Enhancing Chemical Contrast: Latest Trends in Hyperspectral Image Analysis

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Hyperspectral Image Analysis

- Images where every pixel contains complete spectrum
  - Possible with nearly every type of spectroscopy and spectrometry
- Goal of analysis is usually to obtain maps of chemical species
  - Can be for specific analytes, elements or …
  - Seldom have completely specific channels

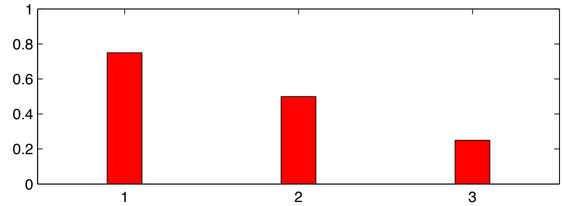
Contrast Enhancing Methods

- Principal Components Analysis (PCA)
  - Nice pictures but not chemically meaningful
- Multivariate Curve Resolution (MCR)
  - Contrast constraints
- Independent Components Analysis (ICA)
  - Homeopathic ICA
- Other methods
  - Maximum Autocorrelation Factors (MAF)
  - Maximum Difference Factors (MDF)
  - Clutter Filters

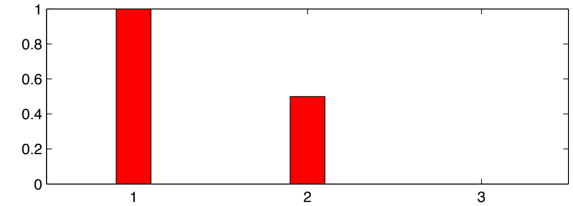
Multivariate Curve Resolution

- MCR attempts to resolve mixtures into pure spectra and concentrations without using prior information
  - MCR typically solved with Alternating Least Squares (ALS)
  - Typically solved with constraints, *e.g.* non-negativity, continuity
  - Other variants and names: SIMPLISMA, Purity, SMCR, SMMA

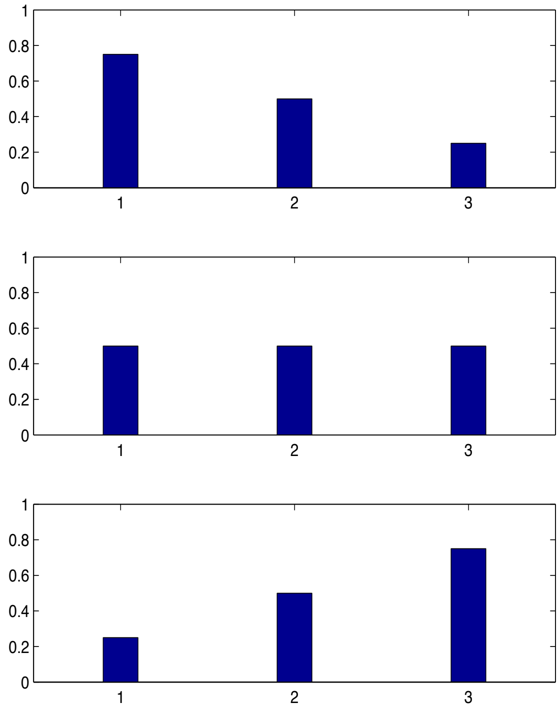
Pure Component 1a



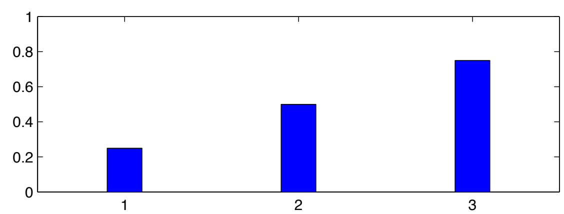
Pure Component 1b



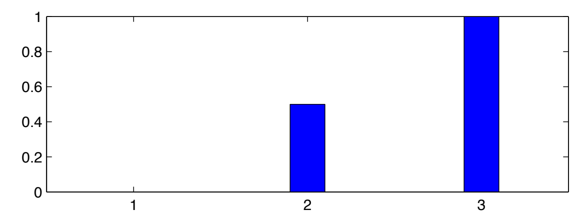
Mixtures



1.0	0.0	0.75	0.25
0.5	0.5	0.5	0.5
0.0	1.0	0.25	0.75



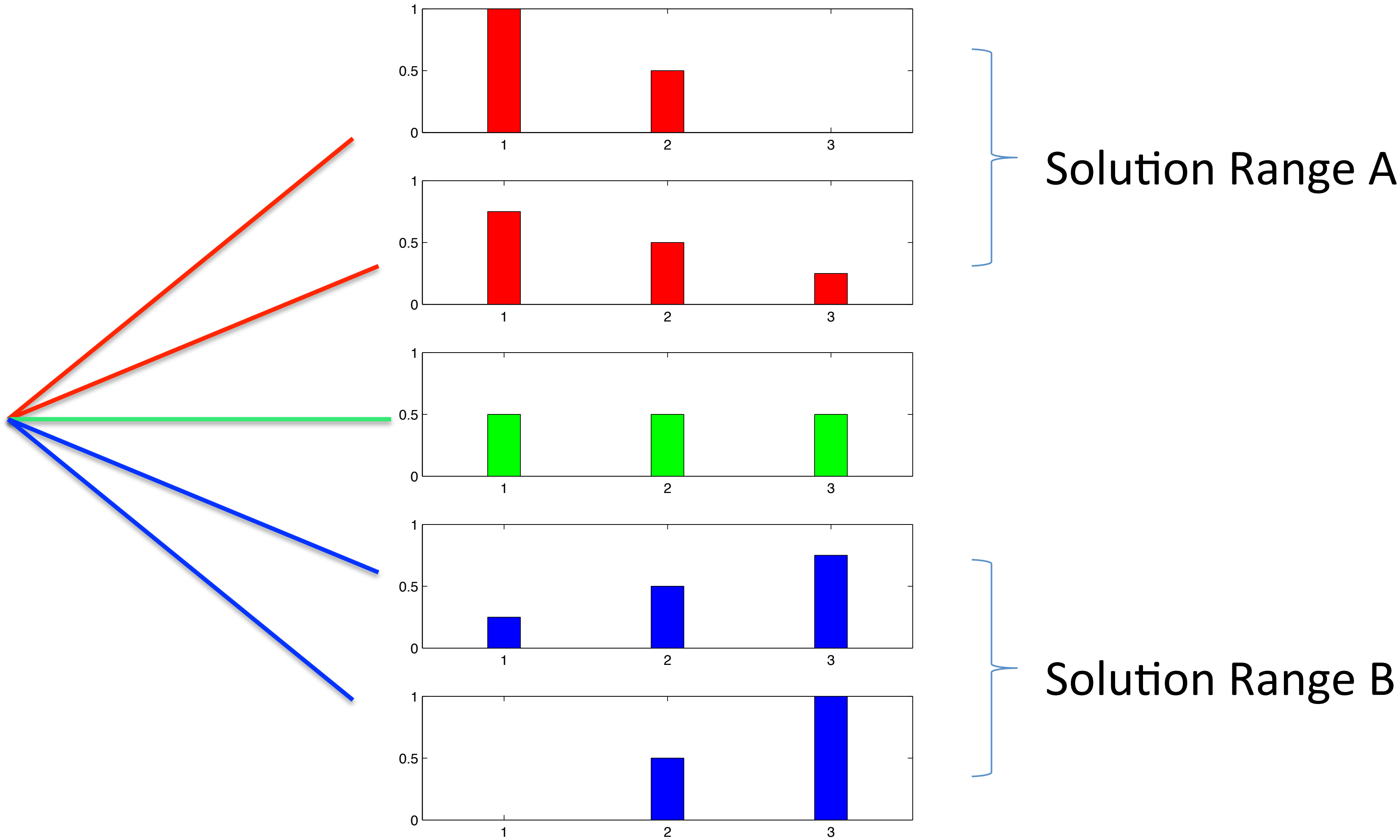
Pure Component 2a



Pure Component 2b

Observations

- "Contrast" is present in data set
- High contrast in resolved contributions gives low contrast in resolved spectra
  - Assumes pure samples
- High contrast in resolved spectra gives low contrast in resolved contributions
  - Assumes pure variables



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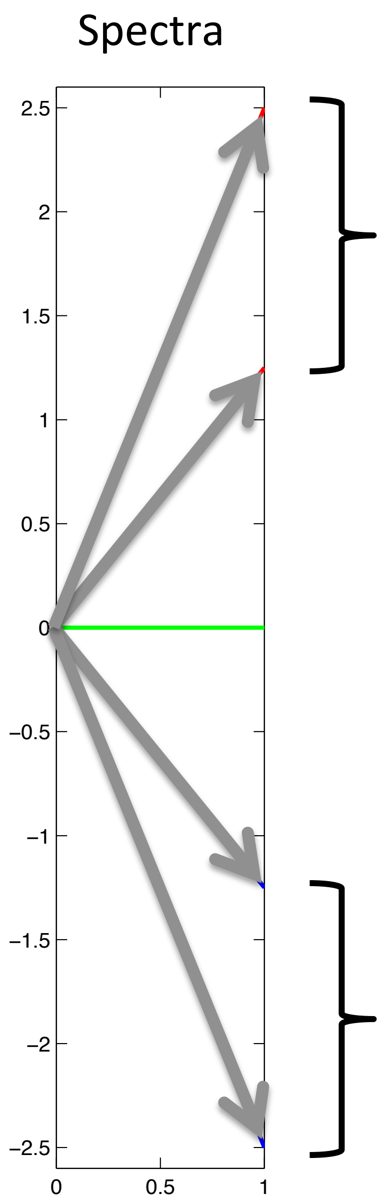
Solution Range



Solution Range A

Pure sample solution

Pure variable solution

Solution Range B

Solution Range

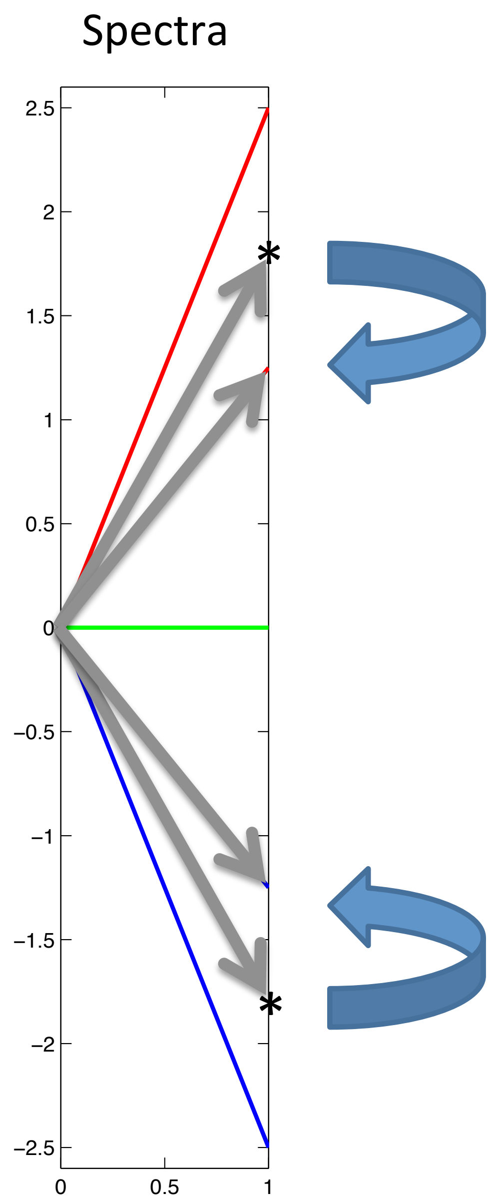
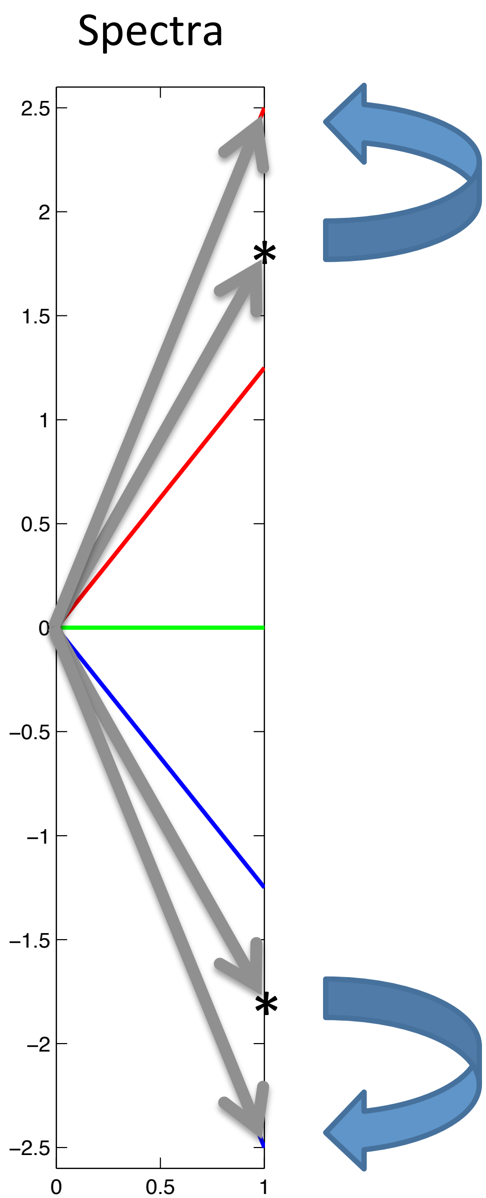


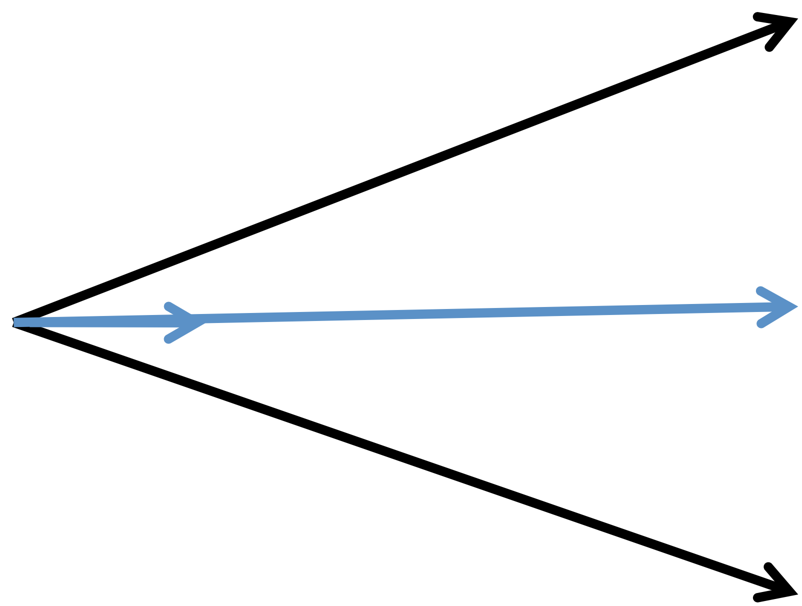
Image (concentration) contrast

Solution Range

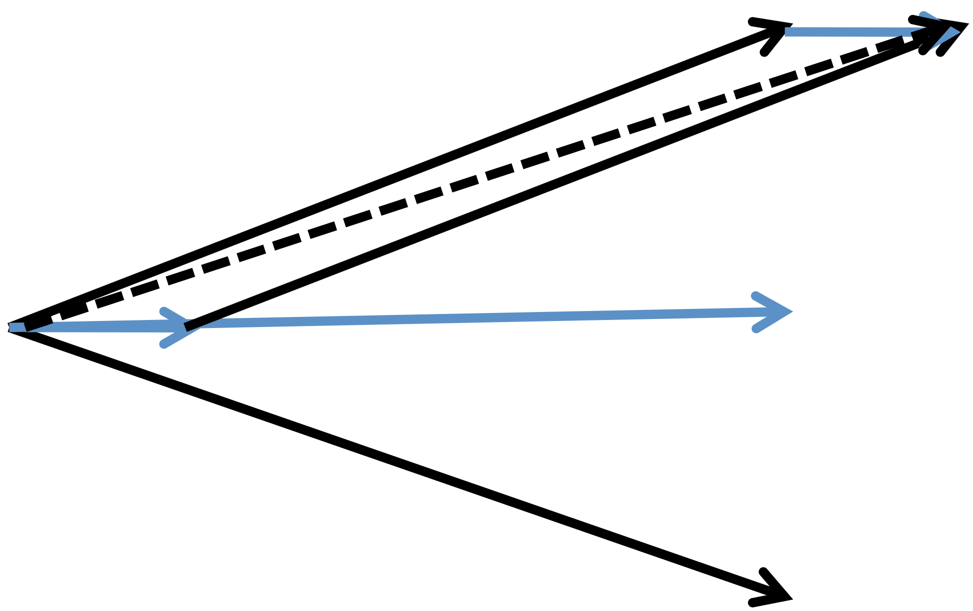


Spectral contrast

Decreasing Angles



Decreasing Angles



Can be done on either the spectra (sample)
or concentration (variable) mode!

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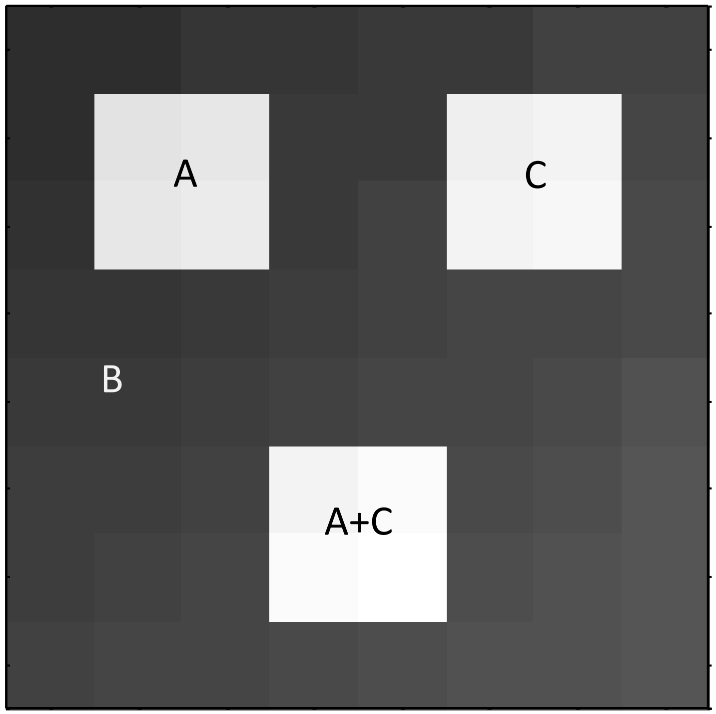
Simulated mixture



Spectral Contrast

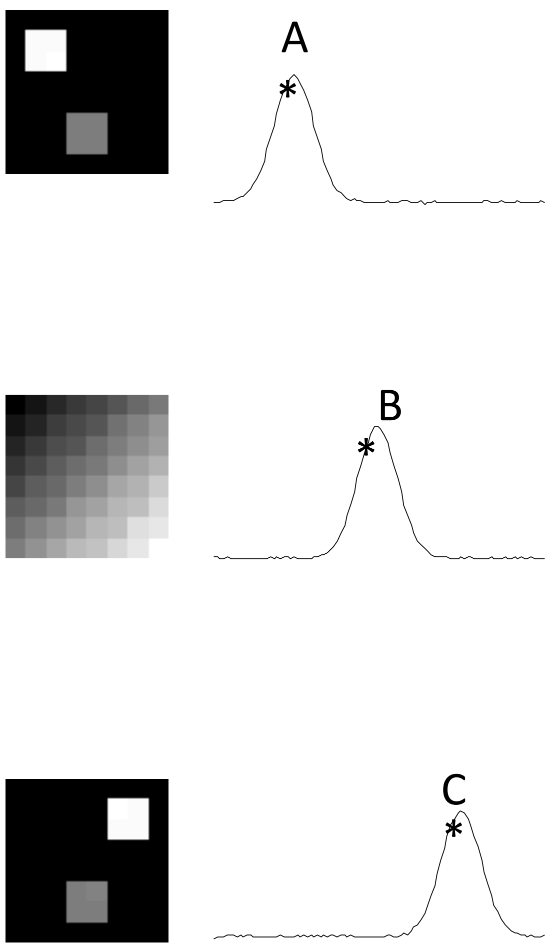
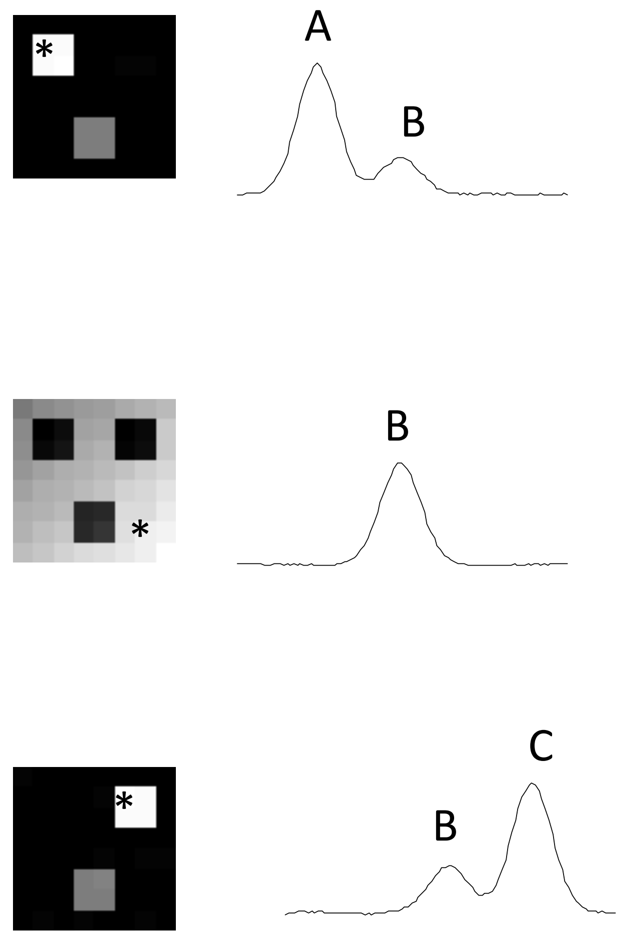


Image Contrast



Weighted Poisson scaling

- Variance in SIMS is expected to follow a Poisson distribution such that the variance is equal to the mean of the data.
- Divide each variable (mass channel) by the square root of the mean of the variable
- Tends to increase emphasis on channels with smaller signals (*e.g.* higher masses)
- Poisson scaling applied before MCR

W. Windig, M. R. Keenan and B. M. Wise, "The effects of pre-processing of image data on self-modeling image analysis," J. Chemometrics 2008; 22: 500–509

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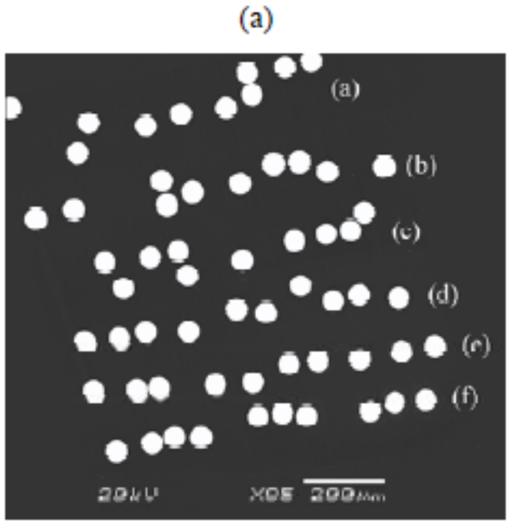
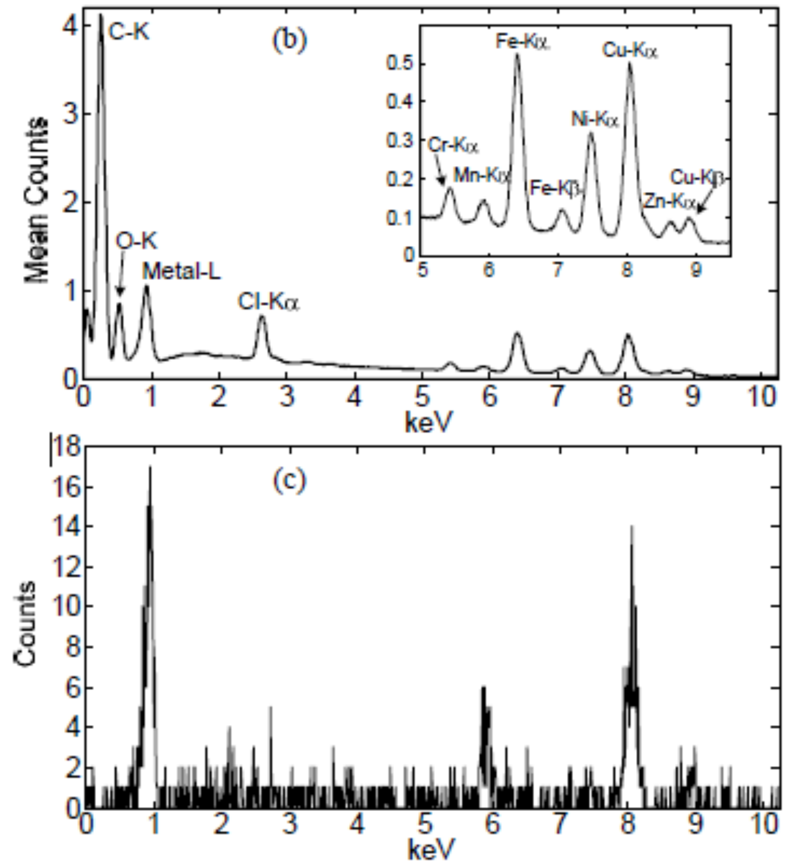
Energy dispersive spectrometry (EDS)



Wire Compositions

(a) 100% Ni
(b) 36% Ni, 64% Fe
(c) 70% Cu, 30% Zn
(d) 16% Cr, 84% Fe
(e) 13% Mn, 4% Ni, 83%Cu
(f) 100% Cu



M.R. Keenan, Multivariate Analysis of Spectral Images Composed of Count Data, In: H. F. Grahn, P, Geladi (eds.), Techniques and Applications of Hyperspectral Image Analysis, pp. 89-126, Wiley & Sons, 2007

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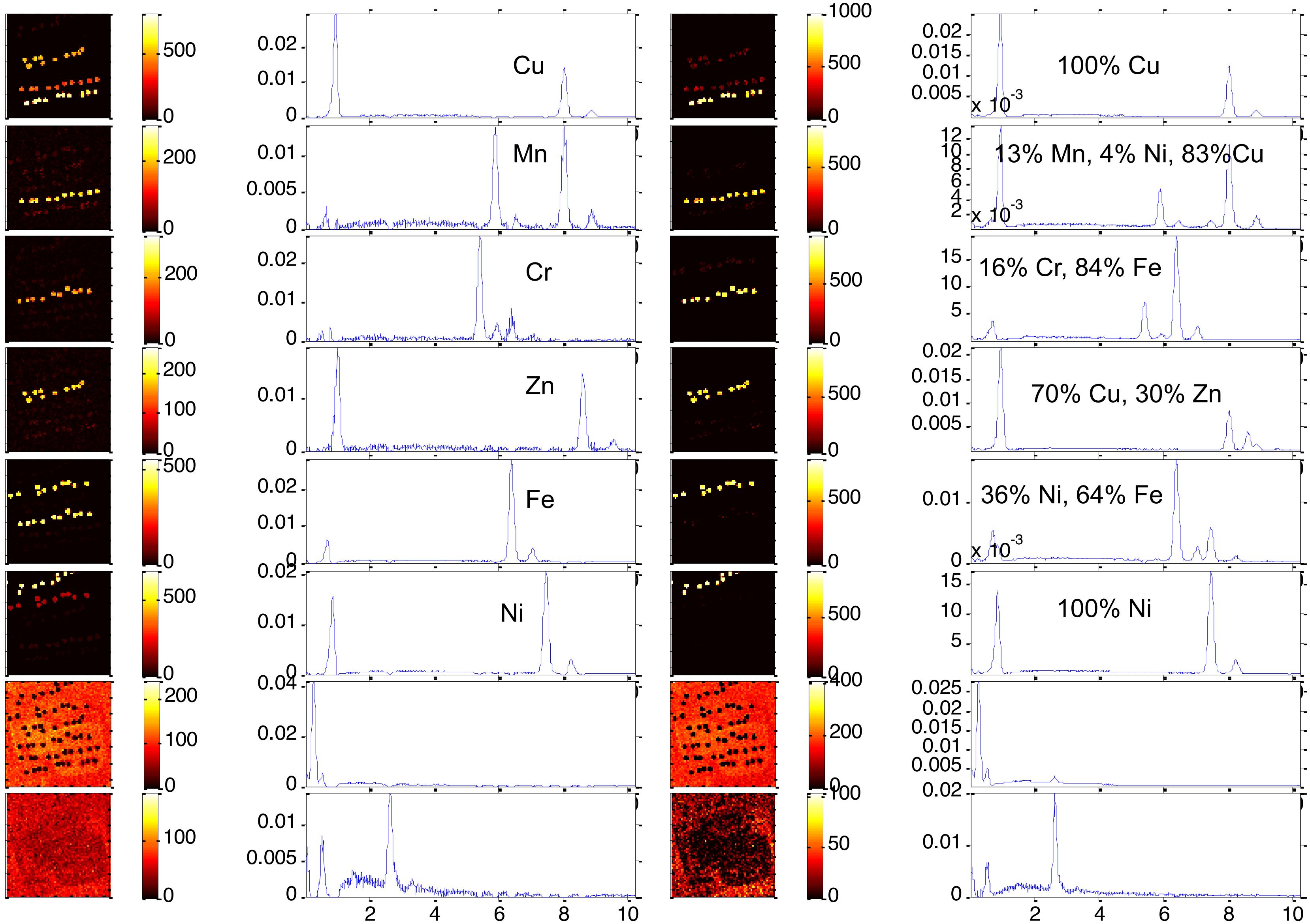
Spectral contrast   Image contrast



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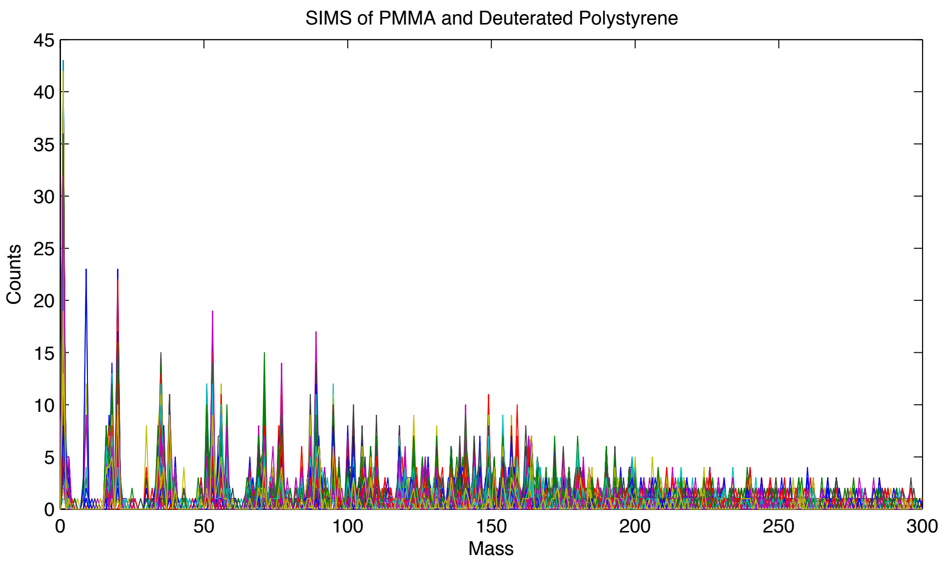
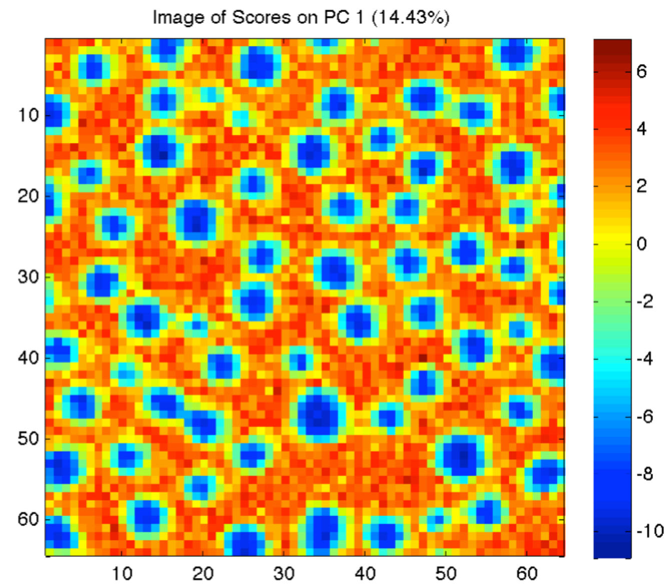
TOF-SIMS of PMMA and Deuterated Polystyrene

- Positive SIMS spectrum on 64x64 grid
- 301 mass channels (AMU)
- Thanks to Physical Electronics for the data





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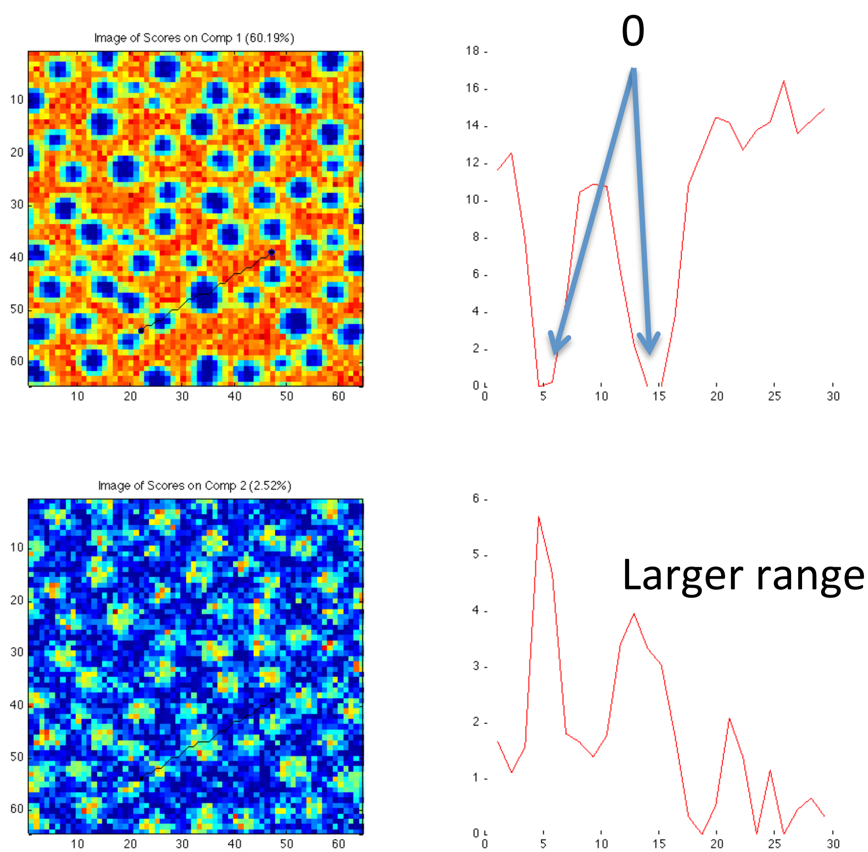
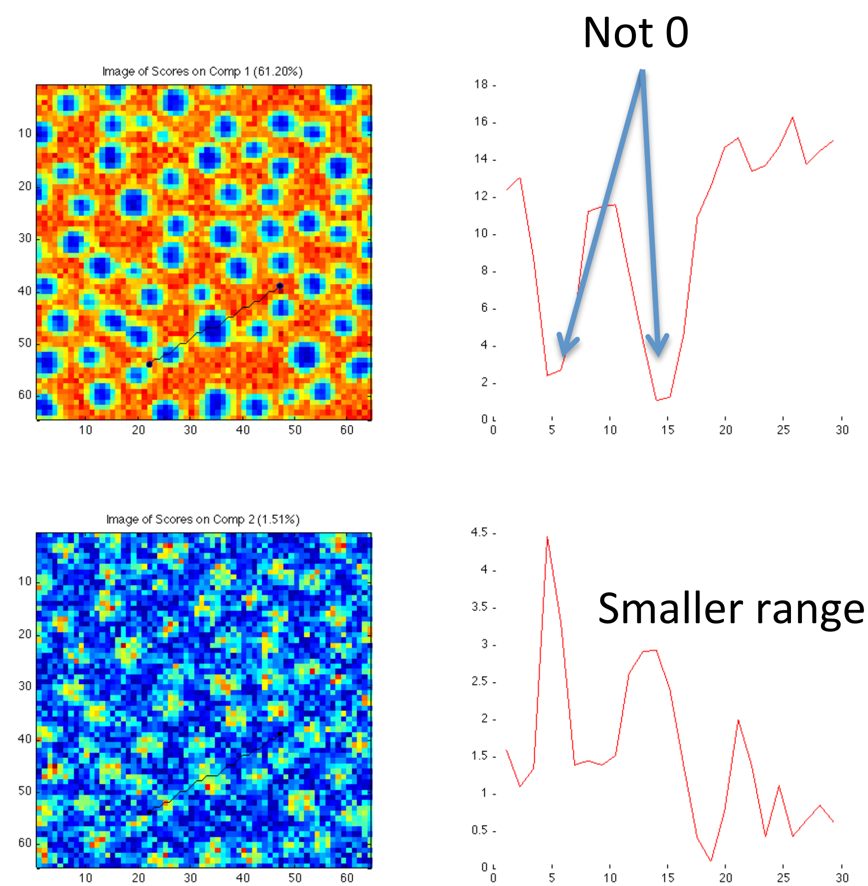
MCR Solutions for Concentrations

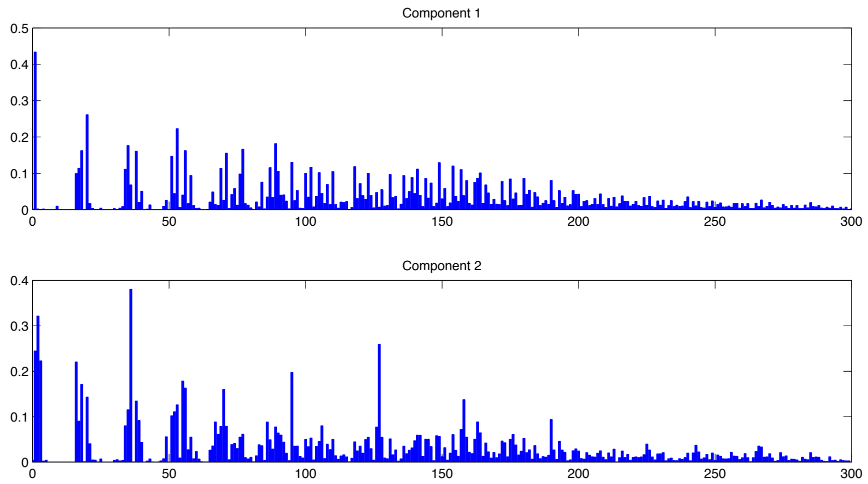


Concentration Contrast

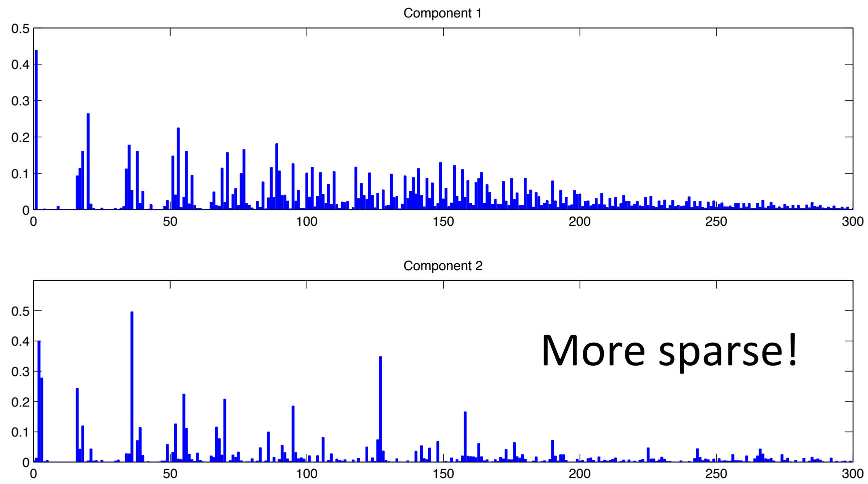


Spectral Contrast

MCR Solutions for Spectra



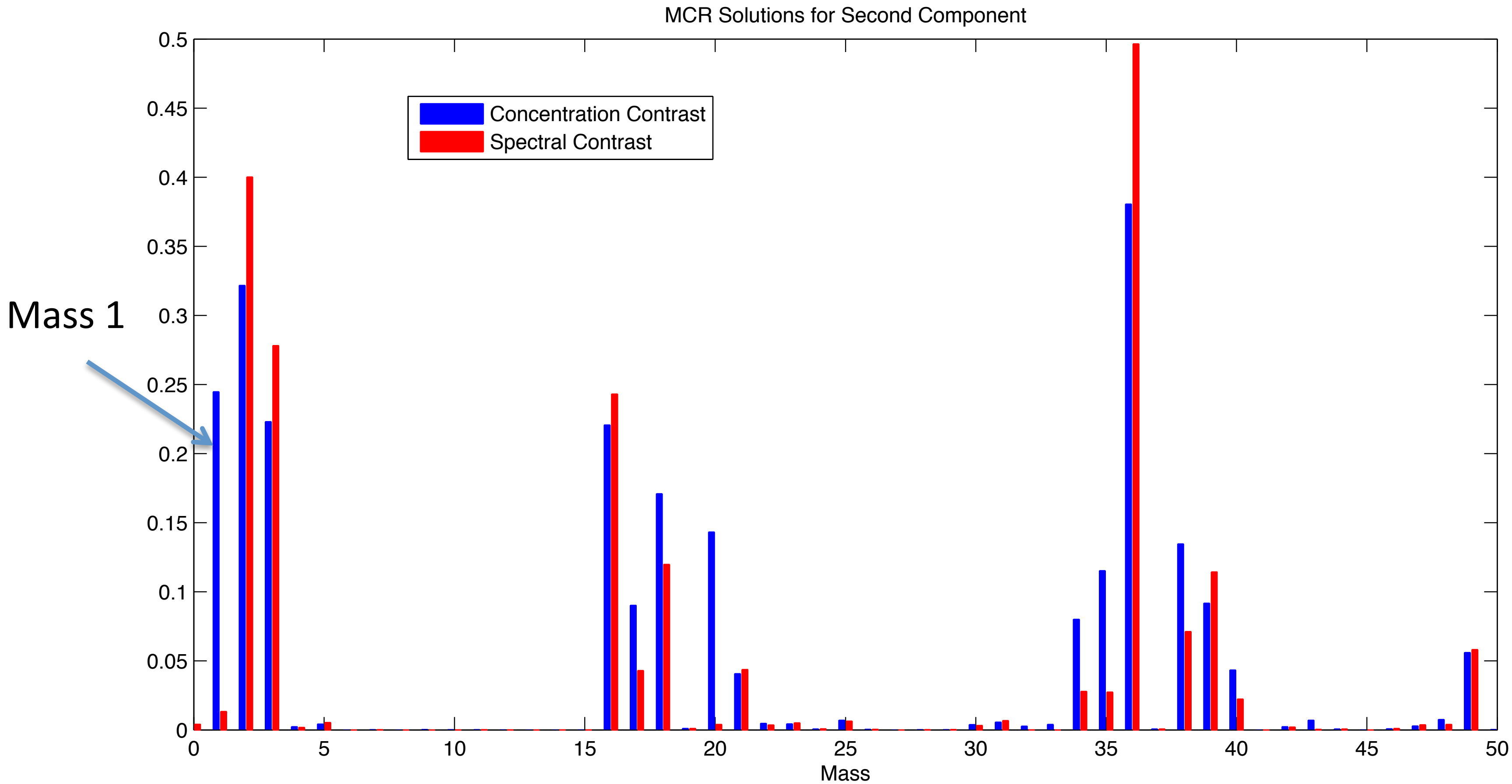
Concentration Contrast



Spectral Contrast

Note: Poisson scaled solutions!

Second Component Comparison



Spectral contrast

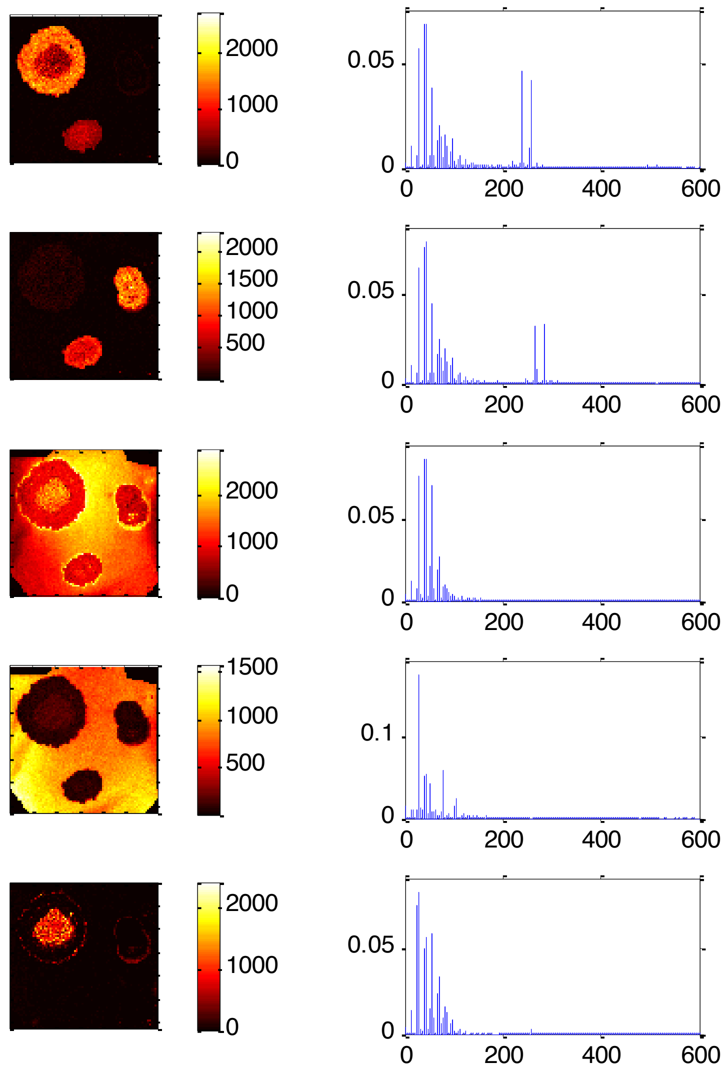
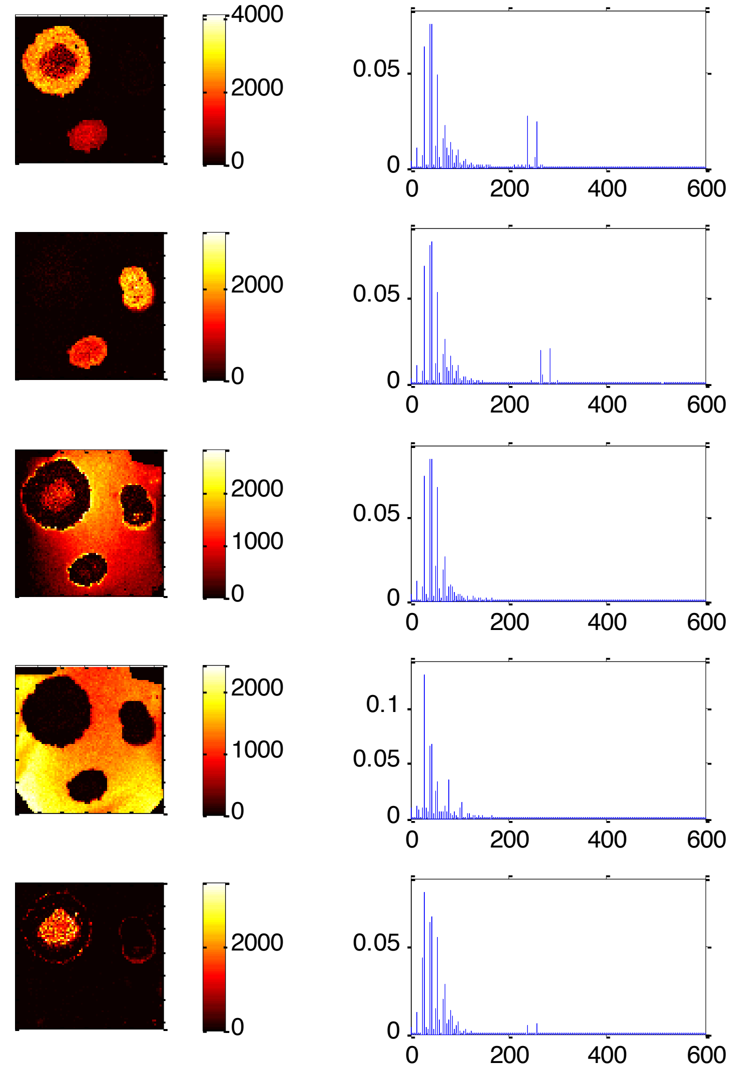
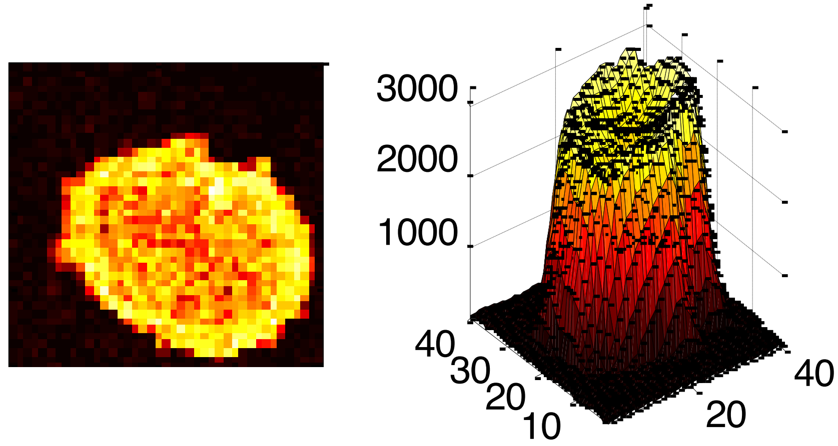


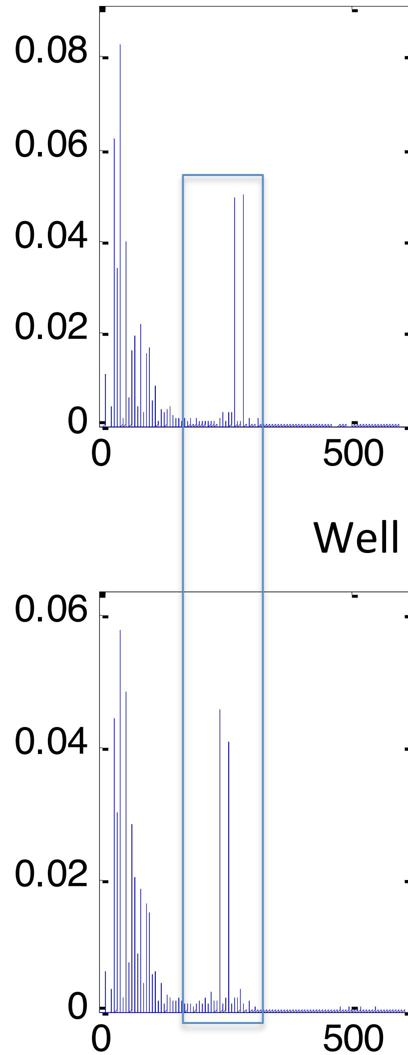
Image contrast



Stearic and palmitic acid spots and mixture

Spectral contrast





But concentration images nearly identical

Well resolved peaks!

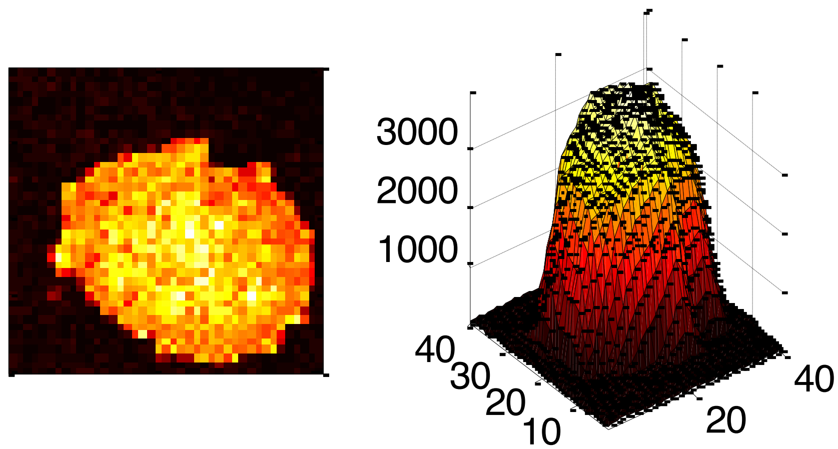


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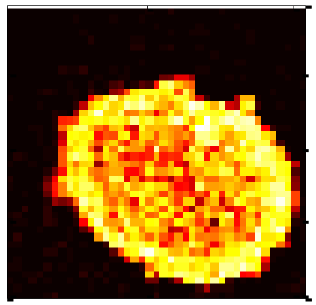
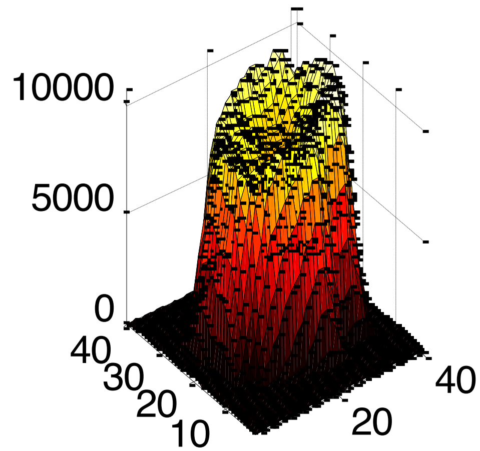
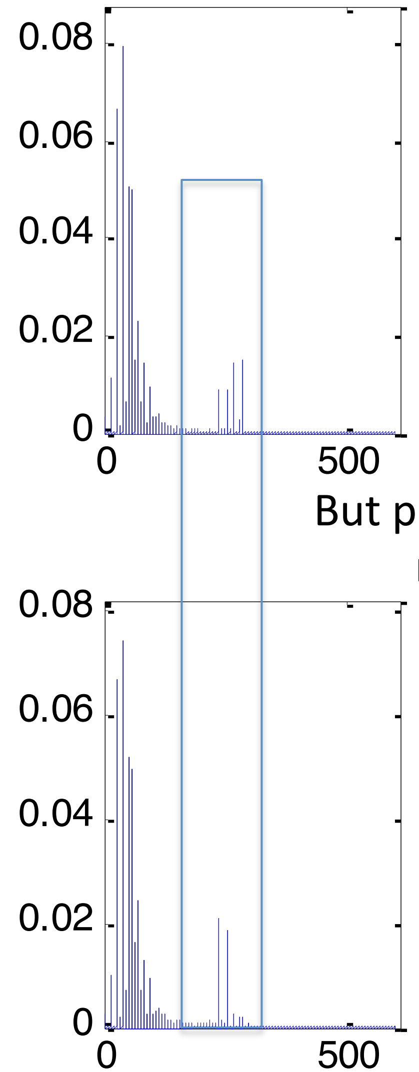
Image contrast

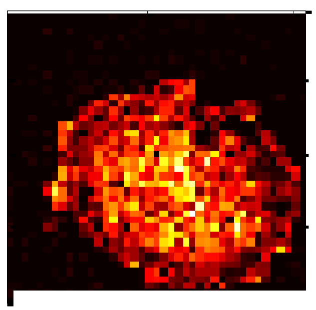


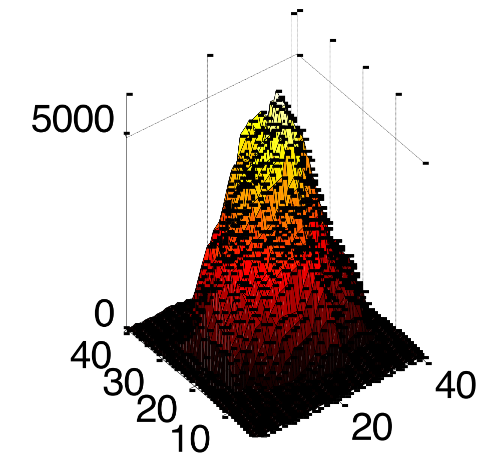




Large contrast in concentration images

But peaks no longer resolved!





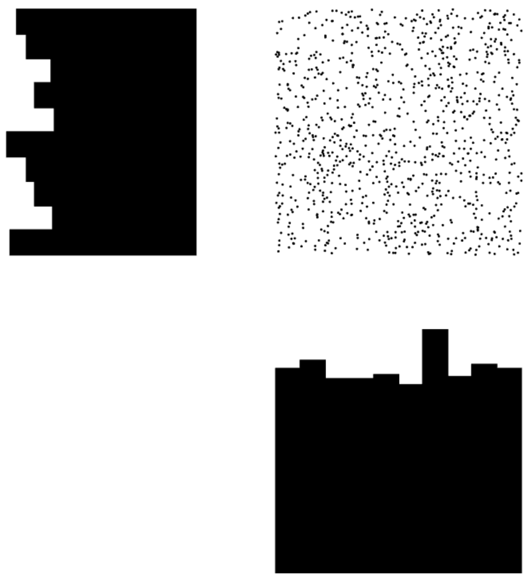
Contrast Constraint Conclusions

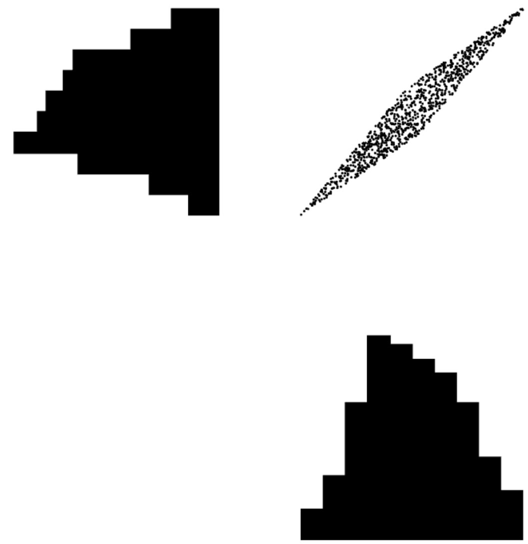
- Contrast in the spectra or images (concentrations) is problem dependent
  - Often one of the extremes is "correct" solution
  - Can be implemented as a constraint in MCR
- Ability to maximize spectral or concentration contrast helps elucidate range in solutions

Homeopathic ICA

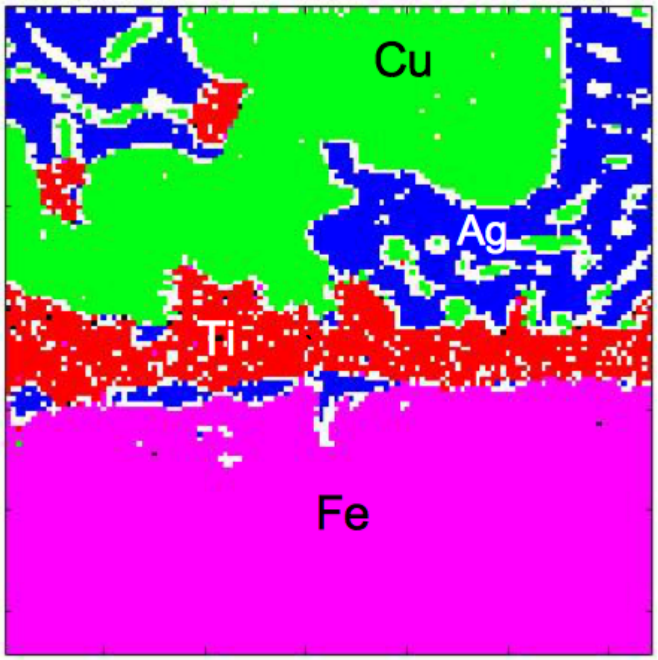
- Are principal components independent?
- Uncorrelated does not mean independent
- Orthogonal does not mean independent
- Independent variables *are* orthogonal and uncorrelated

Homeopathic ICA

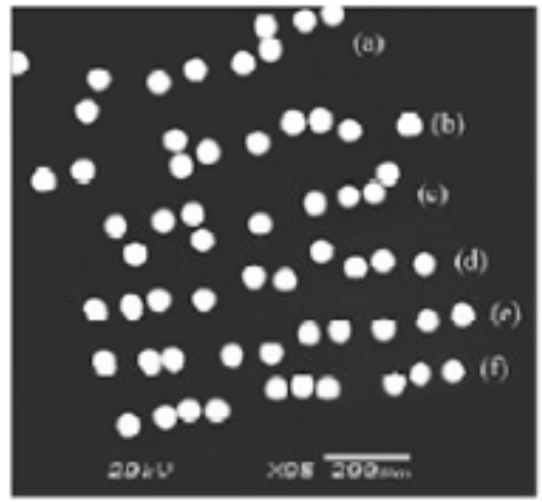




Homeopathic ICA



(a)



Wire Compositions

(a) 100% Ni

(b) 36% Ni, 64% Fe

(c) 70% Cu, 30% Zn

(d) 16% Cr, 84% Fe

(e) 13% Mn, 4% Ni, 83%Cu

(f) 100% Cu

Homeopathic ICA

X1	X2	Prob.	Joint. Prob.	Marg. Prob.
1	0	X1=0, X2=0	1/4	(1/2)x(1/2)
1	1	X1=0, X2=1	1/4	(1/2)x(1/2)
0	0	X1=1, x1=0	1/4	(1/2)x(1/2)
0	1	X1=1, X2=1	1/4	(1/2)x(1/2)

X1	X2		Joint Prob.	Marg. Prob.
1	0	X1=0, X2=0	0	(1/2)x(1/2)
1	0	X1=0, X2=1	1/2	(1/2)x(1/2)
0	1	X1=1, X2=0	1/2	(1/2)x(1/2)
0	1	X1=1, X2=1	0	(1/2)x(1/2)

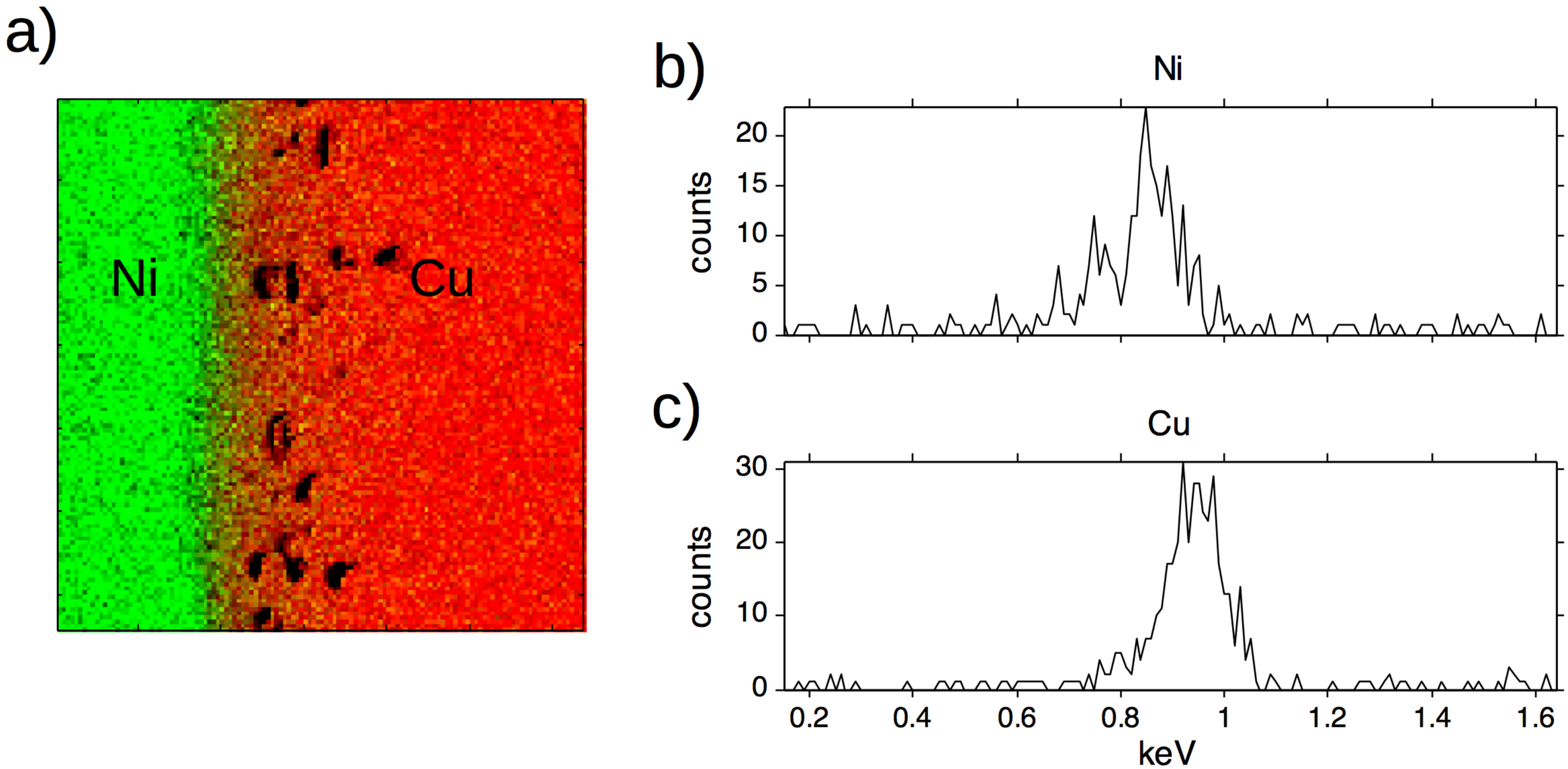
Homeopathic ICA

X1	X2		Joint Prob	Marg. Prob
1	0	X1=0, X2=0	8/12	(10/12)x(10/12)
1	0	X1=0, X2=1	2/12	(10/12)x(2/12)
0	1	X1=1, X2=0	2/12	(2/12)x(10/12)
0	1	X1=1, X2=1	0	(2/12)x(2/12)
0	0			
...	...			
0	0			

Homeopathic ICA

X1	X2		Joint Prob.	Marg. Prob
1	0	X1=0, X2=0	0.67	0.69
1	0	X1=0, X2=0	0.17	0.14
0	1	X1=1, X2=0	0.17	0.14
0	1	X1=1, X2=1	0	0.03
0	0			
...	...			
0	0			

Ni and Cu System



Energy dispersive X-ray spectrometry (EDS)
128x127 pixels, 150 keV values

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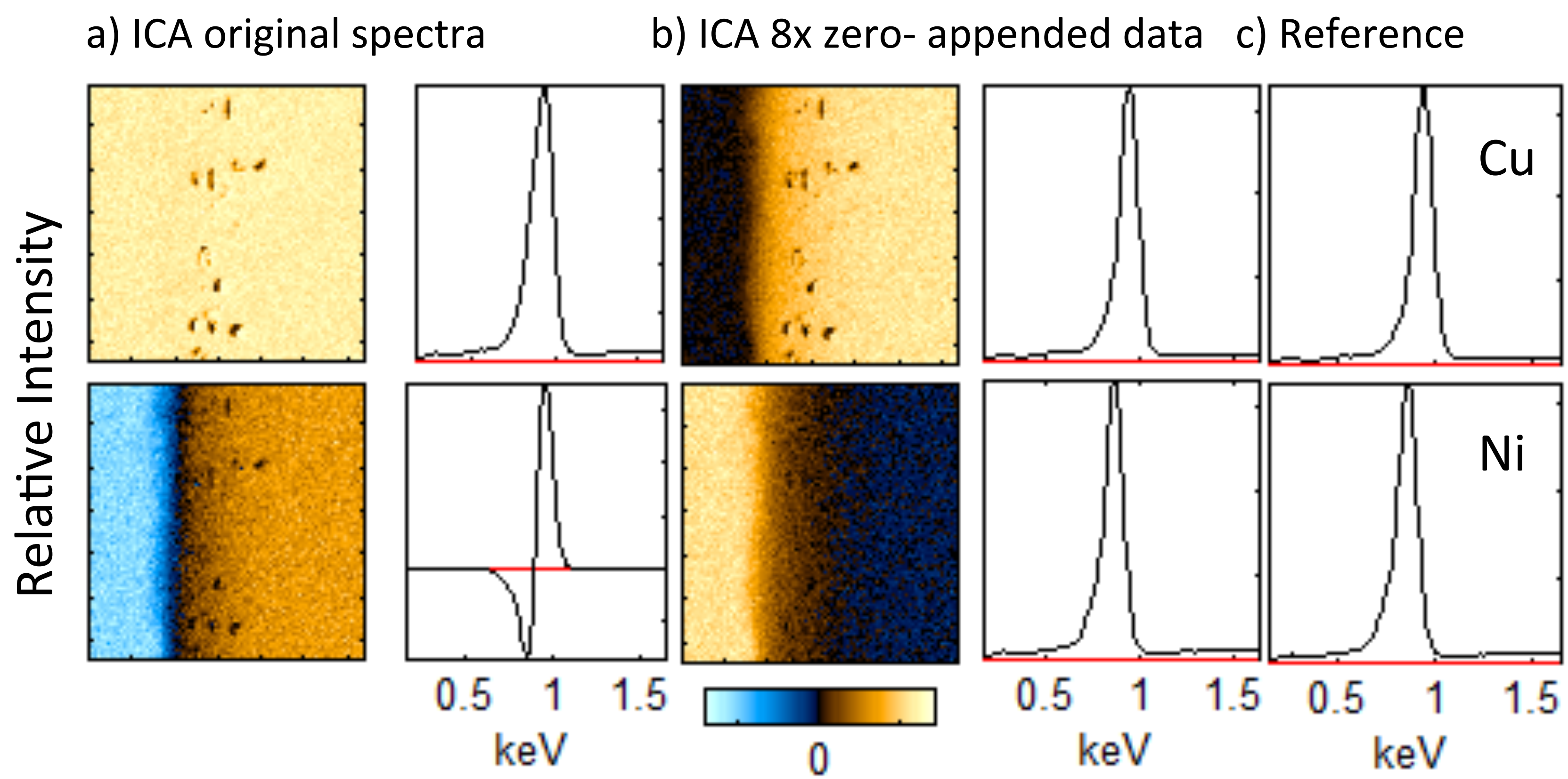

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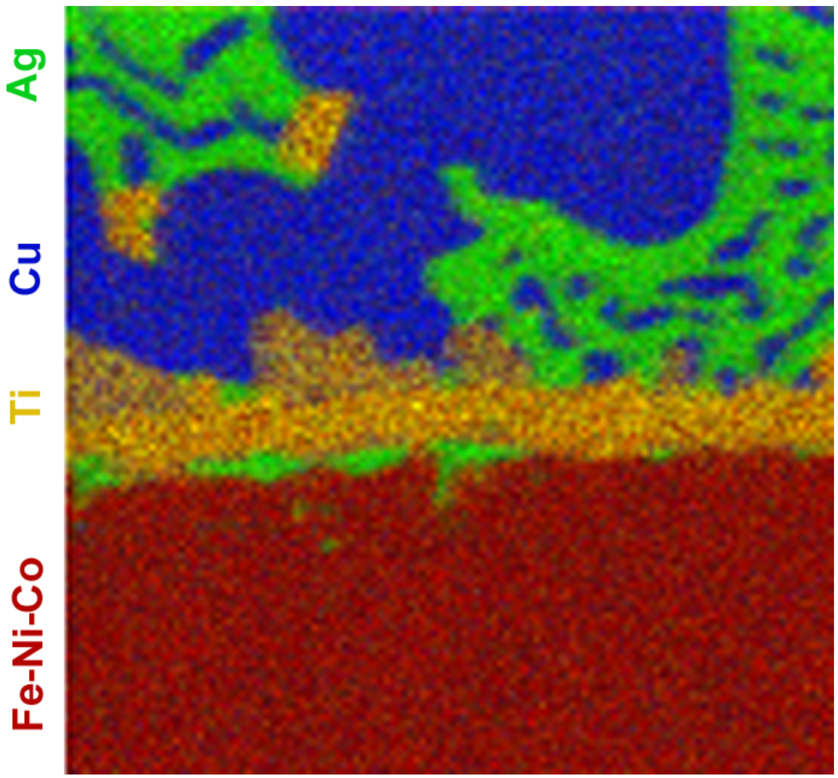

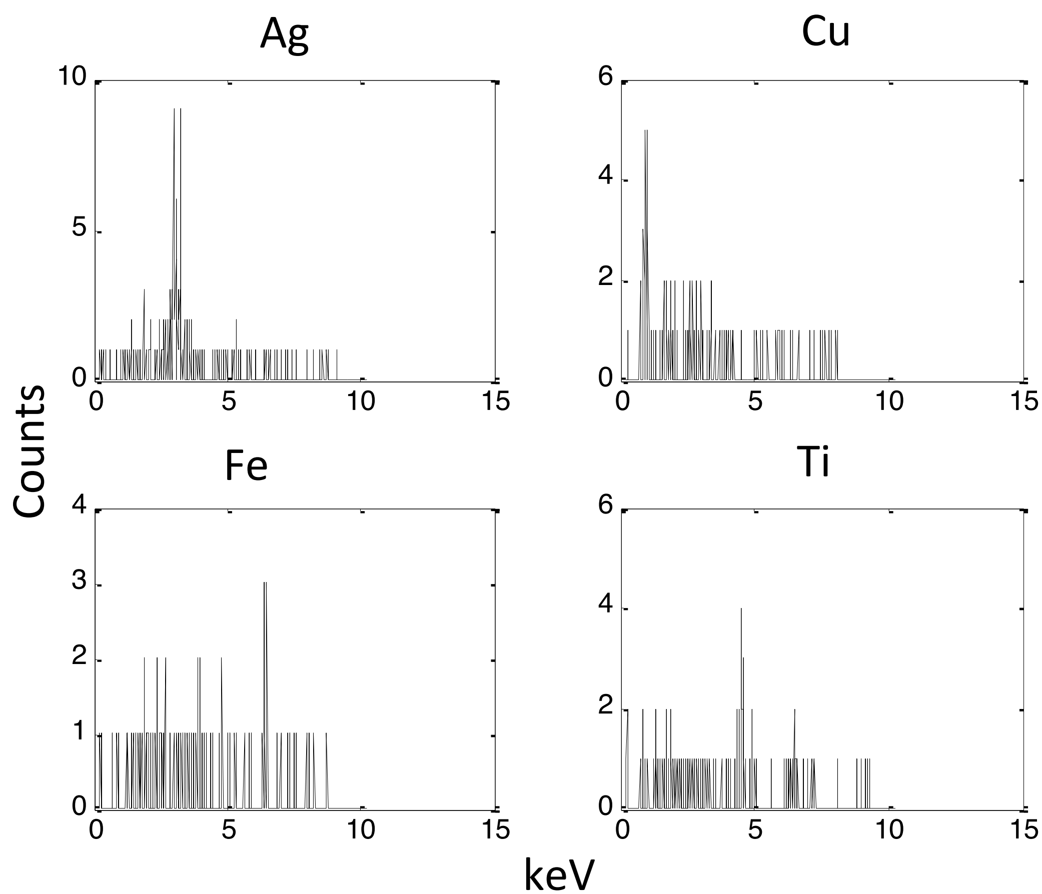

Energy dispersive X-ray spectrometry (EDS)
128x128 pixels, 1005 keV values

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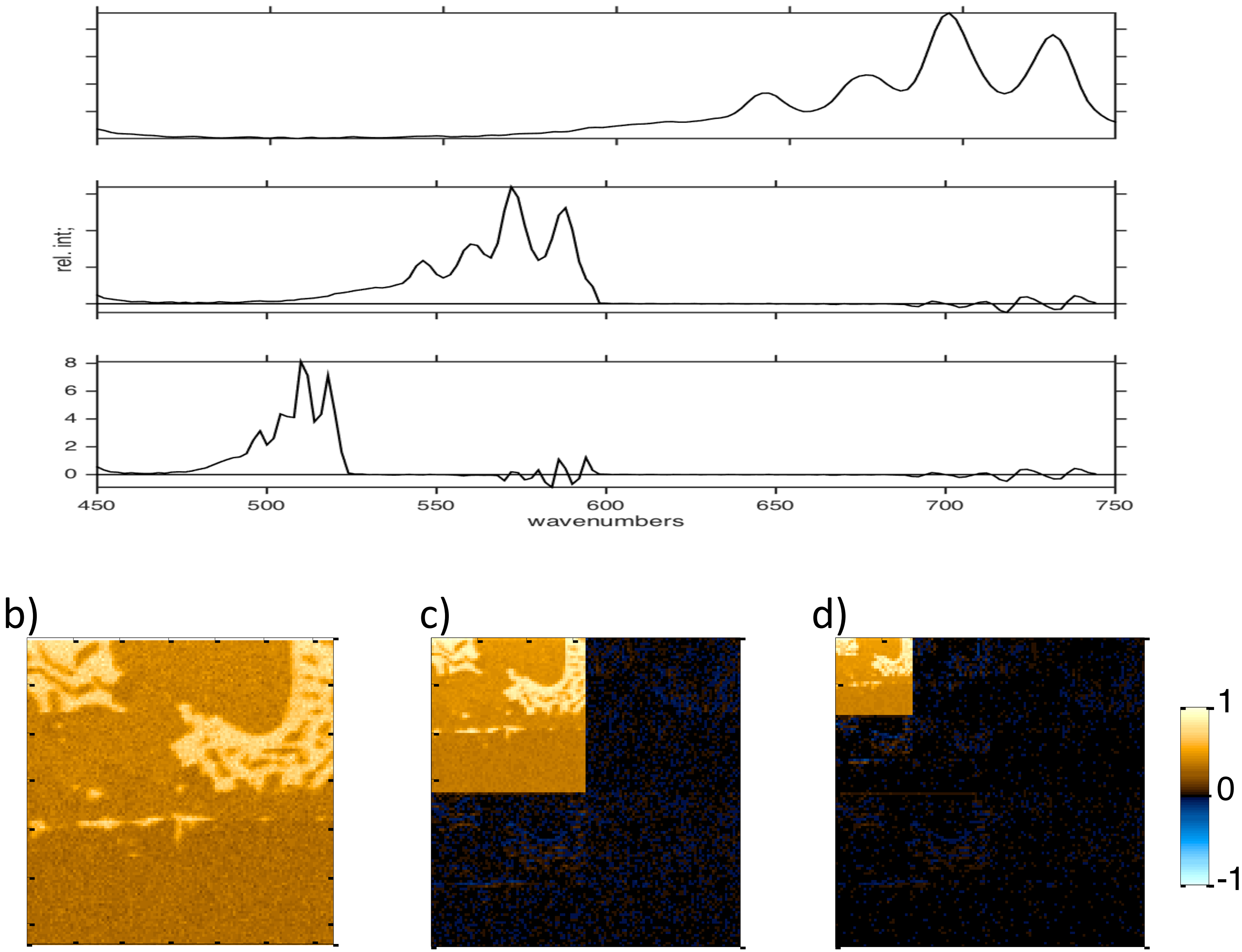
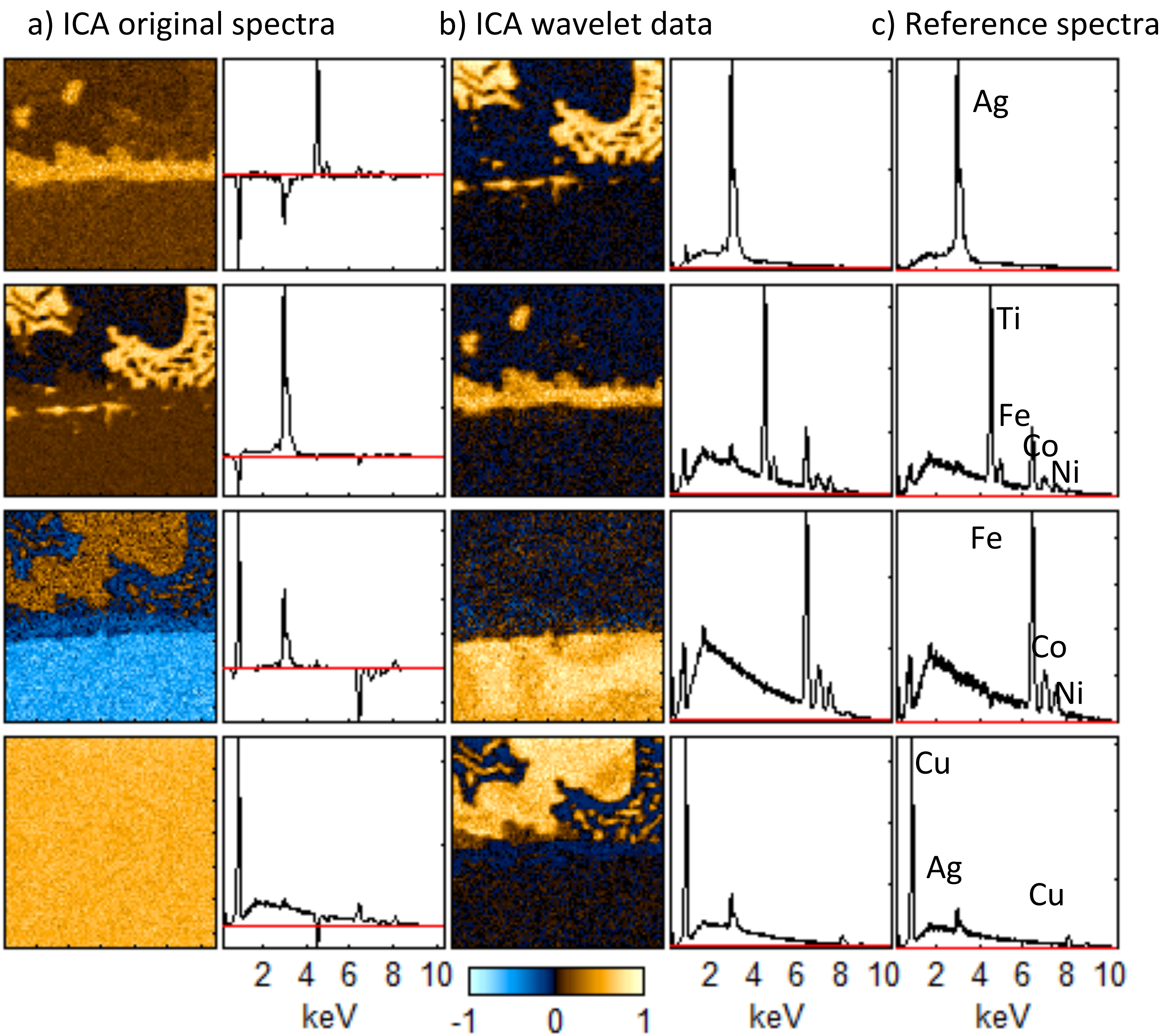

rel. int;
8
6
4
2
0
450
500
550
600
650
700
750
wavenumbers
b)
c)
d)
1
0
-1

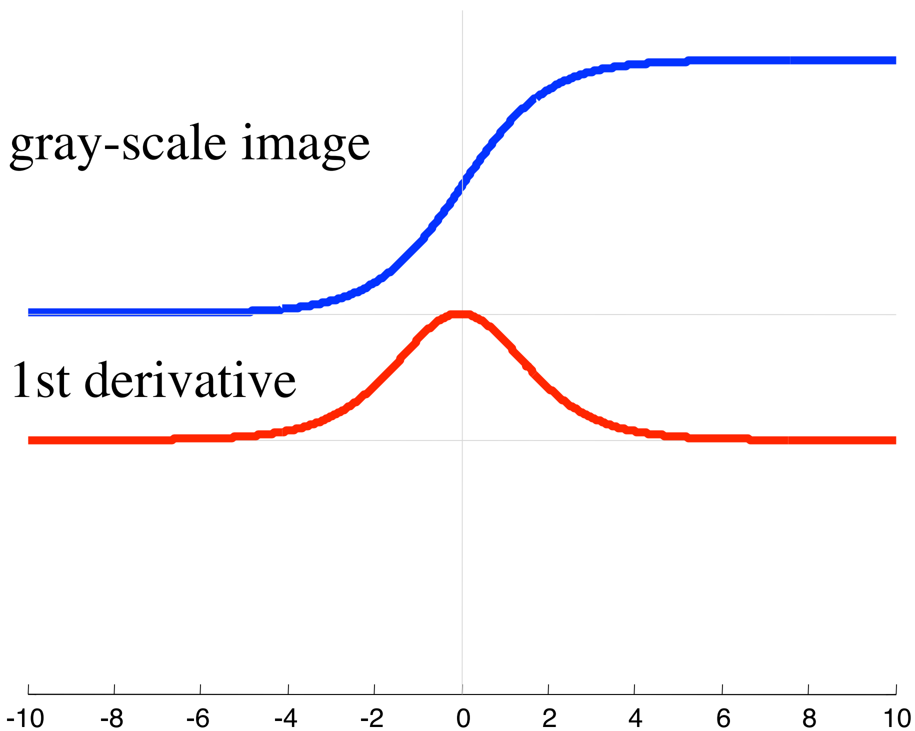


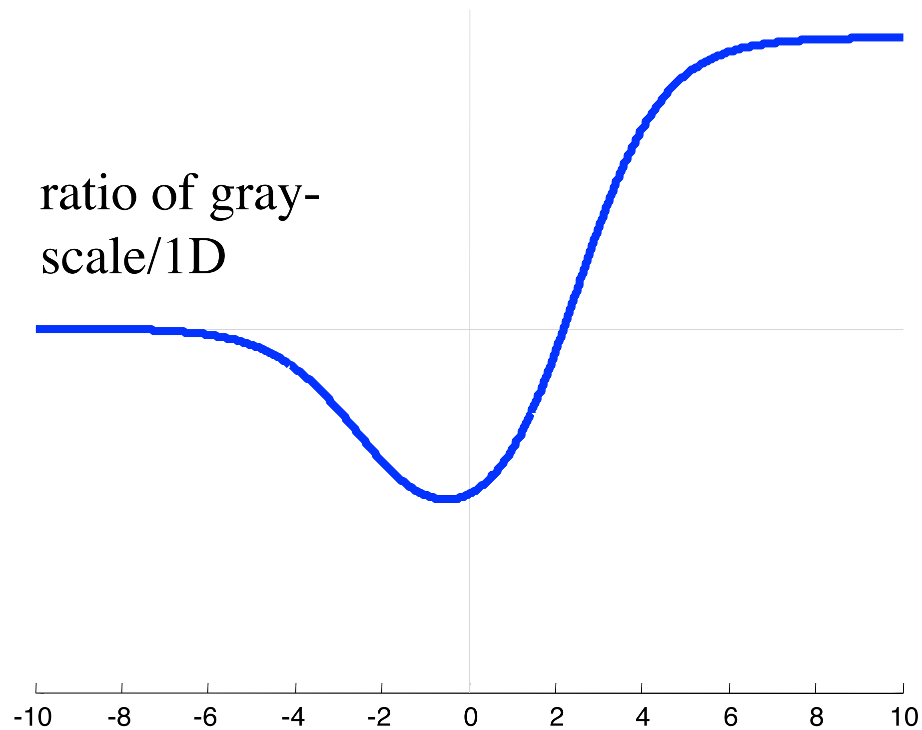
a) ICA original spectra
b) ICA wavelet data
c) Reference spectra
Ag
Ti
Fe
Co
Ni
Fe
Co
Ni
Cu
Ag
Cu
2 4 6 8 10
keV
-1 0 1

Other Ways of Focusing on Variance of Interest

- Maximum Autocorrelation Factors – find variance with spatial correlation
- Maximum Difference Factors – find variance with spatial transitions (multivariate edge detection)
- Clutter filters– ignore variance from specified regions

MAF





MAF finds locations in the image where the ratio of gray-scale to first derivative is a maximum

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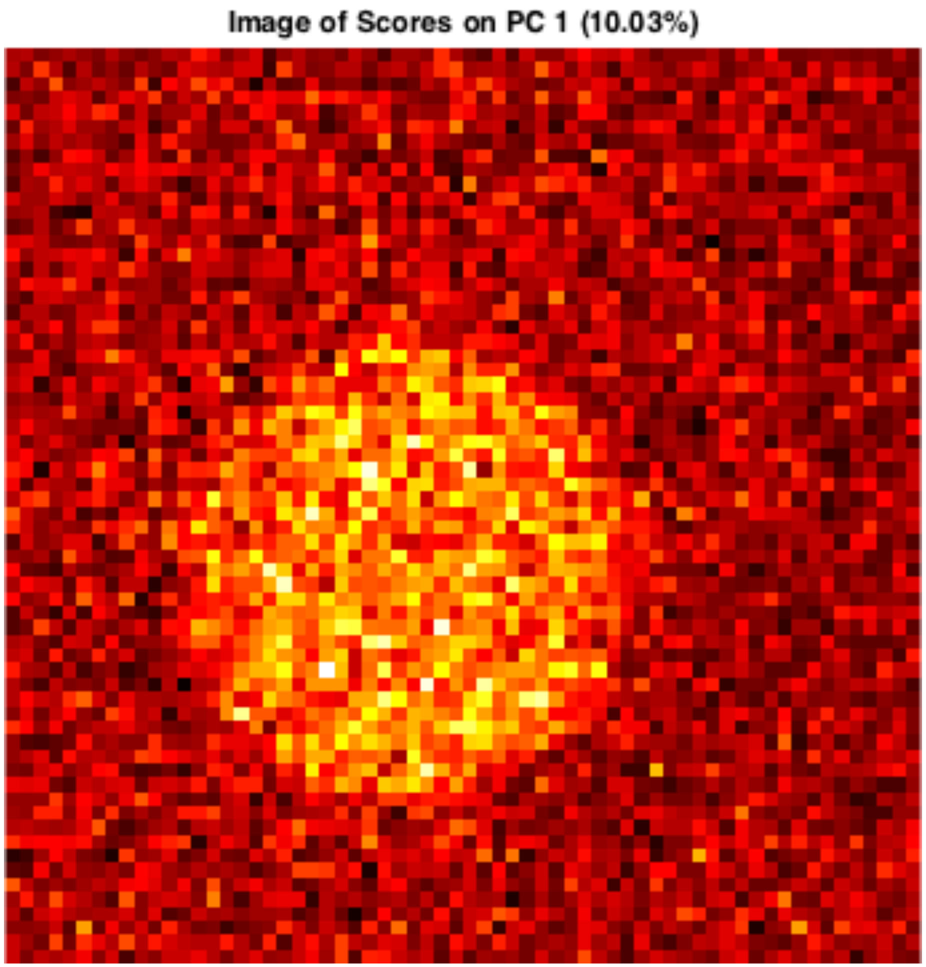
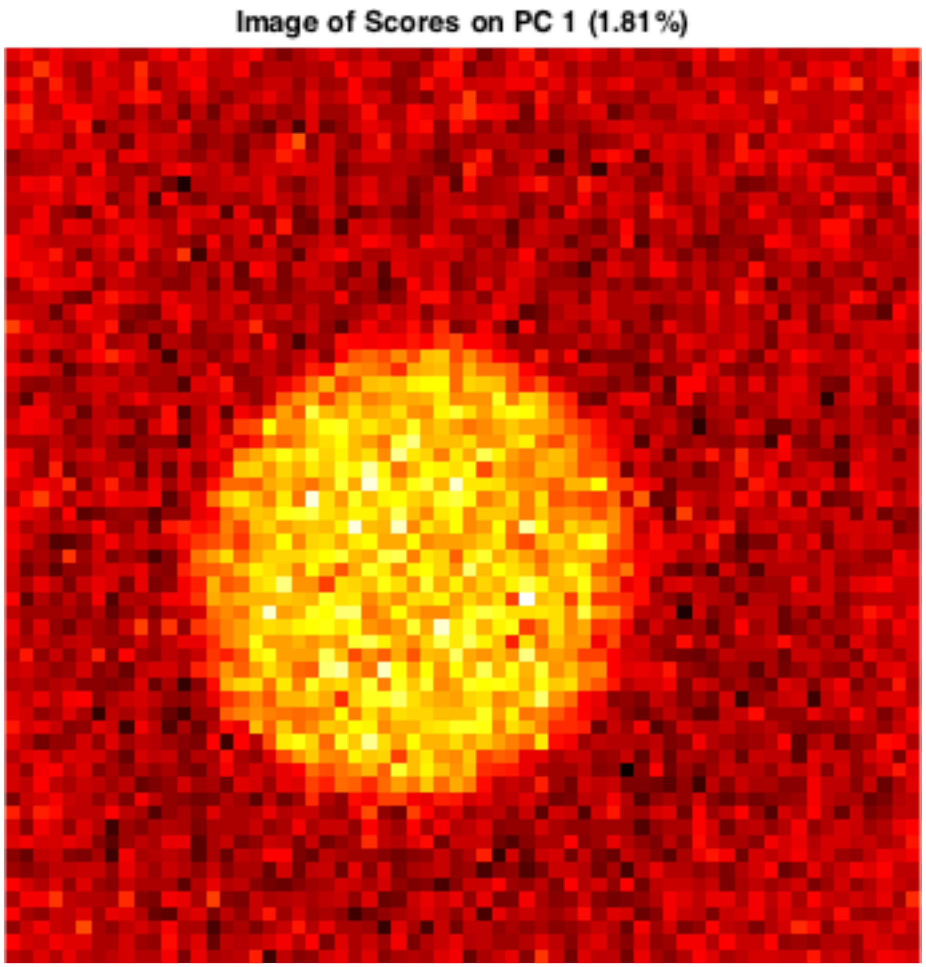
MAF on SIMS Image of PVA



PCA



MAF

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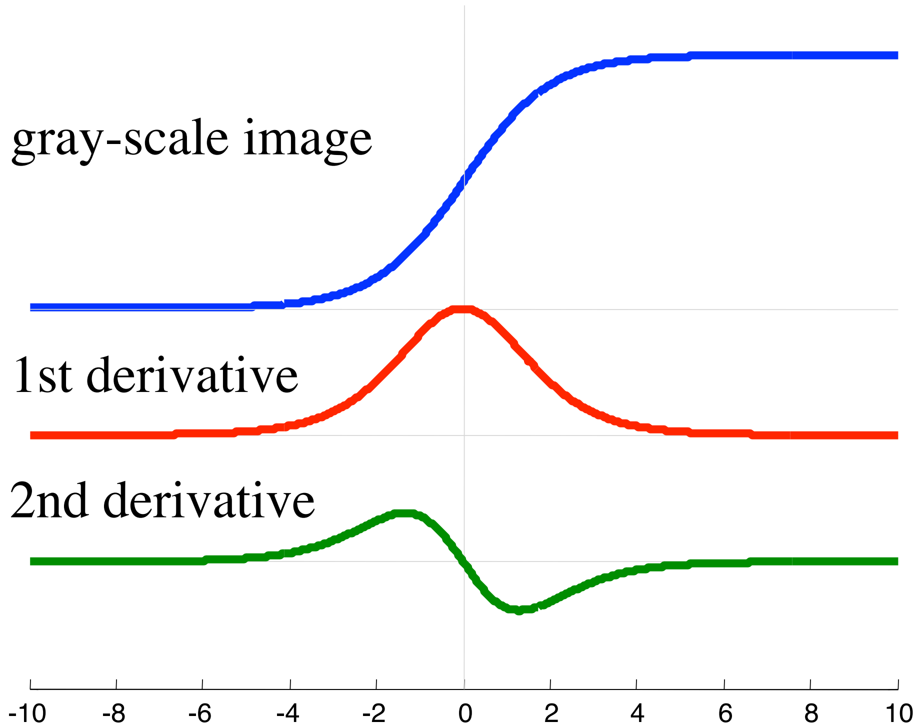
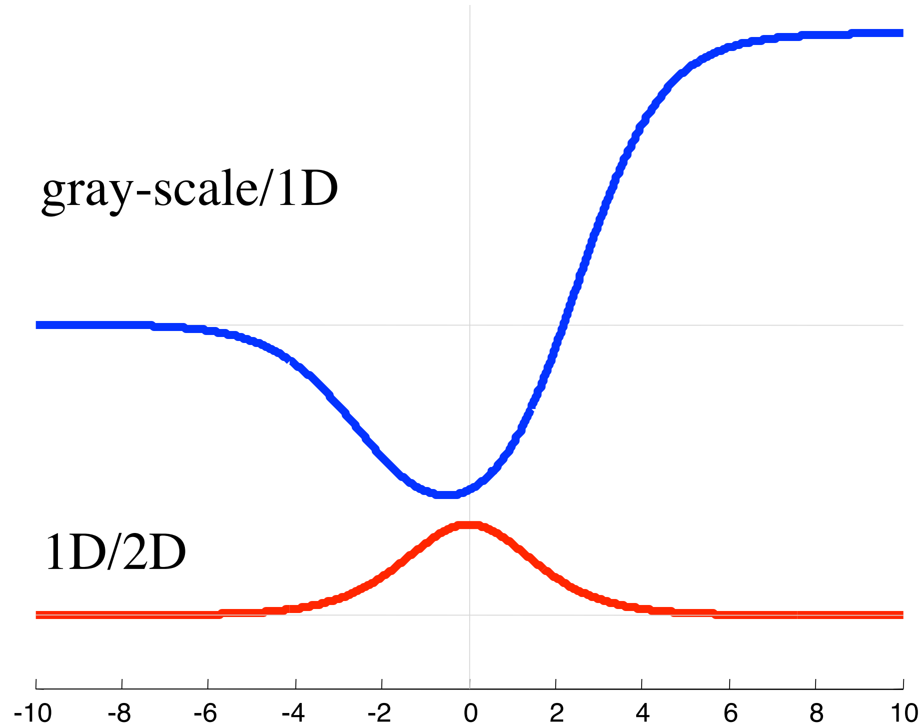
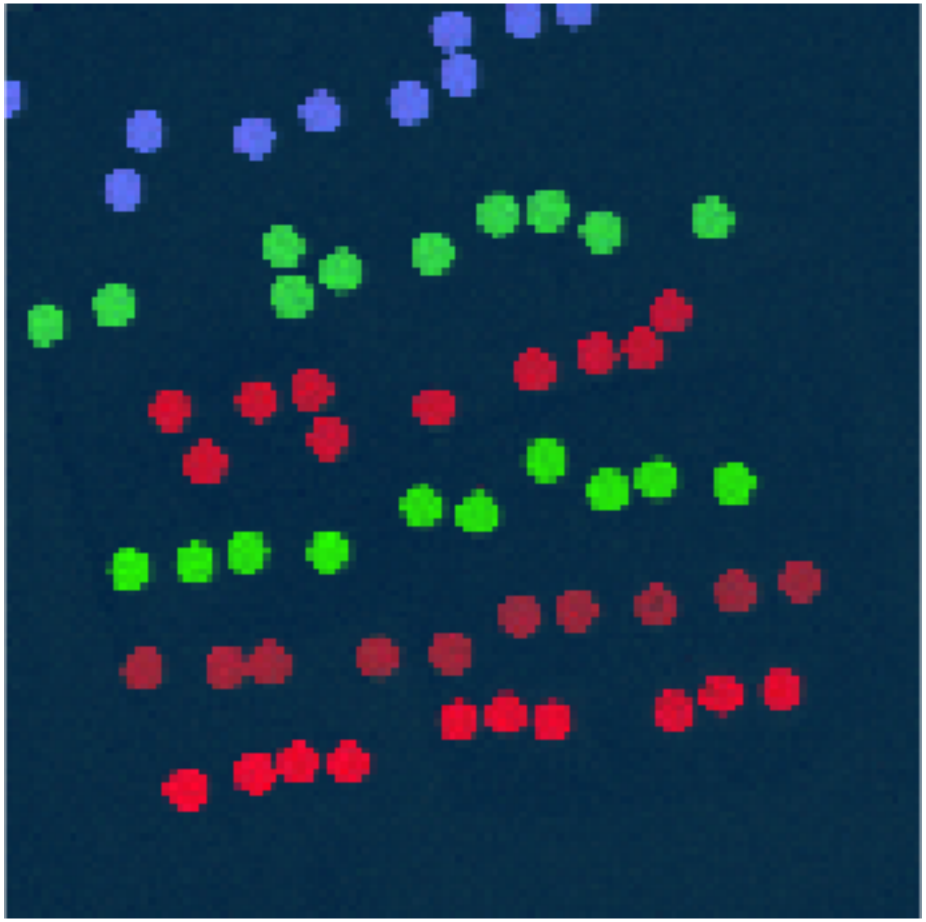
MDF



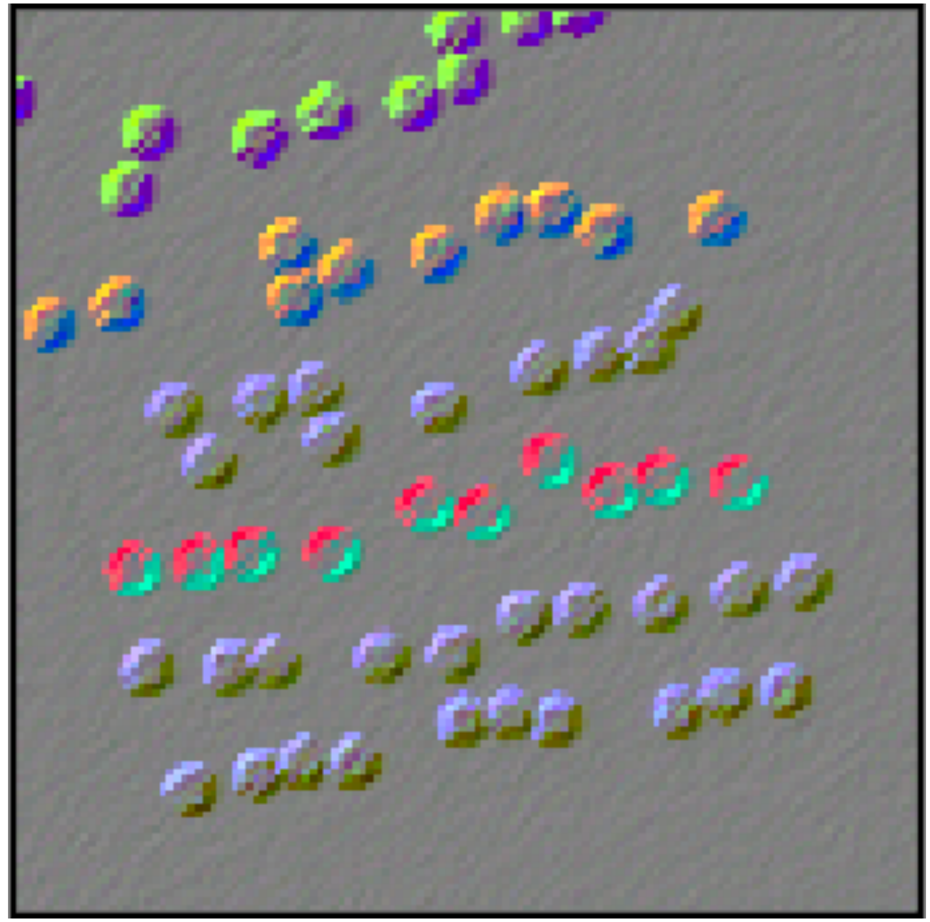


MDF finds locations in the image where the ratio of first to second derivative is a maximum

MDF on EDS of Wires



PCA



MDF

Clutter Filters

- Define areas where only variance is due to noise or other unwanted variation
- Develop filter to minimize this variance
  - Generalized Least Squares (GLS) Weighting
    - Inverse square root of clutter covariance
  - External Parameter Orthogonalization (EPO)
    - Project out first PCs of clutter covariance

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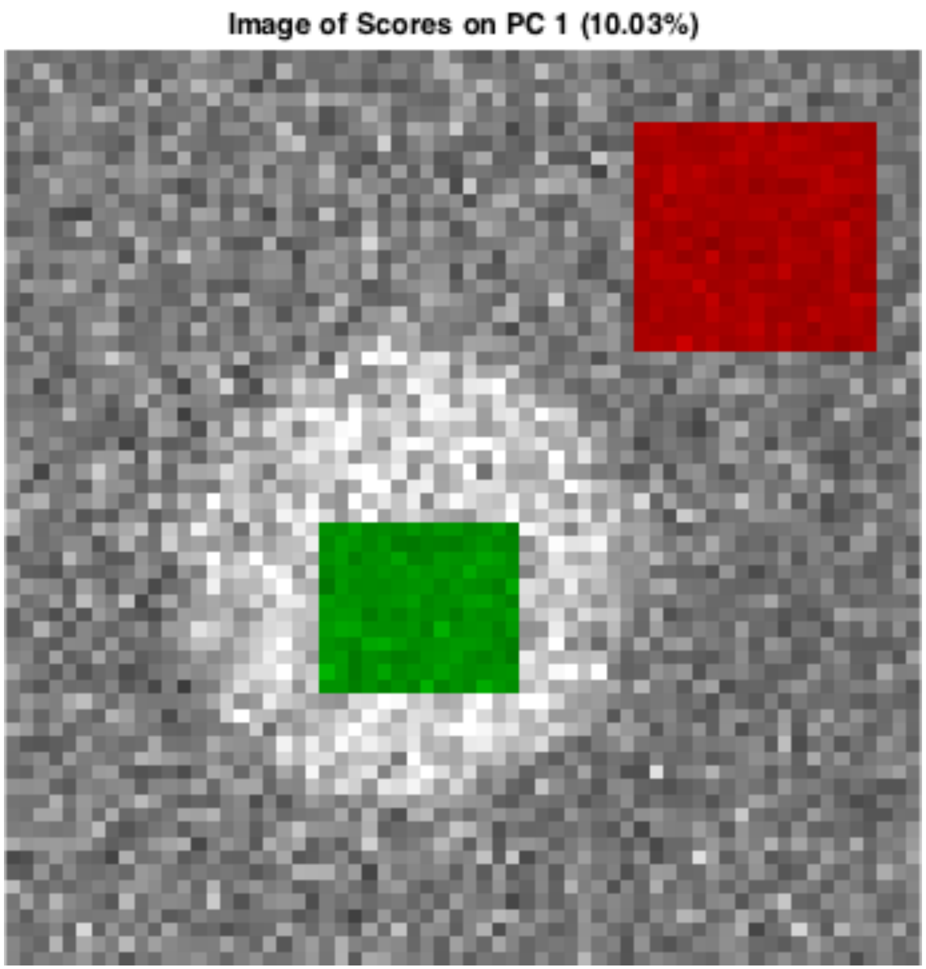
Define Clutter Areas

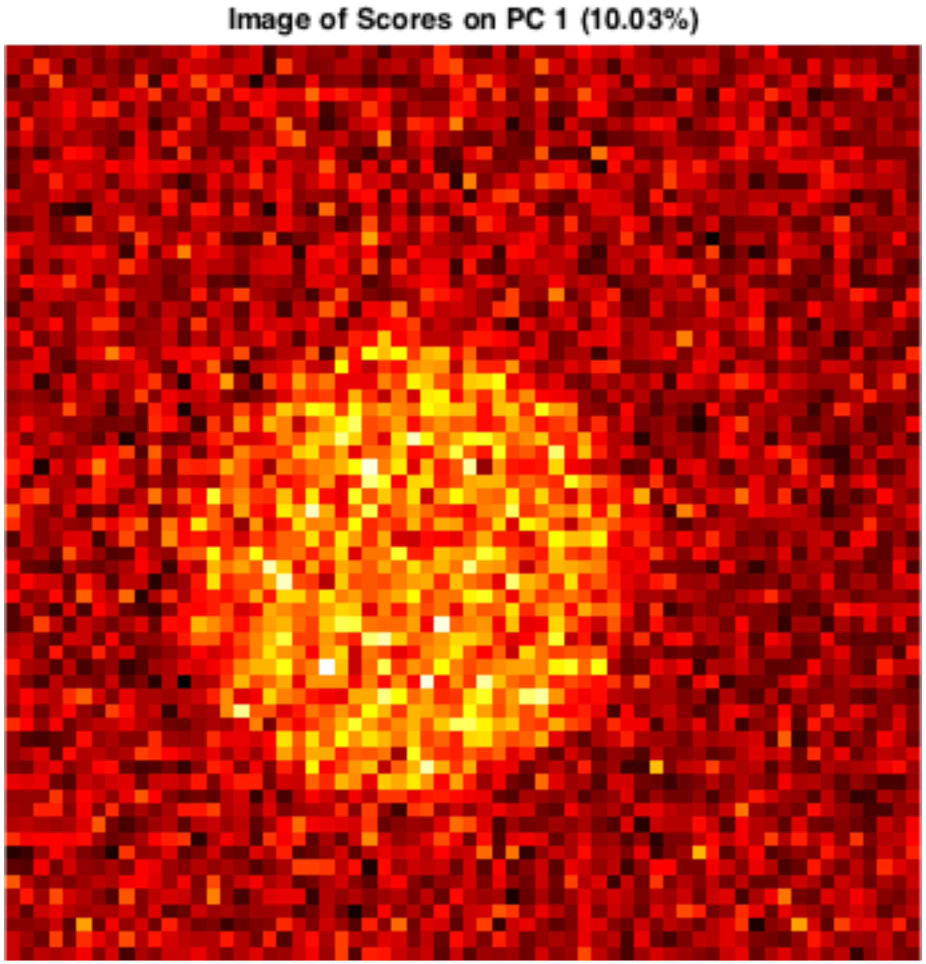


Only variation in marked areas is due to "noise"

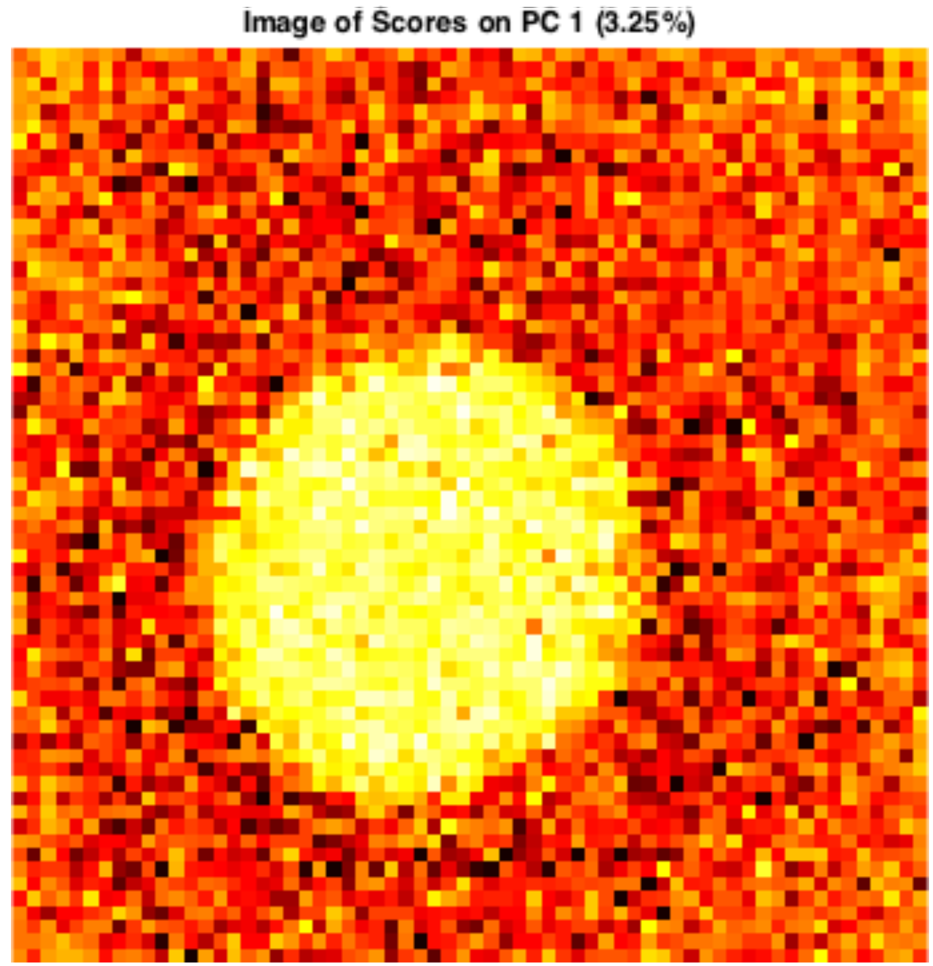
Center each area to its own mean, then combine areas

Develop GLS weighting from combined areas

GLS Filtered PVA



PCA



PCA with GLS

Conclusions

- Many ways to increase the contrast in multivariate images
- Method of choice depends on what features are to be emphasized
  - Spectral contrast
  - Image contrast
  - Continuous areas
  - Edges
  - Specific analytes

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Tools Readily Available

- PLS_Toolbox & MIA_Toolbox
  - for MATLAB users
- Solo+MIA
  - stand-alone for
    - Windows
    - Mac
    - Linux

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Acknowledgements

- Thanks to Mike Keenan for data sets and useful discussions
- Eigenvector software team