Hyperspectral Imaging for Process Monitoring and Process Analytical Chemistry

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Outline

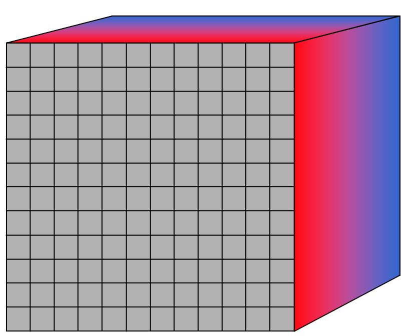
- Hyperspectral images
- Multivariate Curve Resolution for Images
- Process Monitoring and
  Process Analytical Chemistry
- Conclusions

What is a Hyperspectral Image?

- Images are M_xxM_y pixels x N Channels
  - N=1: Univariate (gray scale)
  - N>1: Multivariate
    - N = 3: RGB (JPG)
    - N > 3: Multispectral, Hyperspectral, Ultraspecral, Omnispectral, Megaspectral

Hyperspectral Image (>~10 Variables)

- Spectrum at each pixel
  - could be 100-1000s of variables
  - often not Unsigned 8 bit ⇨ 10-100s Mbytes



mass spectra (pharmaceuticals)

IR (process monitoring and remote sensing)

Visible + (crystallization, parts monitoring, semi-conductor)

Multivariate Curve Resolution

- MCR is most often used with spectra
  - also known as "end member extraction", self-modeling curve resolution, self-modeling mixture analysis
- 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**:

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

X MxN measured responses,

C MxK pure analyte contributions,

S NxK pure analyte spectra, and

E MxN residuals.

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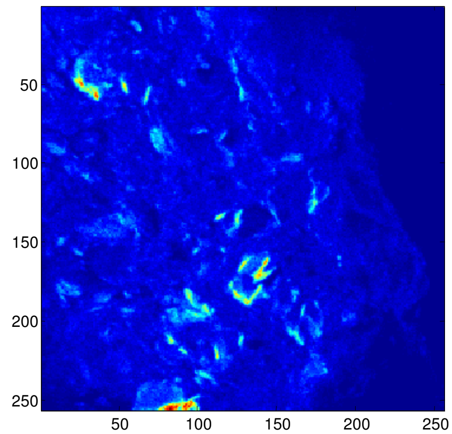
Imaging (TOF-SIMS) Mass Spec

- Drug bead
  - secured to silicon substrate w/ epoxy
  - cross-sectioned w/ sharp blade
- Image 256*x*256 *x*93
  - ~250 x 250 μm^2
  - 41945 mass channels selected and binned into 93 channels
- Image of total ion count



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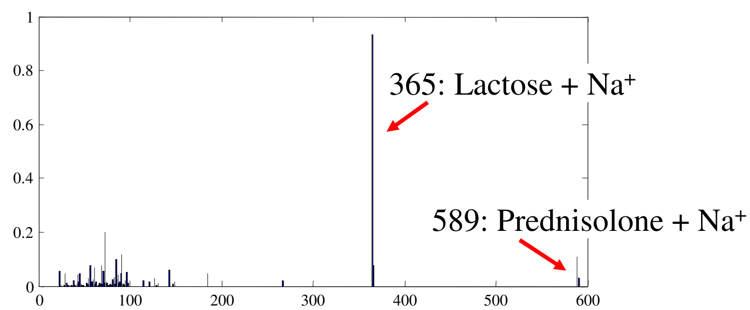
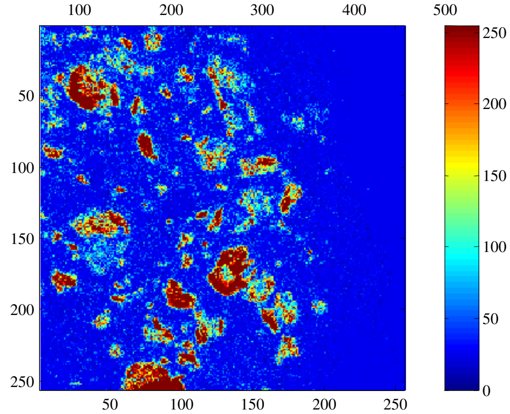


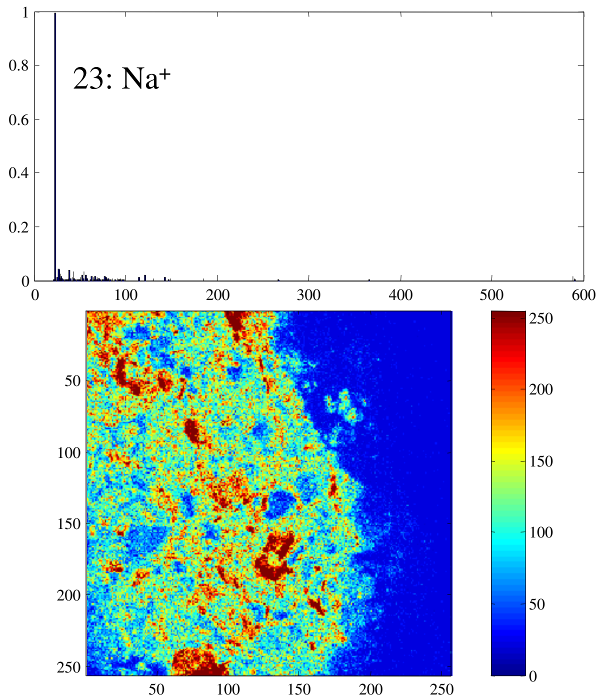
Prednisolone:

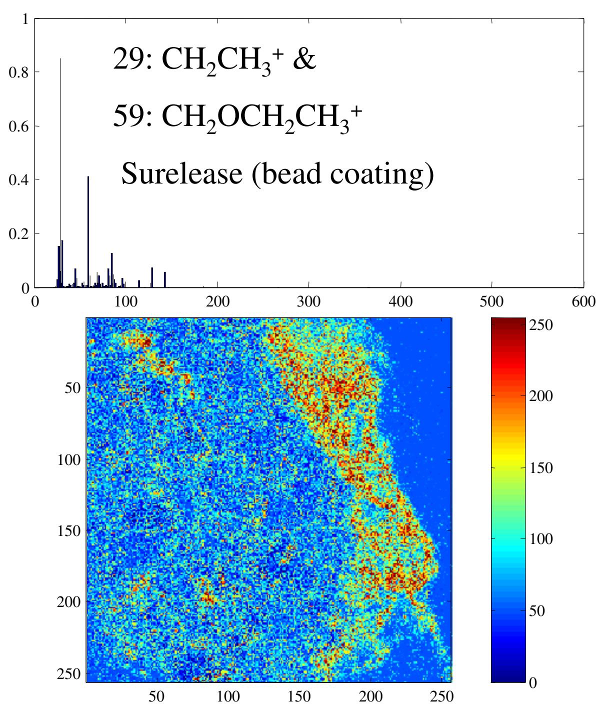
$C_{21}H_{31}NaO_9S$

Lactose:

$C_{12}H_{22}O_{11}$



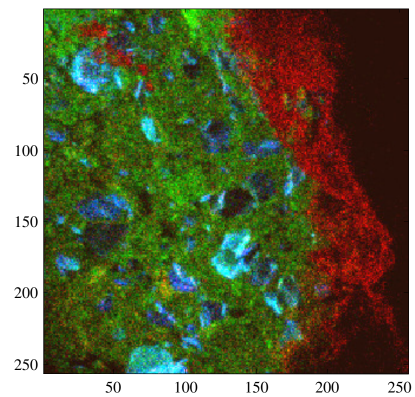

23: Na+


29: CH2CH3+ &
59: CH2OCH2CH3+
Surelease (bead coating)

RGB "Chemical" Image

Red: Surelease (bead coating)
Green: Na
Blue: Prednisolone (drug)

only 3 of 6 factors extracted are shown



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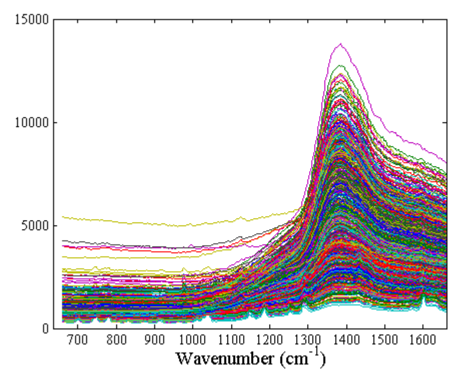
Aspirin in Polymer

- Aspirin in polyethylene on a glass slide
- Raman 22*x*33 *x* 501
  - 660-1660 cm^{-1}
- Background
  - luminescence varies for each pixel



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Functional Constraints

- Constraints for a 6 factor model
- Factors 1, 2, 3
  - **C**>0, [deriv/integ filter (remove baseline), **S**>0, every 10^{th} iteration]
- Factor 4
  - **C**>0, [smooth filter, **S**>0, every 10^{th} iteration]
- Factors 5 and 6
  - **C**>0, [**S**>0, every 10^{th} iteration]

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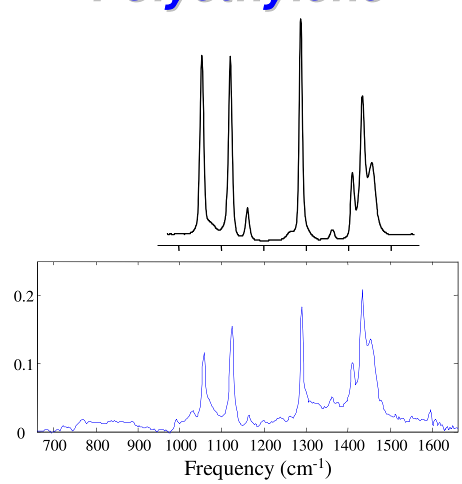
Polyethylene



Polyethylene Spectrum Courtesy of
Kaiser Optical Systems and DOW Chemical

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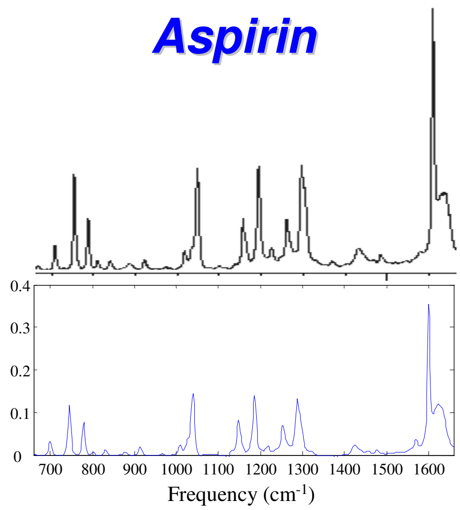
Aspirin



Aspirin Spectrum Courtesy of SDBSWeb:
http://www.aist.go.jp/RIODB/SDBS/ (Jan 2003)

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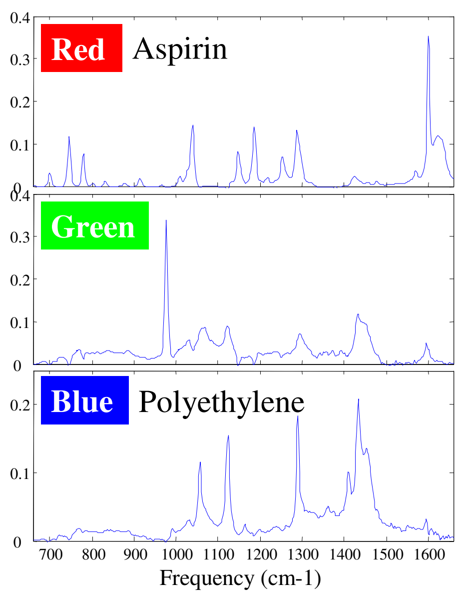
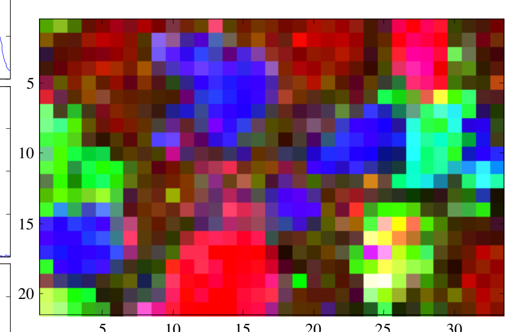


False Color "Chemical" Image



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Statistics for Monitoring

$$T^2 = (\mathbf{c} - \overline{\mathbf{c}})\boldsymbol{\Sigma}^{-1}(\mathbf{c} - \overline{\mathbf{c}})^T$$

$$\boldsymbol{\Sigma} = \tfrac{1}{M_x M_y - 1}(\mathbf{C} - \mathbf{1}\overline{\mathbf{c}})^T(\mathbf{C} - \mathbf{1}\overline{\mathbf{c}})$$

$$T_E^2 = \mathbf{e}\boldsymbol{\Gamma}^{-1}\mathbf{e}^T$$

$$\boldsymbol{\Gamma}_{jj} = \tfrac{1}{M_x M_y - K}\sum_{m=1}^{M_x M_y} \mathbf{e}_{mj}^2 \ ; \ \text{diagonal}$$

$$T_X^2 = T^2 + T_E^2$$

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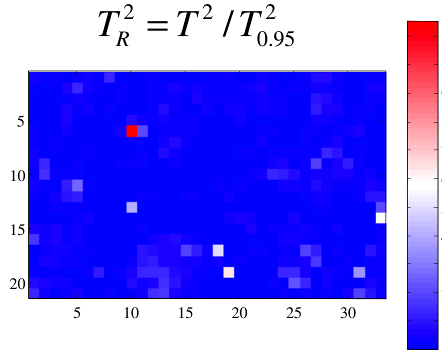
T^2 and T_E^2 Images

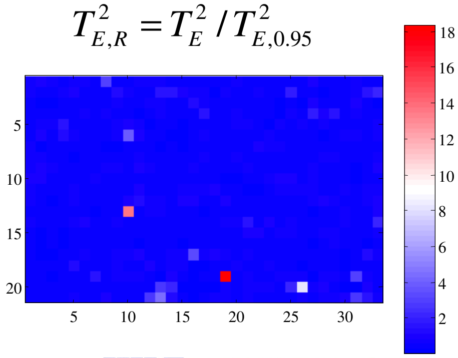
Unusual **c**

$$T_R^2 = T^2 / T_{0.95}^2$$



Unusual **s**

$$T_{E,R}^2 = T_E^2 / T_{E,0.95}^2$$



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Contributions for Diagnostics

- Which variables contribute to the T^2?
  - Why is an unusual pixel unusual?

$$T^2 : \mathbf{t}_{con} = (\mathbf{c}-\bar{\mathbf{c}})\left[\frac{(\mathbf{C}-\mathbf{1}\bar{\mathbf{c}})^T(\mathbf{C}-\mathbf{1}\bar{\mathbf{c}})}{M_x M_y - 1}\right]^{-1/2}(\mathbf{S}^T\mathbf{S})^{-1/2}\mathbf{S}^T$$

$$T_E^2 : \mathbf{t}_{E,con} = \mathbf{x}\left(\mathbf{I}-\mathbf{S}(\mathbf{S}^T\mathbf{S})^{-1}\mathbf{S}^T\right)\mathbf{\Gamma}^{-1/2}$$

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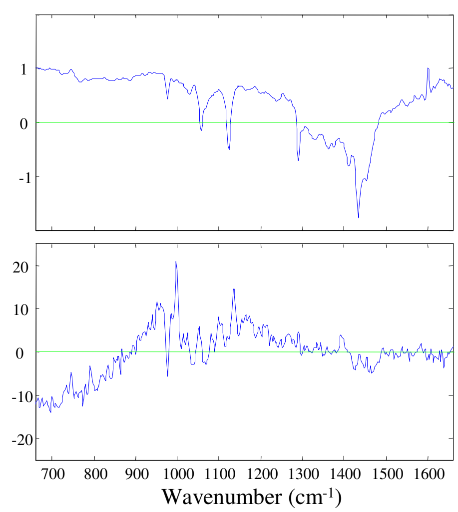
Pixel Contributions



$\mathbf{t}_{con}$ (Pixel 6,10)

$\mathbf{t}_{E,con}$ (Pixel 19,19)

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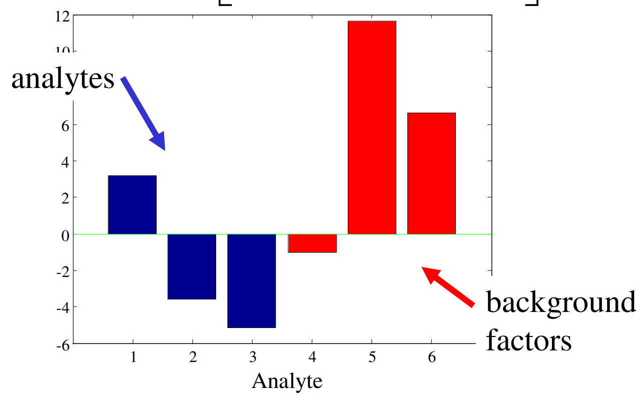
Contribution in C

$$T^2 : \mathbf{t}_{con} = (\mathbf{c} - \bar{\mathbf{c}}) \left[\frac{(\mathbf{C} - \mathbf{1}\bar{\mathbf{c}})^T (\mathbf{C} - \mathbf{1}\bar{\mathbf{c}})}{M_x M_y - 1} \right]^{-1/2}$$



Conclusions

- MCR used to extract "pure component" spectra **S**
  - more difficult than, but similar to, PCA
- Process monitoring can be performed using **S**
  - the result is Process Analytical Chemistry
- Summary statistics and contributions are used to aid monitoring
  - identify faults or unusual compositions
  - interrogation of contributions help diagnose the fault
  - can be tuned to achieve desirable properties