Deconvolving SIMS Images using Multivariate Curve Resolution with Contrast Constraints

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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

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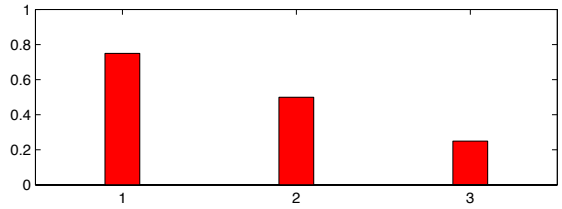
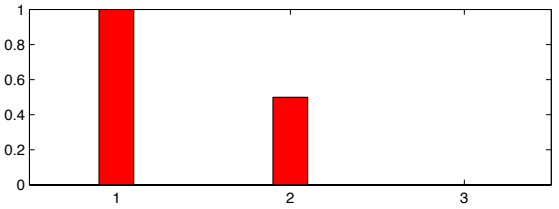
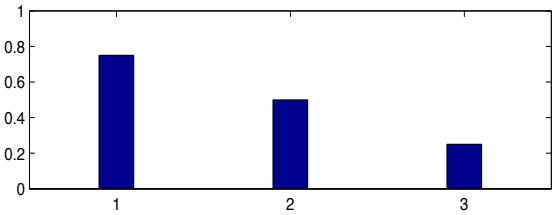
Pure Component 1a



Pure Component 1b

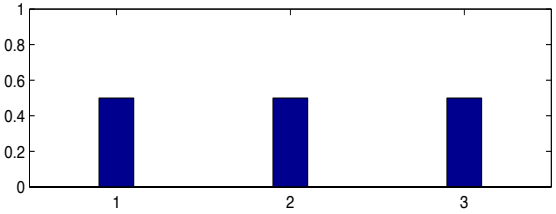


Mixtures



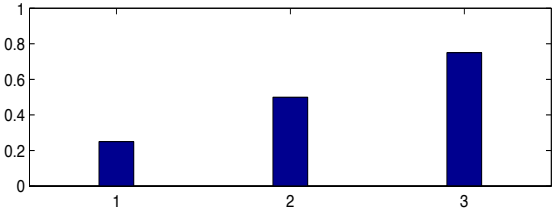
1.0 0.0

0.75 0.25



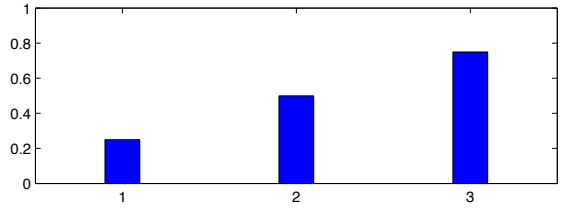
0.5 0.5

0.5 0.5

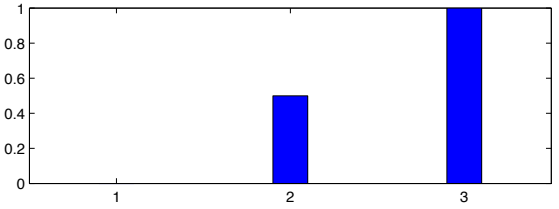


0.0 1.0

0.25 0.75



Pure Component 2a



Pure Component 2b

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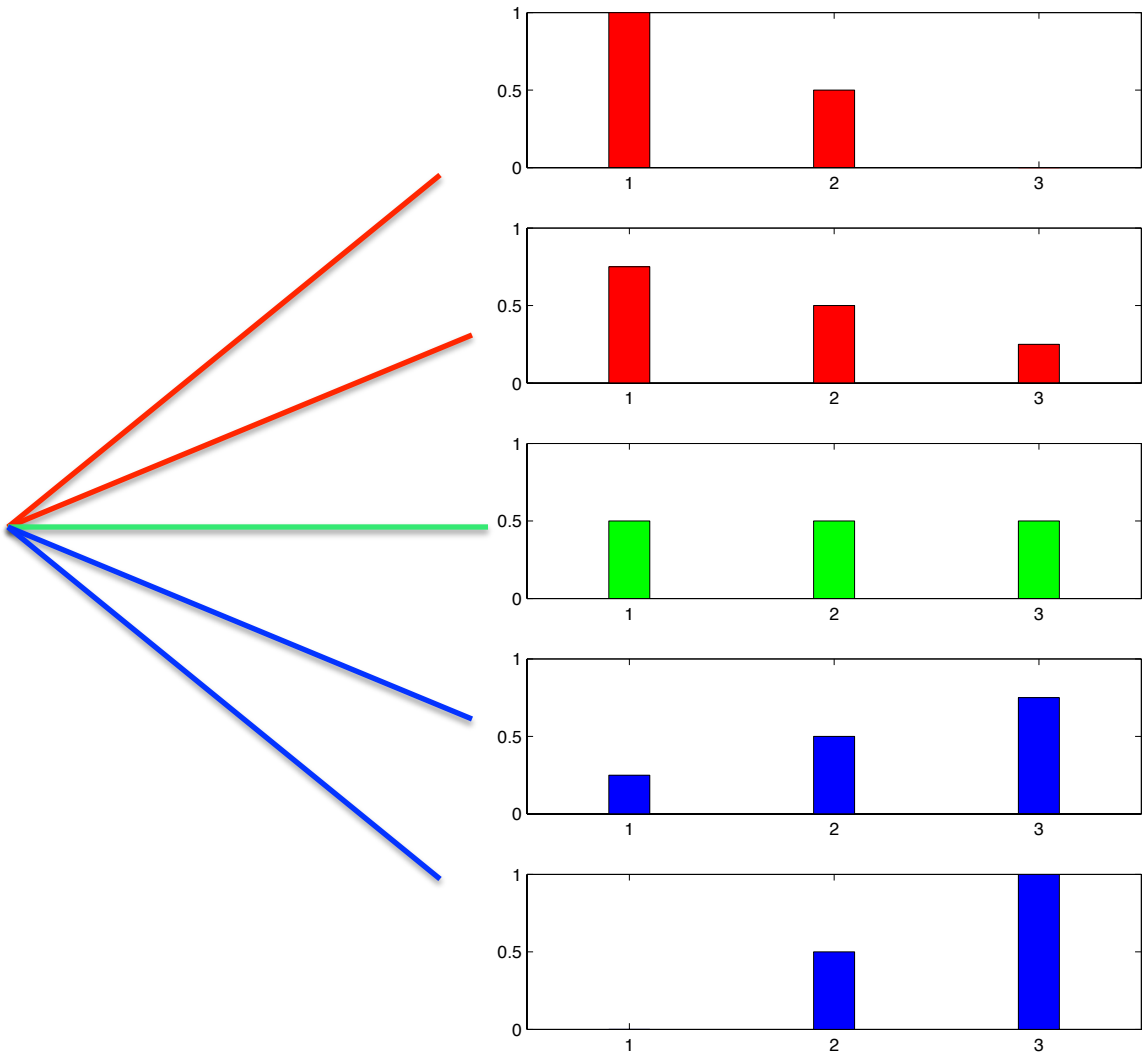
Observations

- "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



Solution Range A

Solution Range B

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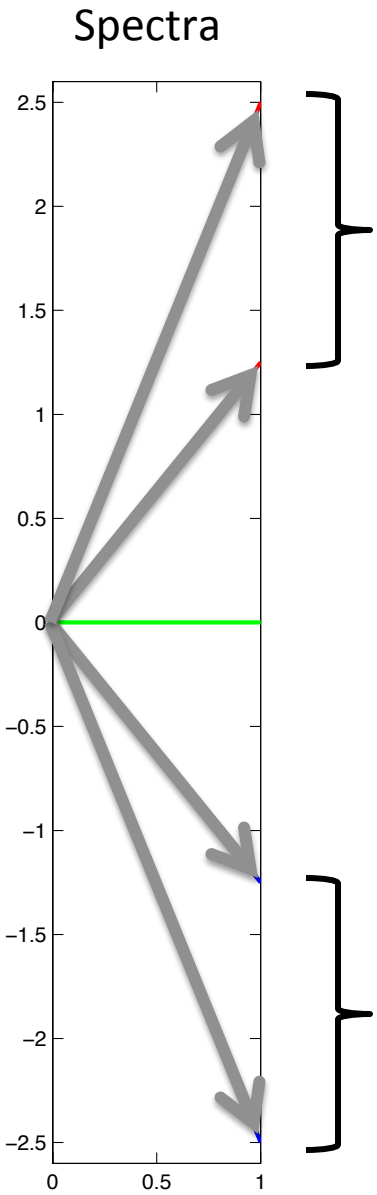
Solution Range



Solution Range A

Pure sample solution

Pure variable solution

Solution Range B

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Solution Range

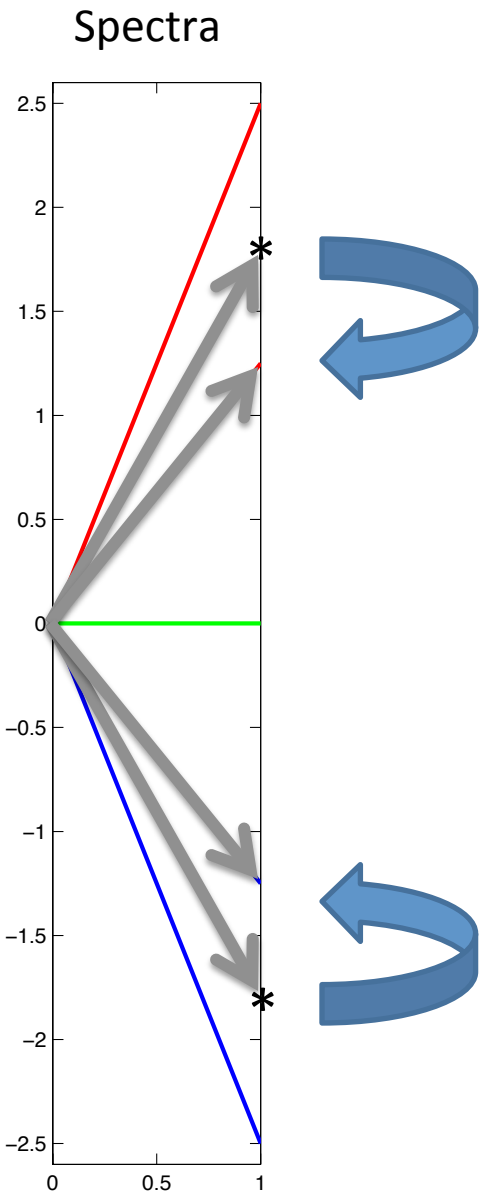

Image (concentration) contrast

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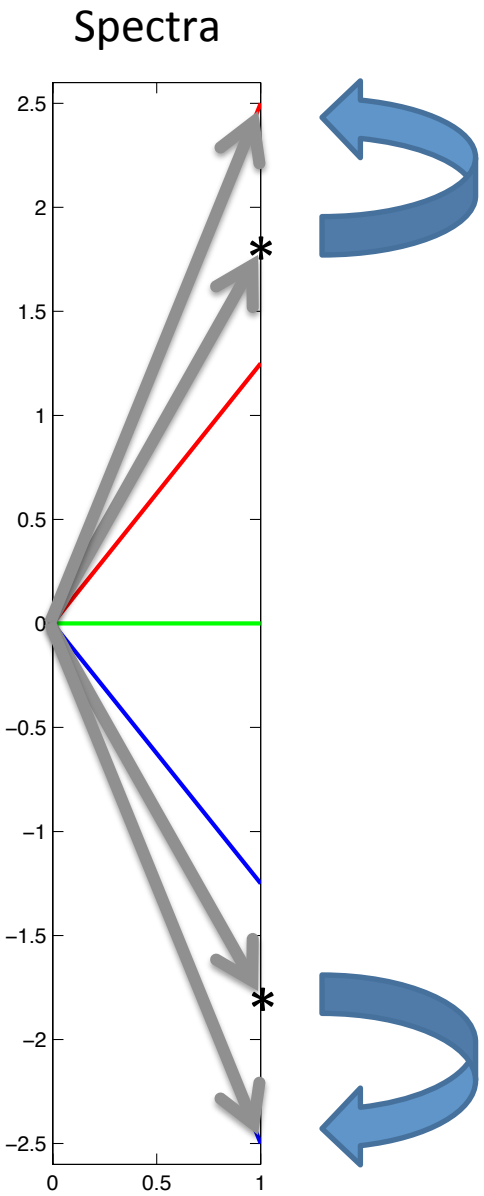
Solution Range



Spectral contrast

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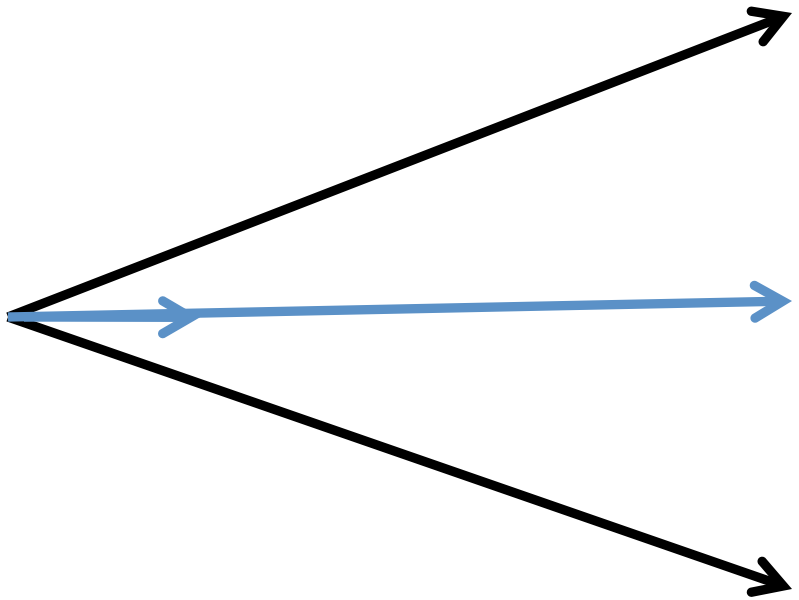
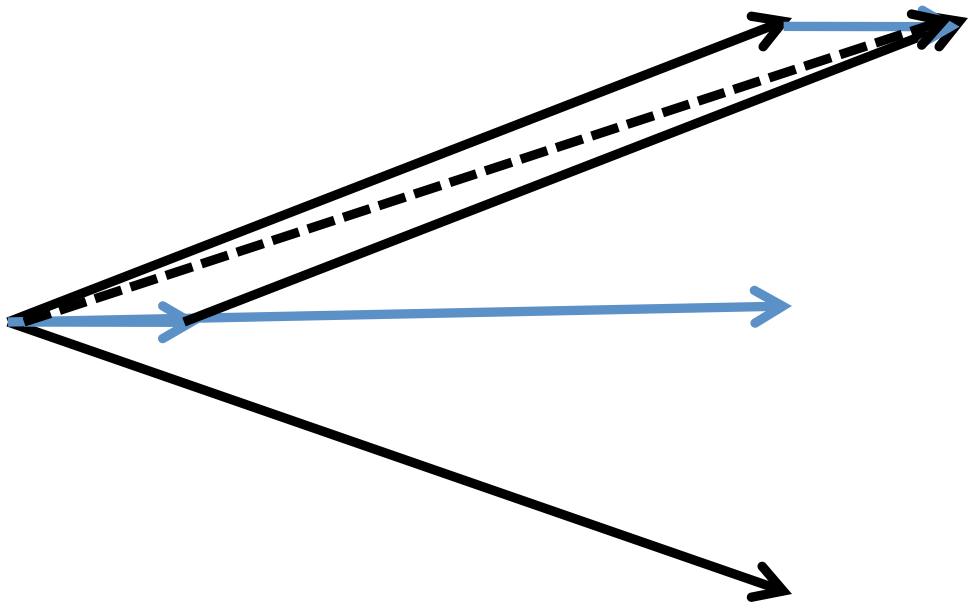
Decreasing Angles



Decreasing Angles



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

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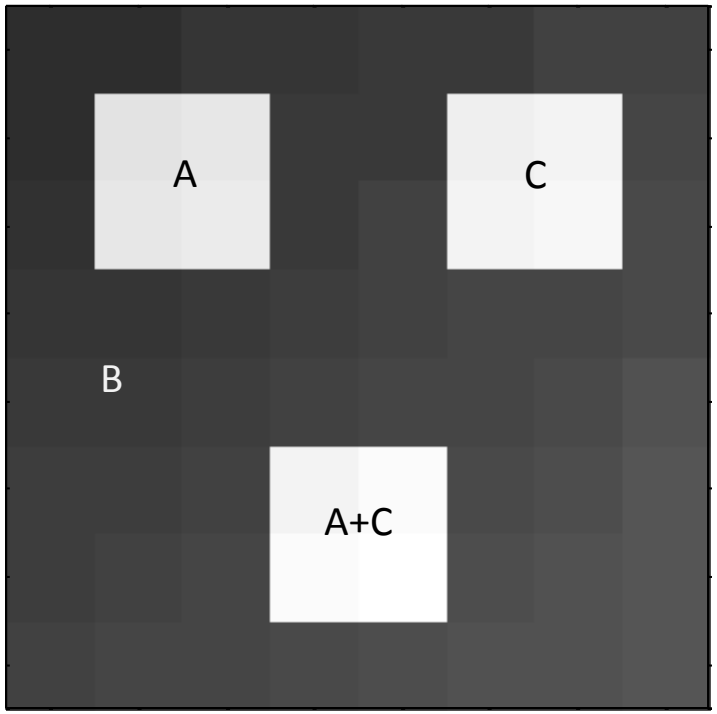
Simulated mixture



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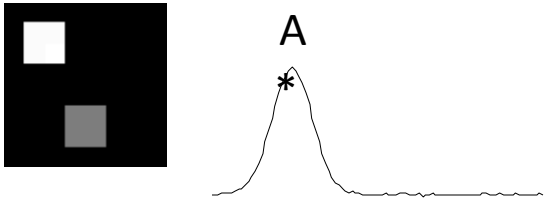
Spectral Contrast



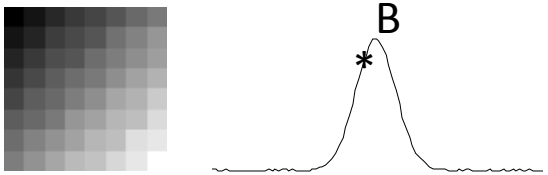
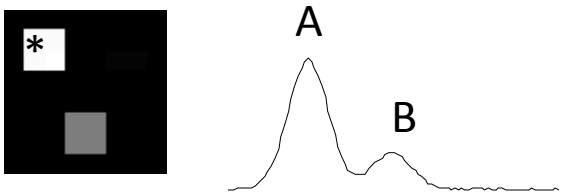
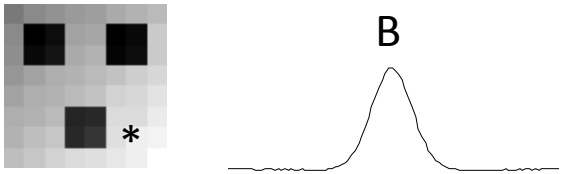
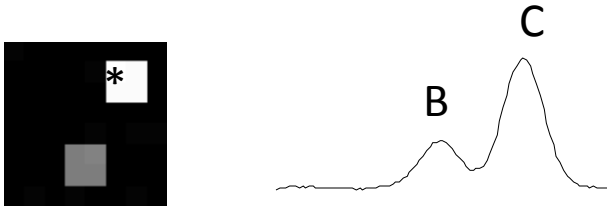


Image Contrast







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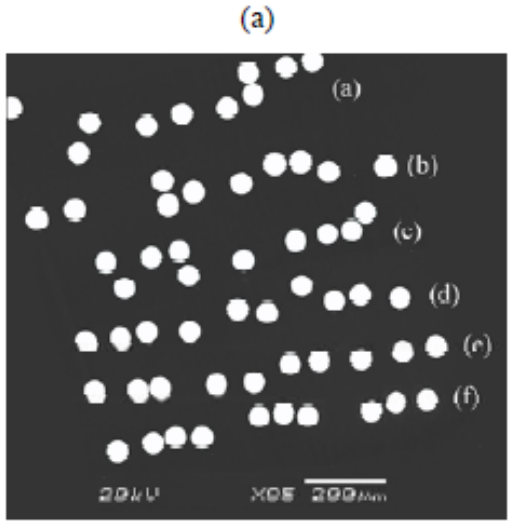
Weighted Poisson scaling

- 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

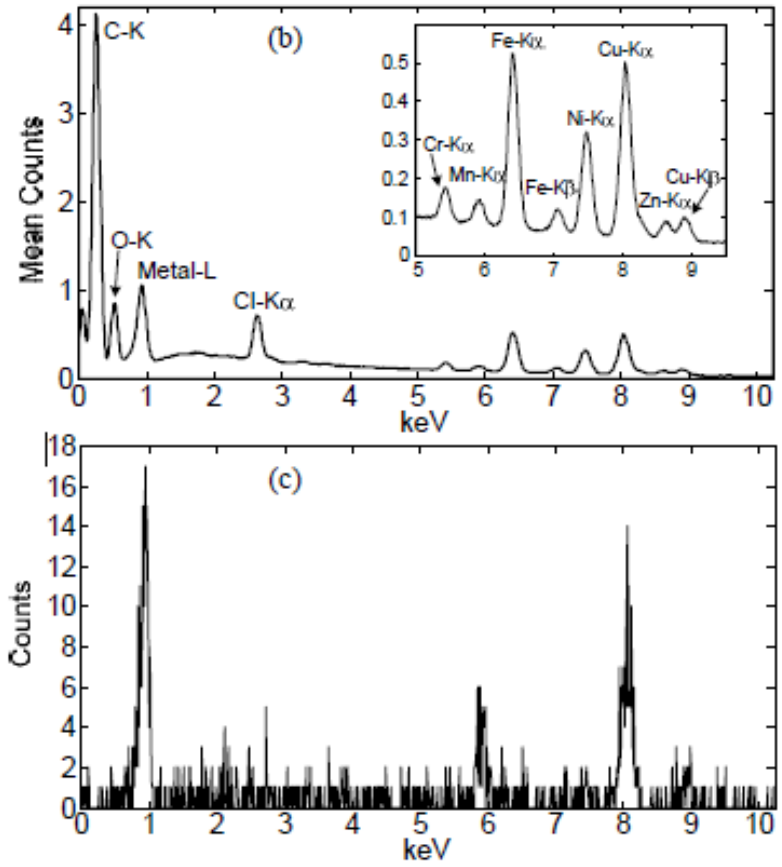
W. Windig, M. R. Keenan and B. M. Wise, "The effects of pre-processing of image data on self-modeling image analysis," J. Chemometrics 2008; 22: 500–509

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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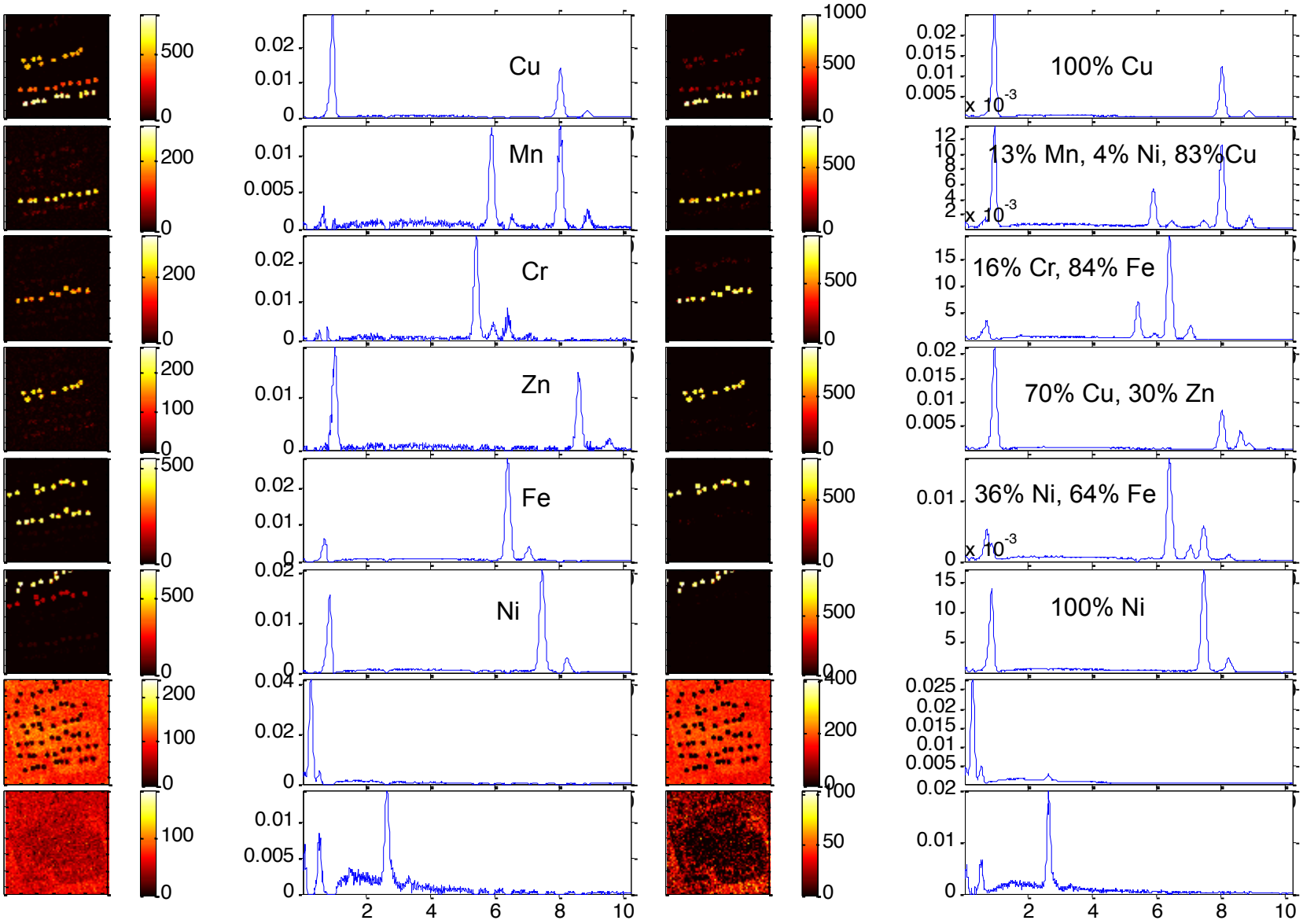
Spectral contrast Image contrast



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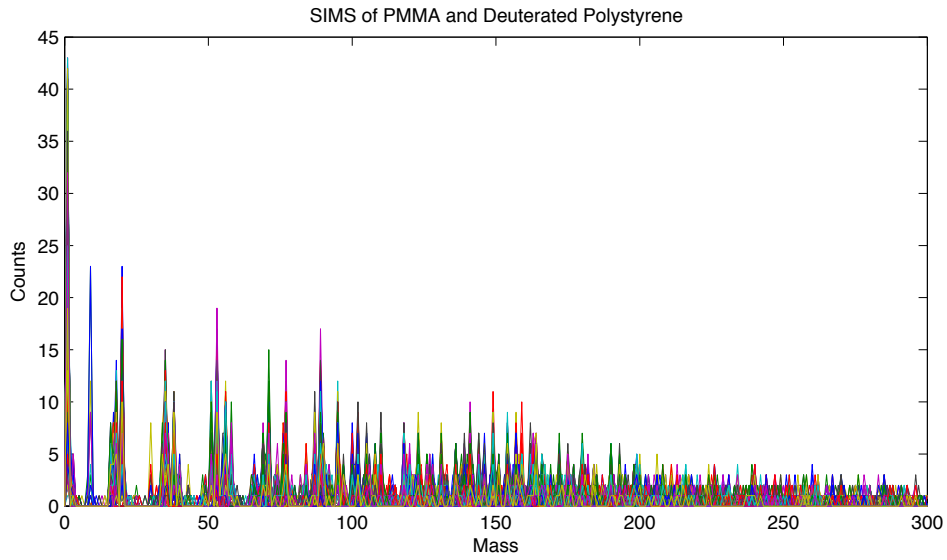
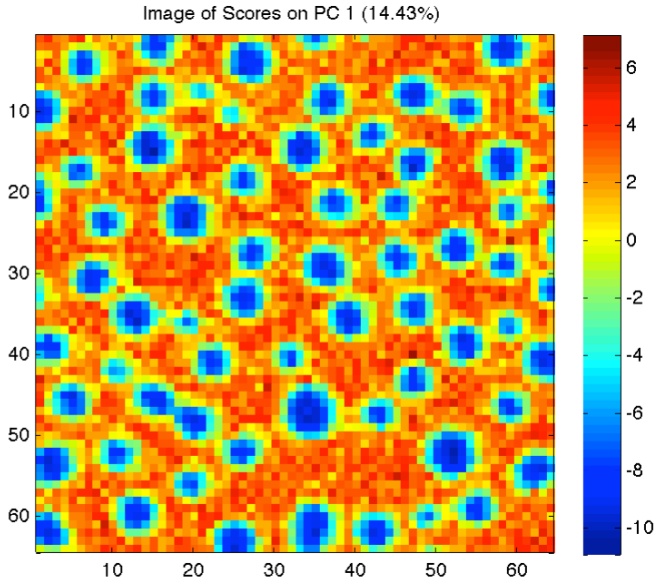
TOF-SIMS of PMMA and Deuterated Polystyrene

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





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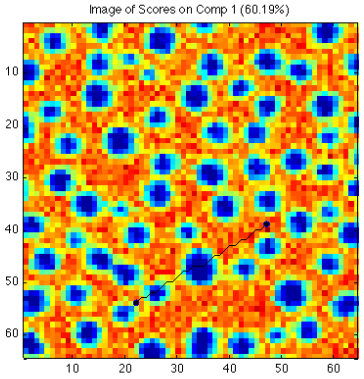
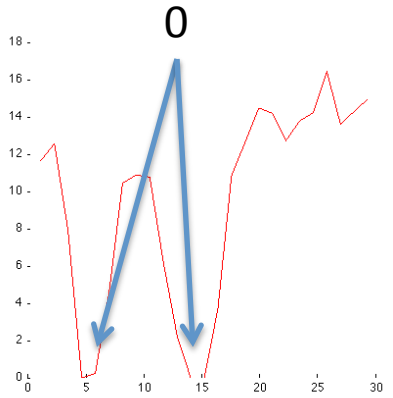
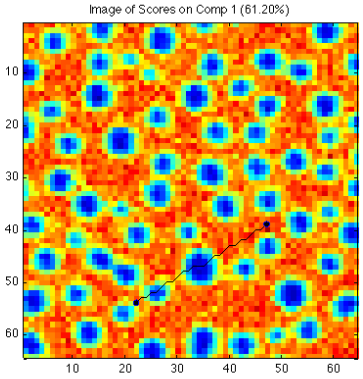
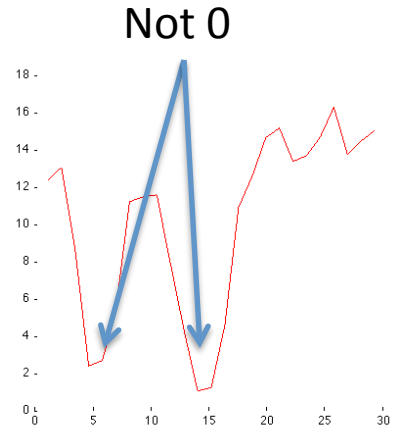
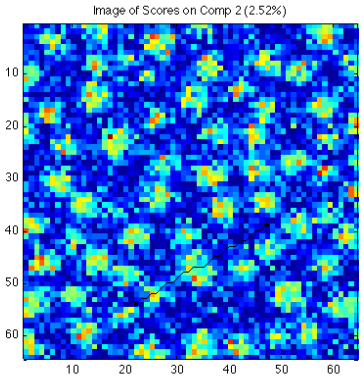
MCR Solutions for Concentrations

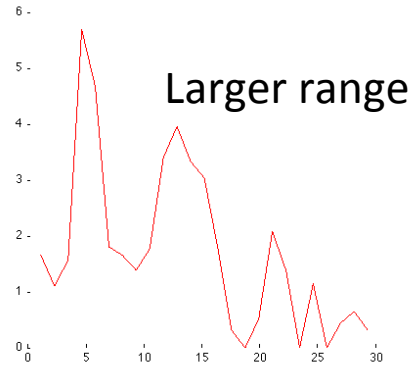


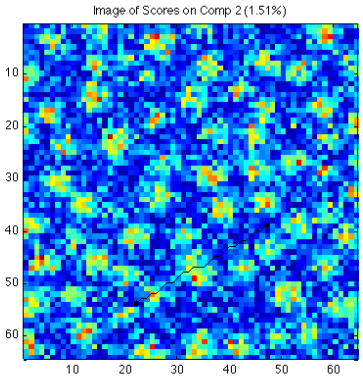


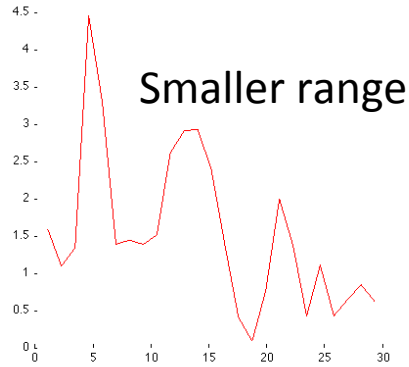












Concentration Contrast

Spectral Contrast

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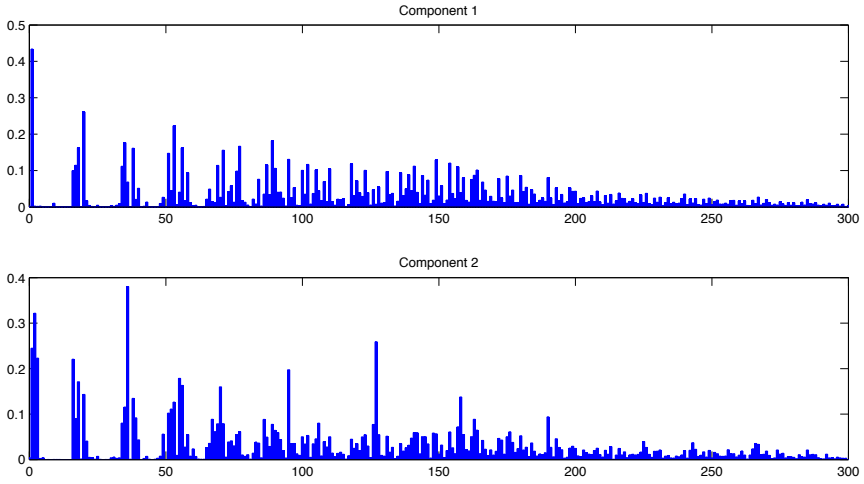
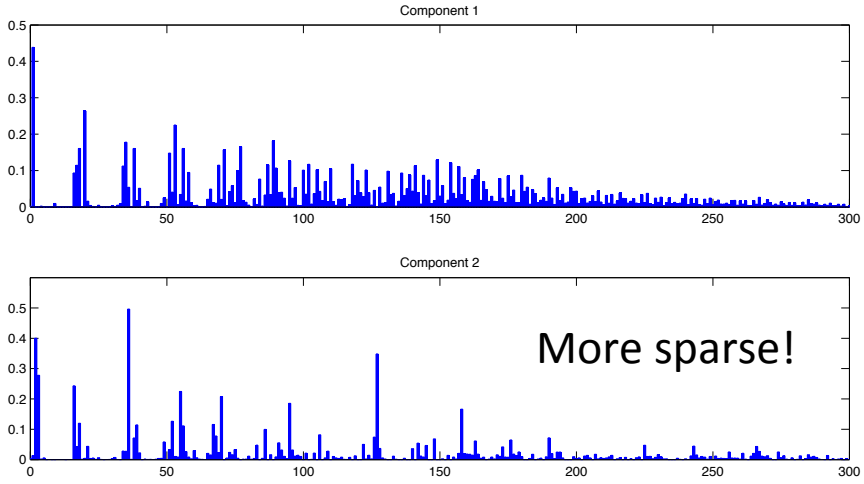
MCR Solutions for Spectra



Concentration Contrast



Spectral Contrast

Note: Poisson scaled solutions!

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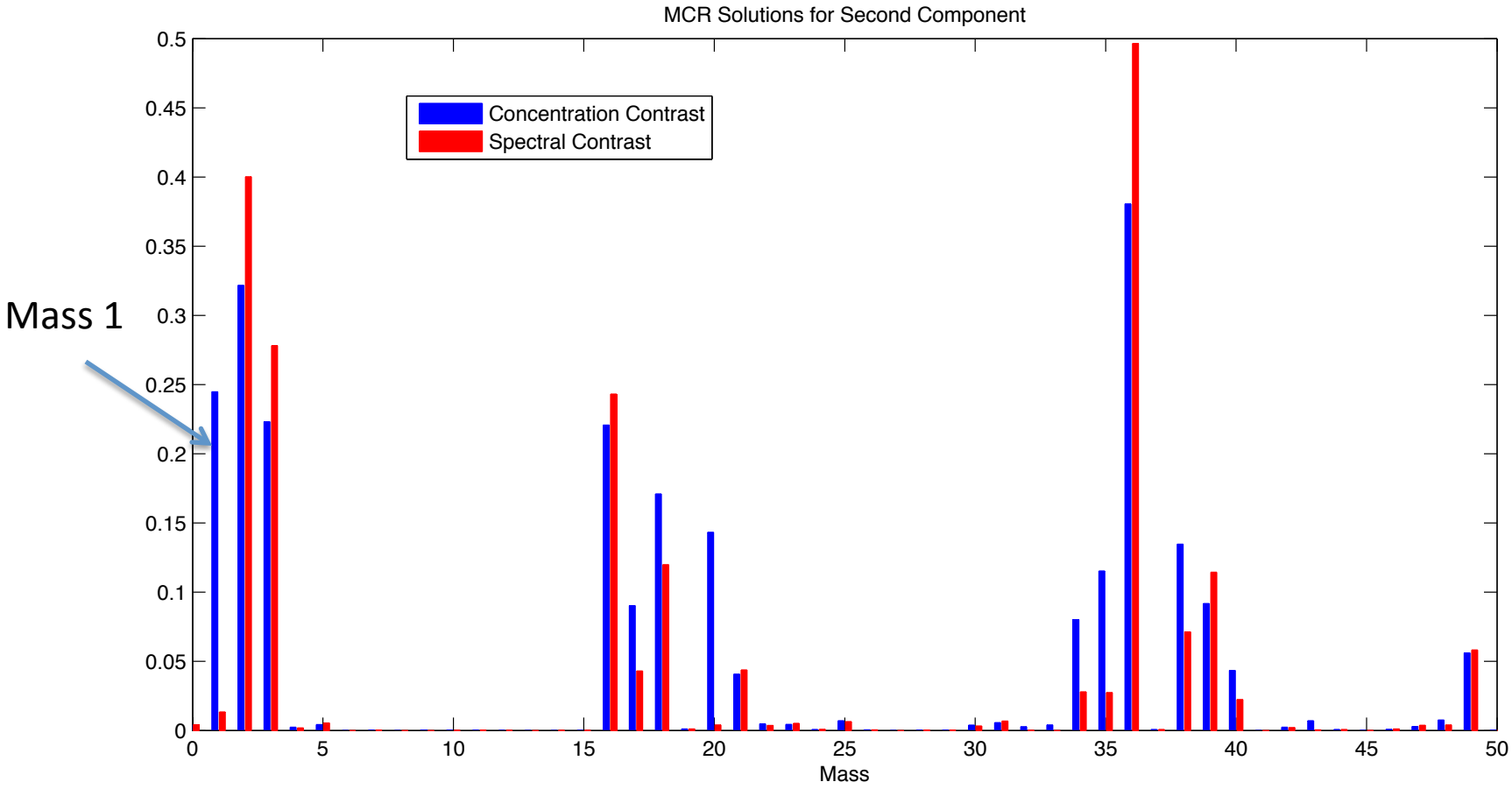
Second Component Comparison



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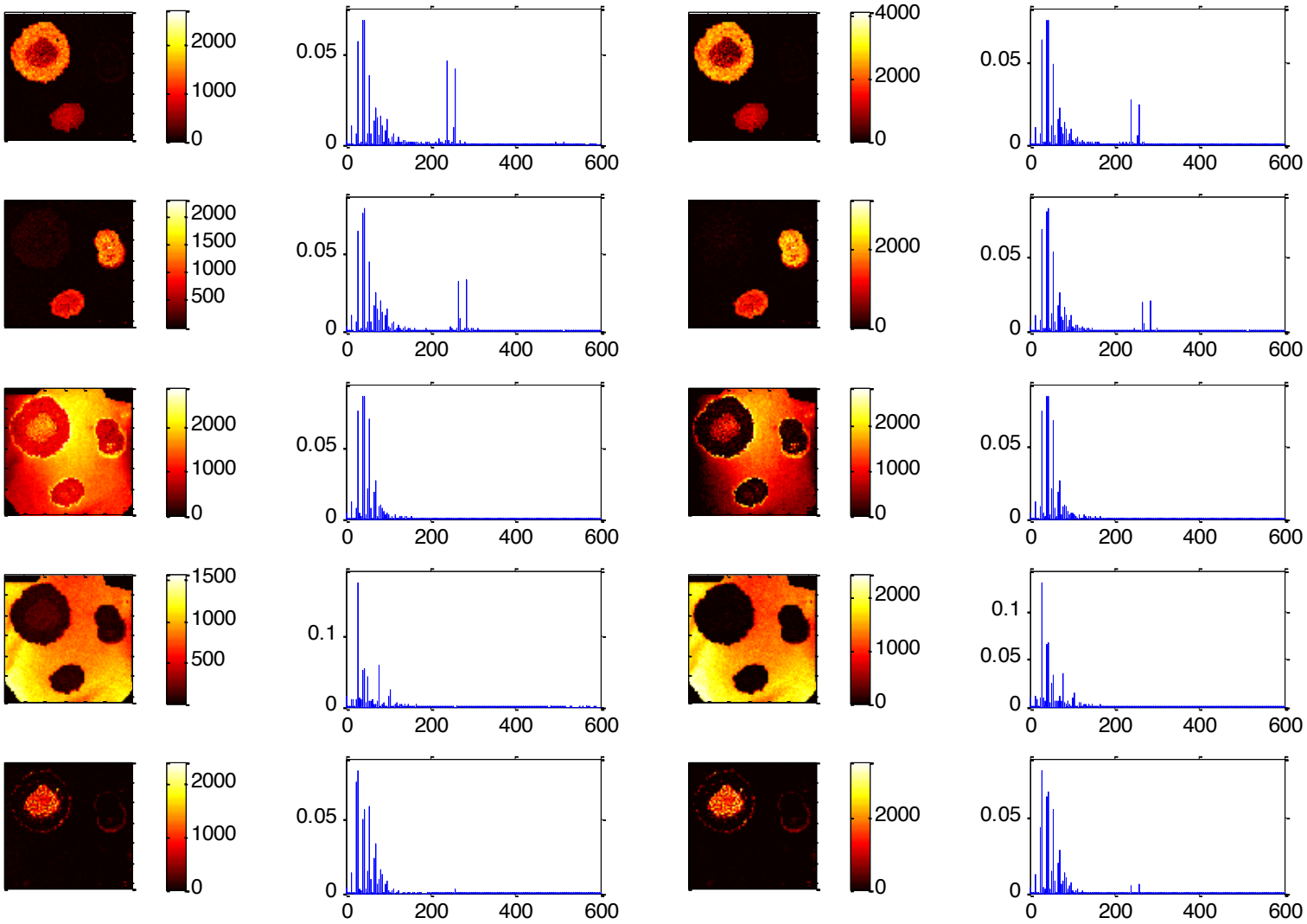
Spectral contrast

Image contrast



Stearic and palmitic acid spots and mixture

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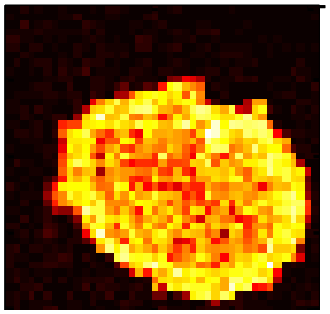
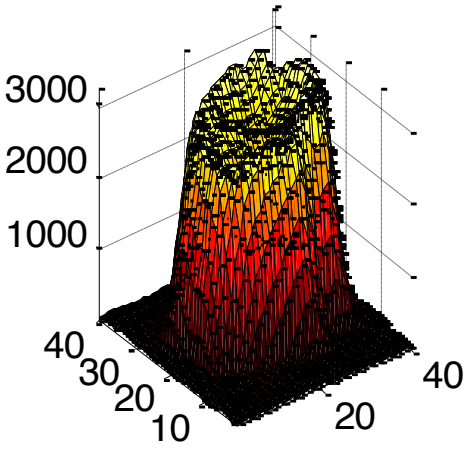
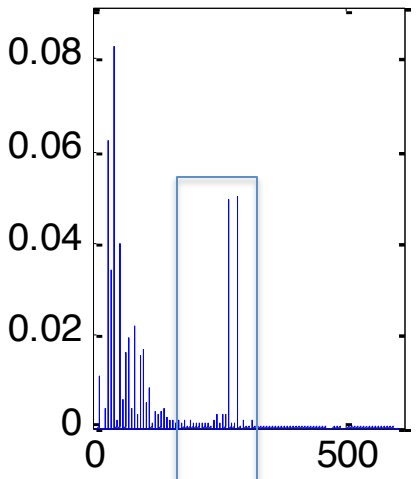
Spectral contrast

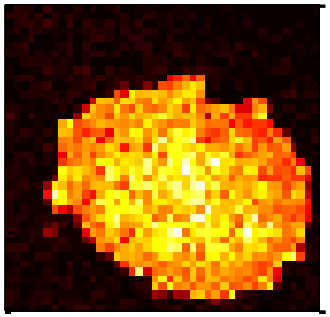


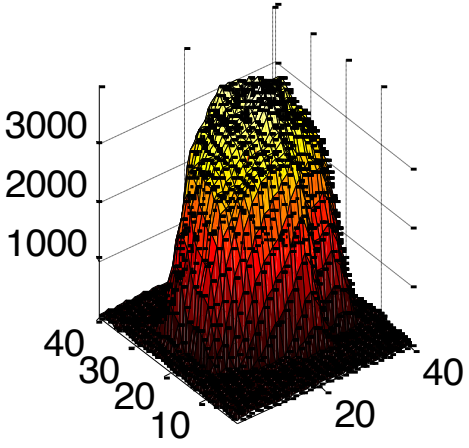




But concentration images nearly identical

Well resolved peaks!





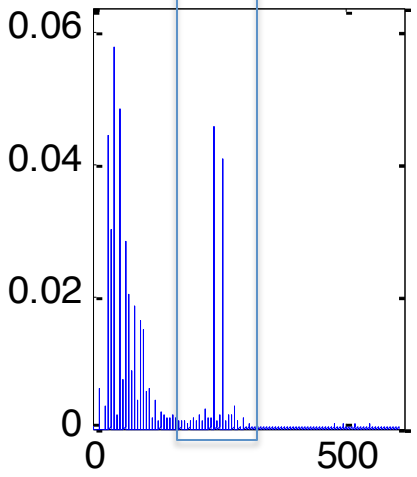


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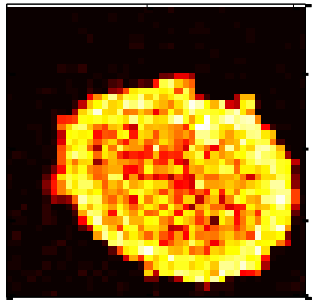
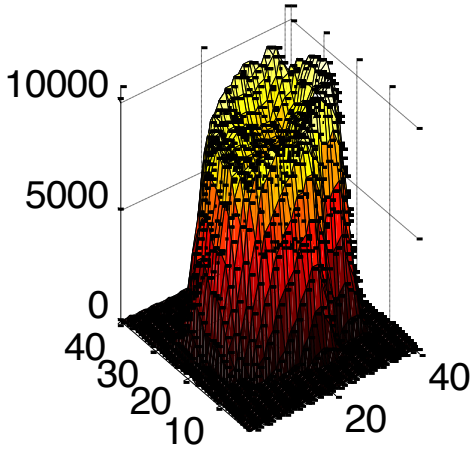
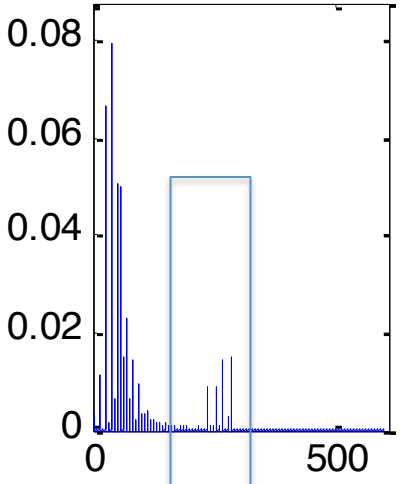
Image contrast

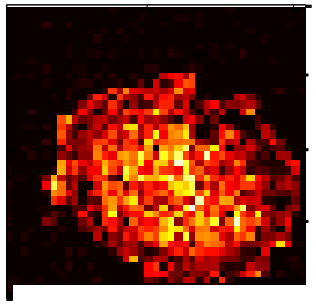


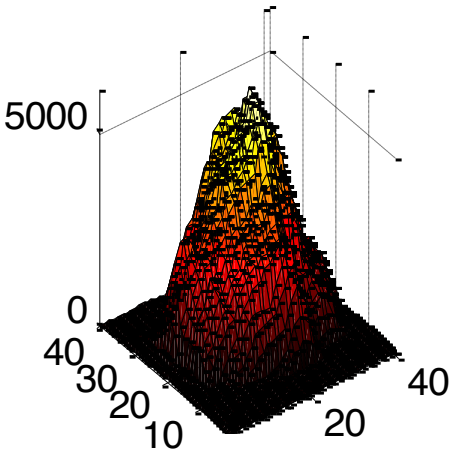


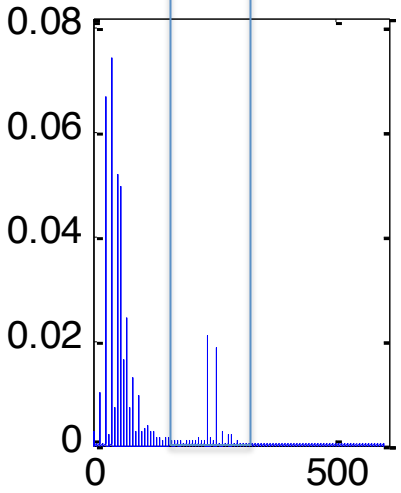


Large contrast in concentration images

But peaks no longer resolved!







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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

Acknowledgements

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

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