Setting the Standard for Automation™

Advantages of Using Raman Spectroscopy to Monitor Key Gasoline Blending Parameters

Standards
Certification
Education & Training
Publishing
Conferences & Exhibits

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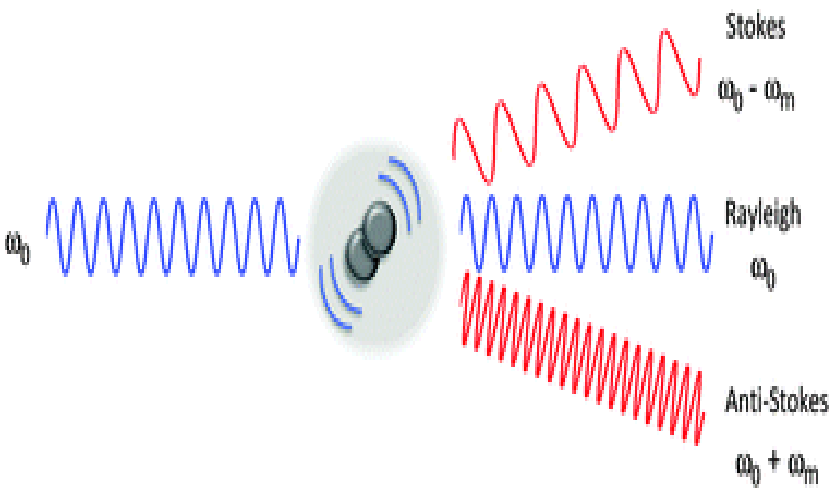
- President - Process Instruments, Inc.
- Located in Salt Lake City, UT, USA
- > 100 On-line Raman Installations since 2000
- Certifications: IEC Ex, ATEX, ETL

Topics

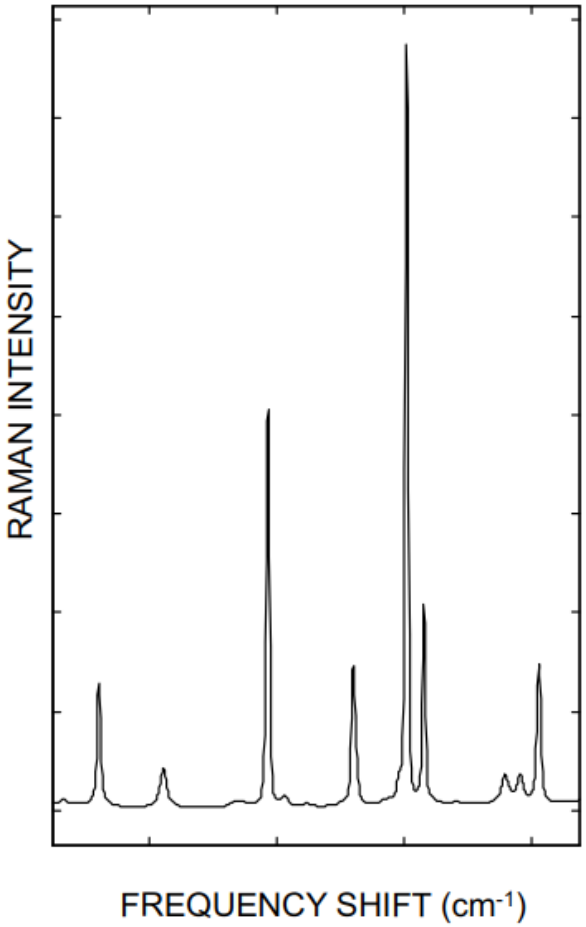
- Raman Scattering Effect and its Interpretation
- Raman's Advantages Within the Refinery
- Typical On-line Setup and Implementation
- Raman Modeling Best Practices
- Refinery Applications and Savings

Raman Effect



- Same Vibrational Modes as MID-IR
- Light Scattering Technology Whereas Infrared Is Absorption
- Different Selection Rules Than IR
- Excellent Spectral Resolution
- Minimum Component Overlap
- Maximum Component Specificity

Interpretation of Raman Spectra

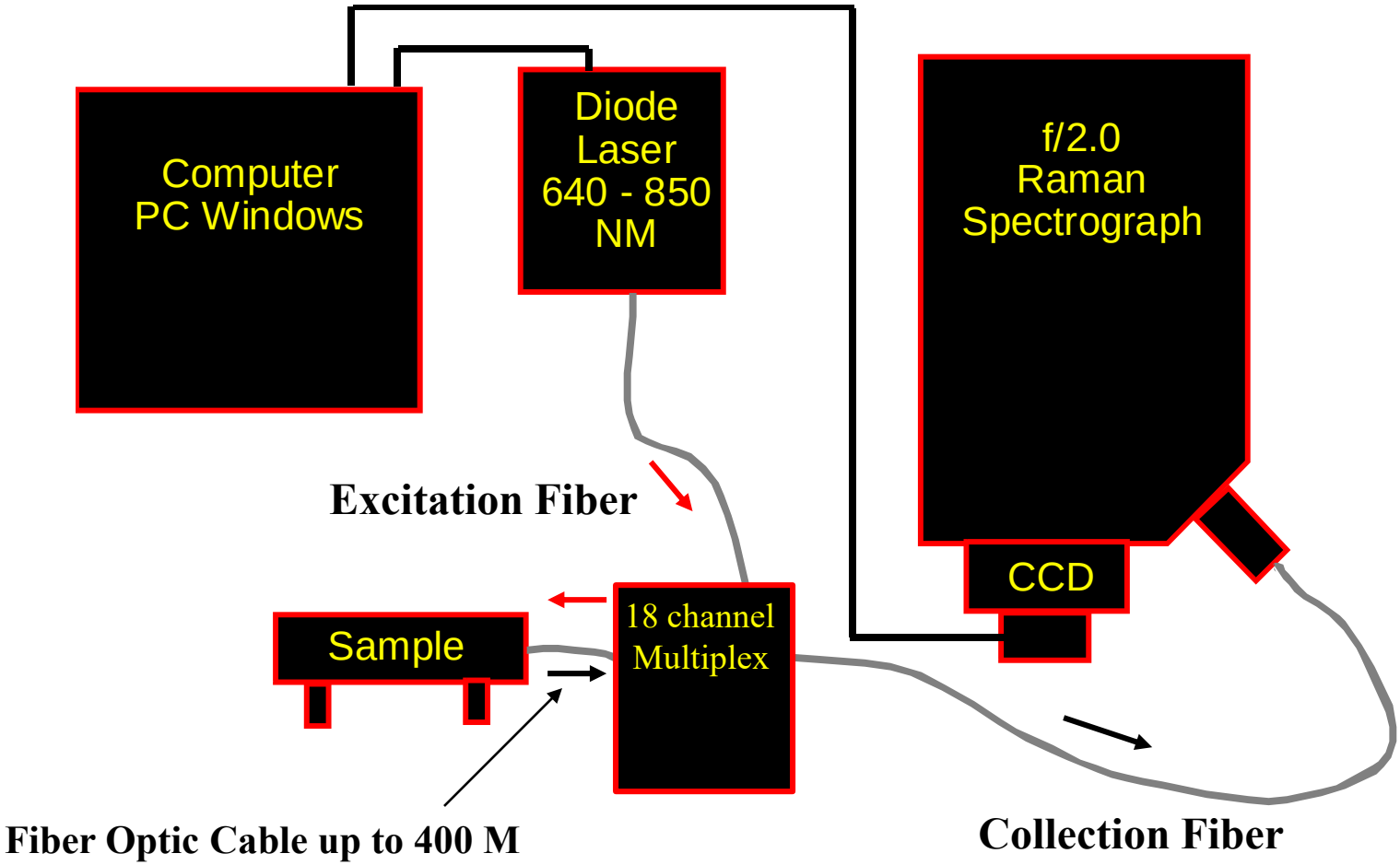


- **Peak Frequency Shifts Yield Sample Composition**
- **Peak Intensities Yield Concentrations**
- **Chemometric Data Analysis for Sample Parameters**
- **Requires Laboratory Data**

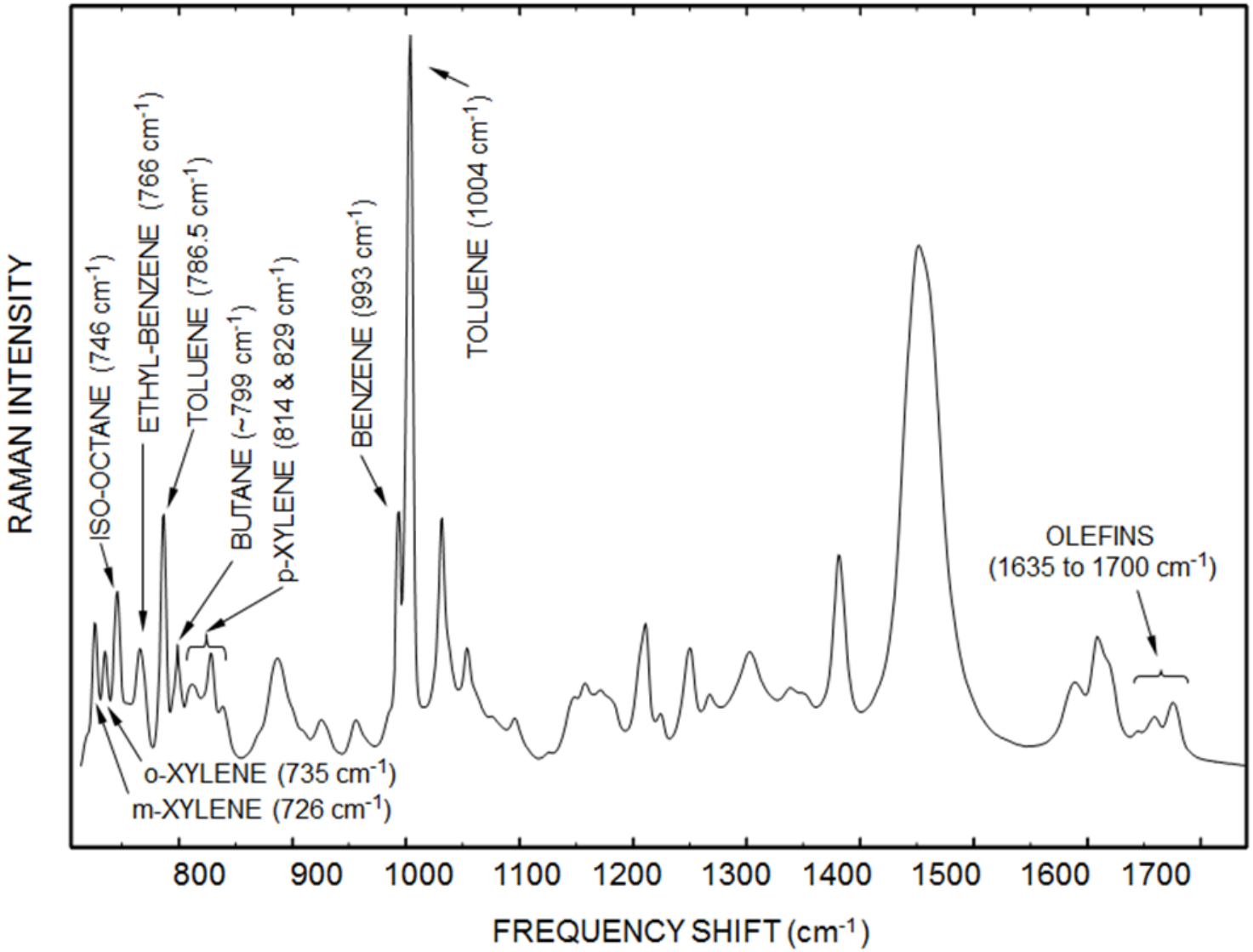
Advantages of Raman Scattering

- **No Interference From H_2O or Process Temp. Changes**
  - **Most Other Spectroscopic Methods Require Extensive Sample Conditioning**
- **Insert Probe Directly Into Process Stream**
- **Multiplex Capable Over Optical Fibers Up To 400 m**
- **Resolution Provides Minimum Component Overlap**
- **Chemometric Models Transfer Easily, Fewer Samples**

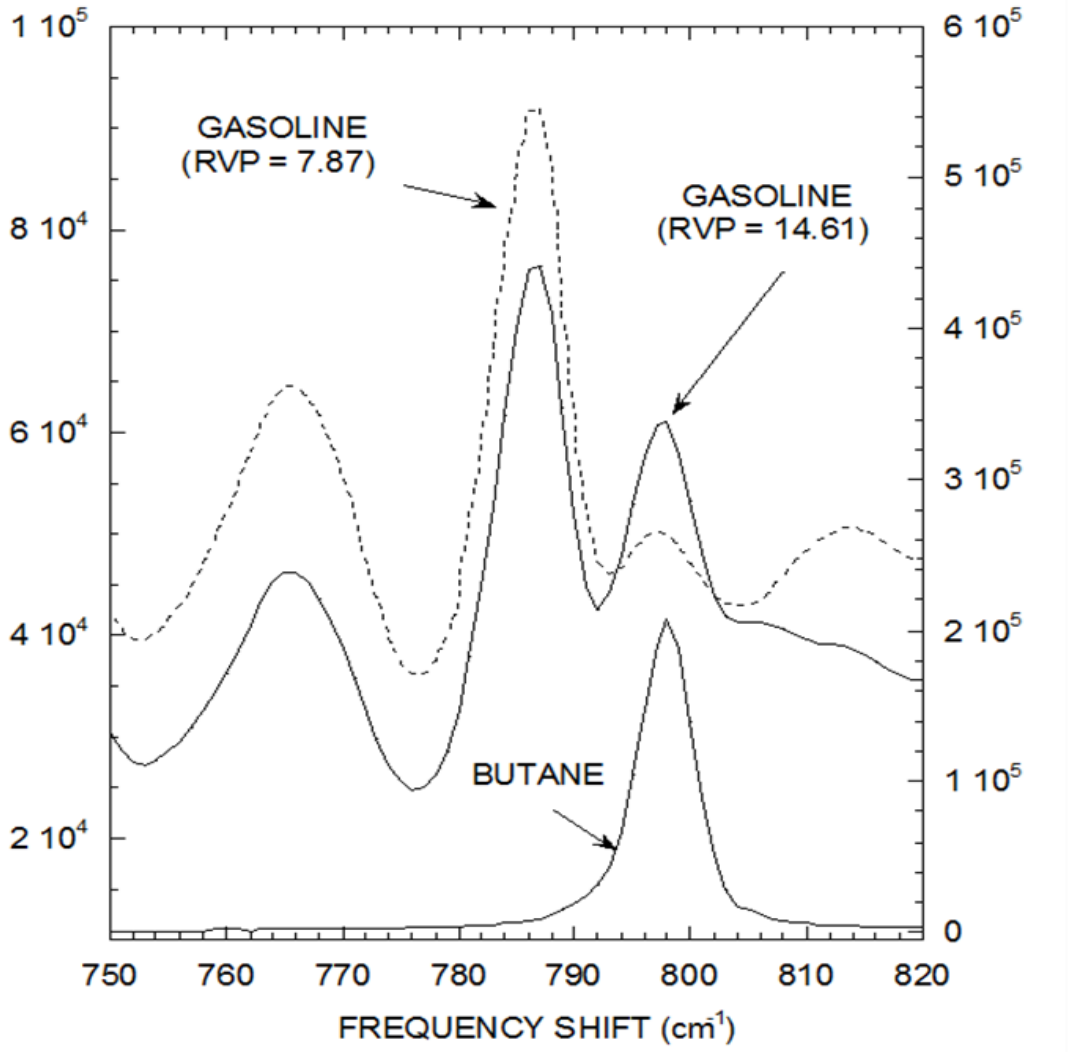
Typical On-Line Raman Setup



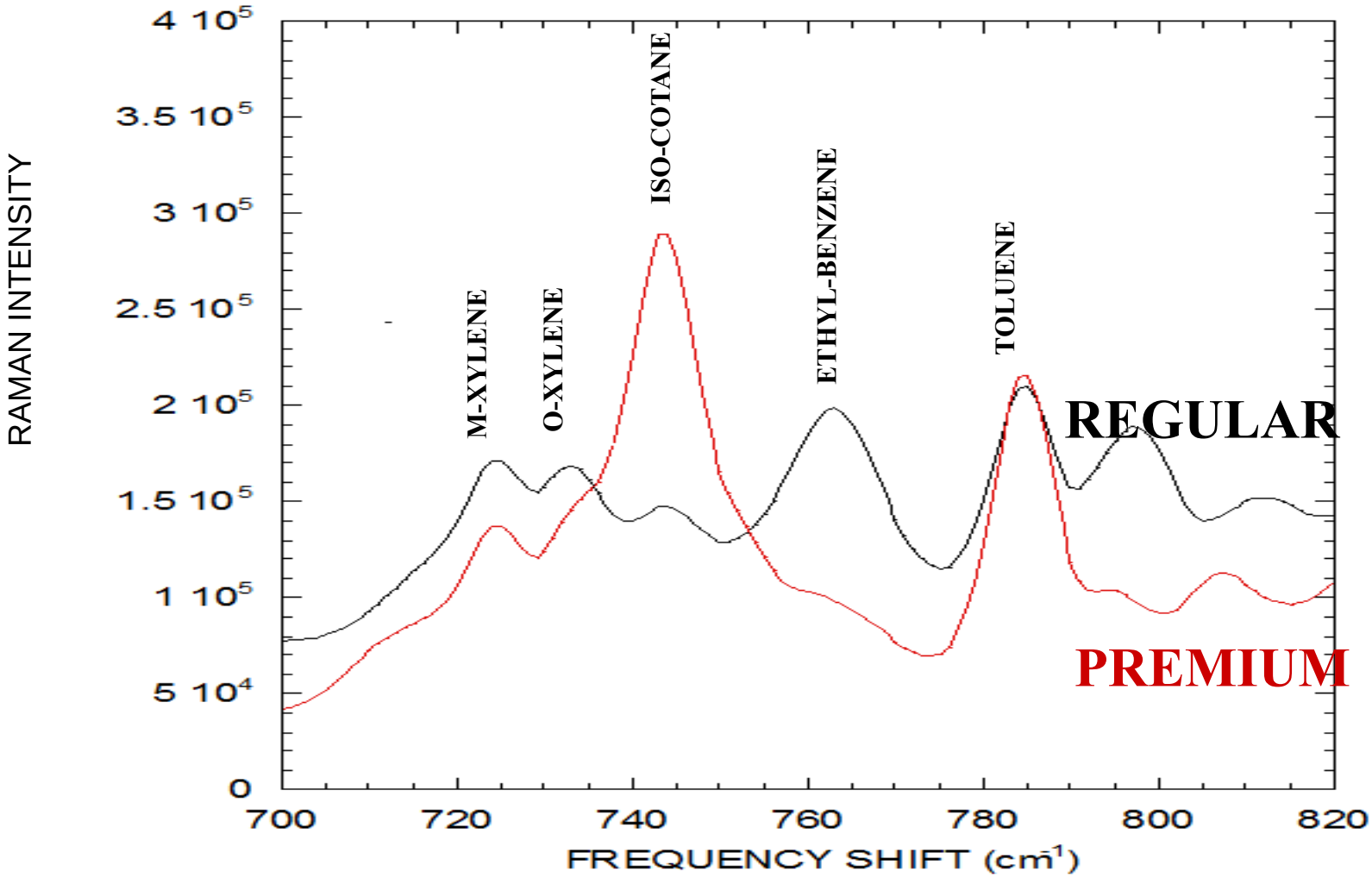
Raman Gasoline Spectrum



RVP Determination Via Raman



Octane Determination Via Raman



Raman Models With Few Samples

PARAMETER	RANGE	r^2	SECV	SAMPLES
RON	87 - 98	0.998	0.175	42
MON	80 - 88.2	0.995	0.174	42
ROAD	83.9 - 92.95	0.998	0.14	42
RVP	6.38 - 9.88	0.997	0.06	45
IBP	85 – 99	0.87	1.36	44
10%	117 – 151	0.99	1.04	44
50%	195 - 235	0.95	1.58	44
90%	304 - 357	0.96	1.27	42
FBP	397 - 429	0.93	2.03	42
E200	29.9 - 48.4	0.991	0.472	46
E300	66.3 - 90.5	0.99	0.448	46
API	54.7 - 64.3	0.996	0.134	44
BENZENE	0.22 - 1.41	0.9991	0.008	45
AROMATICS	15.1 - 36.4	0.99	0.56	46
T(V/L)	128 - 161	0.98	1.36	47
DRIVEABILITY	1032 - 1254	0.98	7.16	47
SULFUR ppm	3 - 22	0.73	2.1	47
OLEFINS	5.2 - 21.9	0.91	1.31	45
TOLUENE	1.52 - 17.44	0.999	0.127	48

Analyzer Precision Over 3 Months

PARAMETER	MEAN	STANDARD DEV.
RVP	9.23	0.019
RON	92.51	0.029
MON	82.51	0.015
ROAD	87.49	0.025
T (V/L)	138.38	0.17
IBP	96.24	0.097
T 10%	126.75	0.22
T 50%	206.71	0.27
T 90%	326.15	0.18
FBP	405.80	0.32
E200	46.48	0.10
E300	81.52	0.073
API	55.96	0.048
BENZENE	2.23	0.0042
AROMATIC	35.32	0.026
OLEFIN	7.63	0.080
DRIVEABILITY	1137	1.22

Raman's Insensitivity To Process Temperatures

Chemometric Model Predictions

	Temp = 0 C	Temp = 22 C	Temp = 48 C
RON	93.78	93.72	93.68
MON	82.99	83.04	82.97
ROAD	88.31	88.26	88.21
RVP	8.17	8.14	8.13
IBP	98.23	99.26	100.30
10%	125.16	124.12	123.57
50%	208.33	207.19	207.08
90%	315.76	316.37	316.52
FBP	397.08	396.36	396.49
DRIV	1131.3	1121.1	1109.5
E200	48.74	49.04	50.01
E300	84.84	85.12	85.67
DENS	0.751	0.750	0.747
BENZ	1.93	1.90	1.87
AROM	28.86	28.25	27.91
TVL	131.60	128.82	129.53
OLEF	10.03	10.03	9.98

Gasoline Is Not Beer…So Do Not Pour It Like Beer.

Grab Sample Collection Techniques To Preserve Octane and RVP

Collect Under Pressure in Sample bomb

If Using Glass Bottle, Use Amber Glass and Chill Bottle First

Ideally Chill Grab Sample

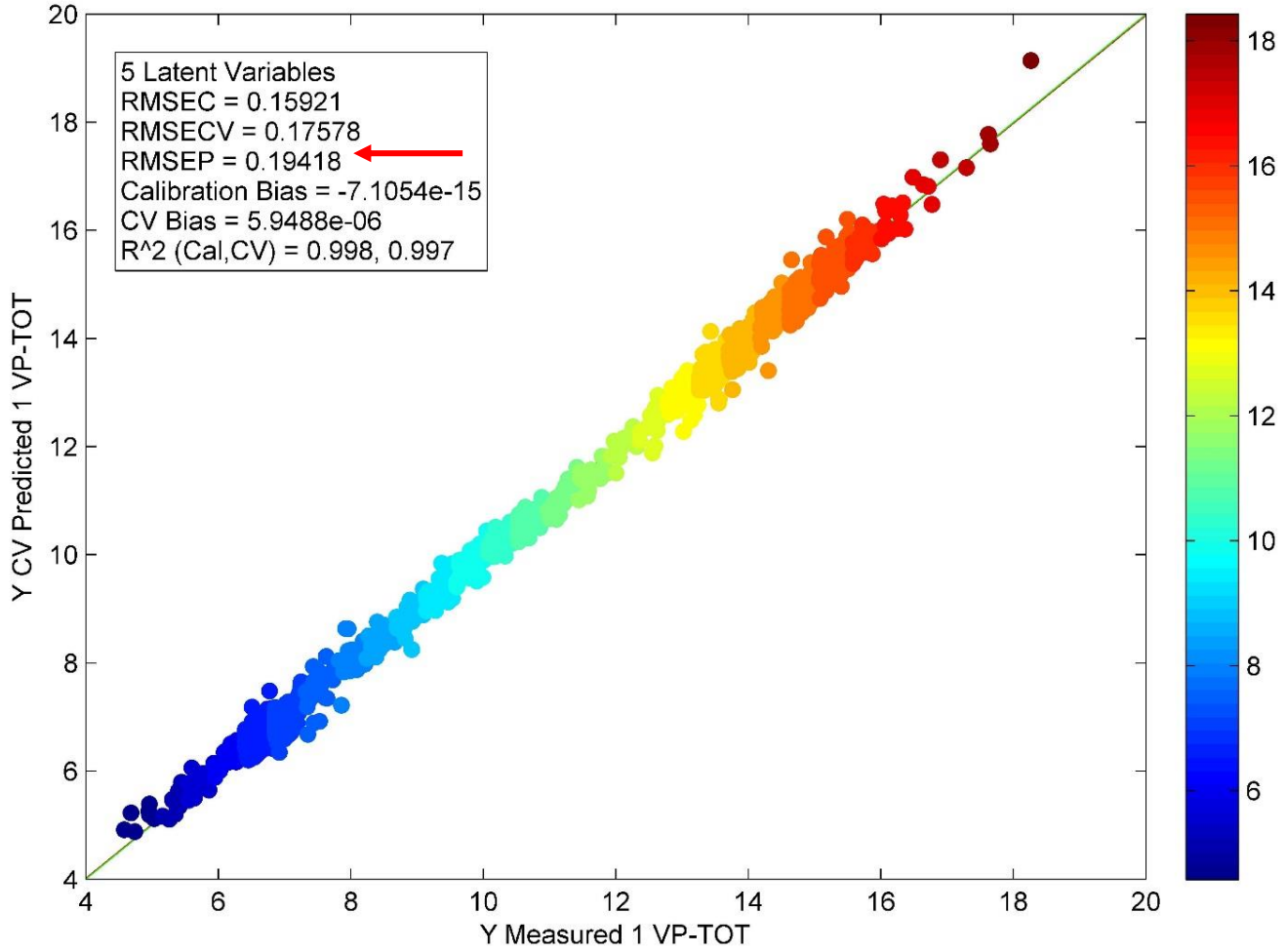
Fill Bottle From Bottom Up

Tightly Seal Bottle

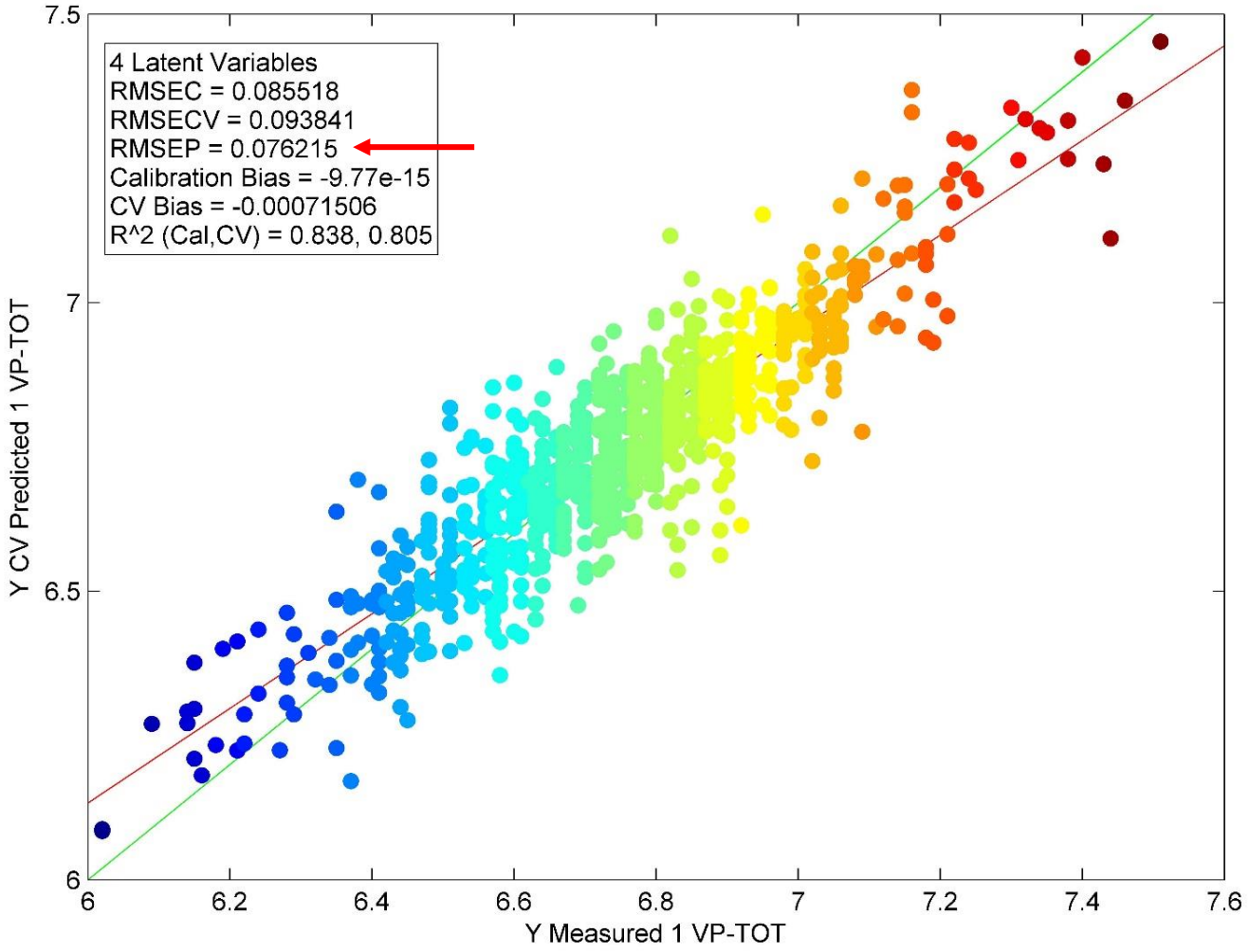
Modeling Best Practices

- **Background correction, area normalization of all spectra, and mean centering**
- **Venetian blind cross-validation**
- **Generalized least squares weighting (GLSW Filtering)**
- **Outliers selected from leverage vs. studentized residuals**
- **Conservative choice of latent variables determined from standard error of cross-validation (SECV) plot**
- **Validation with an independent set of data**

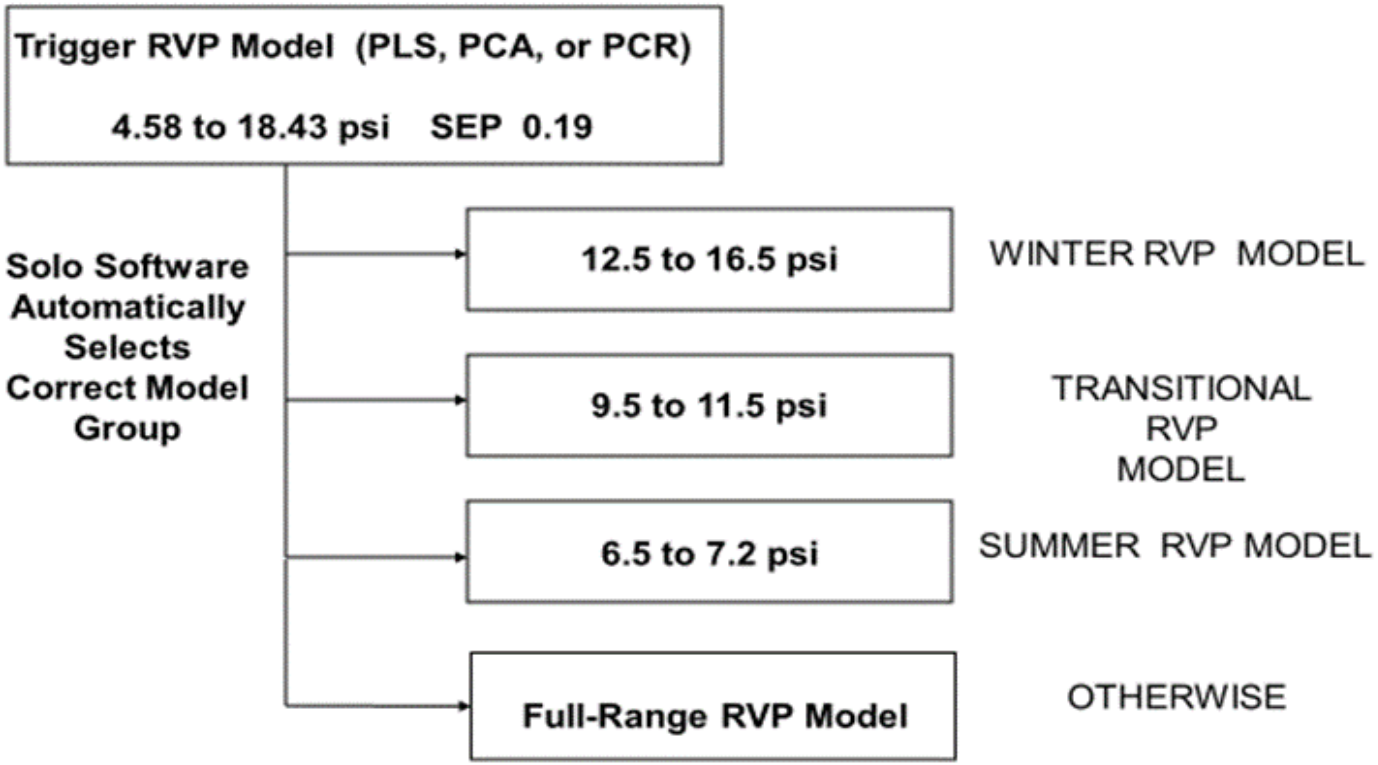
RVP: Full Range
Measured vs Predicted



RVP: Low Range
Predicted vs Measured



Hierarchical RVP Model Tree



One Year Case Study – U.S. West Coast, Refinery

- **Blend Property Control Optimization – Via Raman Refinery Capacity - 240,000 bpd**
  - **$6MM RVP giveaway savings 2014 - 2015.**
  - **Targeting 0.1 psi from spec**
  - **Consistently <0.1 Octane giveaway in summer grades**
  - **$3MM Octane giveaway savings**

Raman Refinery Applications

Monitor/Control Blender

- 24/7 Monitoring
- Reduce Octane and RVP Give-Away
- Eliminate Off-Spec Blends
- Reduce Reprocessing
- Reduce Tankage Requirements
- Reduce On-Line Equipment and Maintenance Needs

Monitor Component Streams

- Alky, Reformer, Hydrotreater, FCC, Ethanol
- Alkylation Acid, MSAT, LPG, Etc.

Monitor Diesel, Kerosene, Jet Fuel, Crude Units

- Customer Documented Payback Periods 1 to 3 Months