Contrasting Spectroscopy and Chromatography for Motor Fuel Assessments

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Infometrix:
39 Years of Chemometrics

- Process analytical technology applications in refining have been evolving for decades
  - Continual improvement in instrument reliability, affordability, speed have led to a wide range of technologies to choose from
    - …. So how do you choose?
- Case study of two technologies investigated, discussion of process

The process is the important part – not the final results!

Raman vs Chromatography, Chemistry

Raman Spectroscopy

- Analysis of functional groups in a whole mixture
  - Response is dictated by vibrational stretches activated in the sample
  - Response is proportional to stretch activity and number of functional groups in sample
- Effectively "counts" C-H stretches, S-O stretches, and any other combination of letter stretches

Gas Chromatography

- Separation of whole compounds from a mixture
  - Separation is dictated by boiling point
    - (polarity / size correlated)
  - Response is proportional to molecule's activity for detection method
- Details on composition of mixture, effectively "counts" molecules

Raman vs Chromatography, Applications

Raman Spectroscopy

- Generally used to predict properties based upon functional groups and aggregate mixtures
  - Manufacturing of target chemicals
  - Pharmaceutical applications
  - Plastics
  - Properties

Gas Chromatography

- Generally used to predict properties based upon molecular composition and distribution
  - Complex mixtures
  - Quantitation of target chemical
  - Investigation of pollutant / contaminant

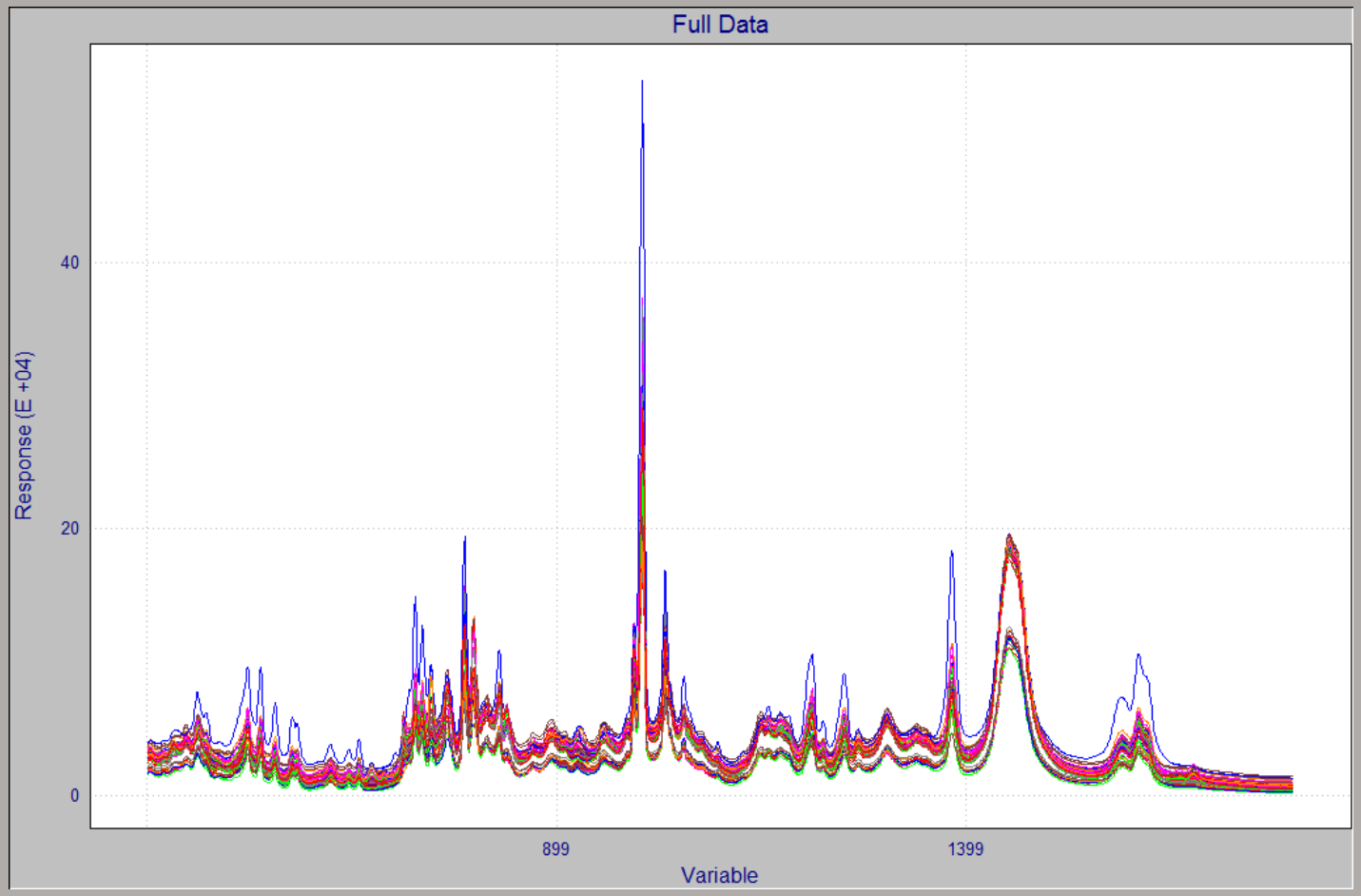
Apply to Gasoline Properties

- IBP
- 10%
- 20%
- 30%
- 50%
- 70%
- 90%
- FBP
- Aromatics
- Benzene
- OLEFINS
- API
- RON
- MON
- SULFUR
- TV/L
- RVP

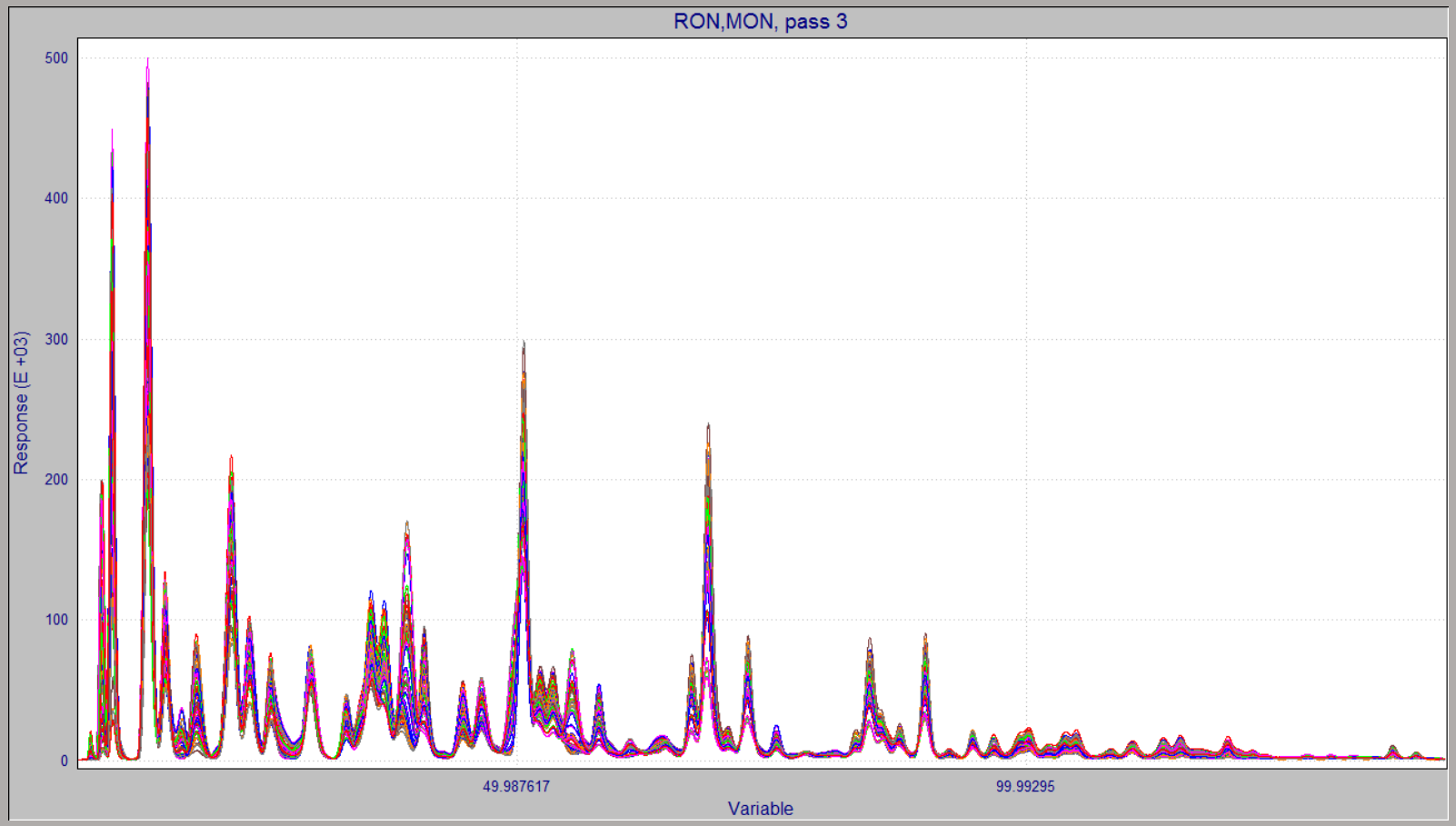
Experiment

- All samples come from ~170 sample superset
  - Some overlap, some don't, all randomly distributed
- 17 independent variables modeled
  - Each one modeled independently
  - Some data not present, those samples are excluded
- **Raman**
- 58 samples acquired
  - 1400 wavenumbers
- **Fast GC**
- 150 samples acquired
  - 250 second acquisition

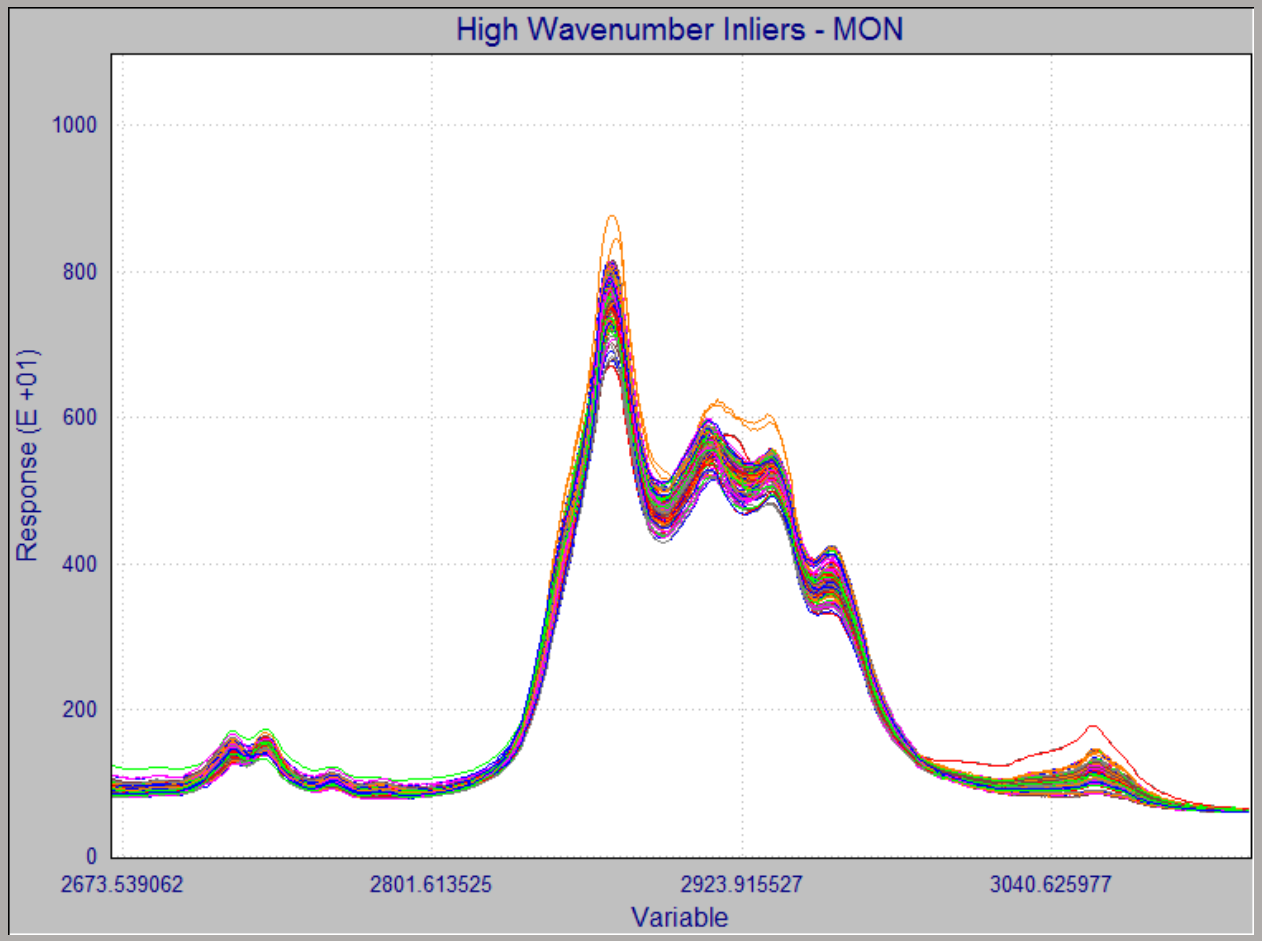
Raman Spectra



Gas Chromatographs



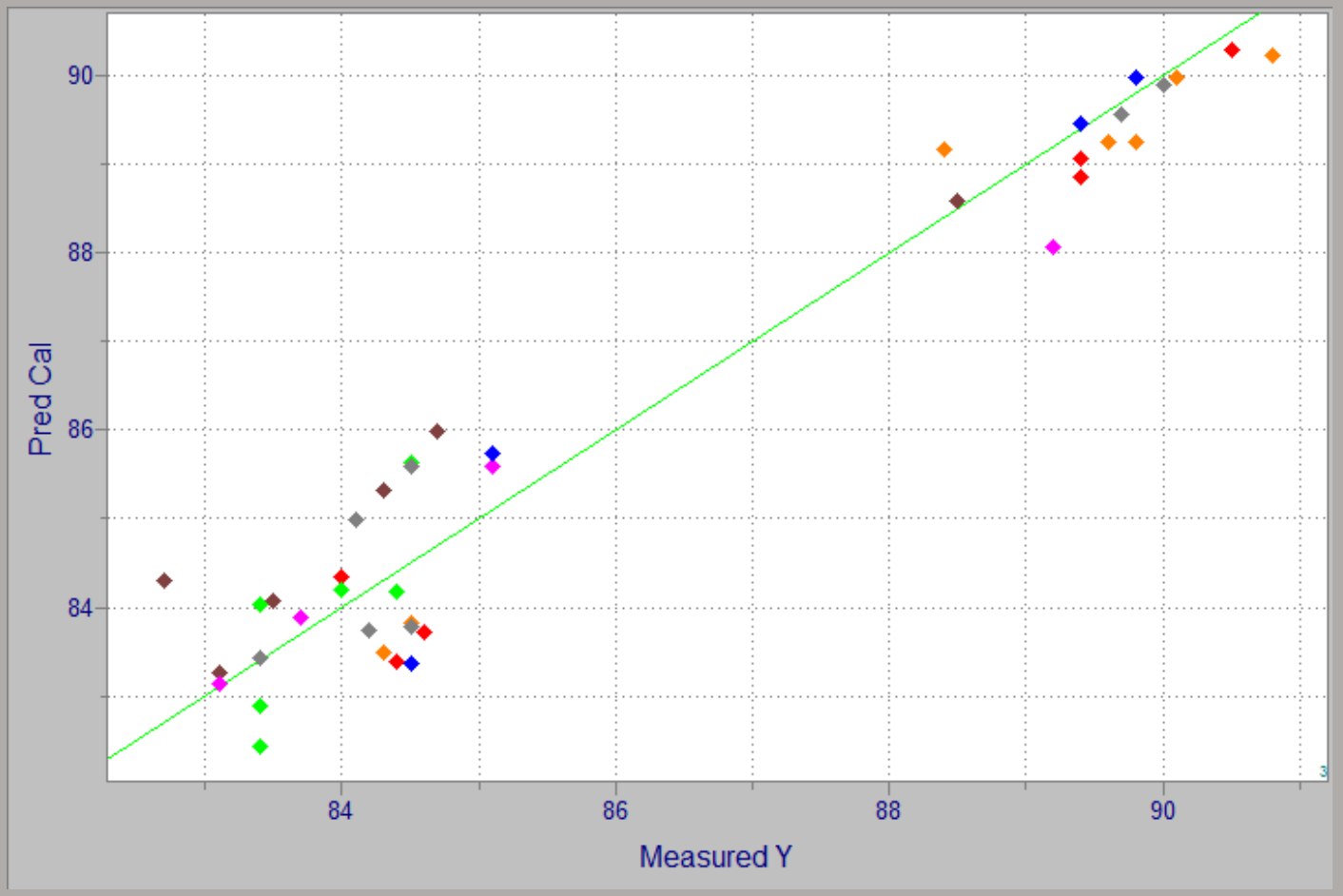
High Wavenumber Raman Region



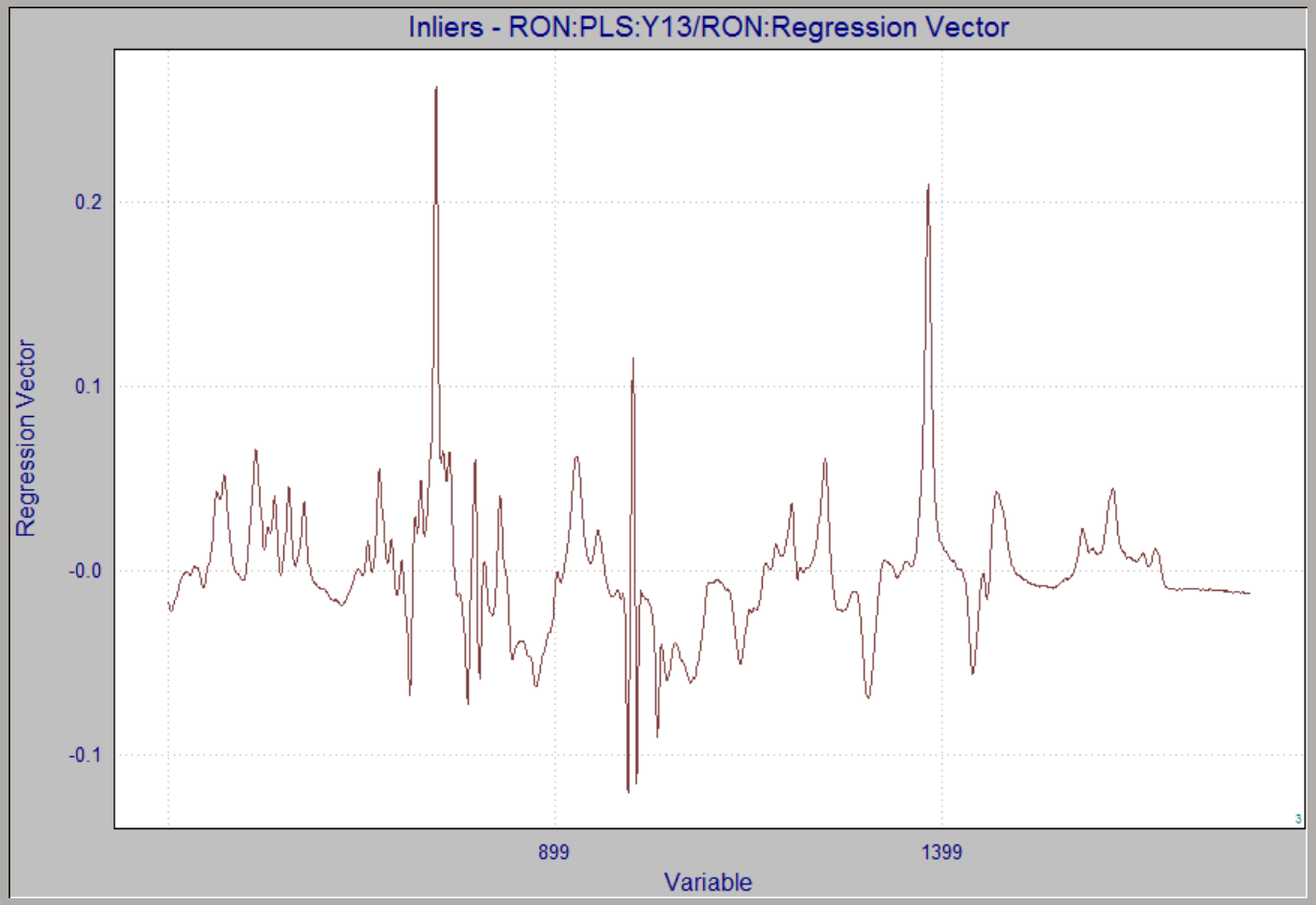
Model Evaluation

- Plug and play, right??
  - Wrong!
- Evaluation of a model is based upon a variety of factors, and each model should be studied in depth
- RMSEP, RMSECV, and RMSEC
- Measured vs. Predicted
- Regression Vector
- Number of Factors
- Outlier diagnostics

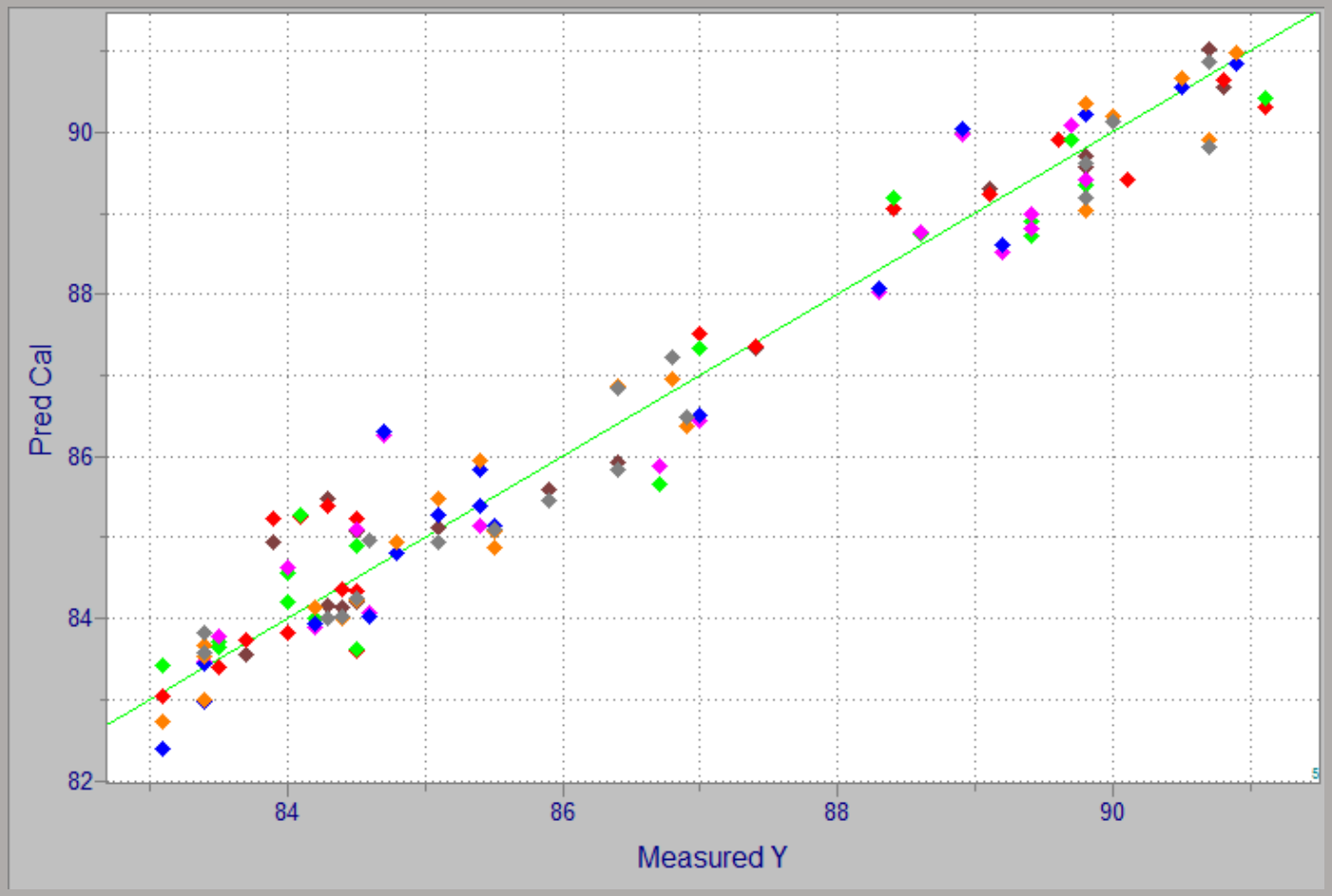
PLS Model of RON on Raman



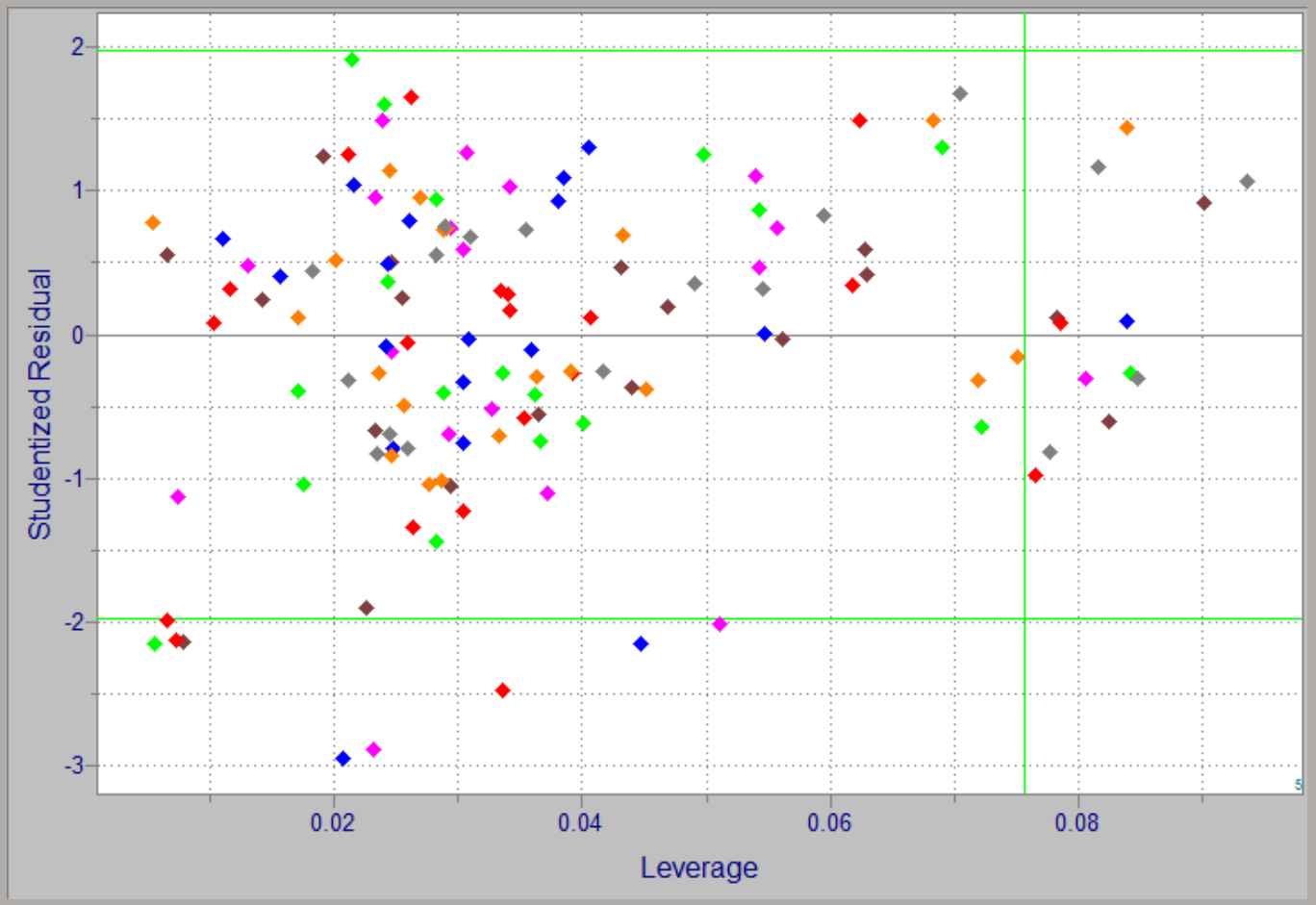
RON Regression Vector



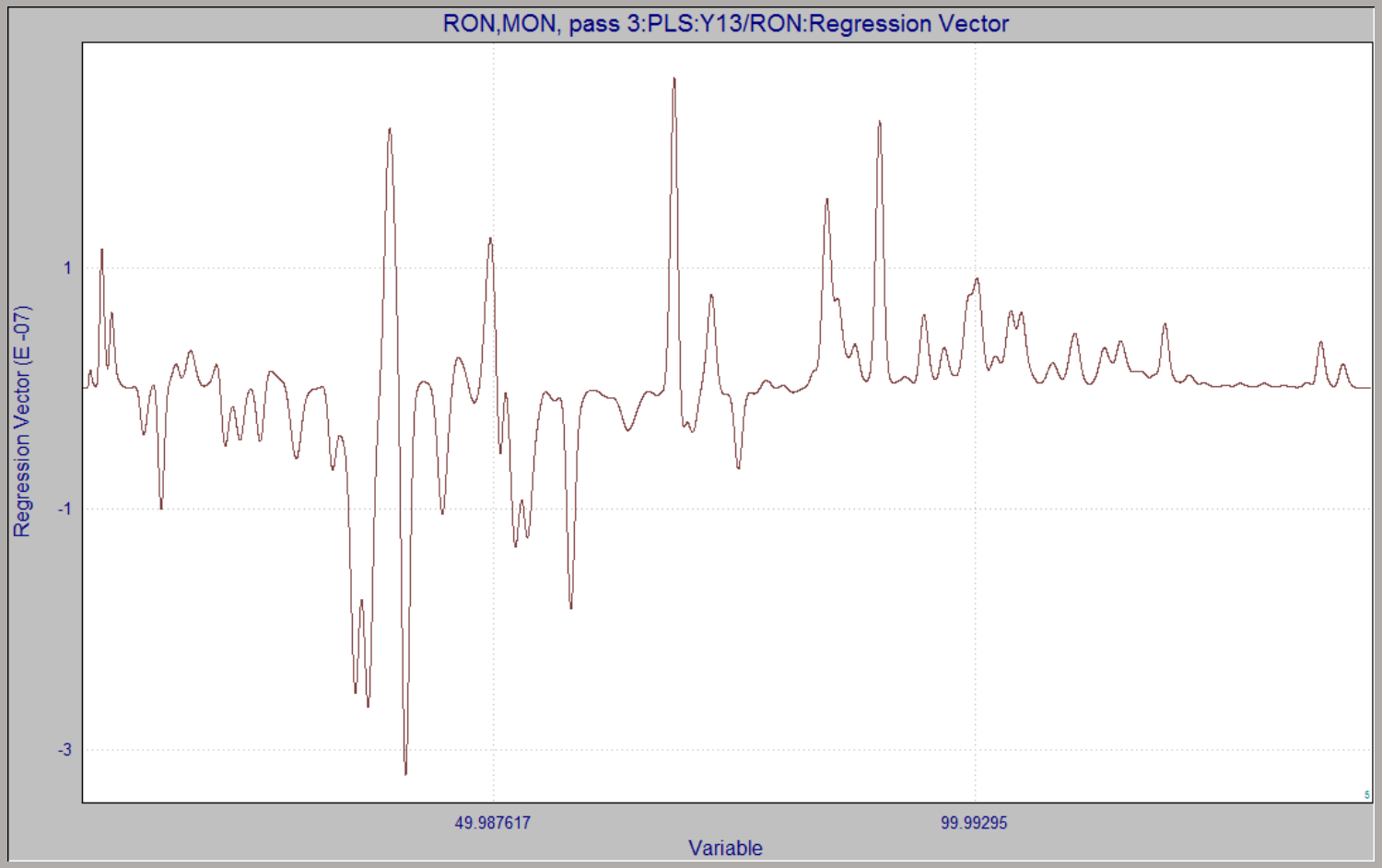
PLS Model of RON on GC



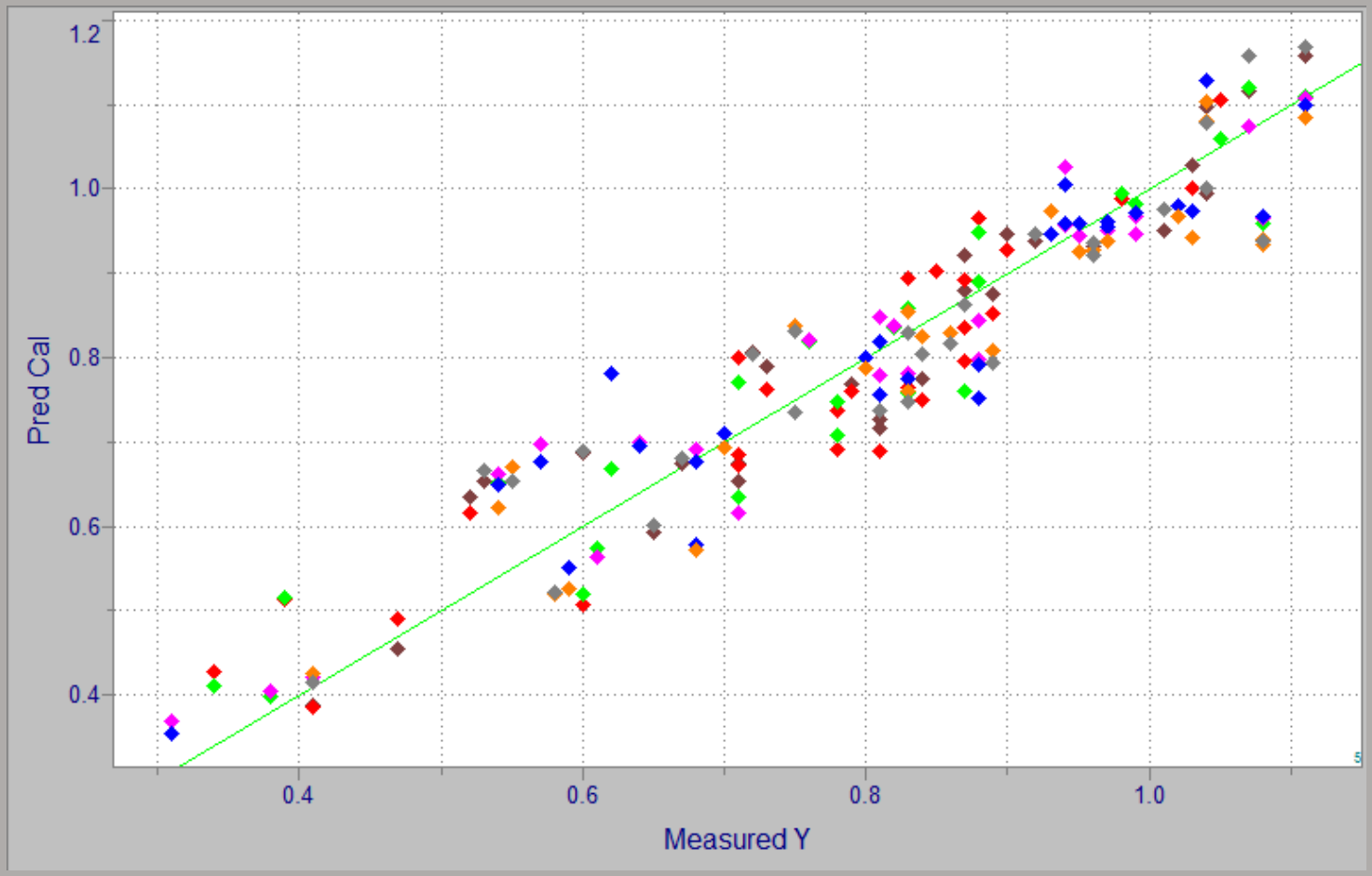
RON on GC - Outliers



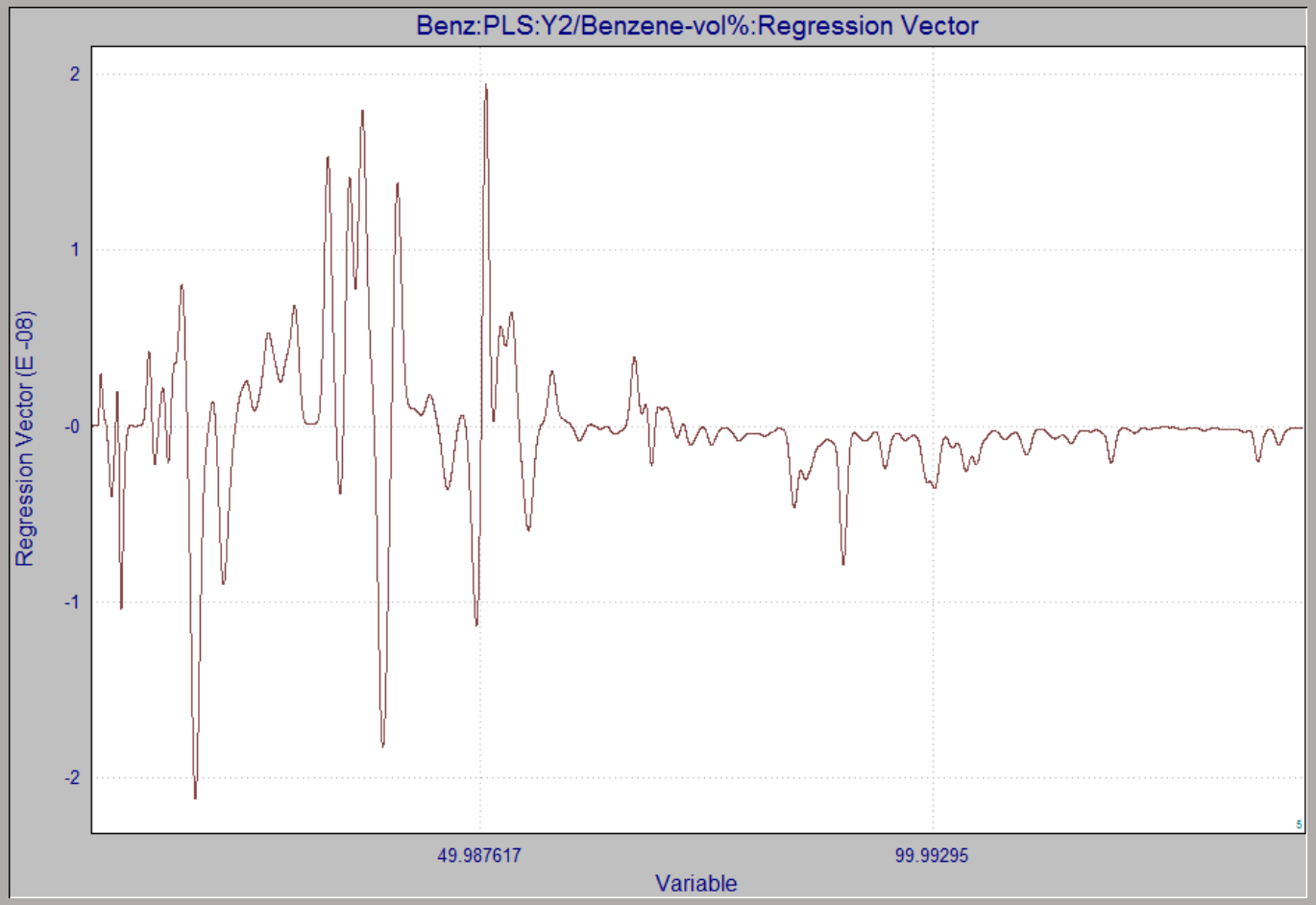
RON Regression Vector - GC



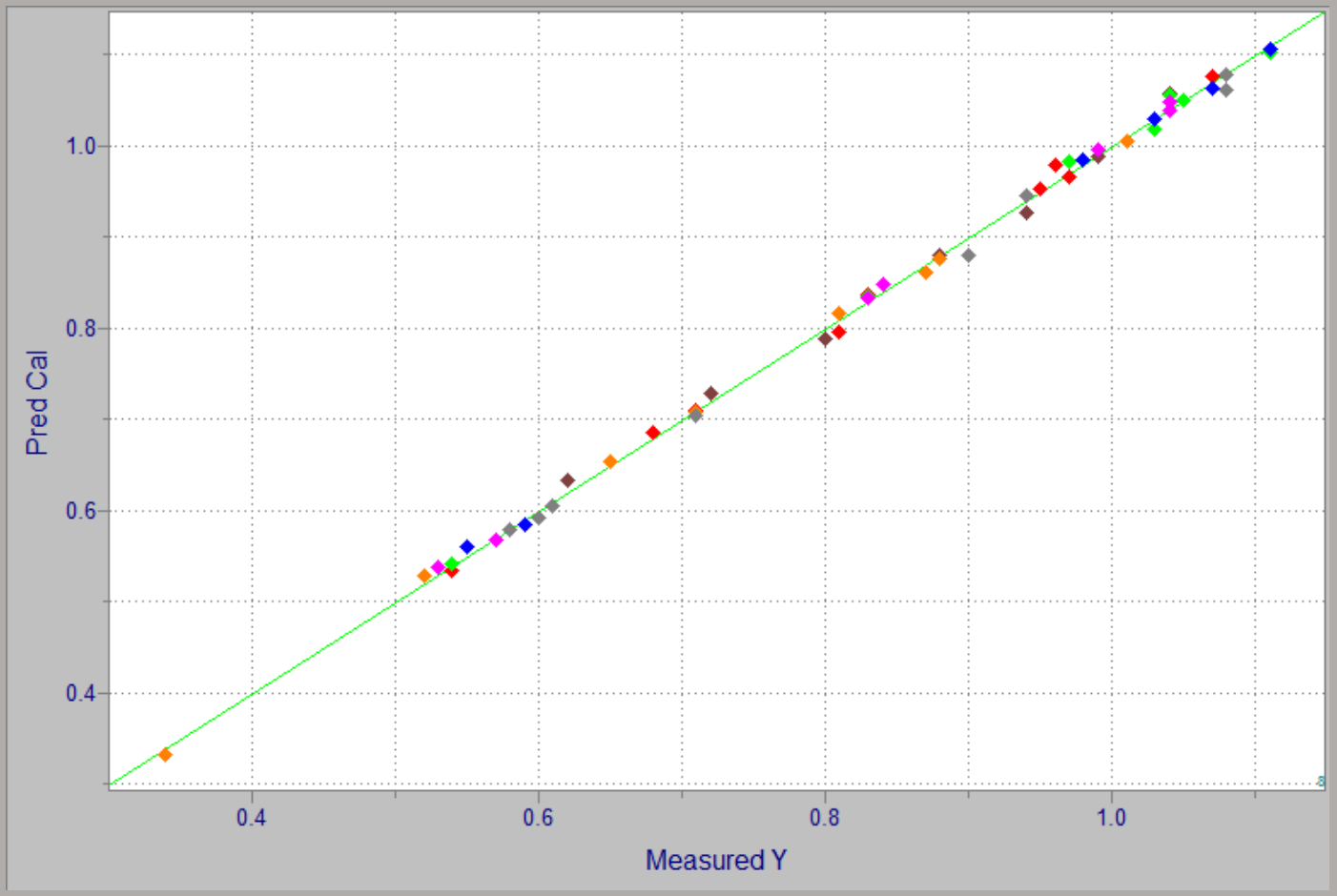
Benzene on GC



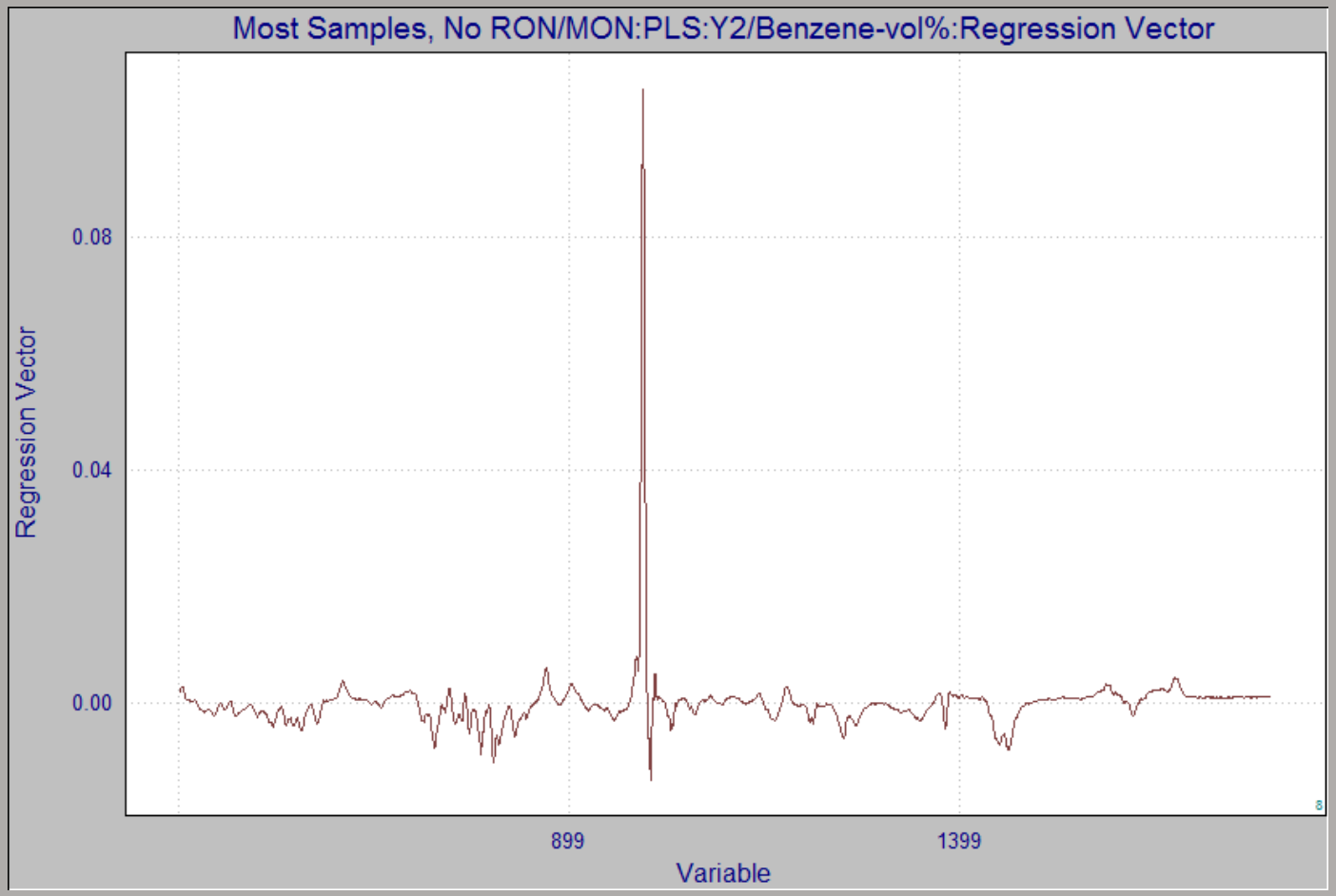
Benzene Regression Vector - GC



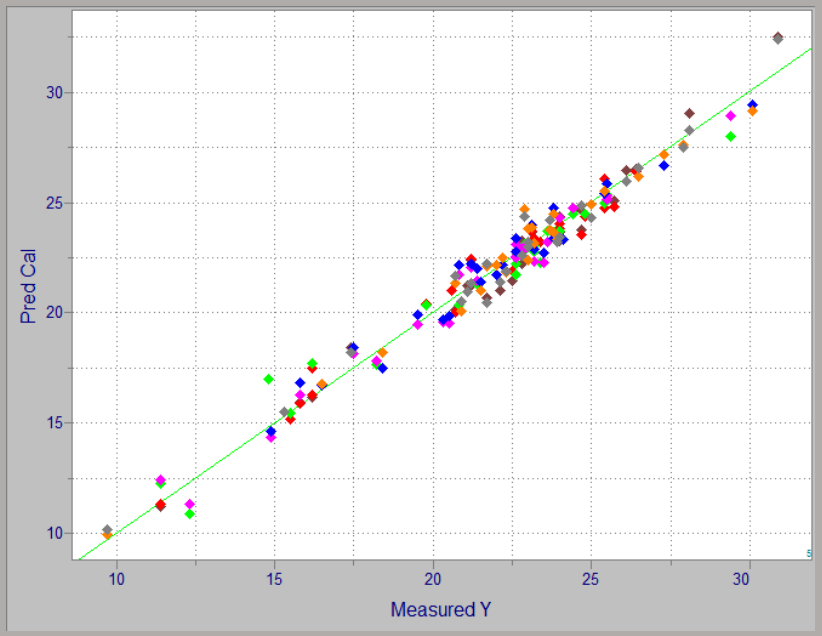
Benzene on Raman

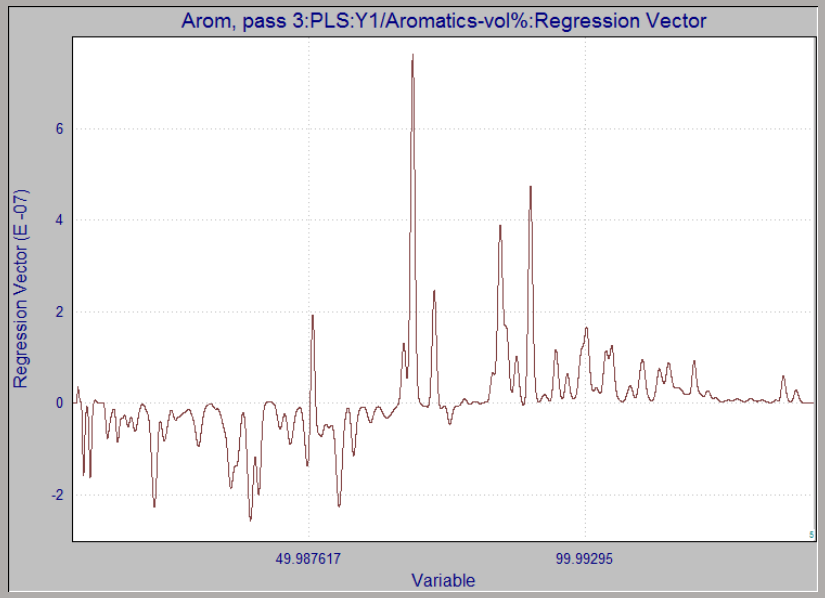


Benzene Regression Vector - Raman

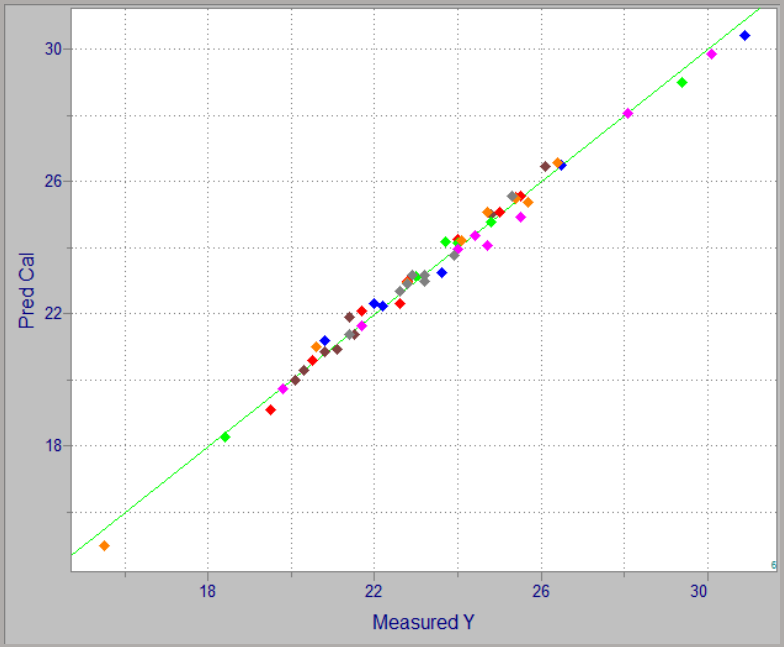


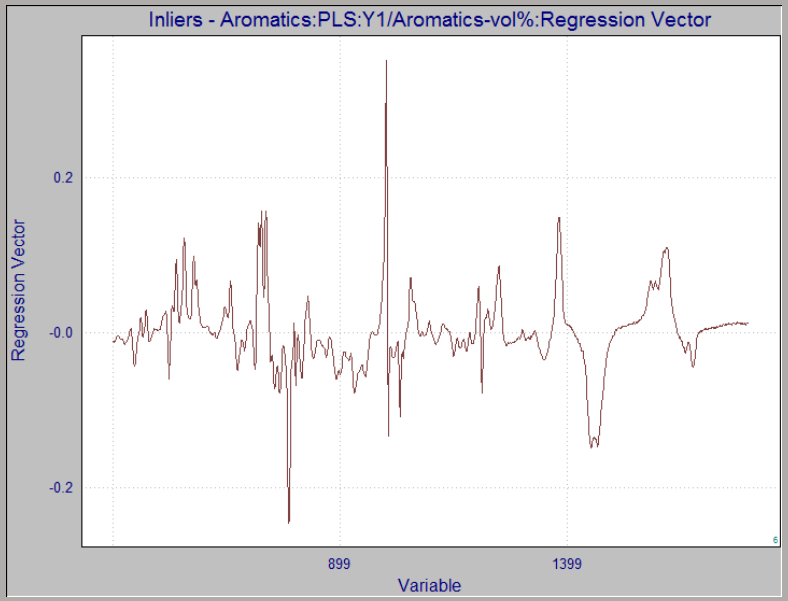
Aromatics - GC





Aromatics - Raman





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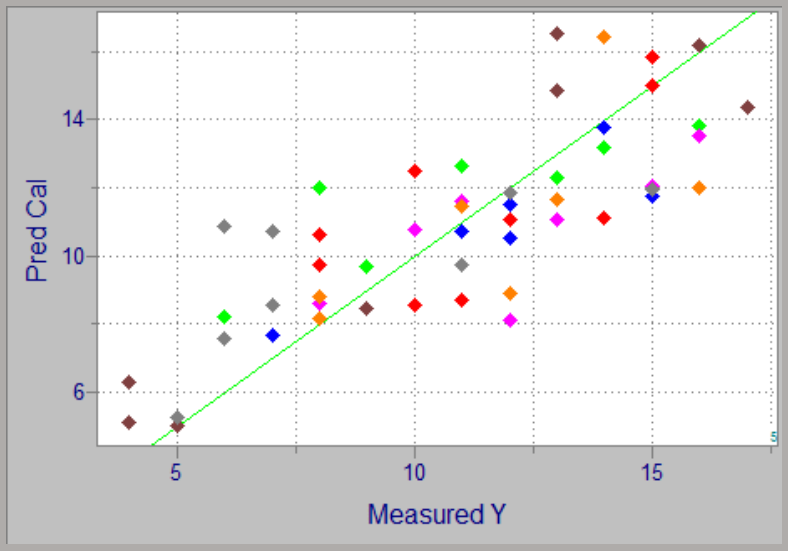
Sulfur with spectroscopy

- Obviously limited by resolution of ref method – 1.0 ppm intervals over 13 ppm range
- Grouping / clustering? May have to do with reference error, spectroscopy LoD, or both



Results comparison

- GC has standout advantage in predictions based on boiling point
- Surprise RON and MON results using GC

	Raman		Gas Chromatography	
	RMSECV	Factors	RMSECV	Factors
IBP	1.53	2	0.89	8
10%	3.69	3	2.29	4
20%	4.41	3	2.16	3
30%	3.71	4	2.10	4
50%	4.01	4	2.01	4
70%	1.57	5	1.31	5
90%	2.36	4	2.10	4
FBP	6.52	4	4.59	5
Aromatics	0.29	6	0.46	6
Benzene	0.01	8	0.06	3
OLEFINS	0.29	4	0.14	5
API	0.22	6	0.35	4
RON	0.49	5	0.17	7
MON	0.32	5	0.15	5
SULFUR	2.53	3	2.46	4
TV/L	1.64	2	1.84	4
RVP	0.32	5	0.46	4

Conclusions

- What does this mean for gasoline analysis?
- "Ideal" is multiple technologies, each used for what it's best suited for
  - Obviously, not practical for most (any?) applications
- What matters most to you?
  - Sampling interface / prep, run time?
  - RON/MON? RVP?
- Most important – follow best practices for chemometrics!