Application Note 7: Determination of Ethanol Content in Water Samples Using a 38-element diode array detector NIR Transmission Instrument.

Introduction

This study was performed to evaluate the use of a 38-element silicon diode array NIR spectrophotometer to develop a rapid alcohol analyser for potential use in the wine industry. The sampling procedure involved the use of a liquid cell in transmission mode and the calibration developed was tested for reproducibility, repeatability and temperature stability.

Description

A preliminary calibration was developed using a set of ethanol solutions made up to the concentrations listed in table 1 prepared in Milli-Q water and buffered with 2.5g/L potassium hydrogen phthalate. Samples were injected into a liquid cell with a pathlength of 30mm and scanned on a NIT 2000 near infrared transmission analyser in the wavelength range 720-1100nm The calibration was optimised and tested for temperature stability with samples equilibrated between 10 and 30^{o}C. This temperature-stabilised calibration was tested for temperature stability, reproducibility and day-to-day repeatability.

Results

1) Calibration

A preliminary calibration was developed using Unscramber™. Principal Component Analysis (PCA) indicated that in the alcohol range 10-20%, there was a good cluster of spectral results. The calibration statistics for the unstabilised calibration are given in table 2.

Table 1: Concentrations of alcohol samples for preliminary calibration

Sample	Concentration (%)	Vol EtOH required (ml)	Mass KHP (g)
1	10.0	5.00	0.125
2	10.5	5..25	0.125
3	11.0	5.50	0.125
4	11.5	5.75	0.125
5	12.0	6.00	0.125
6	12.5	6.25	0.125
7	13.0	6.50	0.125
8	13.5	6.75	0.125
9	14.0	7.00	0.125
10	14.5	7.25	0.125
11	15.0	7.50	0.125
12	15.5	7.75	0.125
13	16.0	8.00	0.125
14	17.0	8.50	0.125
15	20.0	10.00	0.125

To test the temperature stability of this calibration, standard alcohol samples were incubated at 10°C and these samples were continuously measured on the spectrometer until the sample temperature reached 30°C. Temperature was monitored using a thermistor in direct contact with the solution. The results of these experiments are shown in figure 1.

Table 2: Statistics for the alcohol calibrations

	Preliminary Calibration	Temperature Stabilised Calibration
Number of PC's	5	5
Elements	71	110
RMSED	0.087	0.101
SED	0.087	0.102
Slope	0.999	0.998
Correlation	0.999	0.999

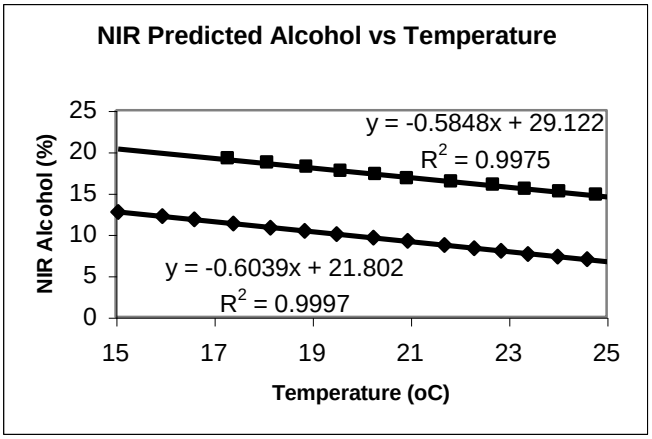

Figure1: Variation of predicted alcohol vs. temperature for a 10% and a 15% alcohol standard.

Figure 1 indicates that the predicted alcohol results vary linearly with temperature and therefore the calibration needed to be corrected for temperature. This was achieved by adding temperature stabilisation samples to the calibration. The statistics are also shown in table 2.

2) Temperature Stability

Figure 2 shows the predictive ability of this calibration with a 13.5% alcohol standard in the temperature range 22.0-30.5°C. Table 3 provides measures of the accuracy, AAD and Standard Deviation for the temperature stability shown in figure 2.

Table 3: Relevant statistics for calibration temperature stability

[ethanol] (%)	NIR Predicted Alcohol (Avg)	Std Deviation	AAD (%)*
13.50±0.1	13.45±0.1	0.05	0.05

*AAD (absolute Average Difference) between consecutive scans

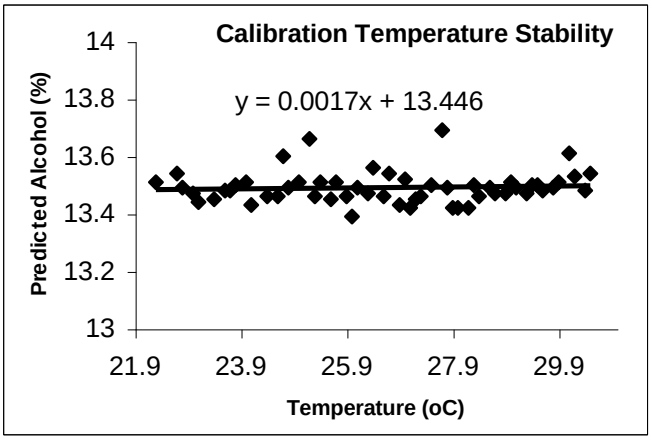

Figure 2: Predictive ability vs. temperature for the stabilised calibration.

3) Predictive Ability

Figure 3 shows the predictive ability of the temperature stabilised calibration for the following ethanol concentrations, 10.0%, 11.0%, 12.0%, 13.0%, 14.0%, 15.0%. All samples were equilibrated to 24.0°C Relevant statistics are also given.

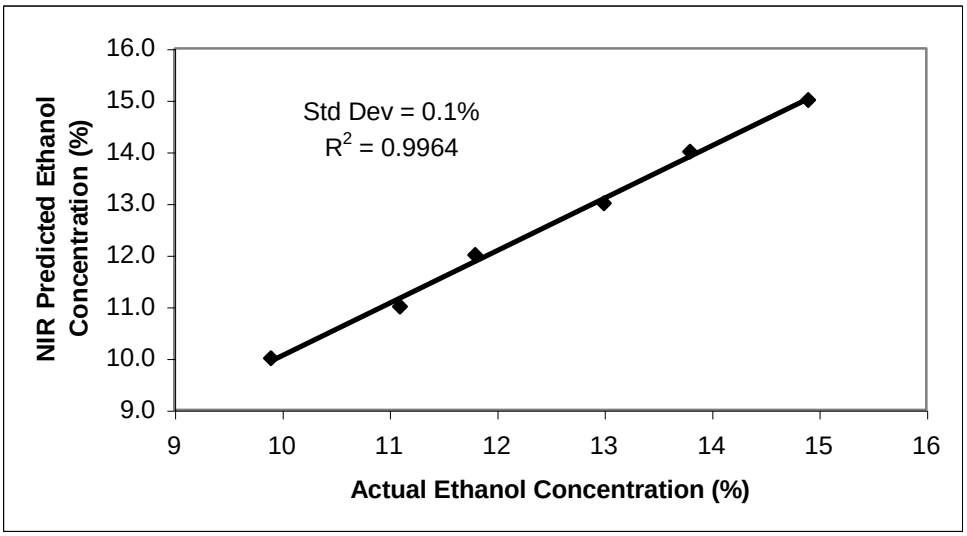

Figure 3: Predictive ability of the temperature stabilised calibration.

4) Reproducibility/Repeatability

a) Reproducibility (between scans): See table 3.

b) Reproducibility/Repeatability (between refills). Table 4 shows the calibration performance between refills and on a day-to-day basis

Table 4: Reproducibility/Repeatability Results

Sample	Temp (°C)	Day 1			Day 2		
		1	2	3	1	2	3
Tap Water	24.0	0.07	0.04	0.05	0.03	0.01	0.04
12.0%	24.0	12.05	12.03	12.04	12.06	12.01	12.00
15.0%	24.0	14.97	15.02	14.93	14.98	14.93	14.95

Reproducibility
AAD between sample refills = 0.03%
Std Dev =0.008%

Repeatability
AAD day-to-day = 0.02%

Conclusions

a) The 38-element silicon diode array NIR instrument can be calibrated to measure alcohol content of a set of ethanol standards.

b) Temperature stabilisation may be achieved within the calibration by the addition of samples measured at the expected sample temperature extremes (i.e. 15-30^{o}C).

c) Reproducibility and Repeatability on a day-to-day basis were found to be within specification (i.e. Within $\pm$0.1%).

d) Although the prediction of actual samples with the ethanol calibration was not successful, the results indicate that the development of a red and a white wine calibration is possible and on the basis of the results in this report, should provide accurate prediction data.

NIR Technology Systems
366 Edgar Street, Condell Park, NSW, 2200, Australia
Tel: 612 9708 5068, Fax: 612 9708 5537
Email: nirtech@nirtech.net, Web: www.nirtech.net