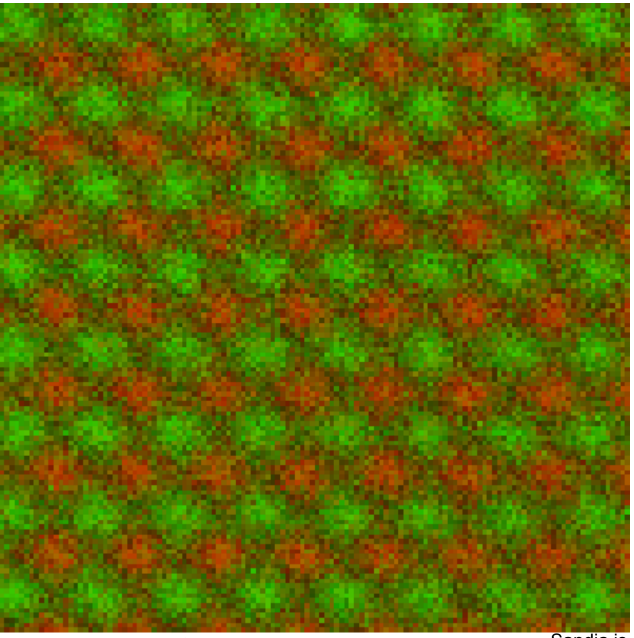
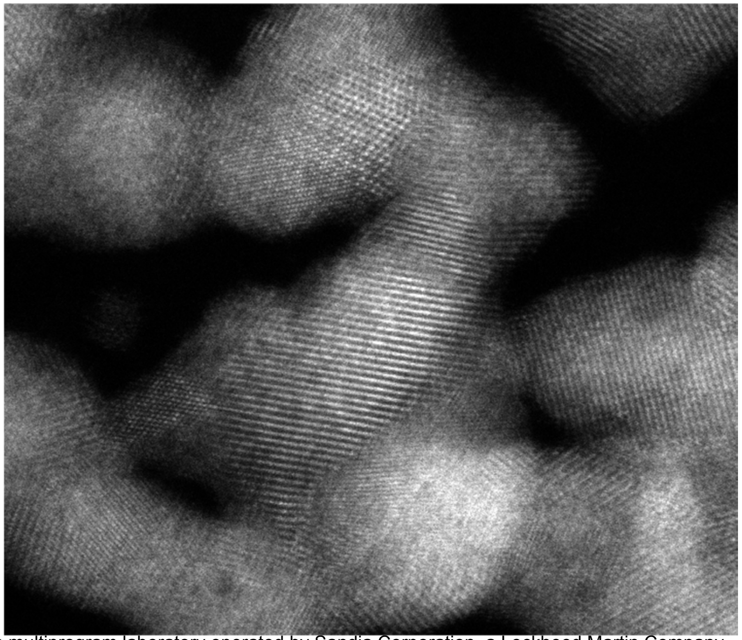
SAND2014-16373PE

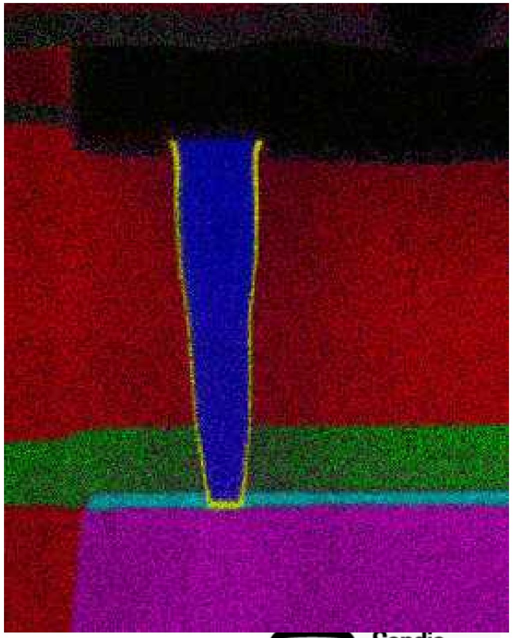
Advances in Acquisition and Analysis of Hyperspectral Images

Paul G. Kotula

Sandia National Laboratories, Albuquerque, NM, USA







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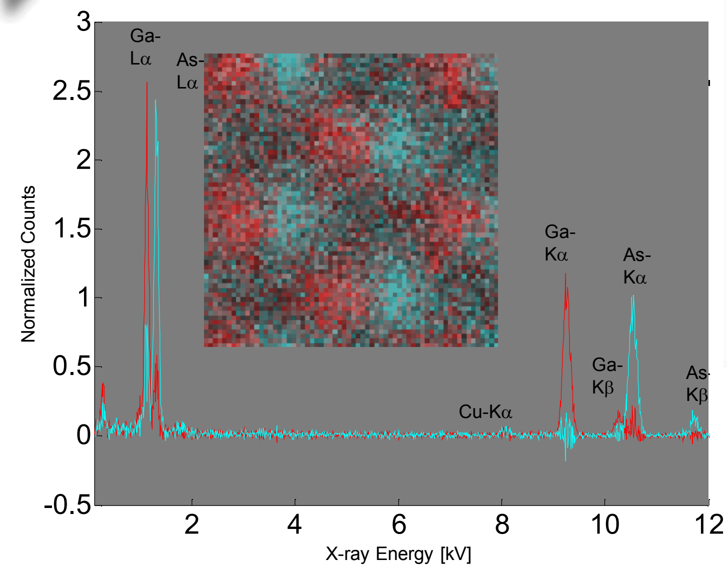
Outline

- Multi vs. hyperspectral definition
  - Multi-spectral…think mapping pre-selected elements
  - Hyper-spectral is collection all the data possible
- Spectral image analysis
- Historical timeline of developments
  - Multi-to-hyperspectral happened 35 years ago
  - Commercial version less than 20 years ago
- Plenty of examples along the way

Materials Characterization Tetrahedron



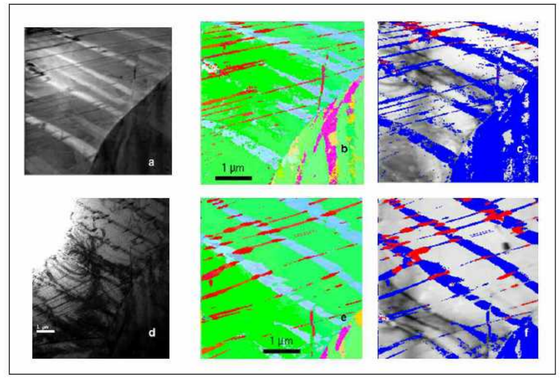
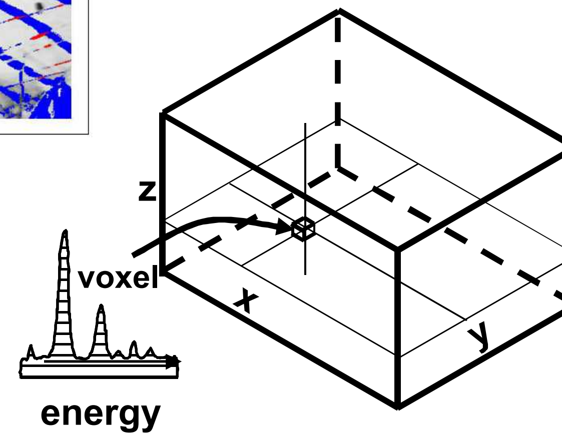
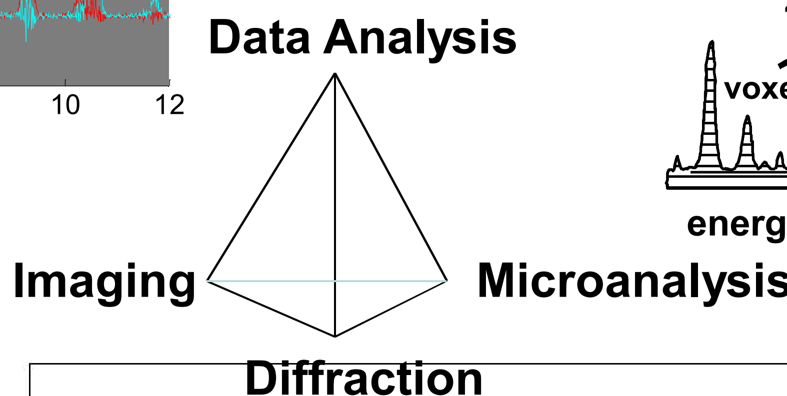
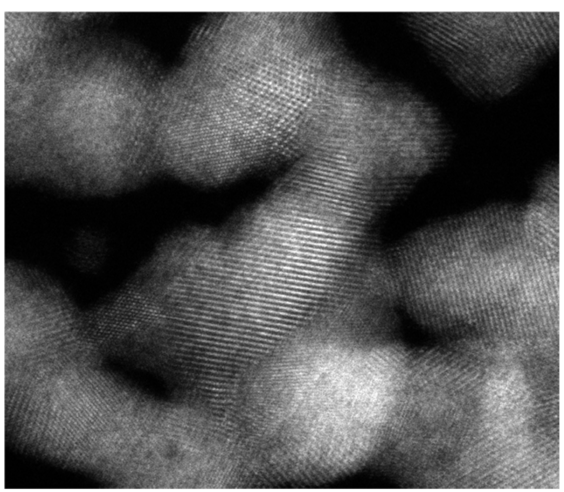
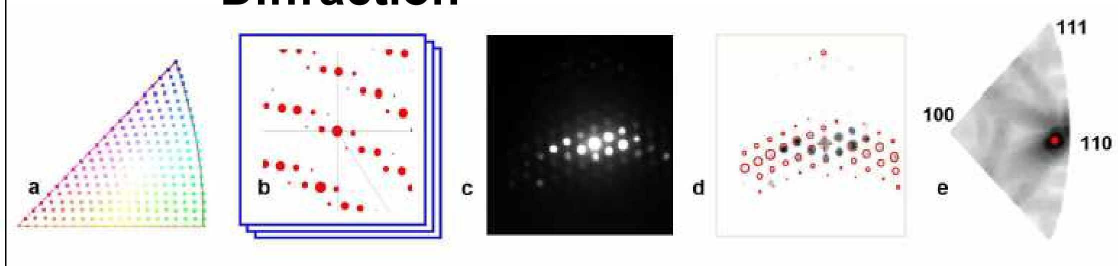


Figure 7:
Austenitic stainless TRIP steel containing three distinct phases: γ fcc matrix, hcp ϵ bands and bcc α' martensite at bands intersections.
(a) Index map coupled to (b) orientation (b) and phase (c) maps acquired without precession.
(d) Brightfield image coupled to orientation (e) and phase (f) maps acquired with precession. Step size 22 nm, precession angle 0.4°, acquisition time 1 hour 9 minutes.



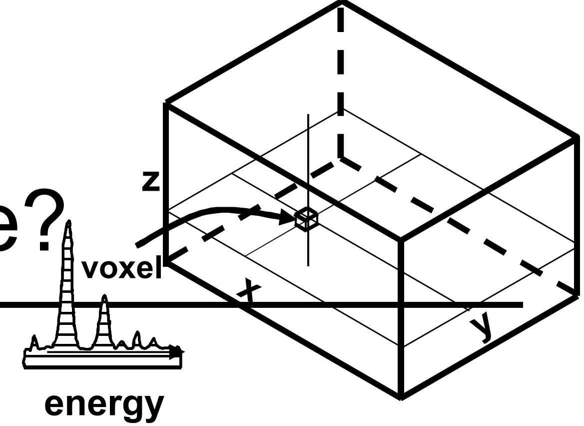




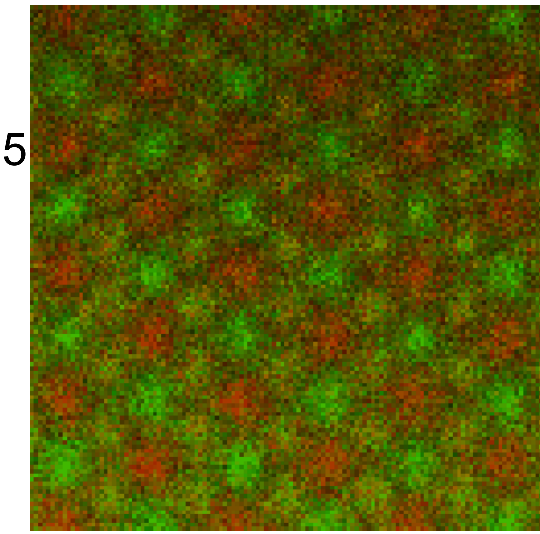


Nanomegas

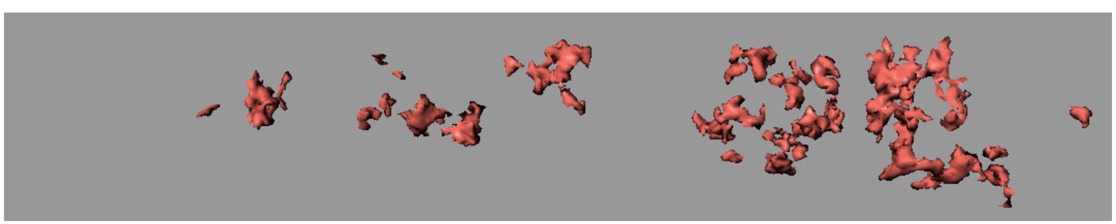
Data analysis primer
What is a spectral image?



- 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.

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*
  - 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 (PCA, factor rotation, MCR)
  - Analysis goal: compact and readily interpreted factors
- 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

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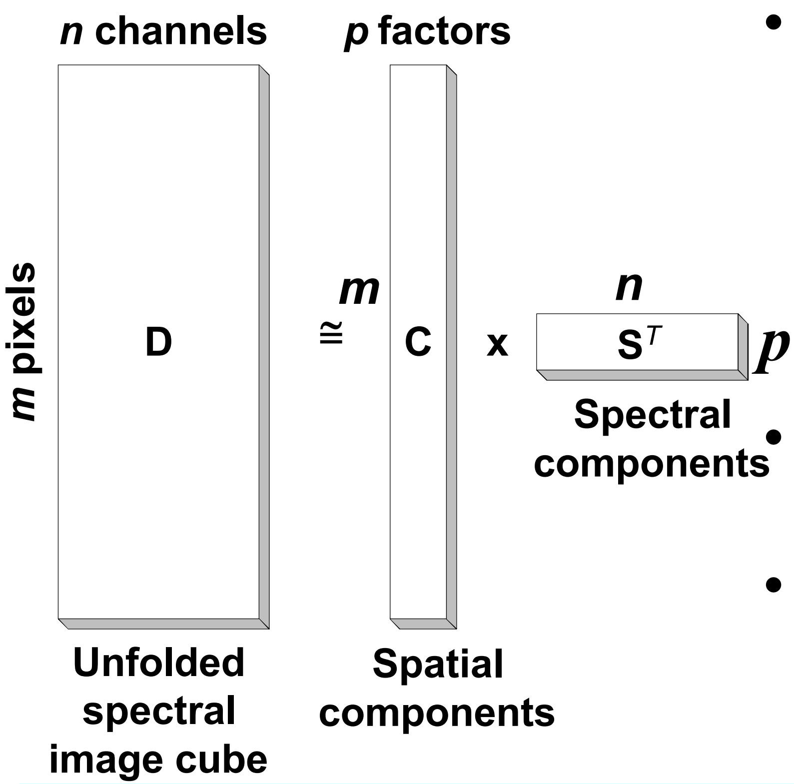
We have several options in our multivariate "Toolbox"



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.

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
  - 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 spatial components are orthogonal and the spectral components are orthonormal
- Rotate the orthonormal spectral components to maximize their mutual simplicity with the VARIMAX procedure
- Apply the inverse rotation to the spatial components which relaxes orthogonally in this domain
- Optionally: Impose non-negativity (e.g. via MCR-ALS)***
- 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*

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
  - 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 (to the component images) in a single classical least-squares calculation**
- **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.

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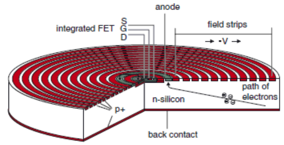
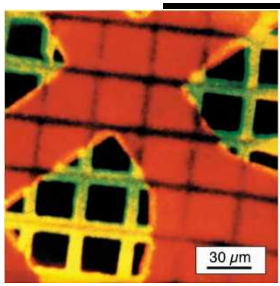
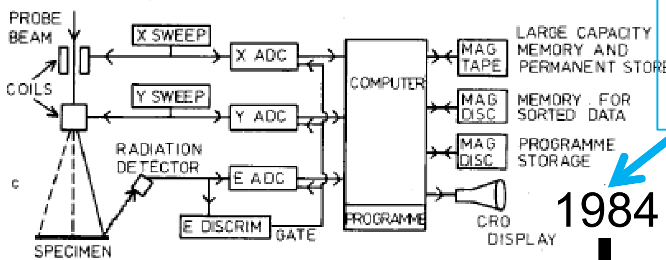
Historical timeline of multi- to hyper-spectral imaging







Gatti & Rehak SDD — 1984

Hunt & William collect an EELS spectrum image — 1991

Kotula et al. collect a 3D spectrum image (FIB-SEM)

PDP 11 IBM PC

1951 1956 1968 1979 1989 1995 2000 2006

Castaing builds the first practical EPMA (single-point analysis) — 1951

Cosslett & Duncumb collect first x-ray maps — 1956

Fitzgerald, et al. develop the Si (Li) EDS detector — 1968

Legge & Hammond acquire the first hyperspectral image — 1979

Jeanguillaume & Colliex describe “spectrum images” — 1989

Mott et al. at PGT commercialize event streaming (PTS) for EDS — 1995

Lechner et al. multi-channel SDD — 2000

Niculae et al. perfect the SDD — 2006

J.J. Friel and C.E. Lyman, *Microsc. Microanal.* 12, 2-25, 2006.

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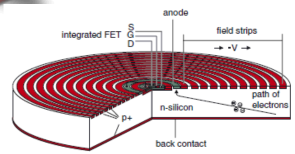
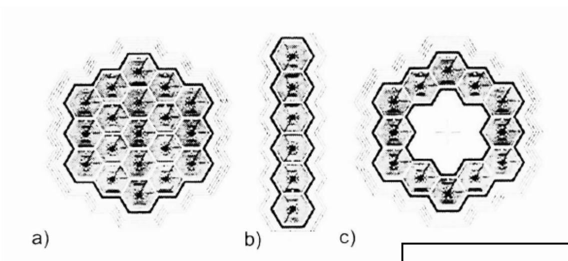
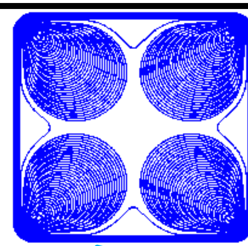
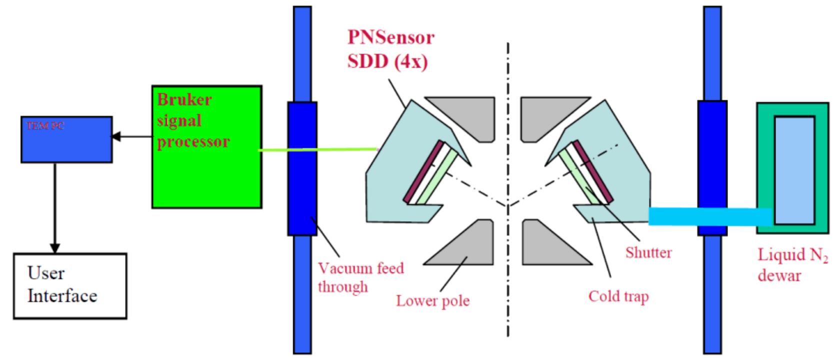
Historical timeline of multi- to hyper-spectral imaging







PNSensor/Roentec

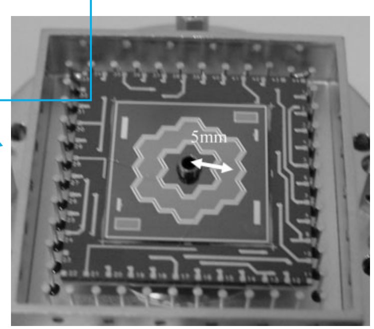


2000

Lechner et al. multi-channel SDD

2005

Doyle et al. demonstrate 1.1 sr annular SDD and spectral imaging

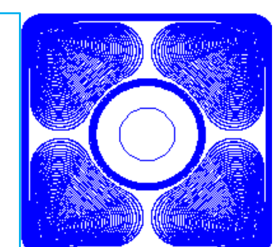


2006

Niculae et al. perfect the SDD

2007

PNSensor/Bruker deliver 'annular' SDD for SEM to Sandia



2010

von Harrach et al. demonstrate 4-channel SDD on AEM (SuperX)

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Historical timeline of hyper-spectral image analysis (partial)

(Specific influences of our early work plus some of our contributions)

PGT-PTS/EmiSpec

1990

Trebbia & Bonnet
EELS-SI and MSA

1995

Titchmarsh et al.
MSA (PCA) of X-ray spectrum line

1998

I joined Sandia and work with Keenan and begin research to develop better tools for spectral image analysis

Anderson et al.
MSA (PCA) of X-ray spectrum images

2002

Sandia's AXSIA commercially licensed/Patents issued 1-years later

2003

Kotula, et al. publish first journal article SEM-EDS SI and MSA /MCR

2004

Keenan, et al. publish Poisson normalization

2006

Kotula, et al. publish 3D EDS by FIB-SEM and MSA analysis

2012

Kotula et al. Atomic-resolution EDS, MSA and quant

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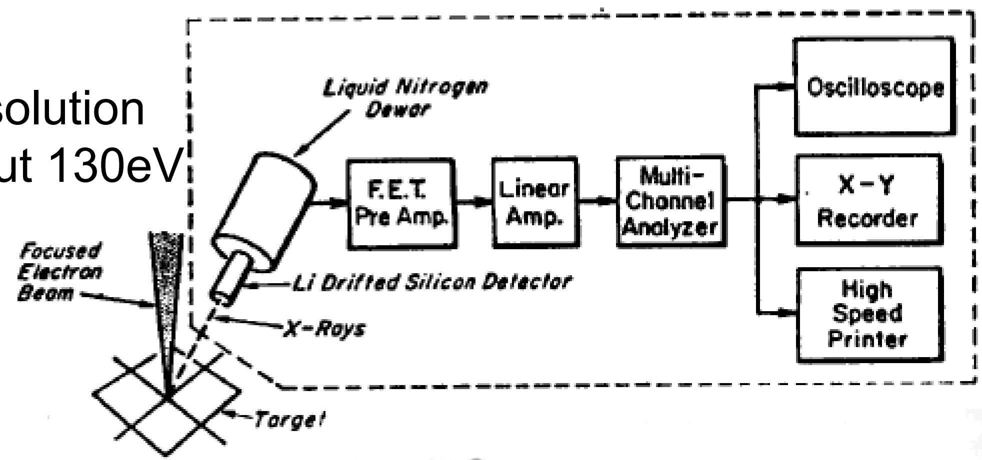
1968, Si(Li) detector…enabling technology for spectral imaging

- Si (Li) EDS started at 600eV resolution
- Over the years improved to about 130eV FWHM at Mn-Kα
- Parallel detection
- Downsides:
  - Liquid nitrogen cooling
  - Lack of flexible geometries
  - You can get either throughput or good spectral resolution but not both



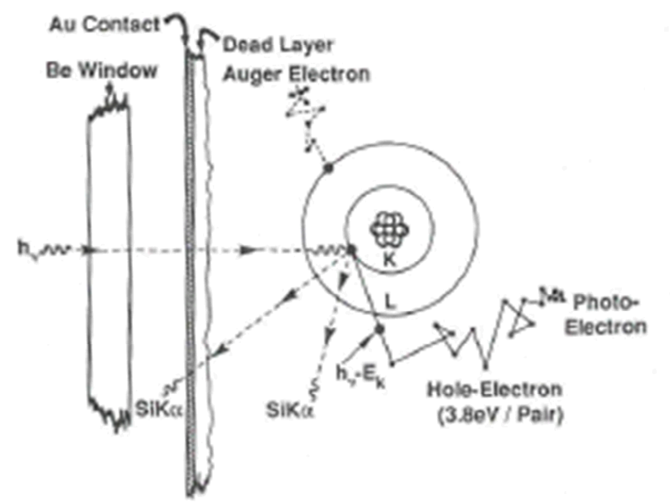


Figure 5.22. The x-ray detection process in the Si(Li) detector.

R. Fitzgerald, K. Keil, K.F.J Heinrich, *Science* (1968) **159** 528-530.

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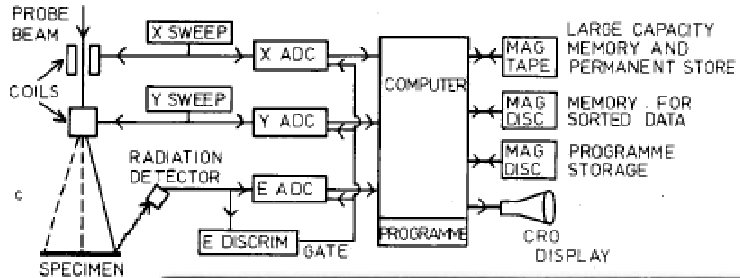
1979, The First Hyperspectral Image

- Proton microprobe with Si(Li) EDS
- Custom-designed beam control and data acquisition
  - Events streamed to magnetic tape

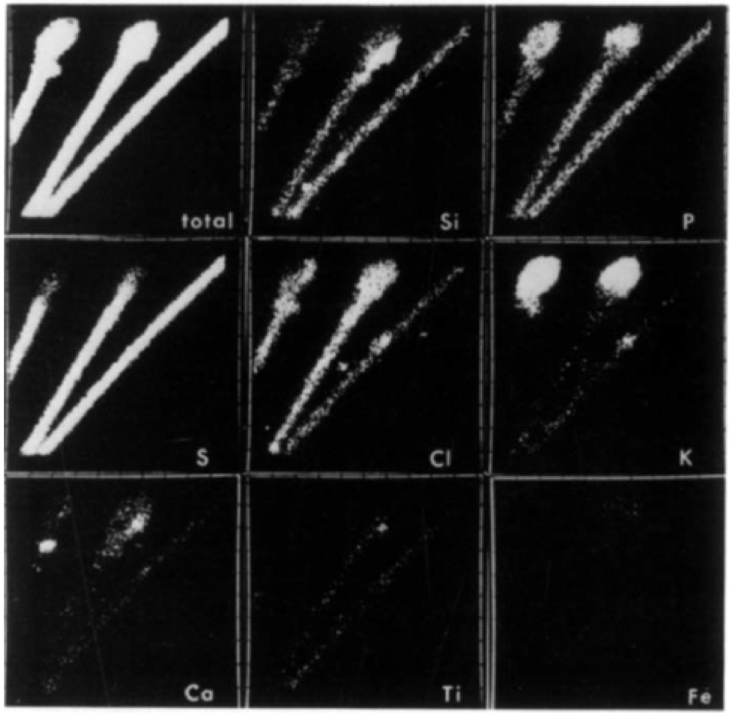


Total quantitative recording of elemental maps and spectra with a scanning microprobe

by G. J. F. Legge and I. Hammond, *School of Physics, University of Melbourne, Parkville, Victoria 3052, Australia*

SUMMARY

A system of data recording and analysis has been developed by means of which simultaneously all data from a scanning instrument such as a microprobe can be quantitatively recorded and permanently stored, including spectral outputs from several detectors. Only one scanning operation is required on the specimen. Analysis is then performed on the stored data, which contain quantitative information on distributions of all elements and spectra of all regions.



© *Journal of Microscopy, Vol.* 117, *Pt* 2, *November* 1979, *pp.* 201–210.
Revised paper accepted 9 *May* 1979

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1984, SDD…eventually a game changer

SEMICONDUCTOR DRIFT CHAMBER – AN APPLICATION OF A NOVEL CHARGE TRANSPORT SCHEME

Emilio GATTI [1)] and Pavel REHAK

Brookhaven National Laboratory, Upton, New York 11973, USA

The purpose of this paper is to describe a novel charge transport scheme in semiconductors, in which the field responsible for the charge transport is independent of the depletion field. The application of the novel charge transport scheme leads to the following new semiconductor detectors:
1) Semiconductor drift chamber;
2) Ultralow capacitance – large area semiconductor X-ray spectrometers and photodiodes;
3) Fully depleted thick CCD.
Special attention is paid to the concept of the semiconductor drift chamber as a position sensing detector for high energy charged particles. Position resolution limiting factors are considered and the values of the resolutions are given.

- The silicon drift detector is born but will take a few decades to hit its stride
- Thin (300 μm to 400 μm thick)
  - Less sensitive to high-energy photons vs. Si(Li)
- Low capacitance allows for very fast read out (short shaping times in the 100s of nsec)
- Several orders of magnitude better throughput
- Issues with peak position and resolution changing with count rate…

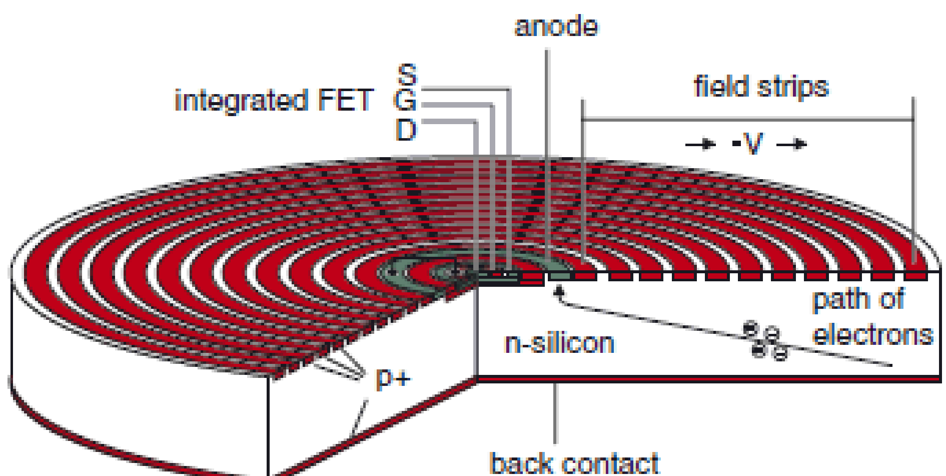
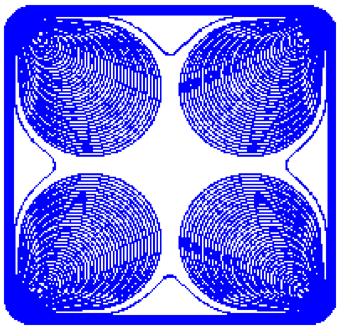


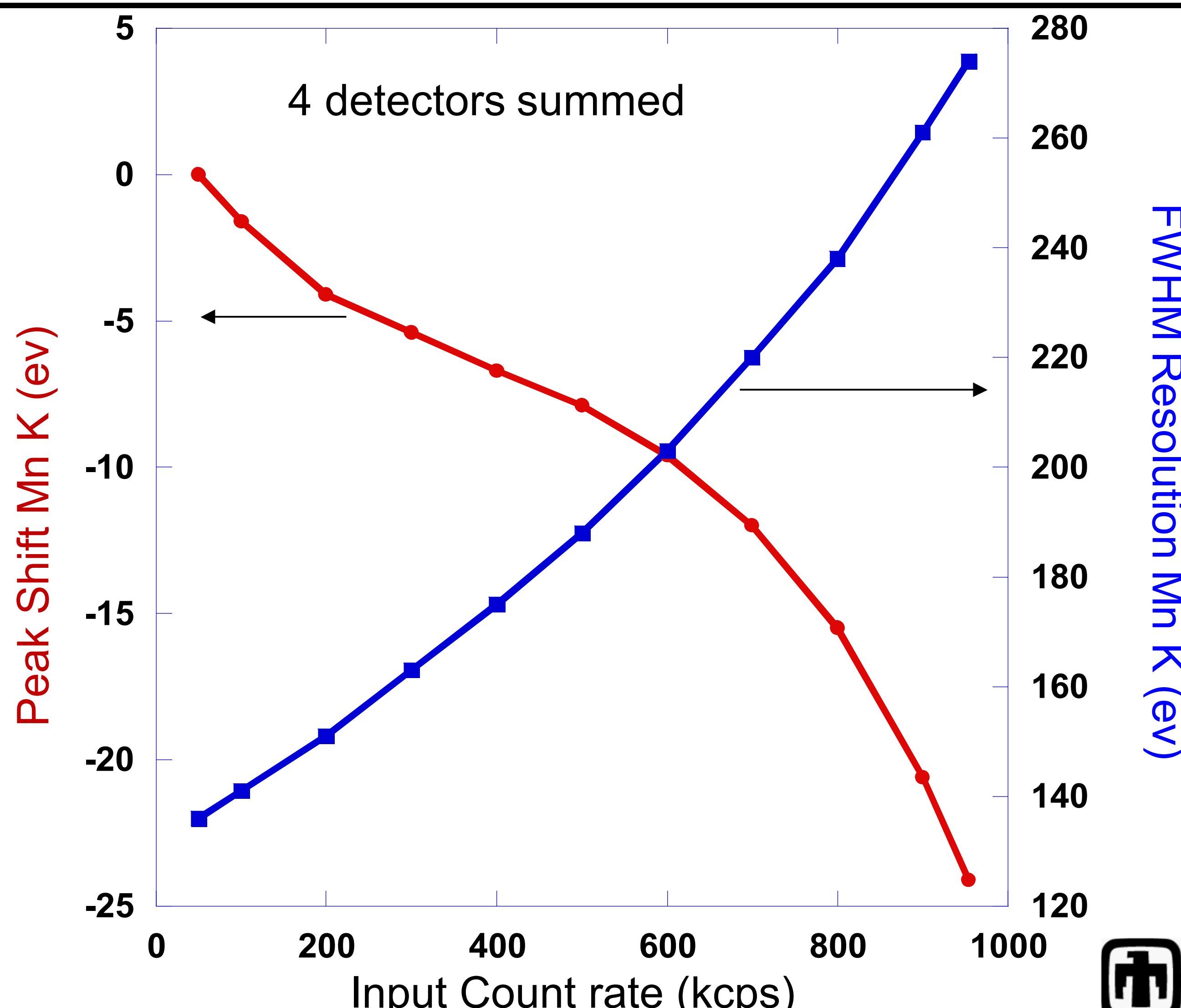
Image courtesy pnSensor

E. Gatti and P. Rehak, *Nuc. Inst. Meth. Phys. Res.* **225** (1984) 608-614.

Early SDDs had issues



Four-channel (each 10mm^2) SDD at Sandia from 2005. Peak distortion was also observed with increasing count rates.



2006, SDDs finally ready for prime time

- The silicon drift detector is finally better in virtually every respect than the Si(Li).
- Improved read-out scheme fixed the stability issues at higher count rates
- Thin (300 μm to 400 μm thick)
  - Less sensitive to high-energy photons vs. Si(Li)
- Low capacitance allows for very fast read out (short shaping times in the 100s of nsec)
- Several orders of magnitude better throughput
- Peltier cooled so flexible geometries are possible

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Nuclear Instruments and Methods in Physics Research A 568 (2006) 336–342
NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH Section A
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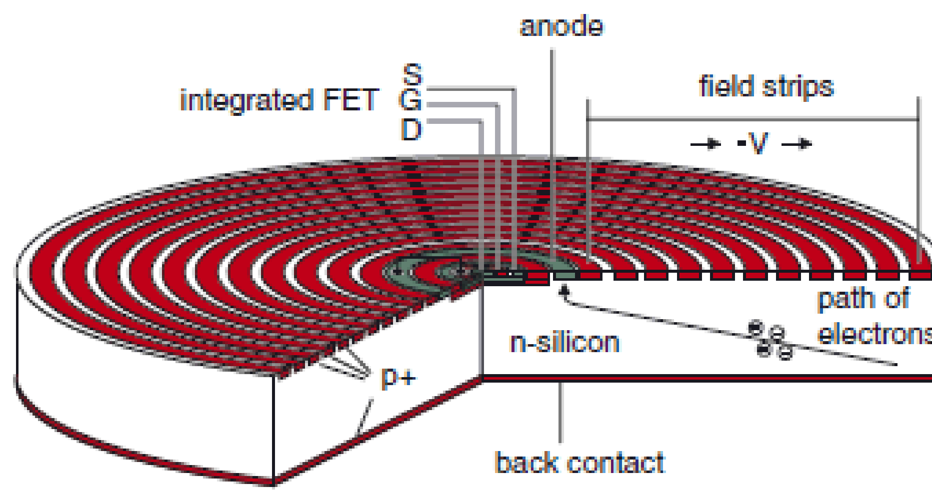
Optimized readout methods of silicon drift detectors for high-resolution X-ray spectroscopy

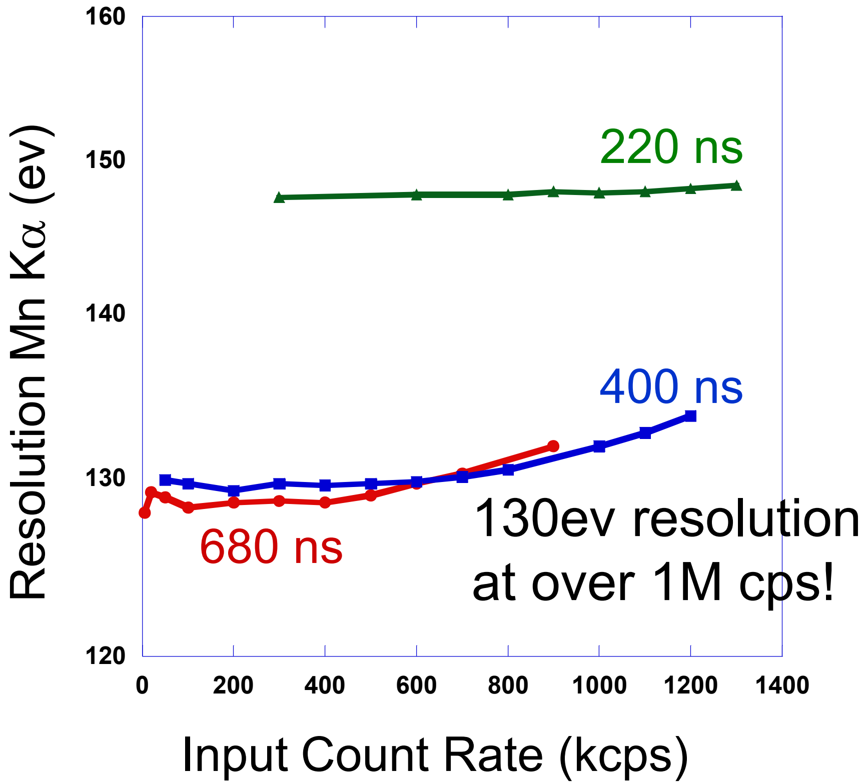
A. Niculae[a,*], P. Lechner[a,b], H. Soltau[a,b], G. Lutz[c,b], L. Strüder[d,b], C. Fiorini[e], A. Longoni[e]

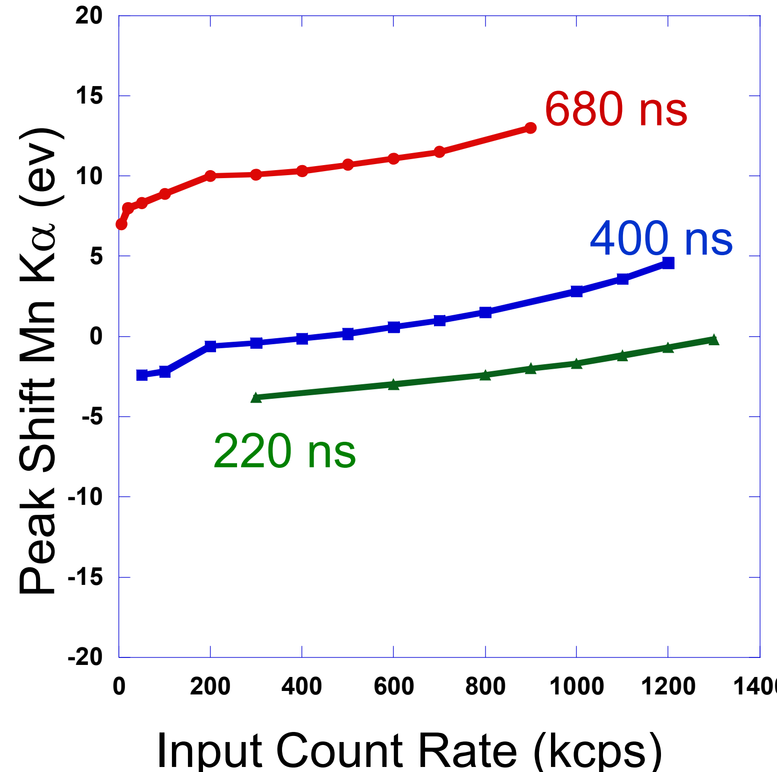
[a] PNSensor GmbH, Römerstraße 28, 80803 Munich, Germany
[b] MPI Halbleiterlabor, Otto-Hahn-Ring 6, 81739 Munich, Germany
[c] Max-Planck-Institut für Physik, 80805 Munich, Germany
[d] Max-Planck-Institut für extraterrestrische Physik, 85748 Garching, Germany
[e] Politecnico di Milano, Dipartimento di Elettronica e Informazione, Via Golgi 40, 20133 Milano, Italy

Available online 7 July 2006

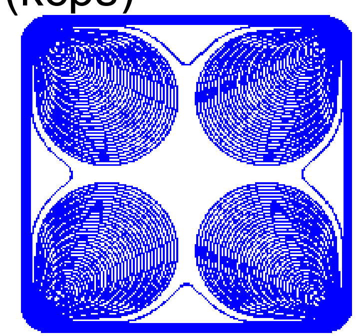


2006, SDDs now excellent performers

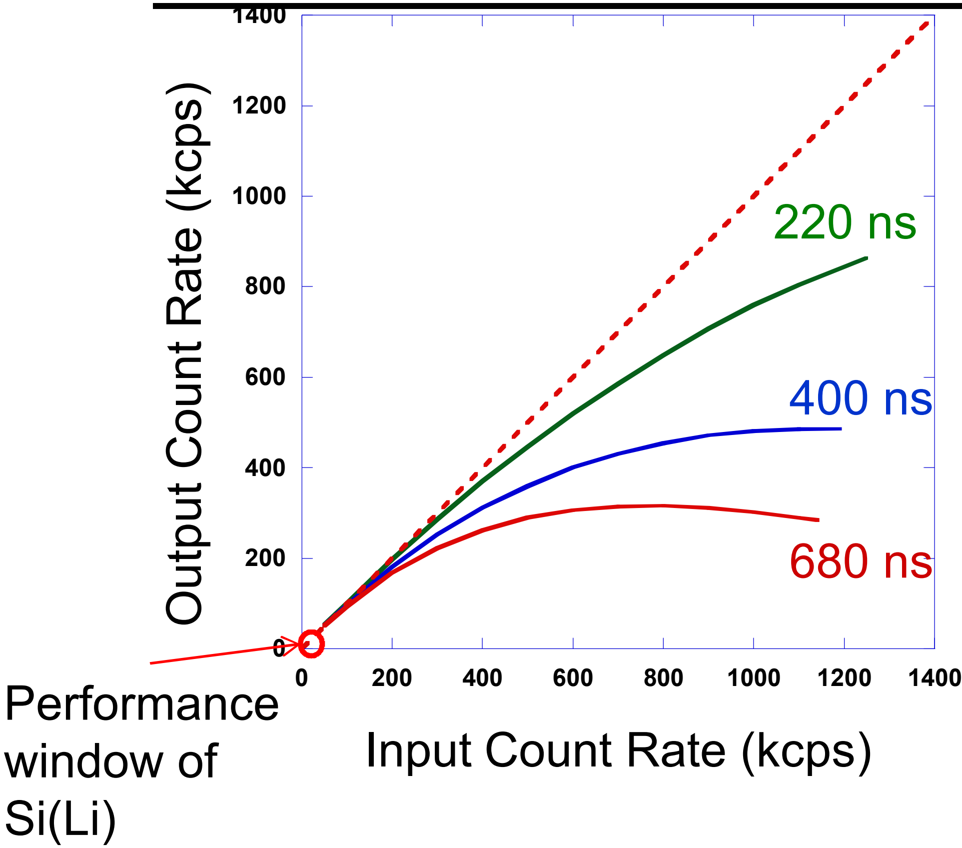


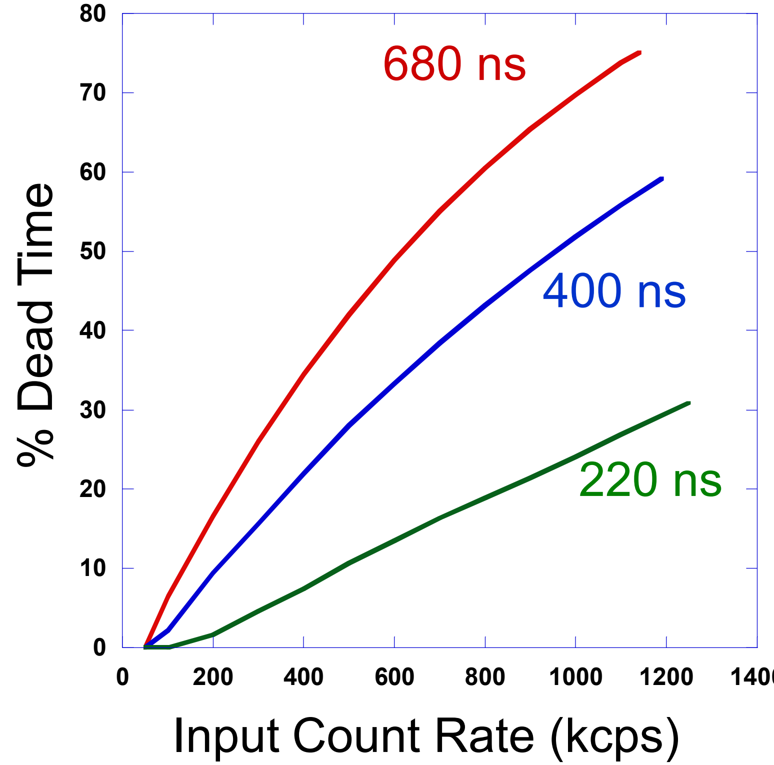


Four-channel (4 by $10mm^2$) SDD at Sandia from 2006. Peak position and spectrometer resolution very stable with count rate

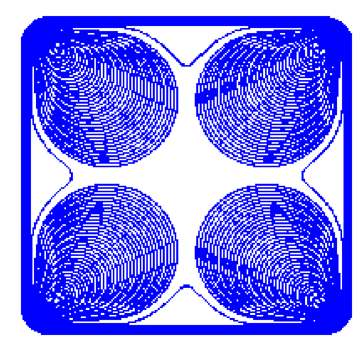


2006, SDDs now excellent performers

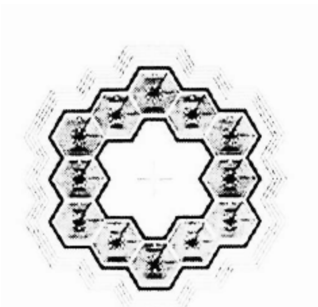




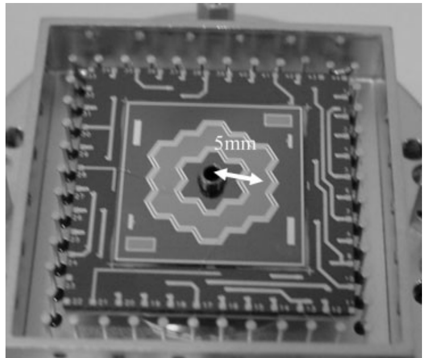
Four-channel SDD at Sandia from 2006. Peak position and spectrometer resolution very stable with count rate

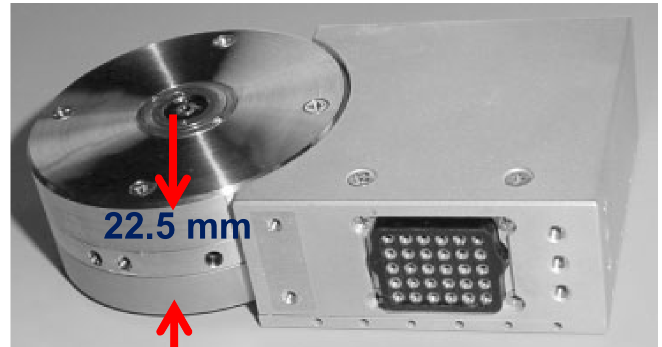


2005, Multi-element SDD and Spectral Imaging

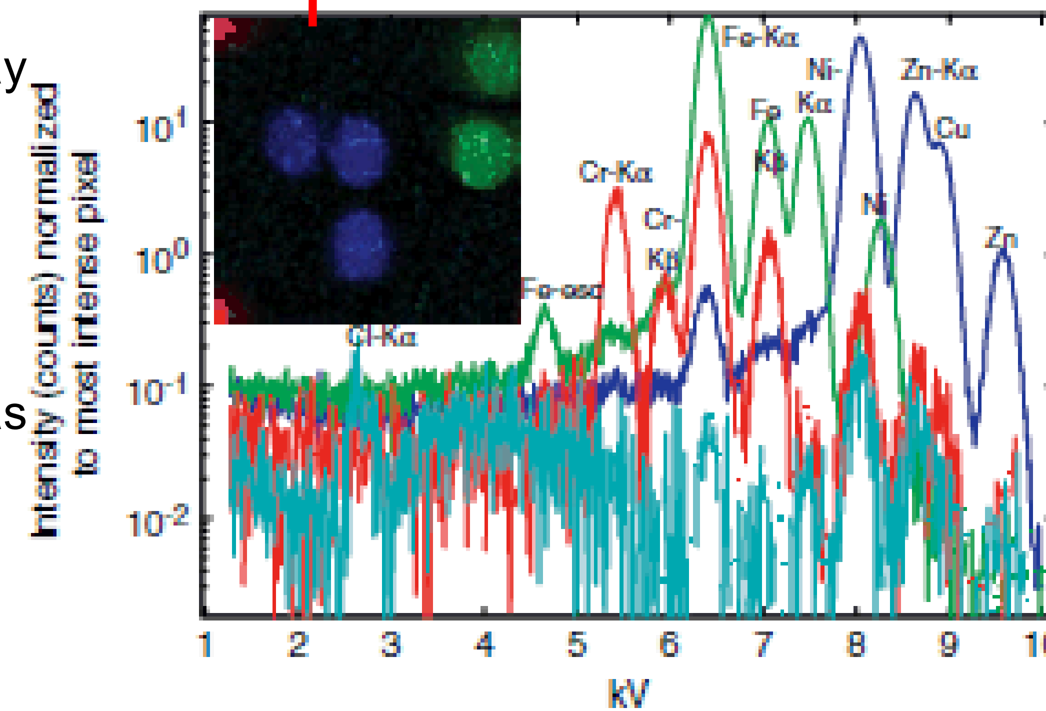


c)



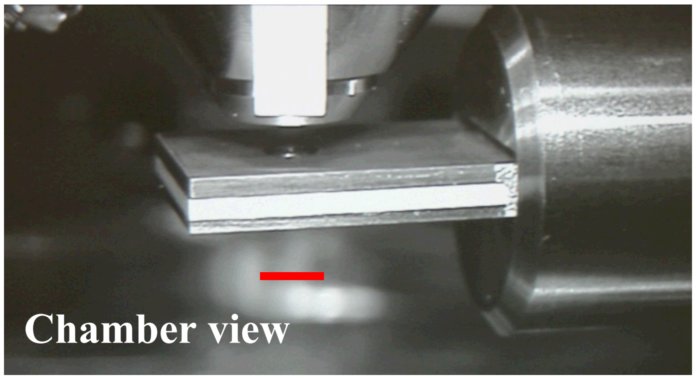


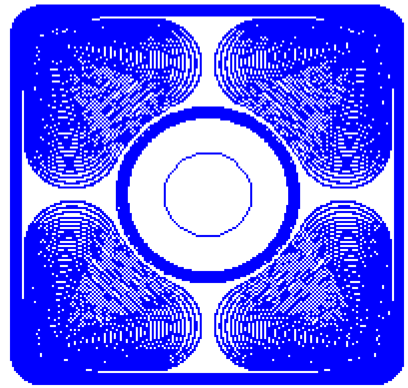
- Sandia/Rontec collaboration
- PIXE microprobe, 1.1 sr SDD array
- 3 MeV Carbon excitation.
- Ionization energies all shift.
- Spectral image acquired with custom-designed system.
- MSA data analysis
  - No *a priori* information such as peak position needed.
  - In fact peak positions were unknown for these conditions prior to this work

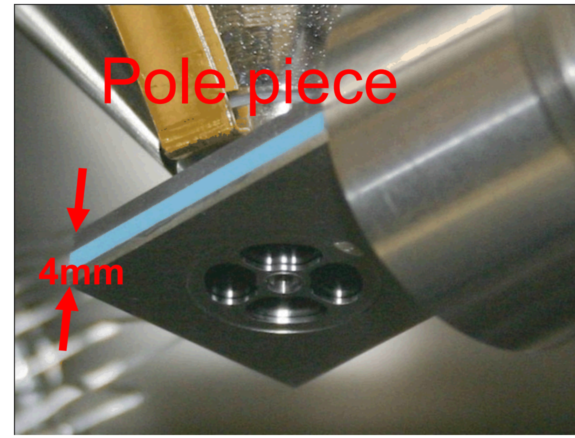


B.L. Doyle, D.S. Walsh, P.G. Kotula, P. Rossi, T. Schulein and M. Rohde, *X-Ray Spectrom.* (2005) **34** 279-284.

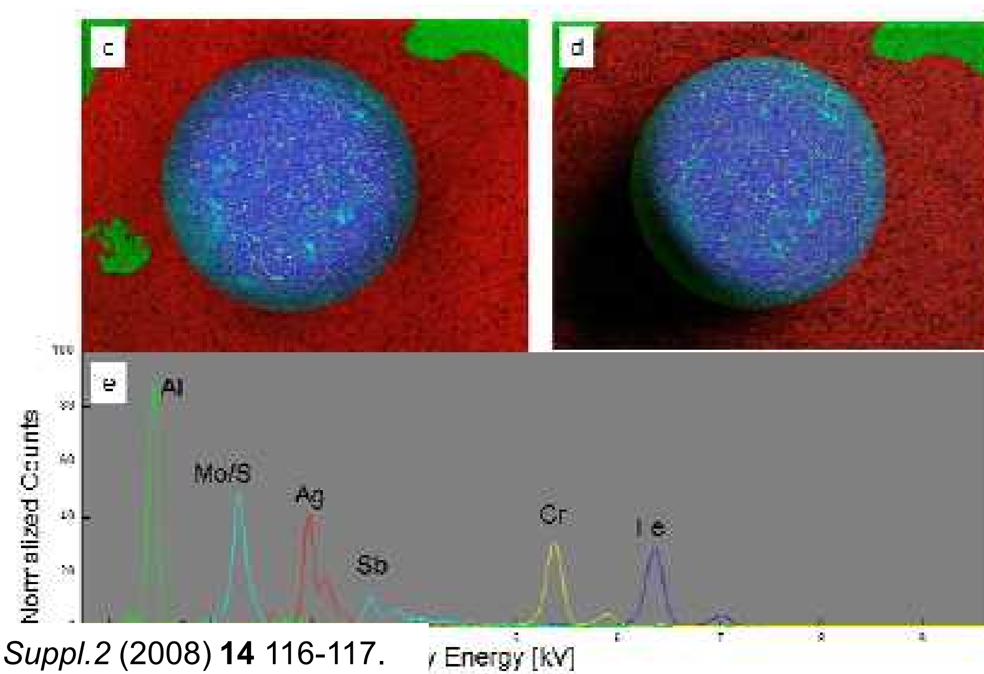
2007, Multi-element SDD and Spectral Imaging







- Collaboration between pnSensor Bruker and Sandia
- Funding from DHS in relation to Sandia's work for the FBI's Amerithrax investigation
- Design existed, Sandia ordered the first for SEM implementation
- 4 x 15 mm^2 sensors with a hole combined solid angle of 1.1sr
- Spectral image of a 750 μm diameter ball bearing. MSA analysis.



P.G. Kotula, J.R. Michael and M. Rohde, *Microsc. Microanal. Suppl.2* (2008) **14** 116-117.

Anatomy of a *Bacillus anthracis* spore

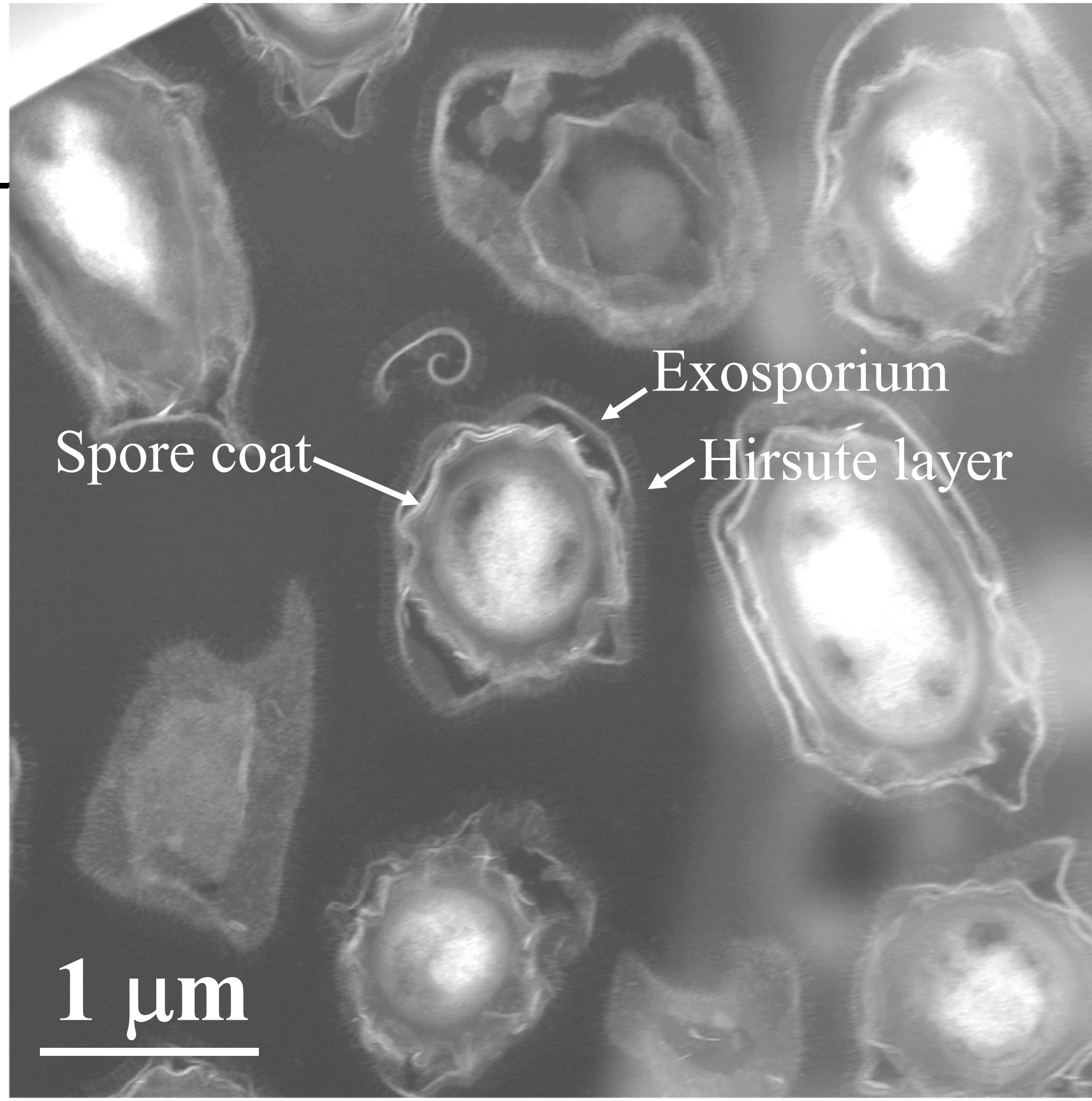
Layers present – Outside to inside

Hirsute Layer

Exosporium

Spore coat

Cortex

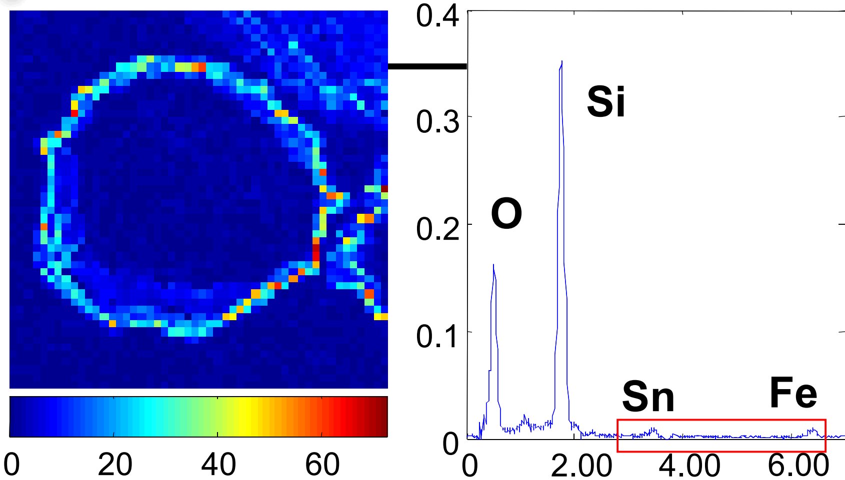


Scanning transmission electron annular dark-field image

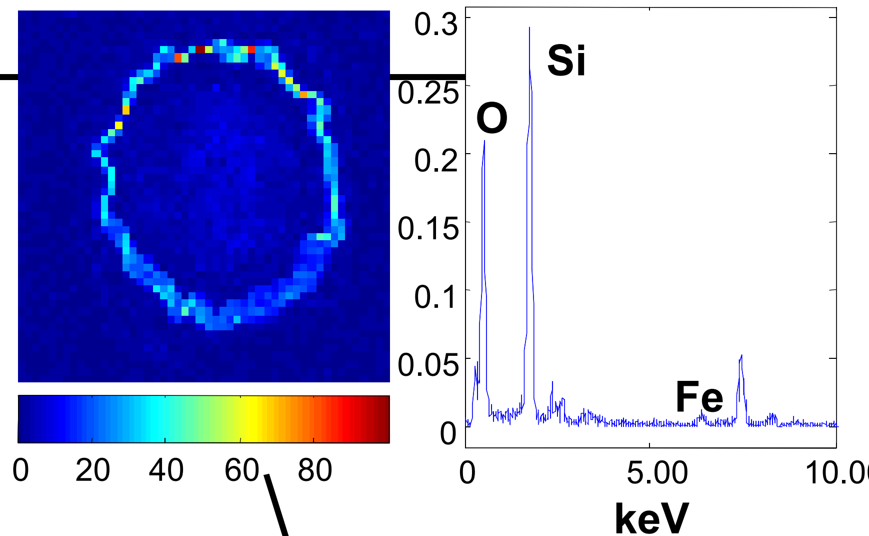
Work for the FBI's Amerithrax investigation with Joe Michael at Sandia.

Bacillus Anthracis chemical signatures from 300kV AEM

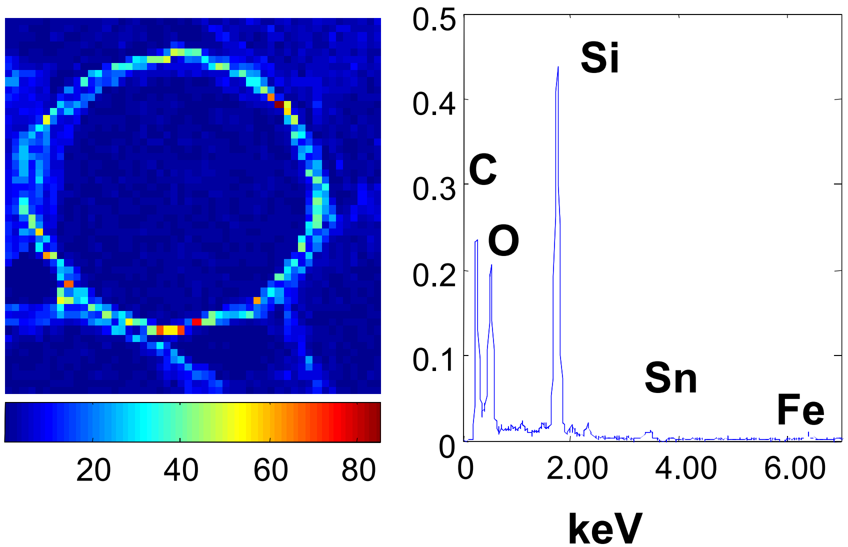
Leahy Material

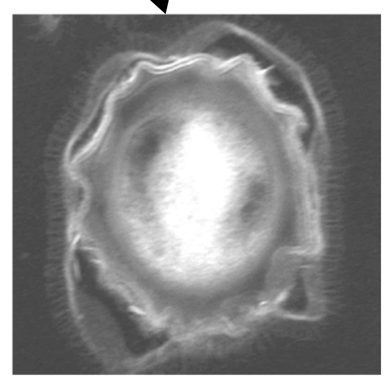


Daschle Material

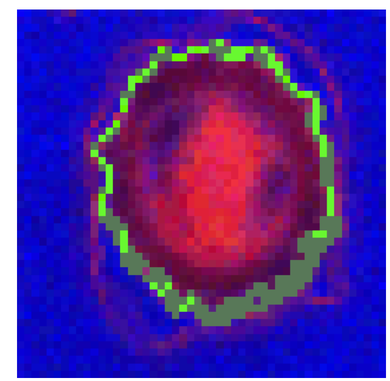


New York Post Material





STEM ADF



MSA results (overlay)

Red = Cortex/stain
Green = Spore coat/Si-O-Sn-Fe
Blue = Plastic

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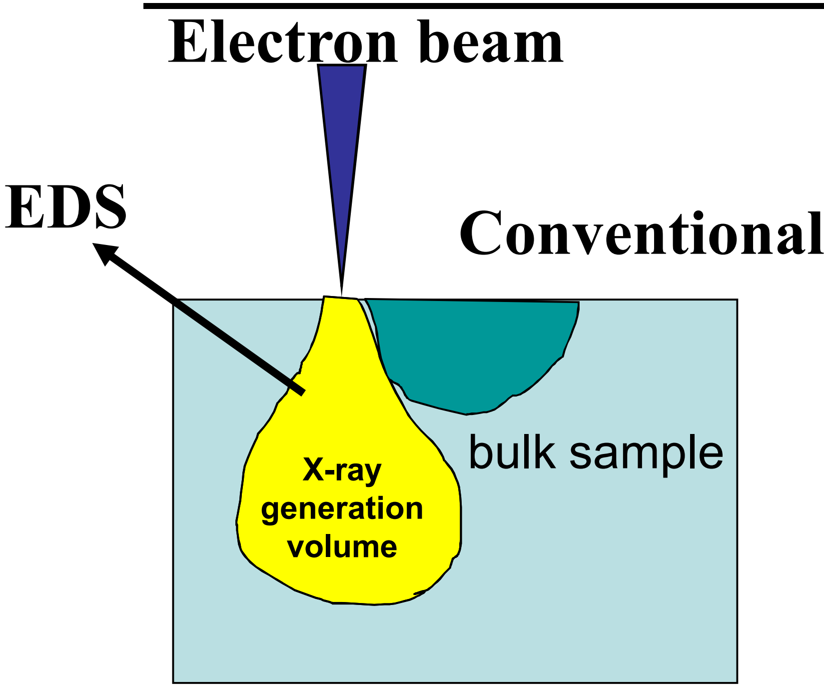
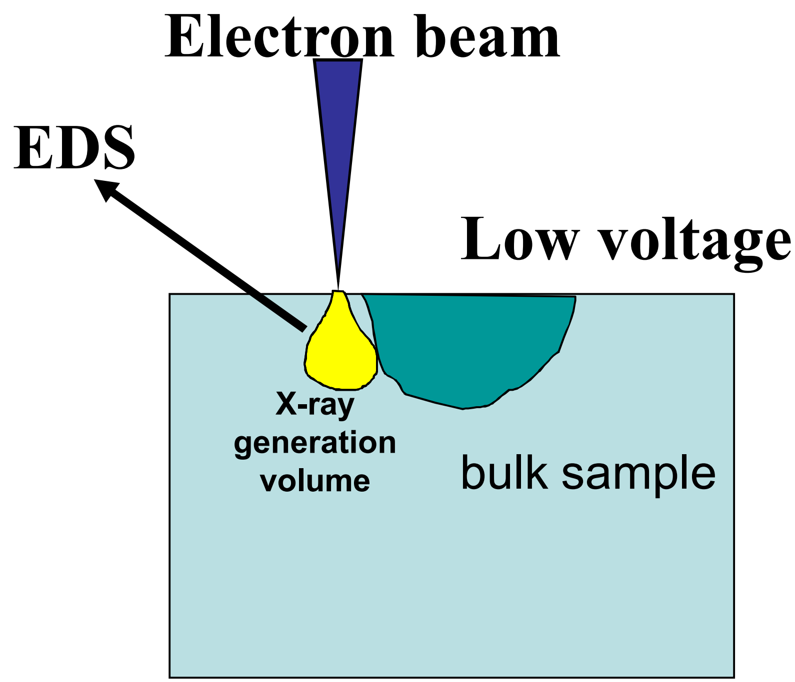
Solving the sample throughput problem

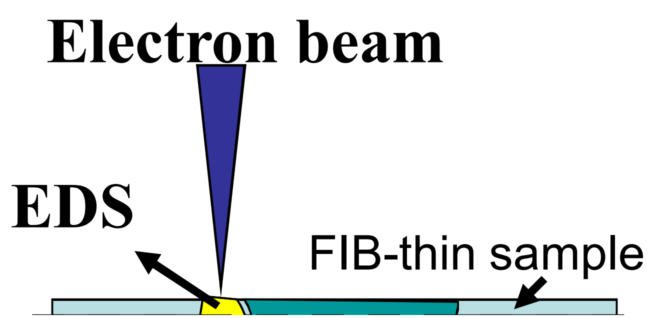
- Not every spore had the Si-O-Sn-Fe signature so we needed to analyze a larger population of spores…in the tens of thousands
- AEM fields of view are small…8-10μm while in SEM it can be millimeters
- Features of interest are 10-20 nm requiring thin samples (STEM in SEM).
- STEM in SEM would be good but typical solid angels for EDS are 60 msrad so count rates are very low for thin samples.
- One solution is a multi-sensor annular SDD

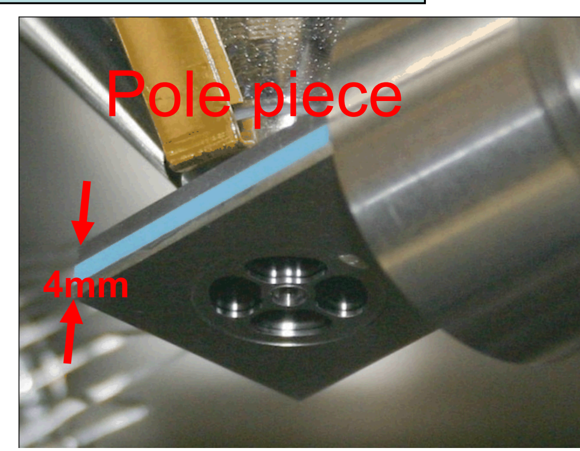
Improved resolution- LV vs. STEM in SEM





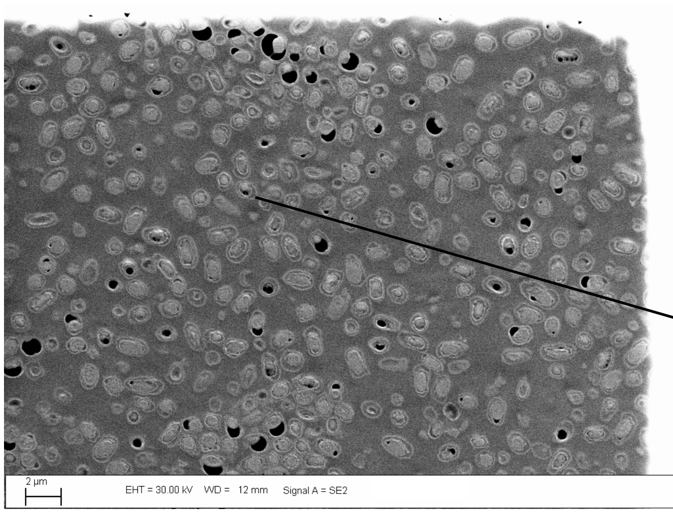
STEM in SEM
(also AEM at higher voltages)



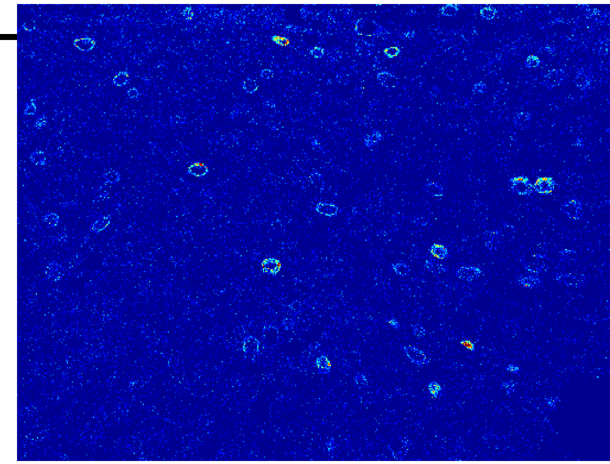


STEM in SEM of unstained, microtomed section

(Samples from Bruce Ivans' lab at USAMRIID)

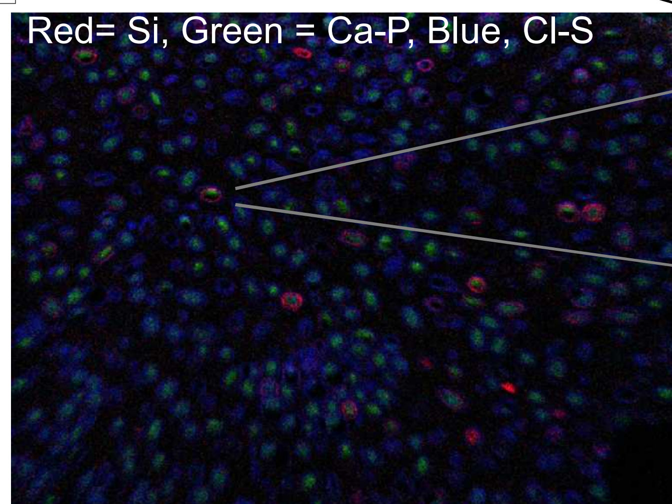


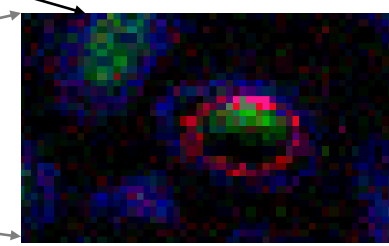
MSA identifies three chemical signatures



Si-containing spore coat

SEM defines field of view for spectral image acquisition

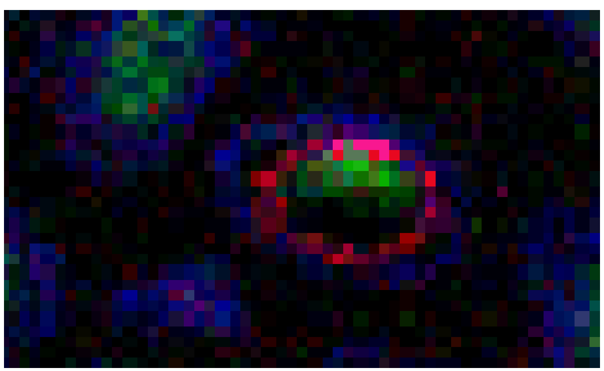


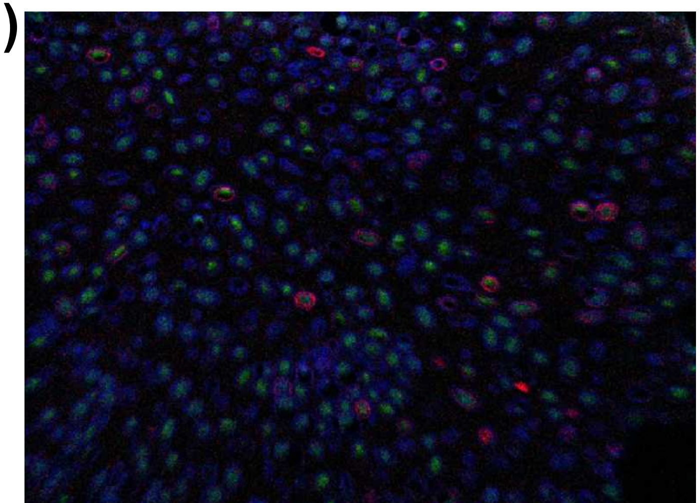


From this it is possible to count *x* and *n*

The true test of the annular detector: 13 samples from the investigation

- **In April of 2008 we were provided 13 samples for analysis**
- **Over 40 STEM in SEM x-ray spectral images were acquired by a Technologist with the new annular x-ray detector**
  - **Over 13,000 spores imaged in 3 work-days (24 hours)**
  - **MSA and counting populations took 7 work-days (56 hours)**
  - **10 days (80h) total for over 13,000 spores**
  - **0.04 seconds per spore for identification (compare with 2 minute per spore for STEM)**





Thanks to Bonnie McKenzie at Sandia for data acquisition.

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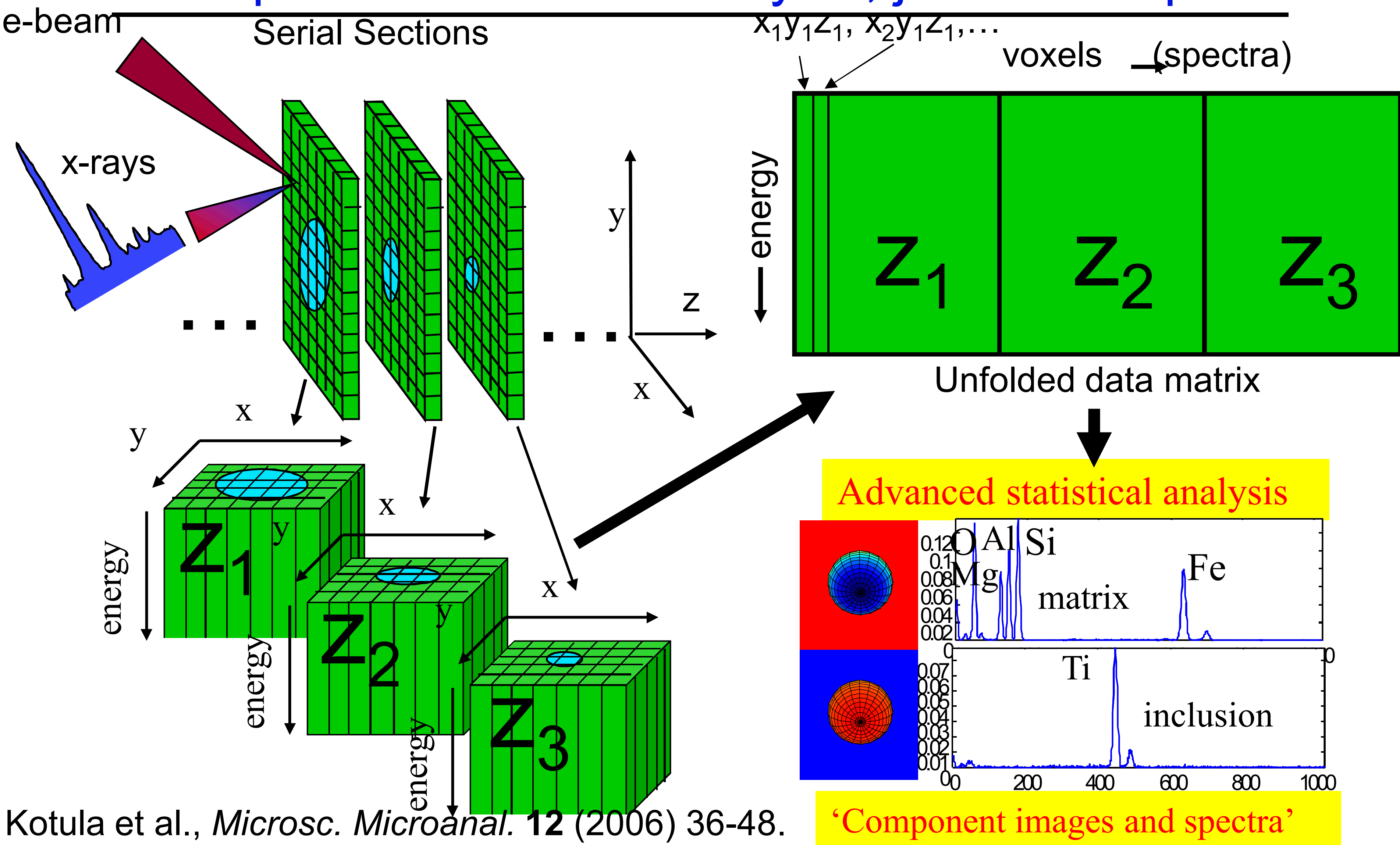
2006, 3D spectral imaging via FIB-SEM/EDS

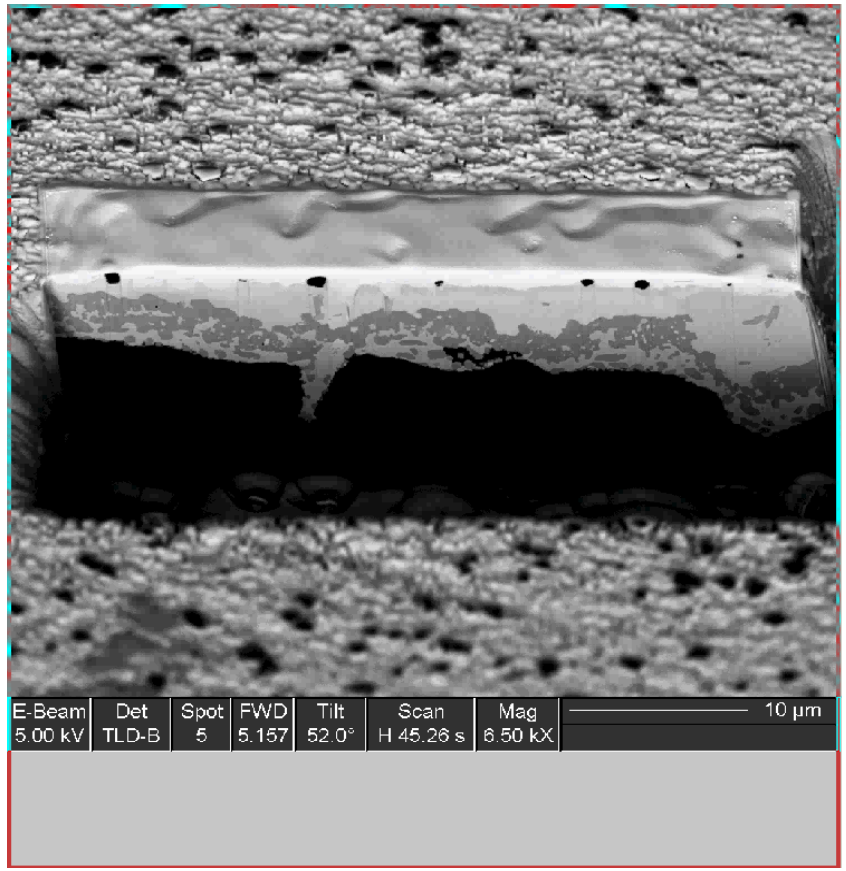
3 spatial dimension analysis, just more spectra



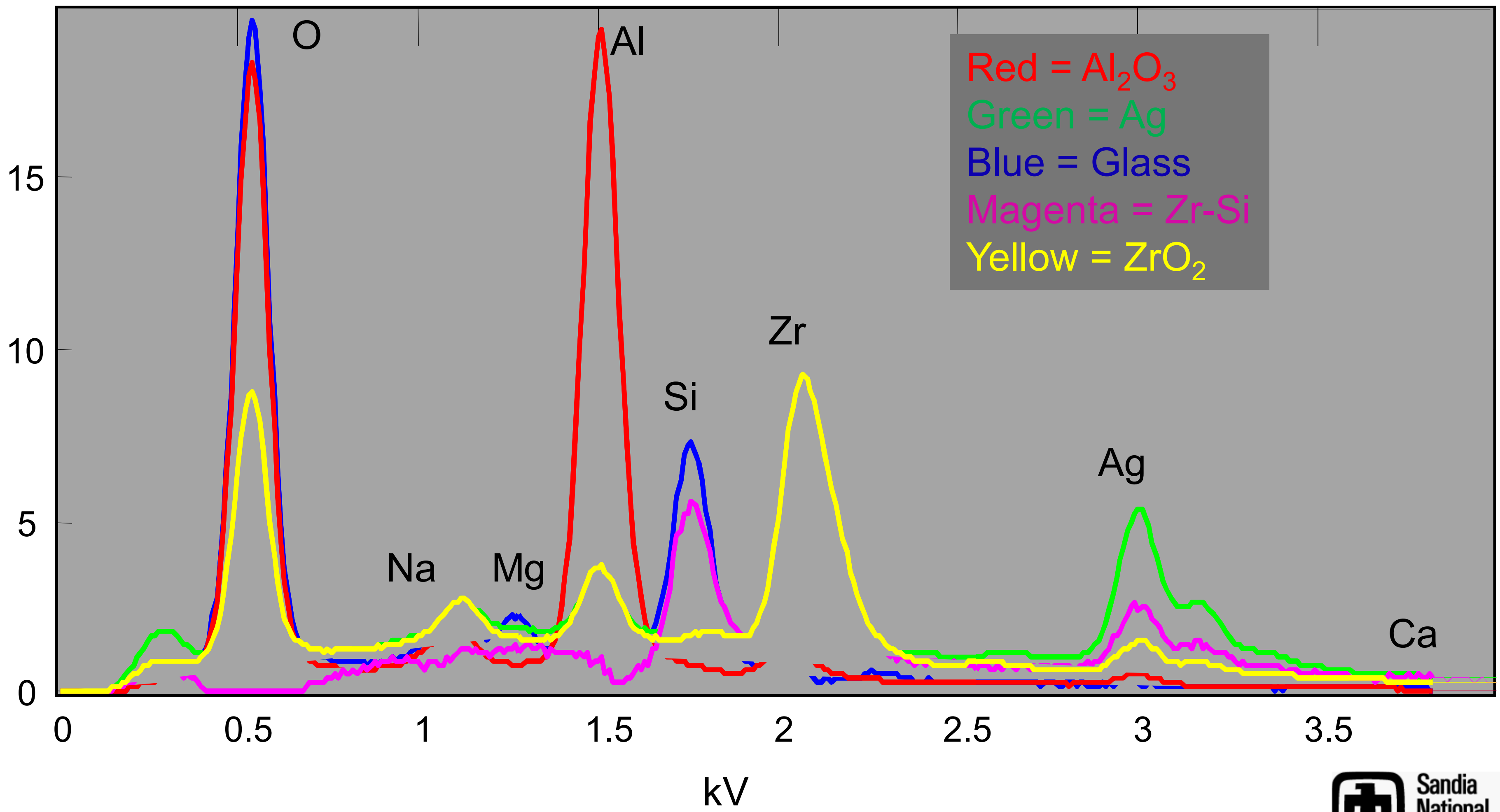
Kotula et al., *Microsc. Microanal.* **12** (2006) 36-48.

3D EDS spectral imaging
Analysis of Ag-2Zr/Alumina Braze

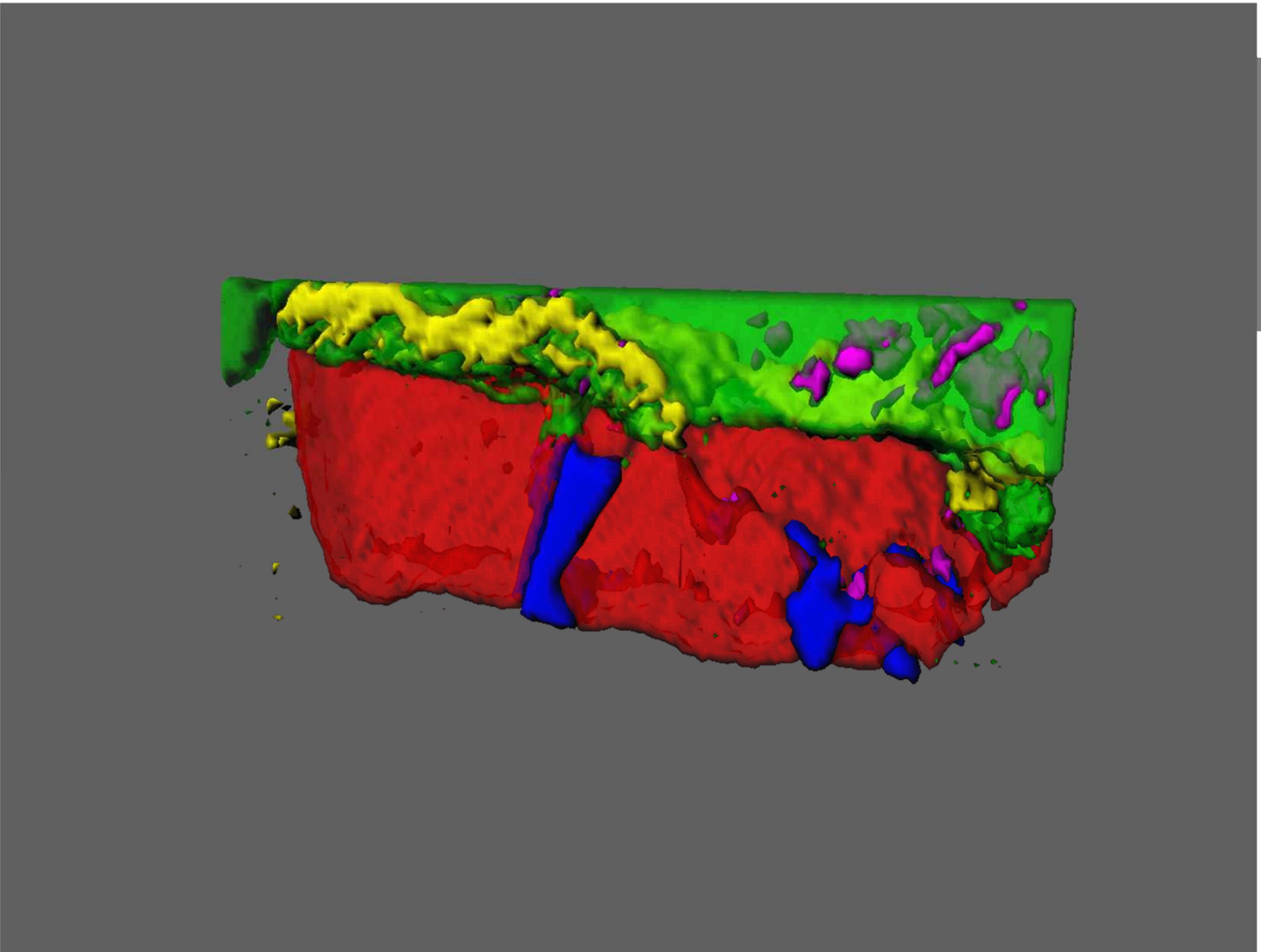
Movie of electron images



MSA Analysis of SI of Ag-2Zr/Alumina Braze (5kV)
Spectral shapes



Analysis of Ag-2Zr/Alumina Braze: 3D Component Images



Red = Al_2O_3
Green = Ag
Blue = Glass
Magenta = Zr-Si
Yellow = ZrO_2

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2010, SuperX™: Large solid angle silicon drift detector array provides more flexible AEM integration

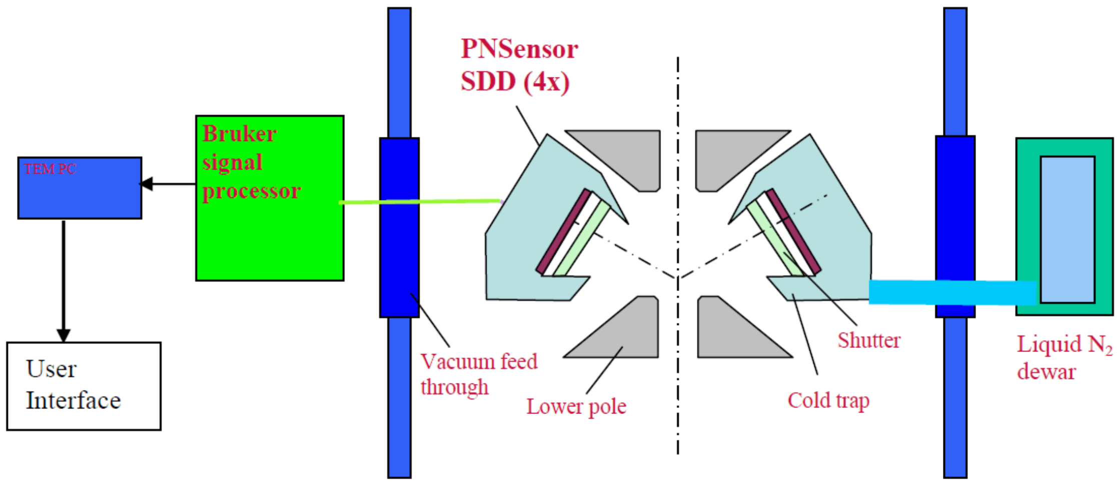
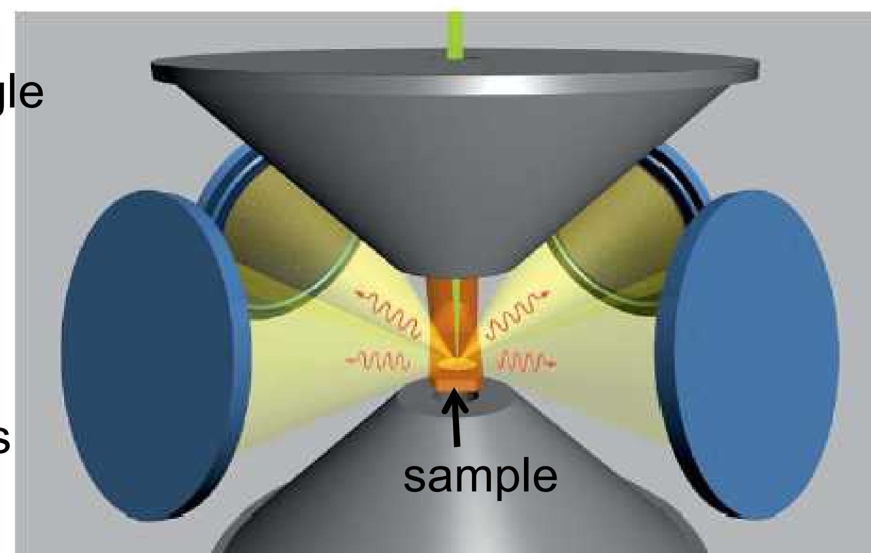


Figure 1. Schematic of Super-X detector

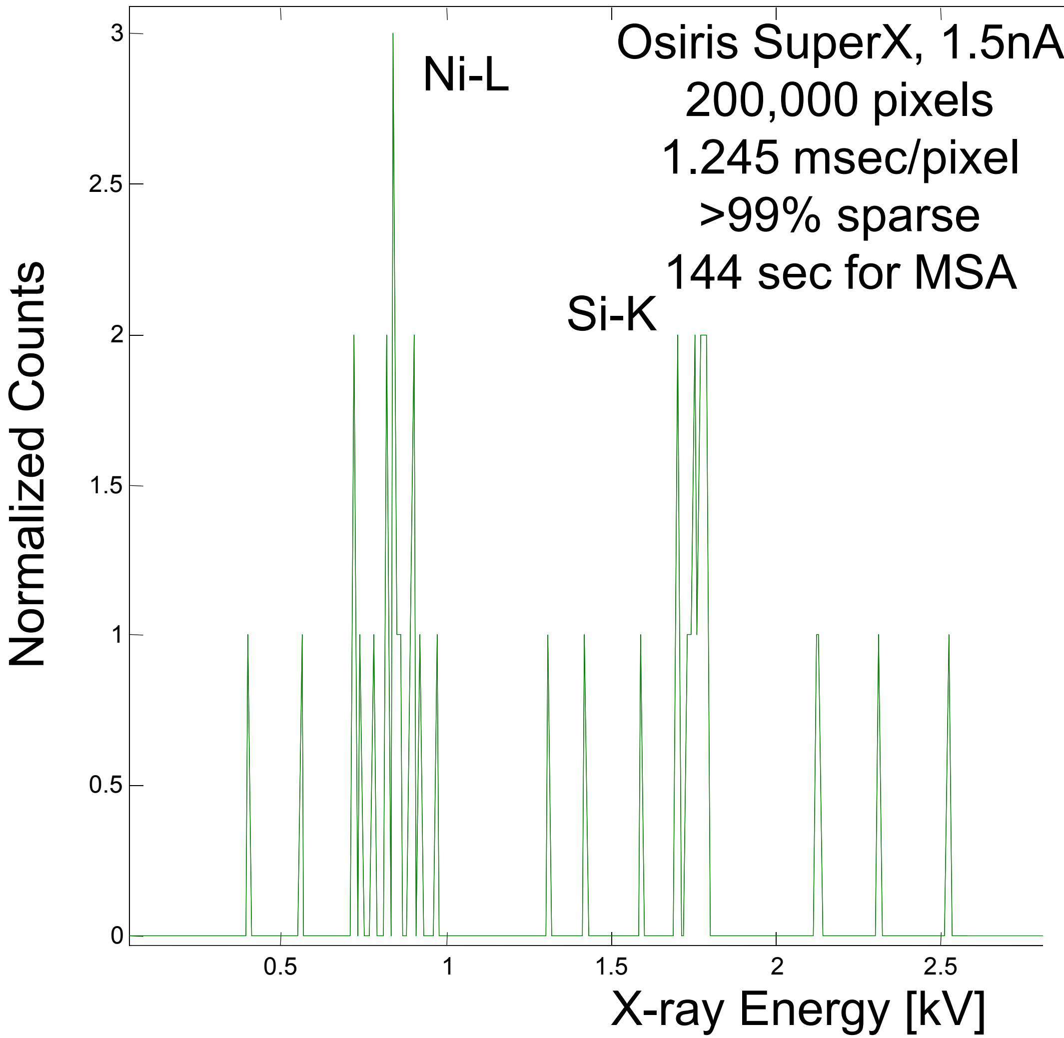
Conceived by FEI with collaboration from Bruker and PNSensor

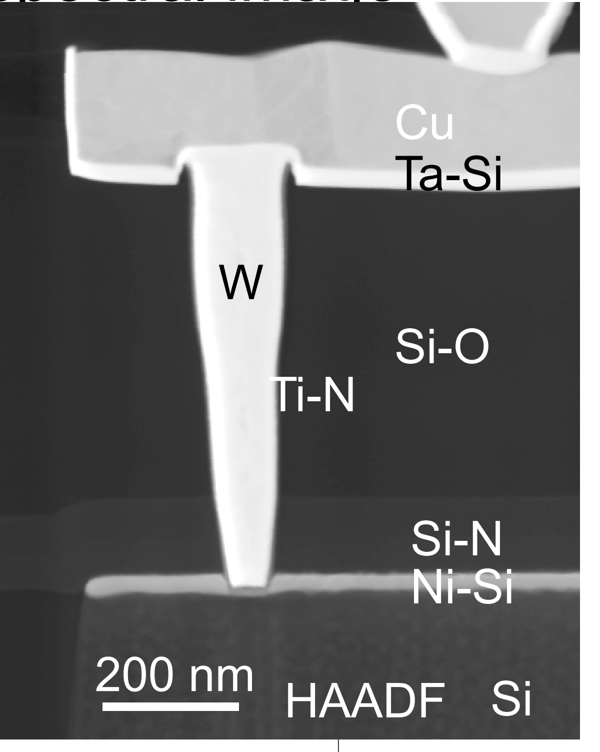
Revolutionary change in AEM-EDS

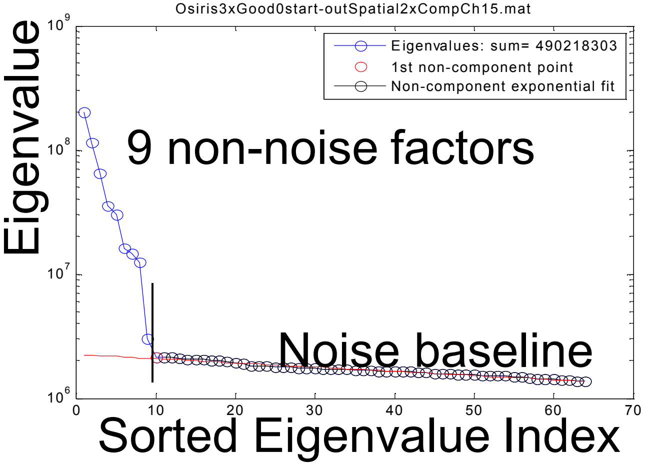
•4-30mm^2 (120mm^2) SDDs with large solid angle
- 0.9 sr (Osiris-uncorrected)
- 0.7 sr (Titan-probe corrected)
- State-of-the-art SDDs
- Windowless & PNWindow…good light-element performance (C, N, O easily)
- High-throughput…10 μsec instantaneous dwell times, multiple pass, drift correction



Low end spatially, high end for sensitivity
Raw spectrum from the CMOS spectral image

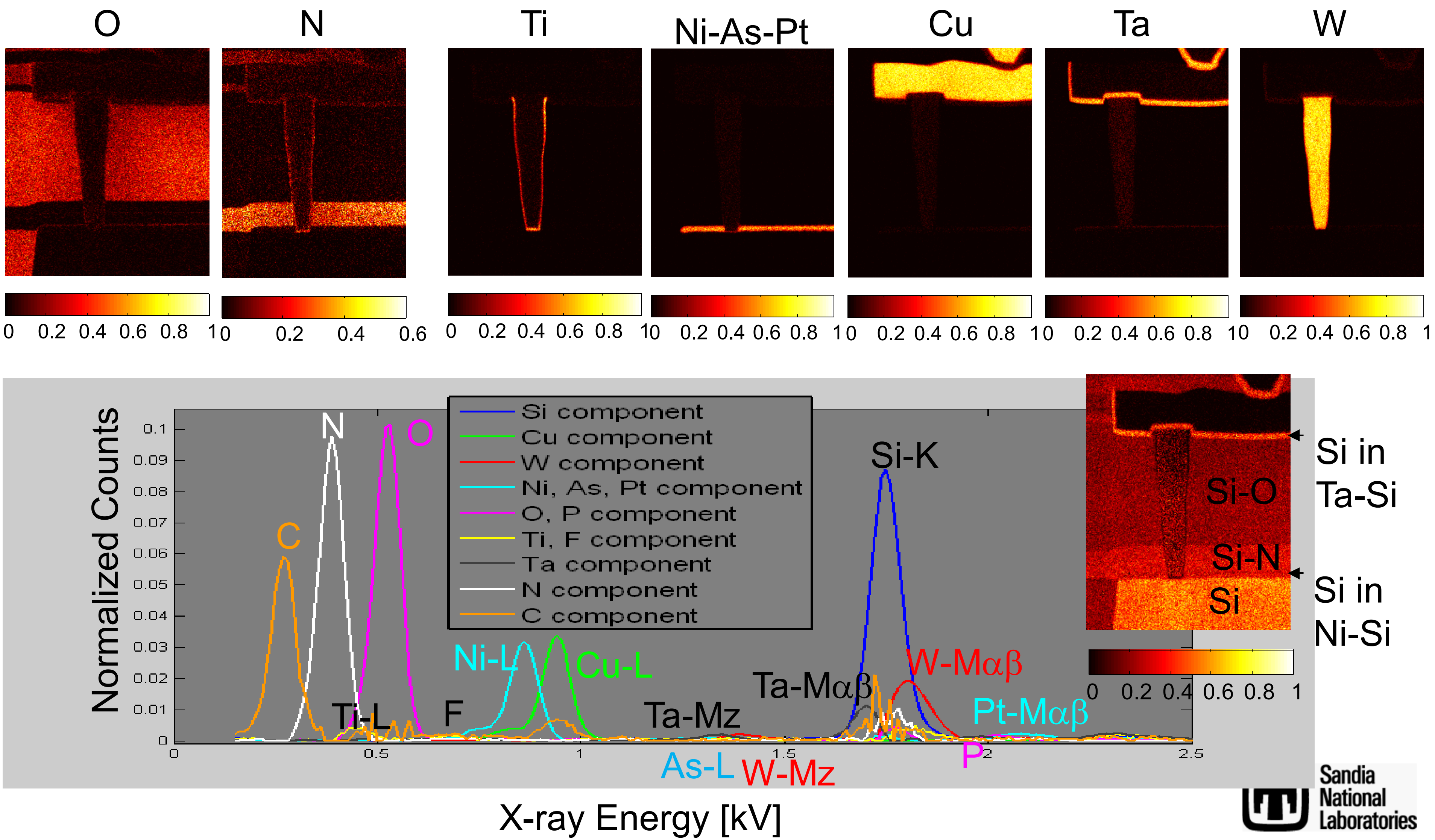






Data courtesy Dmitri Klenov, FEI on sample provide by SNL

Low end, Spectral-Domain Simplicity
Best Spectral or Elemental 'Contrast'



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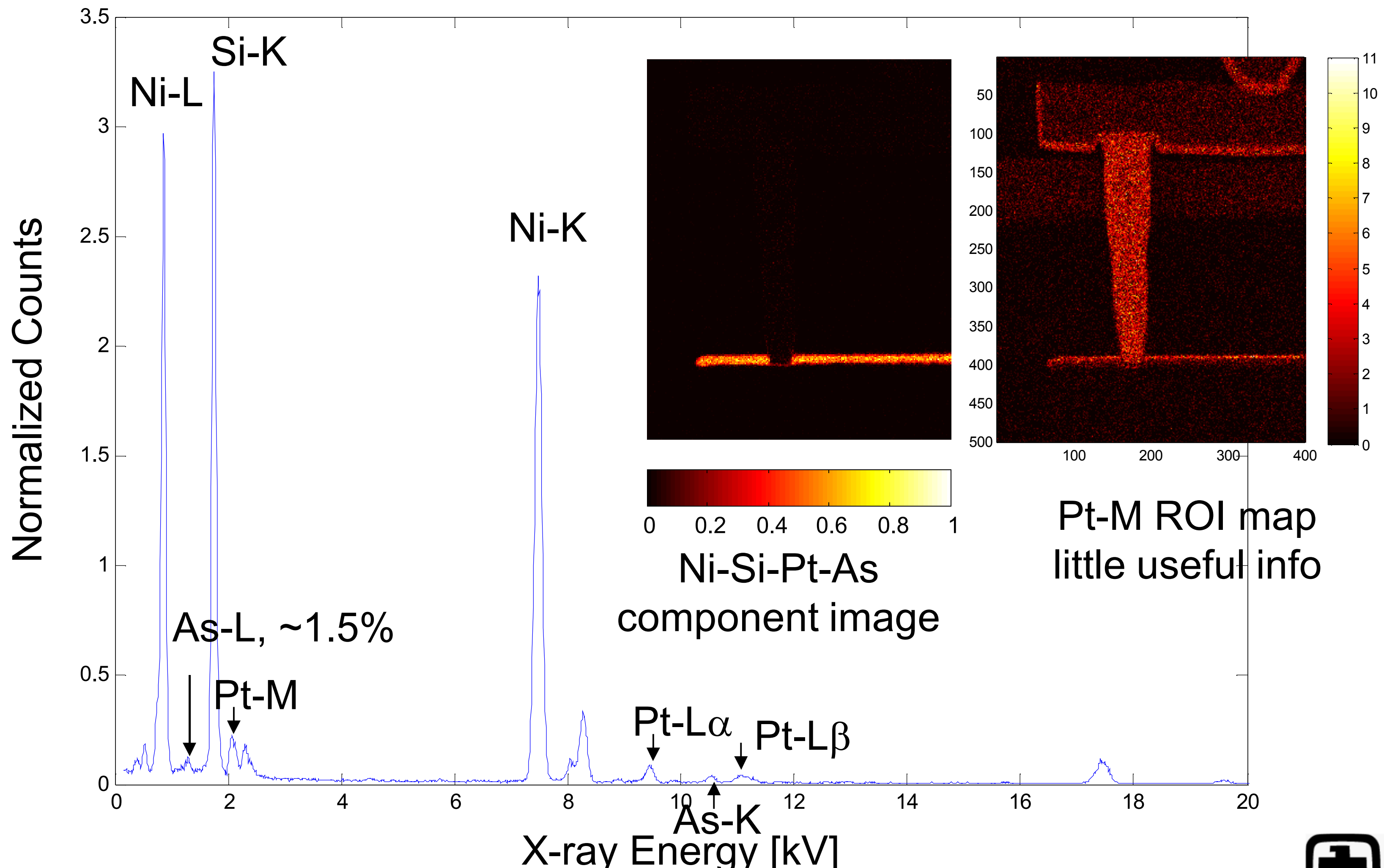
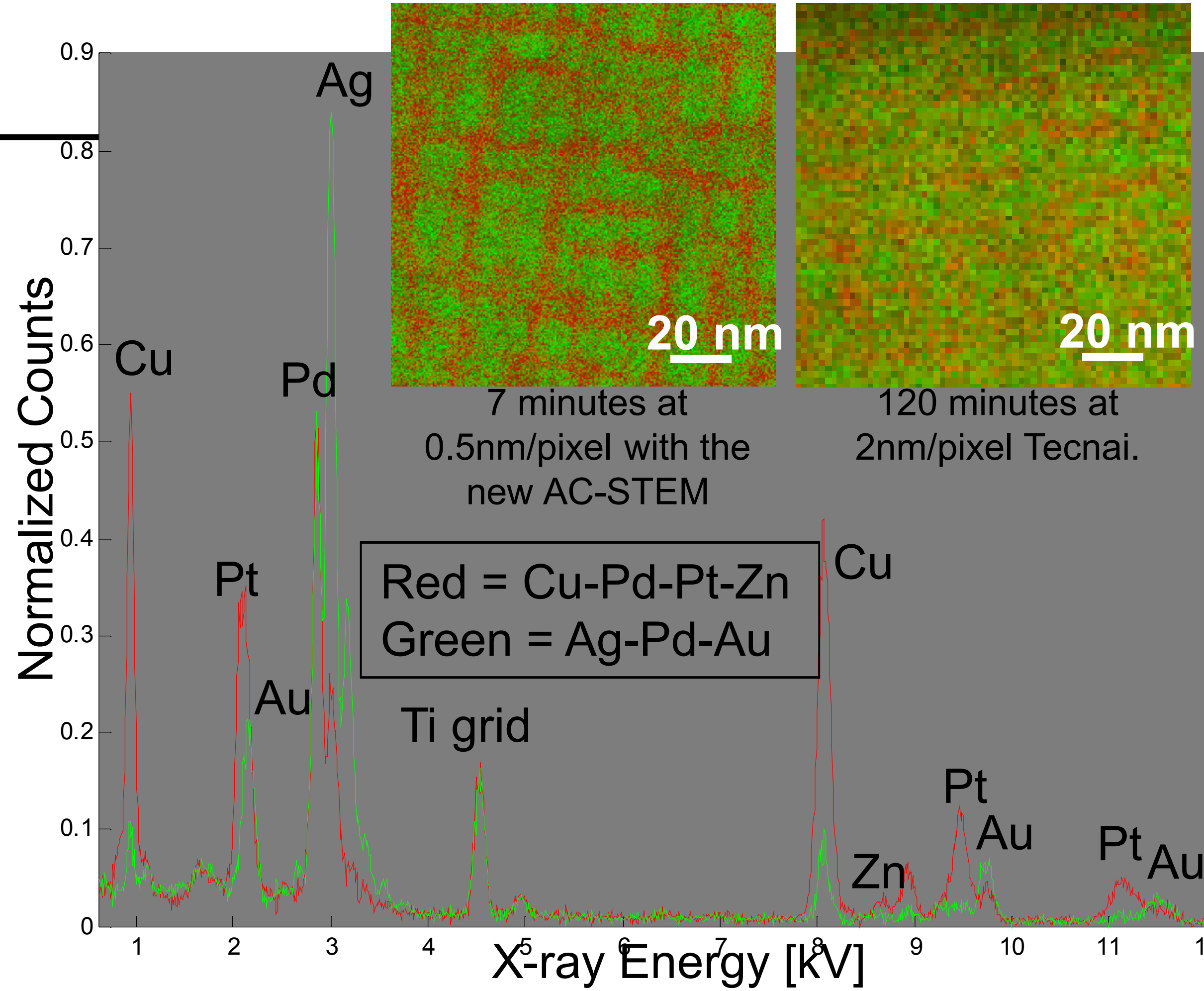
Low end, Spatial-Domain Simplicity
Ni-silicide contact, MSA shows minor elements



Sub-nm microanalysis of electrical contact materials

Titan G2 80-200 Cs probe corrected with ChemiSTEM (SuperX)
MSA analysis

Paliney 7, electrical contact material nanometer-scale spinodal decomposition.



The new AEM is at least **70x** better than our older AEM (Philips/FEI Tecnai F30-ST)

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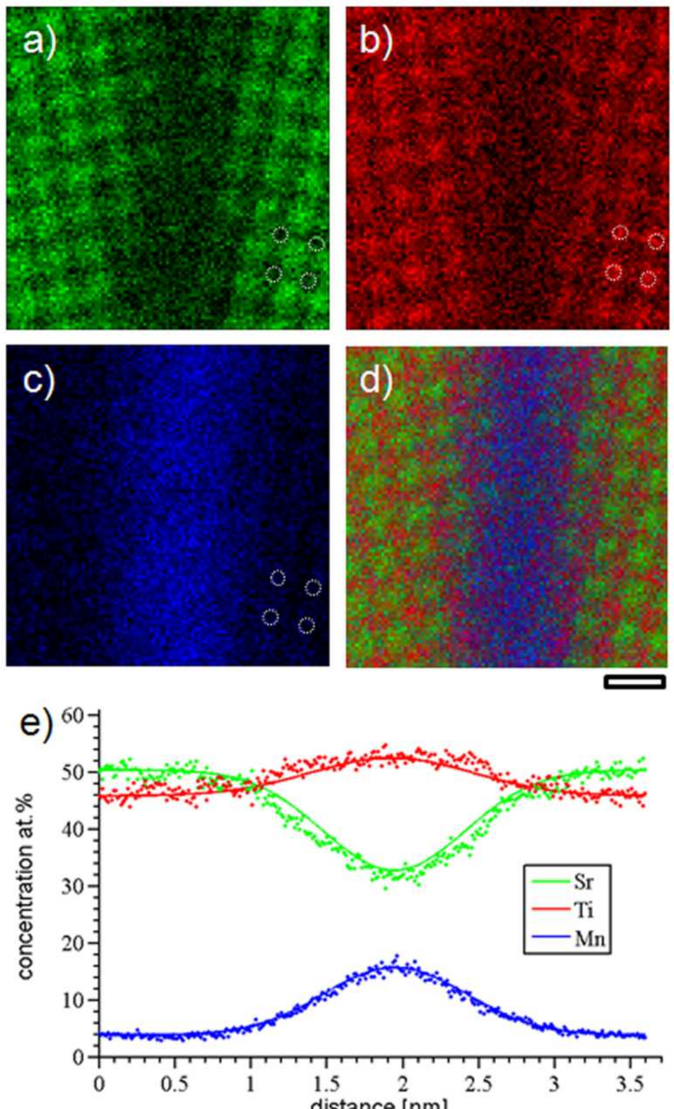
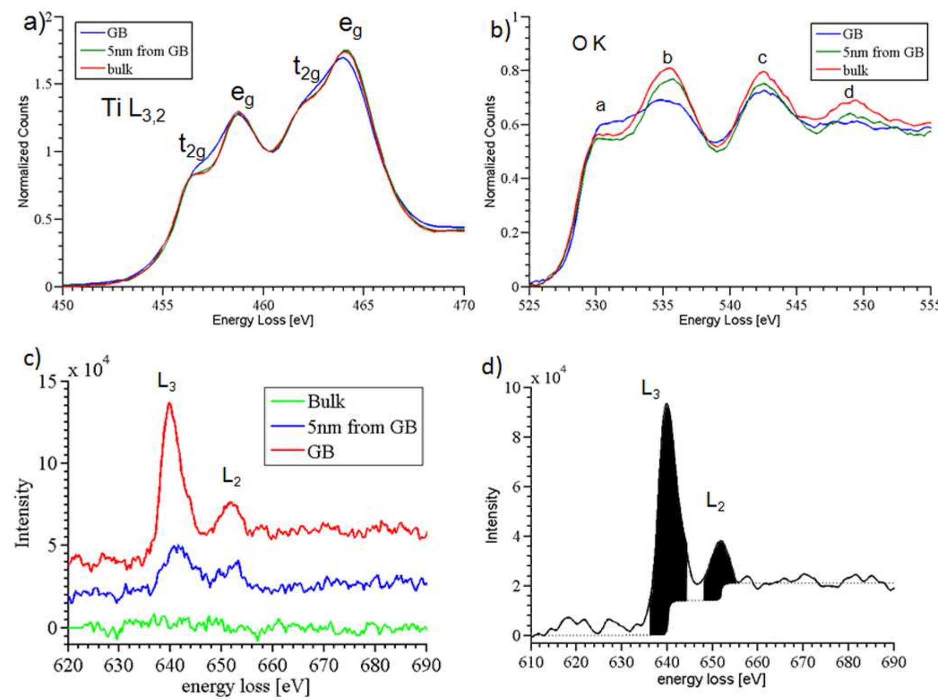
Analysis of Mn-doped STO Σ=13 Boundary

∑13 (510)/[001]

Quantitative EDS and EELS





Mn^{+2} at boundary
Mn^{+4} in bulk near boundary
(subsitutional with Ti)

FWTM enrichment at the boundary less than 2nm

H. Yang, P.G. Kotula, Y. Sato, Y. Ikuhara, N.D. Browning. *Materials Research Letters* (2013). DOI: 10.1080/21663831.2013.856815

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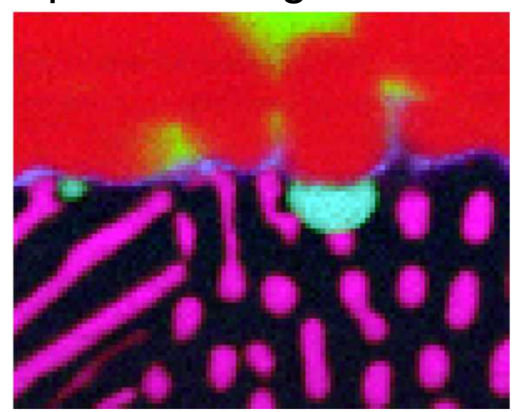
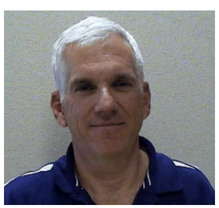
Acknowledgements (partial list)

Barry Carter (Cornell, UMN, UConn, Sandia), firstly my Ph.D advisor but also for making me do a g.b analysis while I was at LANL and introducing me to the guys at Sandia.

Ian Anderson (Cornell, UMN, ORNL, NIST, ?) for helping teach me TEM and getting me interested in microanalysis, spectral imaging and MSA. Also for helping me collect our first spectral image data set…a braze…which is where it all began.





Joe Michael (SNL) for mentoring and much interaction over the years.

Mike Keenan (SNL-Ret.) for being in the right place at the right time for the MSA development and being the chief architect of AXSIA.

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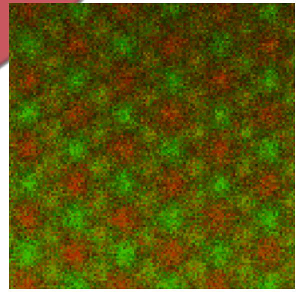
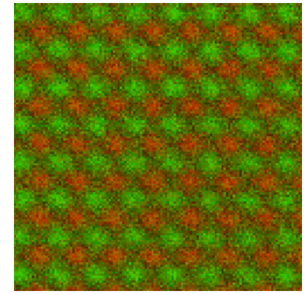
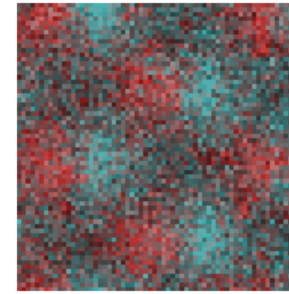


Conclusions





- We live in exciting times and that's good
- In the last 10 years SDDs have come into their own and enabled huge gains in analytical speed and sensitivity
- MSA methods are very useful for simplifying the analysis of large, complex data sets
  - Unbiased analysis powerful for materials science, etc. Needle in the haystack….
  - Quantification can them be performed with added knowledge
- All of these developments have depended upon the availability of inexpensive and powerful computers