(EELS) Data analysis basics

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Université de Lille

Diamond Light Source
2nd of March 2020

Outline

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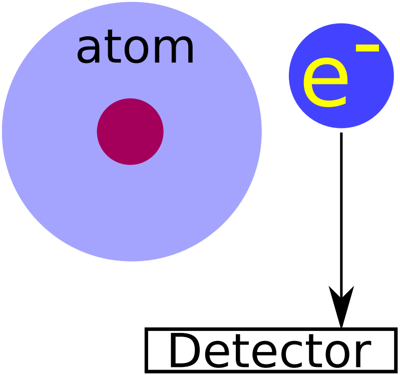
Why do we care about data processing at all?



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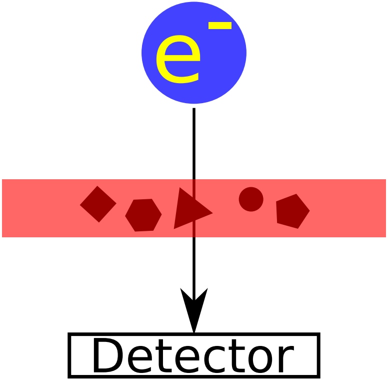
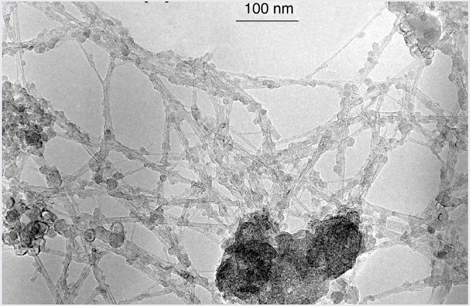
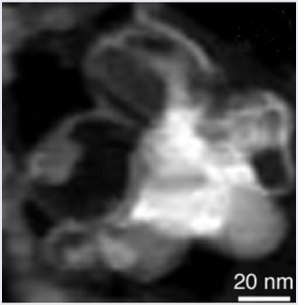


Boron-nitride nano-particles characterisation by EM





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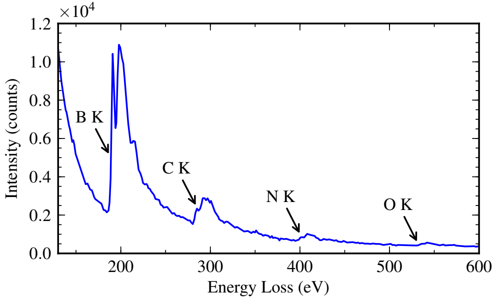
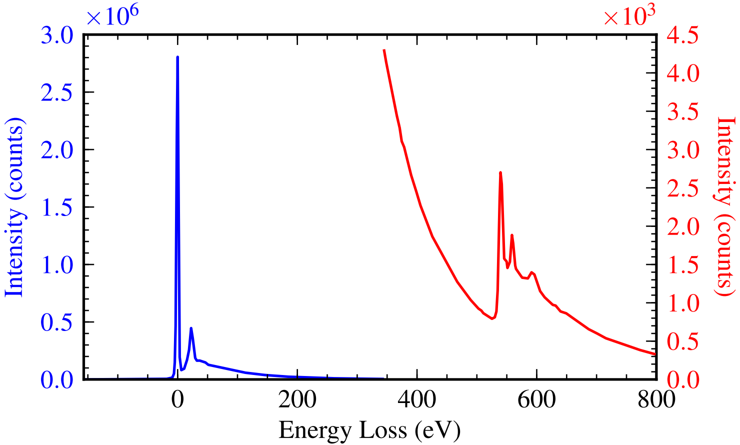
EELS spectrum from BN NPs

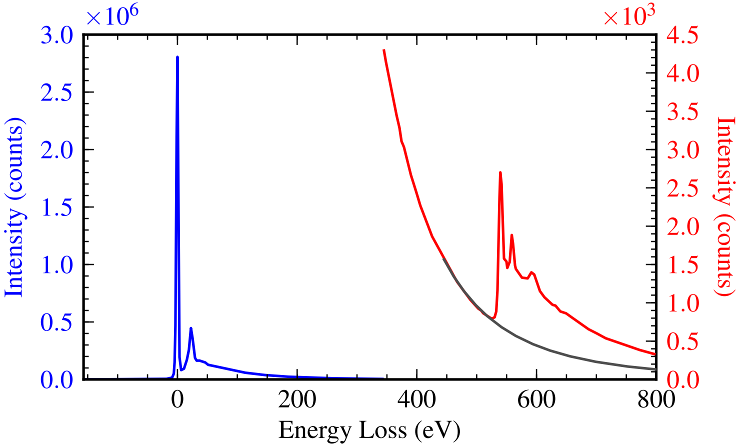


The "windows" method



The "windows" method

$$N_{\mathrm{O}} \approx \frac{}{}$$



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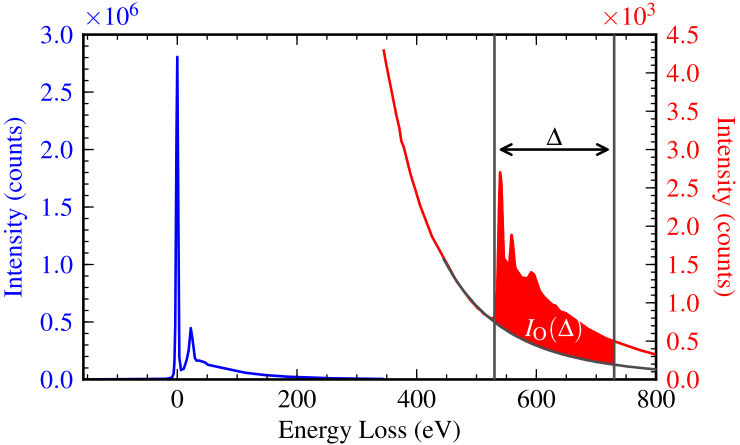
$$N_{\mathrm{O}} \approx \frac{I_{\mathrm{O}}(\Delta,\beta)}{}$$



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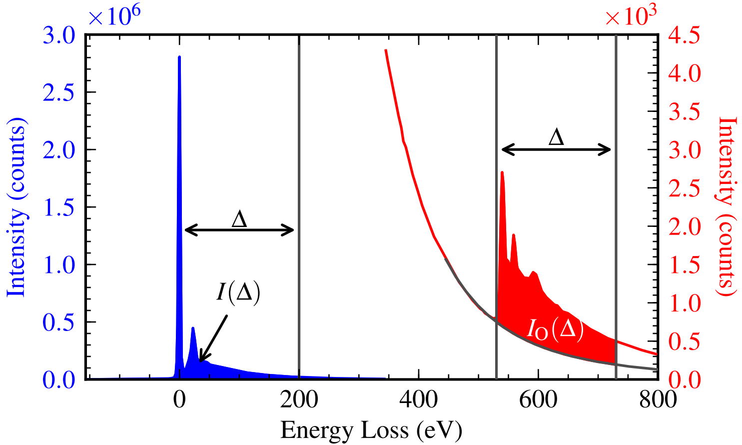
$$N_{\mathrm{O}} \approx \frac{I_{\mathrm{O}}(\Delta,\beta)}{I(\Delta,\beta)} \sigma_{\mathrm{O}}^{-1}(\Delta,\beta)$$



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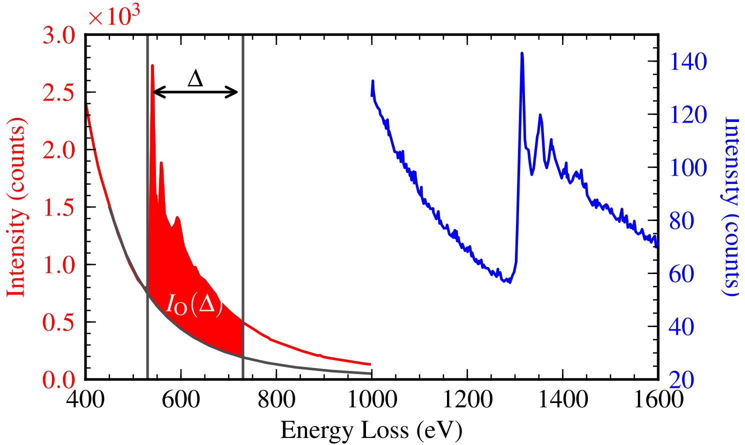
$$N_{\mathrm{O}} \approx \frac{I_{\mathrm{O}}(\Delta,\beta)}{I(\Delta,\beta)}\sigma_{\mathrm{O}}^{-1}(\Delta,\beta) \qquad N_{\mathrm{Mg}} \approx \frac{I_{\mathrm{Mg}}(\Delta,\beta)}{I(\Delta,\beta)}\sigma_{\mathrm{Mg}}^{-1}(\Delta,\beta)$$



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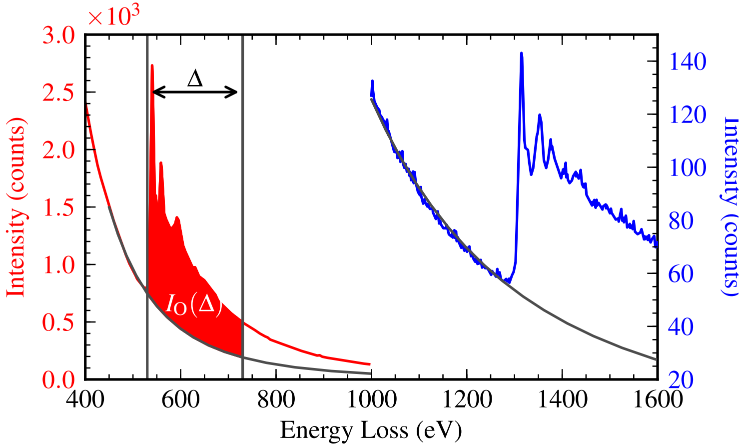

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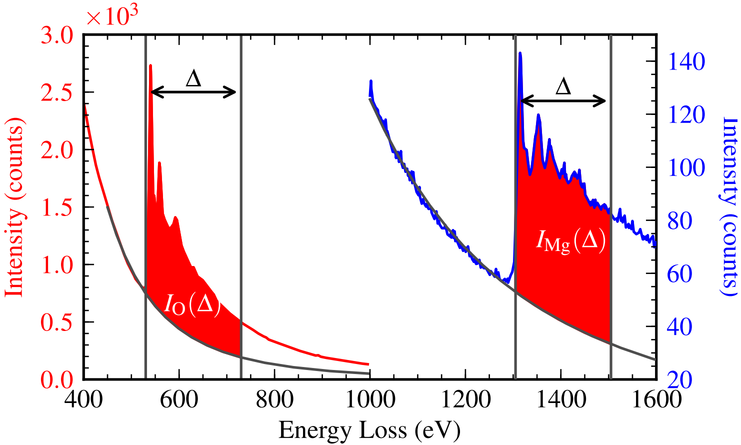

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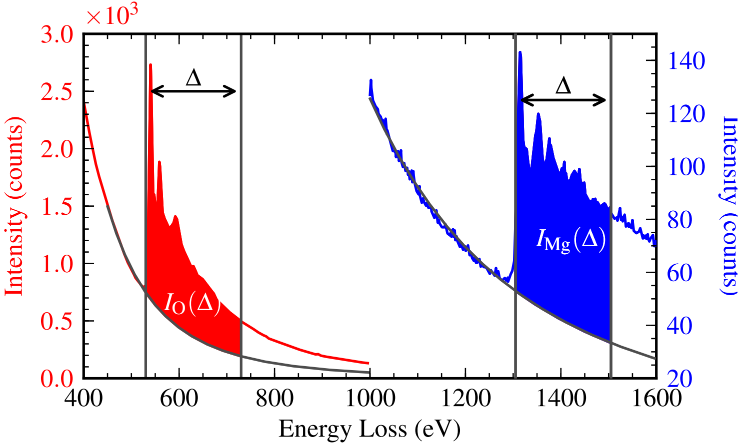
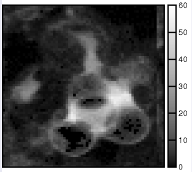
$$\frac{N_{\mathrm{O}}}{N_{\mathrm{Mg}}} \approx \frac{I_{\mathrm{O}}(\Delta,\beta)}{I_{\mathrm{Mg}}(\Delta,\beta)} \frac{\sigma_{\mathrm{Mg}}(\Delta,\beta)}{\sigma_{\mathrm{O}}(\Delta,\beta)}$$

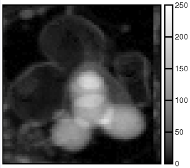


EELS elemental of BN nanoparticle

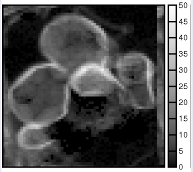
Oxygen



Boron



Nitrogen



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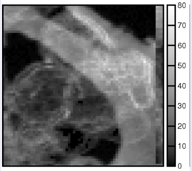

Arenal et al., Ultramicroscopy 2008

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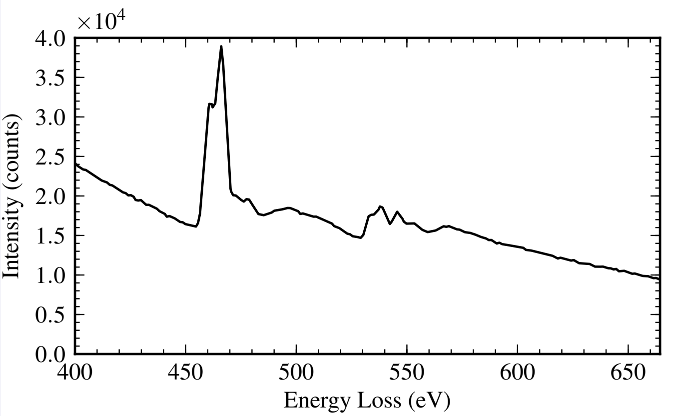
- Overlapping edges
- It always returns a result (what feels good) but,
  how do we know that it is correct?
- Only analyses a fraction of the available signal (non-optimal SNR)
- Useful information gets lost (fine structures changes, energy onset shifts...)

Outline

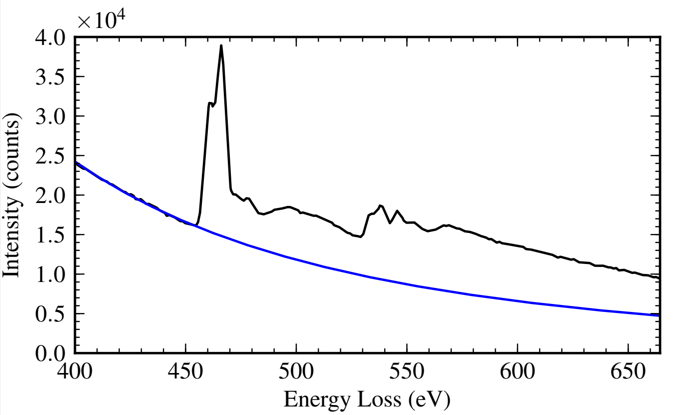
The curve fitting method: an example

$SrTiO_3$ Spectrum



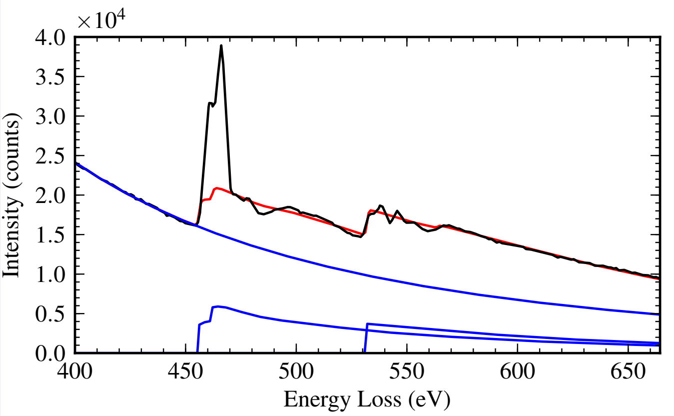
The curve fitting method: an example

$M(E) = AE^{-r}$



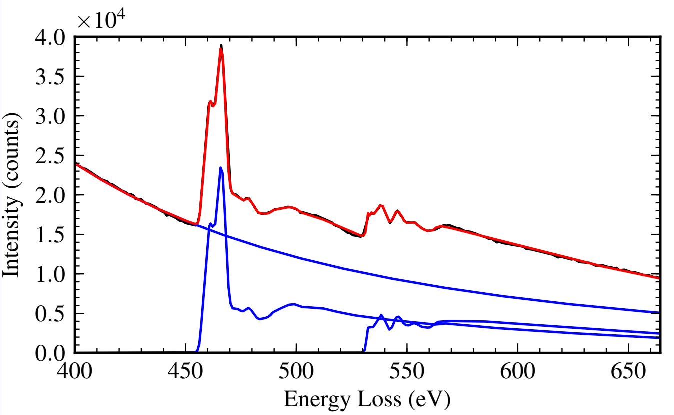
The curve fitting method: an example

$M(E) = AE^{-r} + I_{\mathrm{Ti}}\sigma_{\mathrm{Ti}}(E) + I_{\mathrm{O}}\sigma_{\mathrm{O}}(E)) * L(E)$



The curve fitting method: an example

$$M(E) = AE^{-r} + (N_{\mathrm{Ti}} f_{\mathrm{Ti}}(E)\sigma_{\mathrm{Ti}}(E) + N_{\mathrm{O}} f_{\mathrm{O}}(E)\sigma_{\mathrm{O}}(E)) * L(E)$$



Assumptions

- There is a *known* function, f, that relates the *independent variable* X and the *dependent variable* Y. $Y \approx f(X,\beta) + \varepsilon(f(X,\beta))$

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- The number of unknown parameters, β is *equal or less* thant the number of different observations of the independent variable
- The probability distribution of the statistical error (ε) is known

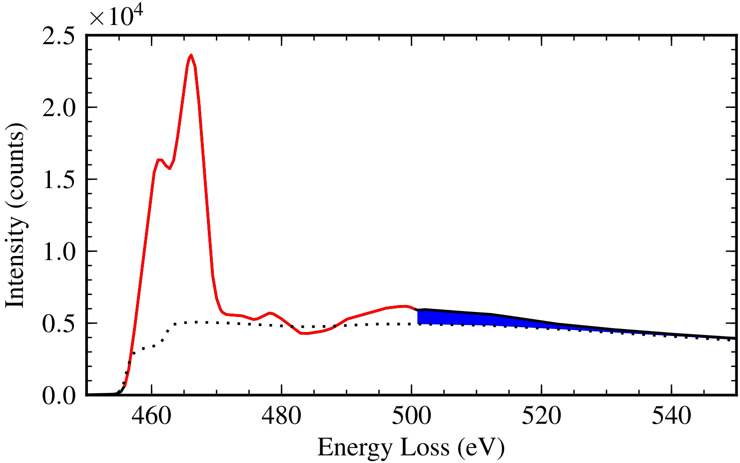
Components of the model

Parametric model of the high energy loss spectrum for elemental and bonding quantification:

$$M(E;\text{parameters}) = AE^{-r} + \left(\sum_i N_i f_i(E) \int_0^{q(\beta)} \sigma_i(E,q)\, dq \right) * L(E)$$

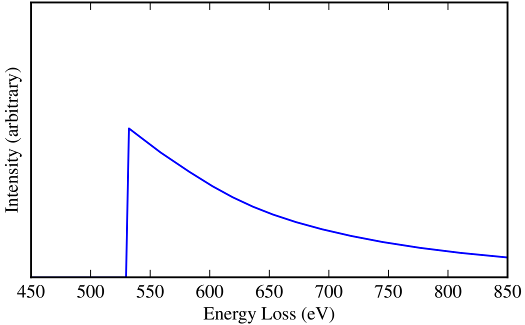
- AE^{-r}: background model
- σ_i^{FS}: cross section of each ionization edge, i
- N_i: $^{\text{atoms}}/_{\text{nm}^2}$
- $f_i(E)$: function that mimics the fine structure of each ionization edge, e.g. gaussian, fingerprints, splines...
- $L(E)$: experimental low loss spectrum.

Why adding the fine structure to the model?



Ionization edge fine structure

Oxygen K ionization edge from MgO



Ionization edge fine structure

- In solids, the first $\sim 40\,\mathrm{eV}$ are strongly modified by the final density of states $\Rightarrow$ carries bonding information

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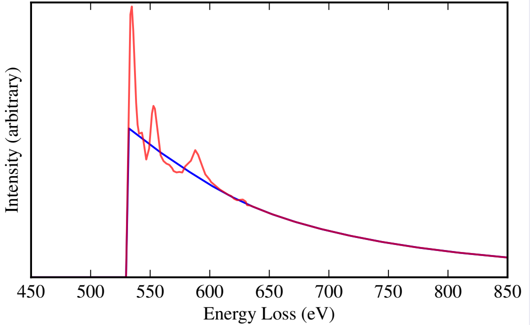
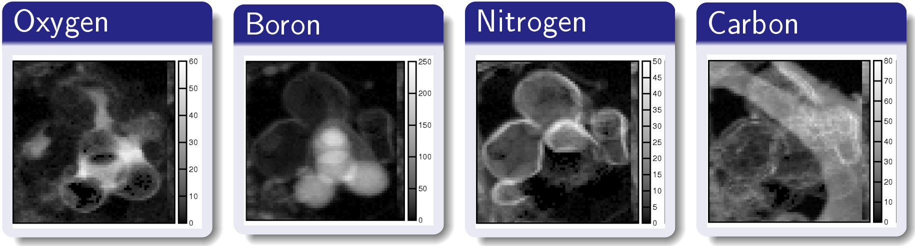


EELS elemental and bonding maps of BN nanoparticle



Arenal et al., Ultramicroscopy 2008

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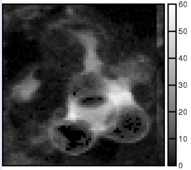

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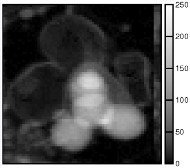

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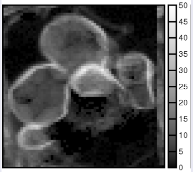

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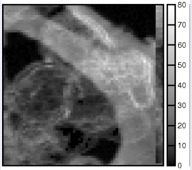
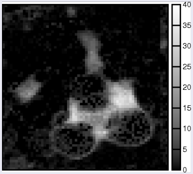
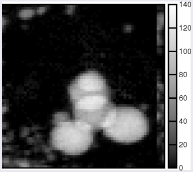


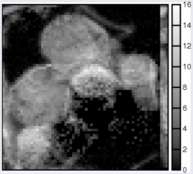
Boron oxide



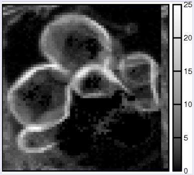
Boron pure



BN $\perp$



BN $||$



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Parameter value and error estimation

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    - Maximum likelihood estimation (ML)

To keep in mind

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- In EELS the noise is a mixture of *Poisson and Gaussian noise.*
- WNNLS can approximate well Poissonian noise when the number of counts is high enough (almost always in EELS)
- Non-linear parameter estimation is an iterative process that *is very sensitive to the starting parameters*

Key articles

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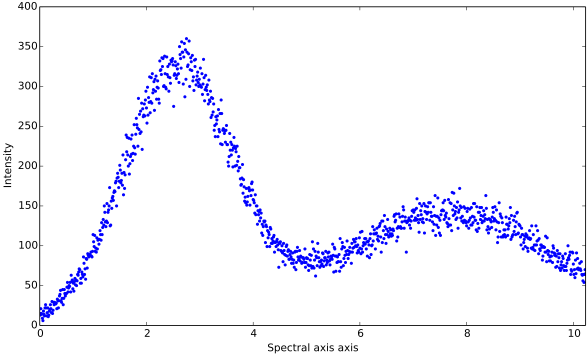
- Verbeeck, J. and Aert, S. V. (2004). Model based quantification of EELS spectra. Ultramicroscopy, 101(2-4):207–224.

Software

- EELSModel http://www.eelsmodel.ua.ac.be/ (open source)
- HyperSpy http://hyperspy.org (open source)
- Digital Micrograph

Outline

Non-linear optimisation routine



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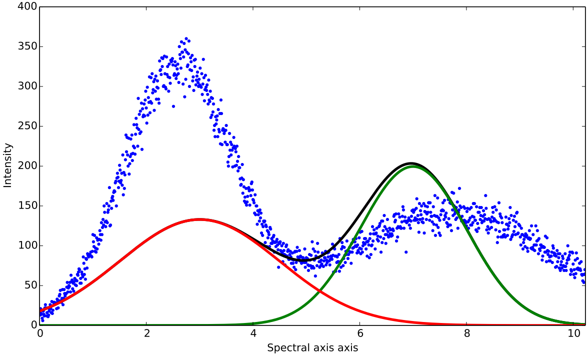

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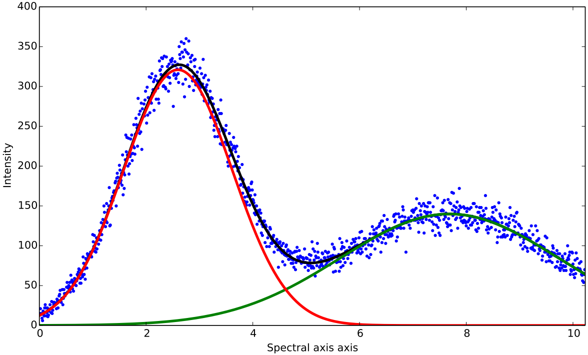

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Fitting routine n-dimensions

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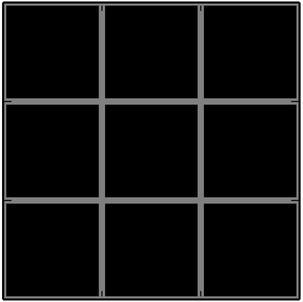

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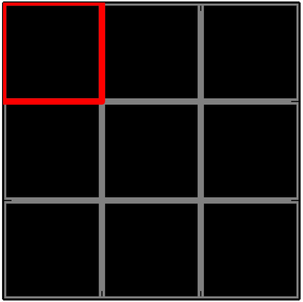

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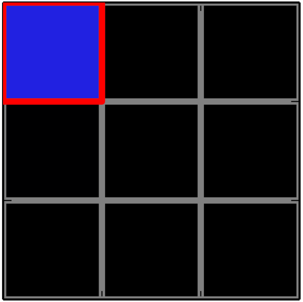

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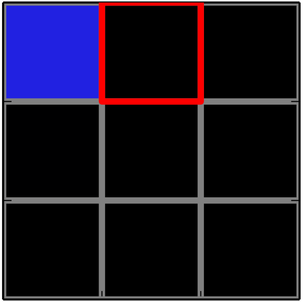

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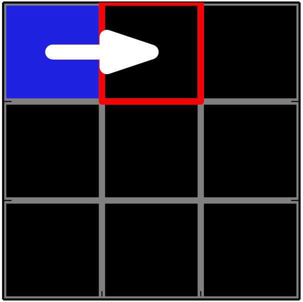

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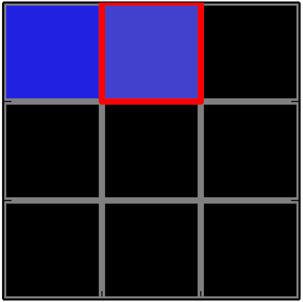

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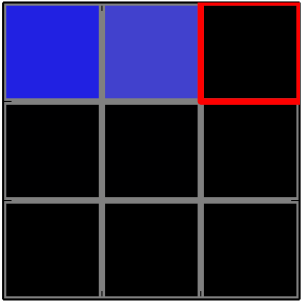

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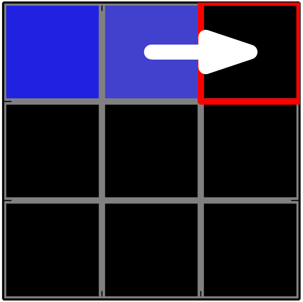

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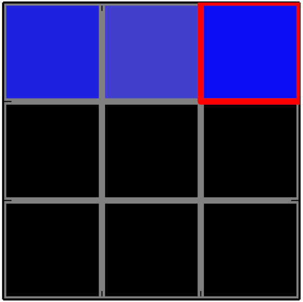

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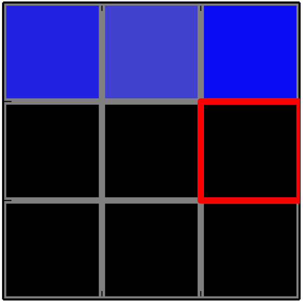

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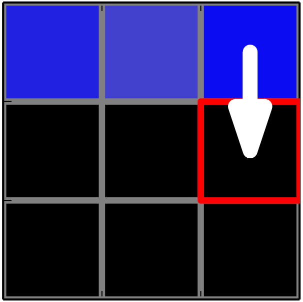

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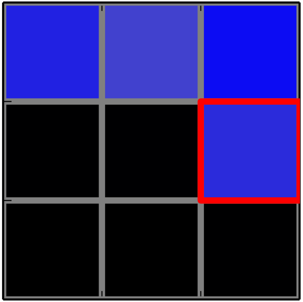

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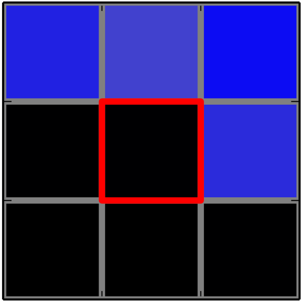

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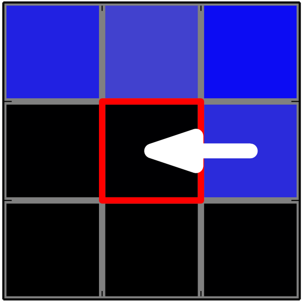

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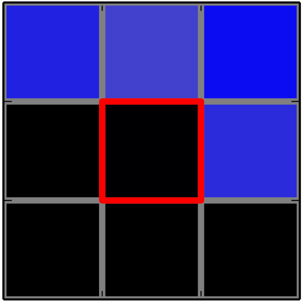

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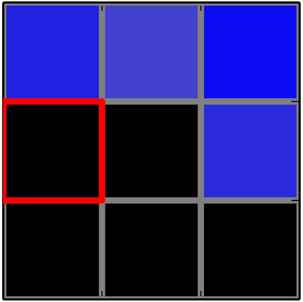

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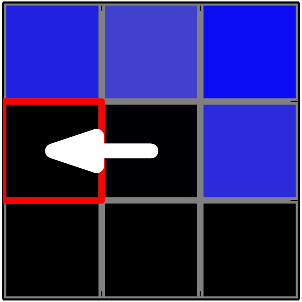

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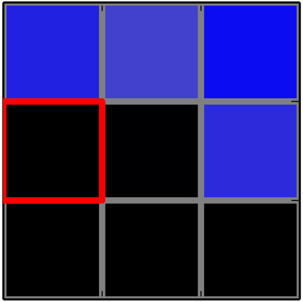

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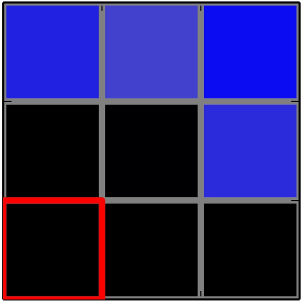

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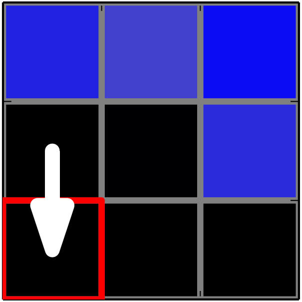

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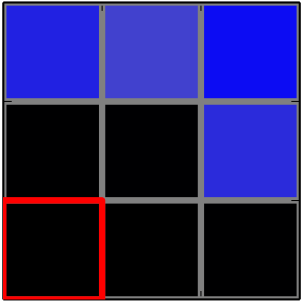

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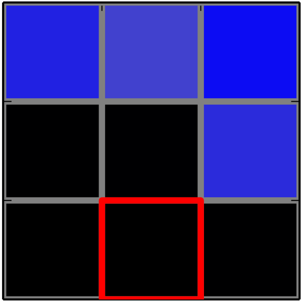

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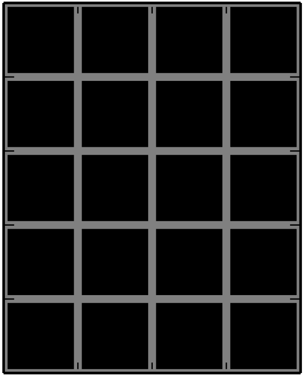

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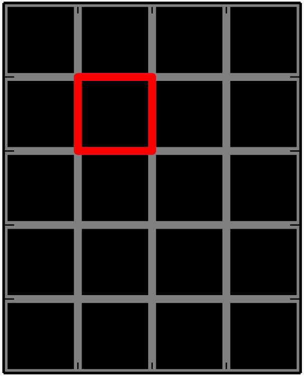

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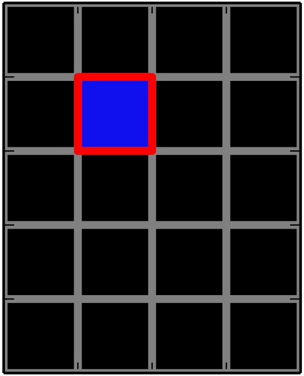

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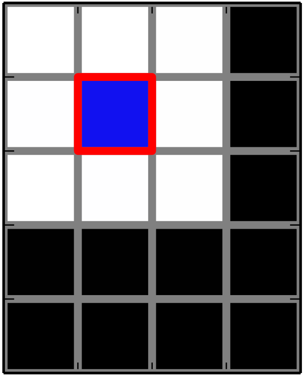

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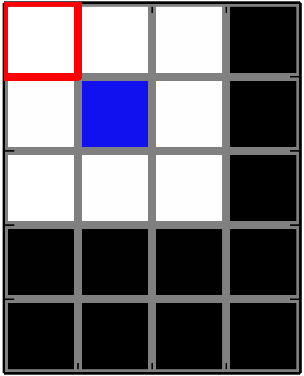

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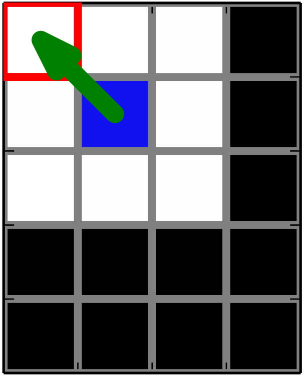

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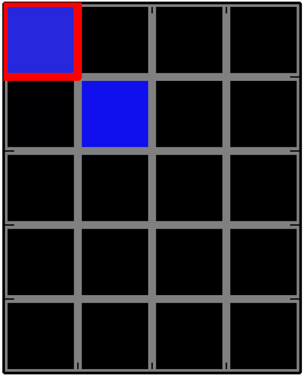

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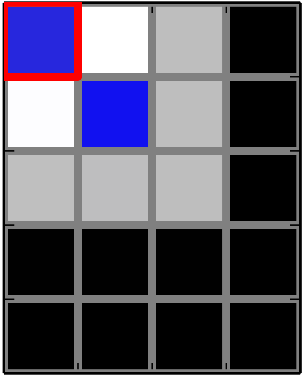

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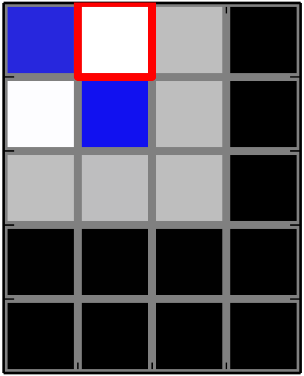

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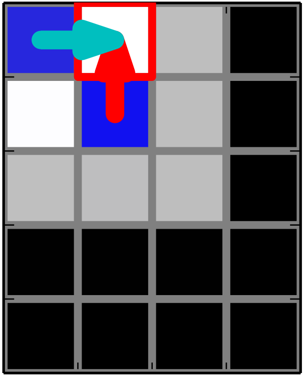

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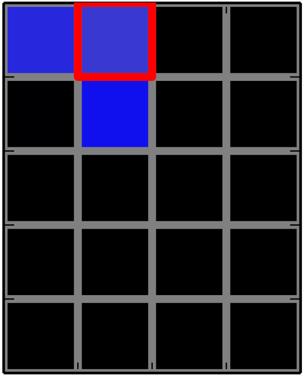

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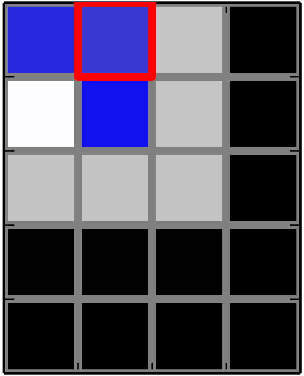

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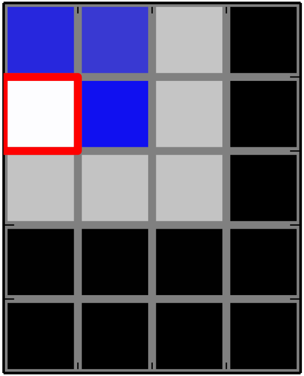

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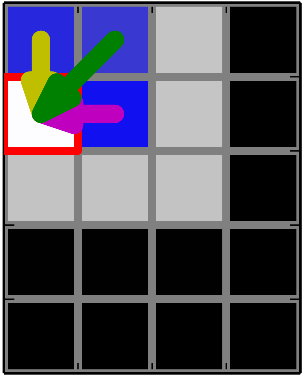

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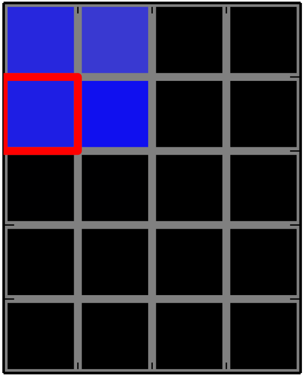

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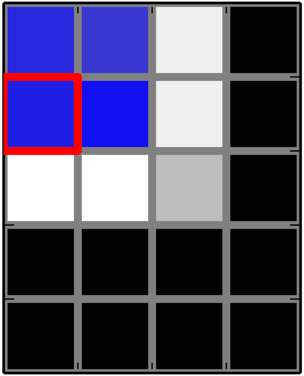

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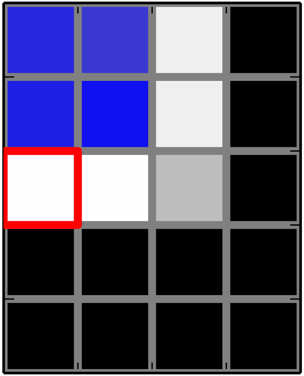

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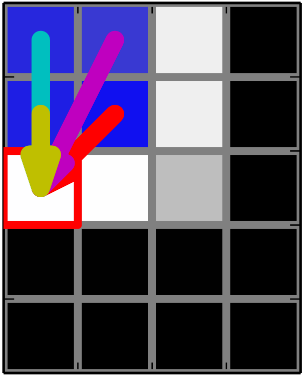

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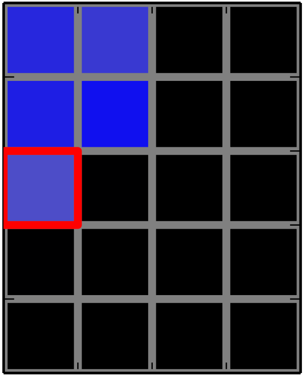

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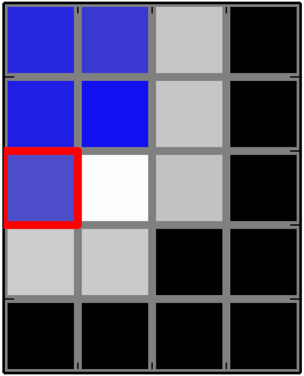

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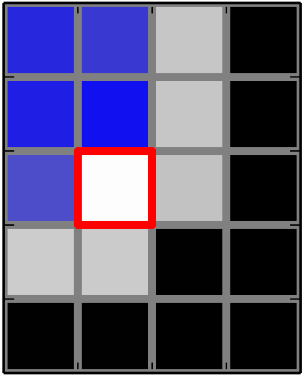

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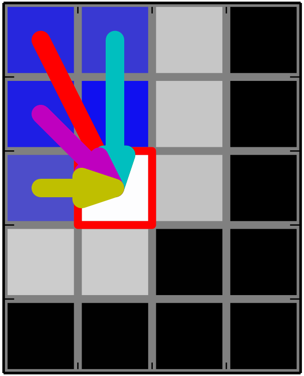

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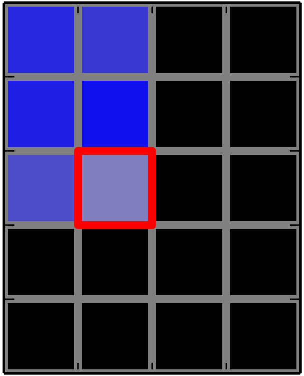

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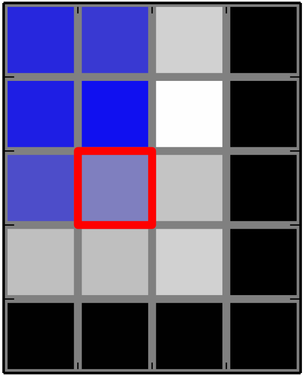

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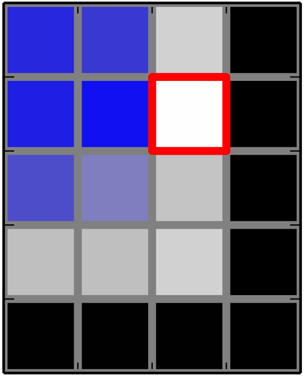

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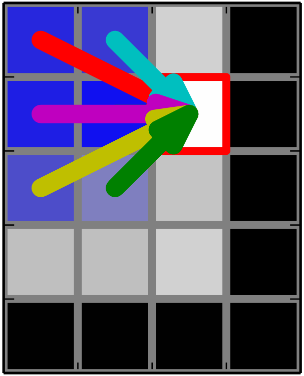

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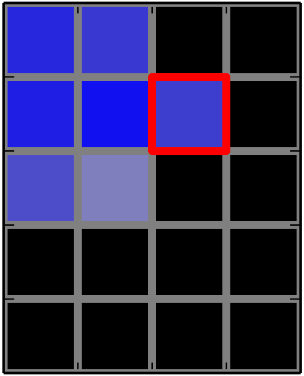

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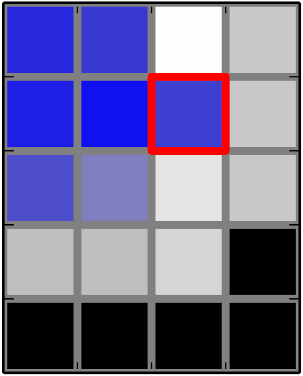

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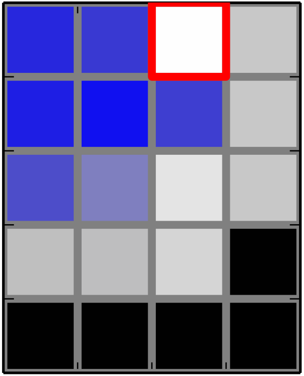

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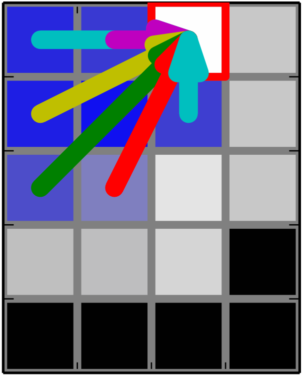

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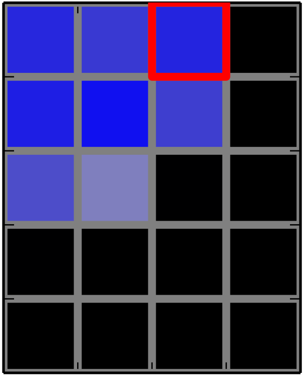

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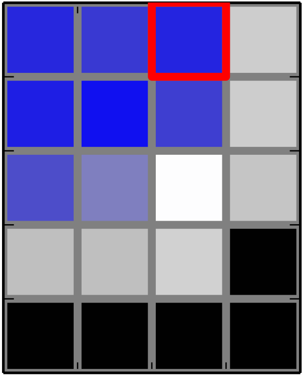

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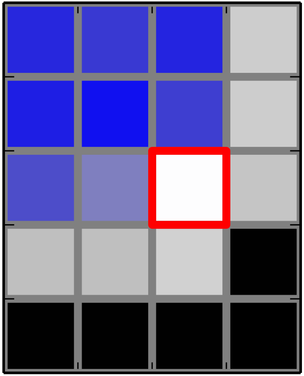

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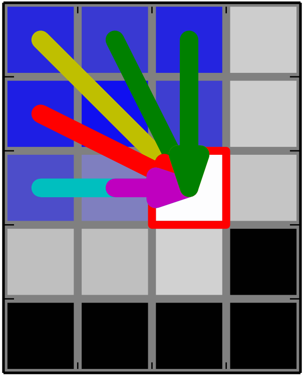

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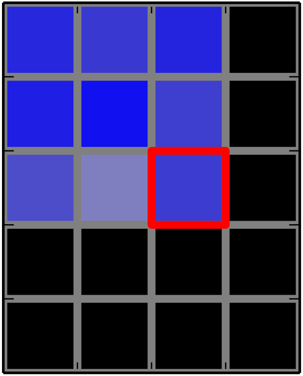

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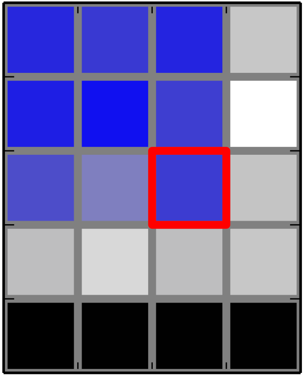

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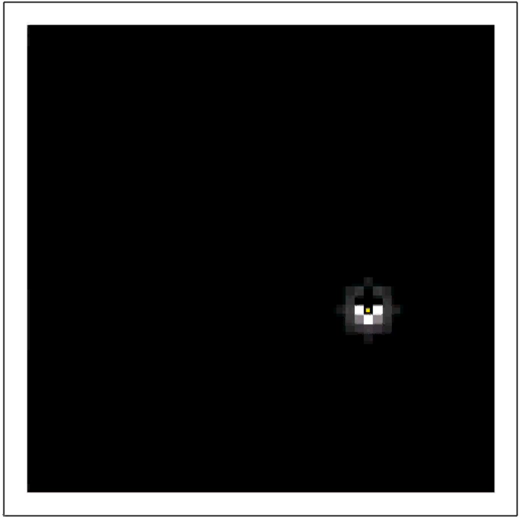
SAMFire parallel fitting example



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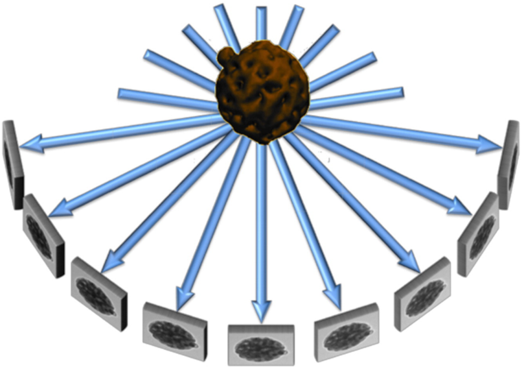
Outline

Transmission electron tomography



Radon transform

$Y_\theta = R_\theta(X) \quad i = -70 \ldots 70$

Figure from O. Ersen et al., *Materials Today* 18, 2015

Tomography as a constrained optimisation problem

$$Y_\theta = R_\theta(X) + \text{noise} \quad \theta = -70, \ldots, +70$$

Tomography as a constrained optimisation problem

$$Y_\theta = R_\theta(X) + \mathrm{noise} \quad \theta = -70, \ldots, +70$$

$$X^* = \arg\min_X \left\{ \| R_\theta(X) - Y_\theta \|_2^2 + \lambda \mathrm{f}(\mathrm{X}) \right\}$$

Tomography as a constrained optimisation problem

$$Y_\theta = R_\theta(X) + \text{noise} \quad \theta = -70, \ldots, +70$$

$$X^* = \underset{X}{\arg\min}\left\{\|R_\theta(X) - Y_\theta\|_2^2 + \lambda \mathrm{f}(\mathrm{X})\right\}$$

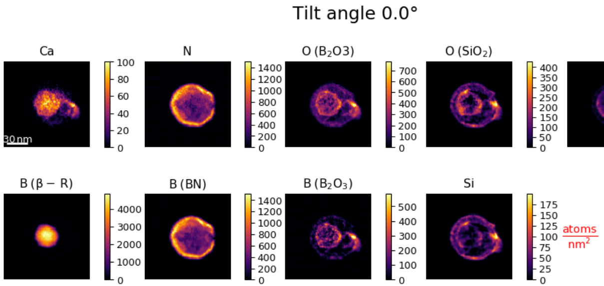
Useful regularisation functions are:

- $\mathrm{L}_1 - \text{norm}$: promotes sparsity
- Total variation: promotes sparsity in the gradient

For EM applications see:

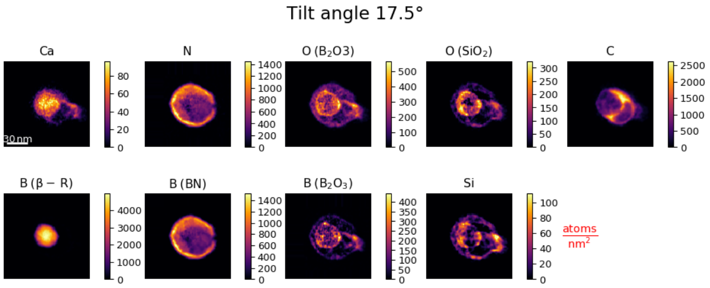
- Leary, Rowan, et al. , *Ultramicroscopy* 131 (2013)
- Goris, Bart, et al. , *Ultramicroscopy* 113 (2012)

SAMFire application - Quantitative bonding tomography



de la Peña, EMC 2016 proceedings

SAMFire application - Quantitative bonding tomography



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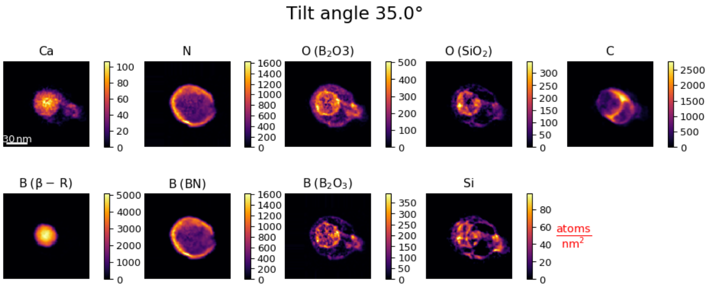

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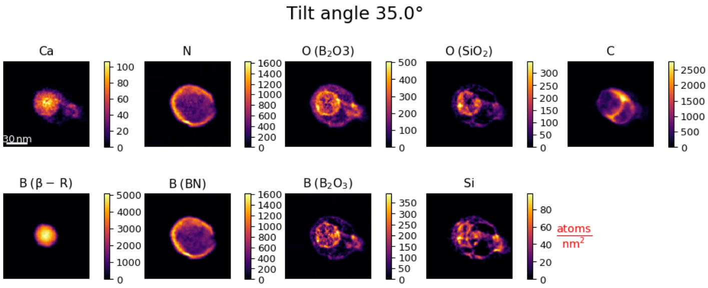

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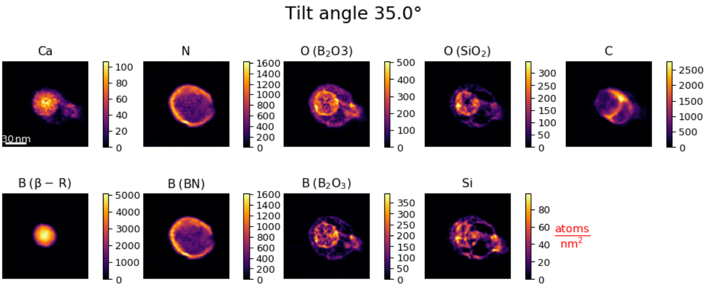

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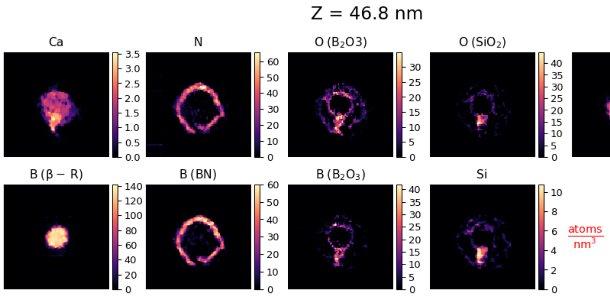

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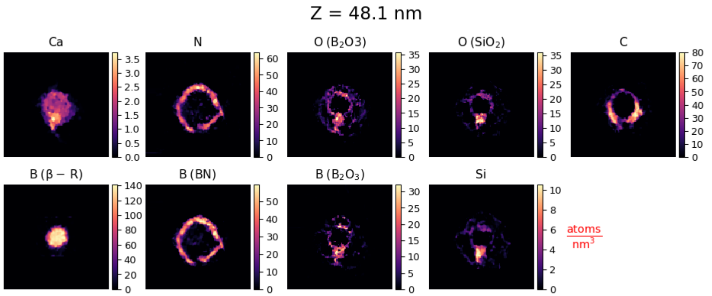
SAMFire application - Quantitative bonding tomography



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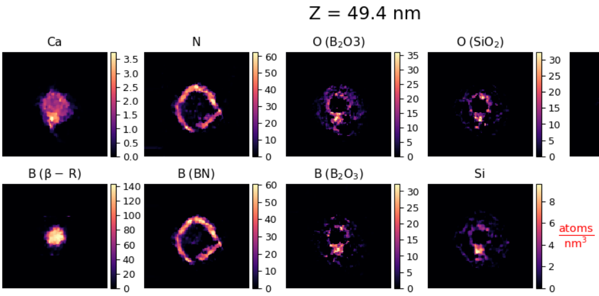

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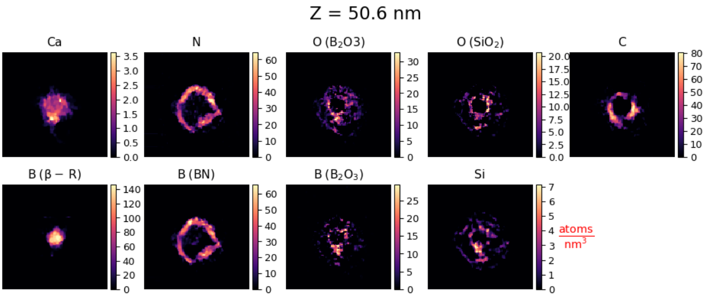
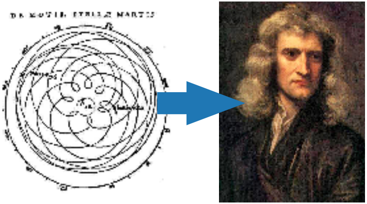


de la Peña, EMC 2016 proceedings

Outline

(Human / Machine) learning

(Human / Machine) learning



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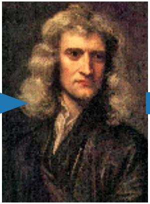
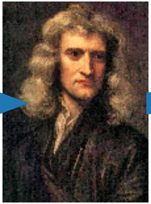


$$F = G\frac{m_1 m_2}{r^2}$$

(Human / Machine) learning



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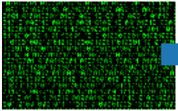

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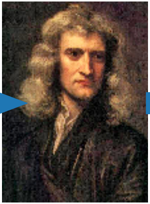

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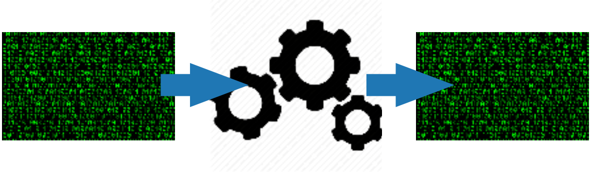

(Human / Machine) learning electron microscopy

Human learning : $$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[\frac{-\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r},t)\right]\Psi(\mathbf{r},t)$$

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Machine learning : $H \cdot X = Y$

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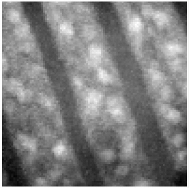
Machine learning : $H \cdot X = Y$

Outline

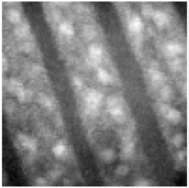
Spinodally decomposed SnO_2/TiO_2 multilayers

HAADF

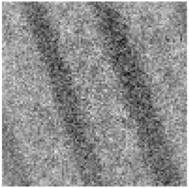


Spinodally decomposed SnO_2/TiO_2 multilayers

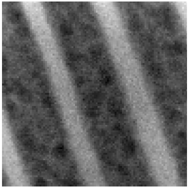
HAADF



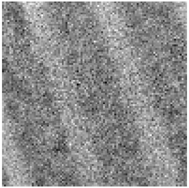
Tin



Titanium

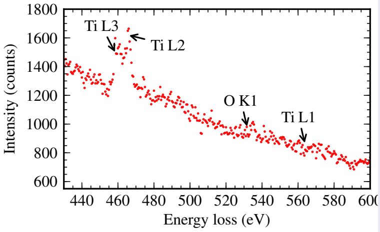


Oxygen

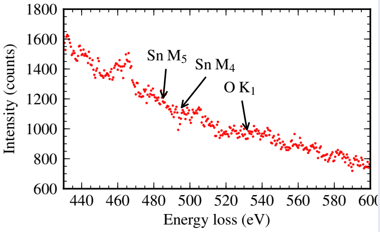


The problem: overlapping peaks and noise

EEL spectrum Ti rich



EEL spectrum Sn rich



Linear mixing
Linearity assumption

$$[a_{i,j}]_{10000\times(64\times64)} = [u_{i,j}]_{(10000)\times 4} \times [v_{i,j}]_{4\times(64\times64)}$$

Paul

Ringo

George

John

Linear mixing

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Paul

Ringo

George

John

Mix 1

Mix 2

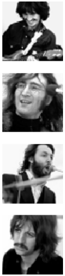
Mix 3

Mix 4

Blind source separation

$$[a_{i,j}]_{I \times I} \times S = \tilde{S}$$

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{pmatrix} \times$$



$$=$$

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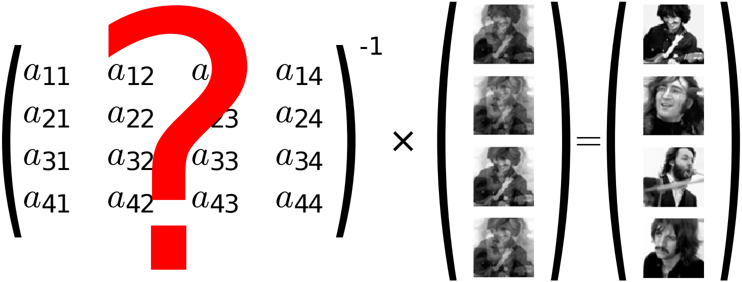

Noisy linear mixing

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Paul

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Mix 1

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Noisy linear mixing

$$[a_{i,j}]_{10000\times(64\times 64)} = [u_{i,j}]_{(10000)\times 4} \times [v_{i,j}]_{4\times(64\times 64)} + \text{noise}$$

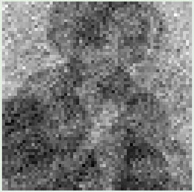
Paul

Ringo

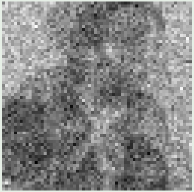
George

John

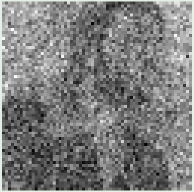
Mix 1



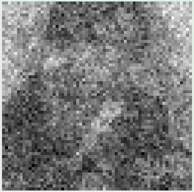
Mix 2



Mix 3



Mix 4



Theorem

Any matrix $A \in \mathbb{R}^{m \times n}$ can be factorised into a singular value decomposition (SVD),

$$A = USV^T \tag{1}$$

where $U \in \mathbb{R}^{m \times m}$ and $V \in \mathbb{R}^{n \times n}$ are orthogonal matrices, and $S \in \mathbb{R}^{m \times n}$ is diagonal with $r = \mathrm{rank}(A)$ leading positive entries. The p diagonal entries of S are denoted σ_i for $i = 1, \ldots, p$ where $p = \min\{m, n\}$ and are called the singular values of A. They satisfy the property $\sigma_1 \geq \sigma_2 \geq \ldots \geq \sigma_p$.

Theorem

Let the SVD of A be given by (1). If $k < r = \mathrm{rank}(A)$ and $A_k = \sum_{i=1}^{k} \sigma_i u_i v_i^T$, then

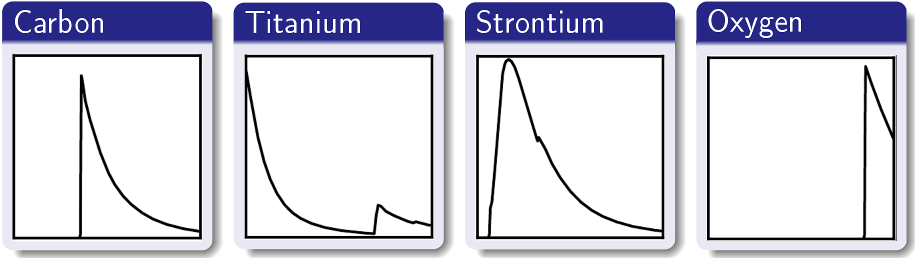
$$\min_{\mathrm{rank}(B)=k} \|A - B\|_2 = \|A - A_k\|_2 = \sqrt{\sum_{i=k+1}^{p} \sigma_i^2}$$

BSS with The Beatles

input image: 1

EELS BSS with The Beatles

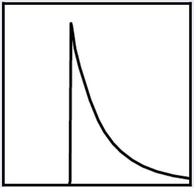
$[d_{i,j}]$ $\times 1024$ $=$ $\times 4 \times [s_{i,j}]_{4 \times 1024}$



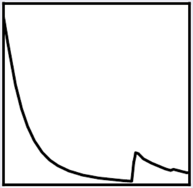
EELS BSS with The Beatles

$$[d_{i,j}]_{(134\times134)\times1024} = [p_{i,j}]_{(134\times134)\times4} \times [s_{i,j}]_{4\times1024}$$

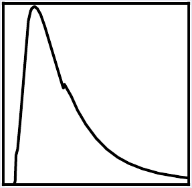
Carbon



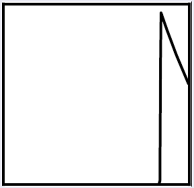
Titanium



Strontium



Oxygen



Carbon

Titanium

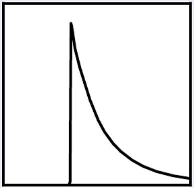
Strontium

Oxygen

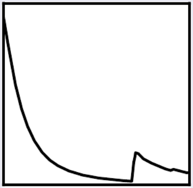
EELS BSS with The Beatles

$$[d_{i,j}]_{(134\times134)\times1024} = [p_{i,j}]_{(134\times134)\times4} \times [s_{i,j}]_{4\times1024} + \text{Poisson noise}$$

Carbon



Titanium



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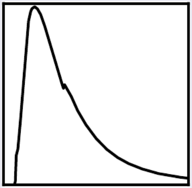
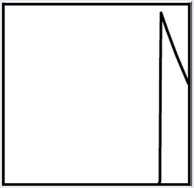


Oxygen



Carbon

Titanium

Strontium

Oxygen

Synthetic SIs for ICA test

- Using the synthetic SIs we will test the performance of ICA at estimating the mixing matrix when using the first and second derivative as pre-treatment

Low SNR SI

- 4 elements: C, Sr, Ti, O
- 134×134 pixels
- 1024 energy channels
- Poisson noise
- Average number of counts: $\sim 10^3$

Synthetic SIs for ICA test

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- 134×134 pixels
- 1024 energy channels
- Poisson noise
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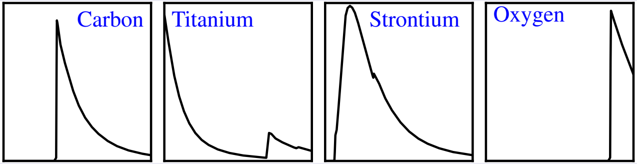
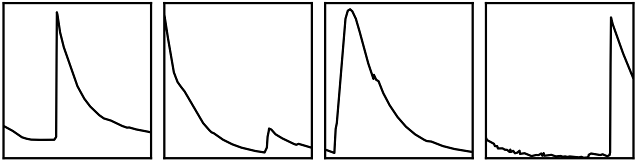
High SNR SI

- 4 elements: C, Sr, Ti, O
- 134×134 pixels
- 1024 energy channels
- Poisson noise
- Average number of counts: $\sim 10^6$

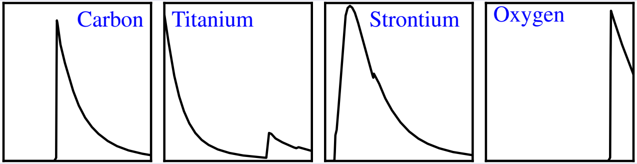
Original spectral components



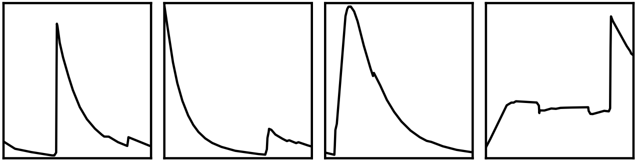
ICA result: Low SNR, first derivative



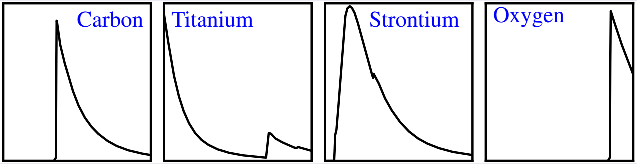
Original spectral components



ICA result: Low SNR, second derivative



Original spectral components



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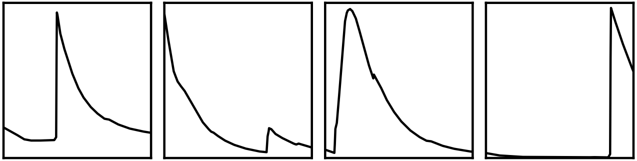
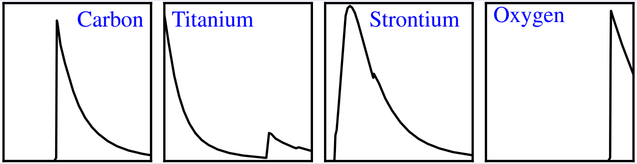
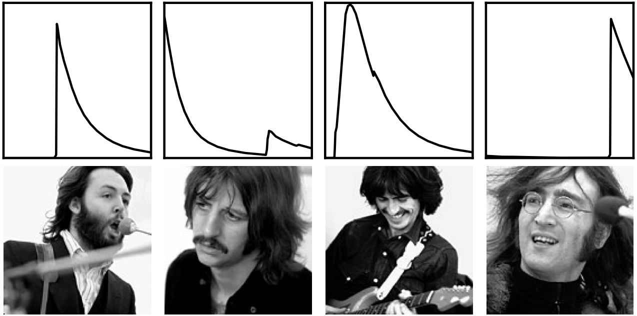


Original spectral components



ICA result: High SNR, second derivative



Original spectral components

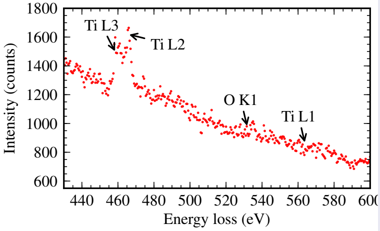
Low SNR: windows methods

ICA result: Low SNR, first derivative

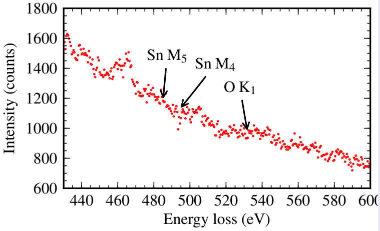
Spinodally decomposed SnO_2/TiO_2 multilayers

Noise reduction by dimensionality reduction

EEL spectrum Ti rich



EEL spectrum Sn rich



Spinodally decomposed SnO_2/TiO_2 multilayers

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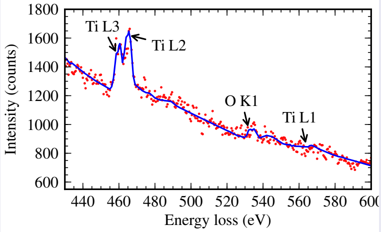

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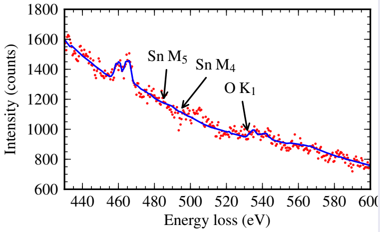
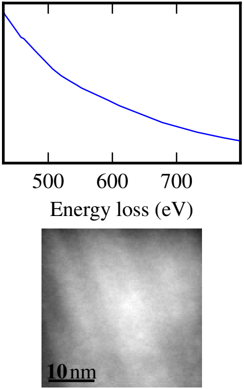
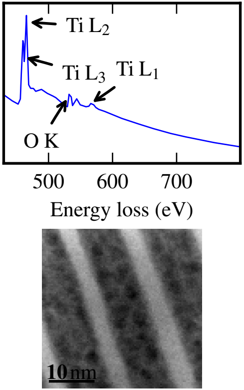


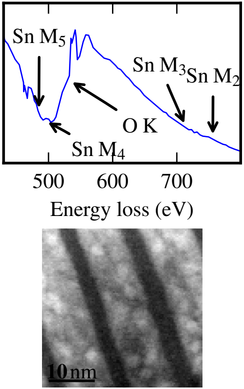
IC 1 Carbon



IC 2 Titanium oxide



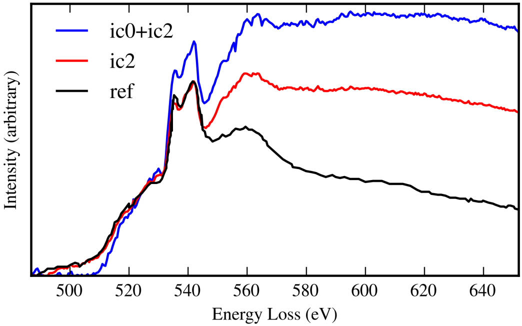
IC 3 Tin Oxide



de la Peña et al., Ultramicroscopy 11 (2011)

Spinodally decomposed SnO_2/TiO_2 multilayers

The effect of plural scatteting



Take home messages

- Singular value decomposition
  - is very useful for
    - Data denoising with no information loss
    - Rank estimation
    - Dimensionality reduction

Take home messages

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  - is very useful for
    - Data denoising with no information loss
    - Rank estimation
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  - The SNR improves with the number of trials in the dataset

Take home messages

- Singular value decomposition
  - is very useful for
    - Data denoising with no information loss
    - Rank estimation
    - Dimensionality reduction
  - The SNR improves with the number of trials in the dataset
- Independent component analysis
  - Separates sources from a mixture
  - The accuracy increases with SNR

Bibliography

- PCA: Jolliffe, Ian. Principal component analysis. John Wiley & Sons, Ltd, 2002.
- weighted PCA: Keenan, Michael R., and Paul G. Kotula. "Accounting for Poisson noise in the multivariate analysis of ToF-SIMS spectrum images." Surface and Interface Analysis 36.3 (2004): 203-212.
- ICA: Hyvärinen, A., Karhunen, J., and Oja, E. (2001). Independent Component Analysis. Wiley- Interscience

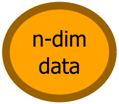
Other methods

- PCA variants: robust PCA, online PCA
- Other BSS methods: non-negative matrix factorization (NMF), vertex component analysis (VCA)
- Tensor decomposition: Spiegelberg, Jakob, Ján Rusz, and Kristiaan Pelckmans. "Tensor Decompositions for the Analysis of Atomic Resolution Electron Energy Loss Spectra." Ultramicroscopy (2017).

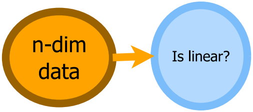
Outline

1. Introduction
   - Introduction
2. Model based quatification
   - The integration method
   - The curve fitting method
   - Multi-dimensional curve fitting
   - Practical application: Analytical tomography
3. Machine learning
   - Introduction
   - EELS core-loss analysis
4. Summary
   - Summary

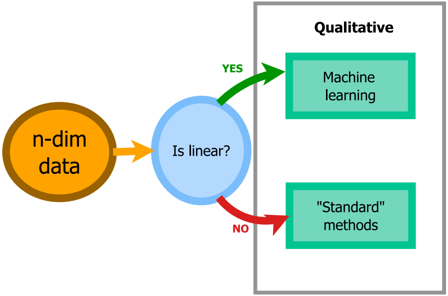
Multi-dimensional data analysis workflow



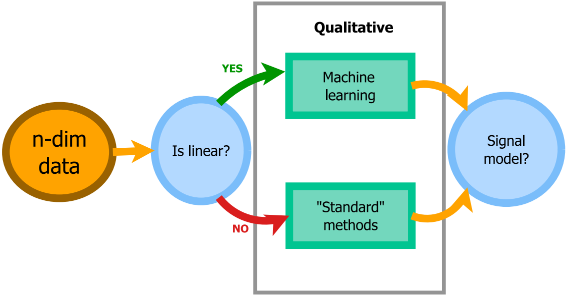
Multi-dimensional data analysis workflow



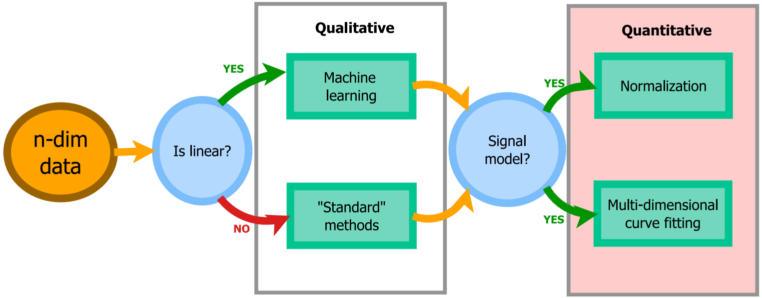
Multi-dimensional data analysis workflow



Multi-dimensional data analysis workflow



Multi-dimensional data analysis workflow



Thank you all for you attention