Introduction

The NIT-38 Near Infrared Transmission Analyser is designed to measure alcohol between the range of .1-30% alcohol in clear and turbid solutions. It was the aim of this study to determine accuracy and precision of the NIT-38 Alcohol Analyser for measuring ethanol in petrol(gasoline).

Description
Analyser:

The NIT-38 Alcohol Analyser scans the near infrared region between 720-1100nm at a resolution of 10nm. Light from a tungsten halogen lamp is passed through a 20mm cuvette(Starna Ltd, G-20) containing the petrol sample. The light passes through a slit to the spectrograph where it is separated into the frequency domain. A 38 element silicon photodiode array detector measures the intensity of the light at each frequency. The 38 pixel(wavelength) spectrum is stored in the instruments computer. A calibration model developed using Partial Least Squares Regression(PLS) is applied to the spectrum and the computer calculates the Ethanol and displays the results on the screen. Typical analysis time is 30 seconds.

Sampling:

5 different samples of unleaded petrol were sourced from local petrol outlets. Approximately 40 mls of each petrol were transferred to separate measuring cylinders. 1ml of Ethanol was added to each cylinder, mixed and allowed to settle until clear. (Note that the mixture tends to become turbid on addition of the ethanol). Each sample was scanned in the NIT-38 and the spectra stored in the instruments internal memory. Another 1ml of ethanol was added to each cylinder, mixed and settled. The samples were scanned again. This process was repeated until 10ml of Ethanol had been added to each sample.

21 samples of Petrol with Ethanol added between 2 and 20% were prepared by addition of Ethanol to 4 samples of the original petrol stocks. Samples were made up to 50 ml, mixed and allowed to settle. These samples were used as a prediction set.

Spectral Data:

Figure 1. presents the spectra of Petrol with Ethanol added between 2 and 20%.

NIR Transmission Spectra of Petrol with 2 to 20% Ethanol Added
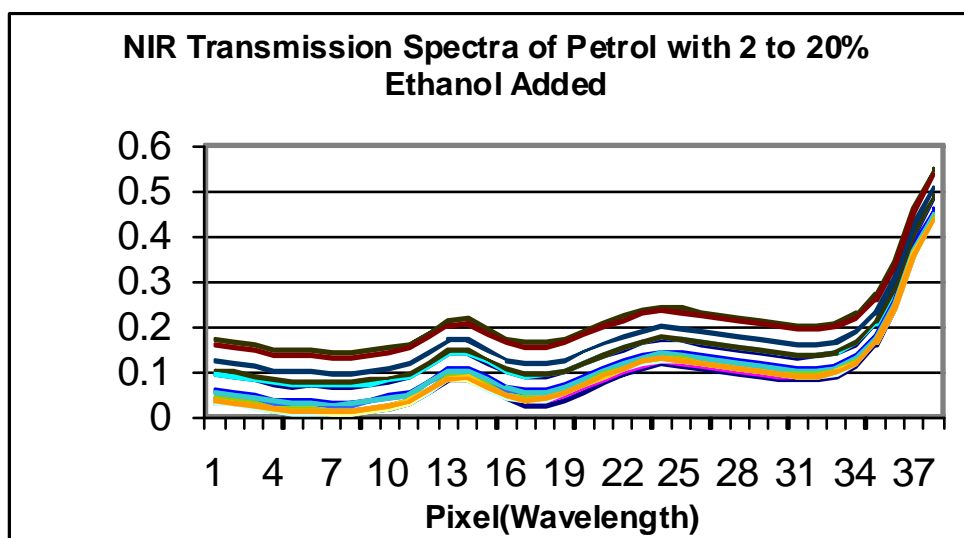
Calibration:

The 50 spectra saved in memory were uploaded from the NIT-38 Alcohol Analyser to a PC using NTAS(NIR Technology Australia Software). In the Calibration, Edit module, the calculated % Ethanol for each sample additions was added to the spectral file. The spectral range was reduced to cover the 750-1060nm since there was no visible absorbance bands lie outside this region.

A PLS calibration was performed. The optimum number of Principle Components (PS's) was determined at 8. The calibration statistics were, SEC = 0.24%, R^2 = .998. The calibration model was saved and downloaded into the NIT-38 Alcohol Analyser.

Results

The Prediction set were analysed using the Ethanol calibration developed above. Each sample was poured into the cuvette and loaded into the sample cell holder, scanned and the results saved in memory.

Table 1. shows the results of the analysis of these 20 samples. (Note that 1 sample was scanned twice and thus 21 data points are shown). The Standard error of Prediction (SEP) for these 21 samples was 0.20% Ethanol.

NIR Ethanol%	Ethanol Additions %	Diff %
20.78	20.83	0.05
2.17	2.08	-0.09
4.47	4.17	-0.30
6.06	6.25	0.19
19.91	19.90	0.00
19.24	19.06	-0.18
18.48	18.28	-0.21
8.07	8.33	0.26
10.35	10.42	0.06
17.36	17.56	0.20
18.75	18.75	0.00
20.83	20.83	0.00
2.36	2.08	-0.27
4.21	4.17	-0.04
6.06	6.25	0.19
8.36	8.33	-0.03
8.33	8.33	0.00
10.76	10.42	-0.34
12.50	12.50	0.00
14.58	14.58	0.00
16.20	16.67	0.47
	SEP	0.20

Figure 2. presents a plot of the NIR predicted Ethanol versus the calculated Ethanol by addition. The linearity (R^2) was determined in Excel as 0.9991.
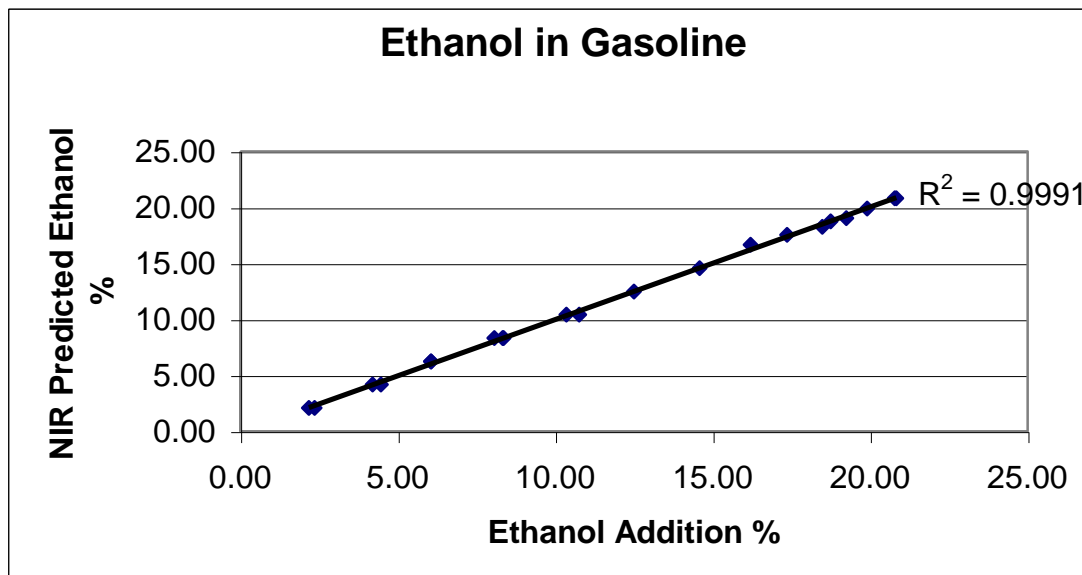
Figure 2. Plot of Ethanol Additions % vs NIR Predicted Ethanol %

2 samples were analysed 5 times to determine the precision. Table 3. presents the results.

Table 3. Precision Study. 2 samples analysed five times.

Sample	Ethanol%	Ave – Sample
1	17.23	0.05
2	17.30	0.12
3	16.98	-0.20
4	17.25	0.07
5	17.14	-0.04
6	9.32	0.01
7	9.28	-0.03
8	9.37	0.06
9	9.26	-0.05
10	9.30	0.01
	SDD	0.09%

Conclusion

The NIT-38 Alcohol Analyser is capable of being calibrated for the prediction of alcohol in petrol. The accuracy of the technique is expected to be better than 0.20% since the procedure described above did not use volumetric flasks but measuring cylinders. As such the error in dilution was the limiting factor. The Precision of analysis is considered typical for the NIT-38 Alcohol Analyser as this is similar to the analysis of alcohol in wine and beer.

It should be noted that to develop a more robust calibration, samples from a specific region or country would be required. These samples should be analysed for alcohol using Gas Chromatography.