Introduction to Instrument Standardization and Calibration Transfer

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Motivation

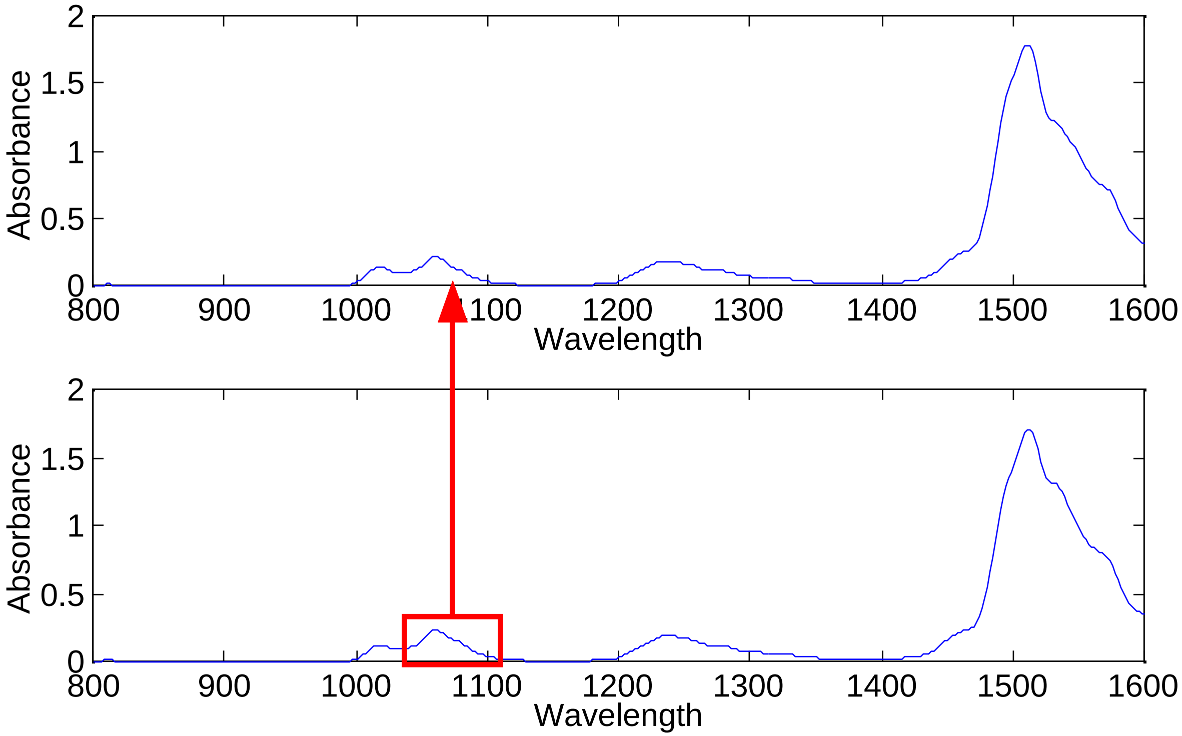
- Calibration models for quantitation or classification often take advantage of relatively small changes in spectra
- Instrument to instrument differences can be substantial, *i.e.* samples look different
- Instruments may drift over time
- Renders models invalid
- Inconvenient to recalibrate instruments or may want to utilize a historical database

Two Main Approaches

- Find a transformation that maps the response of the field instrument onto the standard instrument
  - Direct and piece-wise direct standardization
  - Neural network and other variants
- Process the data from both instruments in a way that makes the differences disappear
  - baselining and derivatizing
  - multiplicative scatter correction, FIR filtering
  - orthogonal signal correction
  - prediction augmented classical least squares
  - generalized least squares
  - explicit deresolution

Piece-wise Direct Standardization (PDS)

- Develop models which use windows on field instrument to predict single channels on standard

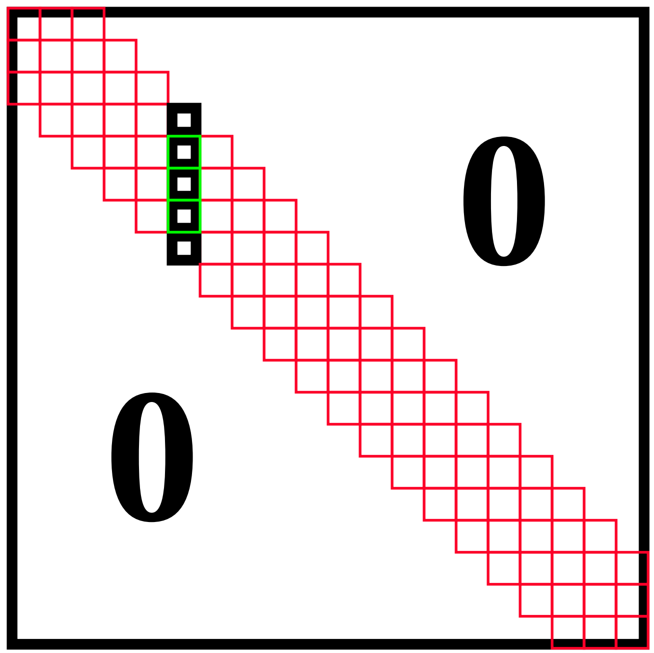


Develop Transfer Matrix F_b

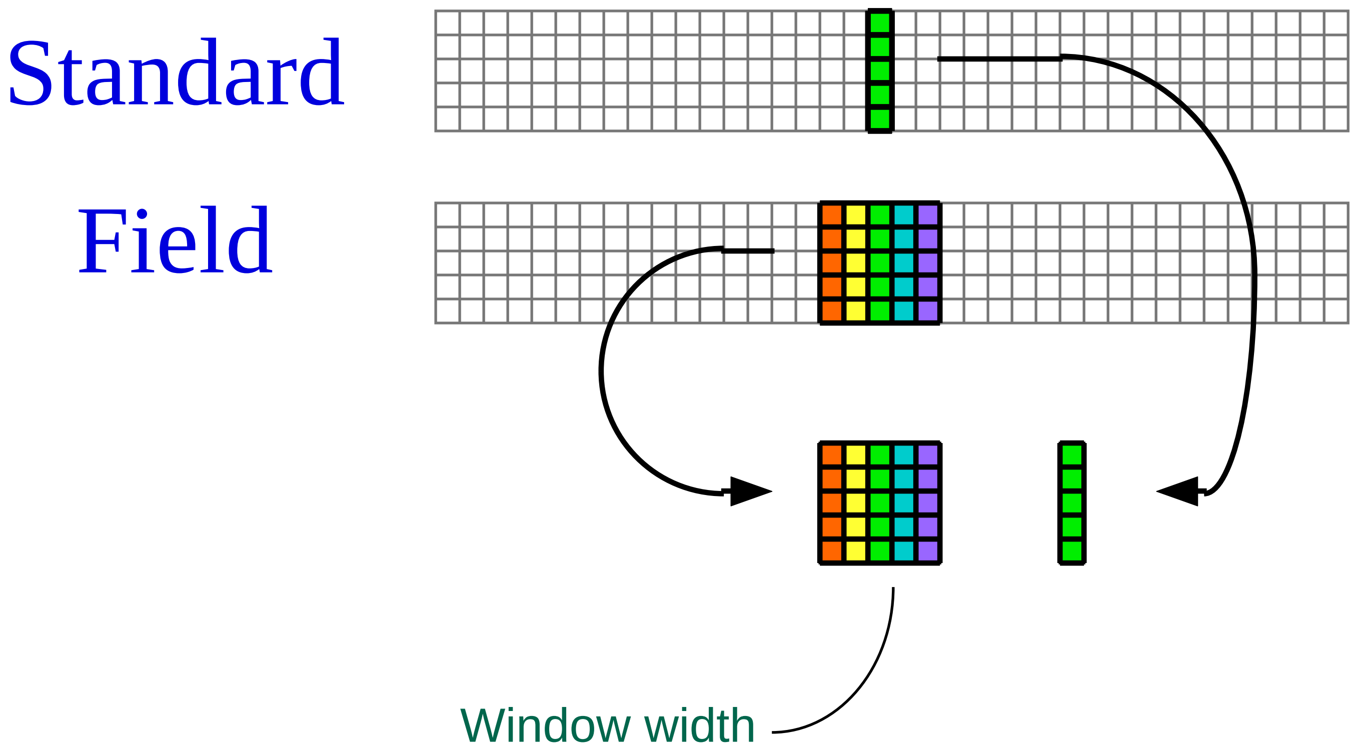
Difference between instruments
modelled as:

$$\mathbf{S}_1 = \mathbf{S}_2\mathbf{F}_b + \mathbf{1}b_s^T$$

$$\mathbf{F}_b =$$



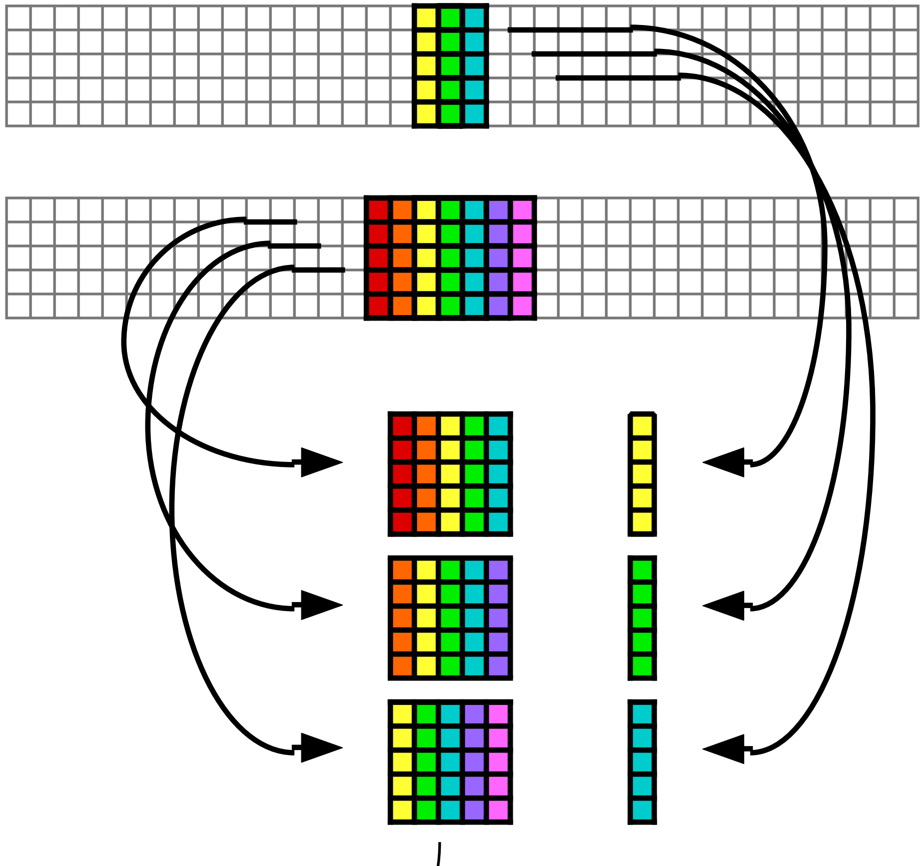
Data Arrangement for PDS



Data Arrangement for Double Window PDS

Standard

Field



Window width

Window 1 = 5
Window 2 = 3

Second window can be spectrum full width = single model PDS

Direct Standardization

- Similar to PDS except $\mathbf{F}_b$ matrix is full:

  $\mathbf{F}_b = \mathbf{S}_2^{+}\mathbf{S}_1$

- Many more parameters in DS compared to PDS

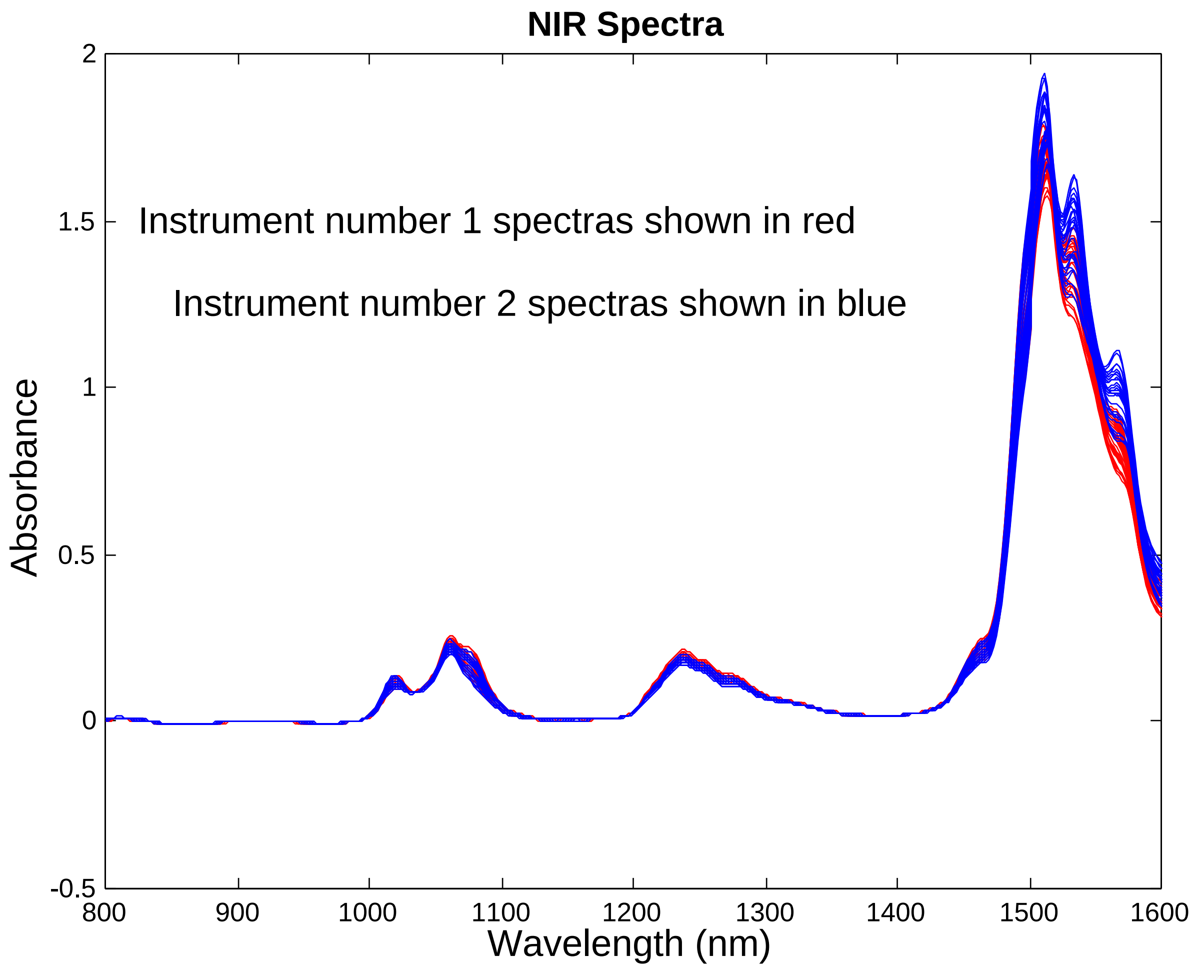
Variations on PDS

- Single model PDS
  - widen second window in DWPDS until it is the width of the entire spectrum
  - model is the same for each channel in master instrument
  - transfer function not a function of wavelength
- Single model PDS with index
  - include the channel number as the parameter in the model
  - use non-linear model such as ANN
  - transfer function is a function of wavelength

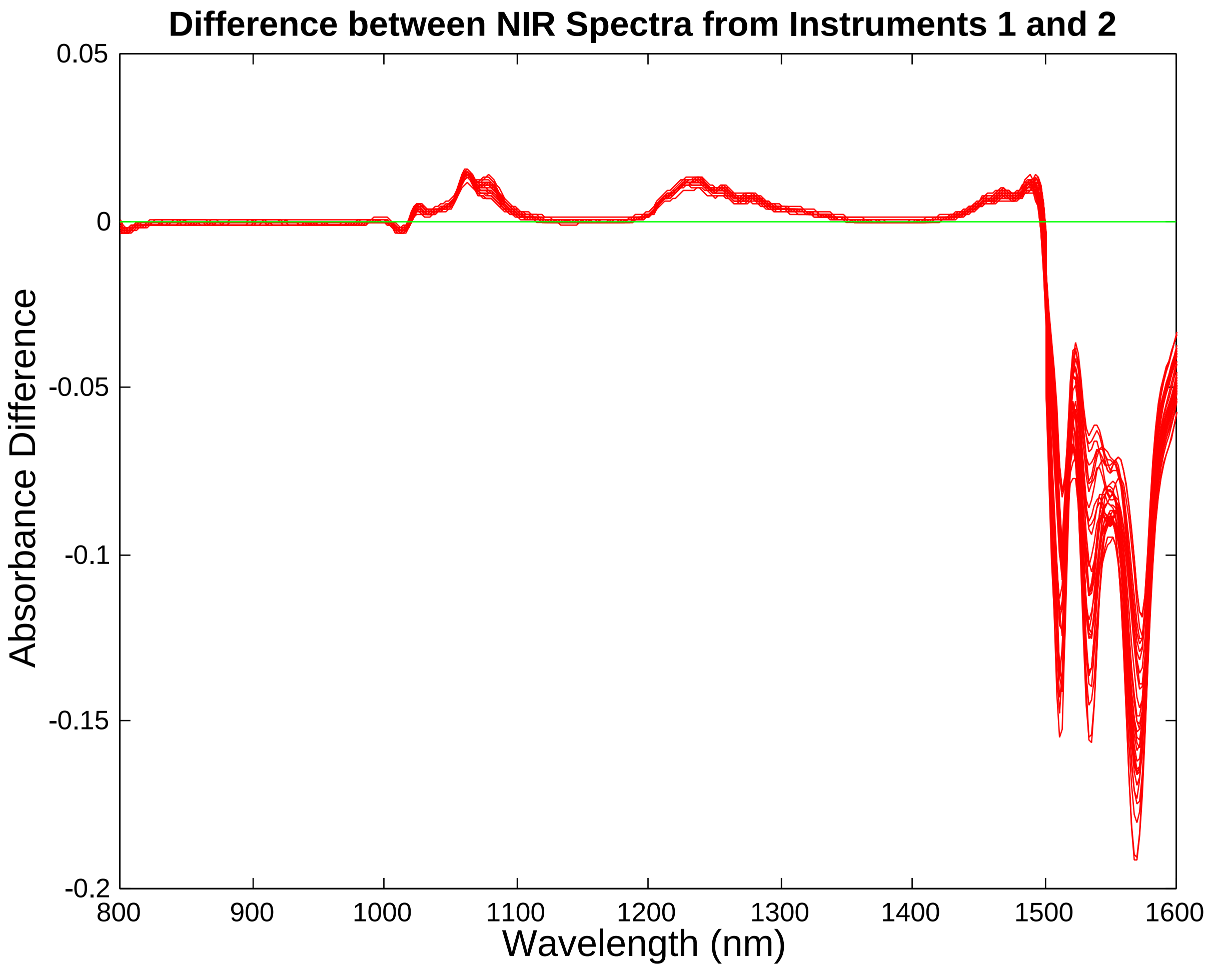
Orthogonal Signal Correction

- OSC attempts to remove extraneous variation unrelated to the property of interest from the predictor variables
- Principal components are calculated for the predictor variables then orthogonalized against the variable(s) to be predicted
- Weighting vectors are determined with PLS which reproduce the orthogonal directions on new data
- To use in standardization, apply to data measured on both instruments

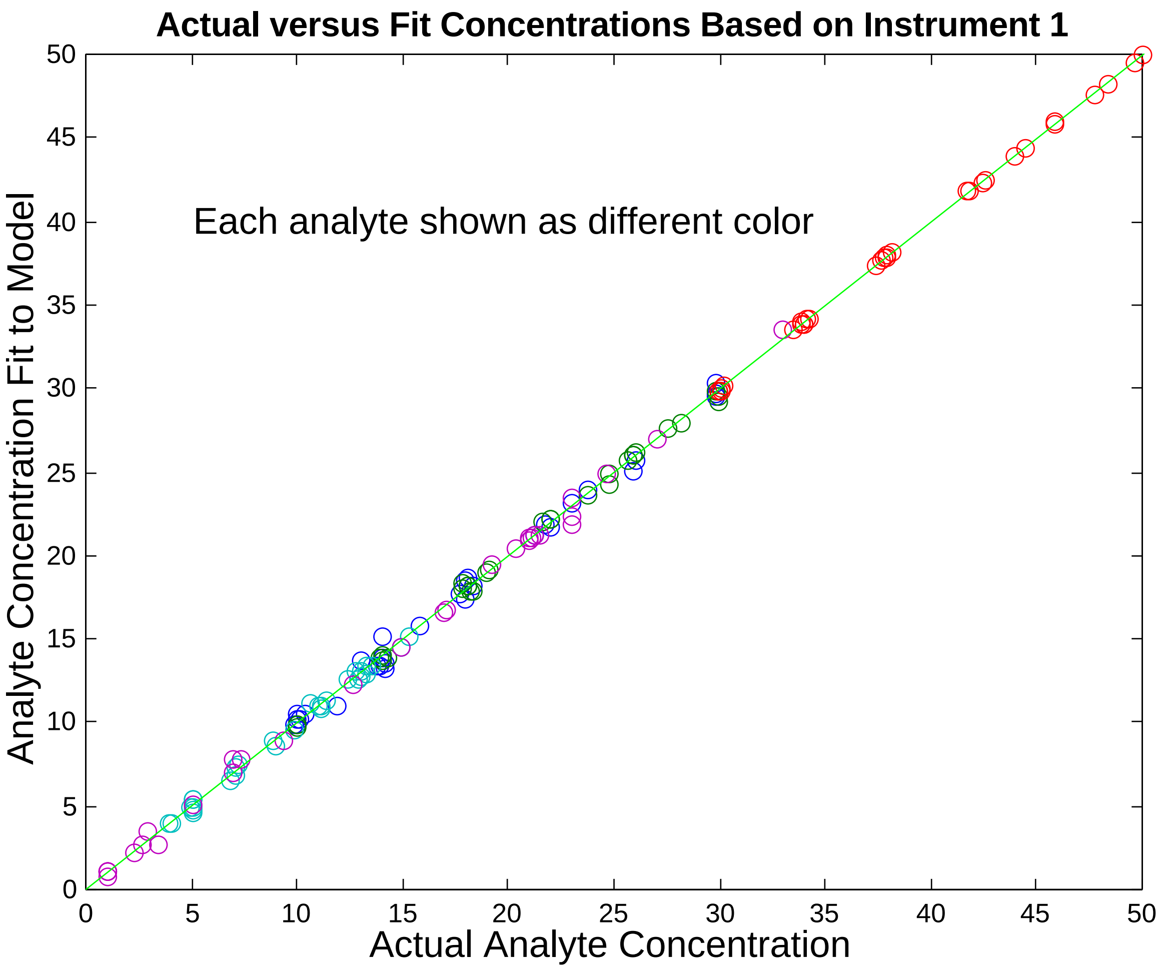
Example From NIR, Pseudo Gasoline Mixtures



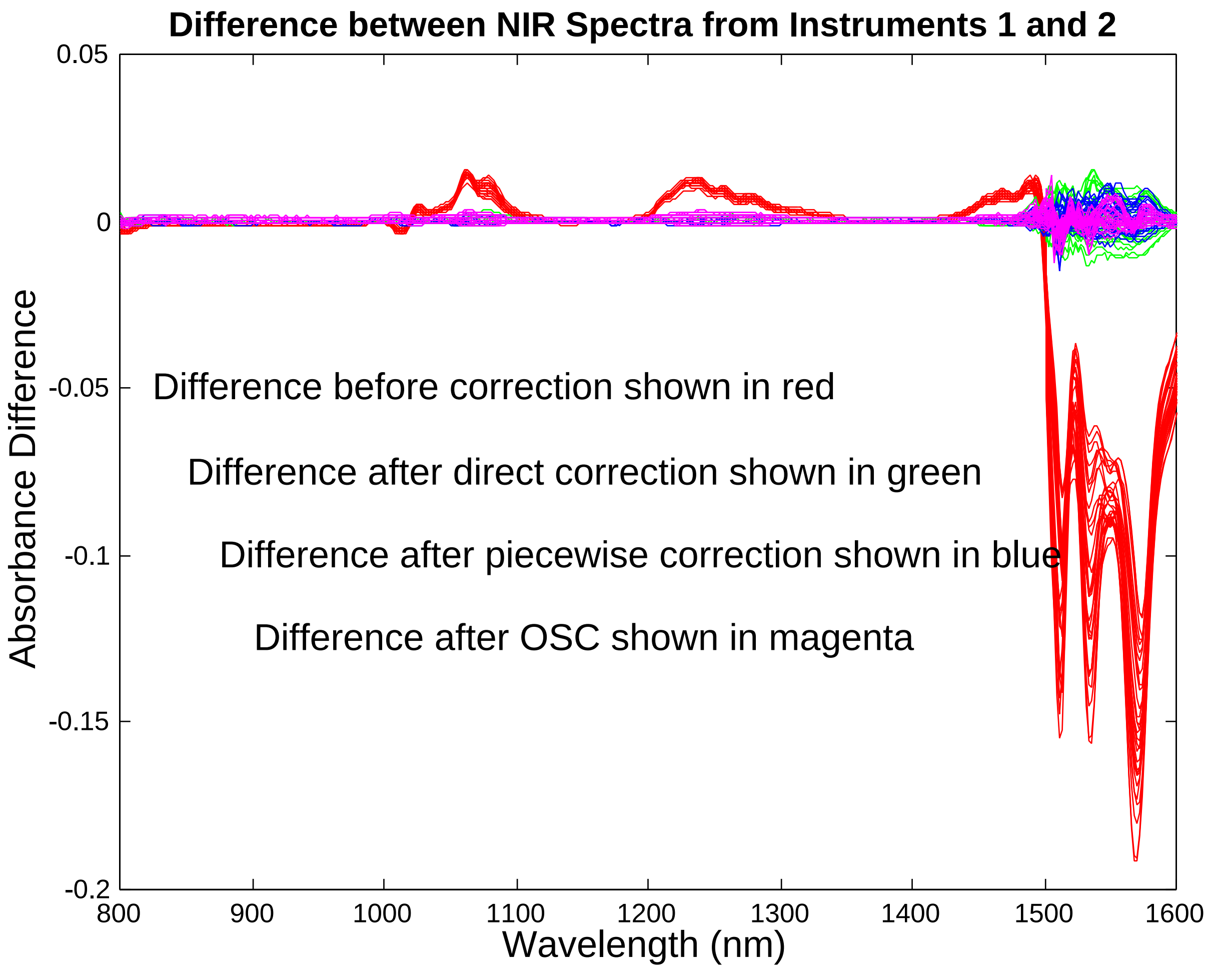
Difference Between Instruments



Instrument 1 Calibration



After Standardization



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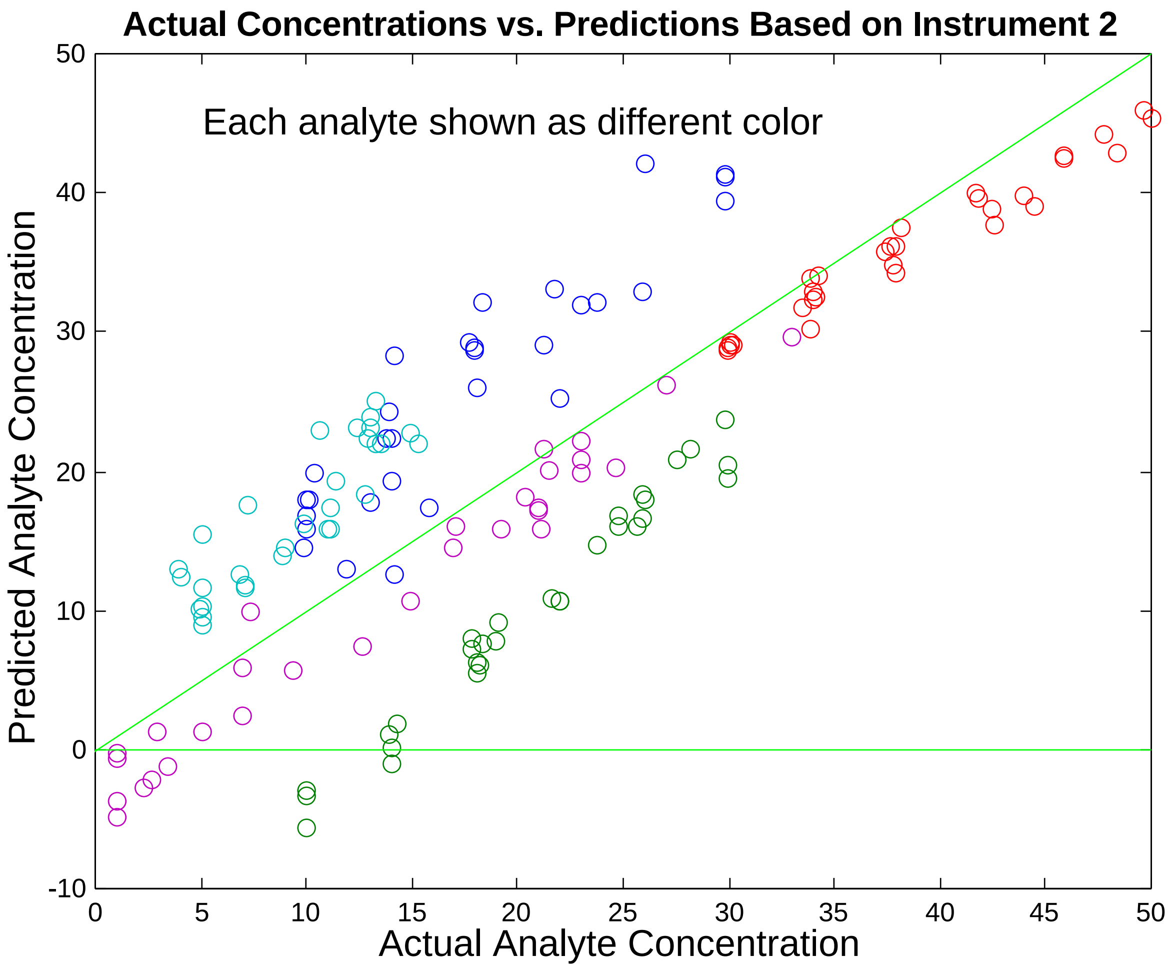
Instrument 1 Calibration on Unstandardized Instrument 2



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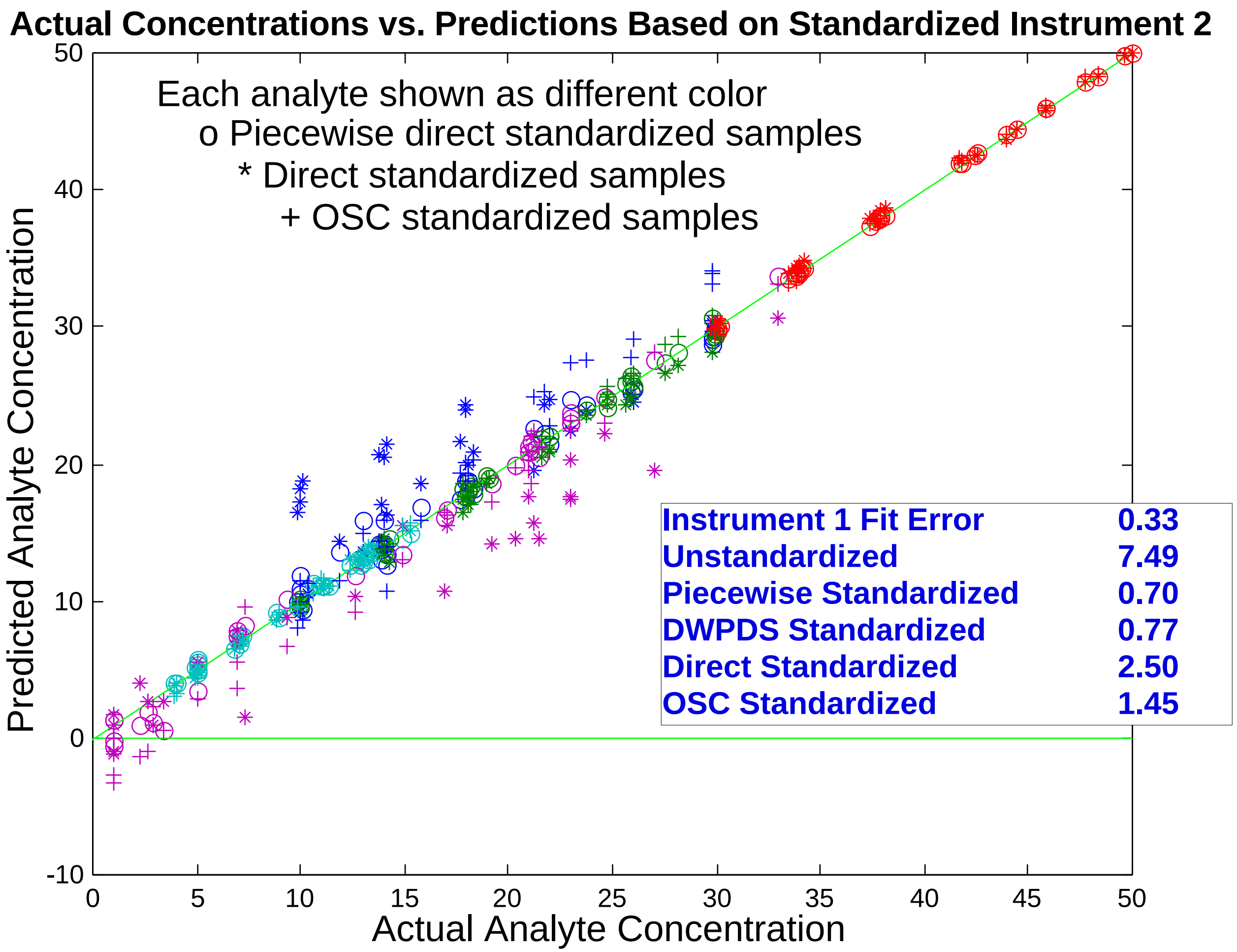
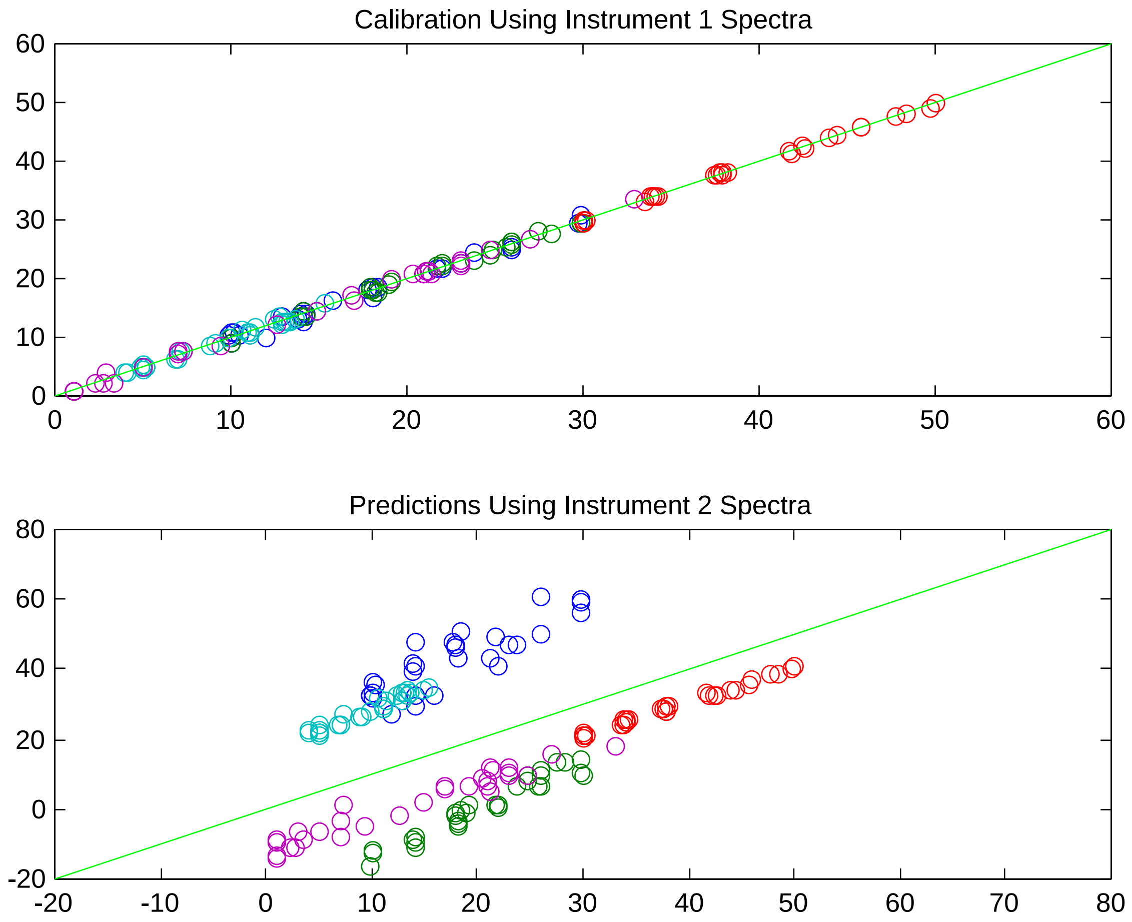
Instrument 1 Calibration on Standardized Instrument 2



Prediction Augmented Classical Least Squares

- If CLS is used for predictive model, new spectra can be added to prediction step to account for differences between instrument
- Augmented spectra can include known new components or estimates of changes such as a baseline offset or mean difference
- Eigenvectors of difference matrices can also be included

CLS: Predictions on Instrument 2 with Instrument 1 Spectra



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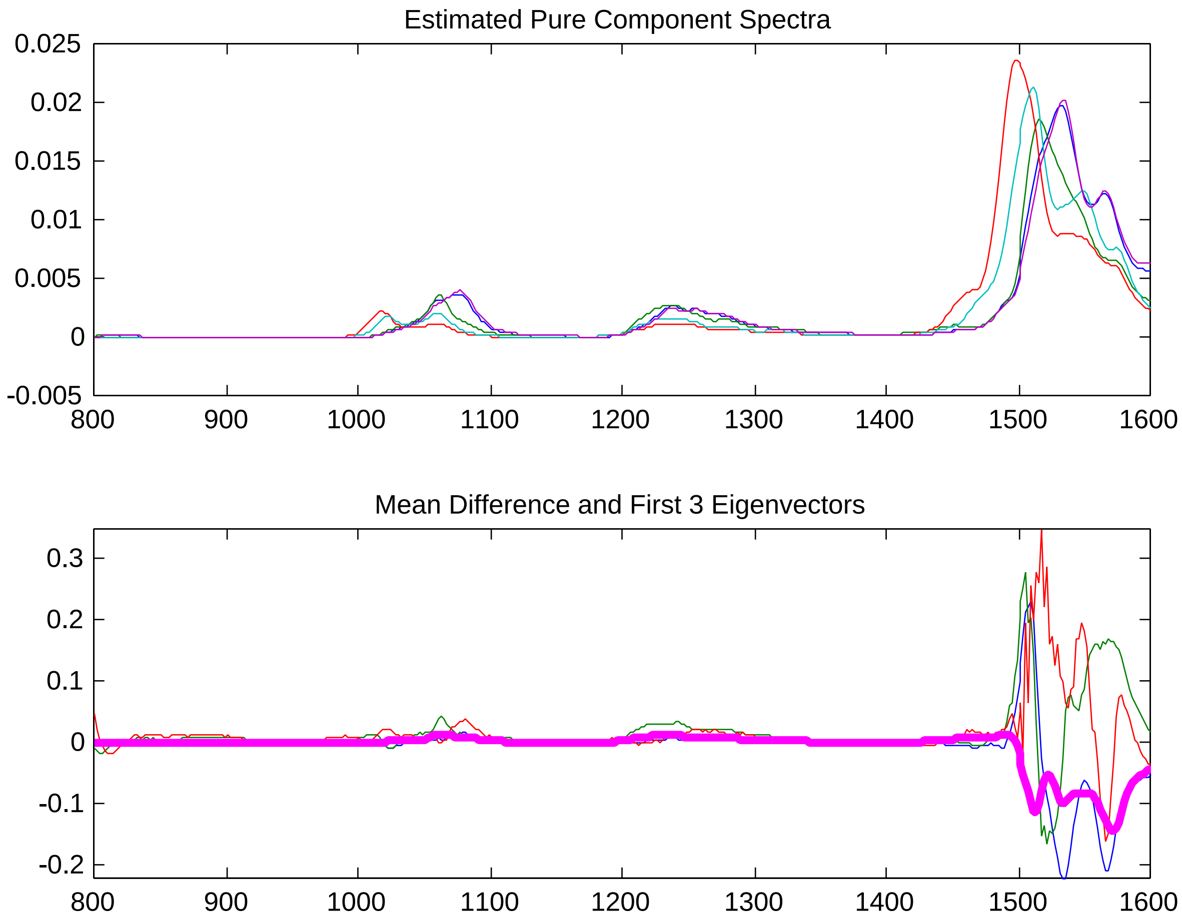
Estimated Pure Component Spectra and Additional Factors



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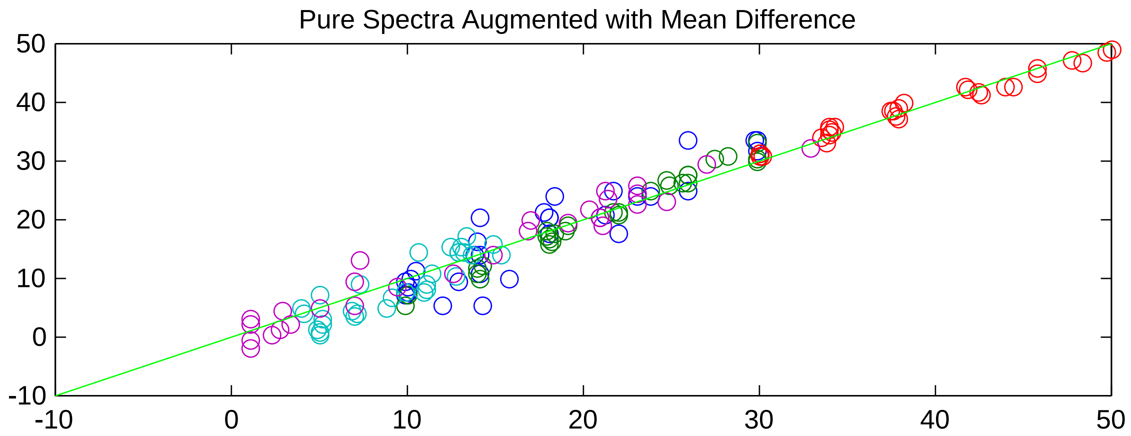
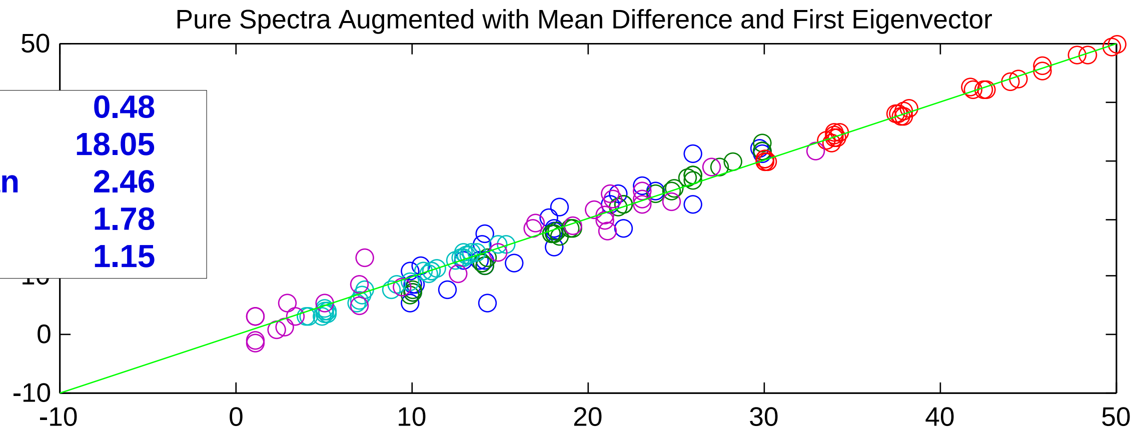
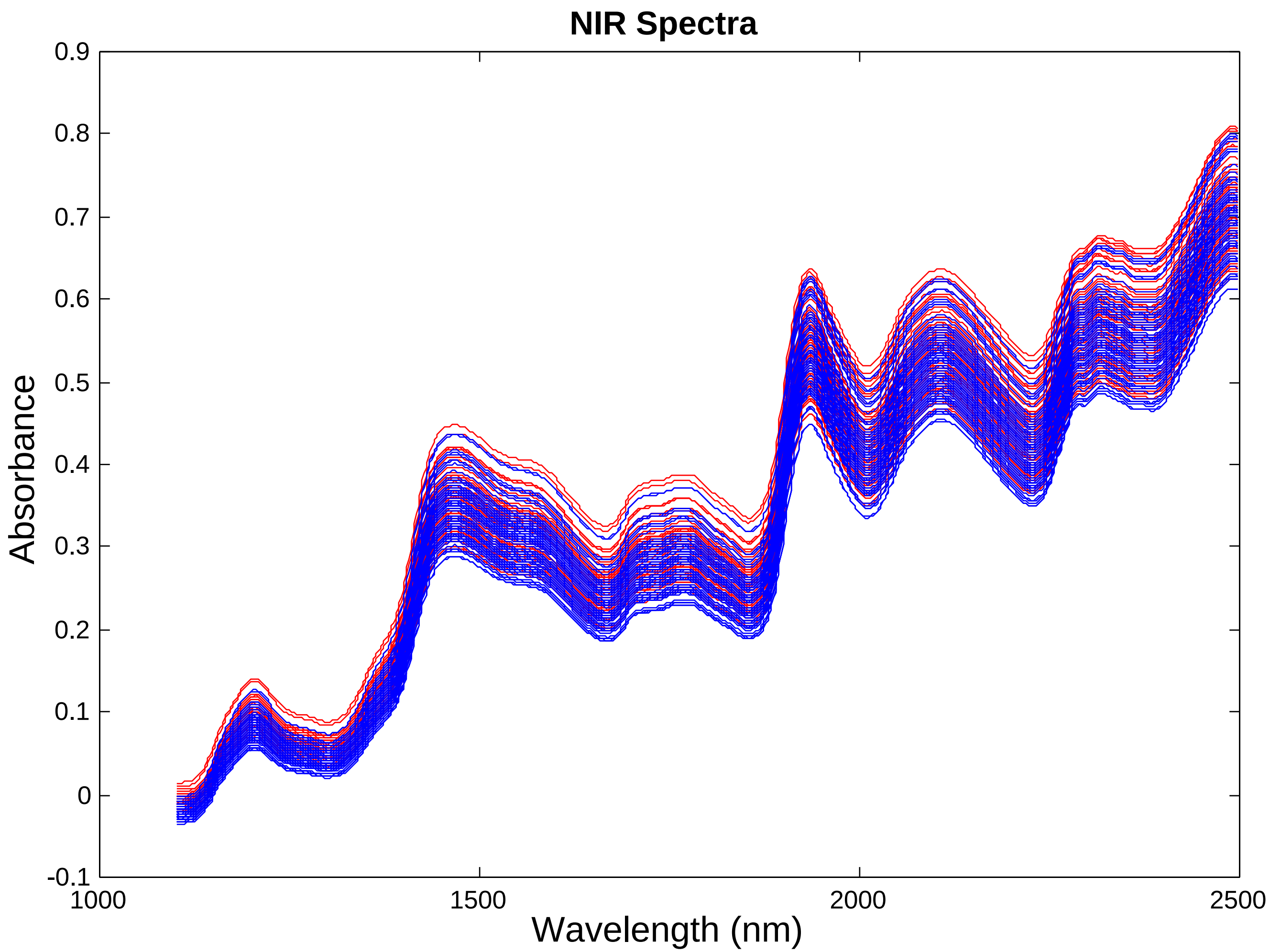
PA-CLS Predictions





Fit Error	**0.48**
Uncorrected	**18.05**
PA-CLS w/mean	**2.46**
PA-CLS 1 EV	**1.78**
PA-CLS 3 EVs	**1.15**

NIR of Corn Samples



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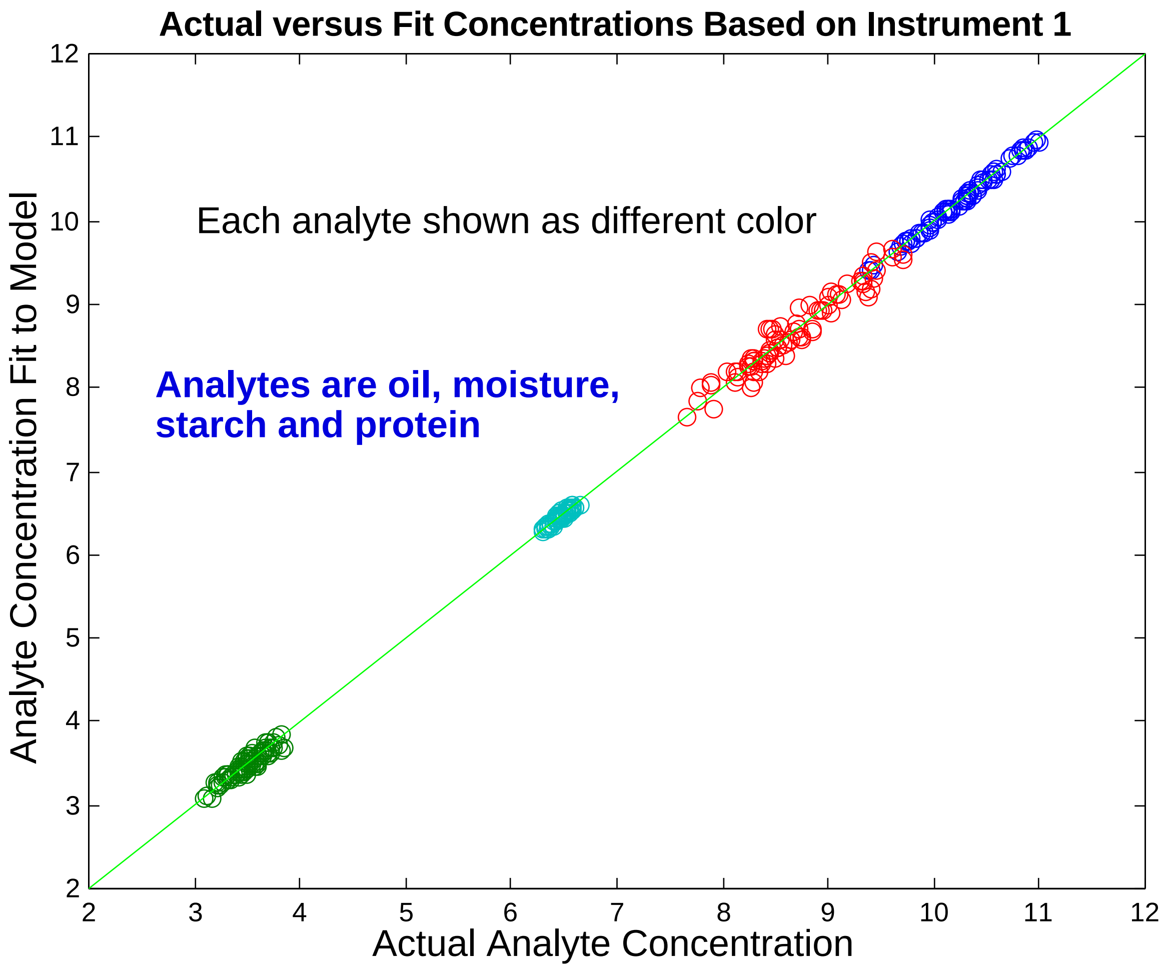
Calibration



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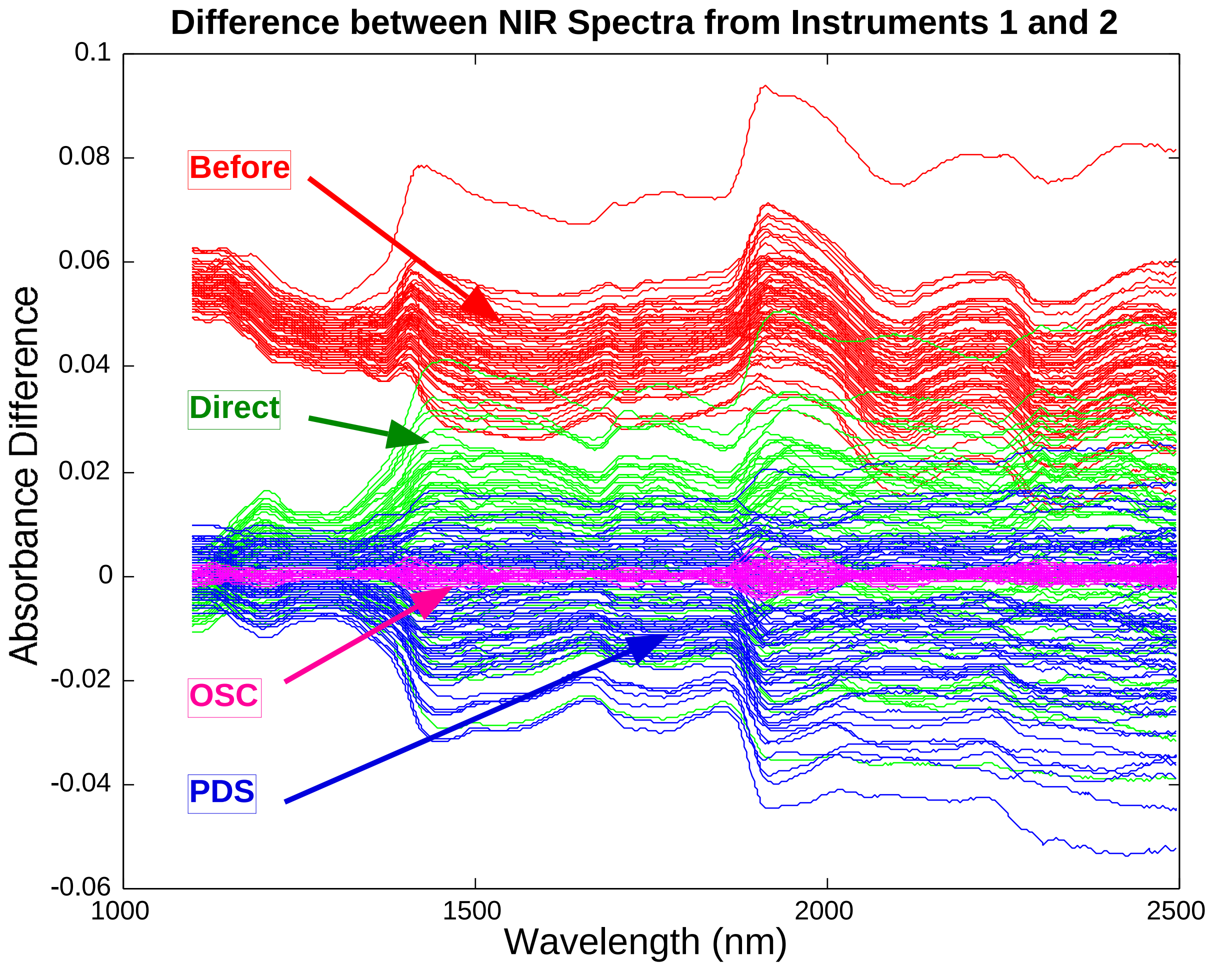
Difference Before and After Standardization



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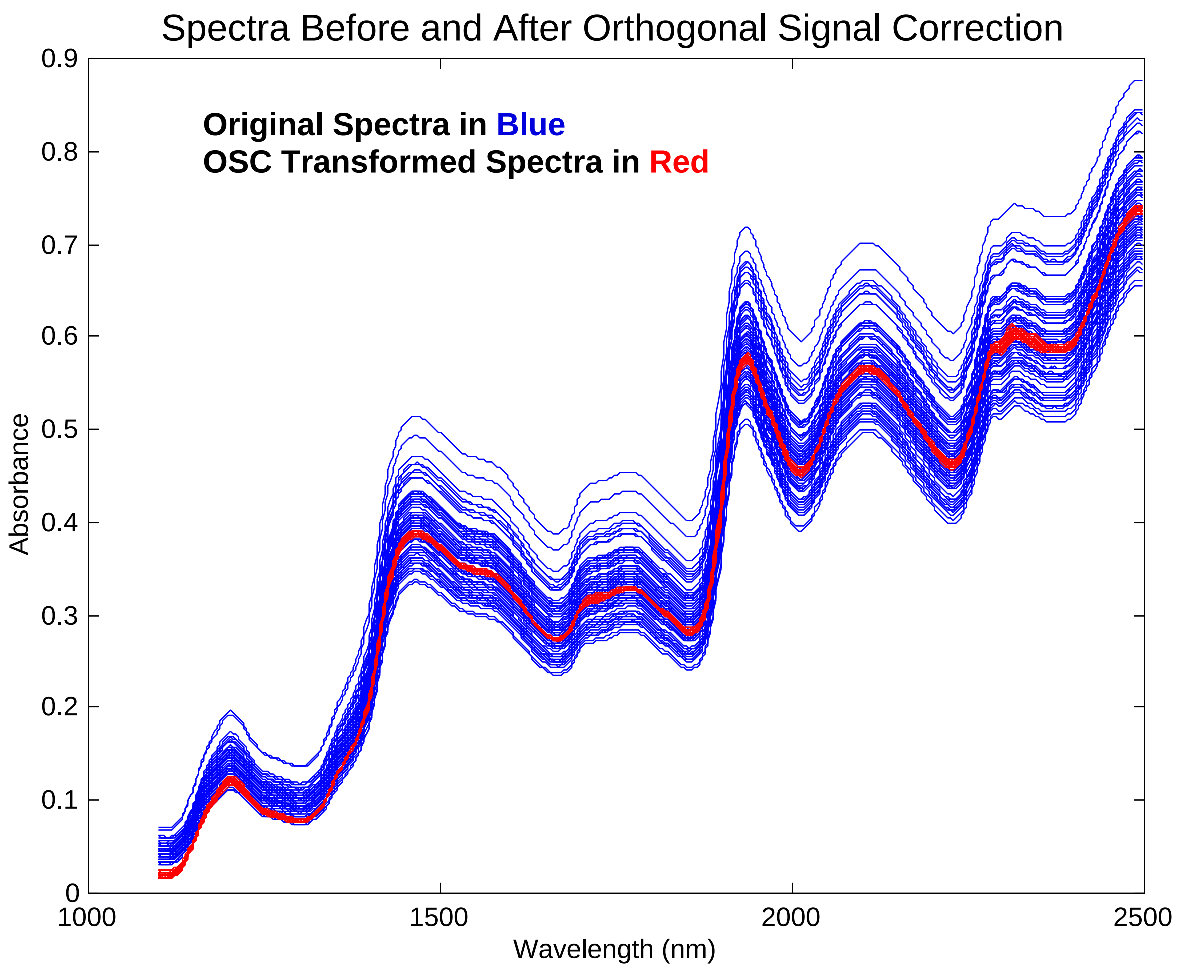
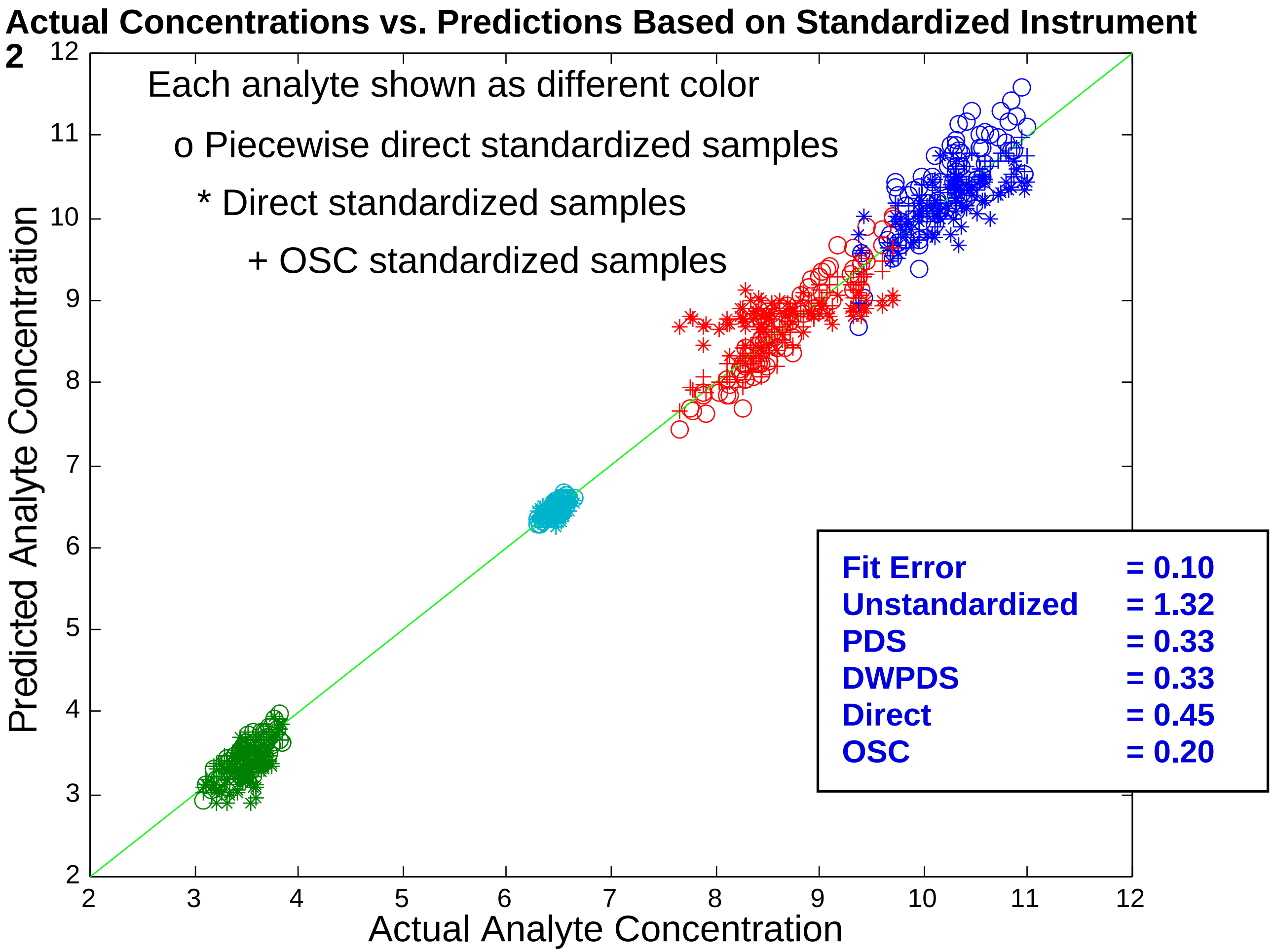
Effect of OSC on Spectra



Results of Corn Standardization



Summary

Method	Transforms?	Standards	Parameters	Uses Y	Comments
Direct	Yes	Real	Lots	No	Many samples
PDS	Yes	Anything	Few	No	Few samples
NN-PDS	Yes	Anything	Moderate	No	Non-linear
Derivative	No	None	None	No	Easy
MSC	Yes	Real, Few	Few	No	Easy
OSC	No	Real	Few	Yes	Requires Y
PA-CLS	No	Anything?	Few	No	Interpretable
GLS	No	Real	Moderate	No	New
Deresolution	No	None	Few	No	FTIR

Conclusions

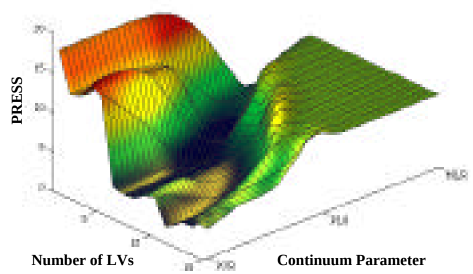
- PDS still the method to "shoot for"
- DS more sensitive to number of transfer samples
- OSC produces especially good results in some data, also useful as a preprocessing technique
- FIR not adequate in situations we've seen

PLS_Toolbox 2.0 for use with MATLAB

- Version 2.0 for MATLAB 5 now available
- Wide selection of multivariate analysis tools
- Used in our Chemometrics Short Courses

MATH BY MATLAB

MATLAB PARTNER



PLS_Toolbox 2.0

for use with MATLAB™

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Neal B. Gallagher