Multivariate Curve Resolution of Hyperspectral Images: Initialization and Functional Constraints

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Multivariate Curve Resolution

- MCR is most often used with spectra
  - aka end member extraction", self-modeling curve resolution
- Literature filled with examples from evolving data
  - LC-MS, GC-NIR, GC-GC …
- Newer examples include multivariate images
  - Image Mid-IR, NIR, UV-Vis ...

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MCR

- Based on the classical least squares (CLS) model, attempt to estimate **C** and **S** given **X**:

$$\mathbf{X} = \mathbf{C}\mathbf{S}^T + \mathbf{E}$$

where

X is a MxN matrix of measured responses,

C is a MxK matrix of pure analyte contributions,

S is a NxK matrix of pure analyte spectra, and

E is a MxN matrix of residuals.

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MCR Similar to PCA

- CLS and PCA look similar but with different mathematical properties

$\mathbf{X} = \mathbf{C}\mathbf{S}^T + \mathbf{E}$	$\mathbf{X} = \mathbf{T}\mathbf{P}^T + \mathbf{E}$
$\mathbf{X}_{M\text{x}N}$	$\mathbf{X}_{M\text{x}N}$
$\mathbf{C}_{M\text{x}K}$, $c_{ij} \geq 0$	$\mathbf{T}_{M\text{x}K}$, $\mathbf{T}^T\mathbf{T}$ KxK diagonal
$\mathbf{S}_{N\text{x}K}$, $s_{ij} \geq 0$	$\mathbf{P}_{N\text{x}K}$, $\mathbf{P}^T\mathbf{P} = \mathbf{I}_{K\text{x}K}$
$\mathbf{E}_{M\text{x}N}$	$\mathbf{E}_{M\text{x}N}$

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ALS

- Alternating and constrained least squares is often used to get estimates of **C** and **S** e.g.
- 0) Start with a guess for $\mathbf{C} = \mathbf{C}_0$ (or $\mathbf{S}_0$)
- 1) Estimate $\mathbf{S}^T_r = \mathbf{C}^\dagger_{r-1}\mathbf{X}$ subject to $\mathbf{S}(i,j) \geq 0$
- 2) Estimate $\mathbf{C}_r = \mathbf{X}\mathbf{S}^{\dagger T}_r$ subject to $\mathbf{C}(i,j) \geq 0$
- 3) Continue Steps 1 and 2 until $\|\mathbf{E}\|$ within some tolerance or $r > r_{max}$

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Initial Estimate

- With evolving data
  - can use Evolving Factor Analysis (EFA) and Evolving Window Factor Analysis (EWFA) to get a first estimate of **C**
  - more difficult to do with images since the pixels are not usually "ordered" in time
- Try to find "extreme" samples/pixels

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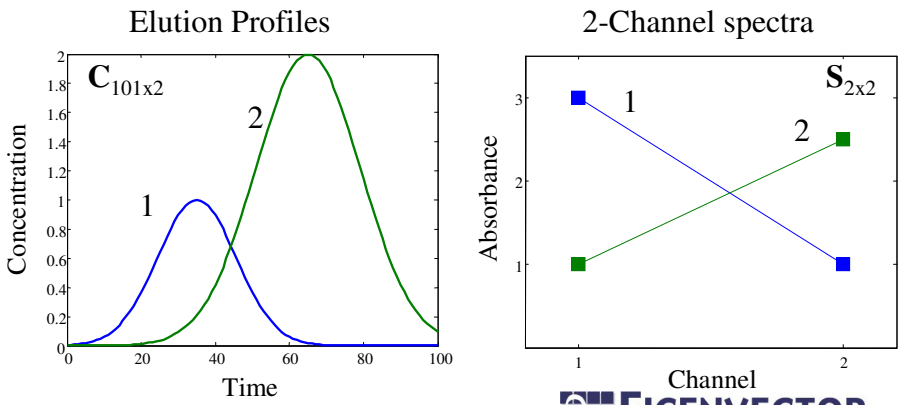
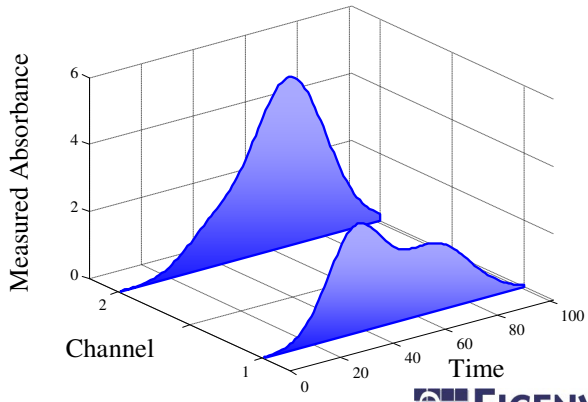
Example with Evolving Data

- Synthetic data from LC-NIR

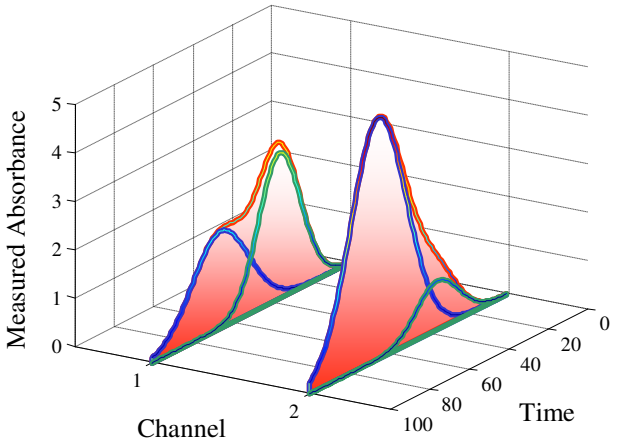


Elution Example No Noise

- Measured response (no noise)



Measured Response (no noise)



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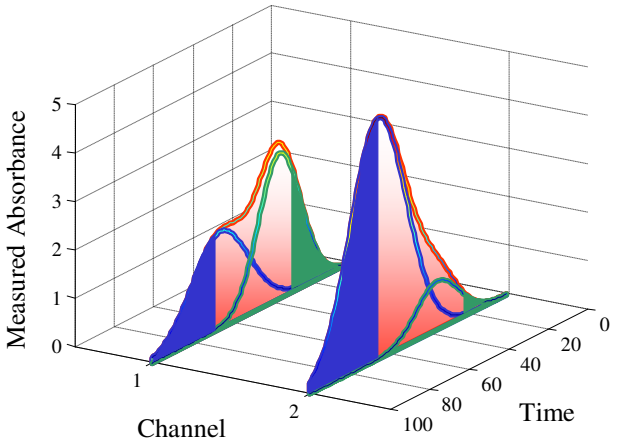
Measured Response (no noise)



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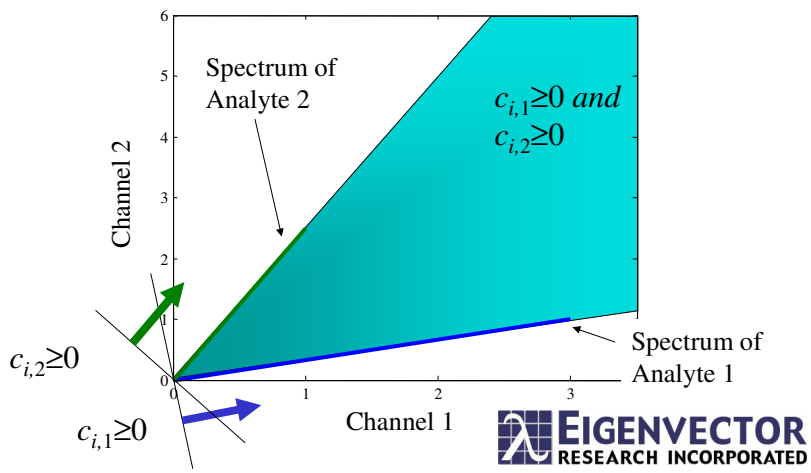
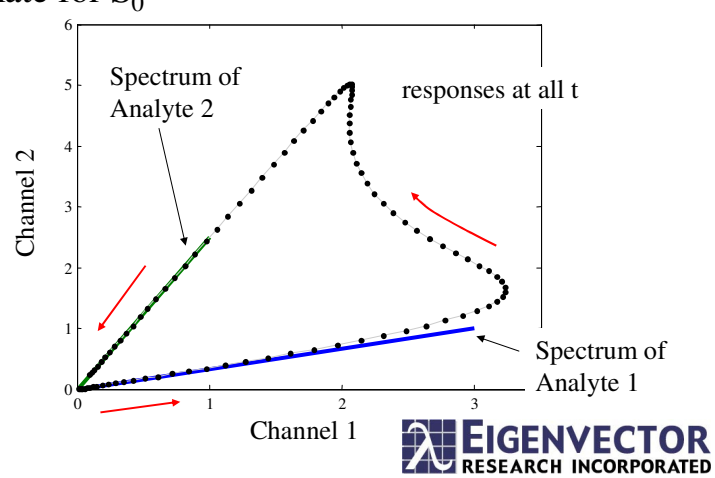
Non-negativity

- Plot **S** (Channel 2 versus 1)



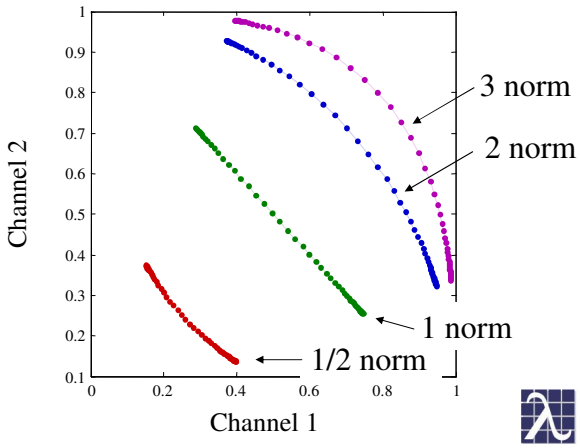
Elution Example No Noise

- Samples at the boudaries (extremes) are best estimate for $\mathbf{S}_0$



How to find the Extremes?

- Normalize each spectrum (which p?)



p norm

$$\mathbf{x} = \mathbf{x}\left(\sum_{j=1}^{N} x_j^p\right)^{1/p}$$

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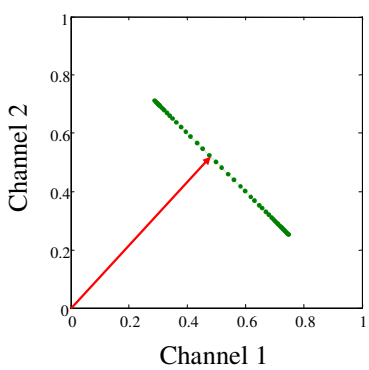
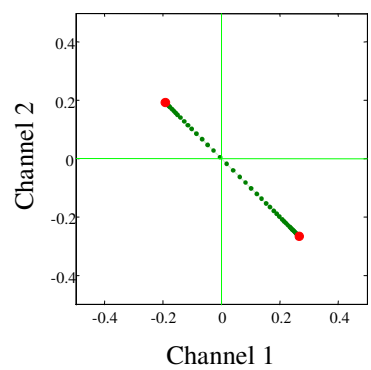
Extreme Samples

- Mean centering the 1 norm spectra drops the rank





the extreme sample spectra are indistinguishable from the original analyte spectra

samples with 0 norm not used

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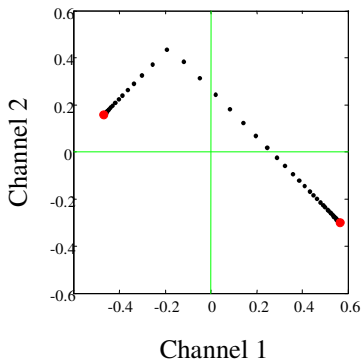
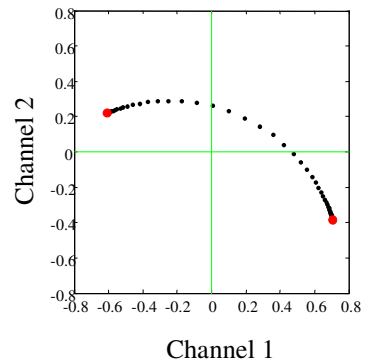
1 and 2 Norm

- Can use 2 norm to find extremes also
  - note that one of the pure spectra has a negative





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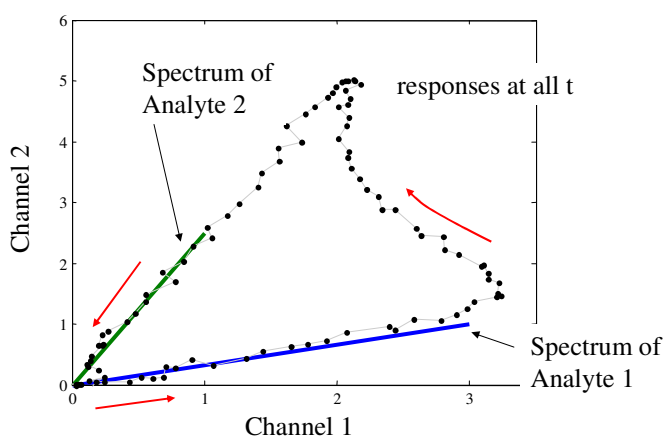
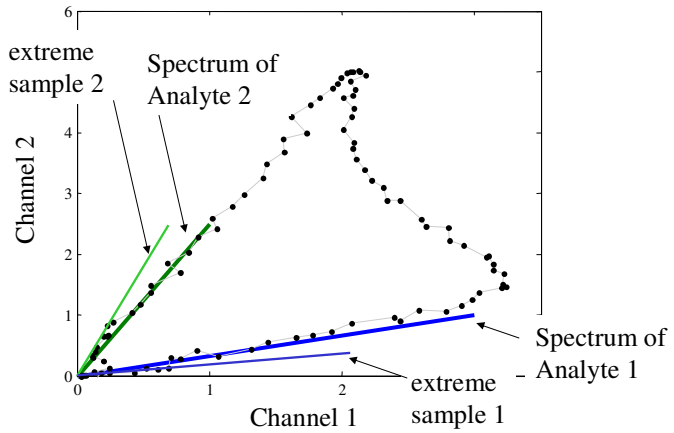
What Happens with Noise?

- Estimate extremes using samples with higher signal



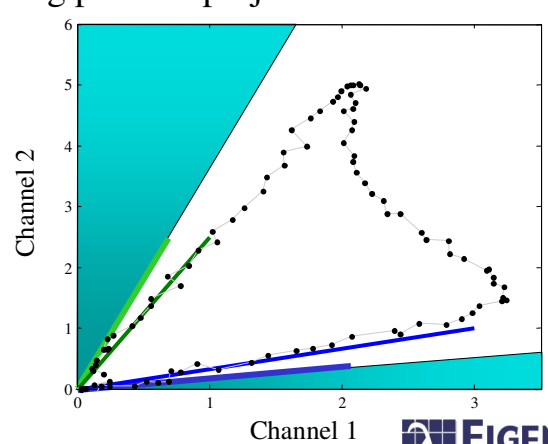
What Happens with Noise?

- Extremes from samples with norm >0.5



Feasible Solution

- Set of spectra (s_{ij}>0) that bounds the data with the c_{ij} having positive projections is a feasible solution



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Rotational Ambiguity

- For an invertible matrix **A**
  - such that constraints are satisfied
- Result is a rotational ambiguity
  - all solutions have the same fitness **E**

$$\mathbf{X} = \mathbf{C}\mathbf{S}^T + \mathbf{E} = (\mathbf{C}\mathbf{A})\left(\mathbf{A}^{-1}\mathbf{S}^T\right) + \mathbf{E}$$

Tauler, R., "Calculation of maximum and minimum band boundaries of feasible solutions for species profiles obtained by multivariate curve resolution", *J. Chemo.*, **15**, 627-646, 2001.

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Multiplicative Ambiguity

- For a diagonal matrix **A**
  - with non-zero elements
- Result is a multiplicative ambiguity
  - all solutions have the same fitness **E**

$$\mathbf{X} = \mathbf{C}\mathbf{S}^T + \mathbf{E} = (\mathbf{C}\mathbf{A})\left(\mathbf{A}^{-1}\mathbf{S}^T\right) + \mathbf{E}$$

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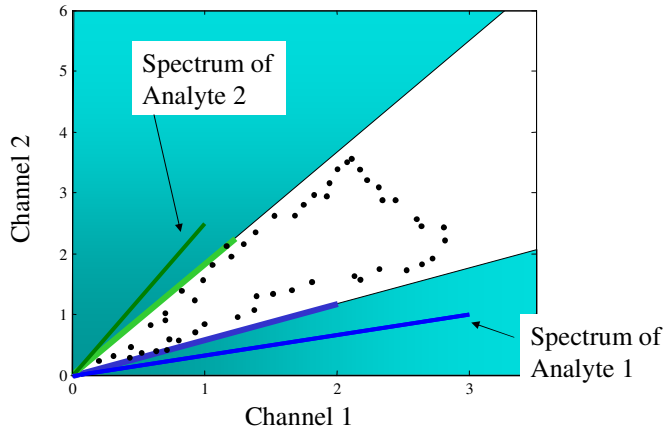
Lack of Selectivity

- Extremes are inside pure spectra



Manne, R., "On the Resolution Problem in Hyphenated Chromatography", *Chemo. Intll. Lab. Sys.*, **27**, 89–94, 1995.

Use What You Know

- Multiplicative and rotational ambiguities, and lack of selectivity can some times be resolved using constraints
  - non-negativity, unimodality, smoothness, equality …
  - functional (chemistry/physics)
  - these can be easily incorporated into an ALS algorithm

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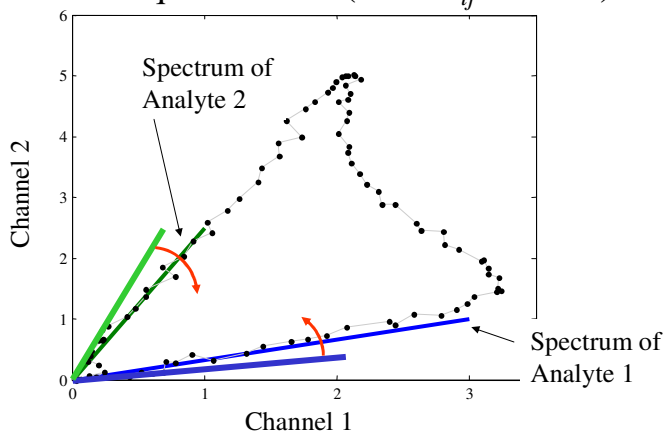
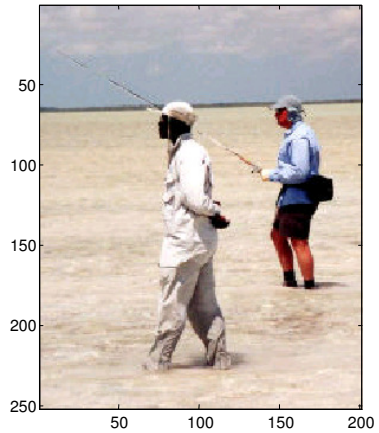
What Happens with Noise?

- With appropriate constraints the ALS also fits the data in a least squares sense (some c_{ij}< ~ 0 ok)



Try an Example with an Image

- RGB image
  - 251x201x3
  - fly fishing for bone fish
- What are the 3 pure component spectra?
  - matricize to (251*201)x3 and look for the extremes



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Three Extreme Pixels

- 3 extreme samples are on the guide's face (red pixels)
  - in the shade where the signal is low
  - values are:

[12 0 0
0 0 5
0 1 0]

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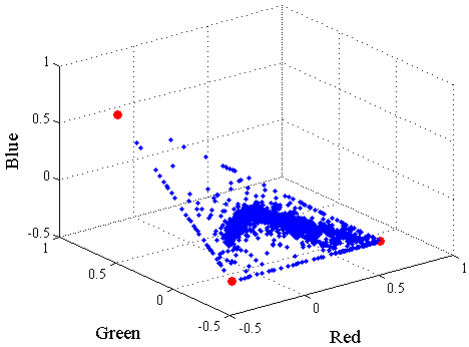
Plot of Normalized Pixels

```
x = imread('c:\program files\qualcomm\eudora\attach\flat_harlan.jpg');
x = x(50:300,150:350,:);
y = double(reshape(x,251*201,3));
tol = 0.05;
[normy,norms] = normaliz(y,0,1);
i1  = find(norms>tol);
ymean = mncn(normy(i1,:));
isel = distslct(ymean,3);
y(isel,:)
  12    0    0
   0    0    5
   0    1    0
```



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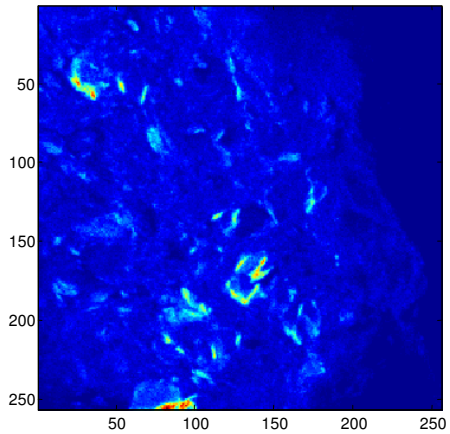
Imaging Mass Spec

- Image is 256x256x90
- The mass spectrum was 41945 mass channels selected and binned into 90 channels
- Image of total ion count
  - false color



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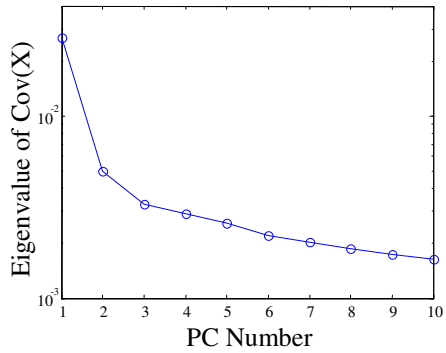
PCA of the Image Data

1 norm, mean center for samples with norm>2

Percent Variance Captured by PCA Model

Principal Component Number	Eigenvalue of Cov(X)	% Variance Captured This PC	% Variance Captured Total
1	2.68e-002	35.40	35.40
2	4.97e-003	6.56	41.97
3	3.29e-003	4.34	46.31
4	2.90e-003	3.83	50.14
5	2.57e-003	3.40	53.54
6	2.22e-003	2.93	56.47
7	2.02e-003	2.67	59.15
8	1.88e-003	2.48	61.63
9	1.74e-003	2.31	63.94
10	1.63e-003	2.16	66.10



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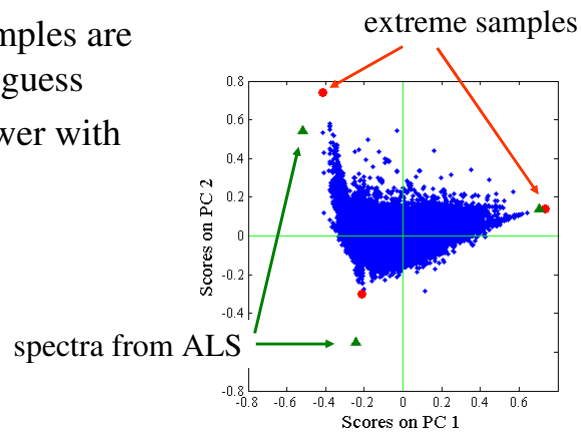
Scores on PC 2 vs. 1

- Extreme samples are a good first guess
- ALS has fewer with $c_{ij}<0$



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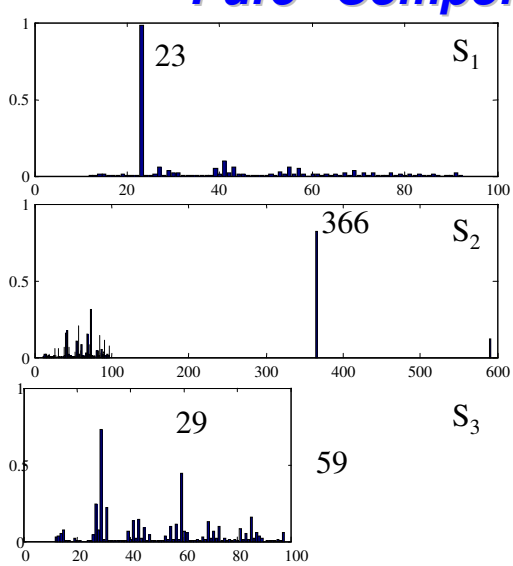
"Pure" Component Spectra



- Make a "true color" image where
  - Red - high at mass 23
  - Green - high at mass 366
  - Blue - high at masses 29 and 59

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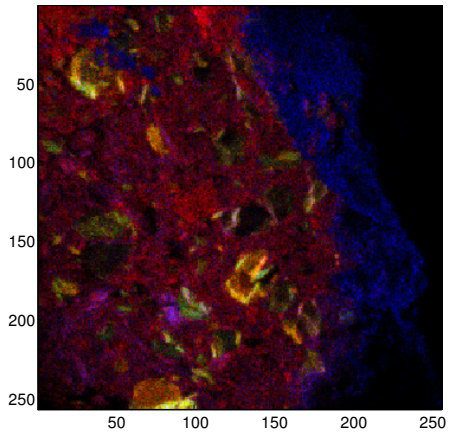
Concentration Image

- Convert **C** to uint8
  - 0 to 255



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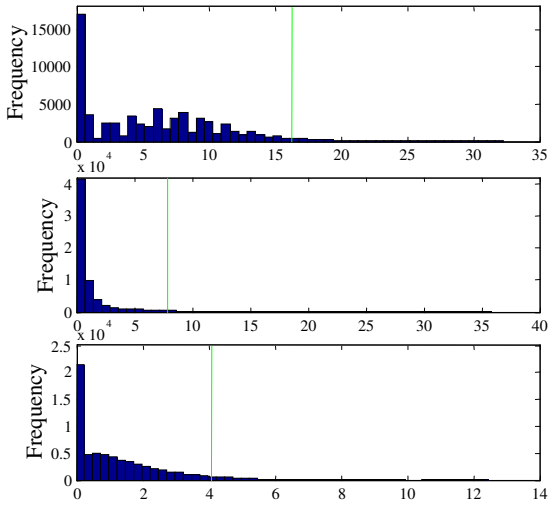
Contrast Enhancement



- Only a few channels use up the dynamic range
  - identify high limit and saturate values above
  - can also use a low limit

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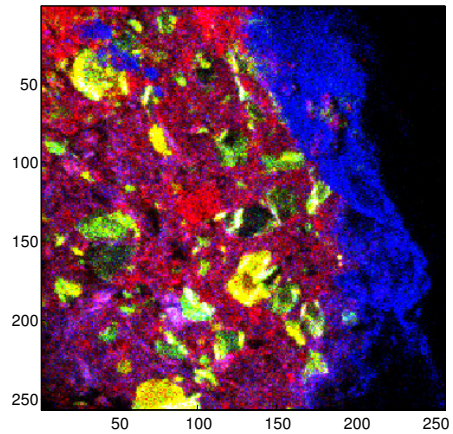
Contrasted Concentration Image

- Convert **C** to uint8
  - "true color" image



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Summary of Procedure

- Normalize rows of $\mathbf{X} \Rightarrow \mathbf{X}_{\text{norm}}$
  - 1 norm easy to use if **C**>0 and **S**>0 (in a single quadrant)
  - use only rows with norm > tolerance (~noise level)
- Mean center the columns of $\mathbf{X}_{\text{norm}} \Rightarrow \mathbf{X}_{\text{norm,mean}}$
- Identify the extreme samples of $\mathbf{X}_{\text{norm,mean}} \Rightarrow i_{sel}$
- Initial guess $\mathbf{S}_0 = \mathbf{X}_{\text{norm}}(i_{sel},:)$ [stop?]
- Use ALS on $\mathbf{X}_{\text{norm}}$ with $\mathbf{S}_0$ as an initial guess
  - include known constraints

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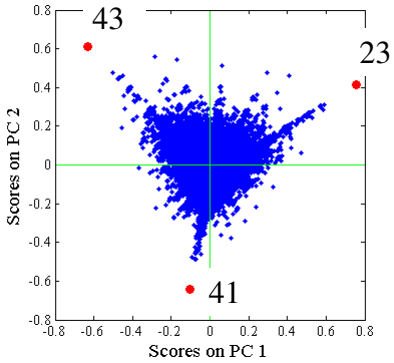
Cloth Example

- Cloth 256x256x34 mass spec
- PCA of 1 norm (for norm>2), mean centered
- The extreme samples represent "single channel spectra"



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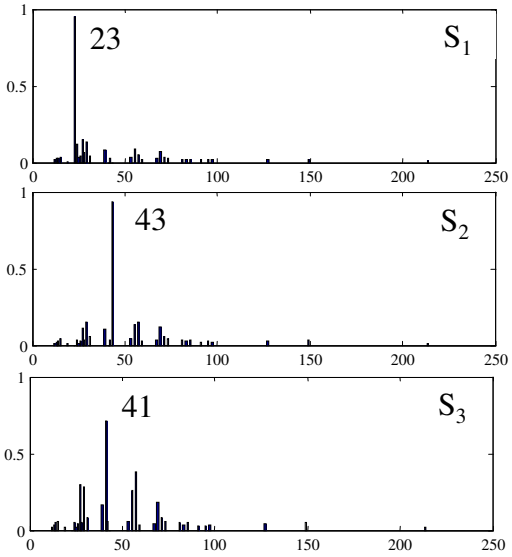
MCR via ALS



- For both the extreme spectra and ALS results
  - Red - high in 23
  - Green - high in 43
  - Blue - high in 41

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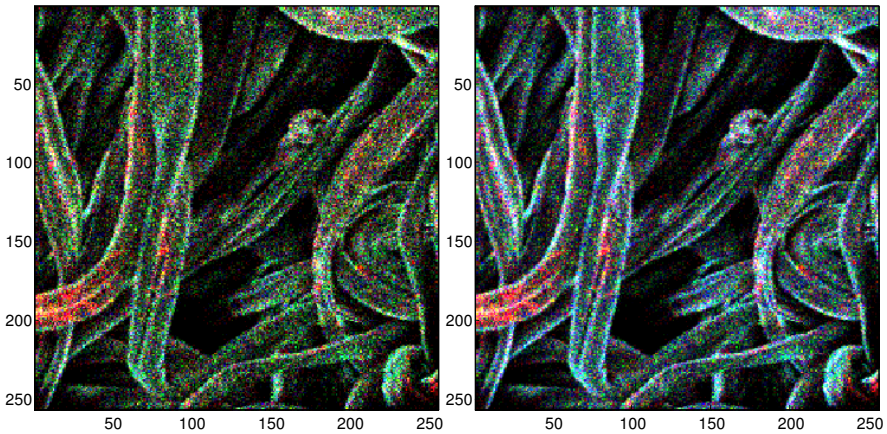
Contrasted Concentration Images

using extreme spectra

using ALS spectra



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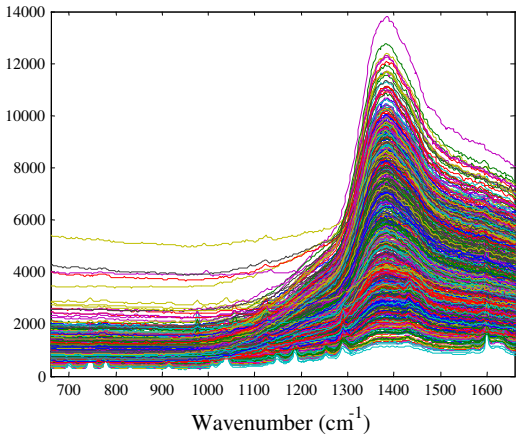
Aspirin in Polymer

- Raman 22x33x501 (635-1660 cm^{-1})



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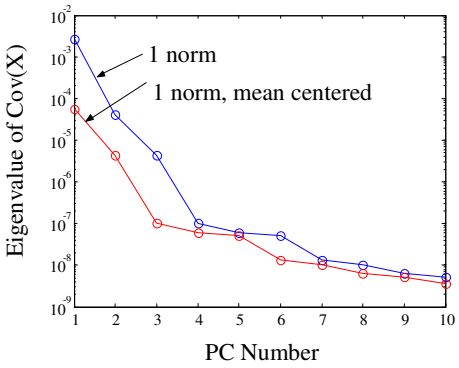
Aspirin in Polymer

- PCA, 1 norm, mean centered

Percent Variance Captured by PCA Model

Principal Component Number	Eigenvalue of Cov(X)	% Variance Captured This PC	% Variance Captured Total
1	5.60e-005	92.20	92.20
2	4.37e-006	7.20	99.40
3	1.04e-007	0.17	99.57
4	5.92e-008	0.10	99.67
5	5.03e-008	0.08	99.75
6	1.35e-008	0.02	99.77
7	1.00e-008	0.02	99.79
8	6.25e-009	0.01	99.80



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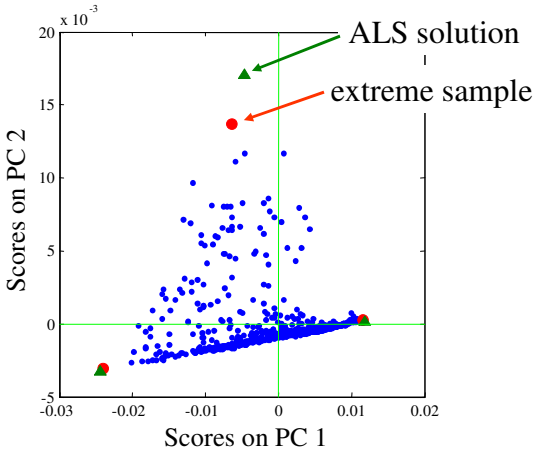
Extreme Samples and ALS



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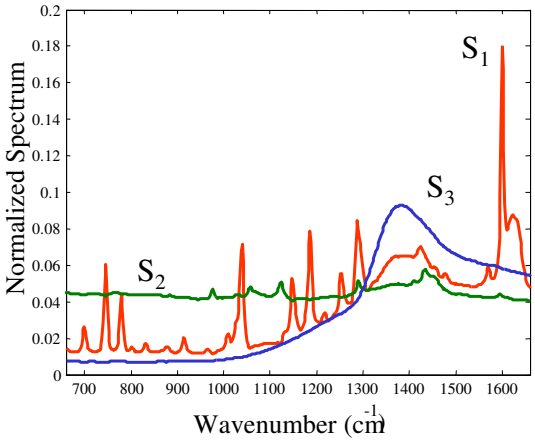
Extracted Spectra



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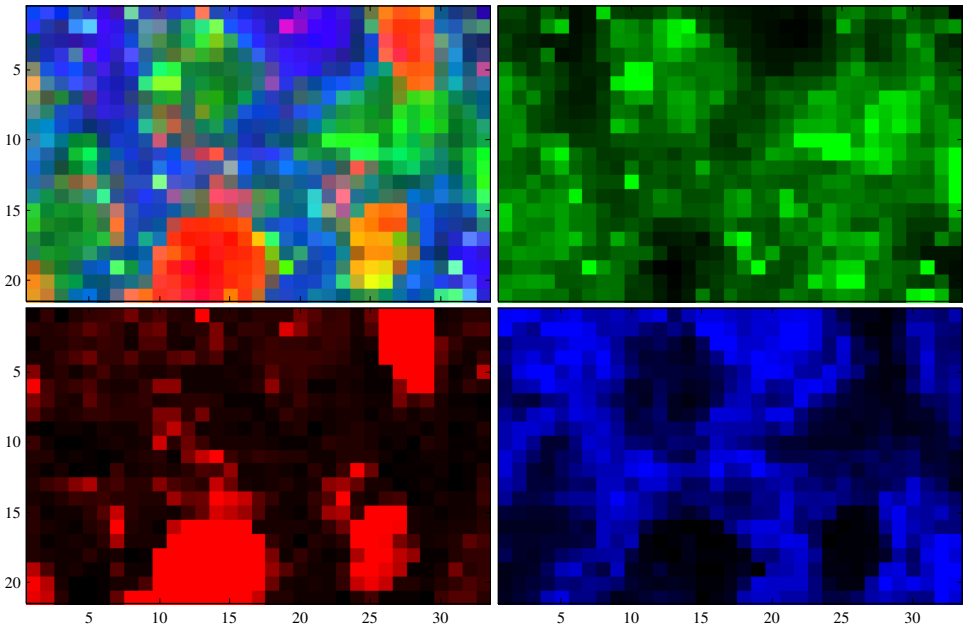
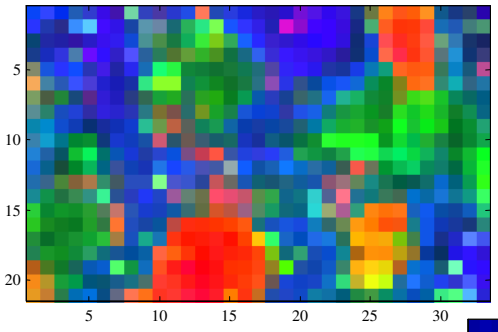
Concentration Images



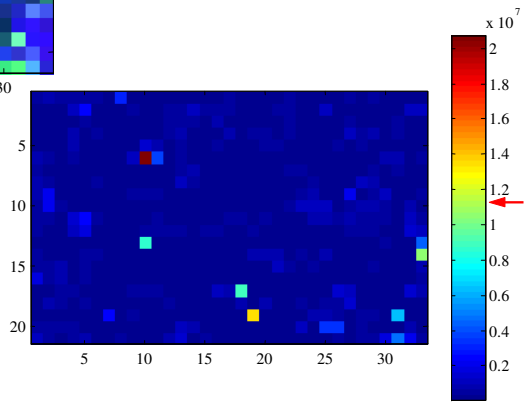
Concentration Images

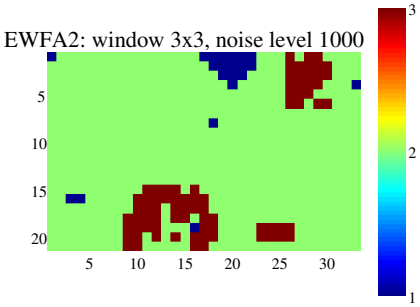


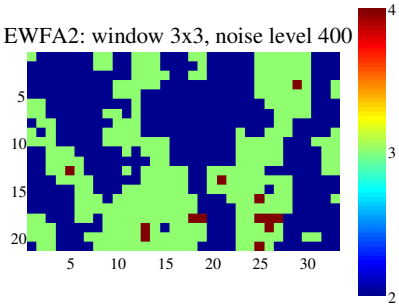
RGB Image of the 3 factors

Sum of squared residuals

arrow indicates ~95% confidence limit line







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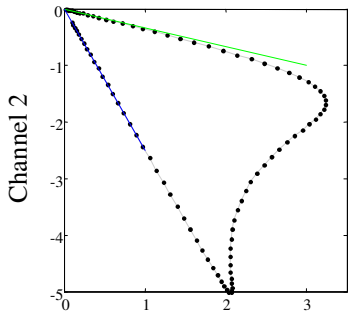
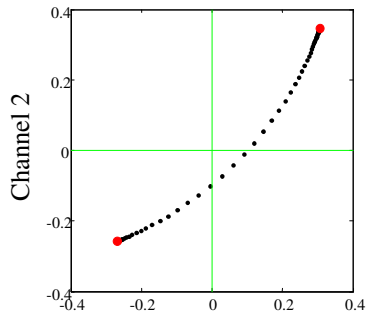
2nd Derivative

- Find the extreme samples of 2 norm of 2nd derivative spectra (positive and negative channels)



non-negativity on **C** means the data lie between the spectra



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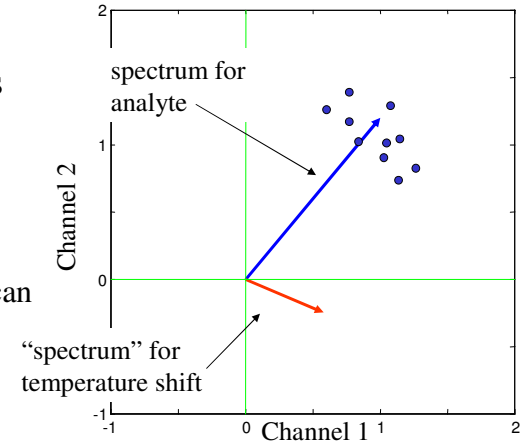
Temperature Shifts

- Temp changes often result in spectral shifts
  - can often be modeled using a low number of "extra factors" or "temperature spectra"
  - but temp contribution can be >0 or <0 ⇒lot's of feasible solutions



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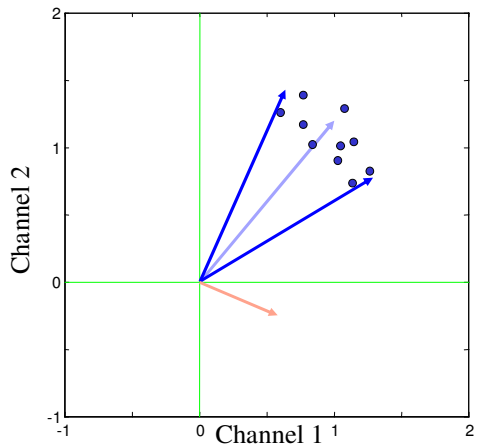
Temperature Shifts

- Non-negativity on **C**
  - rotates the temperature spectrum so a soln can be obtained
  - but also rotates the other spectrum away
    - it is the spectrum at an extreme temperature
    - can constrain if **C** is known



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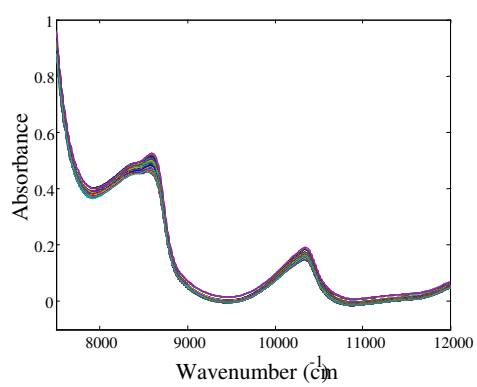
Example: 2nd Deriv and T Shifts

- Caustic data
  - SWIR (7500-12000 cm^{-1})
  - NaCl, NaOH, (wt%) in hot brine with variable T
  - 70 calibration samples
  - 25 test samples



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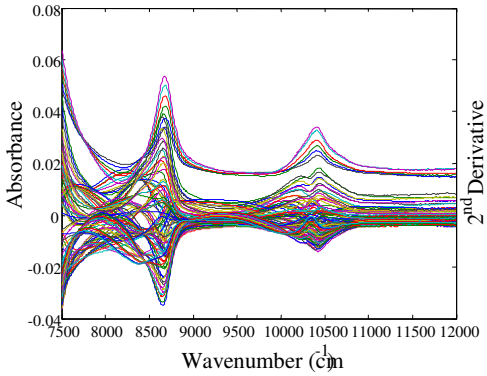
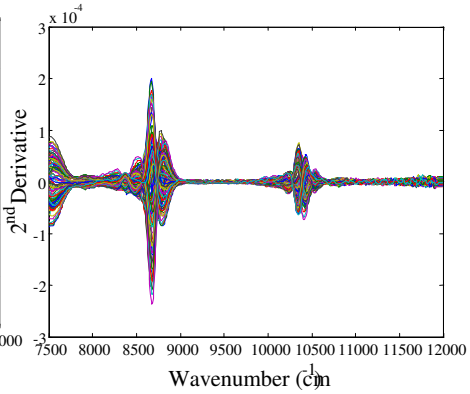
Second Derivative

mean centering shows offsets



2nd derivative removes offsets (mean centered)



savgol(x,15,2,2)

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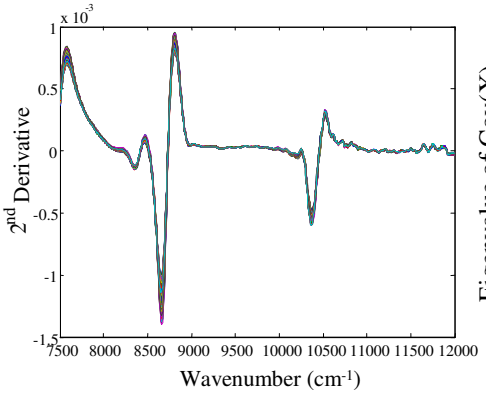
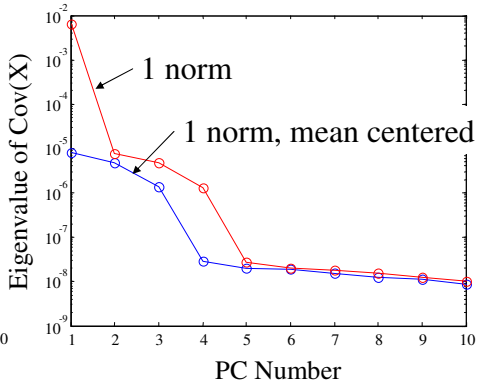
PCA of Normalized 2nd Deriv

2nd derivative (not normalized)





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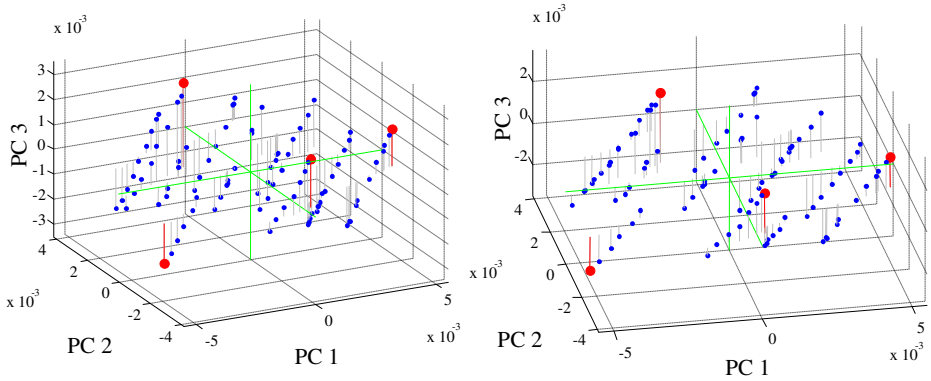
Extreme Samples



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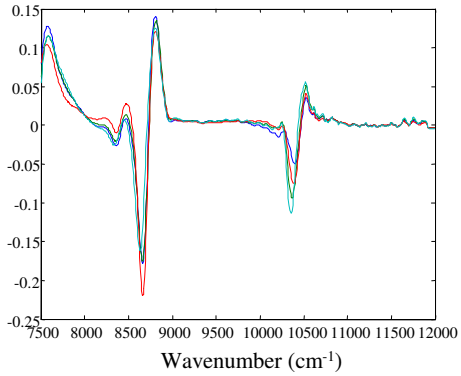
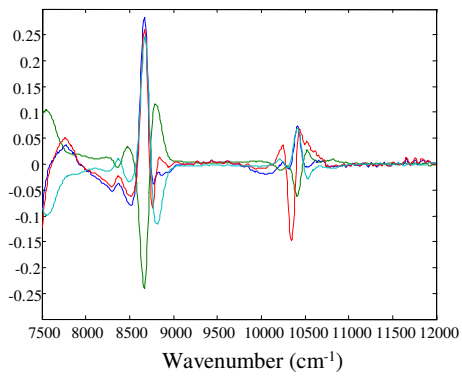
Recovered Spectra

S2: only C constrained >0



S1: C constrained >0, and equality constraints for known NaCl and NaOH



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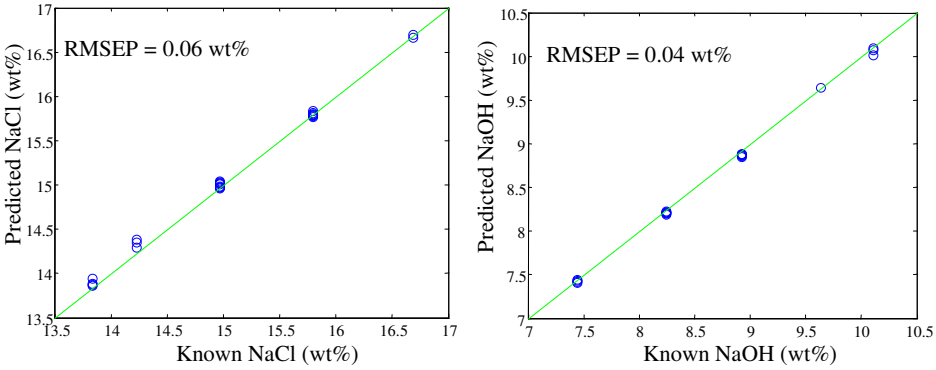
CLS Prediction

S1: used to predict NaCl and NaOH for test samples



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Curve Resolution for Multivariate Images

- Summary ...

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