Combining Instrument Standardization and Data Preprocessing Methods: What Methods, and What Order?

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Original Abstract

Combining Instrument Standardization and Calibration Transfer Methods: What Methods, and What Order?

Note title change--we're going to look at just prepro and transfer methods at this point, not combined transfer methods.

Abstract: Spectroscopic instrument differences can be mitigated by data preprocessing methods (e.g. baselining, derivitization, multiplicative scatter correction) and standardization methods (e.g. piece-wise direct standardization, orthogonal signal correction, generalized least squares weighting). Each of these methods has strengths and weaknesses in the face of different types of instrument non-idealities. Can these methods be used in combinations that are more effective than single approaches? This talk discussed how combinations of techniques can be used. Approaches are tested on 3 NIR data sets with different issues.

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Outline

- The calibration transfer problem
  - Instrument differences, drift, environment changes
- Data sets
  - Pseudo gasoline
  - Corn
- Standardization approaches
  - Generalized Least Squares (GLS) preprocessing
  - Piece-wise Direct Standardization (PDS)
- Preprocessing approaches
  - Multiplicative scatter correction (MSC)
  - Standard normal variate (SNV)
  - Second derivative
- Study Design
- 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, part replacements
  - Temperature, humidity
  - *Standardization*
- New interferences in samples

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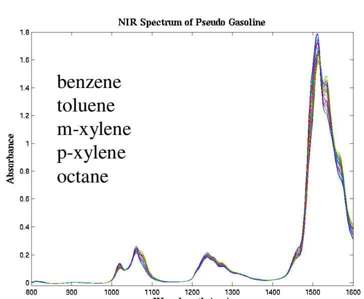
Pseudo Gasoline Data



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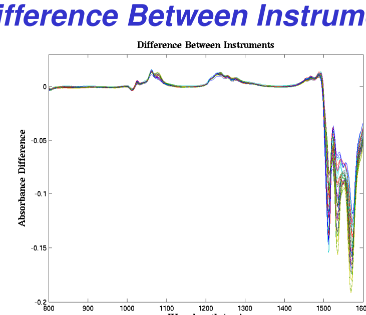
Difference Between Instruments



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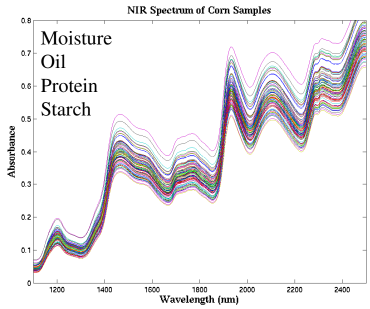
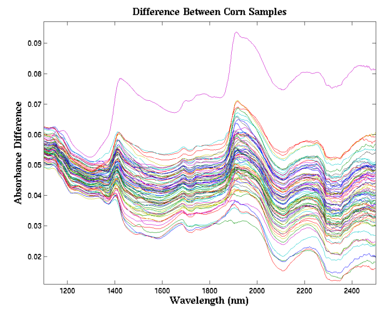
Corn Data



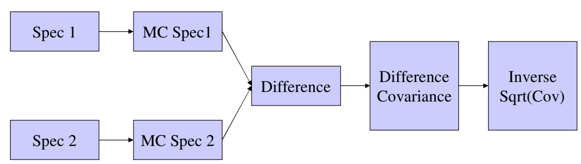
Difference Between Instruments



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

Development of GLS Weighting Matrix



Difference Covariance

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

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

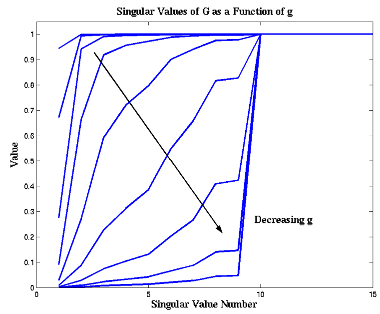
Covariance to Weighting Matrix

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

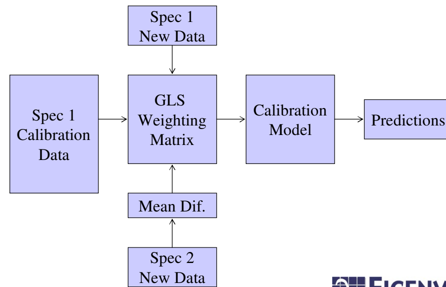
$$\mathbf{G} = \mathbf{V}\mathbf{D}^{-1}\mathbf{V}^{\mathrm{T}}$$

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

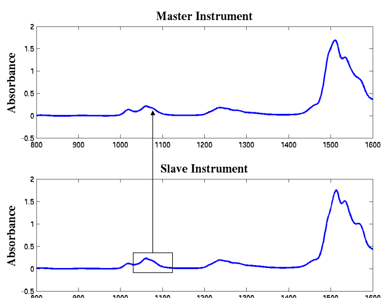
Effect of Parameter g



Application of GLS Weighting Matrix

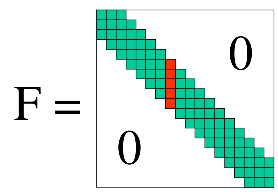


Piece-wise Direct Standardization



PDS Model

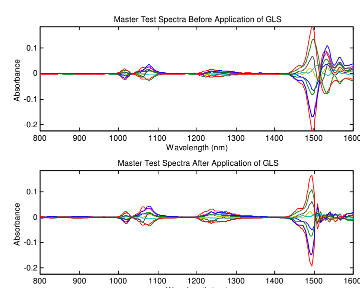
$$\mathbf{X}_1 = \mathbf{X}_2\mathbf{F} + \mathbf{1}\mathbf{b}_{2-1}$$



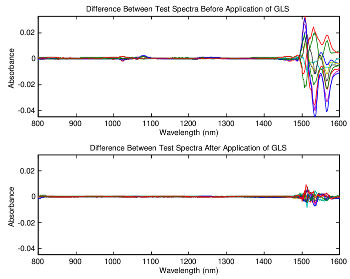
Orthogonal Signal Correction

- 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



Pseudo Gasoline Difference Before and After GLS



⇨movie

Comparison of Methods for Corn Data

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

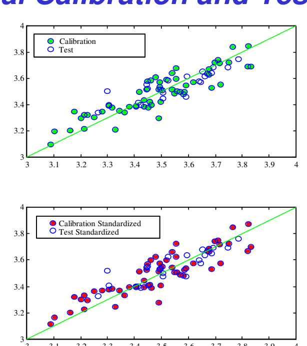
Corn Study Design

- 4 analytes
  - moisture, oil, protein, starch
- 6 ways to transfer
  - between 3 instrumets: m5, mp5, mp6
- 2 methods tested
  - PDS and GLS
- 7 preprocessing options
  - SNV, 2nd deriv, and MSC, before and after, or none
- 336 transfers total (4x6x2x7)

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



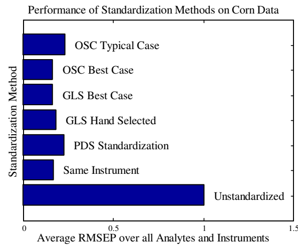
Standardizing MP5 to M5 for Corn moisture

Results from Previous Study on Corn Data

Prediction Instrument (columns); Model Instrument (rows)

	Moisture			Oil			Protein			Starch			Average
Preds	M5	MP5	MP6	M5	MP5	MP6	M5	MP5	MP6	M5	MP5	MP6	
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	-	

Results of Previous Study on Corn Data



Summary- New Results on Corn Data

	NO standardization		GLS		PDS	
	RMSEP	LV	RMSEP	LV	RMSEP	LV
no preprocessing	1.005	7.1	0.217	7.5	0.236	7.3
MSC after standardization	0.949	5.8	0.228	5.3	0.230	5.4
SNV after standardization	0.887	5.6	0.218	5.5	0.229	5.6
2nd derivative after standardization	0.781	5.8	0.209	4.8	0.224	4.6
MSC before standardization			0.225	5.9	0.280	4.3
SNV before standardization			0.241	5.3	0.230	4.7
2nd derivative before standardization			0.203	4.7	0.220	4.5

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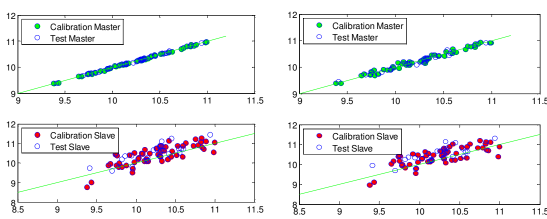
Sample results- corn data

Analyte 1, m5 master/mp5 slave

PDS only | PDS, then 2nd derivative



8LVs, RMSEP = 0.415 | 7LVs, RMSEP = 0.392

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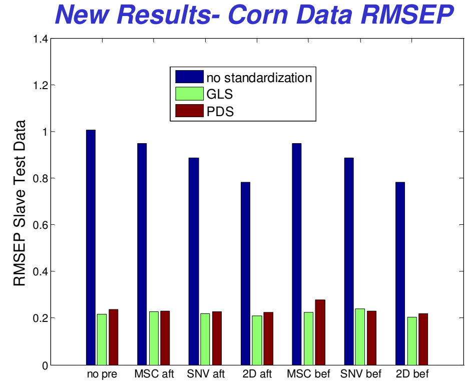
New Results- Corn Data RMSEP



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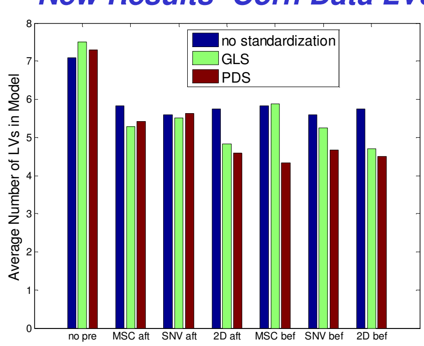
New Results- Corn Data LVs



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PARAFAC model on Corn RMSEP Results

- 4D array
  - Standardization
  - Preprocessing
  - Master/Slave instrument pair
  - Analyte
- 1 PARAFAC component explains 91.4% of the RMSEP data

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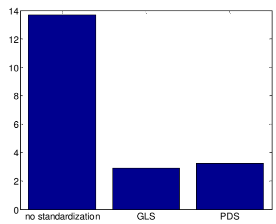
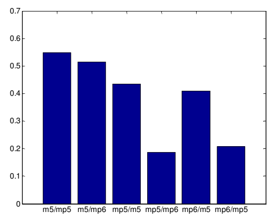
PARAFAC loadings

Mode 1 (standardization method)



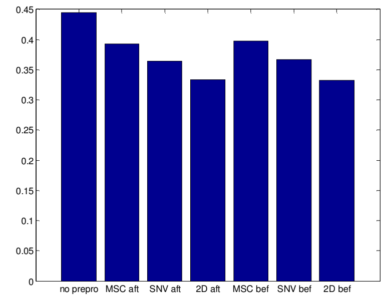
Mode 3 (master/slave instrument pair)



GLS performs slightly better on this data

All transfers involving instrument "m5" have higher RMSEPs

PARAFAC loadings- preprocessing



- *All preprocessing types bring **slight** RMSEP improvement*
- *2nd derivative brings best improvement*
- *NOT much difference between preprocessing BEFORE vs. AFTER standardization!*

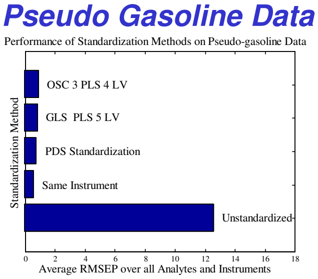
Comparison of Methods on Pseudo Gasoline Data

- 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 both methods on all combinations of instrument and analyte

Pseudo Gasoline Study Design

- 5 analytes (moisture, oil, protein, starch)
- 2 ways to transfer (2 instruments)
- 2 methods tested (PDS and GLS)
- 7 preprocessing options (SNV, 2nd deriv, and MSC, before and after, or none)
- 140 transfers total (5x2x2x7)

Results of Previous Study on Pseudo Gasoline Data



New Results for Pseudo Gasoline Data

Ditto results from corn data here.

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

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Conclusions 1/2

- GLS preprocessing is a simple, effective method for eliminating spectral differences
  - "designed" for correlated sampling issues
  - Can be used in several ways
  - Only one adjustable parameter
  - Potential loss of net analyte signal
- PDS
  - designed to account for instrument differences

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Conclusions 2/2

- GLS slightly better than PDS for corn data, PDS slightly better than GLS for gasoline data
  - More sampling/scattering issues in corn data than gasoline data
- Preprocessing reduces number of LVs needed, and ***slightly*** reduces the RMSEP (slave test data)
  - 2^{nd} derivative gave best improvement
  - For all preprocessing types studied
    - no significant difference observed for preprocessing applied ***before*** vs. ***after*** standardization
- All transfers involving instrument "m5" resulted in higher prediction errors
  - Unique response biases vs. other two instruments studied

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Future Work

- Complete analysis of pseudo-gasoline data
- Expand study to include
  - PDS first to account for instrument differences followed by GLS to handle sampling variance
  - Additional Data Sets

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