Development of a Process NMR Gasoline Analysis System

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Abstract

In recent years near-IR spectroscopy has gained a firm foothold as the on-line process analyzer of choice for gasoline analysis at blending terminals and refineries. We are presently investigating the applicability of ^{1}H process NMR instrumentation to the field of on-line gasoline analysis and have developed multivariate calibration models using partial least squares (PLS) analysis to correlate the NMR data with gasoline properties derived from other techniques. This presentation will demonstrate the accurate prediction of octane number (RON, MON, (R+M)/2) (obtained from ASTM method engine knock data), as well as the saturate, aromatic, olefin, and oxygenate content of a large number of gasolines from various regions of the country. The NMR data obtained from both a process FT-NMR system and a laboratory superconducting NMR system, will be compared along with the results obtained by a near-IR system on the same samples.

Background

The octane number (ON) represents a measure of the degree to which a gasoline is predisposed to cause engine knocking (pre-ignition of the gasoline in the combustion chamber). The higher the value of the ON the less apt the gasoline is to allow knocking. Higher ON gasolines allow use of high compression ratios and advanced ignition timing, resulting in greater power output, improved efficiency, and reduced fuel consumption.

Three different octane numbers are used:
Research Octane Number (RON) - Obtained by ASTM CFR engine test D2699
Typical Values 88-100, Standard error = 0.41
Motor Octane Number (MON) - Obtained by ASTM CFR engine test D2700
Typical Values 79-90, Standard error = 0.61
Road Octane (R+M)/2 - Obtained from average of RON and MON values
Typical Values 84-94, Standard error = 0.36

Octane increasing functionality includes:
aromatics, branched paraffins, olefins(?), oxygenates.

With recent EPA/CARB sanctioned fuel reformulations other properties that need to be analyzed are aromatics/benzene/saturates/olefins/oxygenates/vapor pressure.

Economic Impact of Octane Control

Refinery Gasoline Blend Header Control

Refineries (which can produce up to 4 million gallons of gasoline a day) strive to produce gasoline with a specific target octane which will meet the demands of the motoring public while using a minimum volume of the more expensive high octane blending stocks (such as reformate and alkylate). Optimization of the blending process to within a few tenths of the target octane translates into millions of dollars of octane not being "given away" during the course of a year. At the present time the on-line analyzer of choice is a near-IR instrument which utilizes multiplexing of the near-IR source through a number of fiber-optic cables. Systems costing $650K can effectively control 19 blending streams. However, sample conditioning is required in some situations, and long periods of on-line calibration are a prerequisite.

"At-the Pump" Quality Monitoring Programs

With the introduction of reformulated fuel regulations refiners and fuel marketers must have their products meet multiple physical and property targets or face the possibility of paying hefty fines With this in mind many quality monitoring programs have been developed. At Texaco, for instance FT-IR (both near and mid) are utilized in a mobile testing van program which tests the gasolines at the service station, and in a blending terminal program where gasoline is blended with additive packages before distribution to the service stations.

Present Gasoline Analysis Systems

ASTM CFR Engine Tests

ASTM D2699 - Measures RON, Standard Error = 0.41 ON
ASTM D2700 - Measures MON, Standard Error = 0.61 ON

Aside from the large standard error other problems that are associated with the ASTM tests are that it is not a continuous (on-line) method, it requires a large sample volume (400 ml), there is an obvious spark hazard, substantial maintenance, and an expert operator is required.

Near/Mid-IR Spectrometers

The spectra obtained on a training set of samples are analyzed by partial least squares (PLS) analysis and calibrated against numbers obtained from primary calibration techniques. For octane the primary calibration is the ASTM CFR engine test, for oxygenates it is GC-OFID, for saturates and olefins it is the GS-500 IR analyzer, and for aromatics it is GC-MS.

Typical results obtained on 54 gasolines from Phoenix and Portland (which form the basis of the ^{1}H NMR investigation are:

From Near-IR
RON Std Error = 0.33 $R^2 = 0.985$
MON Std Error = 0.26 $R^2 = 0.977$
(R+M)/2 Std Error = 0.26 $R^2 = 0.985$

From Mid-IR
Aromatics Std Error = 0.77 $R^2 = 0.982$
Saturates Std Error = 0.82 $R^2 = 0.985$
Olefins Std Error = 0.50 $R^2 = 0.976$
MTBE Std Error = 0.33 $R^2 = 0.996$

^{1}H NMR Study

Samples

54 regular, super, and premium unleaded gasoline samples samples from Phoenix & Portland

Primary Calibrations: RON, MON, R+M/2 - ASTM D2699/D2700
MTBE (wt%) - GC-OFID
Aromatics, saturates, and olefins - GS-500 hand-held IR analyzer.

NMR Experiments

^{1}H NMR experiments performed on two instruments for comparison:

Varian UnityPlus-300 Spectrometer
(π/6 pulse, 4 s acquisition, 32 transients)

Elbit-ATI, Series 2000, 54.7 MHz FT-NMR Spectrometer
(π/6 pulse, 12 s acquisition, 16 transients, external ^{7}Li lock)

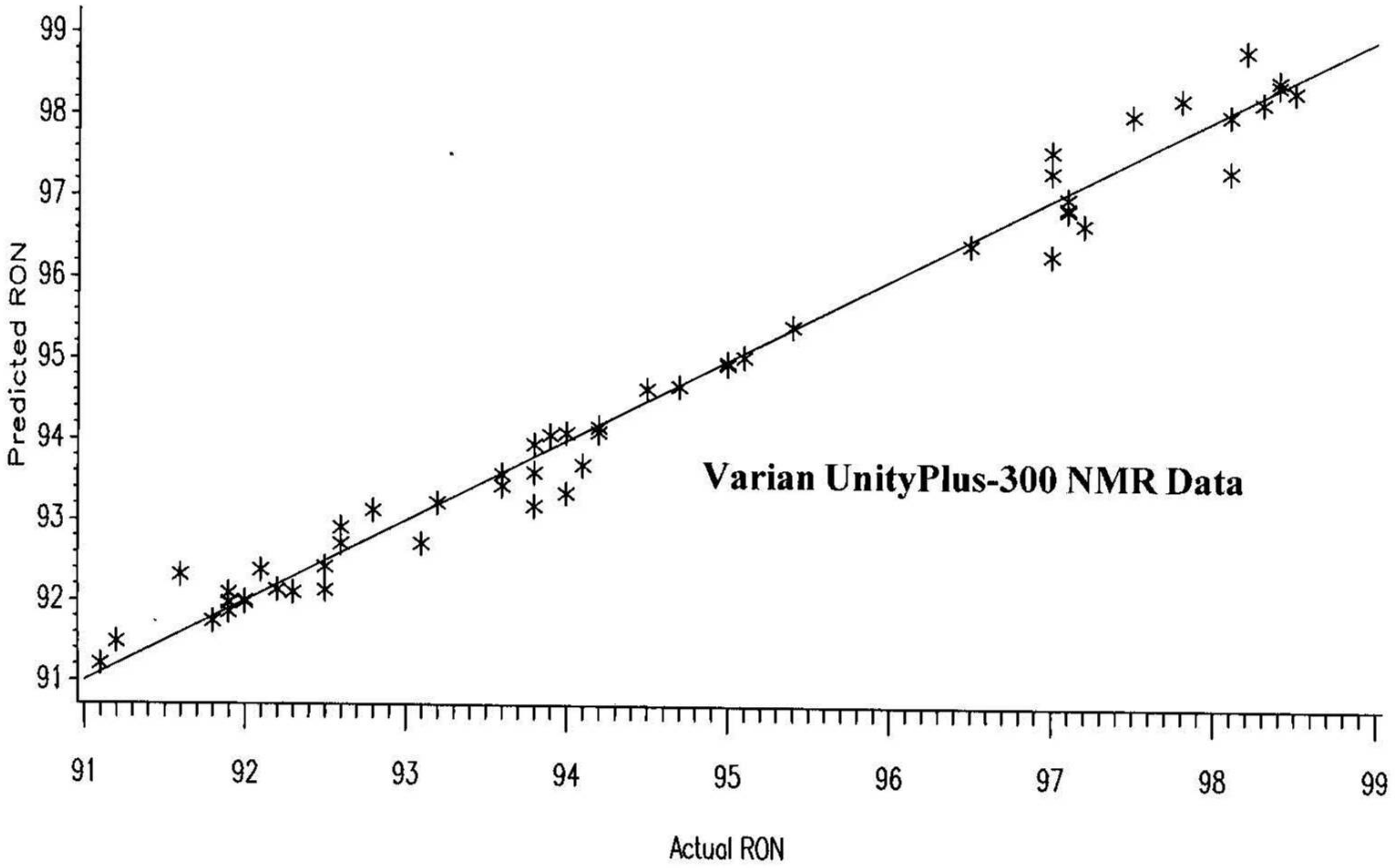
Calibration Method

For each of the 54 ^{1}H NMR spectra, 100 normalized integral values were analyzed by PLS for correlation with RON, MON, (R+M)/2, MTBE, aromatics, saturates, and olefins.

RON – D2699/D2700

Predicted vs. Actual – PLS w/ 14 factors (using centered NMR spectra)

N=54 samples, SEP=0.31, Avg. error=0.22, Max. error=0.73, Bias=–0.005, R–sq=98.2

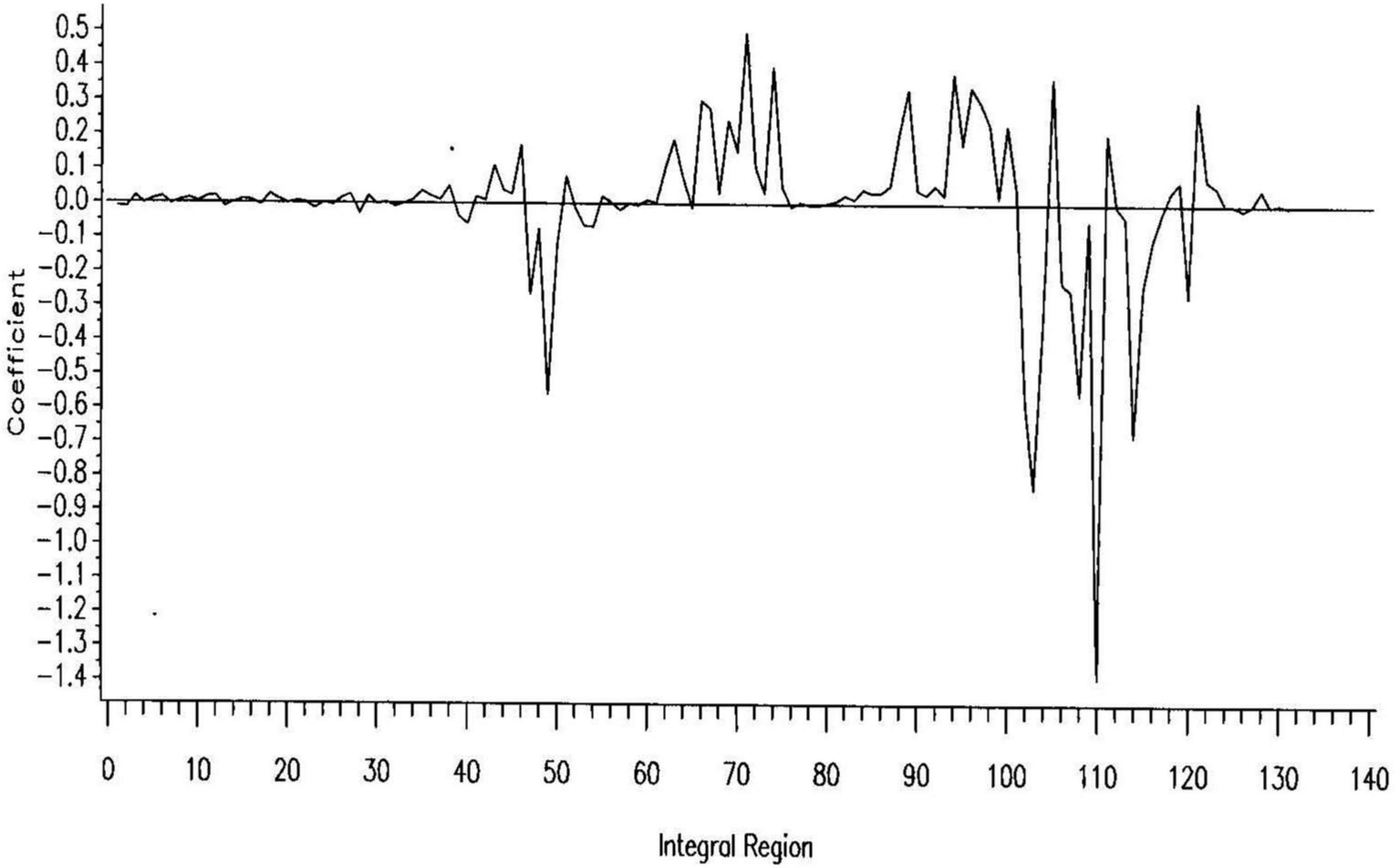


Varian UnityPlus-300 NMR Data

RON – D2699/D2700

Coefficients for NMR spectra – PLS w/ 14 factors (using centered NMR spectra)

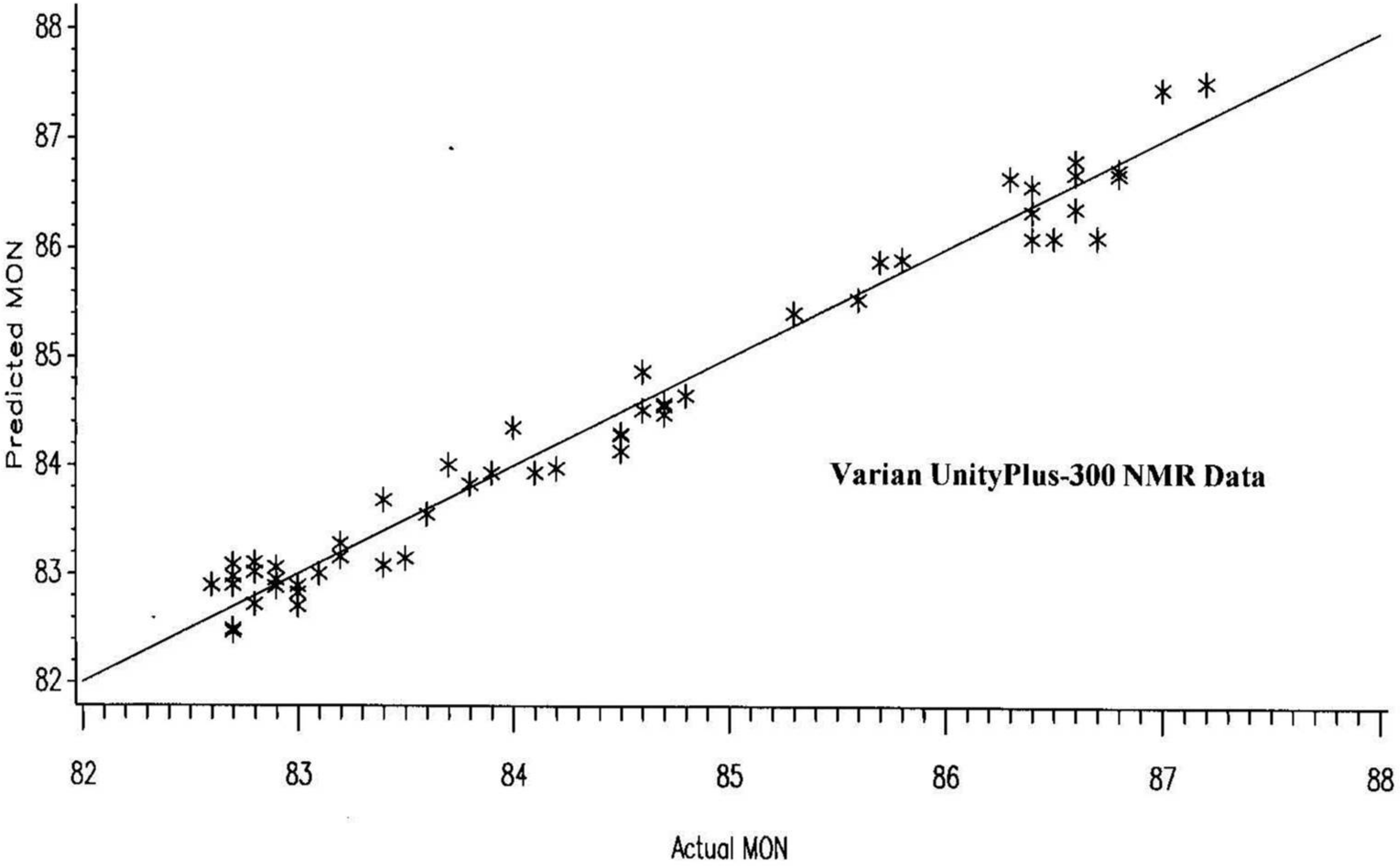
N=54 samples, SEP=0.31, Avg. error=0.22, Max. error=0.73, Bias=−0.005, R−sq=98.2



MON – D2699/D2700

Predicted vs. Actual – PLS w/ 10 factors (using centered NMR spectra)

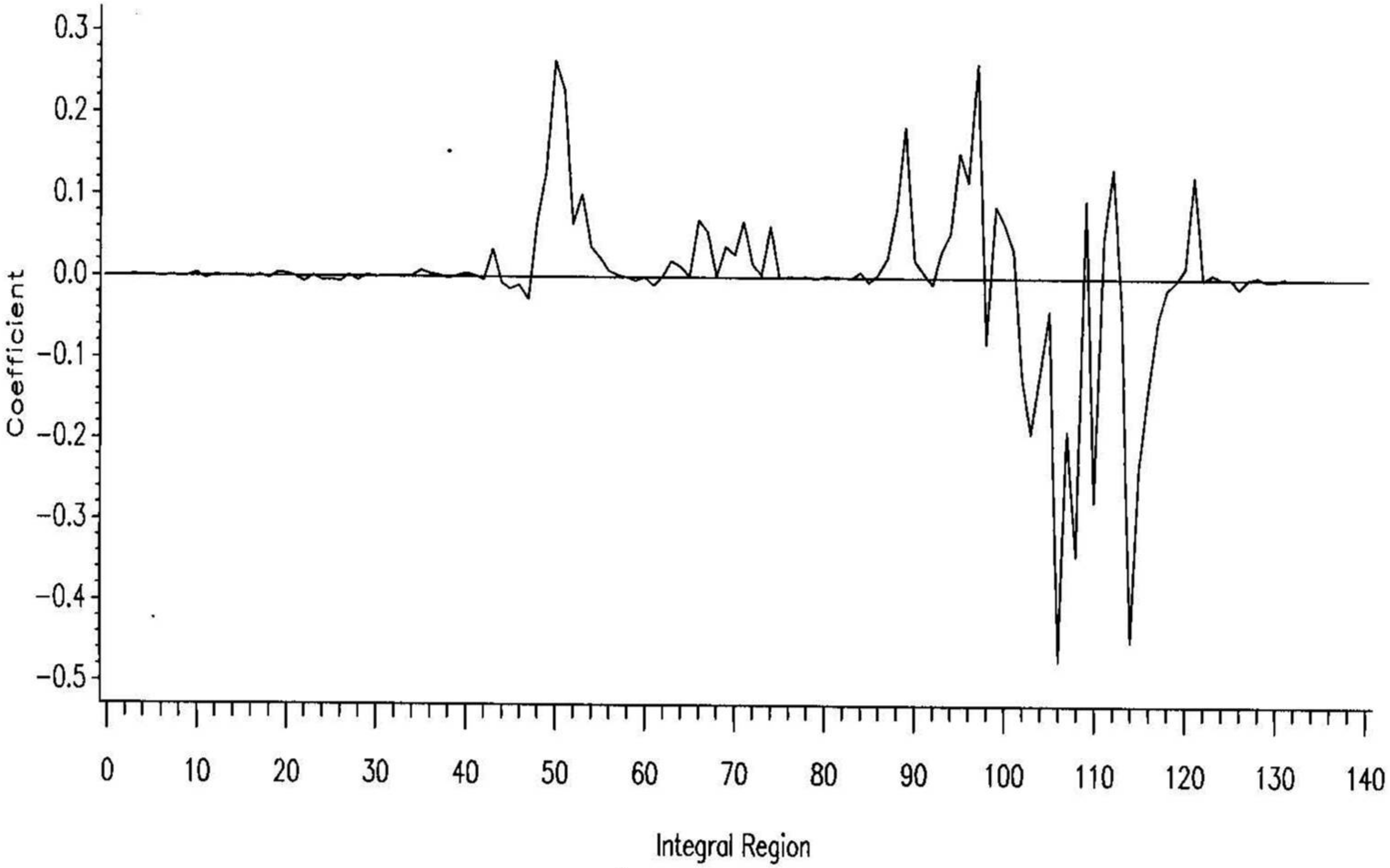
N=54 samples, SEP=0.24, Avg. error=0.20, Max. error=0.59, Bias=–0.007, R–sq=97.5



MON – D2699/D2700

Coefficients for NMR spectra – PLS w/ 10 factors (using centered NMR spectra)

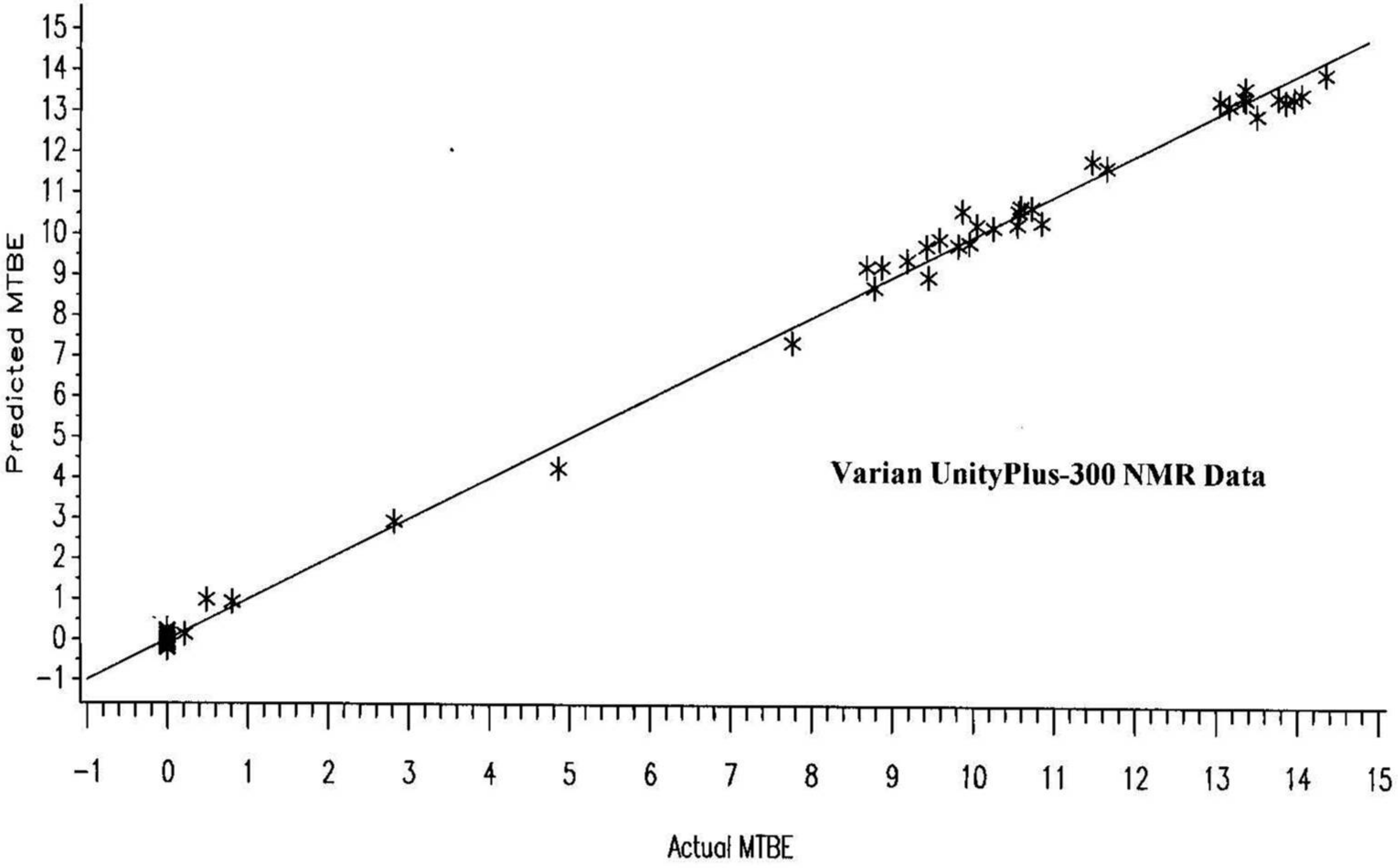
N=54 samples, SEP=0.24, Avg. error=0.20, Max. error=0.59, Bias=–0.007, R–sq=97.5



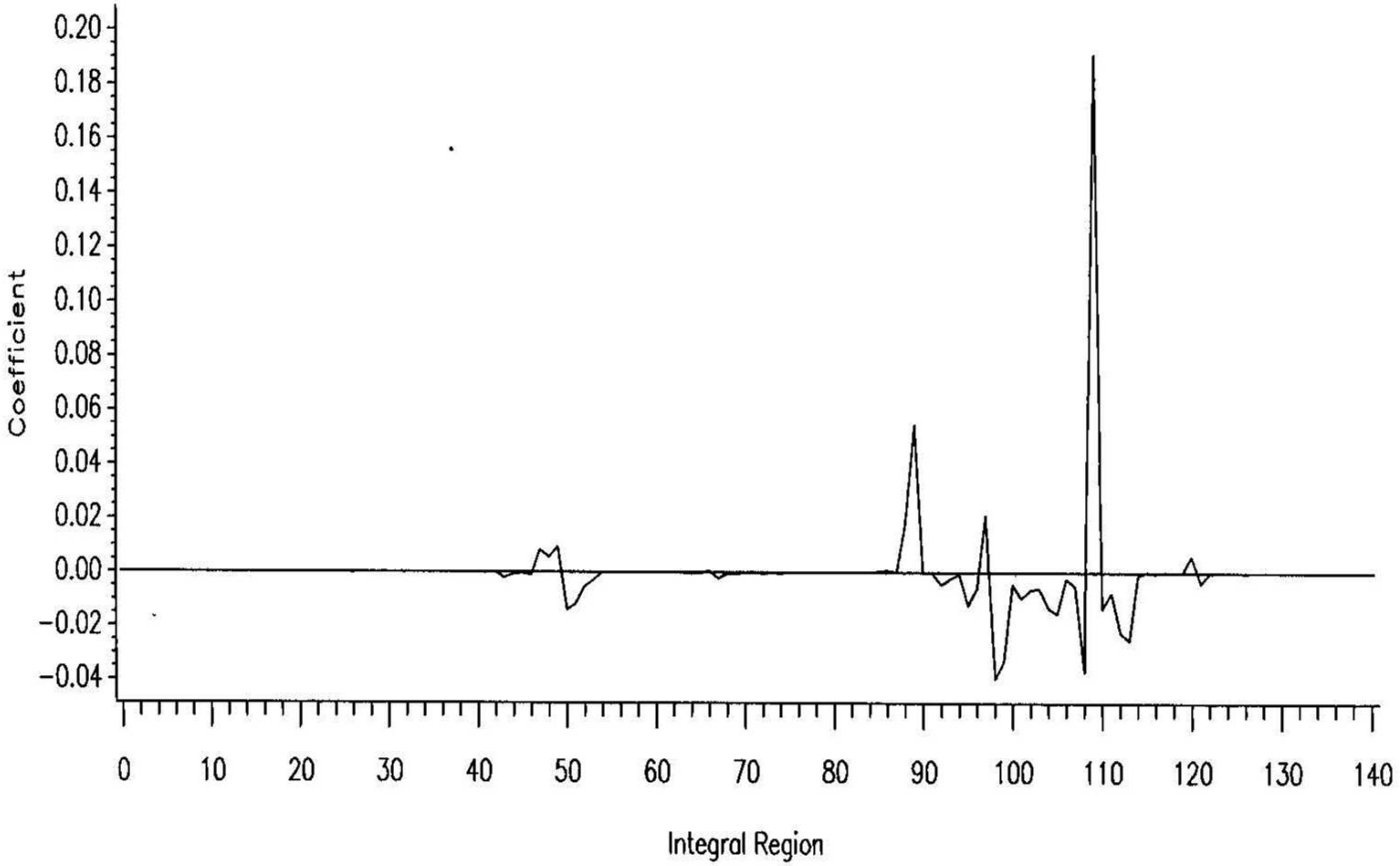
MTBE – GCOFID

Predicted vs. Actual – PLS w/ 4 factors (using centered NMR spectra)

N=54 samples, SEP=0.30, Avg. error=0.23, Max. error=0.79, Bias=+0.004, R-sq=99.7



Varian UnityPlus-300 NMR Data



MTBE – GCOFID

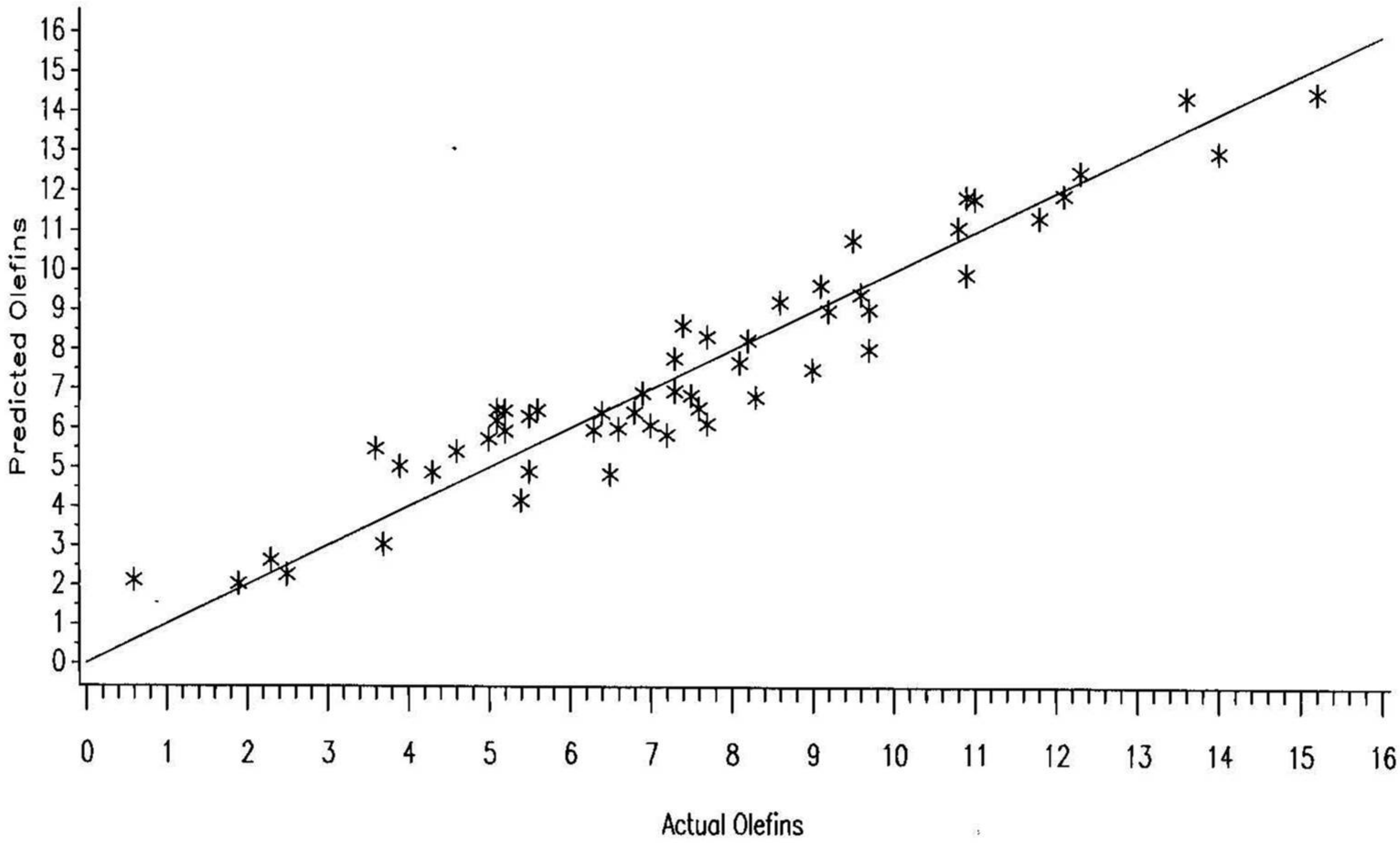
Coefficients for NMR spectra – PLS w/ 4 factors (using centered NMR spectra)

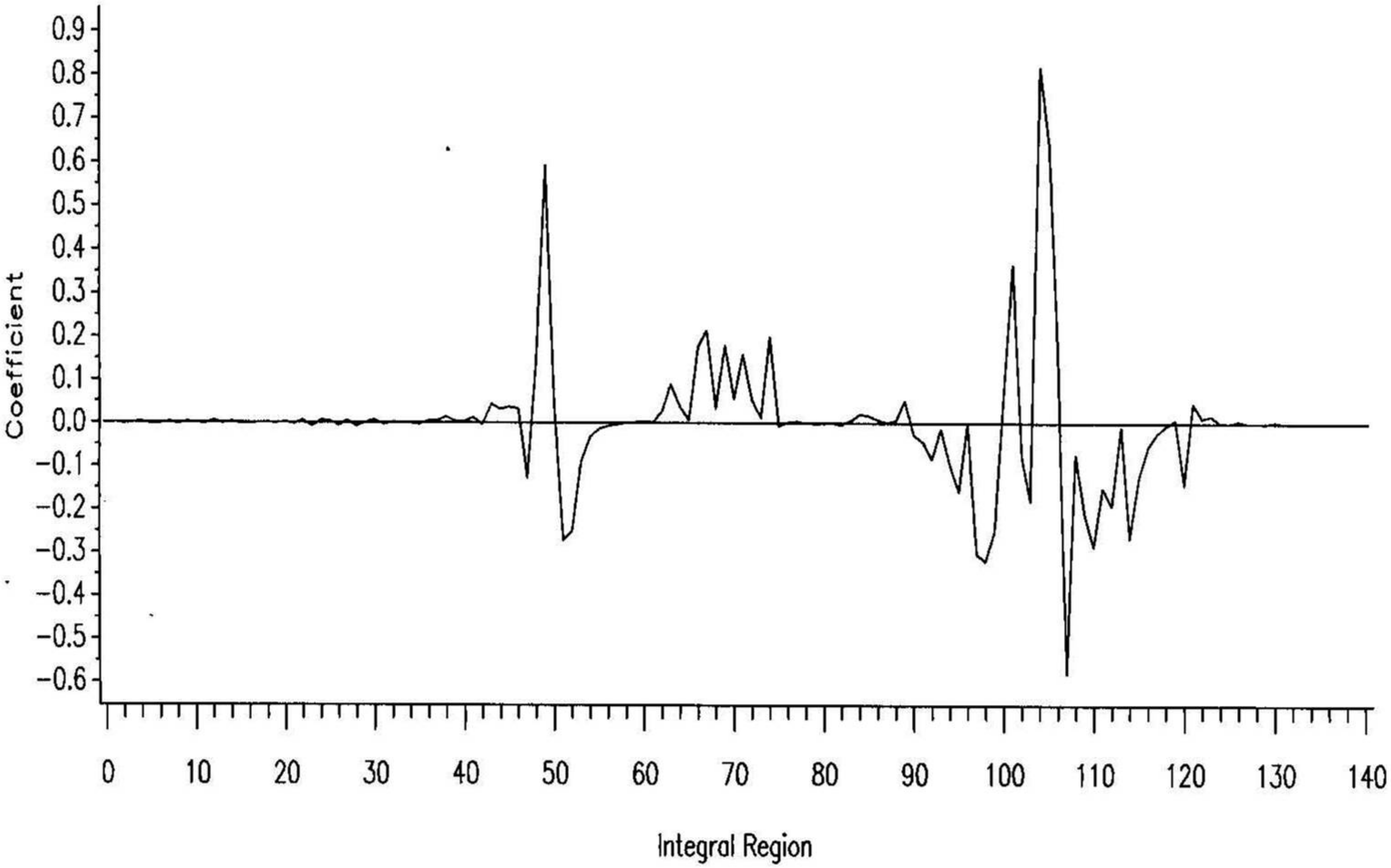
N=54 samples, SEP=0.30, Avg. error=0.23, Max. error=0.79, Bias=+0.004, R–sq=99.7

Olefins – GS-500

Predicted vs. Actual – PLS w/ 9 factors (using centered NMR spectra)

N=54 samples, SEP=0.92, Avg. error=0.78, Max. error=1.88, Bias=+0.006, R-sq=91.2





Olefins – GS-500

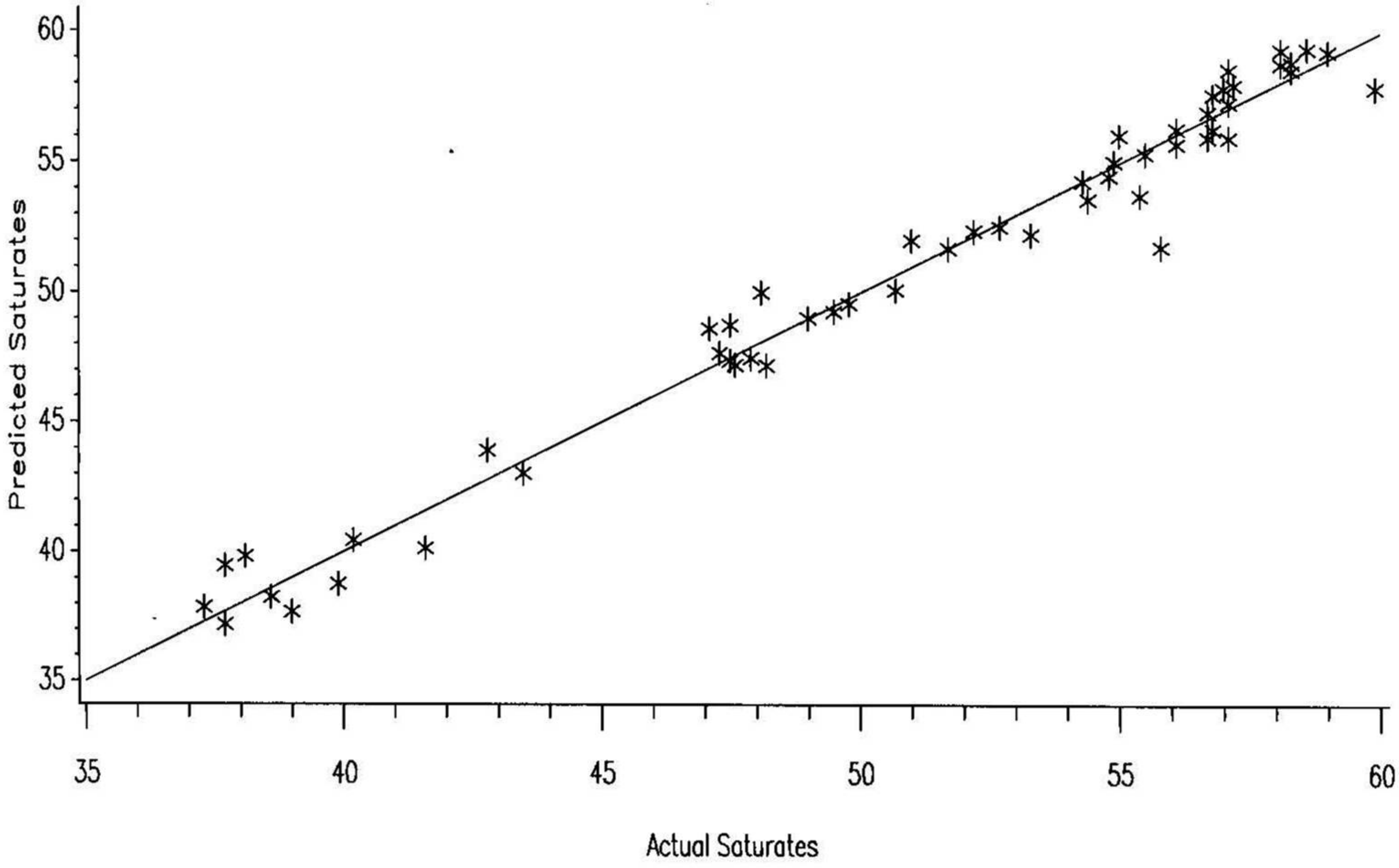
Coefficients for NMR spectra – PLS w/ 9 factors (using centered NMR spectra)

N=54 samples, SEP=0.92, Avg. error=0.78, Max. error=1.88, Bias=+0.006, R–sq=91.2

Saturates - GS-500

Predicted vs. Actual - PLS w/ 8 factors (using centered NMR spectra)

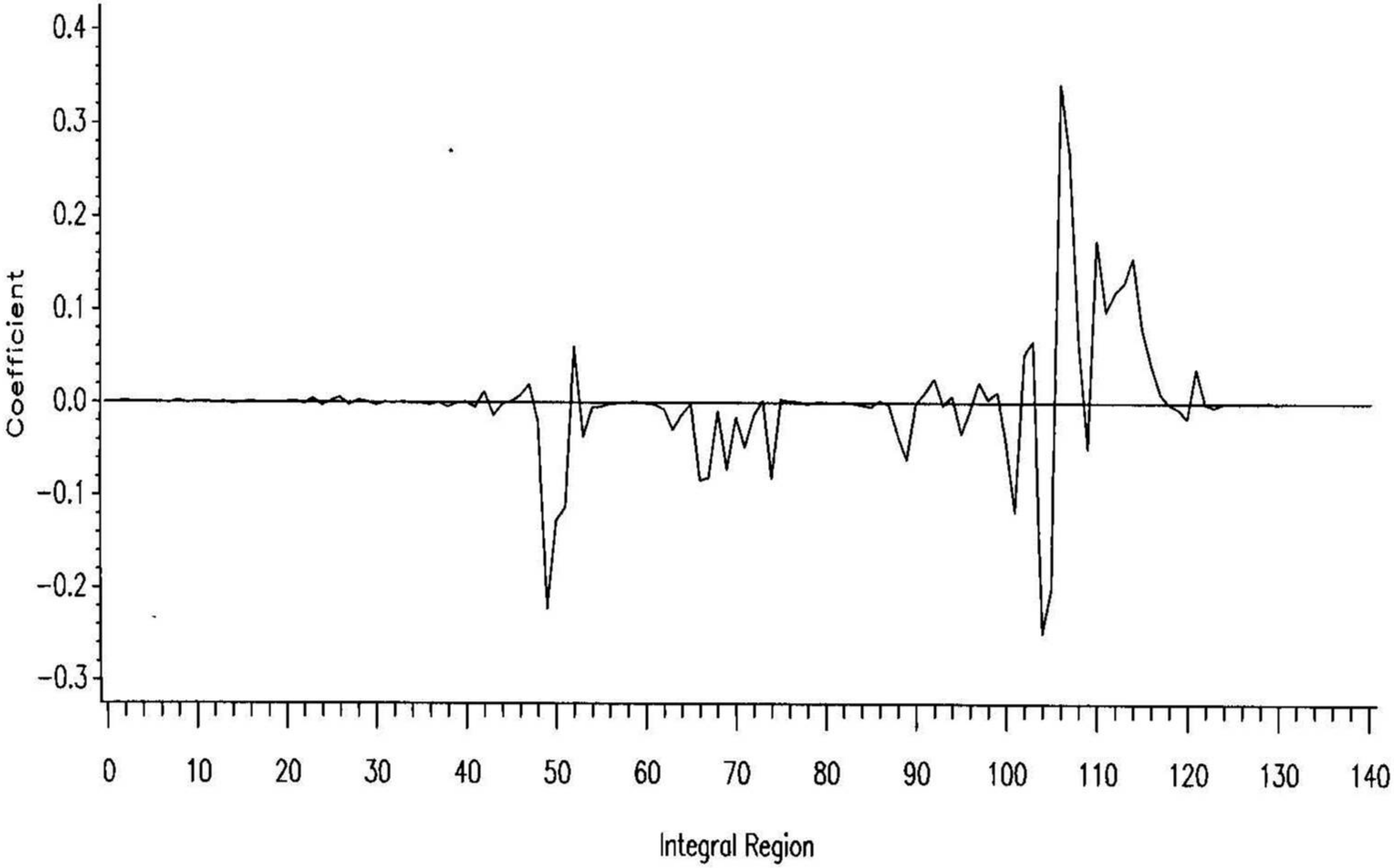
N=54 samples, SEP=1.05, Avg. error=0.79, Max. error=4.04, Bias=+0.004, R-sq=97.6



Saturates – GS-500

Coefficients for NMR spectra – PLS w/ 8 factors (using centered NMR spectra)

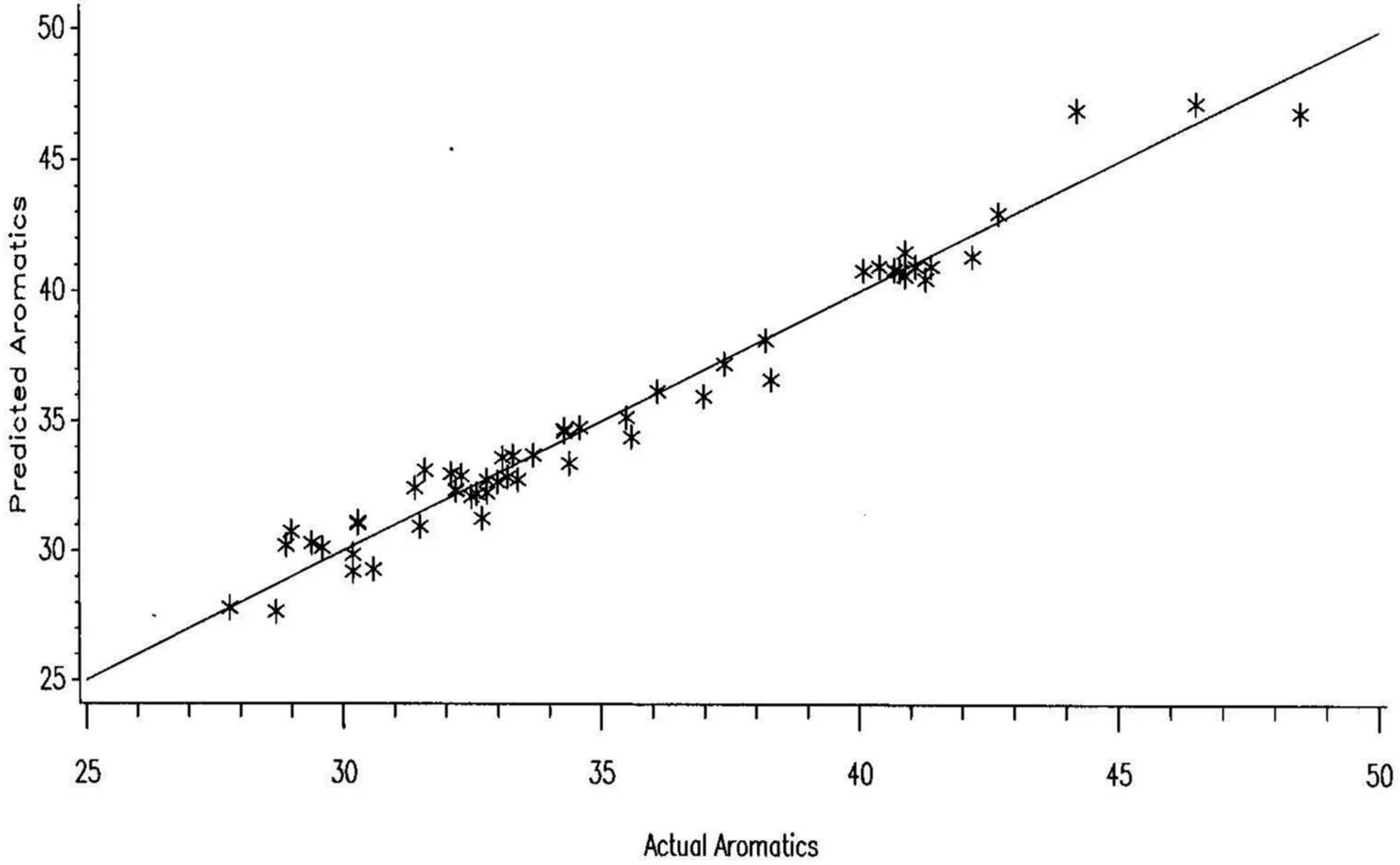
N=54 samples, SEP=1.05, Avg. error=0.79, Max. error=4.04, Bias=+0.004, R–sq=97.6



Aromatics – GS-500

Predicted vs. Actual – PLS w/ 8 factors (using centered NMR spectra)

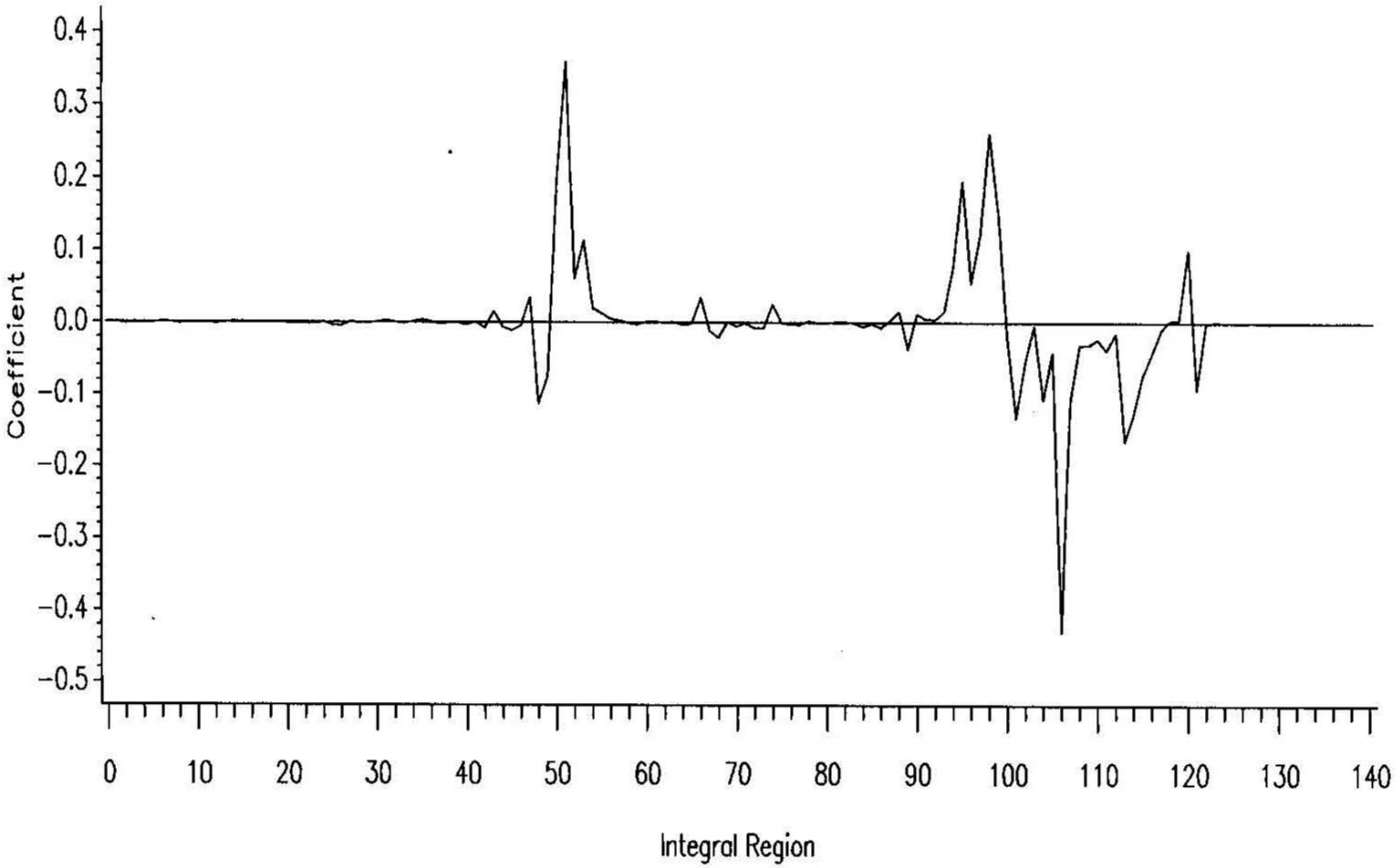
N=54 samples, SEP=0.86, Avg. error=0.67, Max. error=2.77, Bias=+0.007, R-sq=96.9



Aromatics – GS–500

Coefficients for NMR spectra – PLS w/ 8 factors (using centered NMR spectra)

N=54 samples, SEP=0.86, Avg. error=0.67, Max. error=2.77, Bias=+0.007, R–sq=96.9

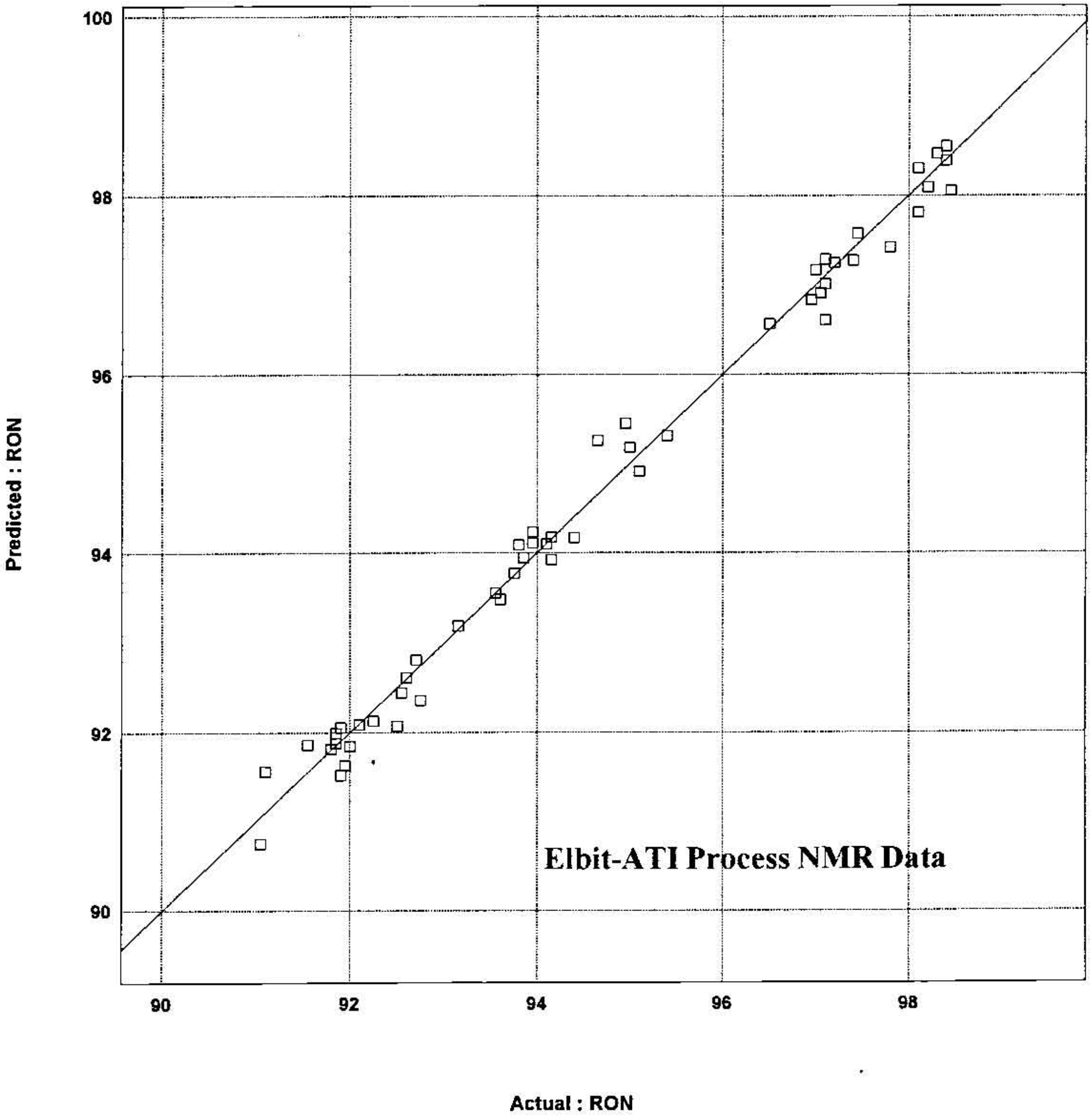


54 Phoenix/Portland Gasolines
Research Octane Number
Primary Calibration ASTM D2699

TE: 1.72875

R^2: .989836

RMSD: .239734



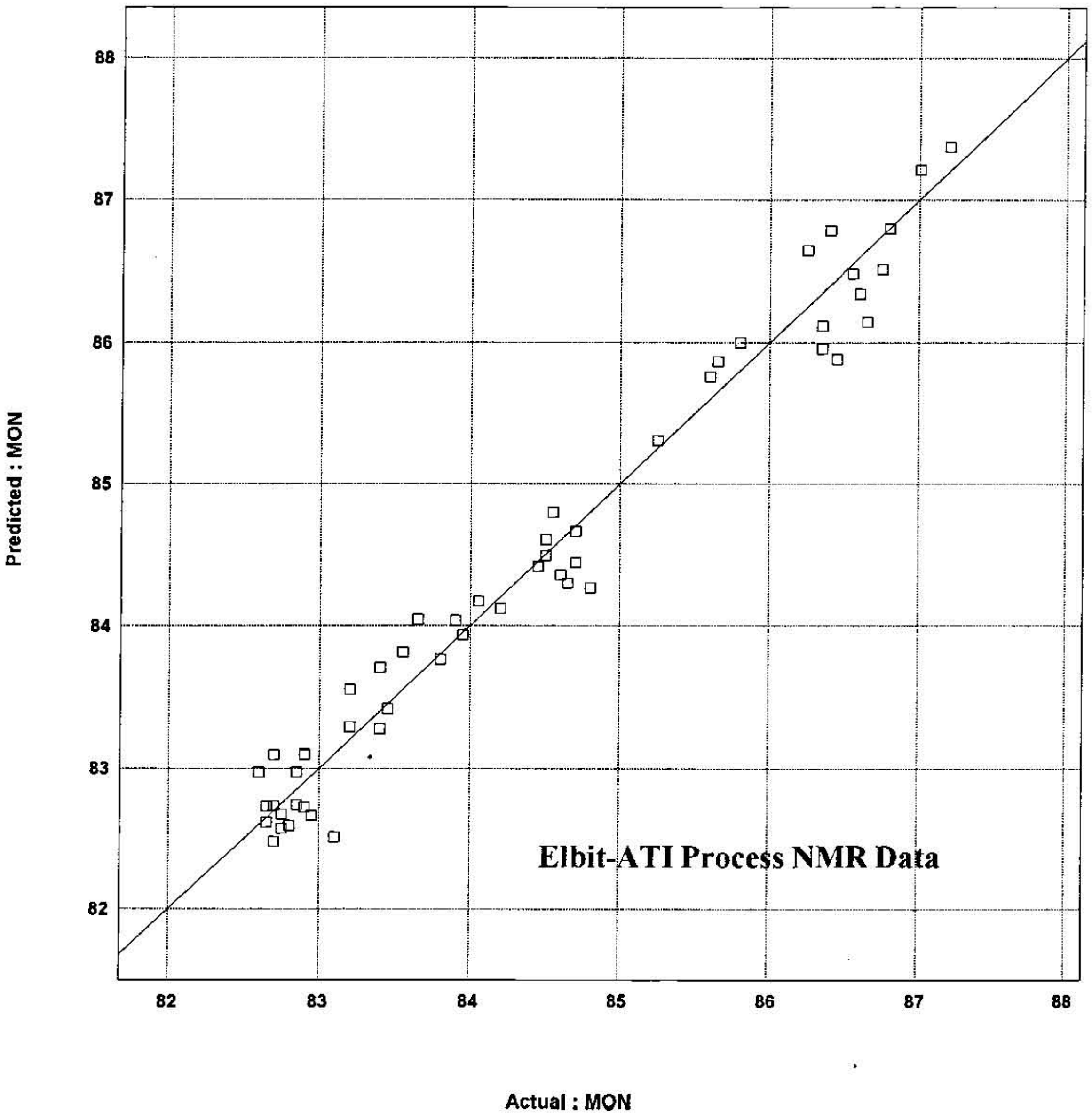
54 Phoenix/Portland Gasolines
Motor Octane Number
Primary Calibration ASTM D2700

TE: 1.87348

R²: .969622

RMSD: .257342

Process NMR Associates



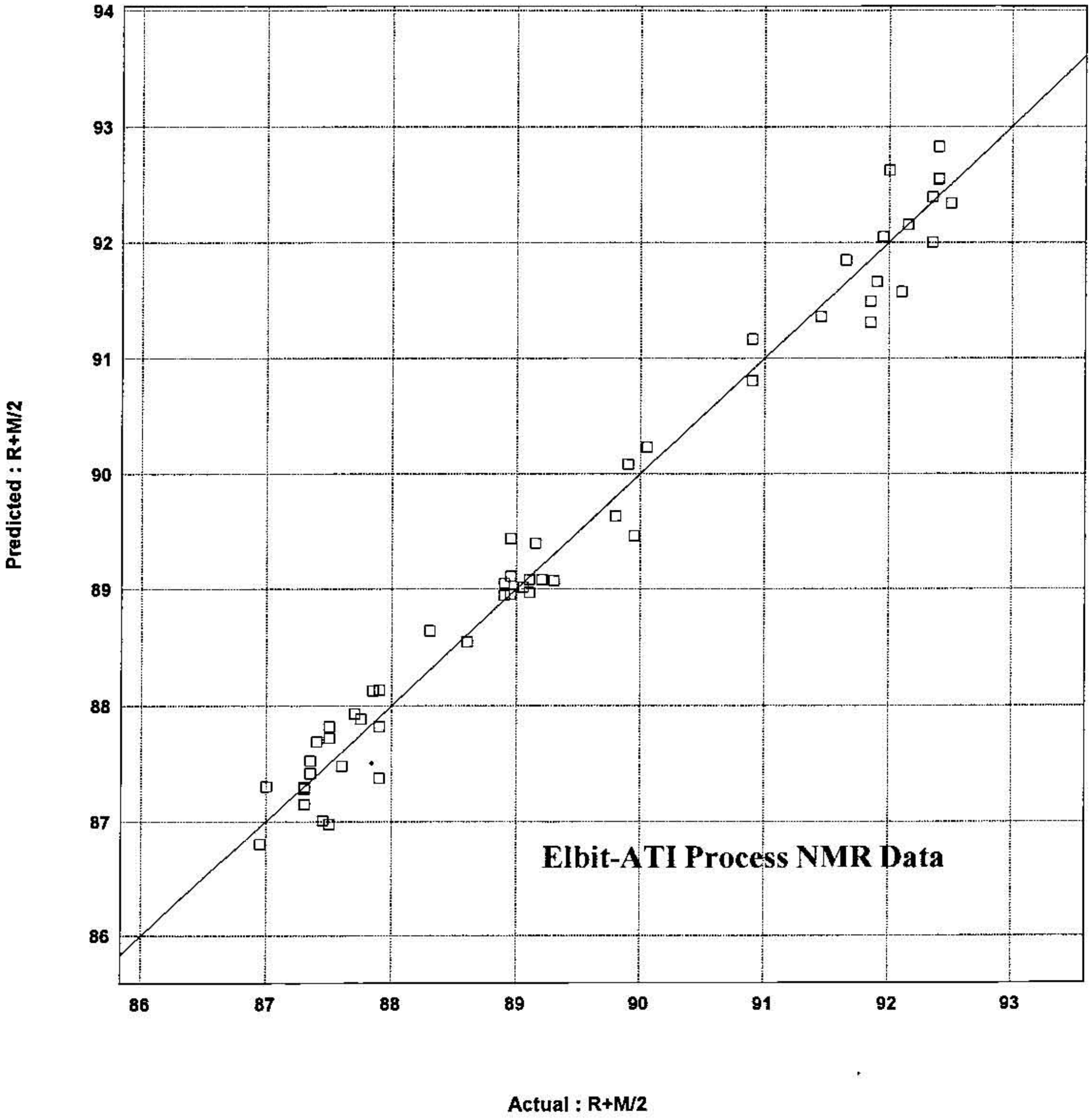
54 Phoenix/Portland Gasolines
Road Octane Number
Primary Calibration ASTM D2700/D2699

TE: 1.9793

R²: .979305

RMSD: .271878

Process NMR Associates

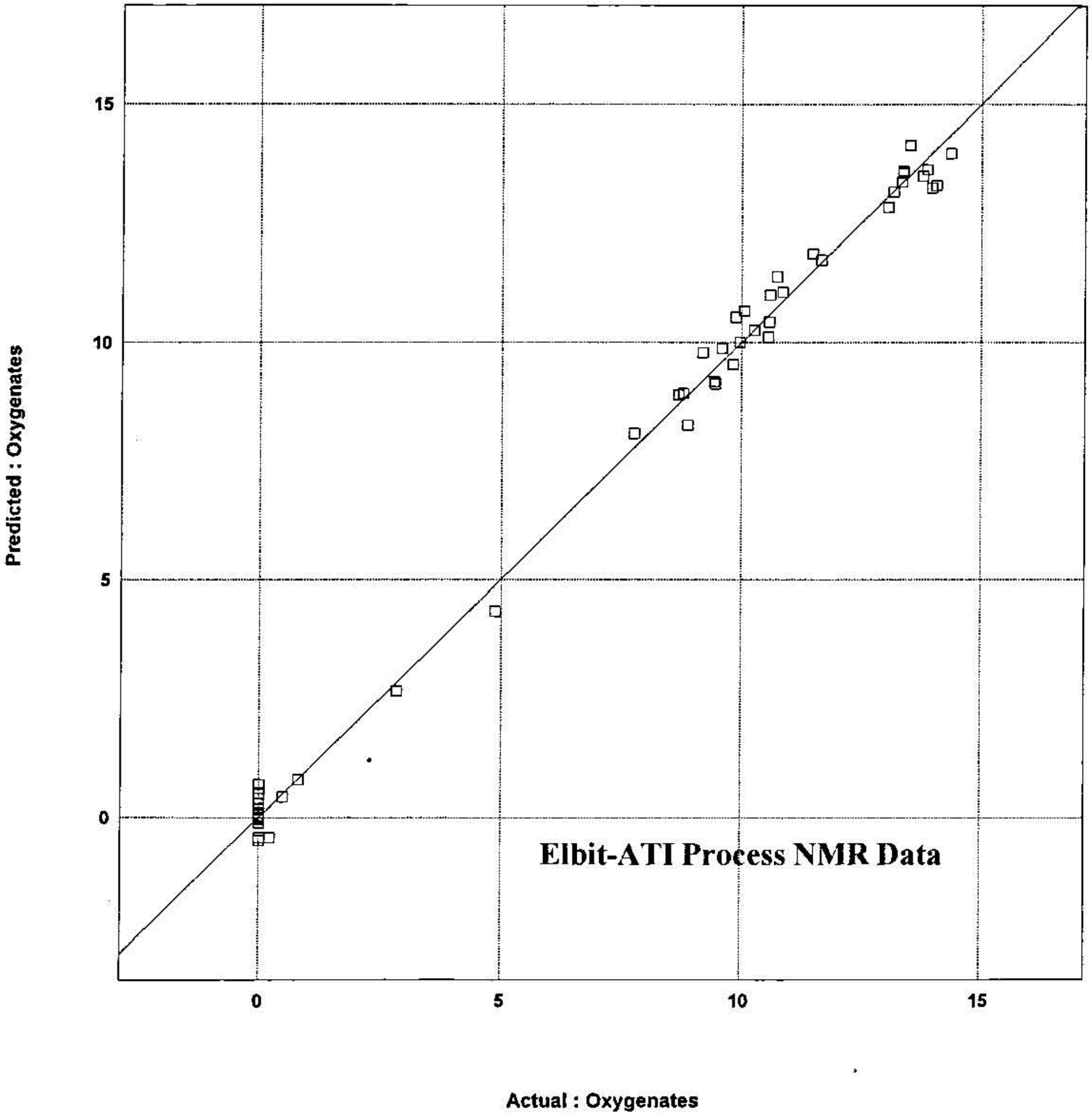


54 Phoenix/Portland Gasolines Oxygenate Content (Wt%) (GC-OFID)

TE: 2.71681

R²: .995534

RMSD: .373183



Process NMR Associates

171 Gasoline Samples From Arizona, Washington, Oregon, California, Oklahoma, Nevada, Alaska, and Hawaii.

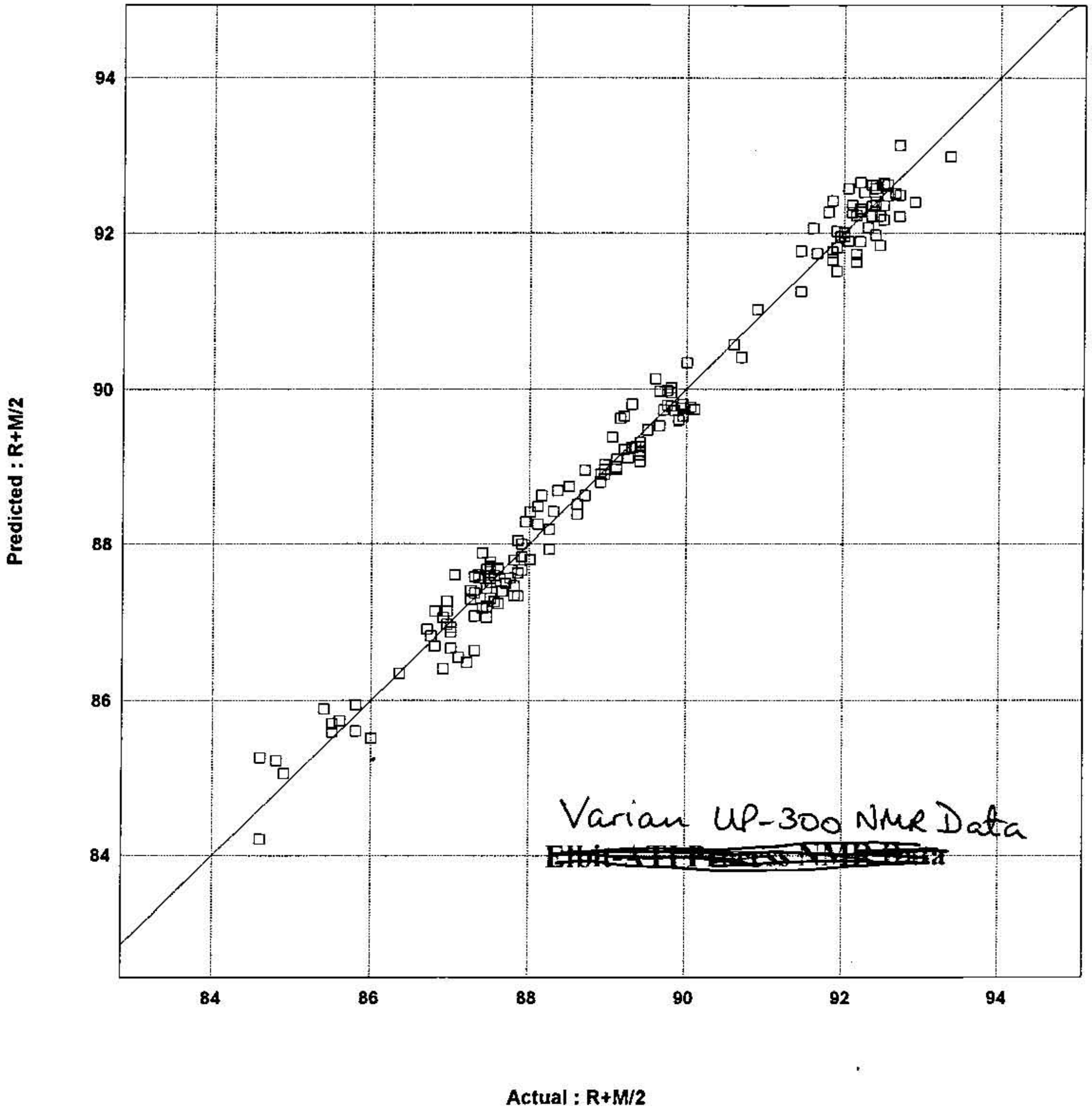
Road Octane Number

Primary Calibration ASTM D2700/D2699

TE: 3.68806

R^2: .983679

RMSD: .282033



Varian UP-300 NMR Data

~~Elbit-ATI Process NMR Data~~

Comparison of Data Obtained From Near/Mid-IR, High Field NMR, and Process NMR Calibrations

Method	RON	MON	R+M/2	MTBE	Aromatics	Saturates	Olefins
Mid/Near-IR	0.33	0.26	0.26	0.33	0.77	0.50	0.82
High Field NMR	0.31	0.24	0.16	0.30	0.86	0.90	1.05
Process NMR	0.24	0.26	0.27	0.37	1.14	0.93	1.53

Conclusions

In the field of gasoline property analysis low field ^{1}H FT-NMR spectrometers can compete favorably with near-IR process equipment, and can also yield results comparable to what can be obtained from high-field NMR instrumentation. The NMR methods have the advantage over near-IR methodologies in that inter-spectrometer calibration is not necessary, the models appear to be less sensitive to crude slate, no sample conditioning is necessary, and the equipment could conceivably be less expensive. Process NMR in combination with the appropriate data processing and chemometric analyses can be readily applied to many on-line analysis processes. The methods applied here can be readily applied to diesel fuel property analysis.