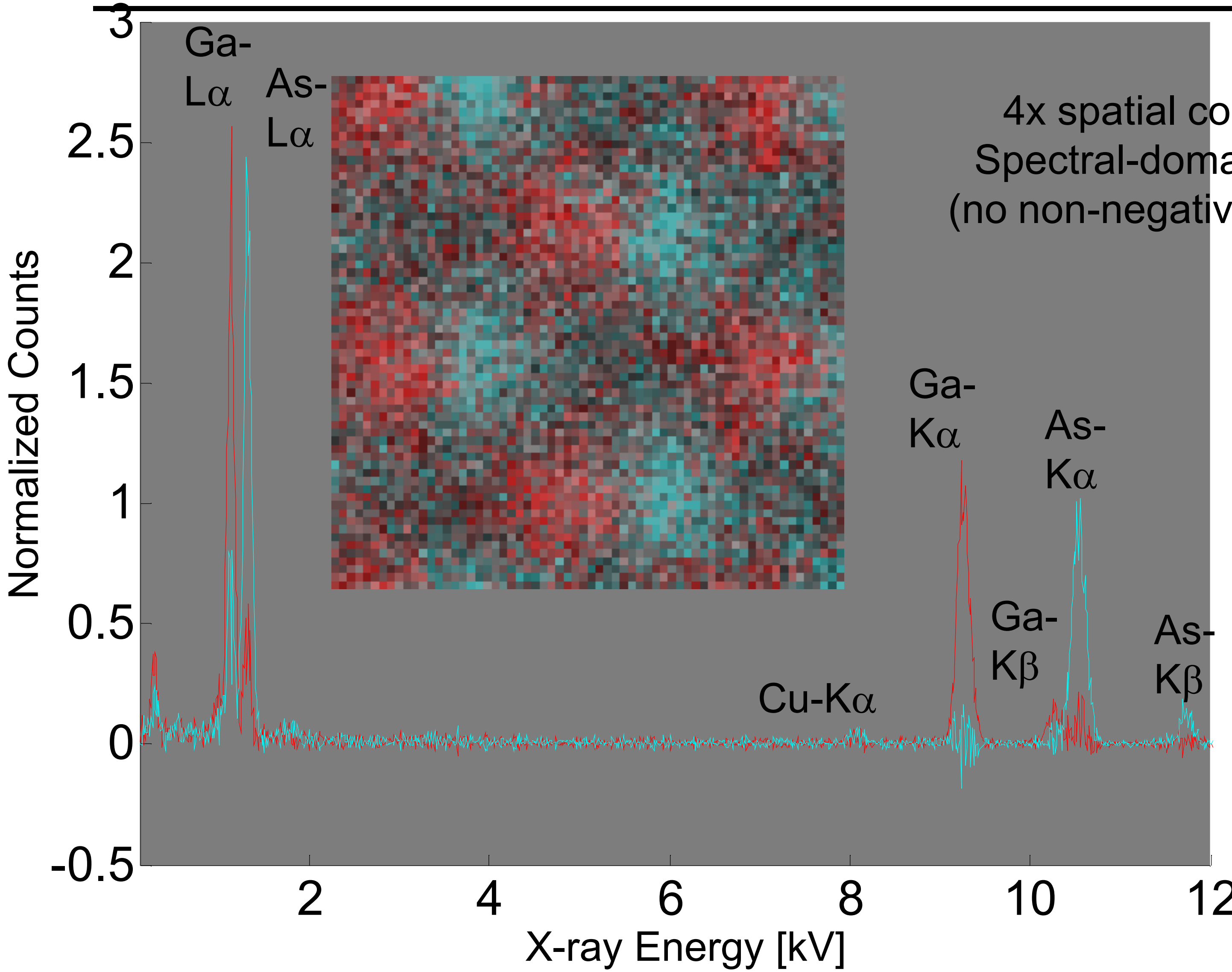
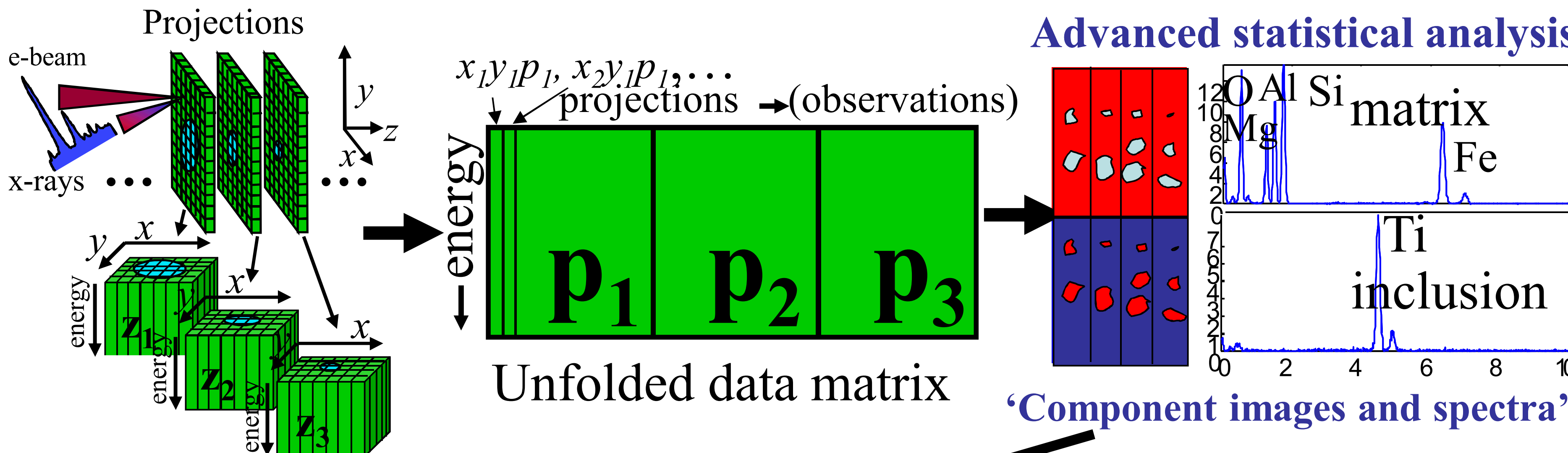
GaAs [110]: MSA component overlay



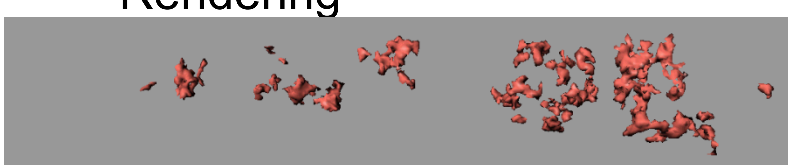
4x spatial compression
Spectral-domain simplicity
(no non-negativity constraint)

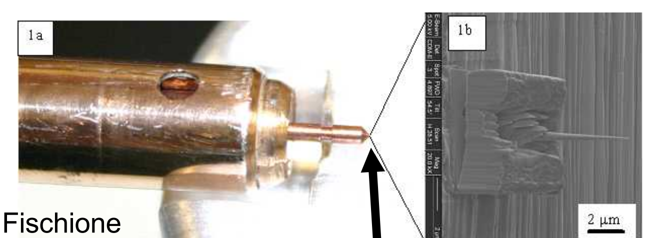
Tomographic Spectral Imaging and Multivariate Statistical Analysis



Reconstruction of component images into 3D model (Inspect 3D)

Rendering





Tip of the Fischione Model 2050 on-axis tomography holder

Atom-probe tip

SEM image of the prepared needle

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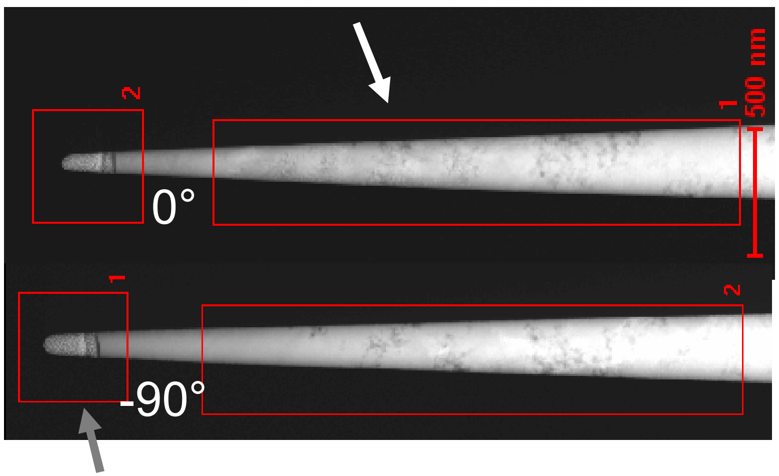
MSA of the entire projection series

FEI Tecnai F30-ST, 0.1sr

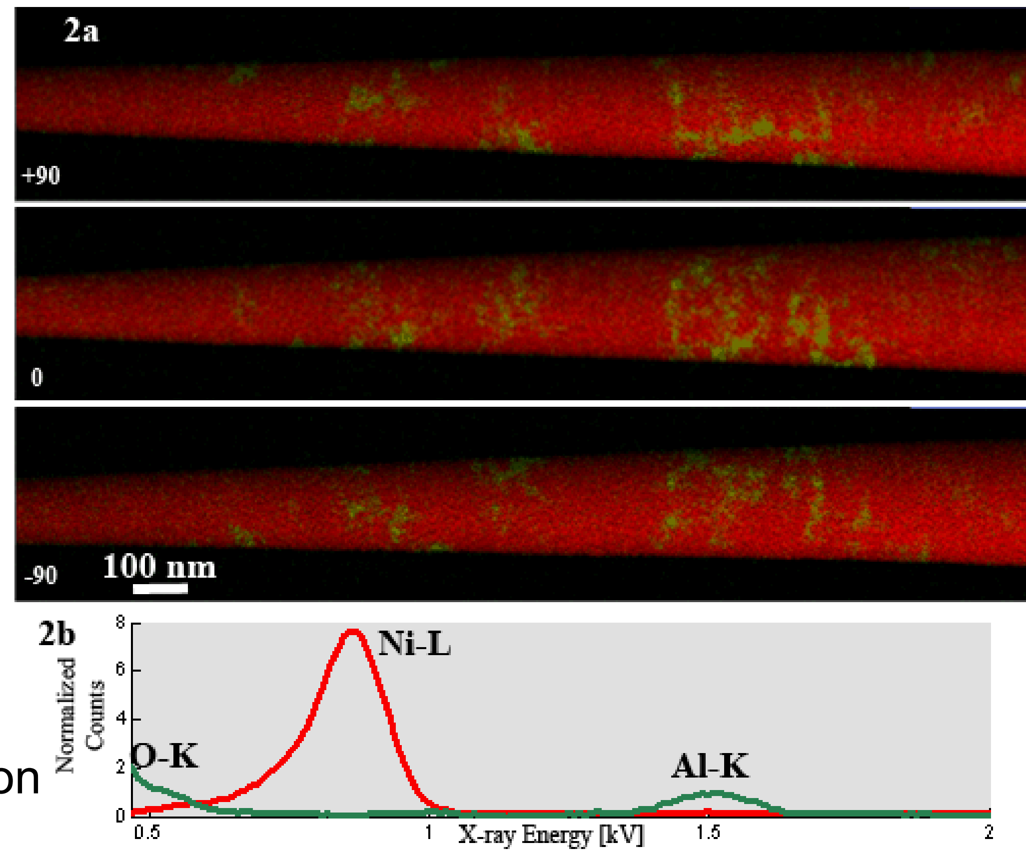
Region of spectral images 2000nm x 400nm



Drift-correction region

19 hours (over 3 days) of data acquisition

Color overlays of component images



P.G. Kotula, et al. Microsc. Microanal. 13 (Suppl2), 2007 1324CD-1325CD

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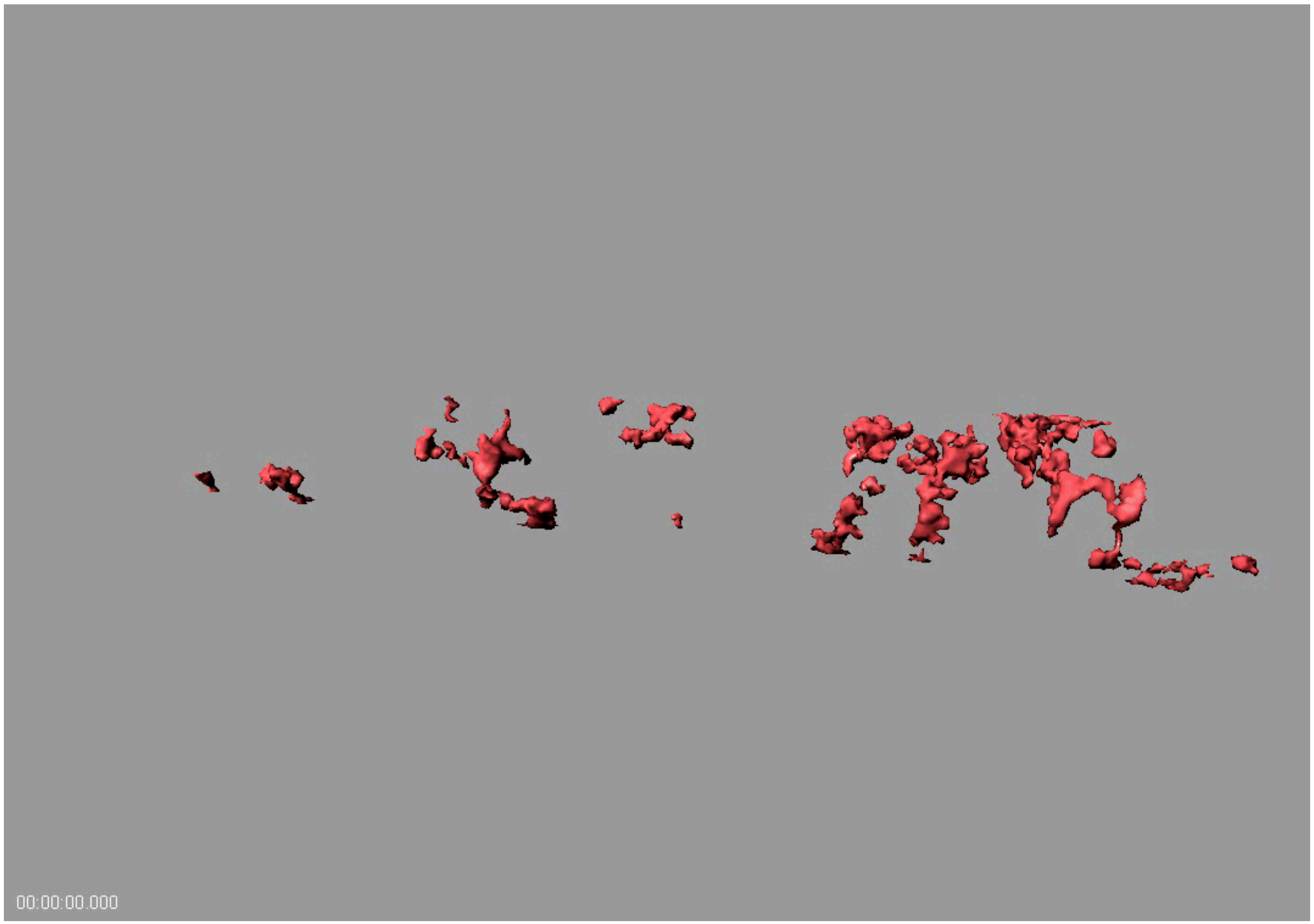
Reconstructed isosurface of the alumina particles



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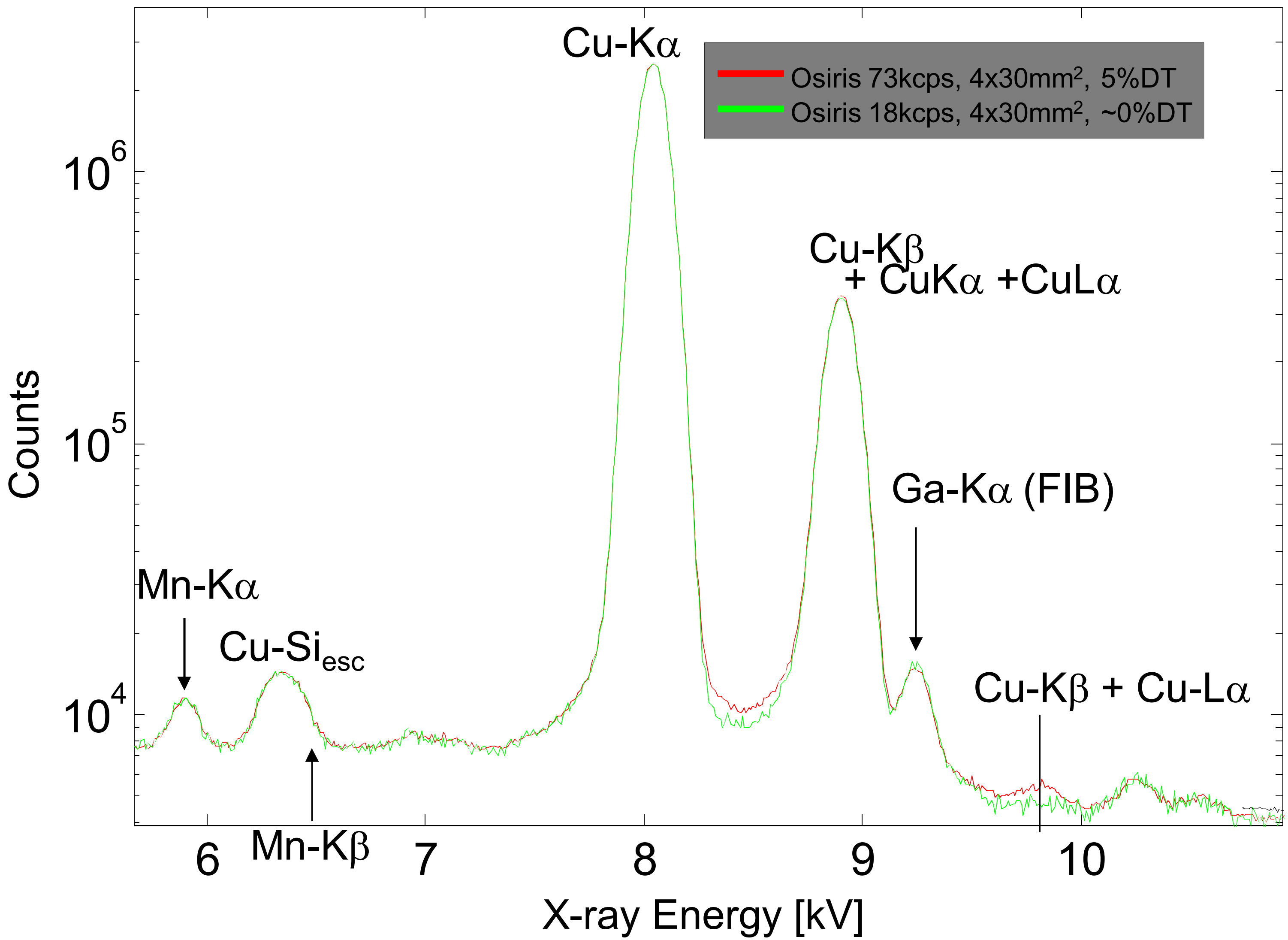
Conclusions

- AEM is undergoing a renaissance with correctors, SDDs, novel diffraction techniques, and better sources.
- Atomic resolution EDS will become more common than EELS. More elements accessible, esp. heavy ones.
- Novel detector geometries for AEM improve sensitivity and throughput.
- MSA methods are very useful for simplifying the analysis of large, complex data sets
  - Importance of Poisson normalization
  - Factor rotation, spatially or spectrally simple viewpoints
  - Unbiased analysis powerful for materials science, etc. Needle in the haystack….single atoms….
- Quantitative analysis pushed to smaller volumes
  - Understanding the spectrum is critical…every bump matters!
  - Potential for 1000 ppm sensitivity at 0.2 nm?
  - 100 ppm sensitivity at 1 nm?
- Practical computed tomographic spectral imaging

Joe Michael's 0.1 wt.% Mn-Cu



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