Automated Peak and Peak-Ratio Selection for Regression and Classification Models of Raman and LIBS Data

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NIR Shootout 2002

- 2002 International Diffuse Reflectance Conference (IDRC) "Shootout" data
  - NIR spectra
  - 654 pharmaceutical tablets
  - Calibration Set, Validation Set, Test Set
  - Two spectrometers
  - **Goal: best model with calibration transfer**
- Won by Karl Norris using "Norris Regression" – selected peaks and peak ratios including gap-segment derivative

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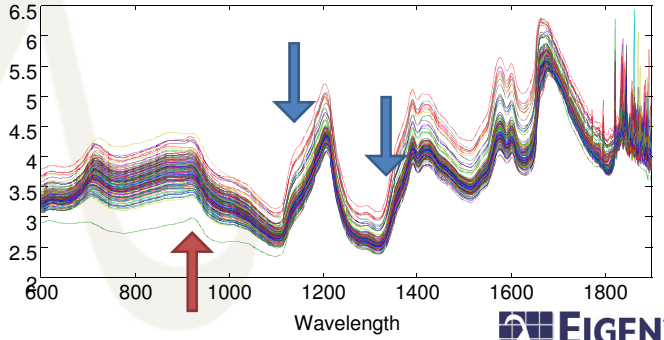
Norris' "Winning" Model

	Term 1			Term 2		
	Wavelength	Smooth	Gap	Wavelength	Smooth	Gap
Numerator	1142 nm	10 nm	26 nm	1338 nm	0 nm	22 nm
Denominator	920 nm	0 nm	30 nm			

Interactive manual selection of regions and smooth/gap parameters



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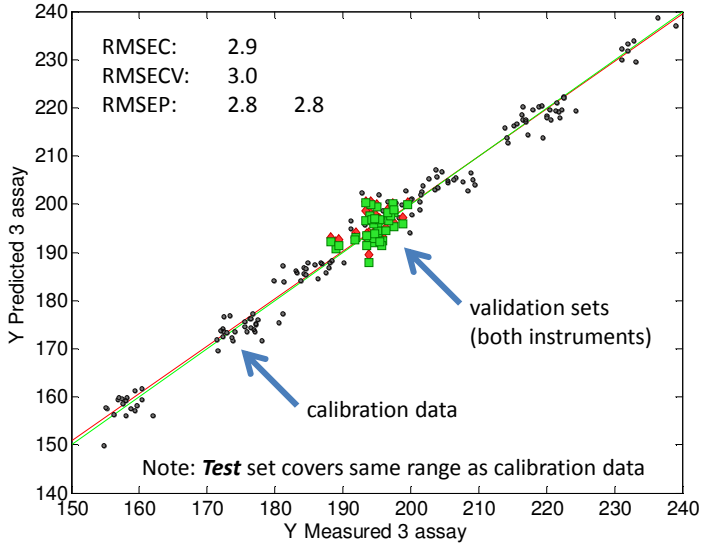
Results using (Approx.) Norris Regression



Preprocessing: 2nd Derivative (gap: 18 nm, segment: 6 nm) + Integrate + Autoscale

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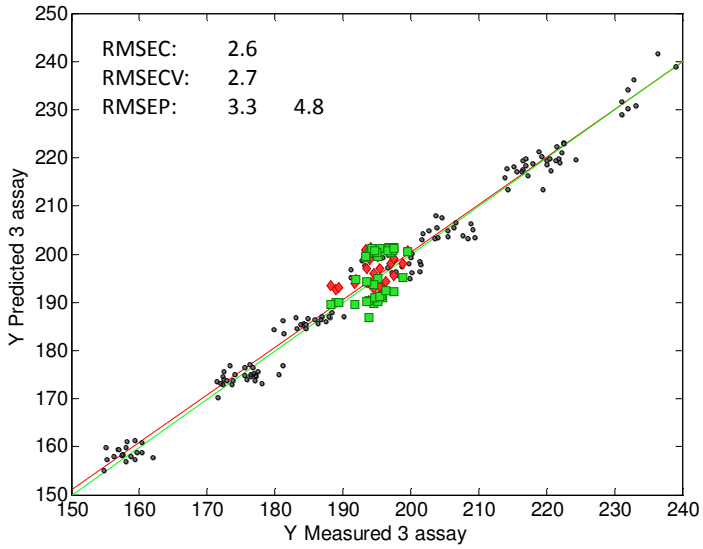
EMSC + 1st Derivative + Mean Centering

EMSC = Extended Multiplicative Scatter Correction



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Tabulated Results

	RMSEC	RMSECV	Val 1	Val 2	Test 1	Test 2
Norris Regression	2.7	2.7	2.8	2.8	3.0	3.3
Expert-Selected Preprocessing	2.6	2.7	3.3	4.8	2.8	4.2

Good Model… but Bad Transfer

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Norris Regression – Generically

Non-linear Regression

$$y = b_1 (x_1)$$

$$y = b_1 (x_1 - x_2)$$ (Gap-Segment 1st Derivative)

$$y = b_1 \frac{x_1}{x_3}$$ (Peak Normalization)

$$y = b_1 \frac{x_1 - x_2}{x_3 - x_4}$$ (Peak Normalization with variable- gap 1st derivative)

$$y = b_1 \frac{x_1 - x_2}{x_3 - x_4} + b_2 (x_5 - x_6) + b_3 x_7 + \ldots$$

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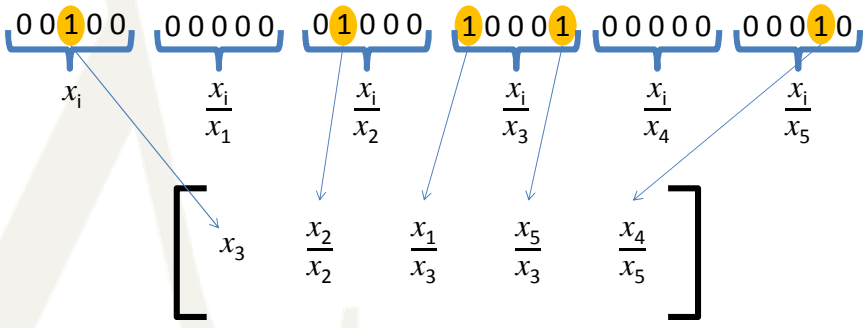
Binary Encoding of Norris Equations

- Example for 5 variables: $[\, x_1 \quad x_2 \quad x_3 \quad x_4 \quad x_5 \,]$



This much could be done by pre-computing…
but at a big memory cost
(525MB for shootout data)

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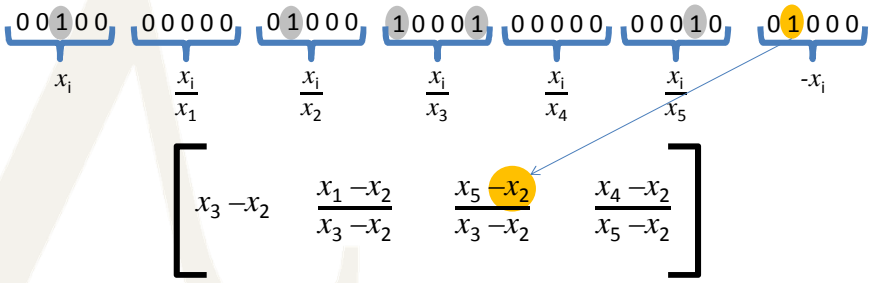
+ Allow Subtraction…

- Example for 5 variables: $[\,x_1 \quad x_2 \quad x_3 \quad x_4 \quad x_5\,]$
- One additional group to identify "baseline"



Pre-computation would now require
2 x10^{201} *variables* (for the shootout data)
variables = 2^n (n^2+n)

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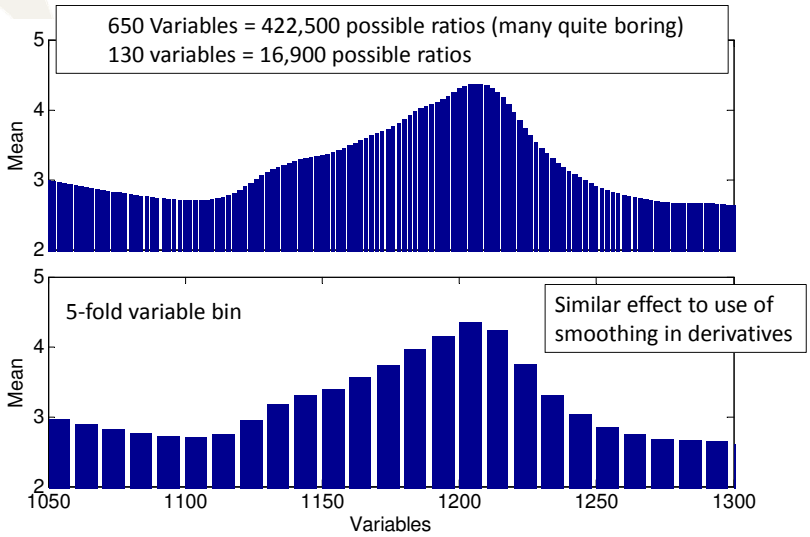
+ Binning to Reduce Dimensionality



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+ Genetic Algorithm to Select Terms

- Try lots of combinations (Calculate variable ratios and offsets on-the-fly)
- Choose best cross-validated results
- Breed (intermix terms) and repeat
- Will refer to this as "GA-Norris"

- **Question:** Can this approach approximate what the interactive Norris approach does?

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Tabulated Results

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Norris Regression	2.7	2.7	2.8	2.8	3.0	3.3
Expert-Selected Preprocessing	2.6	2.7	3.3	4.8	2.8	4.2
GA Norris (Cal 1 only)	2.4	2.5	3.9	5.0	2.8	3.7
GA Norris (Cal 1 & 2)	2.8	2.9	3.0	3.0	3.0	3.3
Simple GA (Cal 1 & 2)	2.6	2.7	3.7	3.8	3.3	3.5

Selecting Variables based on both instruments (building model from ONE) yields GA Norris preprocessing which closely approximates what Karl Norris did.

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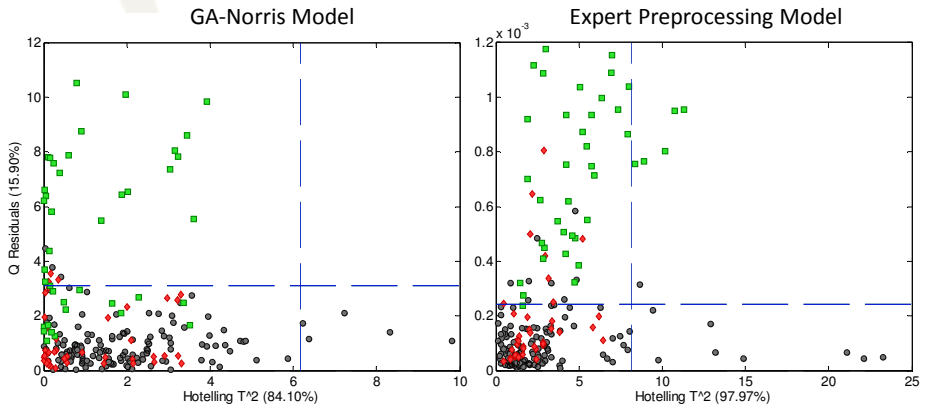
Outlier Detection Achieved…



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Where Else Would Ratios Help?

- Raman – correcting for throughput differences and offsets
- LIBS – correcting for throughput differences and for emphasizing the importance of "relative abundance"

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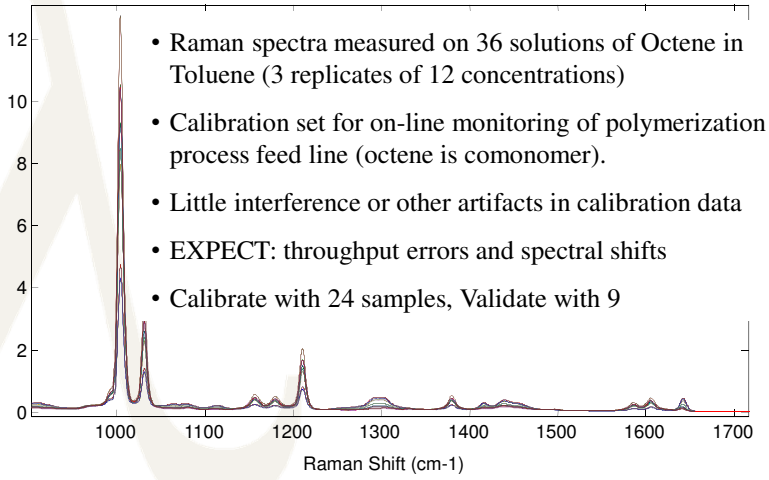
Raman of Octene in Toluene



- Raman spectra measured on 36 solutions of Octene in Toluene (3 replicates of 12 concentrations)
- Calibration set for on-line monitoring of polymerization process feed line (octene is comonomer).
- Little interference or other artifacts in calibration data
- EXPECT: throughput errors and spectral shifts
- Calibrate with 24 samples, Validate with 9

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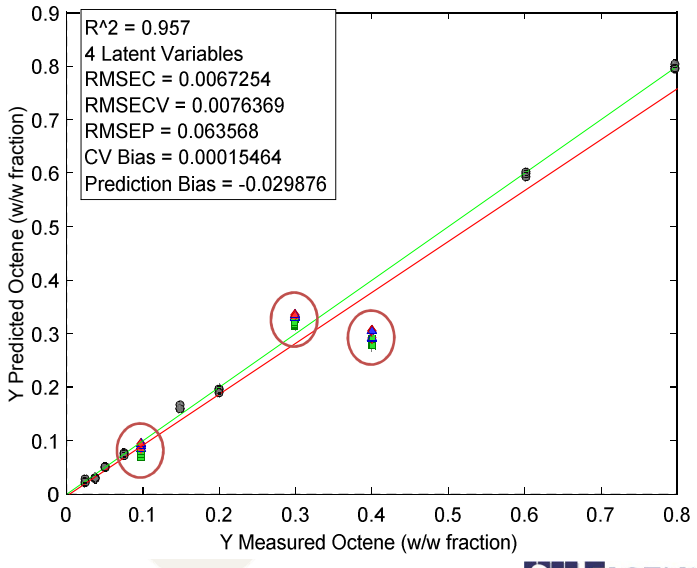

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Prediction Error Vs. Interferences

Autoscale	Scale variables to unit standard deviation
Normalize	Divide by total intensity
Normalize (1000 cm^{-1})	Divide by intensity at 1000 cm^{-1} peak
1st Derivative	Savitzky-Golay 1st Derivative (15 point)
Whittaker Baseline	Automatic baseline subtraction
GA Norris	Binning + GA Norris Variable Selection + Ratios

(All methods also include mean centering)

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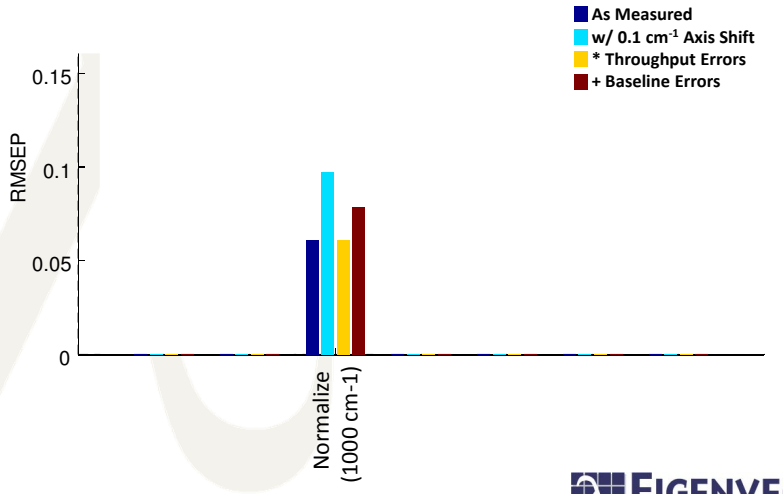
Prediction Error Vs. Interferences



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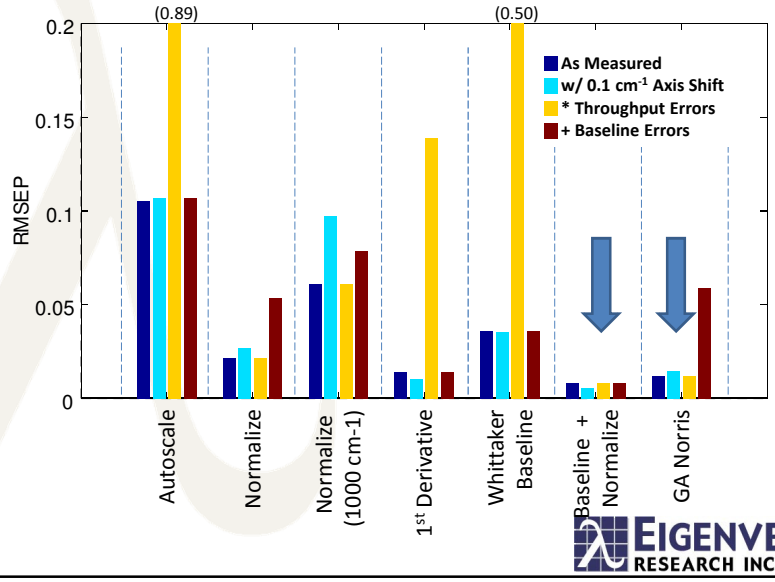
Prediction Error Vs. Interferences



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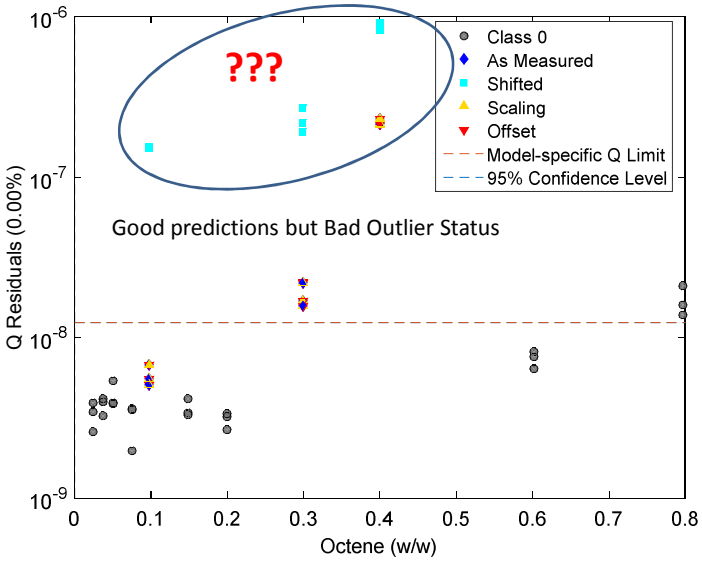
Outlier Detection: Baseline+Norm



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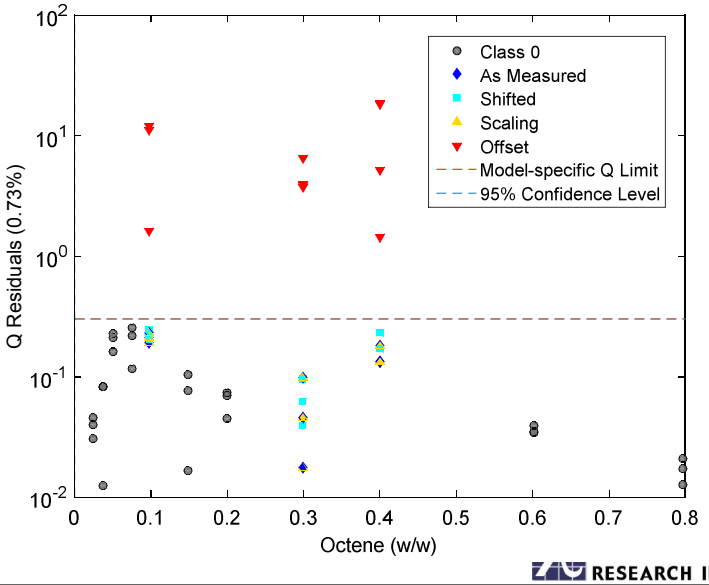
Outlier Detection: GA Norris



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LIBS / Raman Classification

- Mystery classes (natural product, difficult to separate classes)
- Raman data – not much information
- LIBS data – too much information
- Anticipate Peak Ratios should help greatly in LIBS!
- Try GA Norris on LIBS

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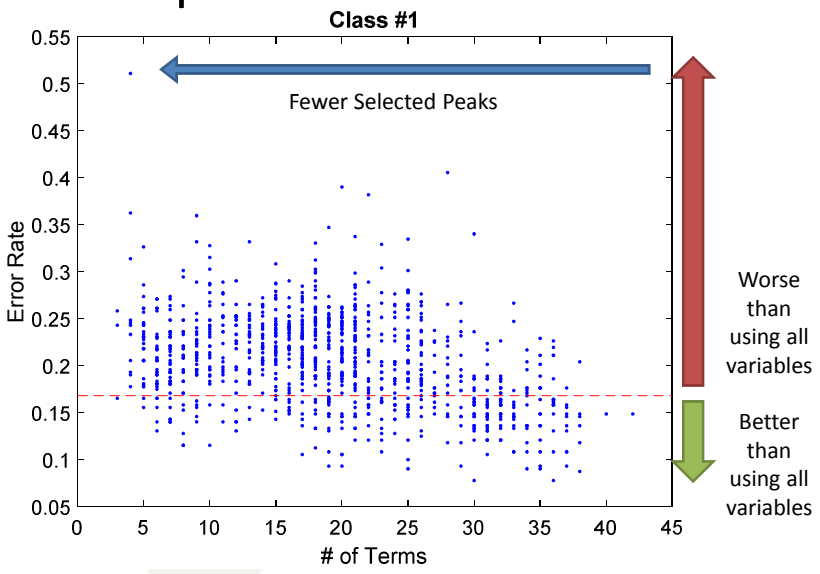
Example GA Norris Results



1000 Selection Results

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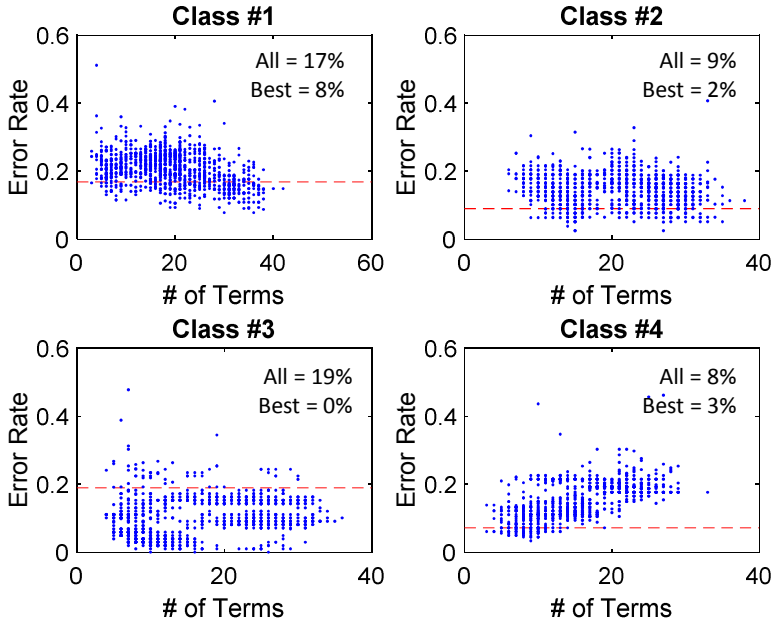
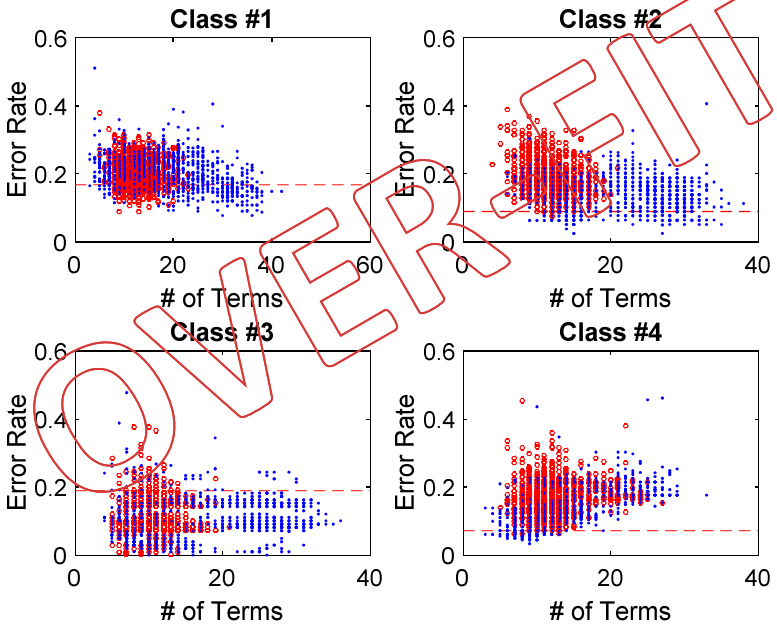
All Classes



With Randomized Classes (Red)



Non-linear model
+ variable selection
+ large domain

= large chance of over-fit

= use caution & permutation tests

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Conclusions

- GA Norris can reproduce Norris Regression results
- Can be used to achieve similar results to standard preprocessing (but with less sound decisions!)
- Large chance of over-fit = use caution & permutation tests, or standard methods!!