Generalized Least Squares for Calibration Transfer

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Outline

- The calibration transfer problem
  - Instrument differences, drift, environment changes
  - Pseudo gasoline
  - Corn
- Generalized Least Squares preprocessing
- PDS and OSC
- Comparison of results
- Conclusions

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Reasons for Calibration Transfer

- No two instruments identical
  - Some calibrations depend on very small changes in data
- Single instruments often drift
  - Aging parts, dirt
  - Temperature
  - *Standardization*
- New interferences in samples

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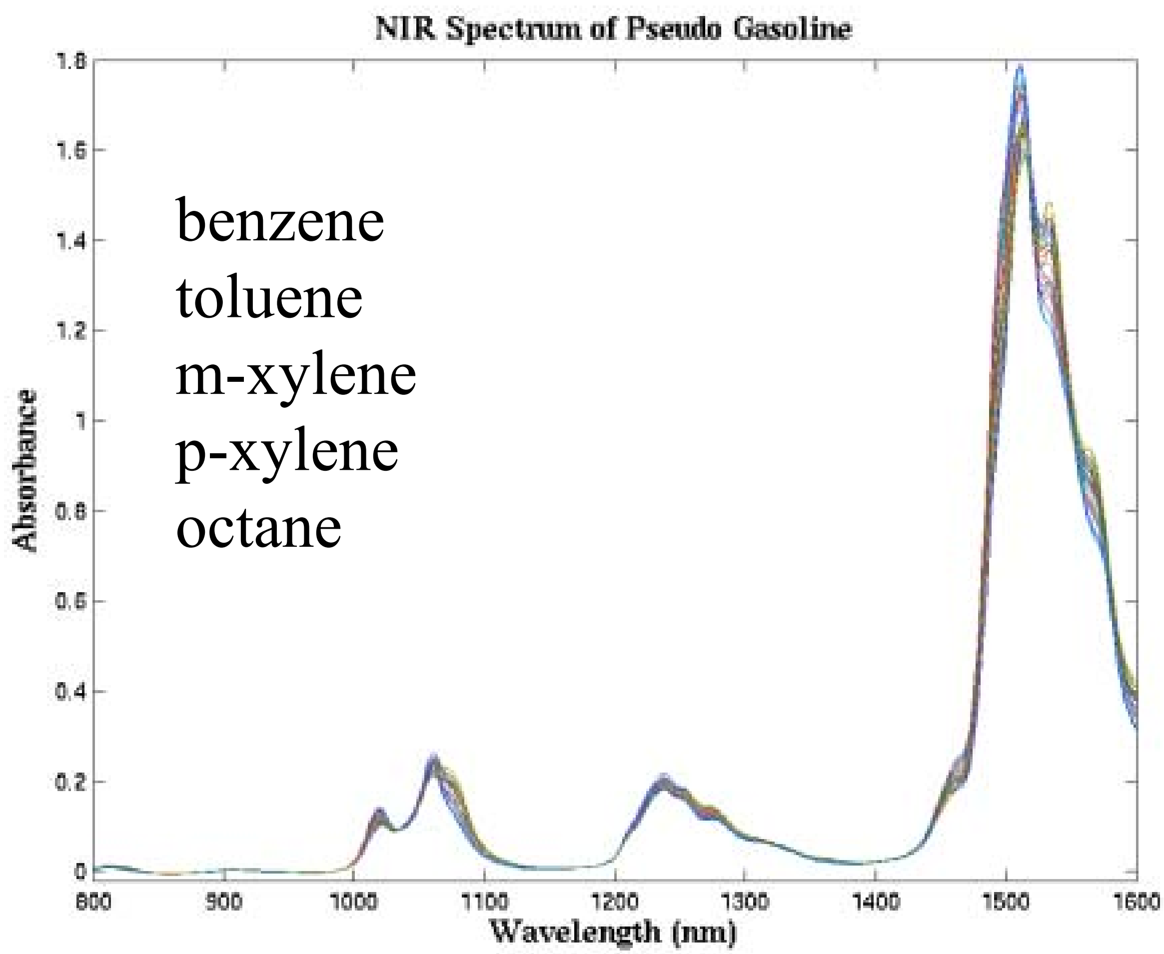
Pseudo Gasoline Data



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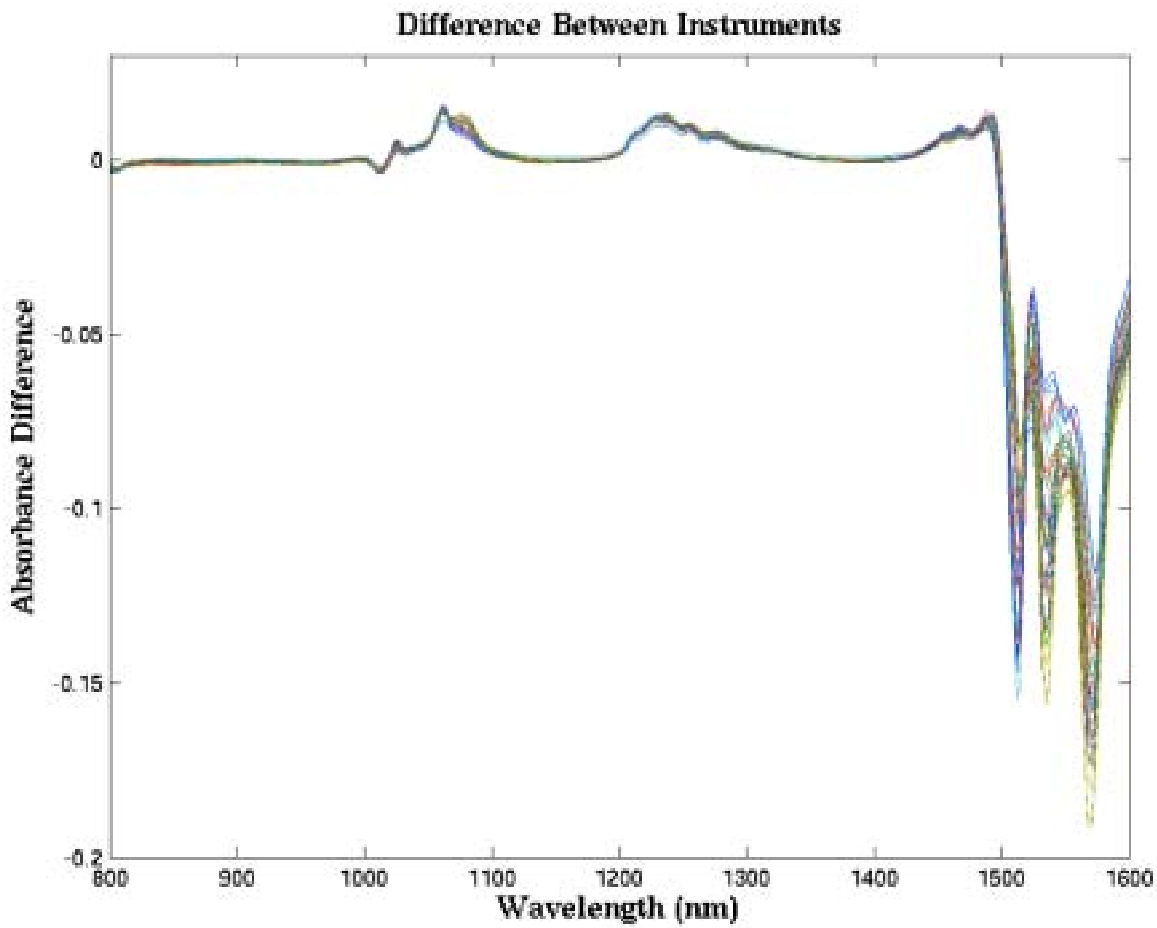
Difference Between Instruments



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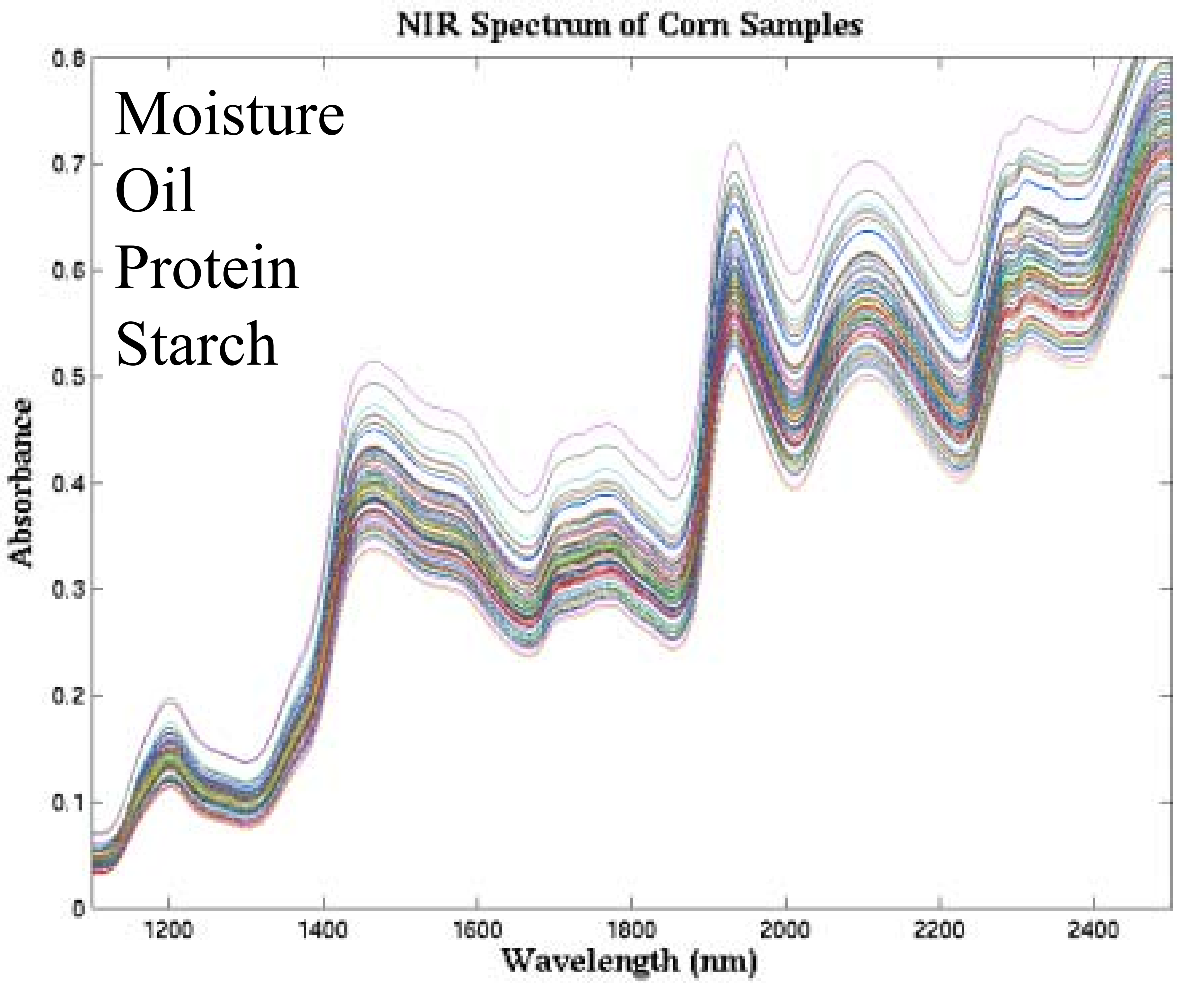
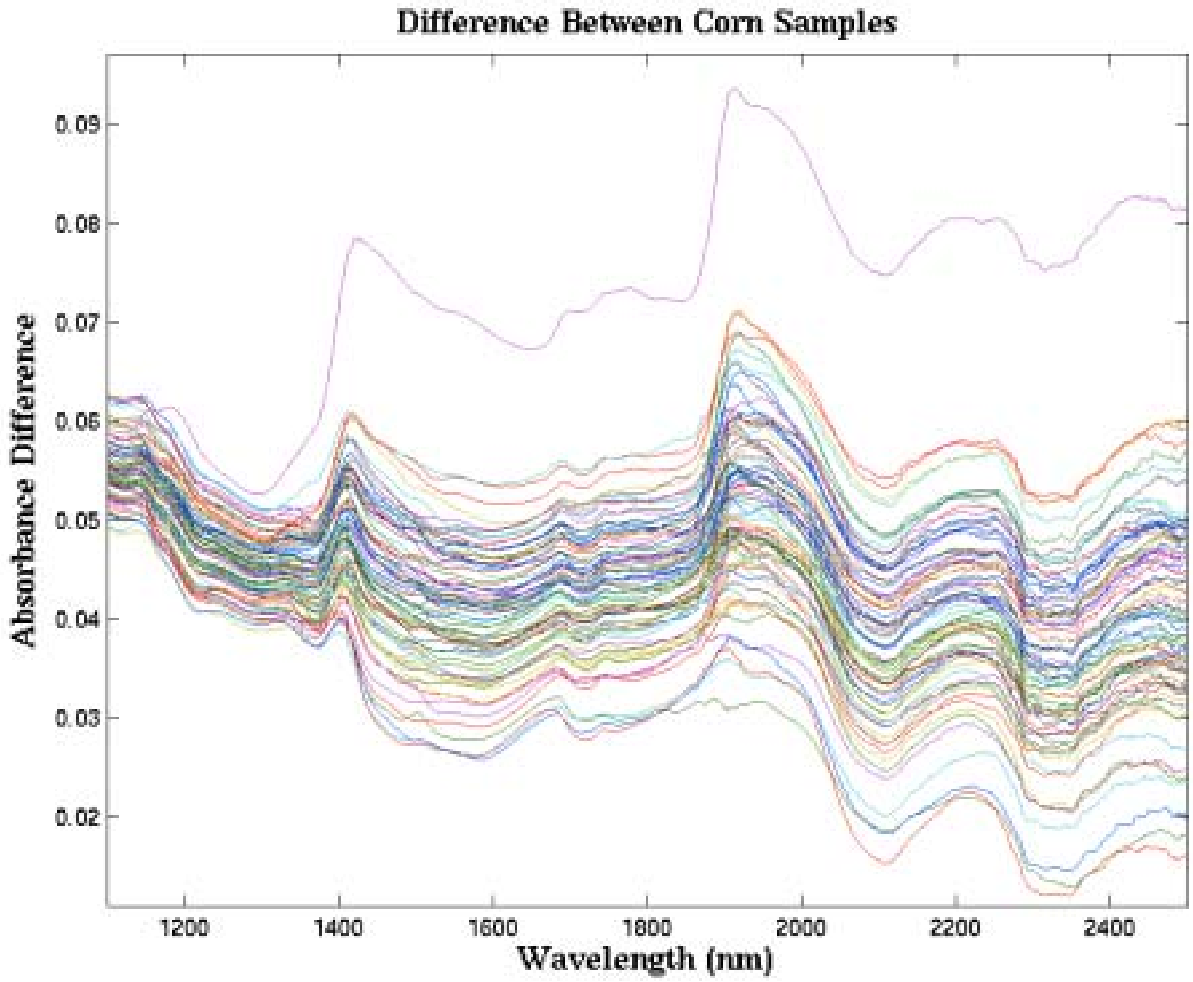
Corn Data


NIR Spectrum of Corn Samples
Moisture
Oil
Protein
Starch
Absorbance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
1200
1400
1600
1800
2000
2200
2400
Wavelength (nm)

Difference Between Instruments



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Selection of Transfer Samples

- Transfer samples should
  - be "high leverage"
  - span the space of differences
- Several ways to choose
  - Hand select (based on PC scores, etc.)
  - Find high leverage in PCA
  - Find high leverage based on calibration model

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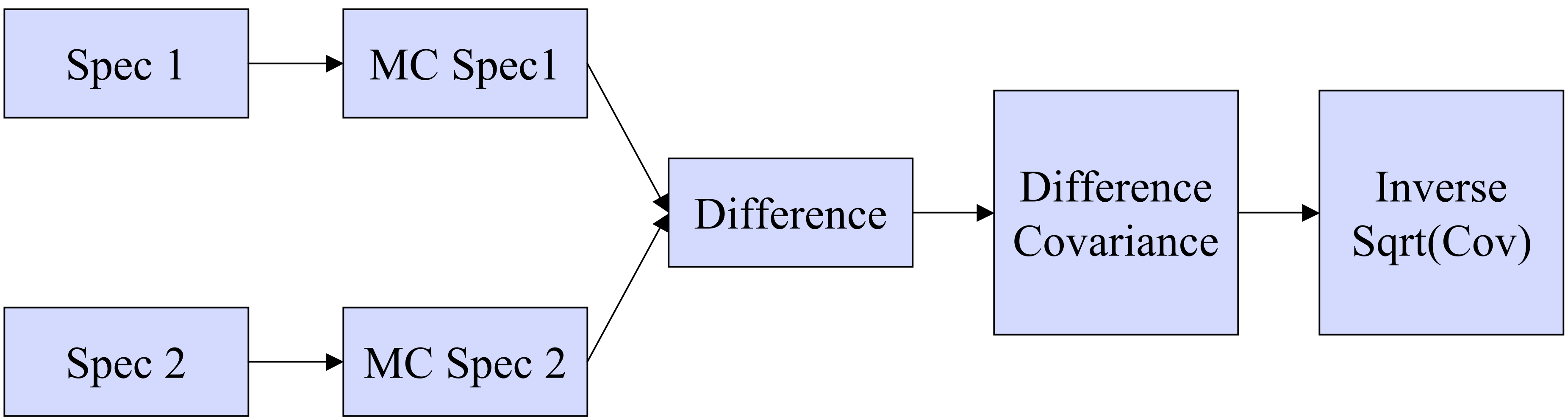
Development of GLS Weighting Matrix



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Difference Covariance

$$\mathbf{X}_d = (\mathbf{X}_{1,tr} - \bar{\mathbf{x}}_{1,tr}) - (\mathbf{X}_{2,tr} - \bar{\mathbf{x}}_{2,tr})$$

$$\mathbf{C} = \frac{\mathbf{X}_d^{\mathrm{T}}\mathbf{X}_d}{N-1}$$

Covariance to Weighting Matrix

$$\mathbf{C} = \mathbf{V}\mathbf{S}^{2}\mathbf{V}^{\mathrm{T}}$$

$$\mathbf{G} = \mathbf{V}\mathbf{D}^{-1}\mathbf{V}^{\mathrm{T}}$$

$$d_{i,i}^{-1} = \frac{1}{\sqrt{\dfrac{s_{i,i}^{2}}{g^{2}} + 1}}$$

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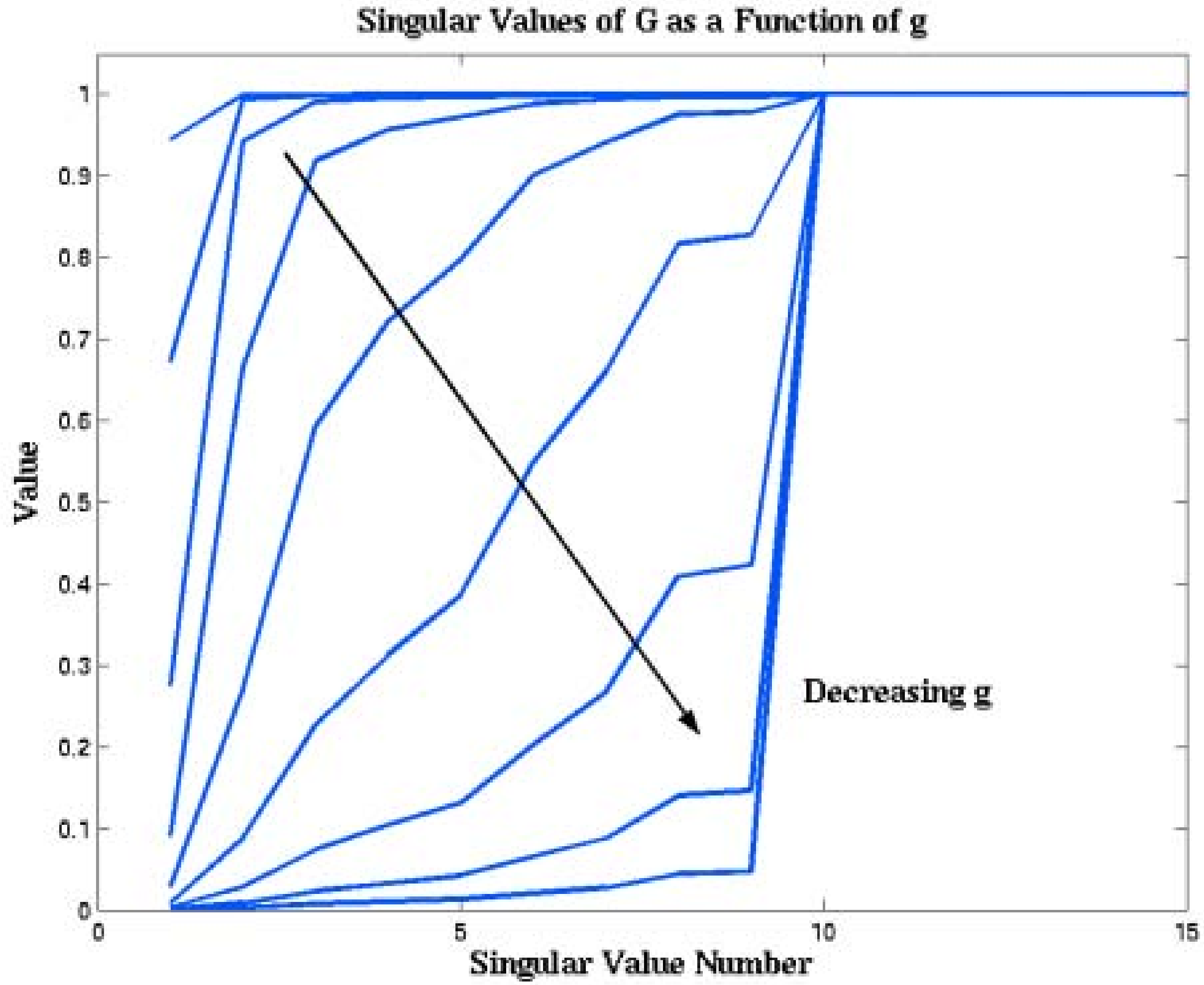
Effect of Parameter g



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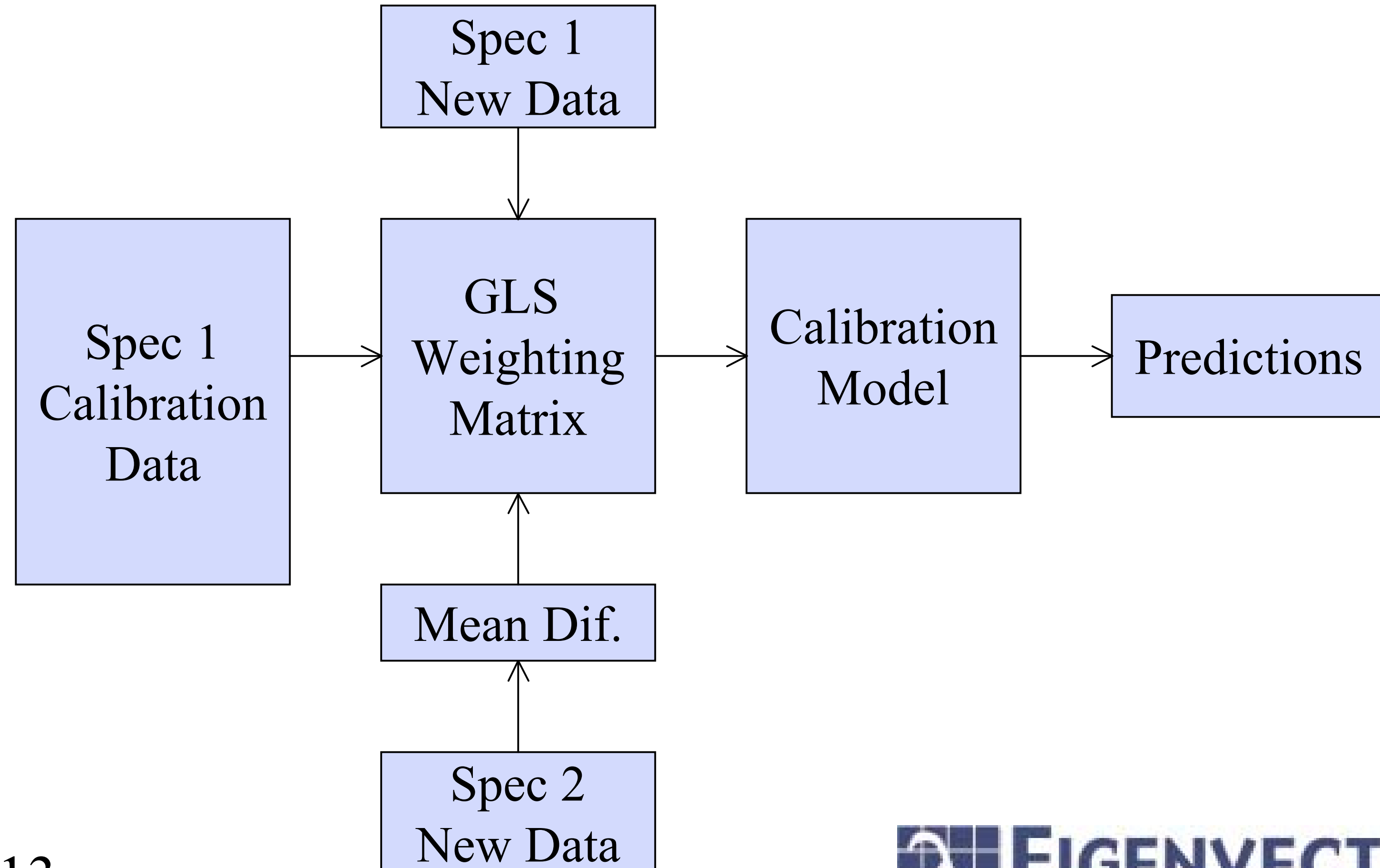
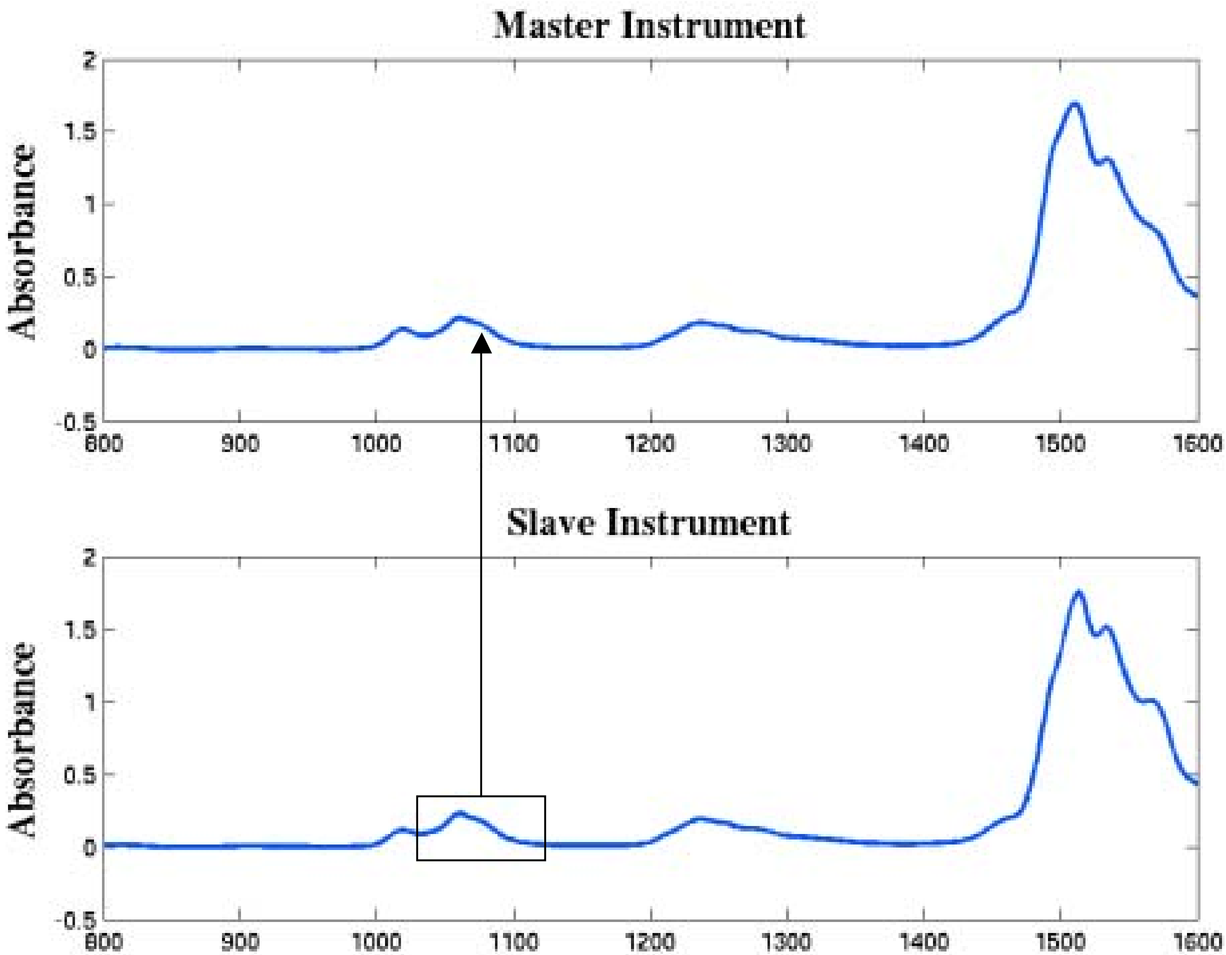
Application of GLS Weighting Matrix



Piece-wise Direct Standardization



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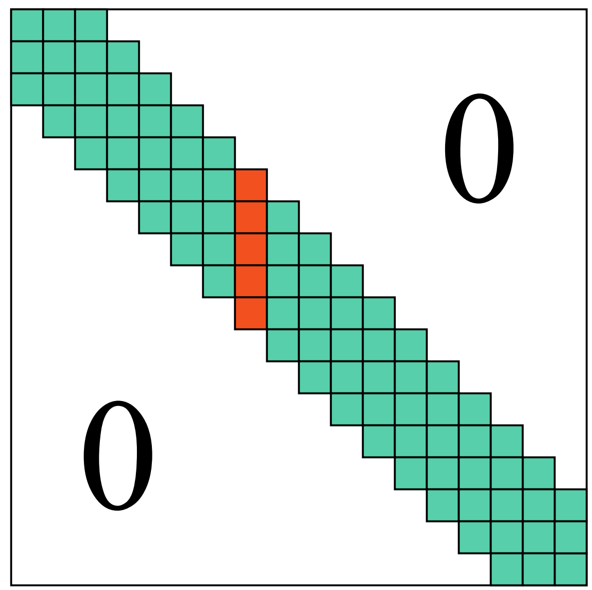
PDS Model

$$\mathbf{X}_1 = \mathbf{X}_2\mathbf{F} + \mathbf{1b}_{2-1}$$

F =



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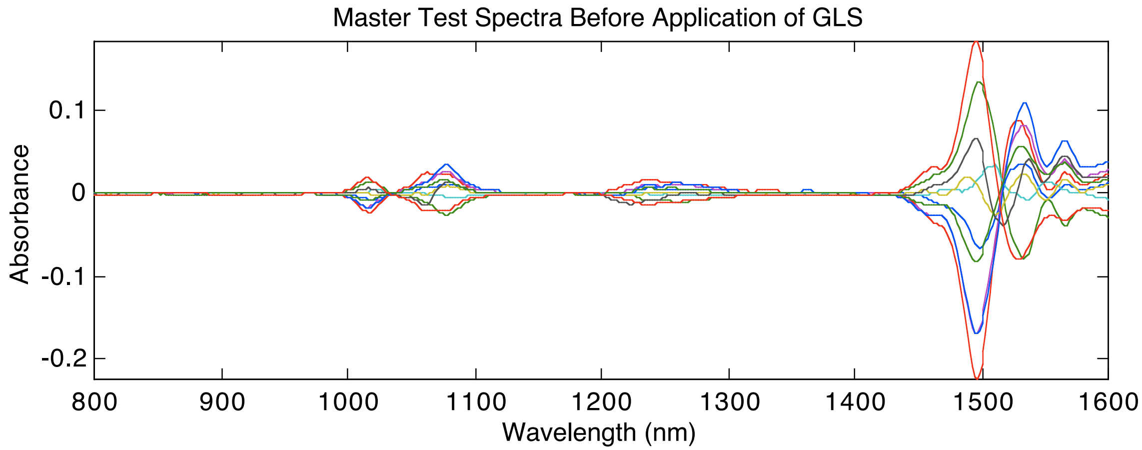
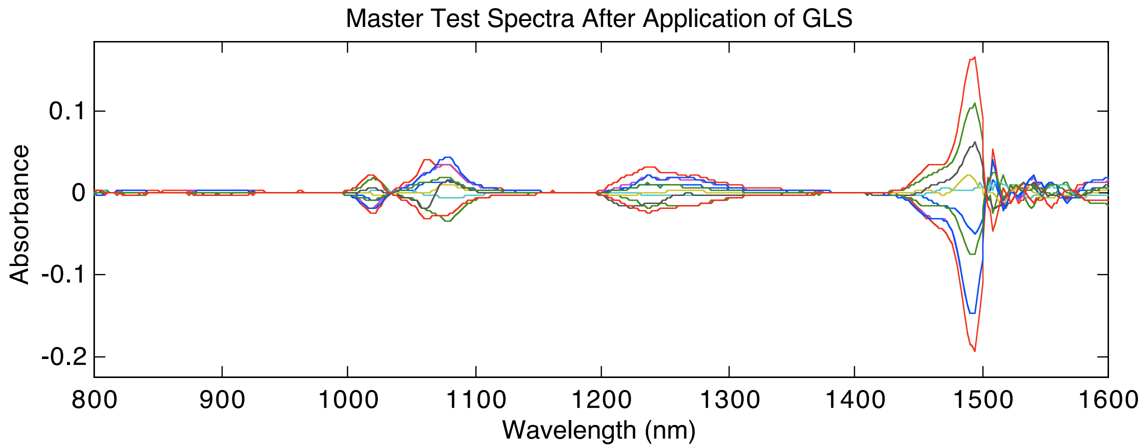
Orthogonal Signal Correction

- Determine factor which describes large amounts of variance in **X** while being orthogonal to **Y**
- Deflate **X**
- Build PLS model that predicts scores of deflation factor
- Use PLS model to estimate amount of factor to remove from new **X**

Pseudo Gasoline Master Before and After GLS





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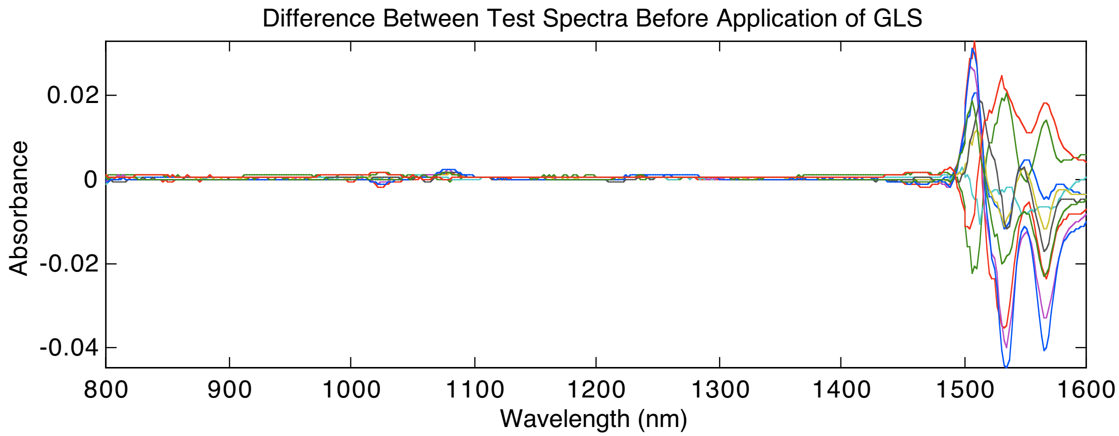
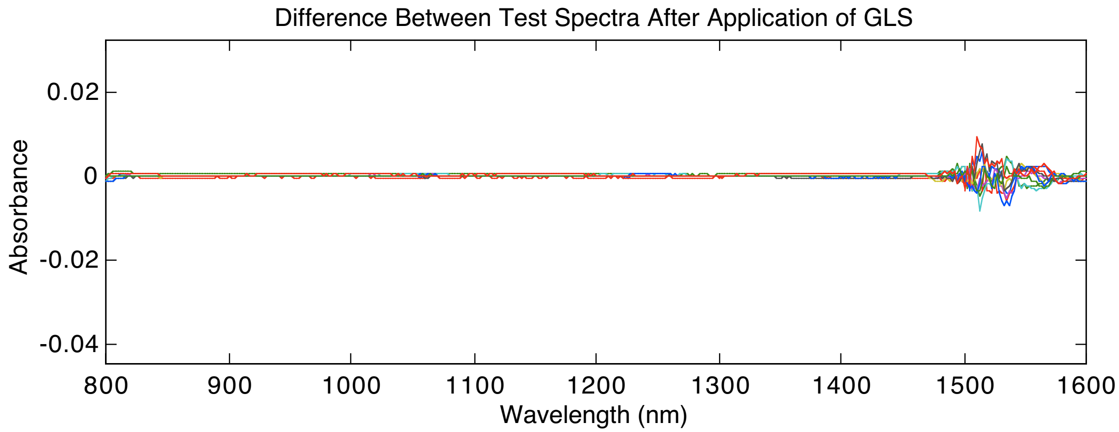
Pseudo Gasoline Difference Before and After GLS





⇨movie

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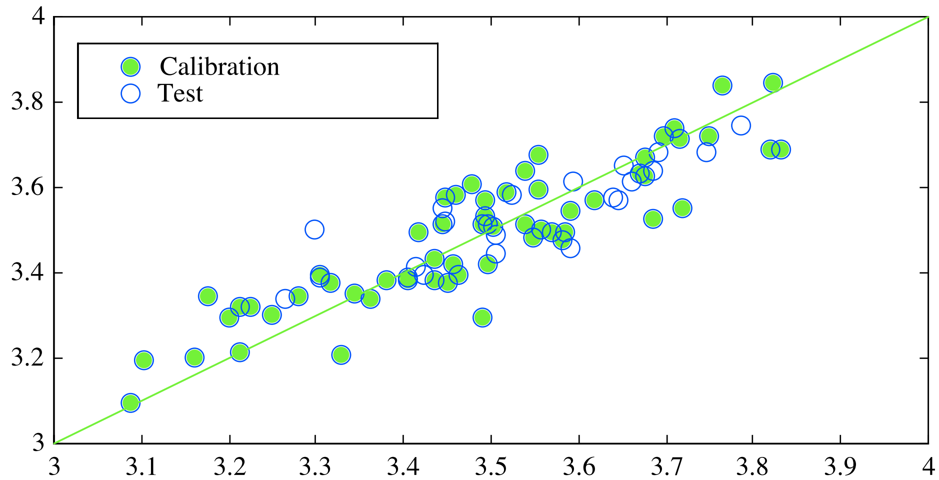
Comparison of Methods on Corn Data

- Available data
  - 80 samples split 60/20
  - 3 instruments
  - 4 analytes
- 5 Transfer samples selected
  - Based on model inverse for PDS
  - Based on PCA leverage for OSC, GLS
- Tested all 3 methods on all combinations of instrument and analyte

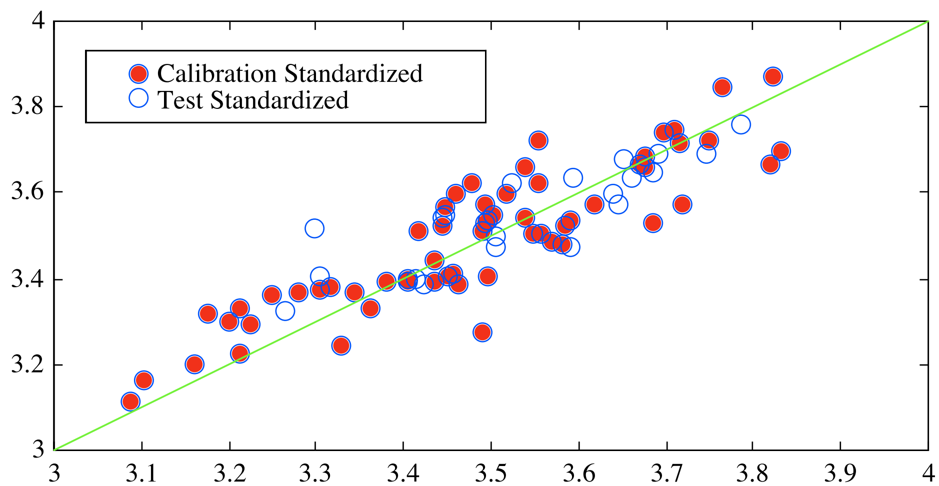
Issues with Meta-parameters

- GLS has only one parameter, g
- PDS
  - Window width
  - Parameters for sub models (LVs or tolerance)
- OSC
  - Number of OSC LVs
  - Tolerance of initial iterations
  - Tolerance on reconstruction
- Number of LVs in PLS calibration models
- *Try to shown each technique in best light!*

Typical Calibration and Test Data



Standardizing MP5 to M5 for Corn moisture



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Results from Corn Data

Prediction Instrument

Model Instrument

Preds	Moisture M5	Moisture MP5	Moisture MP6	Oil M5	Oil MP5	Oil MP6	Protein M5	Protein MP5	Protein MP6	Starch M5	Starch MP5	Starch MP6	Average
M5	0.0187	1.4166	1.5123	0.0361	0.1274	0.1568	0.1302	1.2685	1.3241	0.2077	2.0949	1.6601	
MP5	1.1693	0.1460	0.3547	0.2751	0.0885	0.1516	1.2719	0.1720	0.2782	3.5674	0.4091	0.6119	1.0052
MP6	1.0921	0.2849	0.1667	0.3148	0.1926	0.0819	0.8982	0.2403	0.1876	3.1865	0.6754	0.4031	0.1706
PDS Standardization													
M5	–	0.3951	0.4671	–	0.0932	0.0755	–	0.1699	0.1849	–	0.3362	0.3710	
MP5	0.2342	–	0.1749	0.0876	–	0.0944	0.1401	–	0.1880	0.3455	–	0.3972	0.2289
MP6	0.2068	0.1601	–	0.0920	0.1035	–	0.1553	0.1770	–	0.4147	0.4290	–	
GLS Standardization, LVs hand selected													
M5	–	0.1592	0.1908	–	0.0859	0.0952	–	0.1531	0.1679	–	0.3314	0.3420	
MP5	0.1391	–	0.1477	0.0479	–	0.0770	0.1722	–	0.2110	0.2830	–	0.4381	0.1831
MP6	0.1990	0.1521		0.0603	0.0816		0.1687	0.1570		0.1873	0.3473		
GLS Standardization, best over 5-8 LVs													
M5	–	0.1545	0.1897	–	0.0688	0.0783	–	0.1485	0.1602	–	0.3039	0.3350	
MP5	0.1248		0.1258	0.0479		0.0696	0.1448		0.1721	0.2405		0.3709	0.1662
MP6	0.1902	0.1177	–	0.0590	0.0753	–	0.1358	0.1570	–	0.1873	0.3316	–	
OSC Standardization, best over all cases, 1-3 OSC, 3-8 LVs													
M5	–	0.1630	0.1733	–	0.0816	0.0710	–	0.1433	0.1502	–	0.3002	0.3293	
MP5	0.1945		0.1580	0.0710		0.0739	0.1394		0.1988	0.2640		0.4259	0.1637
MP6	0.1466	0.1320		0.0607	0.0686		0.1568	0.1449		0.2253	0.3744		
OSC Standardization, best single case, 3 OSC 5 LVs													
M5		0.2218	0.2611		0.0835	0.0742		0.1588	0.1502		0.3250	0.3515	
MP5	0.3097	–	0.2176	0.0830	–	0.0834	0.1601	–	0.2388	0.4206	–	0.4506	
MP6	0.3299	0.1379	–	0.0826	0.1157	–	0.1684	0.2154	–	0.5119	0.4363	–	

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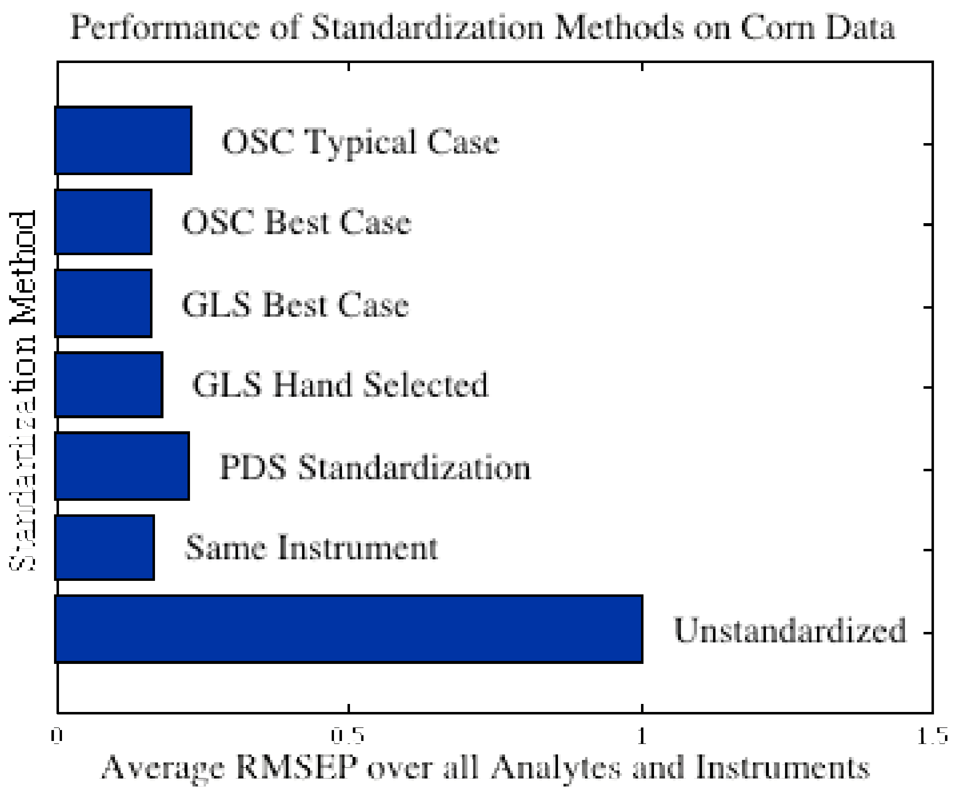
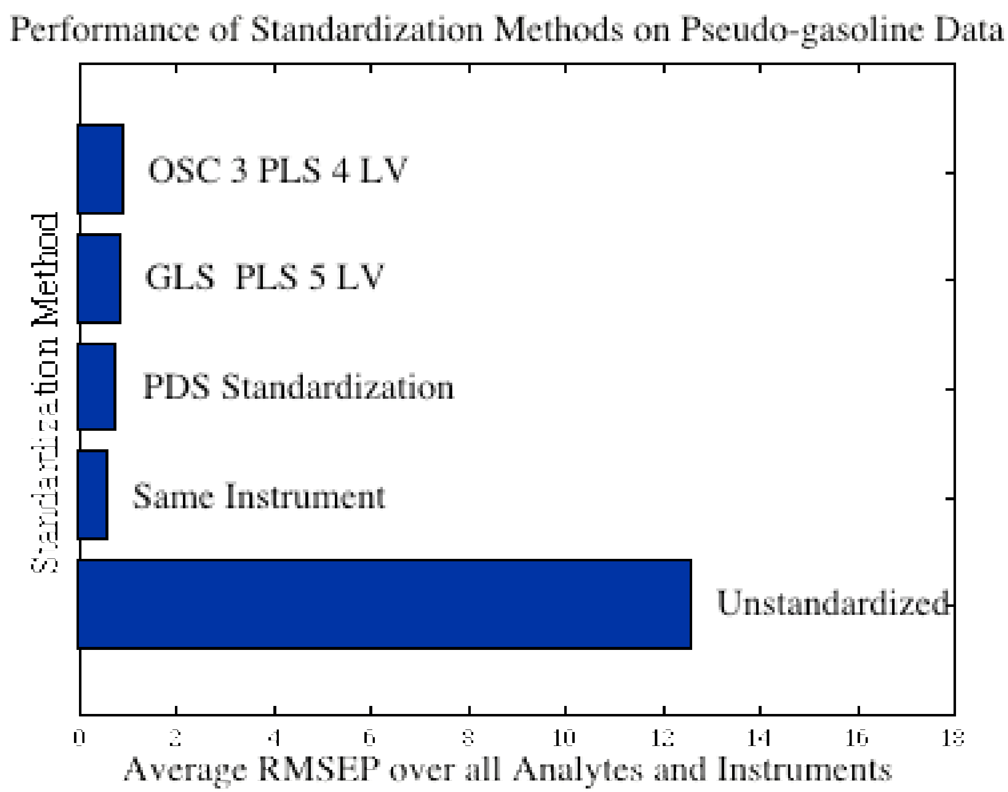
Results on Corn Data



Comparison of Methods on Pseudo Gasoline Data

- Available data
  - 30 samples split 20/10
  - 5 analytes
  - 2 instruments
- 5 Transfer samples selected
  - Based on model inverse for PDS
  - Based on PCA leverage for OSC, GLS
- Tested all 3 methods on all combinations of instrument and analyte

Results on Pseudo Gasoline Data



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Other Ways to Apply GLS

- GLS weighting may be applied directly to model
  - Don’t have to rebuild model!
  - Works well sometimes, but not always (future work)
- Downweight interferents
  - Requires estimate of effect of interferent
  - Image decluttering
- Upweight analyte of interest

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Usability Issues

	Meta-parameters?	Requires Y?	Rebuild calibration model?	Modifies spectra?	Transfer sets function of Y?	Affects net analyte signal?
GLS	1	No	Yes/No	Yes	No	Yes
PDS	2	No	No	No	Yes	No
OSC	3	Yes	Yes	Yes	No	Yes

Conclusions

- GLS preprocessing is a simple, effective method for eliminating spectral differences
- Can be used in several ways
- Only one adjustable parameter
- Potential loss of net analyte signal

Bibliography

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[4] S. Wold, H. Antti, F. Lindgren and J. Öhman, “Orthogonal Signal Correction of Near-Infrared Spectra,” Chemo. and Intell. Lab. Sys., 44, pps 175-185, 1998.

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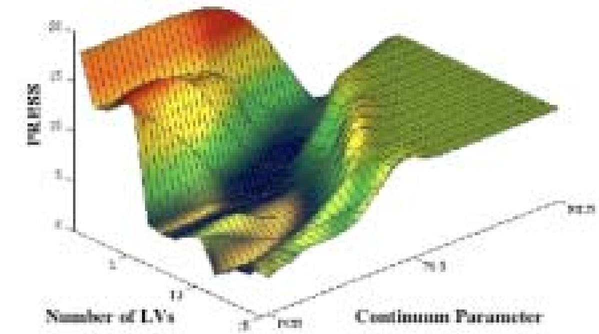

PLS_Toolbox 3.0

for use with MATLAB™

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