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The use of NIR to predict residual ash in the IWTO-19 yield test

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SUMMARY

The determination of ash content as required in IWTO-19 is an energy intensive and environmentally damaging process which contributes approximately 1% to the calculation of the Woolbase result. The use of NIRA (Near Infrared Analysis) technology is already established for determining Ethyl Extractable Matter for IWTO-19. This report investigates the feasibility of extending this technology to the determination of ash content.

A calibration was performed on 1287 scoured wool samples using commercial ash results as reference measurements. 1200 independent samples were measured on both the NIRA calibration and by the reference method and validated using the criteria in IWTO-0 for comparison of test methods. The validation failed all the IWTO-0 criteria, and this was traced to the instrument being unable to accurately predict high ash values (the highest 9% of the data). A validation was performed with these samples removed and passed the criteria for statistical equivalence, except for two statistics which were artifacts of the large amount of data utilised.

The difficulty of measurement of high ash values was traced to the fact that these samples are of relatively low precision, and the trial design was not robust enough to account for the effects of these samples.

Overall the results were promising and it is recommended that further work be carried out with fewer samples of a higher precision and more samples with higher reference values.

INTRODUCTION

The Determination of Ash Content of Scoured Wool Samples (IWTO-19 Appendix D) is a component of the Woolbase test that assesses the percentage of mineral material remaining in the wool sample. This involves combusting 10g wool specimens at 750 +/- 50^{o}C to completion and weighing the residual material. This process is expensive and has some health and safety risks as well as releasing significant volumes of undesirable sulfur and carbon based gases into the environment.

At the 1995 Nice meeting a paper was presented detailing how Near Infra-Red Analysis (NIRA) technology could be used to accurately predict the concentration of Ethyl Extractables in scoured wool. This measurement is also a component of Woolbase and on the basis of that work an alternative method was endorsed as Appendix K of IWTO-19 at that meeting.

This report investigates the feasibility of utlilising NIRA technology for predicting Ash content of scoured wool.

APPARATUS AND EXPERIMENTAL.

The ash results used in this paper were obtained on 10g specimens combusted using a rotary gas furnace. The NIR spectra were collected using an NIRS 6500 spectrophotometer on 10g specimens. Statistical analysis was performed using Win ISI2 software, Statistica, and Microsoft Excel.

RESULTS AND DISCUSSION

Calibration

The instrument was calibrated using commercial data selected for spectral diversity from 5000 samples. The “select” algorithm was utilised and 1287 samples were selected.

The reference values for the calibration were obtained by averaging the results of the 2 commercial ash specimens used in the woolbase determinations.

Several models were examined and the best mathematical treatment was found to be taking the first derivative of the data, using partial least squares regression, and utilising all wavelengths (including the visible spectrum). Reference values ranged between 0.30 and 2.85 % and both commercial and laboratory scoured wools were included.

The calibration was cross-validated by removing 10% of the samples and recalculating the calibration. The removed samples were then predicted with the resulting equation. The process was repeated with the next 10% until all samples have been independently predicted.

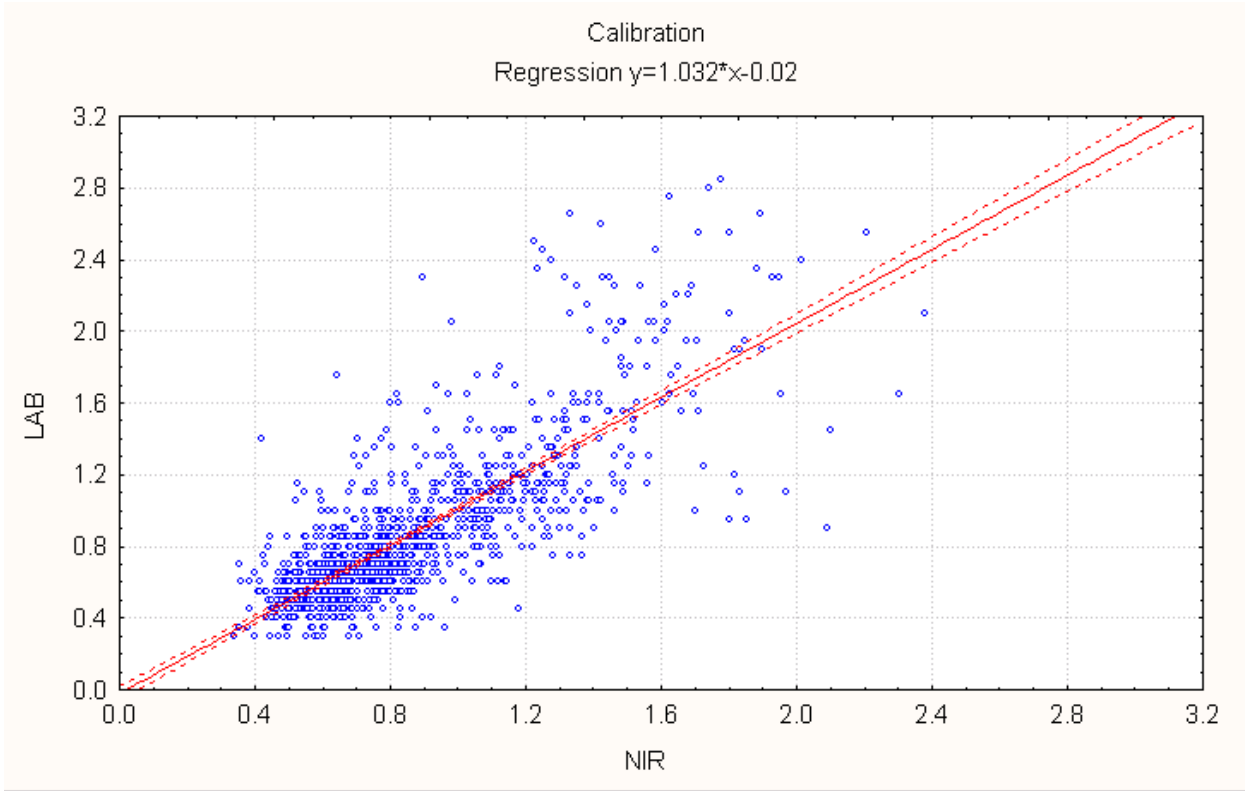
The calibration statistics are given in Table 1

Table 1

	The resulting calibration	Cross validation
Standard error of calibration	0.235%	0.241%
R-squared	0.65	0.64
Number of terms	9	Na

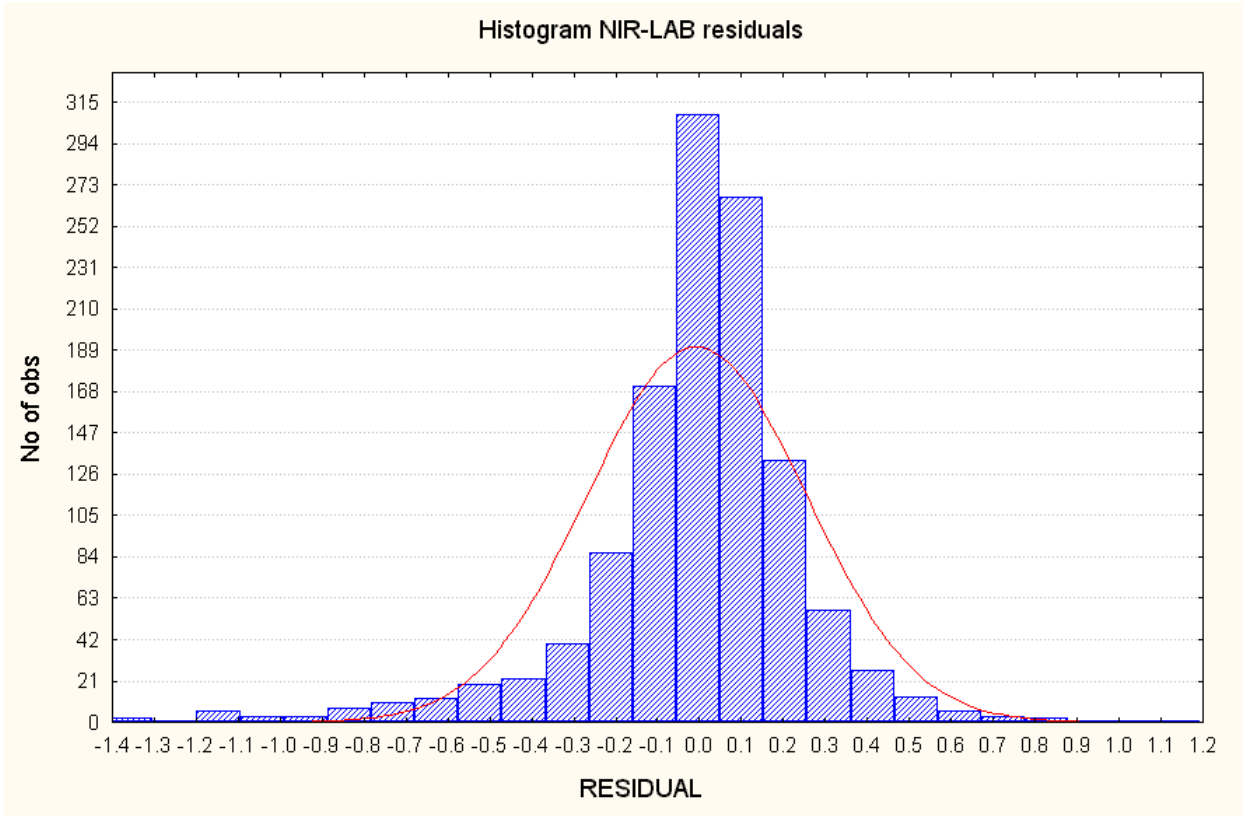
The similar cross-validation statistics indicate that the calibration should perform well in other independent validations. The scatter plot below shows the relationship between the reference and predicted data.

Figure 1



Most of the data is concentrated below 1% residual ash. It can be seen that the regression relationship is close to 1:1 and not biased. It should also be noted that at ash levels higher than 1.5% the precision of the relationship deteriorates. Figure 2 shows a histogram of the calibration residuals

Figure 2



Though most of the data is within 0.3% of zero difference there are a number of outliers which will effect the performance of the calibration, especially on the negative tail (reference values being higher than predicted values).

Validation

1200 samples were selected for spectral diversity from a different data-set. The equation derived above was used to predict ash values and these were compared with the reference values by the methods described in IWTO-0.

Table2

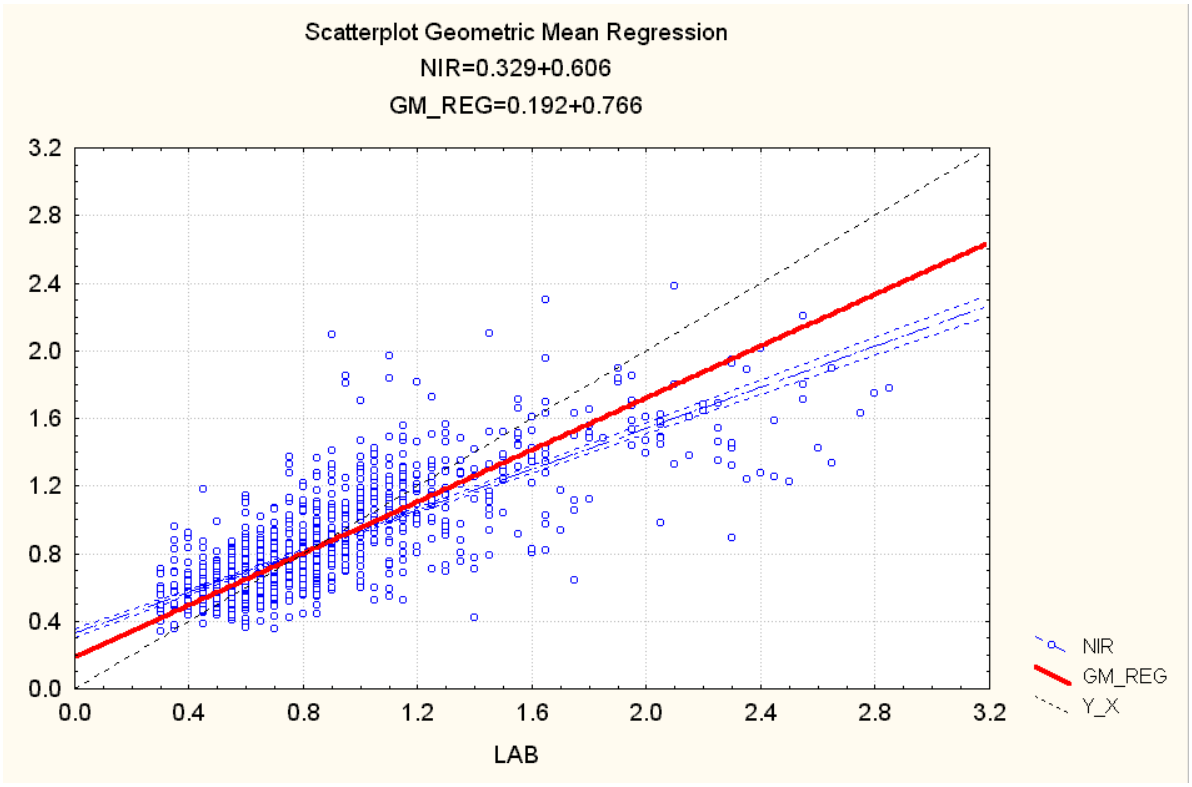
Summary statistics	LAB	NIR	Average	Difference
Number obs.				
Mean ash%	0.853	0.846	0.850	-0.007
SD ash%	0.426	0.327	0.357	0.261
t value				0.935
p-value				0.350
significance				ns

Regression statistics	GM	DVA
Estimated slope	0.766	-0.295
SE slope	0.014	0.019
t value slope	17.242	-15.230
p-value slope	0.000	0.000
significance slope	***	***
Correlation R	0.791	0.403
Correlation t	2535.805	576.873
Correlation p	0.000	0.000
significance	***	***

The slope of the geometric mean regression is highly significant. This is due to the difference in standard deviations between the LAB and NIR data, which were 0.43 and 0.33 respectively.

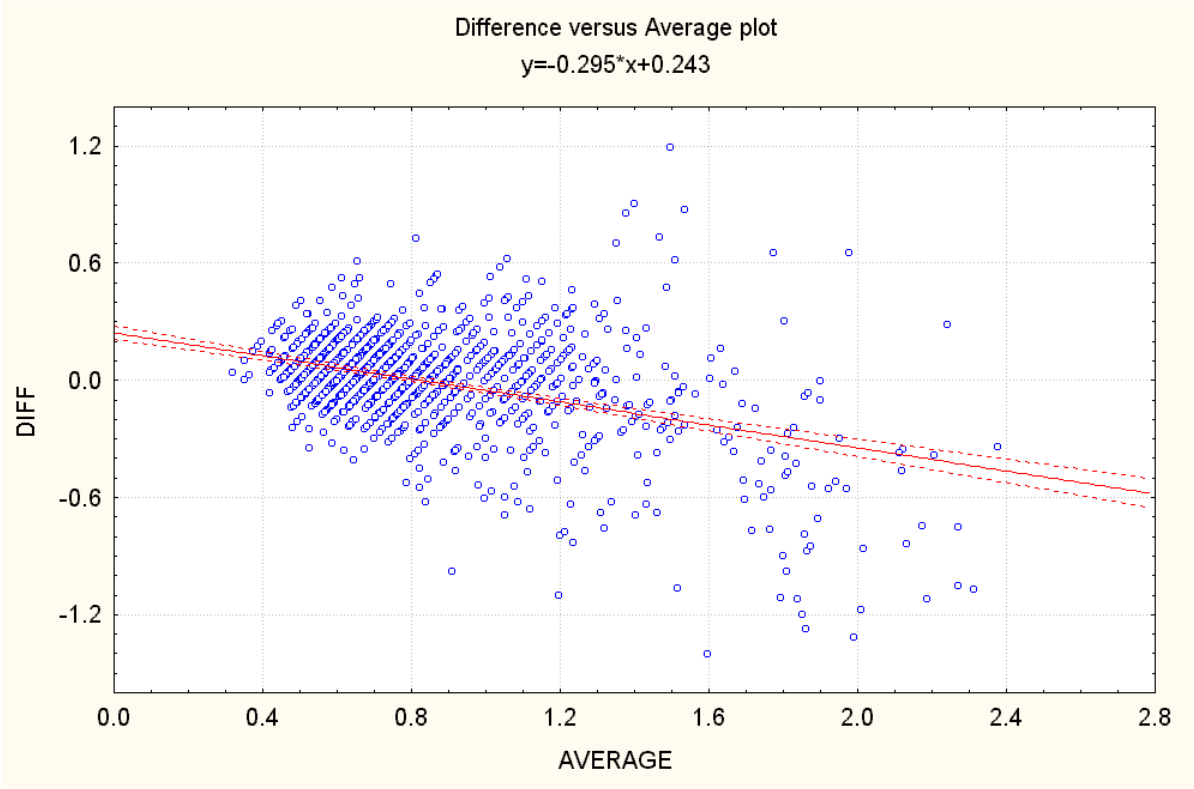
This problem is demonstrated in the GM plot Figure 3

Figure 3



There are 5 points above 2% on the Y axis and 35 points on the X axis. Because of the distance this data is from the mean it has a high degree of leverage on the standard deviation of the population. The GM regression is based on the ratio of the 2 standard deviations. The DVA plot is shown in figure 4.

Figure 4.



Again the relationship is clearly affected by the leverage of the high ash residual samples.

To assess the validity of the predictions at lower levels the analysis was performed with all samples having reference values larger than 1.5 % eliminated (104 samples, 9% of the data) . The results are given in table 3 below.

Table 3

Summary statistics	LAB	NIR	Average	Difference
Number obs.	1096	1096	1096	1096
Mean ash%	0.750	0.787	0.769	0.036
SD ash%	0.254	0.259	0.237	0.196
t value				6.144
p-value				0.000
significance				***

Regression statistics	GM	DVA
Estimated slope	1.019	0.022
SE slope	0.022	0.025
t value slope	0.875	0.883
p-value slope	0.382	0.377
significance slope	ns	ns
Correlation R	0.708	0.027
Correlation t	1703.506	32.051
Correlation p	0.000	0.000
significance	***	***

Without the high values the GM regression passed. The mean difference of 0.036 was statistically significant but this was due to the large amount of data, and is small enough to be of no commercial significance with respect to woolbase results. A similar effect was observed in the DVA statistics with the correlation coefficient of .027 being significant.

The GM and DVA plots are below as figures 5 and 6

Figure 5.

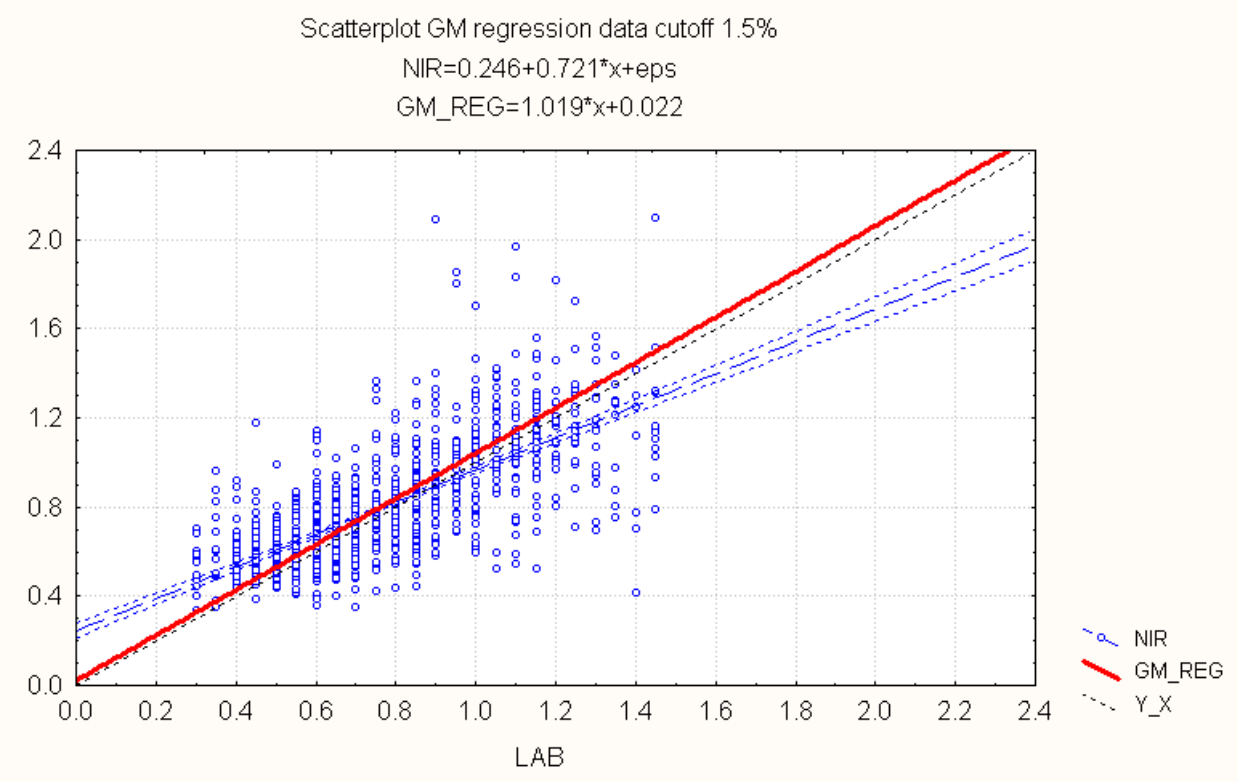
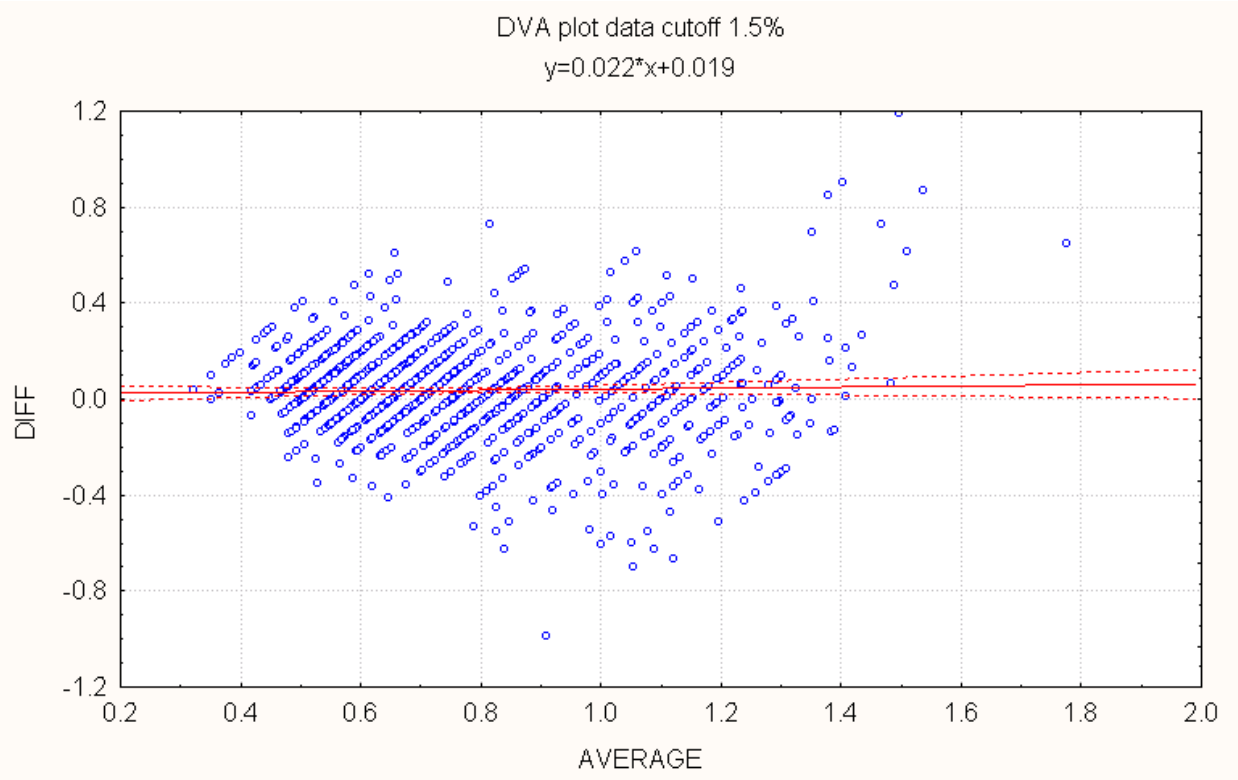


Figure 6



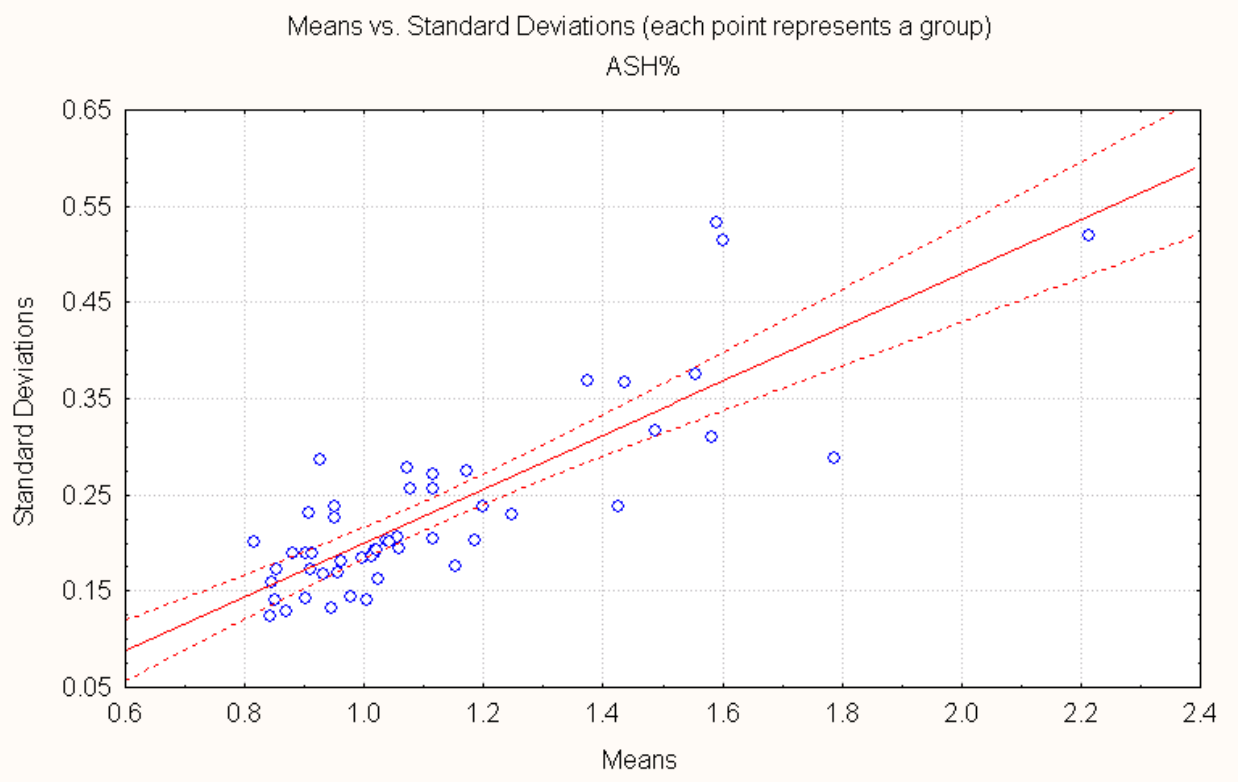
Clearly the calibration derived in this work was not effective at ash levels above 1.5% but complied with the IWTO requirements at lower levels.

PRECISION ISSUES

The standard error of prediction of the original validation was 0.26%. When compared with the average reference value of 0.85% this prediction error is equivalent to about 30% of the mean reference value, and this would normally be considered poor performance for any system of this type.

As no published information could be easily located on the precision of the ash test a small experiment was performed on 20 replicates of 51 typical samples of New Zealand greasy wool. The mean ash value was 1.1% and the pooled standard deviation was 0.37. This performance is slightly poorer than that observed in the validation. The precision was also highly heteroscedastic, with the samples high in ash exhibiting the largest amount of variation. This can be seen in a plot of standard deviations vs means for the data in figure 7 below.

Figure 7



The effectiveness of NIRA calibrations is limited by the quality of the reference data in the calibration set. Based on the variation above it is highly likely that the precision errors observed in the original calibration are due to errors in the reference data, as only 2 specimens were used in their determination.

Similarly the calibration spectra were based on 2 separate specimens which were used for determining the ethanol extractables. If the variation above is caused in part by a lack of homogeneity of ash within the global sample it is possible that many of the high ash subsamples were not observed by the instrument but were obtained by the reference method.

Finally the population structure was not ideal, with only 9% of the data covering half of the working range and most of the samples tending to be close to the mean.

It is recommended that this work be repeated with the following modifications

1. Fewer samples of a higher quality should be used for calibration

2. The same specimens used for ash determination should also be presented to the instrument when collecting spectra

3. At least 4 specimens should be measured for each sample

4. The calibration population should be artificially structured to include more samples with higher ash content and fewer samples close to the mean.

CONCLUSIONS

Overall this work indicated that NIRA technology showed promise in being able to predict ash results to a level where it may provide a suitable alternative to the incineration method used in commercial wool-testing laboratories.

It can also be concluded that NIRA is capable of accurately predicting ASH results at levels lower than 1.5%. The precision of these predictions is at least equivalent to that of the reference method.

At higher ash values the NIRA calibration obtained in this work under-predicted the magnitude of the ash results.

It is recommended that the work be repeated with higher quality reference data and more even population structuring.