Raman Analysis of Concentrated Salt Solutions using Robust Modeling and Data Fusion

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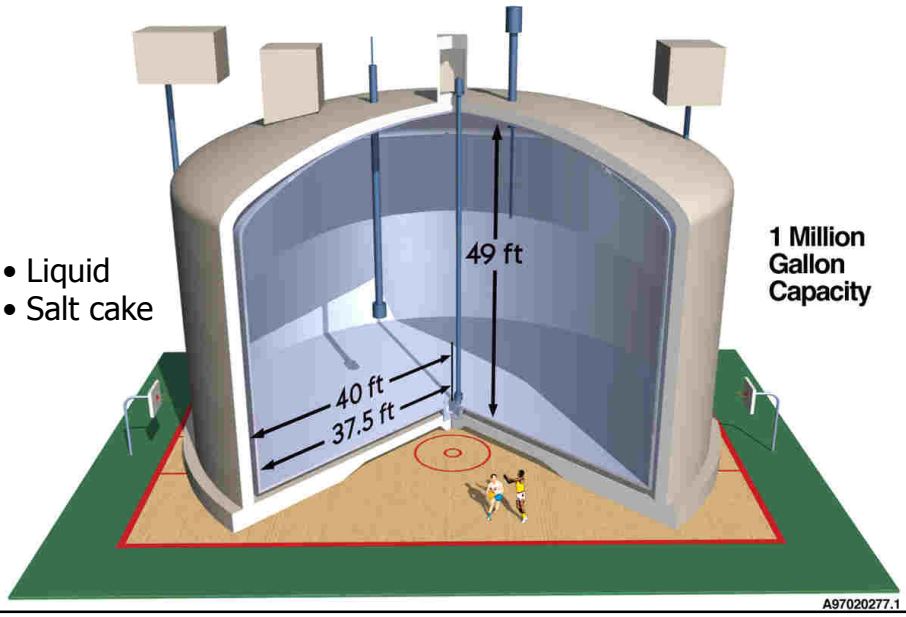
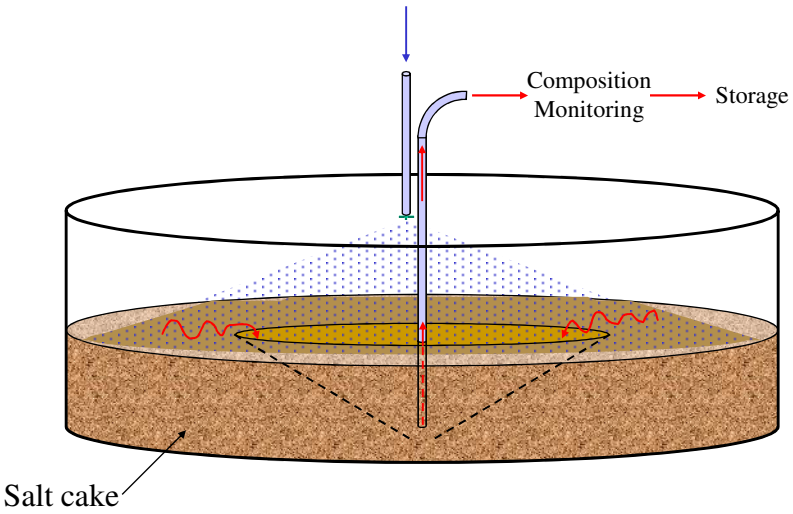
Hanford Double Shell Tank

- Liquid
- Salt cake



Nuclear Waste Storage Tanks



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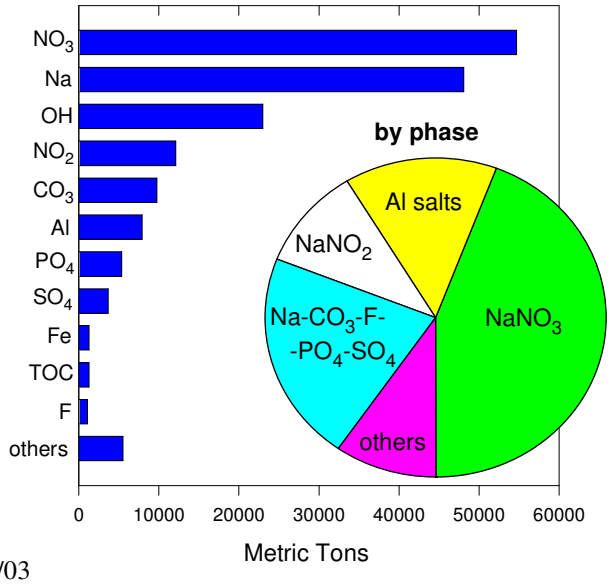
Tank Farm Chemical Inventory



BBI 3/20/03

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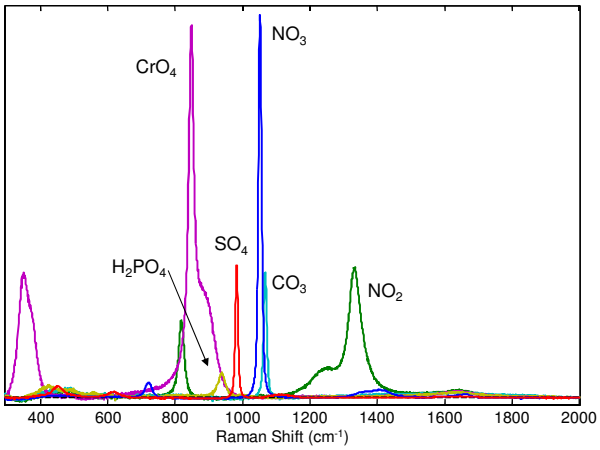
Raman Spectra of Ionic Species



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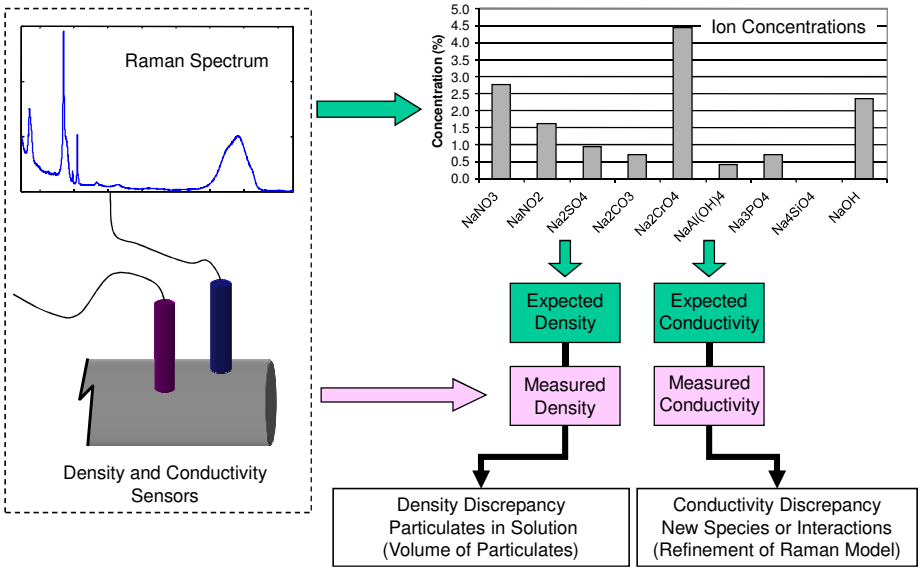
Data and Analysis Flowchart



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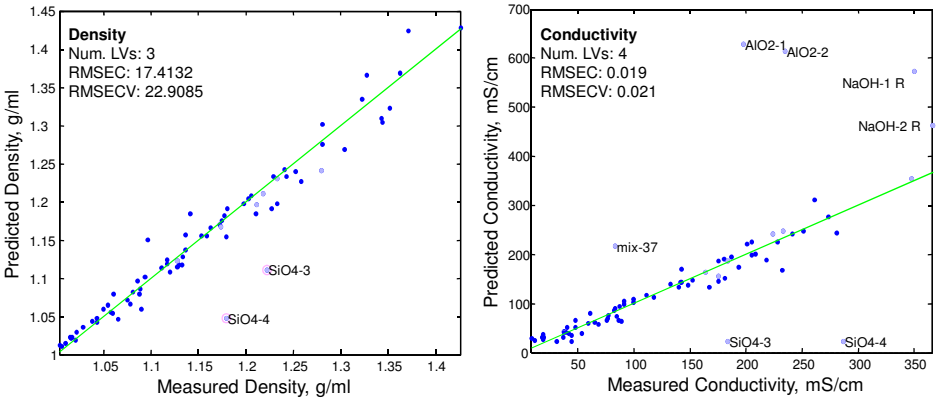
Estimation of Density and Conductivity from Concentrations

(1st generation models)



(dimmed and/or labeled points were ***not*** used in modeling)

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Raman-to-Concentration Model Design Challenges

- Long-Term Model
  - *Months-Years* of Service
- Unknown Field Interferences
  - Updates probably necessary

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Regression Model Options

- ILS – Inverse Least Squares (PLS, PCR, MLR)
  - + Nonlinearities often easily included
  - - Model updating a challenge
- CLS – Classical Least Squares
  - + Model updating straightforward
  - - Does not typically allow for nonlinearities

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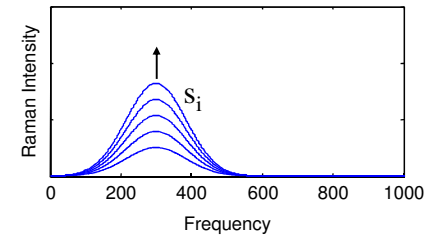
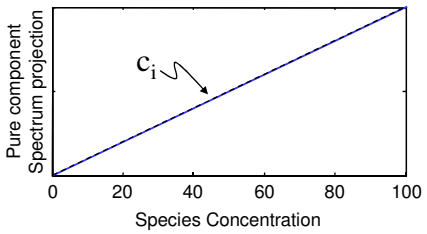
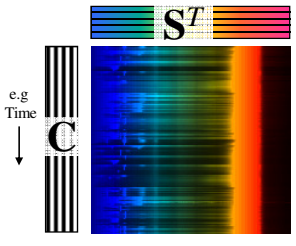
Classical Least Squares Model





As concentration increases, there is a corresponding increase in intensity as a linear response (i.e. **Beer's law**).

The typical CLS model uses a simple response profile (spectrum) to predict concentration of the individual species.



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

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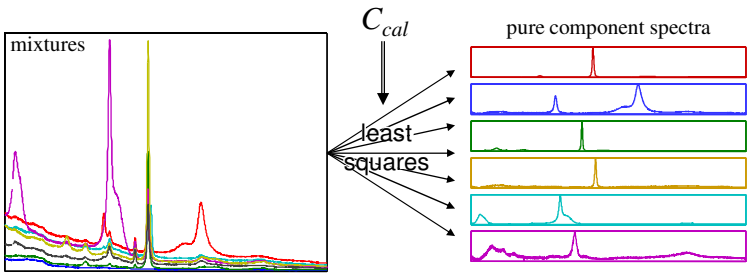
Standard CLS Model
Calibration

$$CS^T = X$$

$$S_{ions}^T = C_{cal}^{\dagger} X_{cal}$$

Determine pure component spectra ($\boldsymbol{S}^T$) from calibration samples by ordinary least-squares regression.



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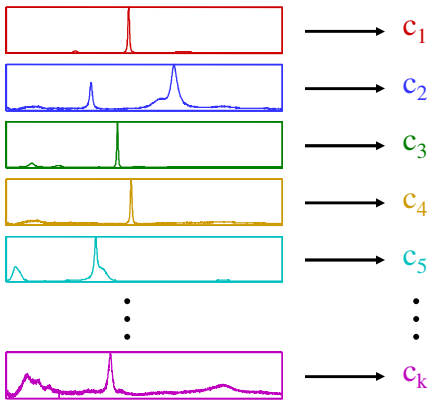
Standard CLS Model
Prediction



Standard "linear" CLS
Each spectrum maps to one concentration.

$$C = X(S_{ions}^T)^{\dagger}$$

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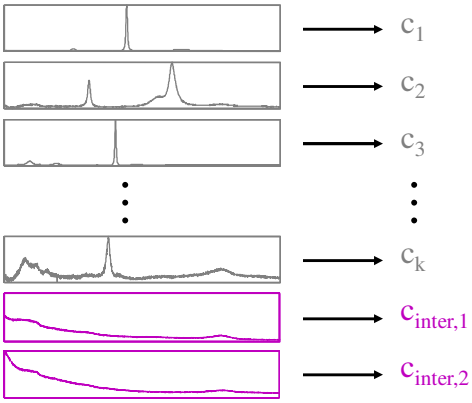
Extended Mixture Model
Prediction



Add additional background or component spectra as needed

$$C = X(S_{ions}^{T})^{\dagger}$$

$$C = X([S_{ions}^{T} S_{inter}^{T}])^{\dagger}$$

Martens & Naes

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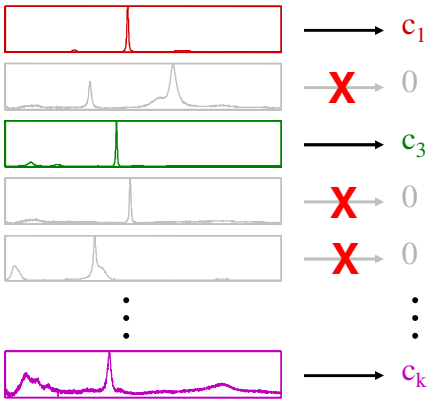
Stepwise Regression
Prediction



Use ONLY those components which improve the spectral residuals by a statistically significant amount

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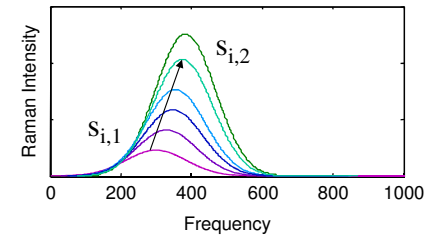
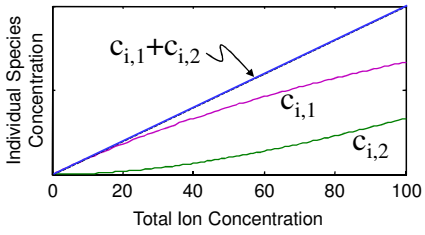
Non-Linear CLS Model





As concentration increases, there is an increase in intensity as well as, eventually, **a shift of the peak position** (due to molecular interactions such as hydrogen bonding)

The typical CLS model expects only a change in intensity and no change in spectral profile. The non-linear CLS model **allows for multiple spectral profiles** as concentration changes.

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Non-Linear CLS Models
Calibration

$$C_c M S^T = C_k S^T = X$$

$$S_{ions}^T = C_{k,cal}^{\dagger} X_{cal}$$

$$C_{k,cal} = C_{c,cal} M$$

If M is diagonal, this is CLS
Otherwise, M imposes closure between underlying factors to known concentration.
e.g. Two factors for first component

$M =$ [1 1 0 0
0 0 1 0
0 0 0 1]

Solve for S_{ions} via ALS
(a) single factors = hard equality constraint
(b) multiple factors = soft closure constraint to species concentration

$$CM^T = C' = X_{cal}(S_{ions}^T)^{\dagger}$$

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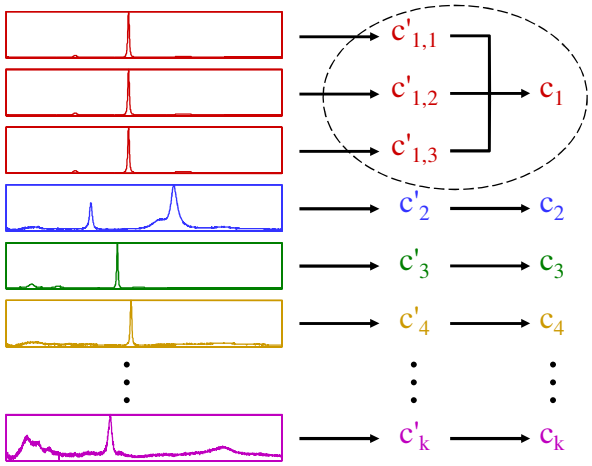
Non-Linear CLS Model

Prediction



"Non-linear" CLS
More than one pure component spectrum can map to an underlying species concentration.

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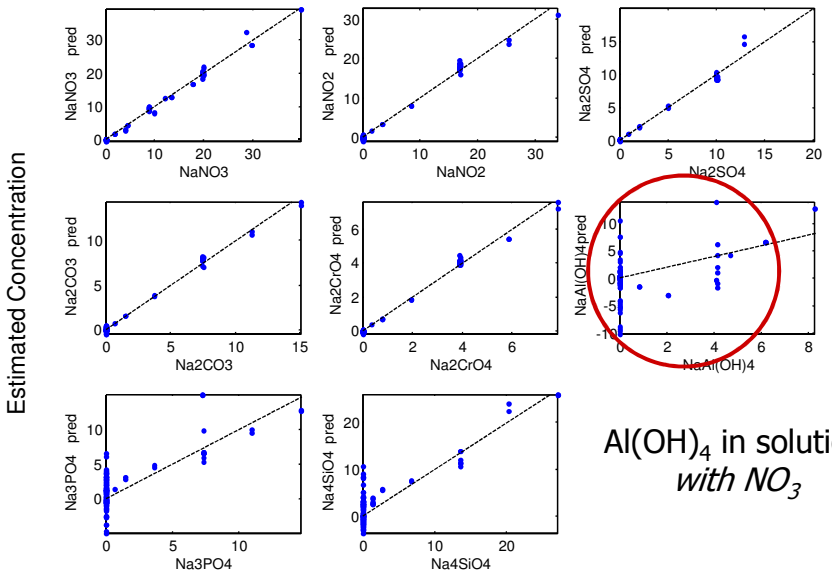
Classical Least Squares (CLS)



$Al(OH)_4$ in solution
with NO_3

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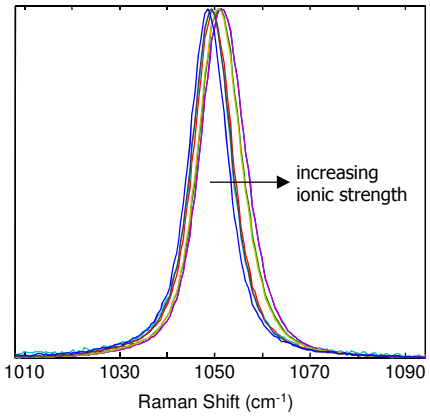
Example: Multiple NO_3 Components

Normalized spectra at different NO_3 concentrations and w/$Al(OH)_4$



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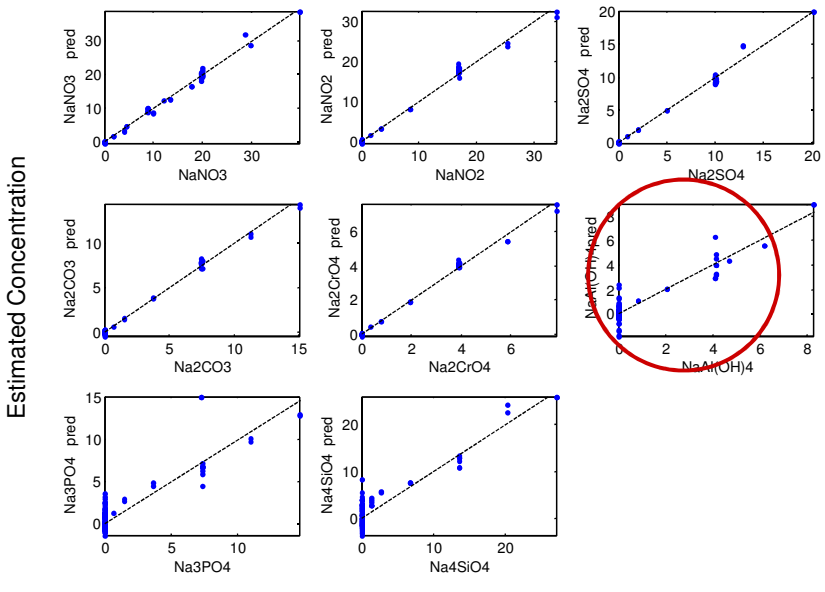
Non-Linear Classical Least Squares (NL-CLS)



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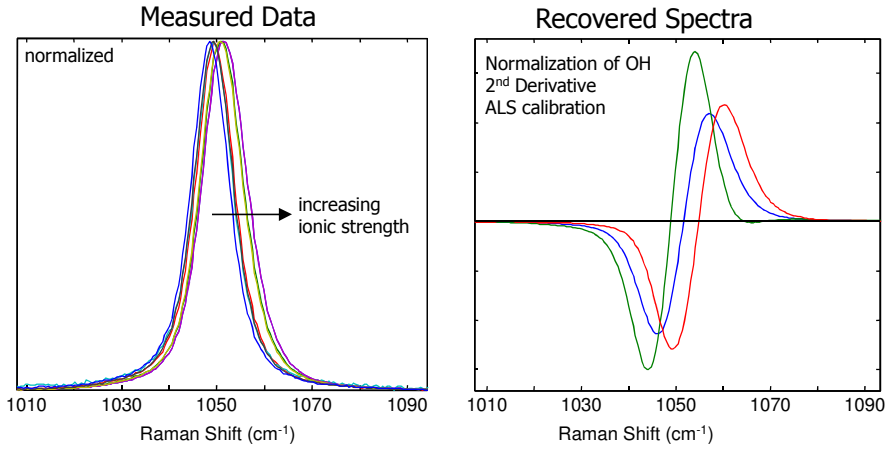
Example: Multiple NO_3 Components



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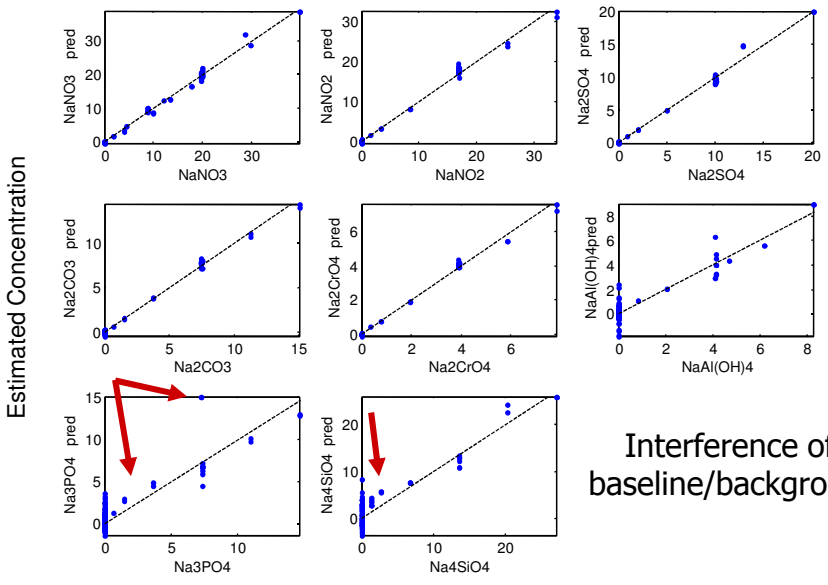
Non-Linear Classical Least Squares (NL-CLS)



Interference of baseline/background

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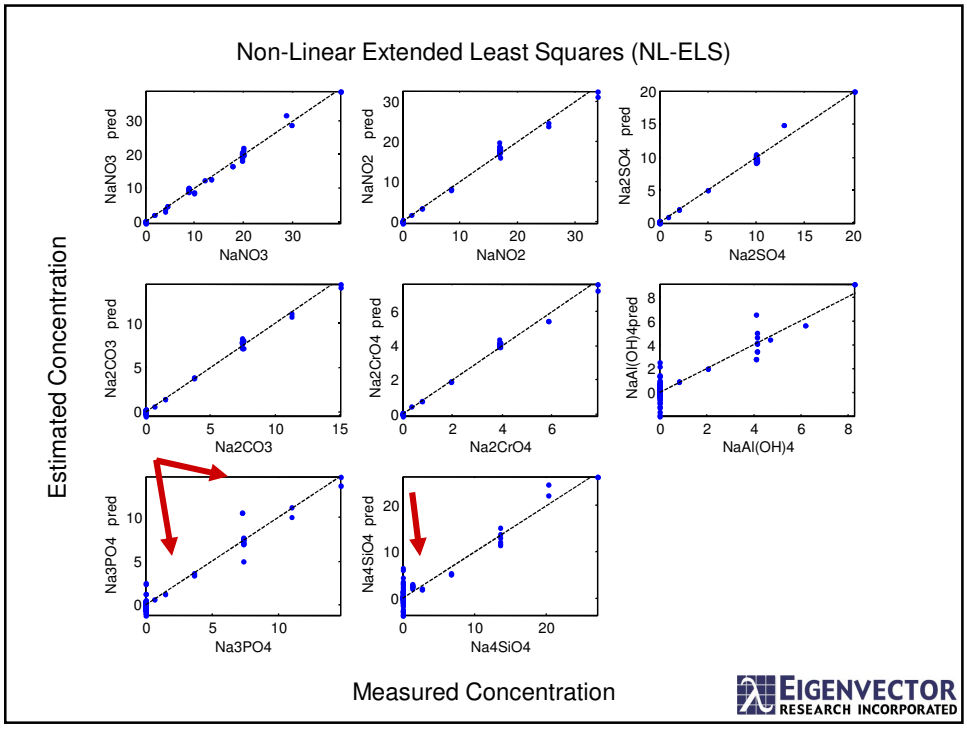
Non-Linear Extended Least Squares (NL-ELS)
Estimated Concentration
NaNO3 pred
NaNO3
NaNO2 pred
NaNO2
Na2SO4 pred
Na2SO4
Na2CO3 pred
Na2CO3
Na2CrO4 pred
Na2CrO4
NaAl(OH)4pred
NaAl(OH)4
Na3PO4 pred
Na3PO4
Na4SiO4 pred
Na4SiO4
Measured Concentration
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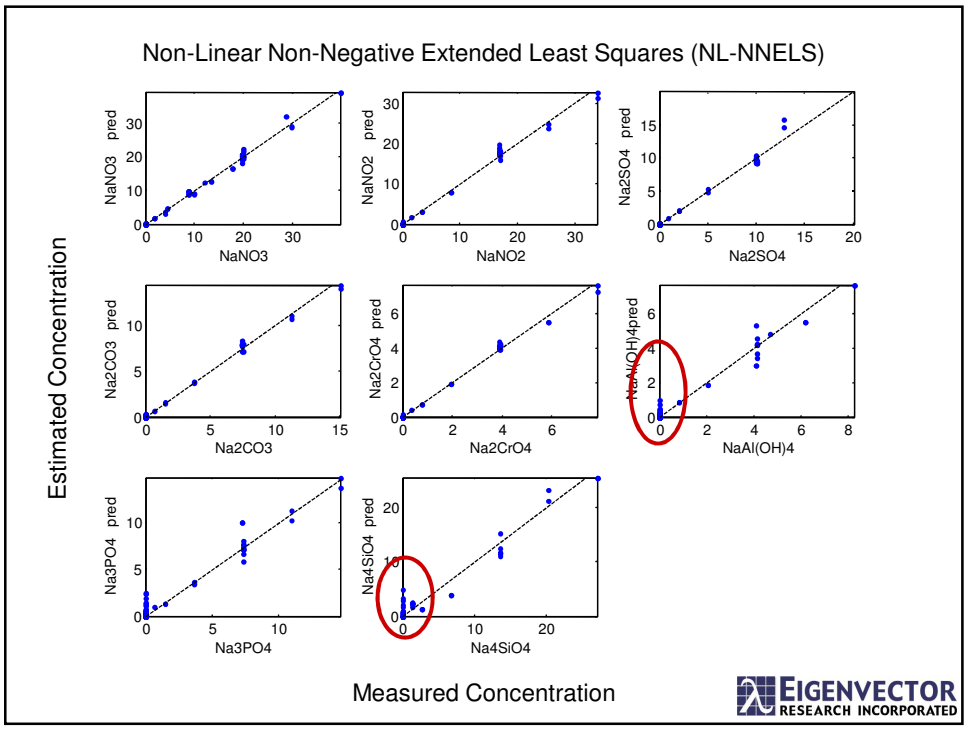
Non-Linear Non-Negative Extended Least Squares (NL-NNELS)
Estimated Concentration
NaNO3 pred
NaNO3
NaNO2 pred
NaNO2
Na2SO4 pred
Na2SO4
Na2CO3 pred
Na2CO3
Na2CrO4 pred
Na2CrO4
NaAl(OH)4pred
NaAl(OH)4
Na3PO4 pred
Na3PO4
Na4SiO4 pred
Na4SiO4
Measured Concentration
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Calibration Results

NO3	NO2	SO4	CO3	CrO4	Al(OH)	PO4	SiO4	
0.18	0.19	0.36	0.11	0.04	**0.43**	0.53	**0.78**	nn
0.19	0.19	0.36	0.09	0.04	**0.42**	0.48	**0.74**	sr,nn
0.18	0.19	0.27	0.13	0.04	0.73	0.56	1.25	
0.18	0.18	0.36	0.12	0.04	0.61	0.49	1.12	sr

(non-negative basis)

NO3	NO2	SO4	CO3	CrO4	Al(OH)	PO4	SiO4	
0.26	0.18	0.35	0.10	0.04	0.38	0.48	0.99	nn
0.26	0.18	0.35	0.09	0.04	0.39	0.45	1.04	sr,nn
0.24	0.23	0.34	0.12	0.04	0.43	0.51	**0.92**	
0.24	0.18	0.39	0.10	0.04	**0.17**	0.44	0.99	sr

Pure samples only
OH Normalization
2nd Derivative
ALS calibration for non-linear components

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Extended and Non-Linear Models Useful?

Ordinary Least Squares

Standard Error of Calibration (SEC)

	NO3	NO2	SO4	CO3	CrO4	Al(OH)	PO4	SiO4
:	0.60	0.59	0.36	0.24	0.12	3.13	2.24	2.77
B :	0.59	0.61	0.36	0.24	0.12	3.15	1.38	1.70
3:	0.57	0.54	0.31	0.21	0.11	0.61	1.50	2.33
B3:	0.57	0.54	0.31	0.21	0.11	0.67	0.67	1.68

Standard Error of Prediction (SEP)

	NO3	NO2	SO4	CO3	CrO4	Al(OH)	PO4	SiO4
:	0.53	0.20	0.06	0.21	0.10	2.06	2.26	2.67
B :	0.51	0.21	0.06	0.21	0.10	2.09	1.26	1.49
3:	0.48	0.19	0.12	0.17	0.09	0.55	1.56	2.03
B3:	0.46	0.18	0.13	0.17	0.09	0.58	0.26	1.55

B: Including 2 Background Factors (from NaOH)
3: Non-linear (3 components) for NO_3

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Extended and Non-Linear Models Useful?

Non-negative Least Squares

Standard Error of Calibration

	NO3	NO2	SO4	CO3	CrO4	Al(OH)	PO4	SiO4
:	0.56	0.66	0.36	0.49	0.13	2.16	4.83	2.03
BG :	0.60	0.74	0.36	0.45	0.12	1.95	1.65	2.42
NL:	0.56	0.53	0.35	0.20	0.10	**0.28**	1.49	2.10
BG,NL:	0.56	0.52	0.35	0.20	0.11	**0.27**	**0.61**	**0.97**

Standard Error of Prediction

	NO3	NO2	SO4	CO3	CrO4	Al(OH)	PO4	SiO4
:	0.41	0.62	0.06	0.42	0.11	0.55	4.73	1.27
BG :	0.38	1.11	0.11	0.39	0.10	0.62	0.87	0.45
NL:	0.43	0.20	0.07	0.17	0.09	0.31	1.54	1.67
BG,NL:	0.40	0.19	0.12	0.18	0.10	**0.20**	**0.31**	**0.38**

BG: Including 2 Background Factors (from NaOH)

NL: Non-linear (3 components) for NO_3

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Stepwise and Non-Negative LS Useful?

Background + Non-linear NO_3

Standard Error of Calibration

	NO3	NO2	SO4	CO3	CrO4	Al(OH)	PO4	SiO4
:	0.57	0.54	0.31	0.21	0.11	0.67	0.67	1.68
SR :	0.56	0.52	0.35	0.20	0.11	0.80	0.61	1.61
NN:	0.56	0.52	0.35	0.20	0.11	**0.27**	0.61	0.97
SR,NN:	0.56	0.51	0.35	0.19	0.11	**0.26**	**0.53**	**0.79**

Standard Error of Prediction

	NO3	NO2	SO4	CO3	CrO4	Al(OH)	PO4	SiO4
:	0.46	0.18	0.13	0.17	0.09	0.58	**0.26**	1.55
SR :	0.45	0.17	0.13	0.17	0.09	0.55	0.55	1.32
NN:	0.40	0.19	0.12	0.18	0.10	**0.20**	**0.31**	**0.38**
SR,NN:	0.40	0.20	0.12	0.18	0.10	**0.22**	0.62	**0.45**

SR: Stepwise regression

NN: Non-Negative least squares

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Best/Worst Results

Standard Error of Calibration

NO3	NO2	SO4	CO3	CrO4	Al(OH)	PO4	SiO4
0.60	0.59	0.36	0.24	0.12	3.13	2.24	2.77
0.56	0.51	0.35	0.19	0.11	0.26	0.53	0.79

Standard Error of Prediction

NO3	NO2	SO4	CO3	CrO4	Al(OH)	PO4	SiO4
0.53	0.20	0.06	0.21	0.10	2.06	2.26	2.67
0.40	0.19	0.12	0.18	0.10	0.20	0.31	0.38

OH Normalization
1st derivative
Non-linear CLS model
Extended Mixture model
Stepwise regression
Non-negative Least Squares

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Conclusions and Future

- CLS models can be adapted to handle non-linear single-component responses
- Updating of CLS models straightforward

- Evidence for fusion of conductivity and Raman for correction
- On-line statistics for evaluation

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