Chemometrics II: Regression and PLS

(Building Predictive Models)

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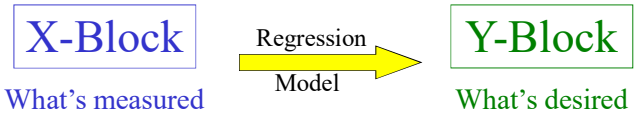
Regression



Regression analysis creates a mapping between two blocks of data.

In contrast, PCA was used to explore the correlation structure within a single data block.

Regression models are often used to obtain estimates (or predictions) for one block of data from the other.

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What Can Be Done with Regression?

- Analyte concentrations from spectra or other sensors
  - CH_4, H_2O, CO_2 in natural gas (NIR)
  - H_2, NH_3 in waste tanks (FTIR)
  - Sugar content of fruit (NIR)
- Prediction of property values
  - Octane of gasoline (NIR)
  - Ozone forming potential of automobile exhaust (FTIR)
- Sample classification (e.g., PLS-DA)
  - Detection of cervical cancer (ETF)
  - Detection of atherosclerotic (vulnerable) plaques (NIR)

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Outline

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Course Materials

- These slides
- PLS_Toolbox or Solo 8.1 or later
- Data sets
  - From DEMS folder (installed with software)
    - plsdata (SFCM)
  - From EVRIHW folder (additional data sets)
    - EigenU_nir_data, SBRdata_EU

Conventions & Notation

- *Rows* correspond to *samples*, *columns* correspond to *variables*
- Notation:
  - **X** = matrix of predictor variables
  - **Y** = matrix (or vector **y**) of predicted variables
  - M = number of samples (observations)
  - N_x = number of **X** variables, N_y = number of **Y** variables
  - **T** = **X**-block scores matrix, $\mathbf{t}_1$, $\mathbf{t}_2$, ..., $\mathbf{t}_K$ score vectors
  - **U** = **Y**-block scores matrix, $\mathbf{u}_1$, $\mathbf{u}_2$, ..., $\mathbf{u}_K$ score vectors
  - **P** = **X**-block loads matrix, $\mathbf{p}_1$, $\mathbf{p}_2$, ..., $\mathbf{p}_K$ loadings vectors
  - **Q** = **Y**-block loads matrix, $\mathbf{q}_1$, $\mathbf{q}_2$, ..., $\mathbf{q}_K$ loadings vectors
  - **W** = **X**-block weights matrix, $\mathbf{w}_1$, $\mathbf{w}_2$, ..., $\mathbf{w}_K$ loadings vectors
  - Θ = ridge parameter

Data Preprocessing

- Everything that was said about preprocessing for PCA goes double for regression
- Data should be linearized, if possible
- Data is often mean-centered
- Variance scaling used when variables are in different units or greatly different magnitudes
- Many preprocessing methods available!
  - Goal: reduce extraneous variance, emphasize relevant variance
- Outlier elimination is critical to regression models

Classical Least Squares

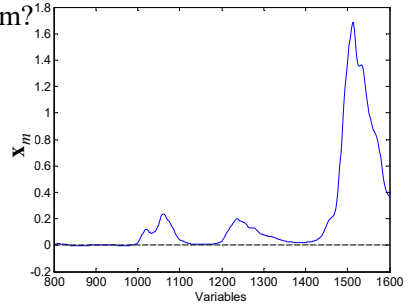
- CLS can be used to develop calibration models
  - often used in spectroscopy
- The CLS model assumes the data follows:

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

where **X** (MxN_x) is the measured response, **S** (N_xxK) is a matrix of pure component responses, **C** (MxK) is a matrix of weights (*e.g.*, concentrations) and **E** (MxN_x) is noise or an error matrix.

The CLS Model

- Given known pure component spectra, how much of each does it take to make up the observed m^{th} spectrum?
- $\mathbf{x}_m = \mathbf{c}_m\mathbf{S}^T + \mathbf{e}_m$
- $m = 1,\ldots,M$
- $\mathbf{c}_m=[c_{m,1}, c_{m,2}, \ldots, c_{m,K}]$
- $k = 1,\ldots,K$



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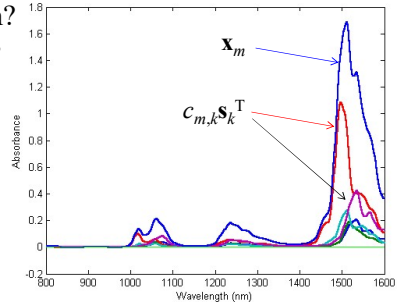
The CLS Model

- Given known pure component spectra **S**, how much of each does it take to make up the observed spectrum?
- *i.e.,* what are the $c_{m,k}$?



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CLS (cont.)

- Once **S** (the spectral "basis") is known, **c**, the degree to which each component contributes to a new sample **x**, can be determined from

$$\mathbf{c} = \mathbf{x}\mathbf{S}^+$$

where $\mathbf{S}^+$ is the pseudo-inverse of **S**, defined in CLS as

$$\mathbf{S}^+ = \mathbf{S}(\mathbf{S}^T\mathbf{S})^{-1}$$

- Problem: How to get **S**?
  - library, estimate from calibration measurements

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Classical Least Squares

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

- Note that $\mathbf{S}^T\mathbf{S}$ is KxK (analytes by analytes) and square

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Estimating S

- Sometimes, **S** can be compiled *a priori* from a data base/spectral library, or from direct measurements of pure components
  - Problem: must account for all components that can contribute to **X**!
- **S** can also be estimated from mixtures, provided all **C** are known and enough samples are available:

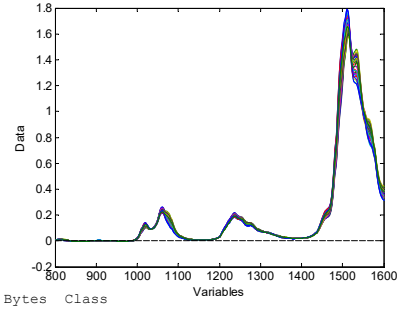
$$\mathbf{S}^T = (\mathbf{C}^T\mathbf{C})^{-1}\mathbf{C}^T\mathbf{X}$$

  - Problem: The concentration of *every analyte that contributes to* **X** must be known!*

*Interferences and unknowns can be handled with GLS or ELS type models, but their basis must be estimated.

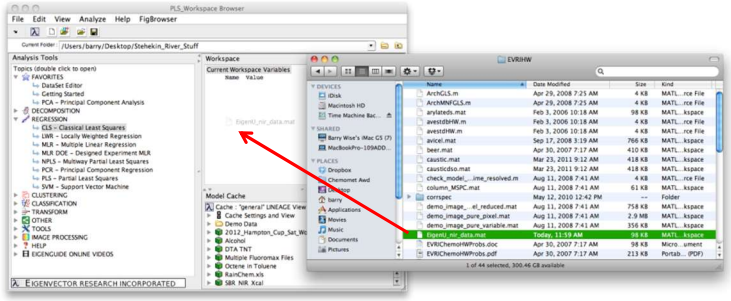
CLS Example

- NIR data of pseudo-gasoline samples
  - absorbance at 401 channels
  - 30 samples
  - 5 analytes
- EigenU_nir_data.mat
- Data broken into
  - 25 calibration samples and
  - 5 test samples

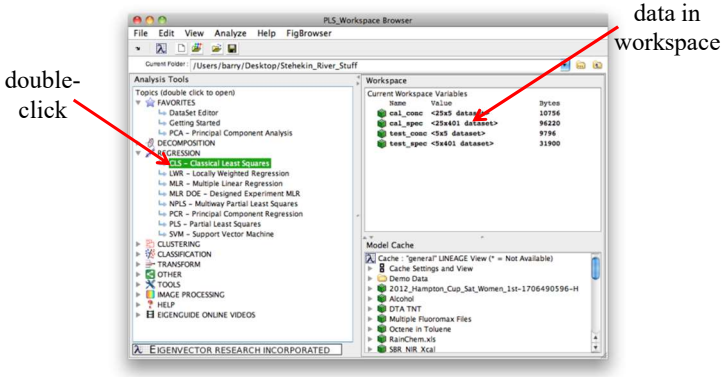



```
>> load EigenU_nir_data
>> whos
  Name            Size              Bytes  Class
  cal_conc        25x5              11002  dataset
  cal_spec        25x401            96466  dataset
  test_conc       5x5               10042  dataset
  test_spec       5x401             32146  dataset
```

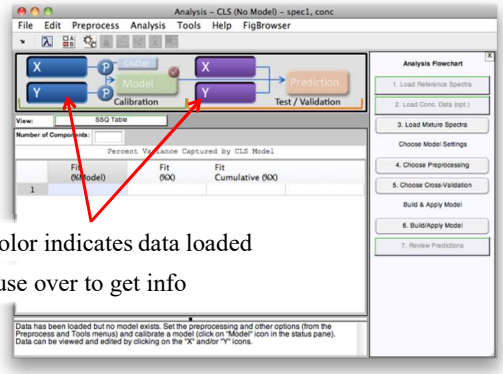

Load Data Into Browser



Start CLS Interface



Data Loaded



darker color indicates data loaded

mouse over to get info

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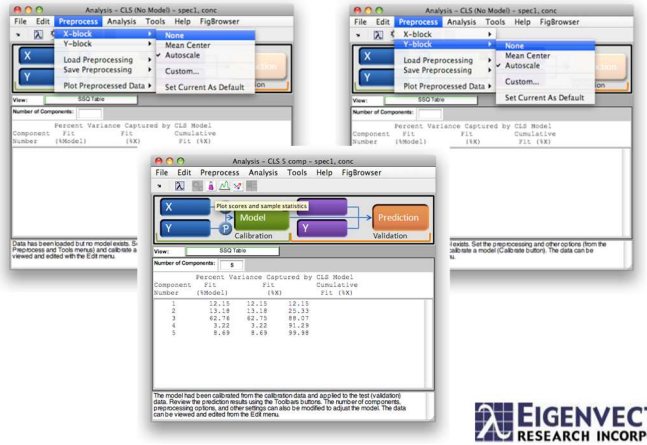
Set Preprocessing to "none," calculate model



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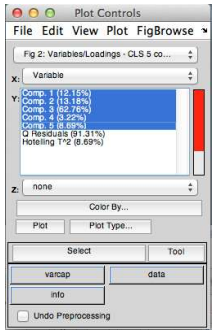
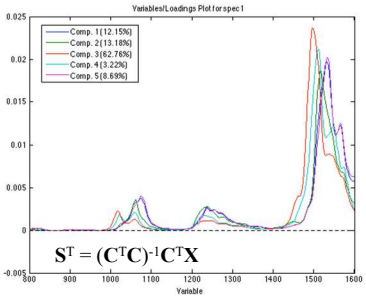
Pure Component Spectra

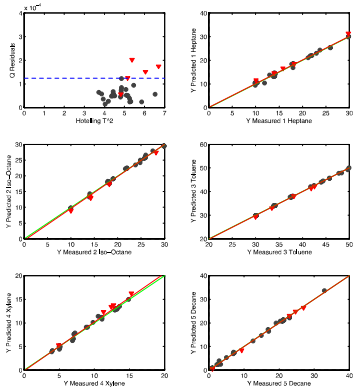
Click loadings "spectrum" icon, select all 5 components



S, estimated from mixtures, using known concentrations of all 5 analytes



Fit to Calibration and Estimate for Validation Samples



Click scores "flask" icon to get fits and predictions (test set).

Check "Show Cal Data with Test".

Calibration data (**black**)

Predicted test (**red**).

All analytes fit and predicted well.

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CLS Problem

- What if the concentration of 1 analyte was unknown?
- Repeat the CLS procedure using only the first 4 (of 5) analytes
- Attempt to predict concentrations of unused (test) samples

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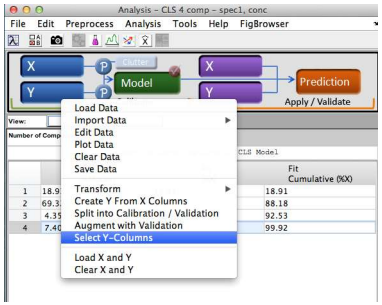
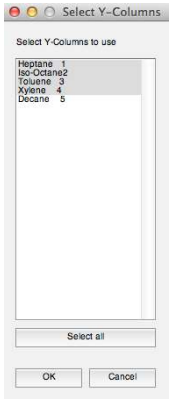
Select only the first four analytes and repeat





click 'cal Y: select Y-columns'

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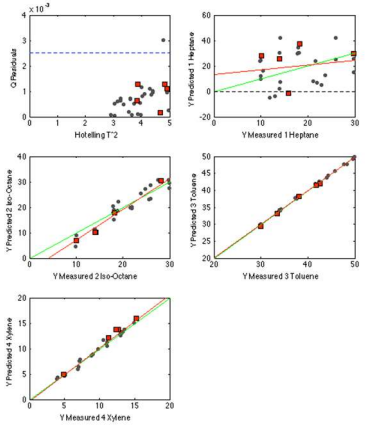
CLS Solution with One Analyte "Missing"



Click scores "flask" icon to get fits

Some analytes not fit (**black**) and not predicted (**red**) well, especially heptane

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Inverse Least Squares

- Inverse least squares (ILS) models assume that the model is of the form:

$$\mathbf{Xb} = \mathbf{y} + \mathbf{e}$$

where $\mathbf{y}$ (Mx1) is a property to be predicted, $\mathbf{X}$ (MxN_x) is the measured response, $\mathbf{e}$ (Mx1) is an error vector, and $\mathbf{b}$ (N_xx1) is a vector of coefficients

- Unlike CLS, ILS methods associate the noise with the predicted property, not the measured response

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Advantage of ILS Methods

- ILS methods (including MLR, PCR, PLS, CR) don't require the concentration of all analytes, including interferents, be known …
- …however, interferents must vary in the calibration data set for the ILS regression model to be robust against them

Interferent: Any substance whose presence interferes with an analytical procedure and generates incorrect results (wiktionary)

Estimation of b: MLR

- It is possible to estimate **b** from

$$\mathbf{b} = \mathbf{X}^{+}\mathbf{y}$$

where $\mathbf{X}^{+}$ is the pseudo-inverse of $\mathbf{X}$

- There are many ways to obtain a pseudo-inverse; the most obvious is multiple linear regression (MLR), a.k.a., Ordinary Least Squares (OLS)
- In this case, $\mathbf{X}^{+}$ is estimated from

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

Multiple Linear Regression

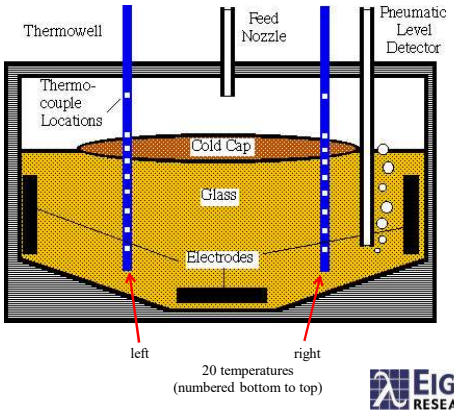
$$\mathbf{Xb} = \mathbf{y} + \mathbf{e}$$
$$\mathbf{Xb} = \mathbf{y}$$
$$\mathbf{X}^{T}\mathbf{Xb} = \mathbf{X}^{T}\mathbf{y}$$
$$\mathbf{b} = \left(\mathbf{X}^{T}\mathbf{X}\right)^{-1}\mathbf{X}^{T}\mathbf{y}$$
$$\mathbf{X}^{+} = \left(\mathbf{X}^{T}\mathbf{X}\right)^{-1}\mathbf{X}^{T}$$

- Note that $\mathbf{X}^{T}\mathbf{X}$ is N_xxN_x and square

Problem with MLR

- Inverse of $\mathbf{X}^{T}\mathbf{X}$ only exists if …
  - Rank(**X**) = N_x, however rank(**X**) ≤ min (M,N_x)
  - **X** has more samples than variables *i.e.,* if M>N_x, and
    - problem with spectra
  - Columns of **X** are not co-linear.
- Inverse may exist but be highly unstable if **X** is nearly rank deficient (a.k.a., ill-conditioned).
- In these cases, small perturbations in the data (possibly due to noise) can produce very different results.

Slurry Fed Ceramic Melter: SFCM



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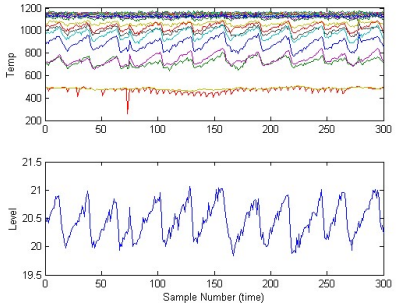
MLR Example

- Use MLR to obtain a relationship between temperature and level in a SFCM



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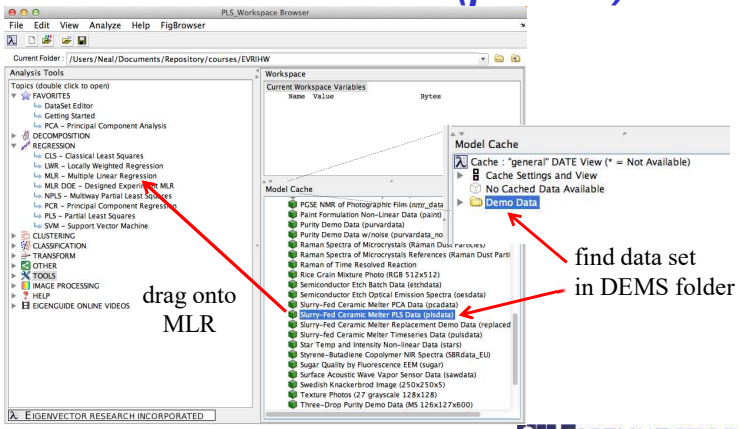
Load SFCM Data (plsdata)



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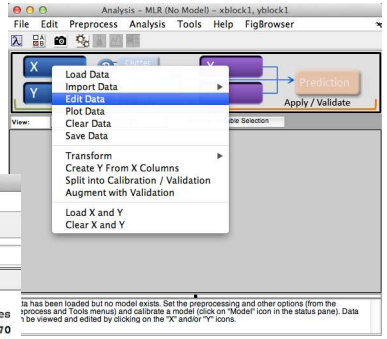
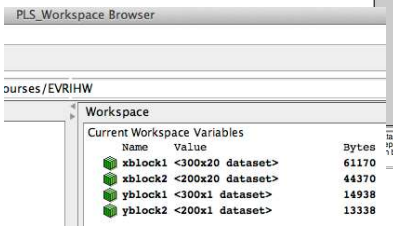
Edit Data

`xblock1` and `yblock1` will load as calibration

`xblock2` and `yblock2` will load as validation set

Edit calibration X-block data





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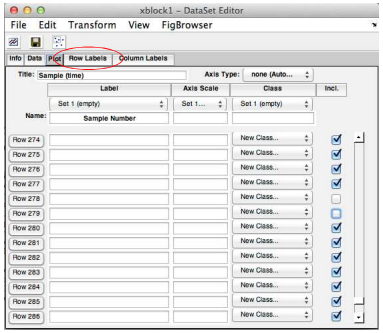
Remove Outliers

Select "Row Labels" tab in DataSet Editor

Exclude samples 73, 167, 278 and 279 from `xblock1`



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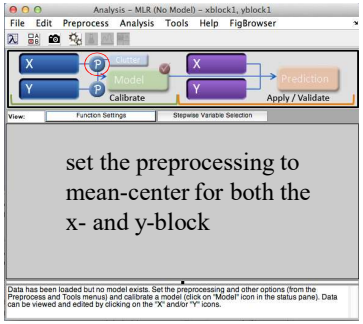
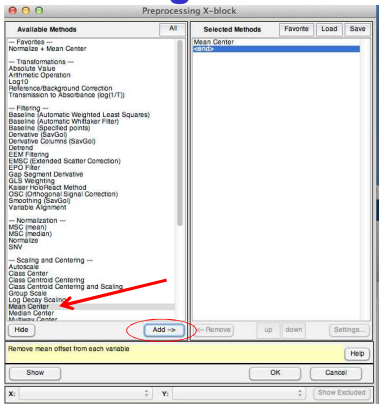
Set Preprocessing



Mean-centering allows for an offset in the linear regression. Not centering is a force fit through zero.



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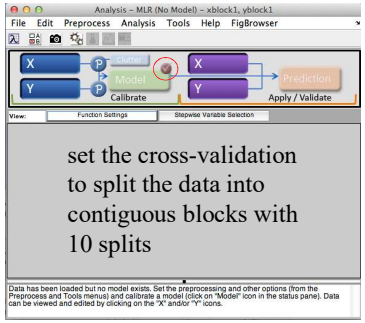
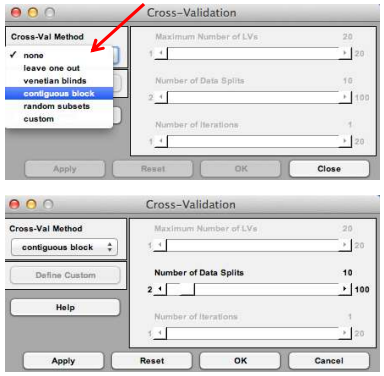
Set Cross-Validation





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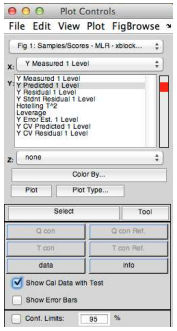
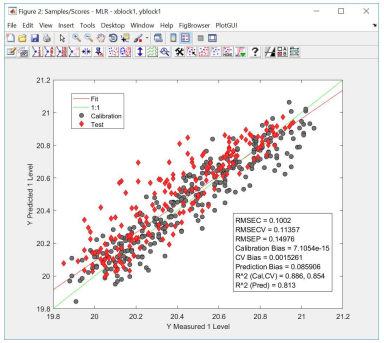
MLR Fit to Calibration and Prediction on Validation Data

Click calculate model 

Click scores "flask" 





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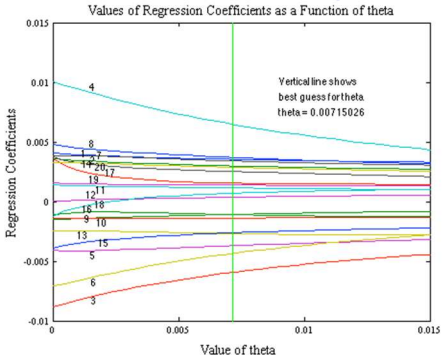
Ridge Regression

- Ridge Regression (RR) is one way to deal with ill-conditioned problems
- RR gets its name because a constant is added to the "ridge" of the covariance matrix in the formation of the pseudo-inverse:

$$\mathbf{X}^{+} = \left(\mathbf{X}^{T}\mathbf{X} + \mathbf{I}\theta\right)^{-1}\mathbf{X}^{T}$$

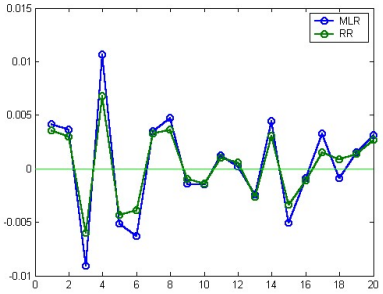
- The addition of the ridge ($\mathbf{I}\theta$ term) stabilizes the inverse and shrinks the values of the coefficients
  - this "ridging" is known as matrix regularization

RR Shrinkage




```
[brr,theta] = ridge(mx,my,0.015,31);
```


RR and MLR Regression Vectors



Problem with MLR and RR

- RR helps stabilize the inverse
  - ridging biases the regression
  - how to determine the ridge parameter θ?
- MLR does not work when $M<N_x$
- Possible solution: eliminate variables
  - how to choose which variables to keep?
    - stepwise regression or other variable selection
  - lose multivariate advantage - signal averaging
- Another solution: use PCA to reduce original variables to some smaller number of factors
  - retains multivariate advantage
  - noise reduction aspects of PCA

Principal Components Regression

- Principal Components Regression (PCR) is one way to deal with ill-conditioned problems
- Property of interest **y** is regressed on PCA scores:

$$\mathbf{X}^{+} = \mathbf{P}_K \left(\mathbf{T}_K^T \mathbf{T}_K \right)^{-1} \mathbf{T}_K^T$$

- Problem is to determine *K* the number of factors to retain in the formation of the model

Principal Components Regression

$$\mathbf{T}_K \mathbf{b}_{pc} = \mathbf{y} + \mathbf{e} = \mathbf{X}\mathbf{P}_K \mathbf{b}_{pc} \Leftrightarrow \mathbf{b} = \mathbf{P}_K \mathbf{b}_{pc}$$

$$\mathbf{T}_K \mathbf{b}_{pc} = \mathbf{y}$$

$$\mathbf{T}_K^T \mathbf{T}_K \mathbf{b}_{pc} = \mathbf{T}_K^T \mathbf{y}$$

$$\mathbf{b}_{pc} = \left(\mathbf{T}_K^T \mathbf{T}_k \right)^{-1} \mathbf{T}_K^T \mathbf{y}$$

$$\mathbf{b} = \mathbf{P}_K \left(\mathbf{T}_K^T \mathbf{T}_K \right)^{-1} \mathbf{T}_K^T \mathbf{y}$$

$$\mathbf{X}^{+} = \mathbf{P}_K \left(\mathbf{T}_K^T \mathbf{T}_K \right)^{-1} \mathbf{T}_K^T$$

- Note that $\mathbf{T}_K^T \mathbf{T}_K$ is *K*x*K* and square

Cross-Validation

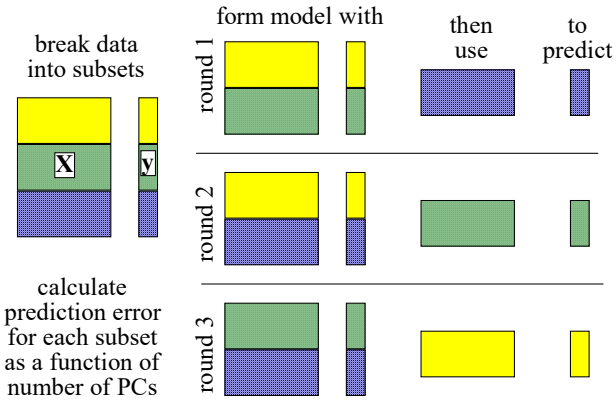
- Divide data set into *J* sample subsets
- For ***each subset*** (*j*=1,…, *J*):
  - Build PCA model using samples in the ***remaining*** subsets
  - Apply the model to subset *j* samples
  - Calculate PRESS (Predictive Residual Sum of Squares) for the subset samples:

$$\mathbf{e}_j^2 = \left(\mathbf{y} - \mathbf{X}\mathbf{b} \right)_j^2$$

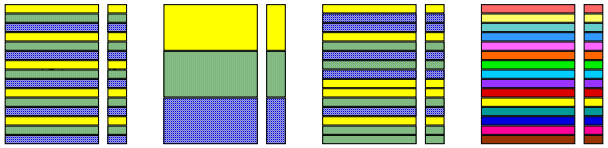
- Look for minimum or "knee" in CumPRESS curve

$$\text{RMSECV} = \left(\frac{1}{M} \sum_{j=1}^{J} \mathbf{e}_j^2 \right)^{1/2}$$

Cross-Validation Graphically



Formation of Test Sets



"Venetian blinds" - OK when data already in random order

contiguous blocks-best for time series

random selection-usually repeated several times

leave-one-out, used when not much data available

What else?

Custom selection, based on prior knowledge!

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Cross-Validation Considerations

- Cross-validation method selection criteria
  - *Number* of objects in dataset, *M*
  - *Order* of objects in dataset
  - *Objective* of cross-validation (specific type of error?)
  - Presence/absence of *replicates*
  - Remember the objective is to mimic future performance
- "Traps" to avoid
  - "Replicate sample trap"
    - Different replicates in both model and test set
  - "External subset selection trap" - extrapolation
    - Test set "space" outside of model set "space"

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Cross-validation Usage Matrix 1/2

DATASET TYPES	CROSS-VALIDATION METHODS				
	Venetian Blinds	Contiguous Blocks	Random Subsets	Leave-One Out	Custom
GENERAL CV Method Properties	• Easy • Relatively quick	• Easy • Relatively quick	• Easy • Can be slow, if m or number of iterations large • Selection of subsets unknown	• Easiest! (Only one parameter) • ***Avoid using if m>20***	• Flexible • Requires time to define splits
Small data sets (<~20 objects)	•	•	• OK, if many iterations done	• Good choice.... • ....unless DOE data	• often needed to avoid the ***external subset selection trap***
randomly-distributed objects	• Good choice	• Good choice	• Good choice • Can take a while with large m, many iterations	• OK, but.... • Can take a while with large m	•

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Cross-Validation Usage Matrix 2/2

DATASET TYPES	CROSS-VALIDATION METHODS				
	Venetian Blinds	Contiguous Blocks	Random Subsets	Leave-One Out	Custom
time-series data	• Useful for assessing ***NON-temporal*** model errors • Can be optimistic with low number of data splits	• Useful for assessing ***temporal*** stability of model	•	•	•
Batch data	• Useful for assessing predictability ***within*** batches/parts of batches	• Useful for assessing predictability ***between*** batches/parts of batches	•	•	• Can manually select "batch-wise" test sets
Blocked data (replicates)	• Beware the ***replicate sample trap*** (optimistic results)!	• Good way to avoid ***replicate sample trap*** • Beware the ***external subset selection trap***!	• Can use to avoid ***replicate sample trap*** (high number of splits, high iterations preferable)	• overly optimistic results, due to ***replicate sample trap***	•
Designed Experiment (DOE) data	• Dangerous, unless object order is randomized	• Dangerous, unless object order is randomized	•	• Not recommended (***external subset selection trap***)	• often needed to avoid the ***external subset selection*** *trap*

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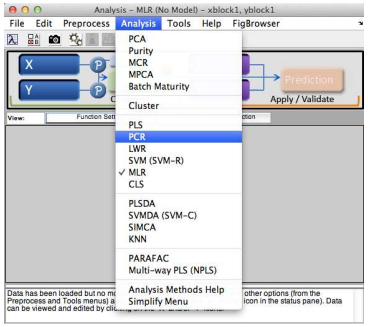
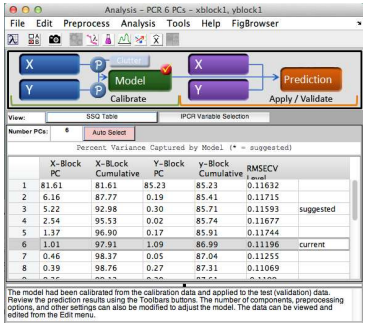
Switch Analysis from MLR to PCR, Calculate Model





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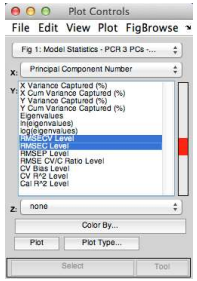
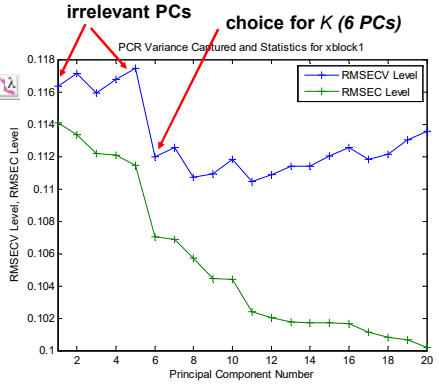
PCR Cross-Validation Example

Recall: time series data so contiguous block CV

Click variance "lambda" icon to get CV results





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PCR Variance Captured

Percent Variance Captured by PCR Model

PC #	X-Block This PC	X-Block Total	Y-Block This PC	Y-Block Total
1	81.61	81.61	85.23	85.23
2	6.16	87.77	0.19	85.41
3	5.22	92.98	0.30	85.71
4	2.54	95.53	0.02	85.74
5	1.37	96.90	0.17	85.91
6	1.01	97.91	1.09	86.99
7	0.46	98.37	0.05	87.04
8	0.39	98.76	0.27	87.31
9	0.36	99.12	0.30	87.61
10	0.24	99.37	0.02	87.63

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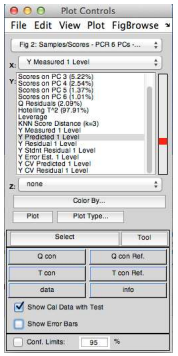
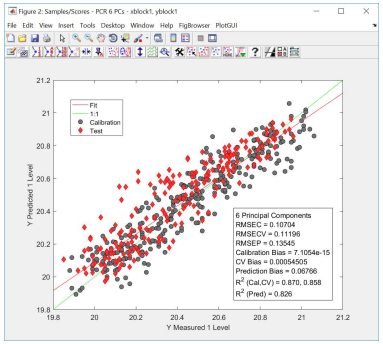
PCR Model Fit to Calibration Data and Validation Predictions

Click scores "flask" to get prediction results

Adjust Plot Controls to get desired plot





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Problems with PCR

- Some PCs not relevant for prediction, but are only relevant for describing variance in **X**
  - leads to local minima and increase in PRESS
- This is a result of PCs determined without using information about property to be predicted **y**
- A solution is to find factors using information from **y** and **X**

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Partial Least Squares

- PLS is related to PCR and MLR
  - PCR captures maximum variance in **X**
  - MLR achieves maximum correlation between **X** and **Y**
  - PLS tries to do both by maximizing covariance between **X** and **Y**
- Requires addition of weights **W** to maintain orthogonal scores
- Factors calculated sequentially by projecting **Y** through **X**

$$\mathbf{X}^{+} = \mathbf{R}_K\left(\mathbf{T}_K^{\mathrm{T}}\mathbf{T}_K\right)^{-1}\mathbf{T}_K^{\mathrm{T}} = \mathbf{W}_K\left(\mathbf{P}_K^{\mathrm{T}}\mathbf{W}_K\right)^{-1}\left(\mathbf{T}_K^{\mathrm{T}}\mathbf{T}_K\right)^{-1}\mathbf{T}_K^{\mathrm{T}}$$

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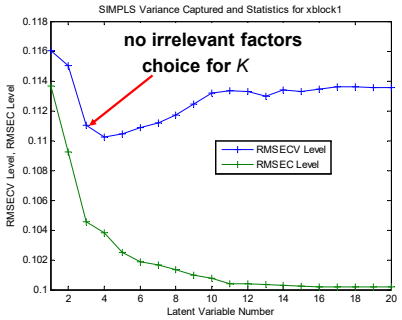
PLS Cross-Validation Example

Set Analysis to PLS

Calculate model

Click variance "lambda" to get CV results 



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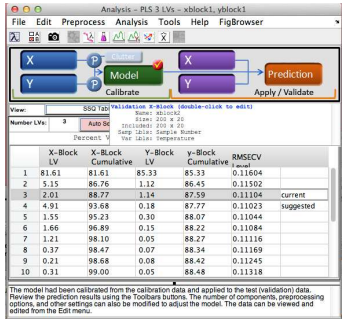
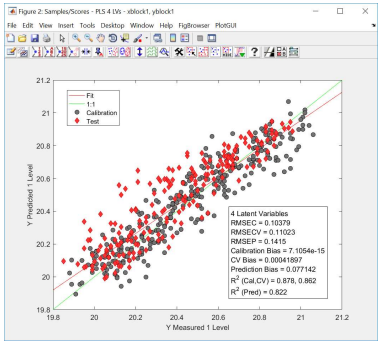
PLS Model Fit to Calibration Data and Validation Predictions

Set number of LVs to 4





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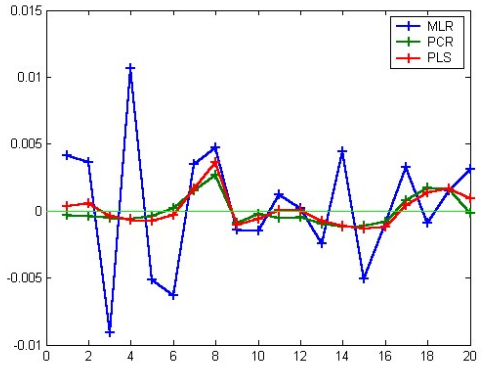
PLS Variance Captured

Percent Variance Captured by PLS Model

LV #	X-Block This LV	X-Block Total	Y-Block This LV	Y-Block Total
1	81.61	81.61	85.33	85.33
2	5.15	86.76	1.12	86.45
3	2.01	88.77	1.14	87.59
4	4.91	93.68	0.18	87.77
5	1.55	95.23	0.30	88.07
6	1.66	96.89	0.15	88.22
7	1.21	98.10	0.05	88.27
8	0.37	98.47	0.07	88.34
9	0.21	98.68	0.08	88.42
10	0.31	99.00	0.05	88.48

Regression Vectors



NIPALS: PLS Algorithm

Choose $\mathbf{u}_1 = \mathbf{y}$ or one column of $\mathbf{Y}$

$$\mathbf{w}_1 = \frac{\mathbf{X}^T\mathbf{u}_1}{\|\mathbf{X}^T\mathbf{u}_1\|} \quad (1)$$

$$\mathbf{t}_1 = \mathbf{X}\mathbf{w}_1 \quad (2)$$

$$\mathbf{q}_1 = \frac{\mathbf{u}_1^T\mathbf{t}_1}{\|\mathbf{u}_1^T\mathbf{t}_1\|} \quad (3)$$

$$\mathbf{u}_1 = \mathbf{Y}\mathbf{q}_1 \quad (4)$$

Check for convergence by comparing $\mathbf{t}_1$ to previous $\mathbf{t}_1$. If $\mathbf{Y} = \mathbf{y}$ skip (3) and (4) and continue

$$\mathbf{p}_1 = \frac{\mathbf{X}^T\mathbf{t}_1}{\|\mathbf{t}_1^T\mathbf{t}_1\|} \quad (5)$$

$$\mathbf{p}_{1new} = \frac{\mathbf{p}_{1old}}{\|\mathbf{p}_{1old}\|} \quad (6)$$

$$\mathbf{t}_{1new} = \mathbf{t}_{1old}\|\mathbf{p}_{1old}\| \quad (7)$$

$$\mathbf{w}_{1new} = \mathbf{w}_{1old}\|\mathbf{p}_{1old}\| \quad (8)$$

Find the regression coefficient for the inner relation:

$$b_1 = \frac{\mathbf{u}_1^T\mathbf{t}_1}{\mathbf{t}_1^T\mathbf{t}_1} \quad (9)$$

After calculating scores and loadings for first Latent Variable, the X and Y-block residuals are calculated:

$$\mathbf{E}_1 = \mathbf{X} - \mathbf{t}_1\mathbf{p}_1^T \quad (10)$$

$$\mathbf{F}_1 = \mathbf{Y} - \mathbf{u}_1\mathbf{q}_1^T \quad (11)$$

Repeat entire procedure replacing $\mathbf{X}$ and $\mathbf{Y}$ with their residuals

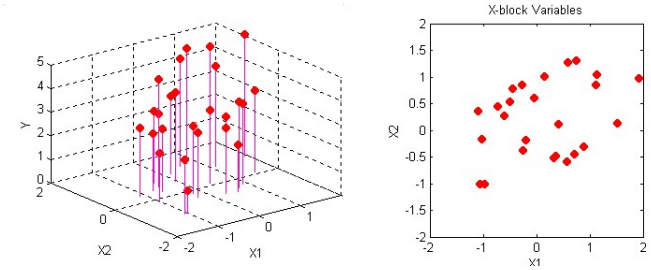
Non-linear iterative patial least squares (NIPALS).
Geladi, Paul; Kowalski, Bruce (1986), "Partial Least Squares Regression:A Tutorial", *Analytica Chimica Acta* **185**: 1–17, doi:10.1016/0003-2670(86)80028-9

Other PLS Algorithms

- It can be shown that $\mathbf{w}_1$ is given by
$$\mathbf{X}^T\mathbf{Y}\mathbf{Y}^T\mathbf{X}\mathbf{w}_1 = \lambda\mathbf{w}_1$$
- The SIMPLS algorithm uses an orthogonalization of a Krylof sequence (faster than NIPLS algorithm)
- The important thing to remember is:
  PLS finds factors in **X** which are correlated with **Y** while describing large amounts of variance in **X**

Sijmen de Jong, "SIMPLS: an alternative approach squares regression," *Chemometrics and Intelligent Laboratory Systems*, **18** (1993) 251-263

Y Projected onto X Plane



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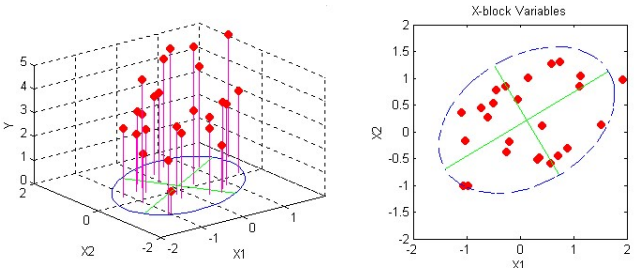
PCA of X-Block



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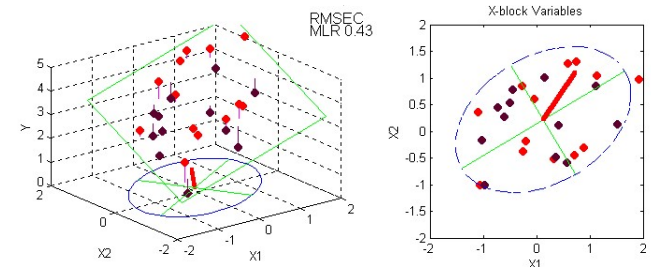
MLR Regression Vector and Surface



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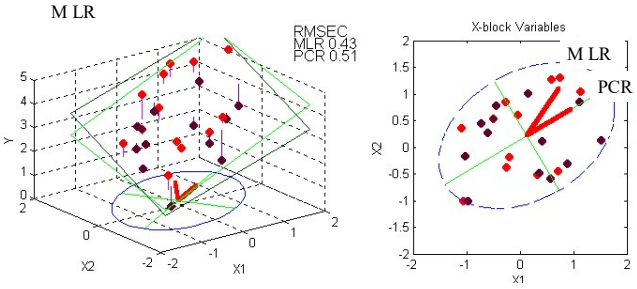
PCR Regression Vector and Surface



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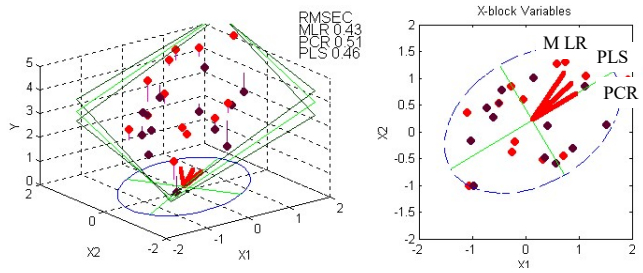
PLS Regression Vector and Surface



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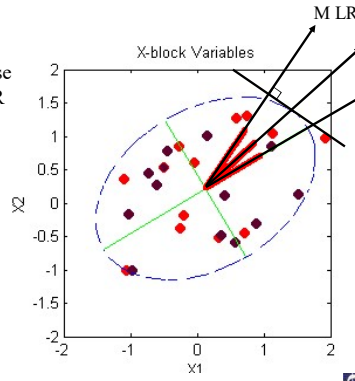
Geometric Relationship of MLR, PCR, and PLS

PLS is the vector on the PCR ellipse upon which MLR has the longest projection



Line perpindicular to the MLR regression vector

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PLS for Multivariate Y

- PLS can be used to relate multivariate **X** to multivariate **Y** (*a.k.a.*, PLS2)
  - outer relationships

$$\mathbf{X} = \mathbf{T}_K\mathbf{P}_K^T + \mathbf{E}$$

$$\mathbf{Y} = \mathbf{U}_K\mathbf{Q}_K^T + \mathbf{F}$$

  - inner relationship

$$\mathbf{U}_K = \mathbf{T}_K\mathbf{B}_K$$

  - *i.e.,* the scores in **Y** are linear combinations of the scores in **X**

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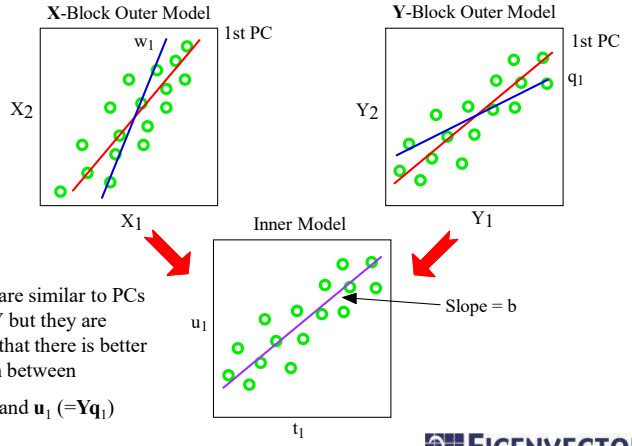
PLS2



$\mathbf{w}_1$ and $\mathbf{q}_1$ are similar to PCs in **X** and **Y** but they are rotated so that there is better correlation between

$\mathbf{t}_1$ (=$\mathbf{Xw}_1$) and $\mathbf{u}_1$ (=$\mathbf{Yq}_1$)

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Model Quality Measures

- Root Mean Square Error (RMSE) Metrics
  - RMSE**C**
  - RMSE**CV**
  - RMSE**P**
  - In units of the **Y** variable!
- Correlation Coefficient (r)
  - Unit-less
  - Considers the range of **Y**

$$\sqrt{\frac{\sum_{i=1}^{m}\left(y_i-\hat{y}_i\right)^2}{m}}$$

$$\frac{\sum_{i=1}^{m}\left(\hat{y}_i-\hat{\bar{y}}\right)\left(y_i-\bar{y}\right)}{\sqrt{\left[\sum_{i=1}^{m}\left(\hat{y}_i-\hat{\bar{y}}\right)\sum_{i=1}^{m}\left(y_i-\bar{y}\right)\right]}}$$

Root Mean Square Error (RMSE) Metrics

- These are used to assess a model's *fit to the data* and *predictive ability on new data*
- Measures "average" deviation of model estimates from the measured data
- Measure of *fit* - root mean squared error of ***calibration*** (RMSE**C**)

$$\text{RMSE}\mathbf{C}=\sqrt{\frac{\sum_{i=1}^{m}\left(y_i-\hat{y}_i\right)^2}{m}}$$

*i's refer to all samples **used to build the model***

Cross-Validation Error

- RMSE**C** measures *fit to the model data*. RMSECV (root mean squared error of cross-validation) is an estimate of *predictive power on new data*.
- RMSE**CV** is a function of the number of factors *k and* how the test sets were selected

$$RMSECV=\sqrt{\frac{\sum_{j=1}^{J}\sum_{i=1}^{m_j}\left(y_i-\hat{y}_i\right)^2}{m_J}}=\sqrt{\frac{PRESS}{m_J}}$$

J's refer to different CV subsets

*i's refer to CV subset samples- **not used to build CV models***

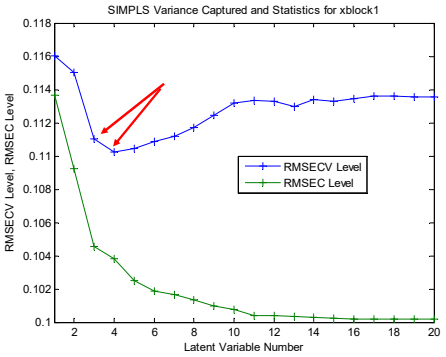
Prediction Error

- Prediction error is often used to validate a model and is a true measure of the *predictive power on new data*
- Measure of *prediction error* - root mean squared error prediction (RMSE**P**)

$$\text{RMSE}\mathbf{P}=\sqrt{\frac{\sum_{i=1}^{m}\left(y_i-\hat{y}_i\right)^2}{m}}$$

*i's refer to samples **NOT** used to build the model*

RMSE metrics, as a function of factor (PC, LV)



RMSEC and RMSECV can also be used to determine the optimal number of factors (LVs, PCs) to be used in a model

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Comparison of Models

- MLR, PCR, and PLS models were constructed using SFCM data: Calibration used (xblock1) and test used (xblock2).

	MLR	PCR	PLS
RMSEC	0.1002	0.1070	0.1038
RMSECV	0.1136	0.1120	0.1102
RMSEP	0.1498	0.1355	0.1415

- ***Fit*** and ***prediction*** are two entirely different aspects of a model's performance

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Number of PCs or LVs

- Choice is not always simple
- A few rules of thumb
  - sqrt(*M*) a good choice for number of splits
  - useful to do repeated CVs with different data ordering
  - if data is time series use block CV due to correlated noise
  - be conservative, models are more often over-fit than under-fit
  - best choice is often not the global minimum PRESS
  - look for minimum of PRESS and work backwards if improvement is not at least 2%
  - RMSEC<RMSECV by more than ~20% indicates overfit
  - look at variance captured in **X** and **Y**. Is it significant with respect to what you know about the data?

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Model Diagnostics

- Diagnostics useful for finding outliers/uniques
- **X**-block Q residual and T^2
- **X**-block leverage and studentized **Y**-block residuals
- Try SFCM example ***without removing outliers***

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Build PLS Model on SFCM Data

- Construct a linear regression for yblock1 from xblock1 (time series data)
  - predict level of slurry fed ceramic melter (Y-block)
  - using melter temperatures (X-block)
- Test the model on xblock2 and yblock2

IF data still loaded, can do:
- Edit/Calibration/X-block Data
- Row Labels Tab
- right-click on "Incl" : "Clear/Reset" (checks all rows)
- calculate model

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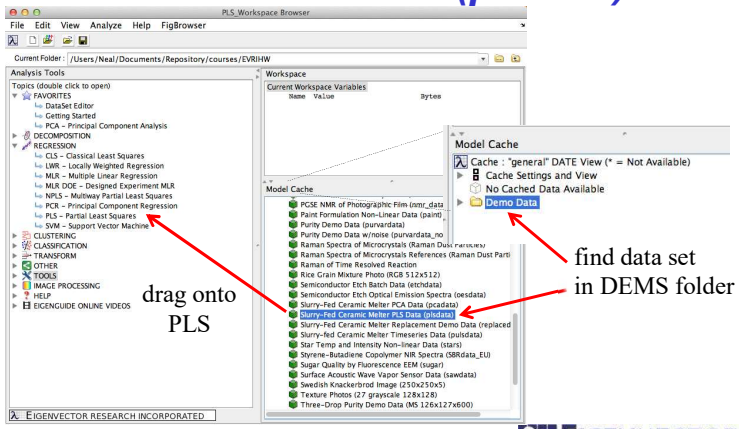
Load SFCM Data (plsdata)



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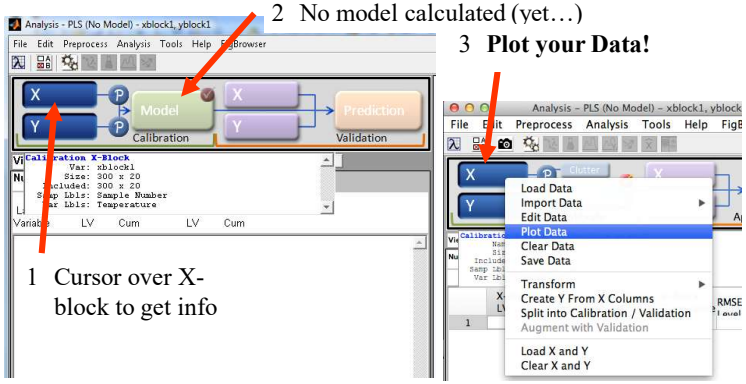
Data: loaded but not analyzed



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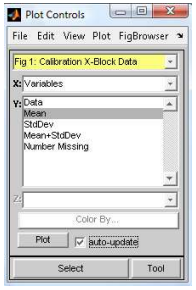
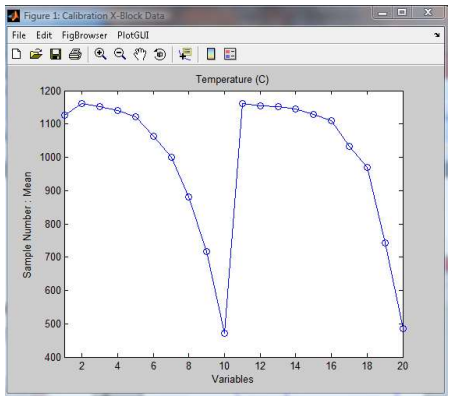
Plot Your Data

Default plot

Column / Variable mean





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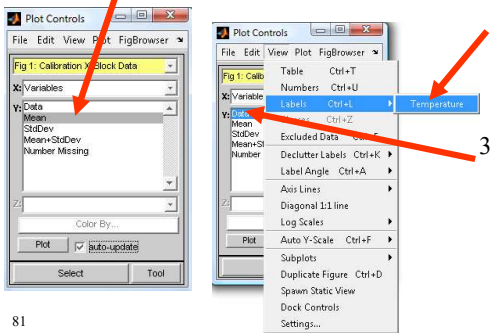
Plot Your Data

1 Plot control default

can look at summary stats

the Plot control generates plots in MATLAB figure windows



2 under view menu check labels:Temperature

3 under Y: menu highlight Data

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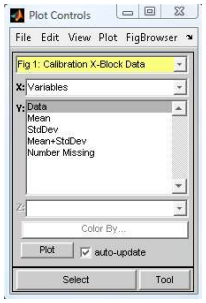
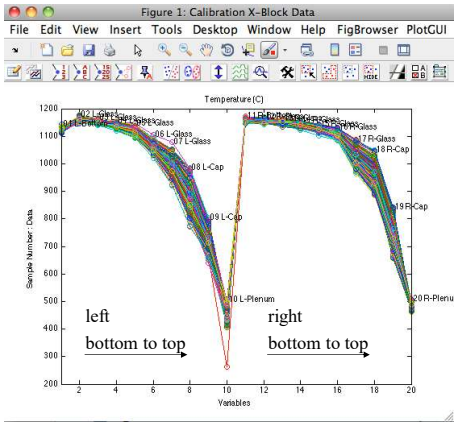
Plot Your Data

all samples vs. variables





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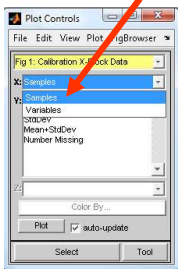
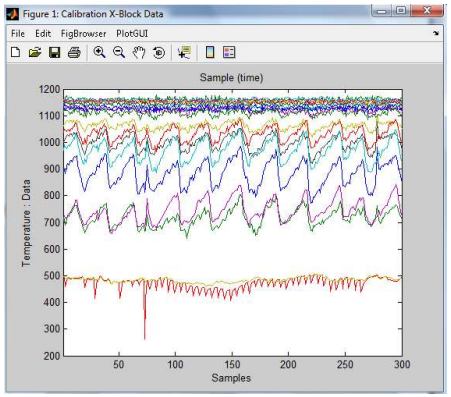
Plot Your Data

all variables vs. samples (time)

under X: menu highlight Samples





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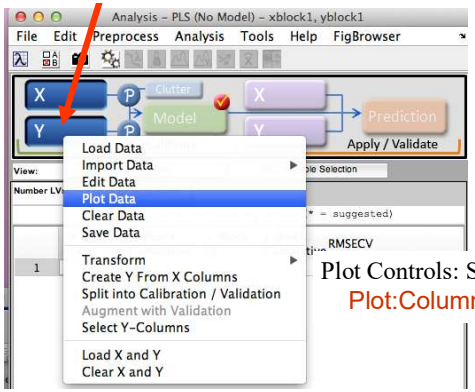
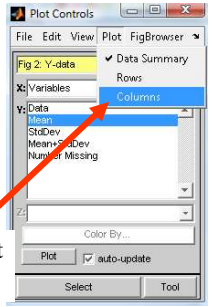
Plot Y data

Click



Plot Controls: Select Plot:Columns



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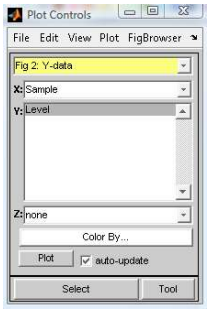
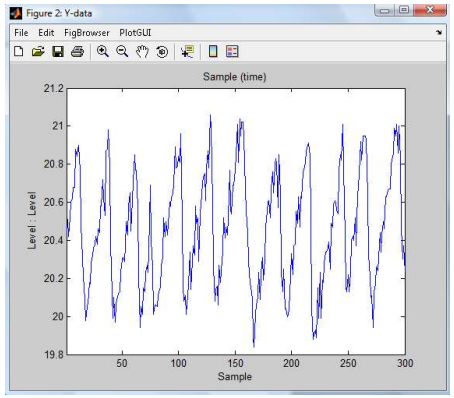
Plot Y Data





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Plot Your Data: Summary

- Bottom temperatures higher than top temperatures
  - surface and plenum space is cooler than the bottom
- Trend in time
  - "saw-tooth" pattern showing correlation between some temperatures and level

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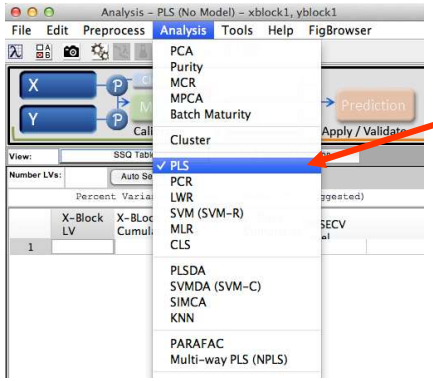
Which Regression?

- BACK to Analysis Window, then Analysis menu
- Choose PLS...



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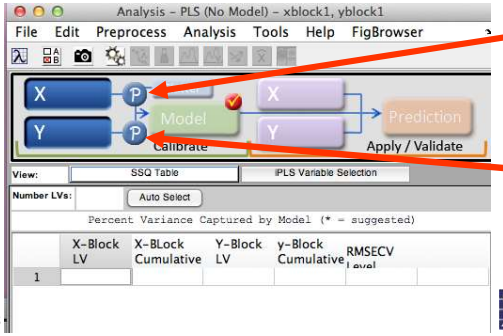
How Should We Scale the Data?

- Variables are in same units and there's and reason to believe that variance is associated with signal: Suggests mean-centering.
- X Preprocessing is set under Preprocess:X-block



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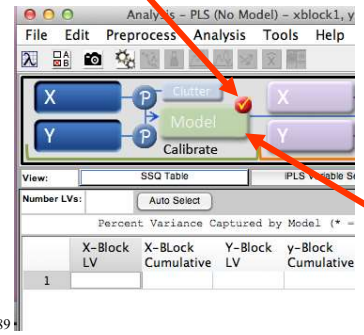
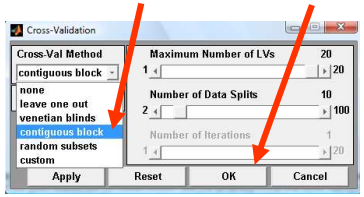
How to Cross-Validate?

- Time series data suggests contiguous block cross-validation

1 click check for Cross-Validation



2 contiguous block, then OK



3 click Model button to perform cross-validation *and* build the regression model

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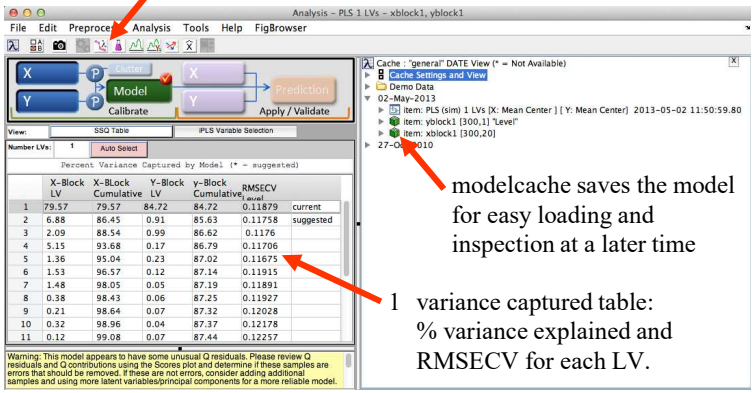
Regression Results

2 Click Eigenvalue button to plot RMSEC and RMSECV

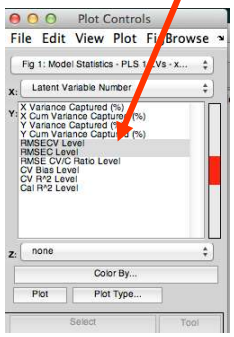


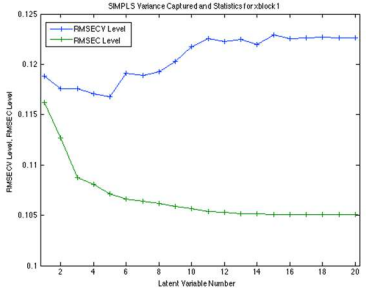
modelcache saves the model for easy loading and inspection at a later time

1 variance captured table: % variance explained and RMSECV for each LV.

RMSECV Plot

Plot RMSEC and RMSECV vs. LV.





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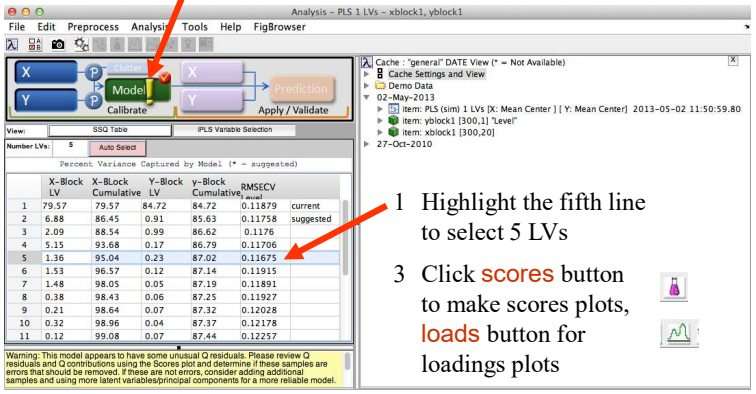
Choose Number of LVs

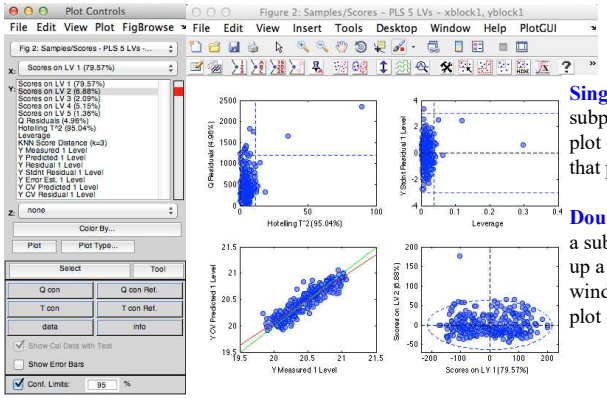
2 Click Model button to reconstruct the model with 5 LVs



1 Highlight the fifth line to select 5 LVs

3 Click scores button to make scores plots, loads button for loadings plots

Scores Summary Plot



Single-click on a subplot: brings up plot controls for that plot

Double-click on a subplot: brings up a new figure window with that plot only

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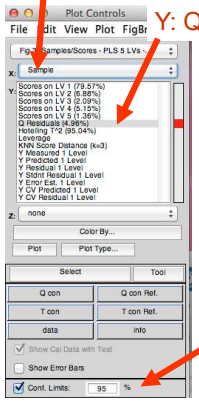
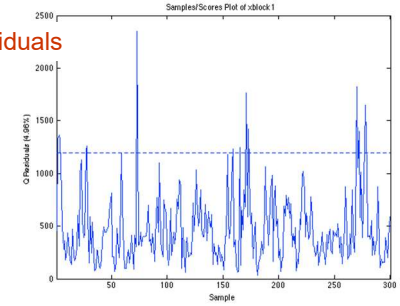
X-Block Q Residuals (by sample)

1 set plot controls

X: Sample

Y: Q Residuals





2 Check Conf. Limits

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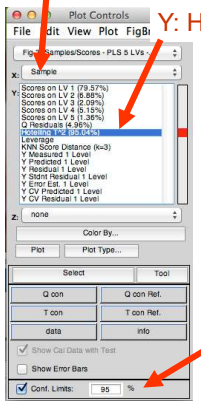
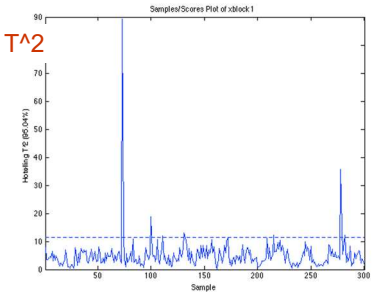
X-Block Hotelling T^2 (by sample)

1 set plot controls

X: Sample

Y: Hotelling T^2





2 Check Conf. Limits

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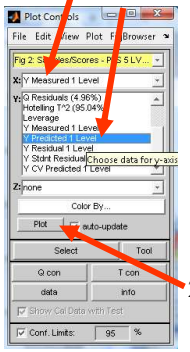
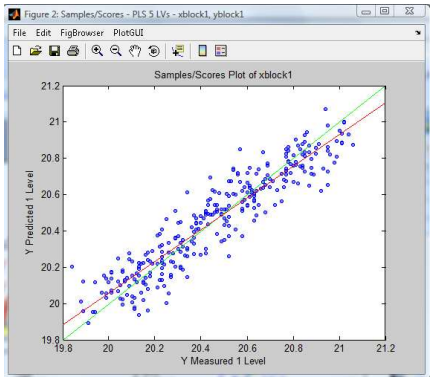
Calibration Curve (Predicted vs. Measured)

1 Click Scores Button

X:Y Measured

Y:Y Predicted





2 Click Plot if auto-update is not checked

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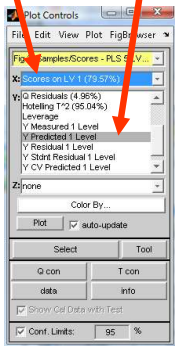
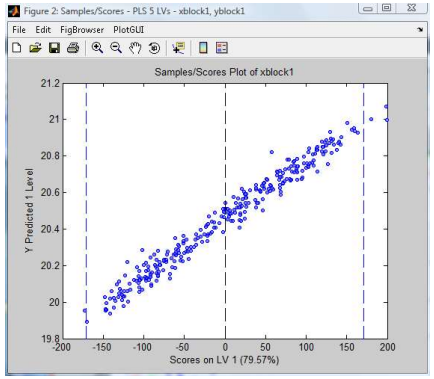
Predicted Y vs. LV 1

1 Click Scores Button

X:LV 1

Y:Y Predicted





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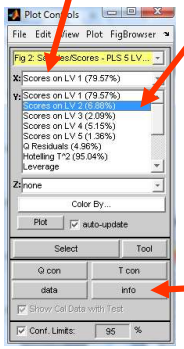
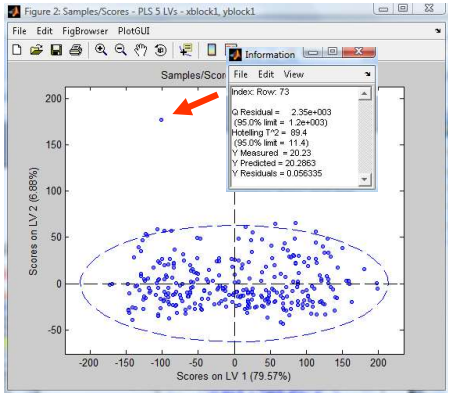
LV 2 vs. LV 1

1 Click Scores Button

X:Scores on LV 1

Y:Scores on LV 2





2 Click info Button and select sample

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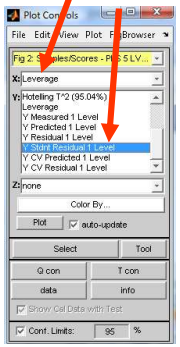
Studentized Y Residual vs. Leverage

1 Click Scores Button

X:Leverage

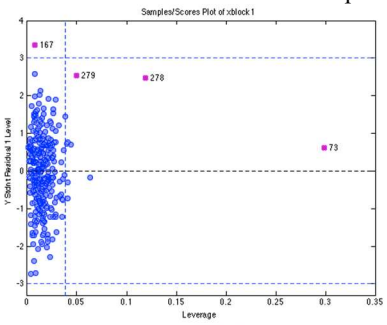
Y:Y Stdnt Residual



2 select outliers

3 view numbers

samples removed in first example



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Calculation of Studentized Residuals

- Given the pseudo-inverse $\mathbf{X}^+$ the leverage for a sample $\mathbf{x}_m$ = x(m,:) and column $\mathbf{X}^+(:,m)$ is

$$l_m = \mathbf{x}_m \mathbf{X}^+(:,m)$$

- Studentized residuals for column m^{th} of $\mathbf{y}$, $t_{e,m}$

$$e_m = \hat{y}_m - y_m$$

$$\sigma = \left(\frac{1}{M-K}\mathbf{e}^T\mathbf{e}\right)^{1/2}$$

$$t_{e,m} = \frac{e_m}{\sigma(1-l_m)^{1/2}}$$

A studentized residual is the quotient resulting from the division of a residual by an estimate of its standard deviation and is a form of t-statistic.

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How Much Leverage is Too Much?

- In PLS and PCR a good rule of thumb is $3K/M$, where K is the number of LVs or PCs, and M is the number of samples
- In MLR, use $2N_x/M$, where N_x is the number of X-block variables

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Regression Example


1,2-


cis-


trans-


styrene

- NIR transmission spectra of styrene-butadiene copolymers
- Different amounts of 4 analytes
  - **All 4** are known for **all** samples (by NMR)
- Data file: SBRdata_EU.mat
  - 60 calibration samples in arrays Xcal, Ycal
  - 10 test samples in arrays Xtest, Ytest

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Regression Methods

- Compare the styrene predictions using the four different regression approaches below.
- CLS – no centering
- MLR (stepwise) – no centering
- PCR – no centering
- PLS – no centering
- Additionally: show results with mean centering

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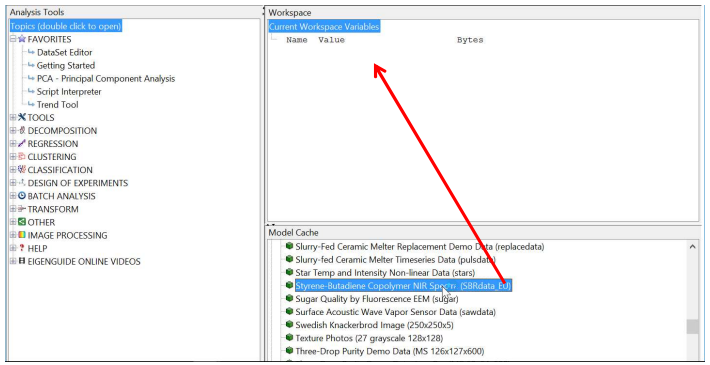
Load Into Workspace



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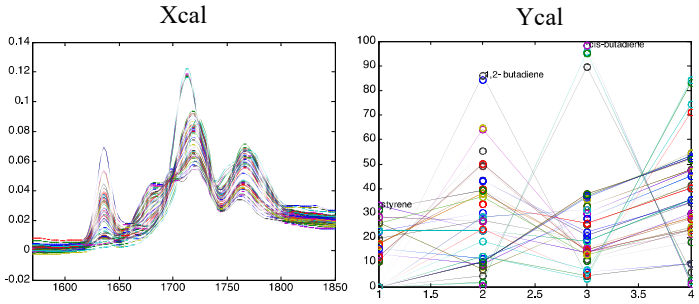
Load and Plot Calibration Data



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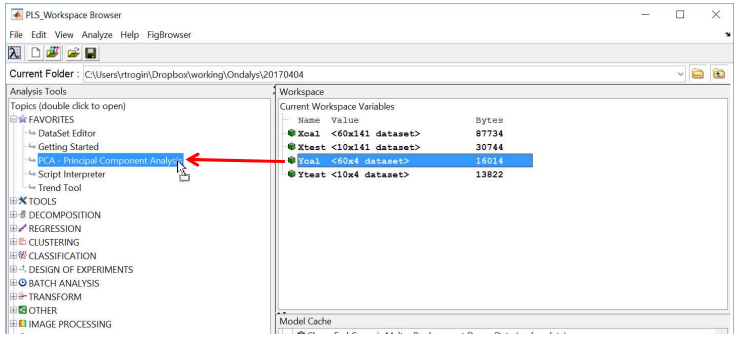
Try This:



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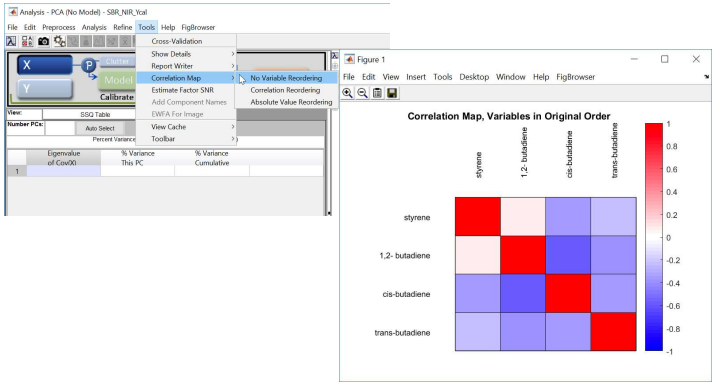
Correlation Map



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Loading Data

- Calibration data
  - Xcal as x-block
  - Ycal as y-block
- Validation data
  - Xtest as x-block
  - Ytest as y-block

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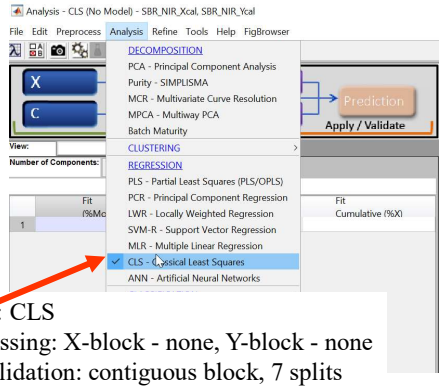
CLS Regression



1 Analysis: CLS
2 Preprocessing: X-block - none, Y-block - none
3 Cross-validation: contiguous block, 7 splits
4 Calculate model

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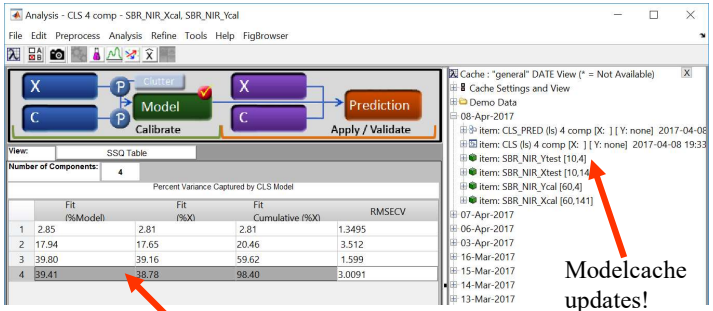
CLS results



Modelcache updates!

4 components determined "automatically" (because of 4 Y variables)

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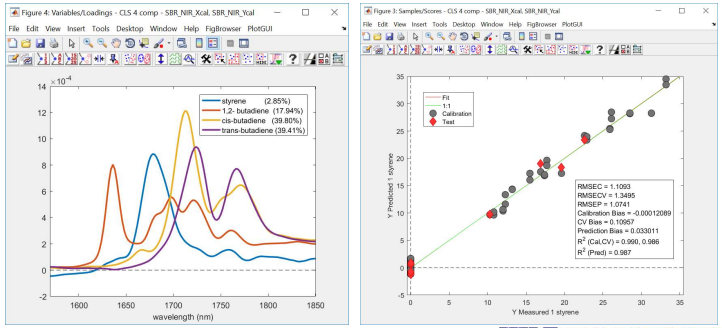
CLS Results

Loadings: **all 4 components**

Scores: Styrene predicted vs. Styrene measured, Cal data included



This is the **S** matrix!

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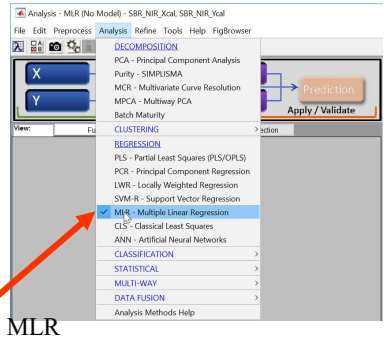
MLR- styrene



1 Analysis: MLR
2 Preprocessing: X-block - none, C-block - none
3 Cross-validation: contiguous block, 7 splits
4 Right-click calibration Y-block =>Select Y Columns => Styrene
5 Stepwise Variable Selection button

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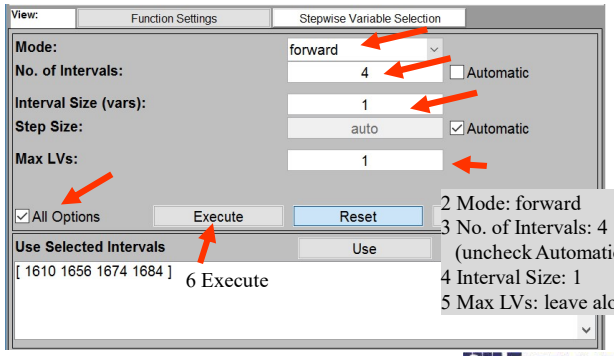
Stepwise Variable Selection

1 Check "All Options"
6 Execute



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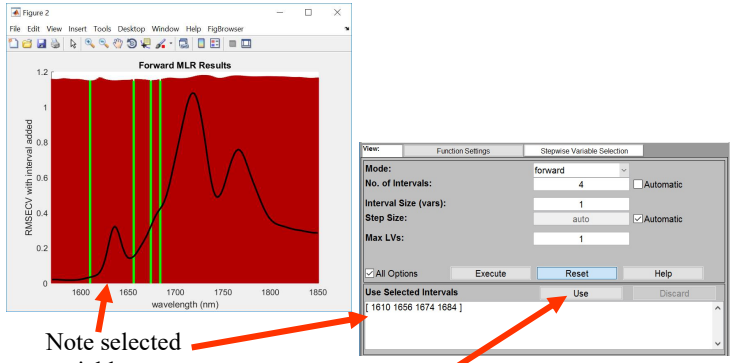
Forward MLR Results



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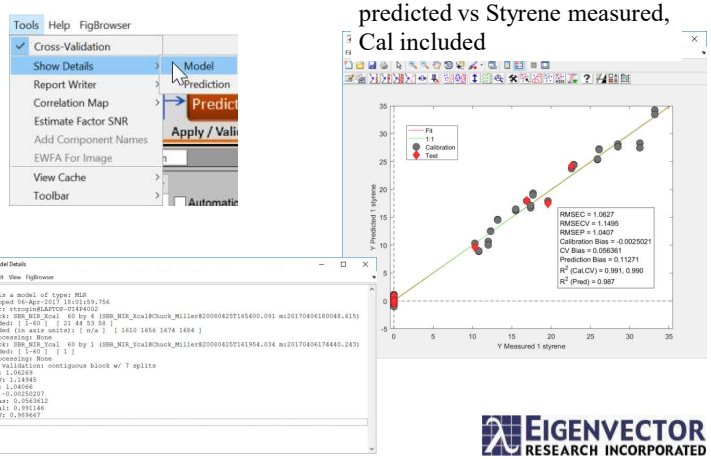
MLR results

Scores button: Styrene predicted vs Styrene measured, Cal included



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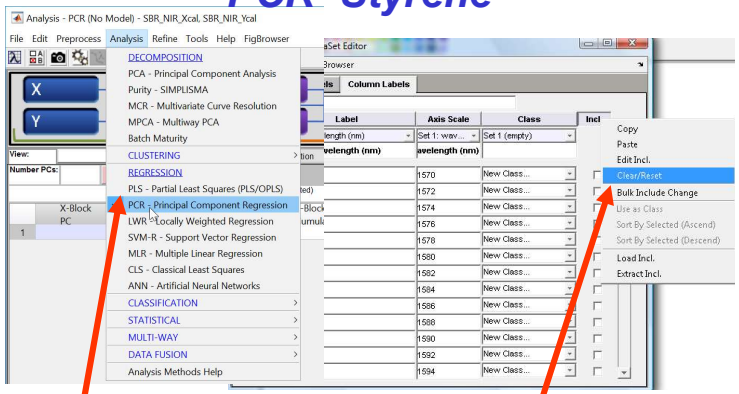
PCR- Styrene



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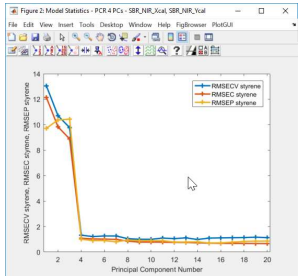
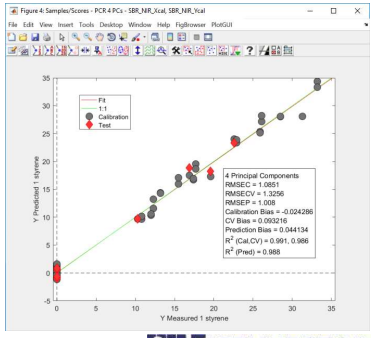
PCR Results

Eigenvalue button:
RMSE[C], [CV], and [P]



Scores: Styrene predicted vs.
Styrene measured



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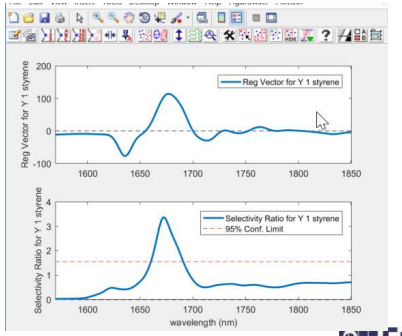
PCR Results

Loadings button: Regression Vector for Styrene
Type "2" (creates second plot)
Second plot: Selectivity Ratio for Styrene



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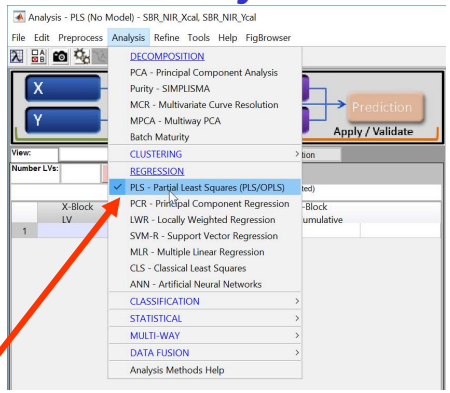
PLS Styrene



1 Analysis: PLS
2 Calculate

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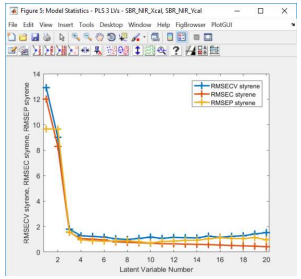
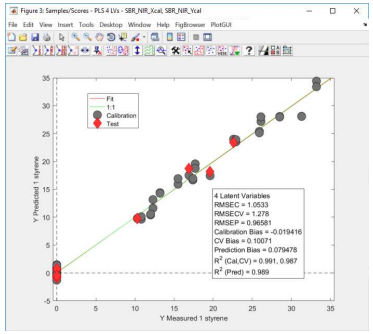
PLS Results

Eigenvalue button:
RMSE[C], [CV], and [P]



Scores button: Predicted vs.
Measured Styrene



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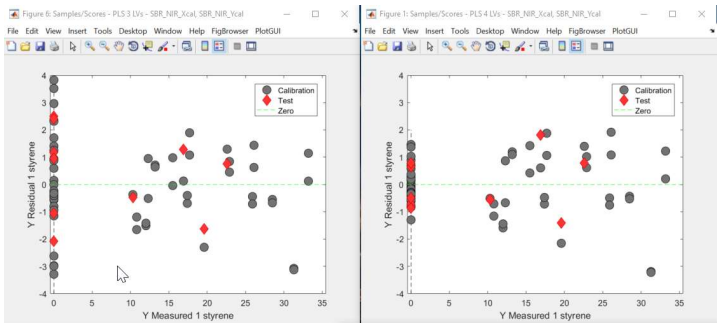
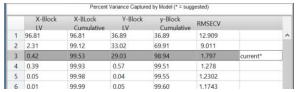
PLS – 3 vs 4 LVs





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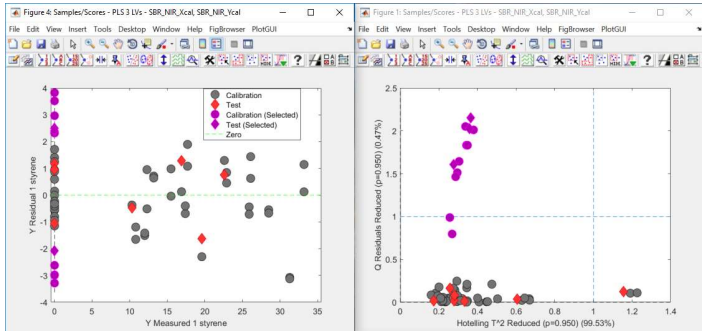
Back to 3 LVs



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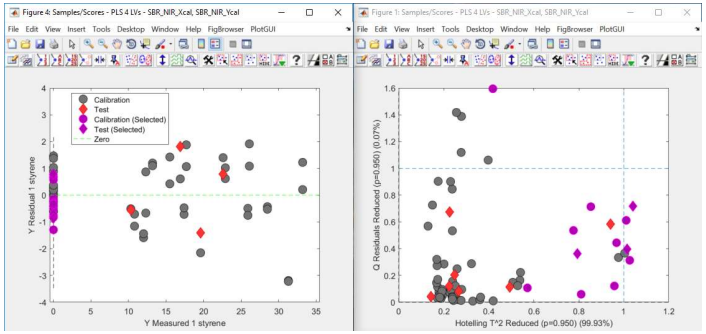
And at 4 LVs



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Regression Summary- Styrene

	RMSEC	CV	P	Comments
Not centered				
CLS	1.11	1.35	1.07	4 factors
MLR	1.06	1.15	1.04	4 stepwise-selected variables
PCR	1.08	1.33	1.01	4 factors
PLS	1.05	1.28	0.97	4 factors
Mean centered				
CLS	1.39	1.61	1.33	4 factors
MLR	0.89	1.07	0.97	4 stepwise-selected variables
PCR	0.84	0.94	0.73	4 factors
PLS	0.84	0.95	0.73	4 factors

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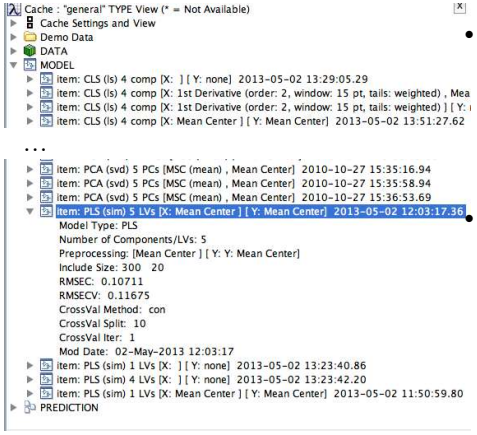
Modelcache



- Can list recent work in 3 ways:
  - By type (shown here)
  - By lineage
  - By date
- Also, can load/show/save any item in the cache

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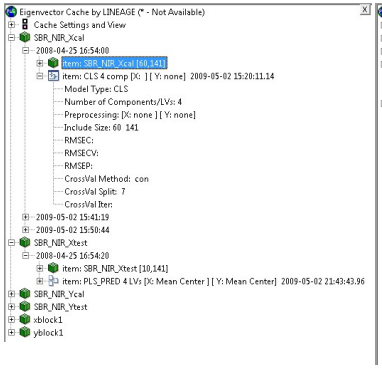
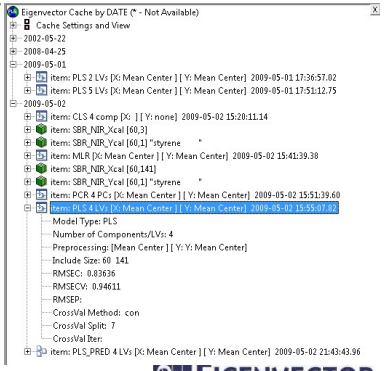
Modelcache by lineage and date

By lineage



By date



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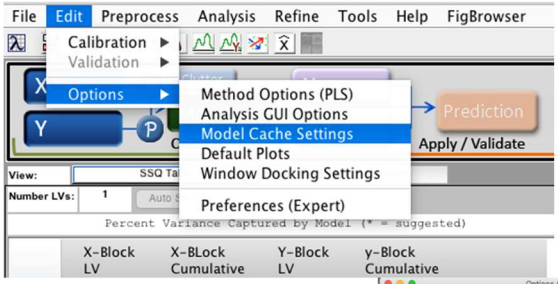

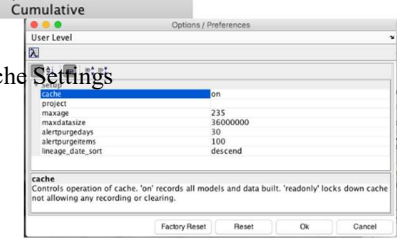

Step 1: Edit: Options: Model Cache Settings

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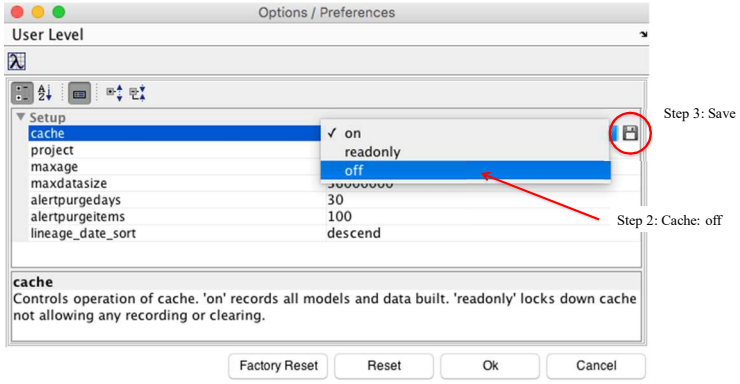

Step 2: Cache: off
Step 3: Save

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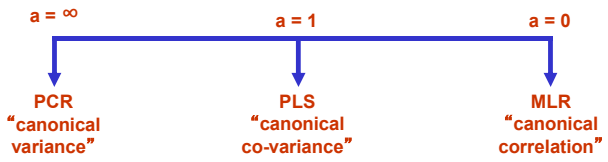
Continuum Regression

- PCR, PLS and MLR can be unified under the single technique Continuum Regression (CR)
- CR is continuously adjustable and encompasses PLS and includes PCR and MLR at the extremes



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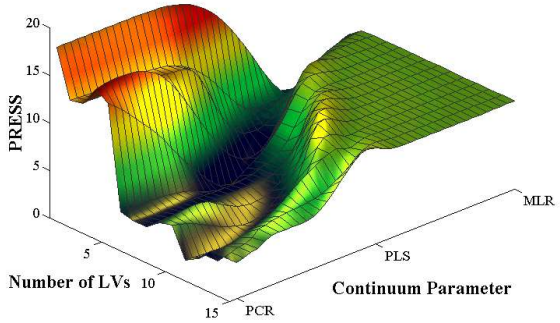
CR Press Surface



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Missing Data

- MDCHECK
  - Checks data sets for `'NaN'` and `'inf'` and replaces with values consistent with a PCA model (if desired)
    - *e.g.*, see the ISFINITE function
  - This is an iterative method
  - Example, use some data from SFCM

```
>> x = xblock1.data(1:50,[6:9 16:19]);
>> x2 = x(:,2);
>> x(2:4:50,2) = NaN;
```

every 4th sample of column 2 removed

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Call *MDCHECK*

- Change the options to reduce the number of PCs

```
>> options = mdcheck('options')
options =
        max_pcs: 5
       frac_ssq: 0.9500
     meancenter: 'yes'
         output: 'no'
      tolerance: [1.0000e-006 100]
    max_missing: 0.4000
>> options.max_pcs = 3;
>> [flag,mismap,xfill] = mdcheck(x,options);
```


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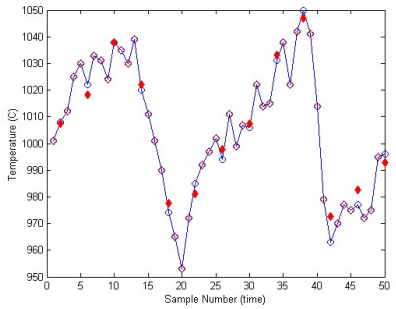
MDCHECK Results

```
>> plot(1:50,x2,'ob-',1:50,xfill(:,2),'rd'), hold on
>> plot(2:4:50,xfill(2:4:50,2),'rd','markerfacecolor',[1 0 0])
```



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Regression Summary

- Regression models can be divided into CLS (used when pure analyte spectra are available) and ILS models (MLR, PCR, PLS, RR, CR, ...)
- PCR and PLS work with ill-conditioned data by reducing to a smaller number of factors
  - has advantage of signal averaging
- Cross-validation is used to determine number of factors
- Fit and Prediction are two different things

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Model Development

- Developing PCR or PLS models
  - center and scale the data (as appropriate)
  - cross-validate to determine number of factors
  - check **X**-block Q, T^2, leverage, and **Y**-block residuals for outliers
    - remove / explain outliers
  - check RMSEC and RMSECV values for overfit
  - repeat as necessary
- PCR or PLS models consist of
  - mean and scaling vectors
  - **X**-block loadings **P**, scores **T**, and weights **W** (if PLS)
  - **Y**-block loadings **Q**, and scores **U**
  - inner coefficients **b**
  - all of this can be reduced to y = **xb**+a form for prediction with new data

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Model Application

- A PCR or PLS model is applied by
  - centering and scaling to the model mean and variance
  - multiply measurements by regression vector to get scaled predictions
  - rescale the predictions back to original units using model mean and variance
- Prediction outliers can be found by
  - calculating Q and T^2 values for new samples
- All the modeling and application is packaged:
  - the model is an object that contains all the parameters
  - validation *e.g.*:

```
valid = pcr(x,y,model,options); %pred's with new X- & Y-block
```

  - prediction *e.g.*:

```
pred = pcr(x,model,options);  %predictions with a new X-block
```


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Model Application – Object Form

- All the modeling and application is packaged:
  - the model is an object that contains all the parameters
  - validation *e.g.*:

```
valid = model.apply(x,y); % this creates a prediction object
pred = model.apply(x);  % this does too

valid_scores = valid.plotscores(options);
pred_scores = pred.plotscores(options);
```

This will create dataset objects containing all of the information that you'll see in a scores plot when using the Analysis interface