LT INDUSTRIES Inc.

Methanol in Crude Using Near-Infrared Analysis

EVCO Analytical Services

Intertek Caleb Brett

Prepared for the Crude Oil Quality Group by
Intertek Caleb Brett and EVCO Analytical Services
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Methanol in Crude Test Setup

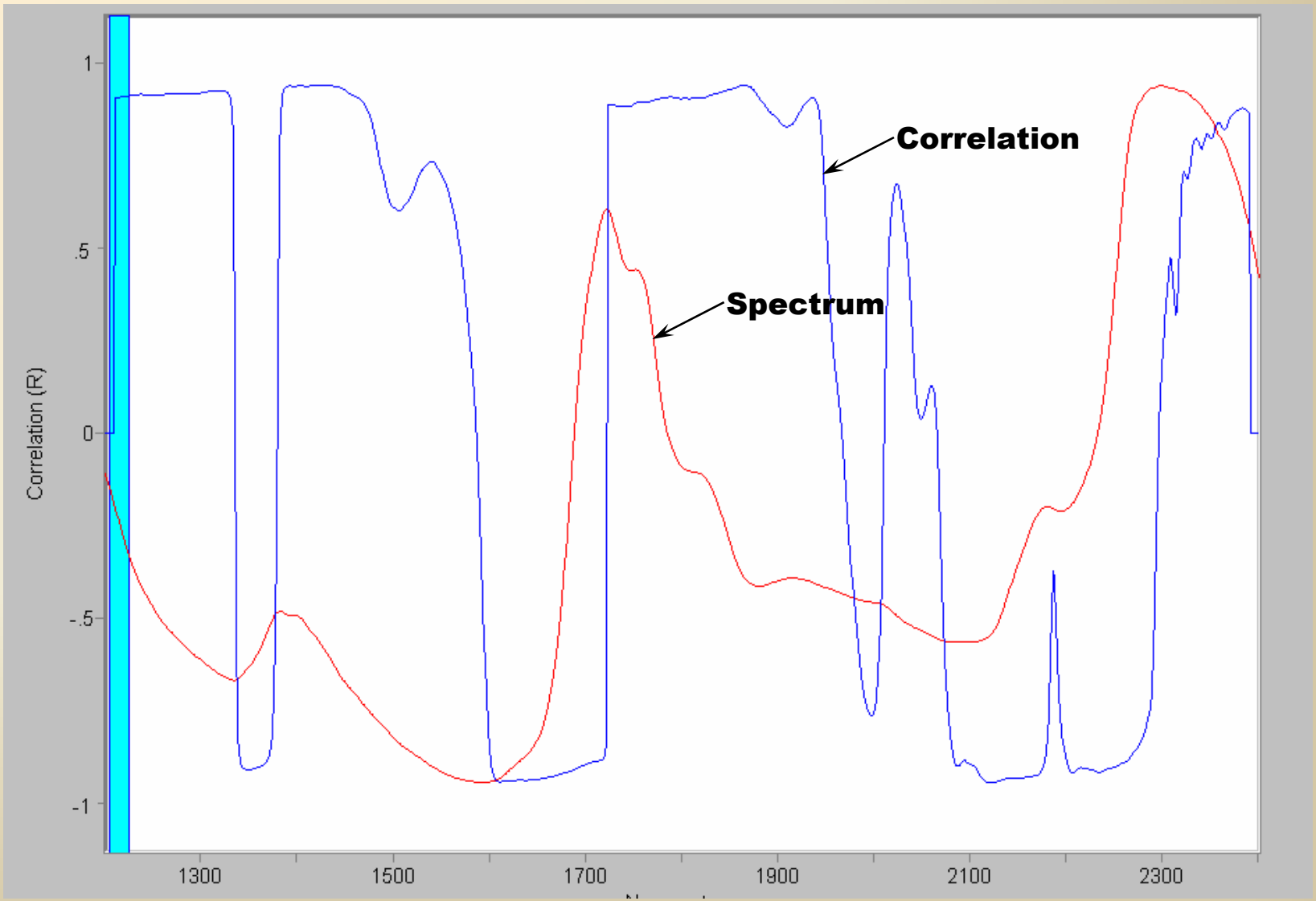
- Methanol was gravimetrically added to washed crude provided by Shell Pipeline to create a set of samples from 50 to 500 PPM by weight.
- These were analyzed using an LTI ParaFuel 1800 NIR analyzer with a fiberoptic transflectance probe.
- The scanned results were used to create a chemometrics model. The properties of the model and the results of tests are shown in the following slides.

LTI ParaFuel 1800

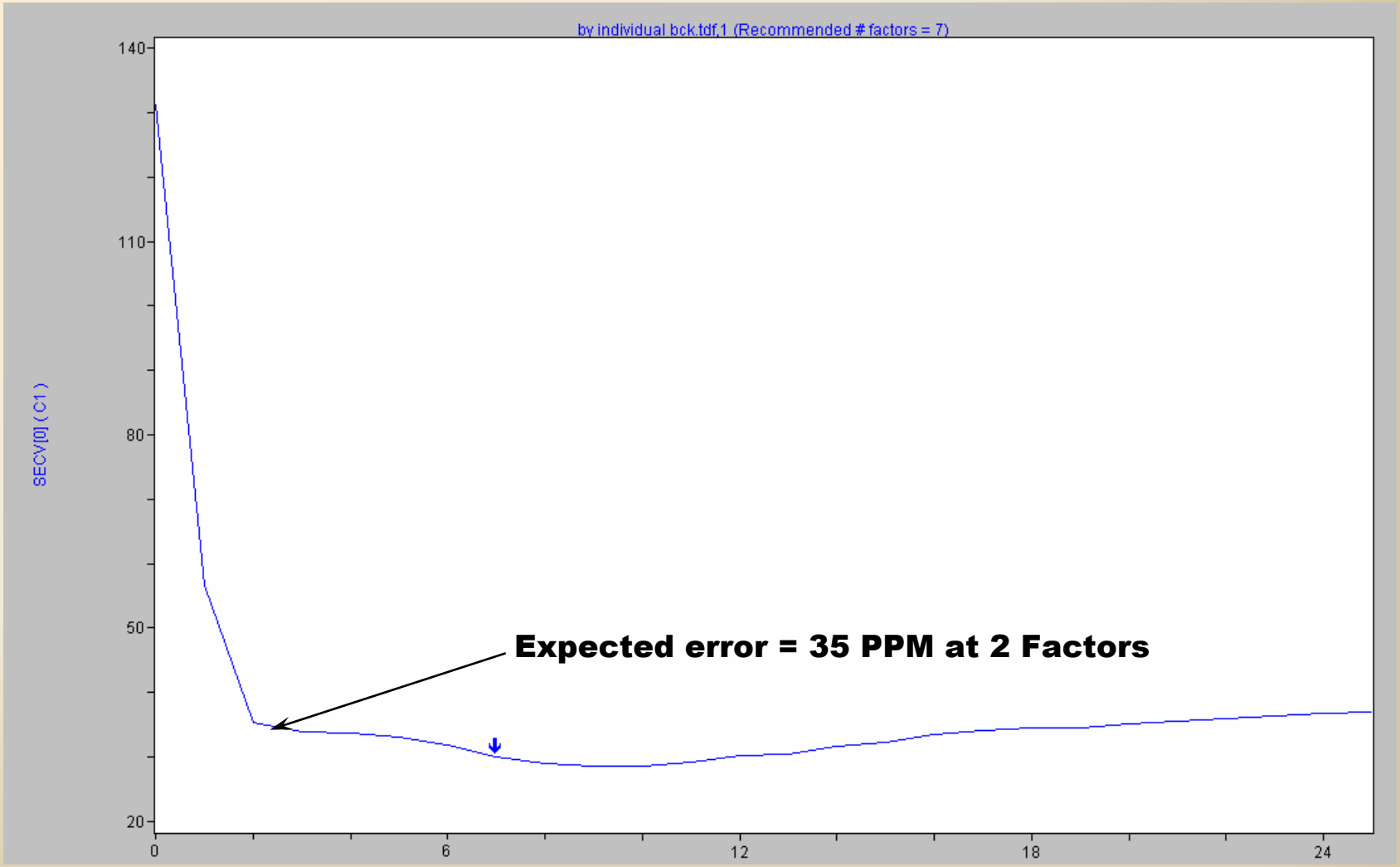
Methanol in Crude Test Results

- The spectra show many areas of high correlation between the methanol content and spectral features, as shown in the next slide.
- The SECV graph shown next suggests 2 factors and an expected error of 35 ppm for this model.
- The correlation of the model is 0.92, a better fit than the GC methods. Later slides show the correlation of the NIR method and the GC method.
- Five samples were then taken out of the model and predicted in triplicate. This is shown following the correlations.

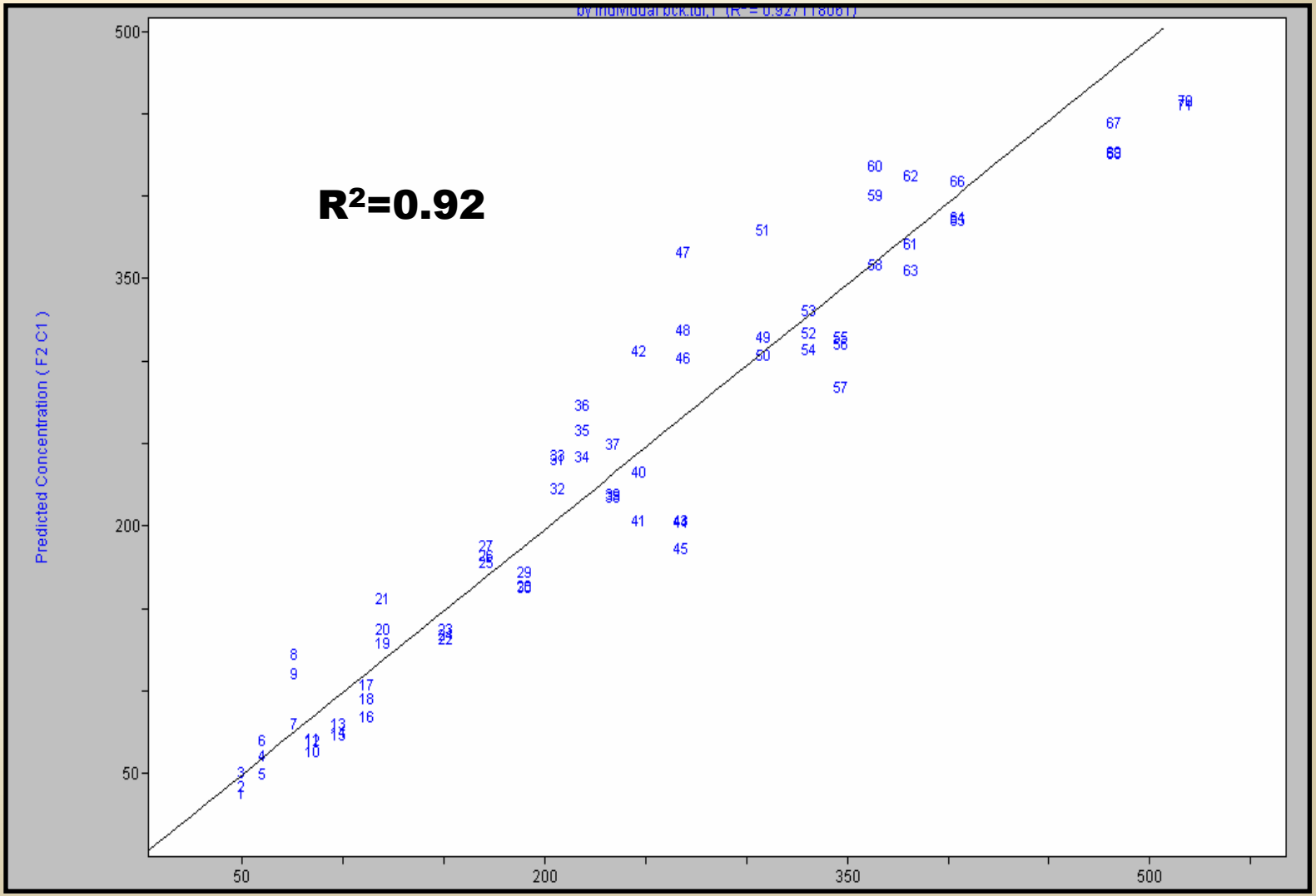
Spectral Correlation



SECV Graph


by individual bck.tdf,1 (Recommended # factors = 7)
SECV[0] (C1)
140
110
80
50
20
0
6
12
18
24
Expected error = 35 PPM at 2 Factors

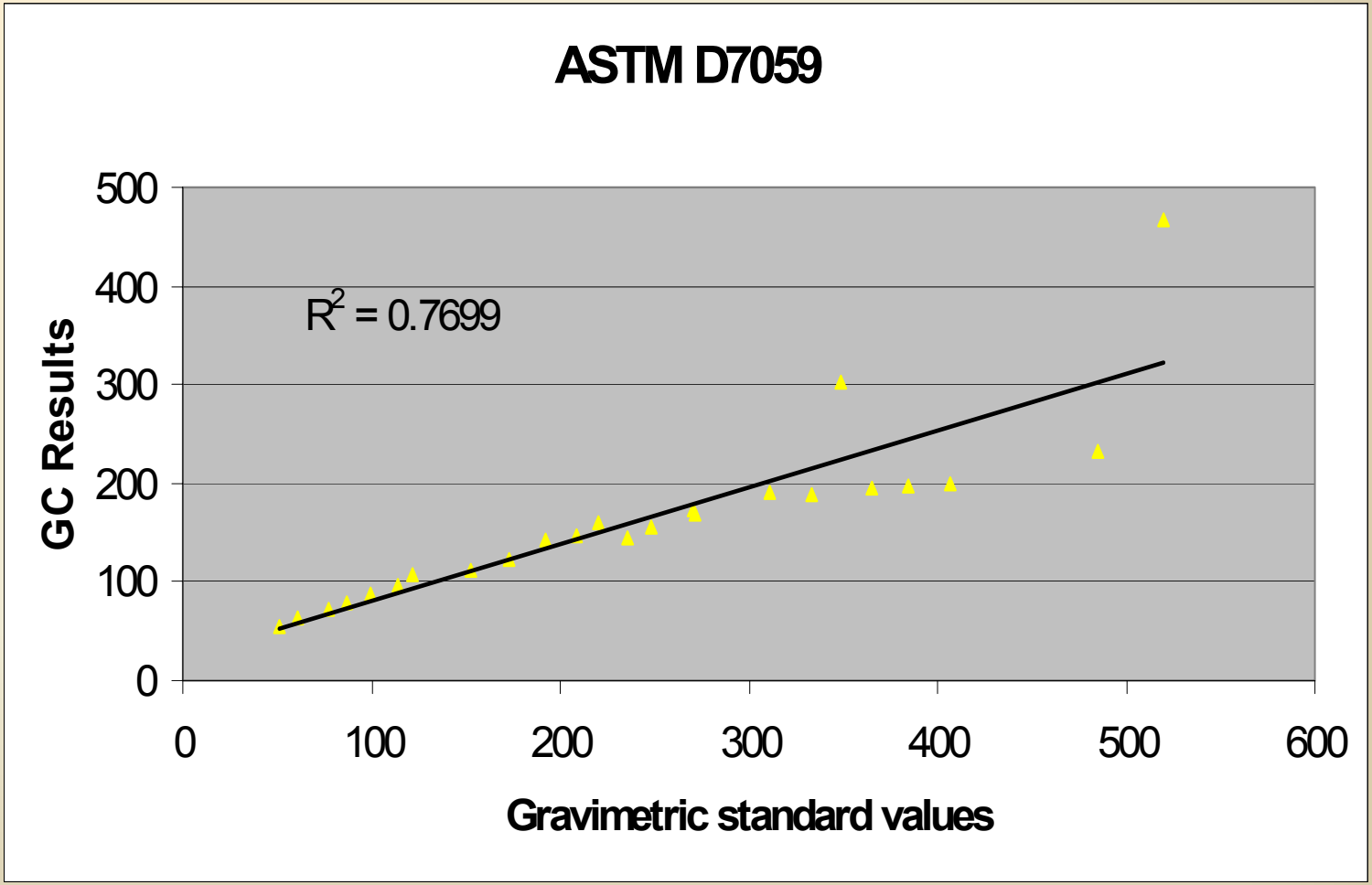
NIR Correlation – Act. vs Predicted



Predicted Samples

Sample	Pred_Value	Actual Value	Residual
153ppm a.spc	135.3	153.0	17.7
153ppm b.spc	141.1	153.0	11.9
153ppm c.spc	137.1	153.0	15.9
270ppm a.spc	212.4	270.0	57.6
270ppm b.spc	213.2	270.0	56.8
270ppm c.spc	195.0	270.0	75.0
366ppm a.spc	360.5	366.0	5.5
366ppm b.spc	402.4	366.0	-36.4
366ppm c.spc	419.7	366.0	-53.7
485ppm a.spc	454.5	485.0	30.5
485ppm b.spc	435.4	485.0	49.6
485ppm c.spc	435.3	485.0	49.7
77ppm a.spc	84.0	77.0	-7.0
77ppm b.spc	121.7	77.0	-44.7
77ppm c.spc	111.2	77.0	-34.2
		Standard Deviation of the Residual	41.1

ASTM Correlation – Act. vs Predicted



What Happened?

- ASTM D7059 is restricted in scope for crude samples containing less than 0.1 wt% water.
- The EIC samples sequestered for this study had various levels of methanol already present. The methanol was washed out of the samples in order to create a viable matrix for the gravimetric standards.
- The residual water content of the washed crude (after centrifugation) was approximately 1.0 Vol%. The added methanol was also diluted with water, creating a variable amount in the samples. Methanol almost certainly migrated preferentially to the water and dropped out during the GC prep.

What Happened ? (cont)

- The NIR model was taught to look for methanol in a crude matrix with a higher (and variable) water concentration than permitted in the scope of the ASTM method. It overcame a limiting factor of the GC procedure.
- This indicates that crude oil water content will not be a significant detriment to accurate determination of methanol concentration. This can be further improved by modeling water content explicitly if required.

What Happened ? (cont)

- These results from a relatively minor modeling effort strongly suggests that significant improvement in accuracy is likely with more extensive modeling. Given that the lowest samples modeled were 50 ppm, a lower LDL can also be expected by modeling lower levels of methanol.

Next Steps

- **Development of a more extensive model, taking into account water and crude source variations.**
- **A field test using the more extensive model and an on-line version of the analyzer on an off-shore platform.**