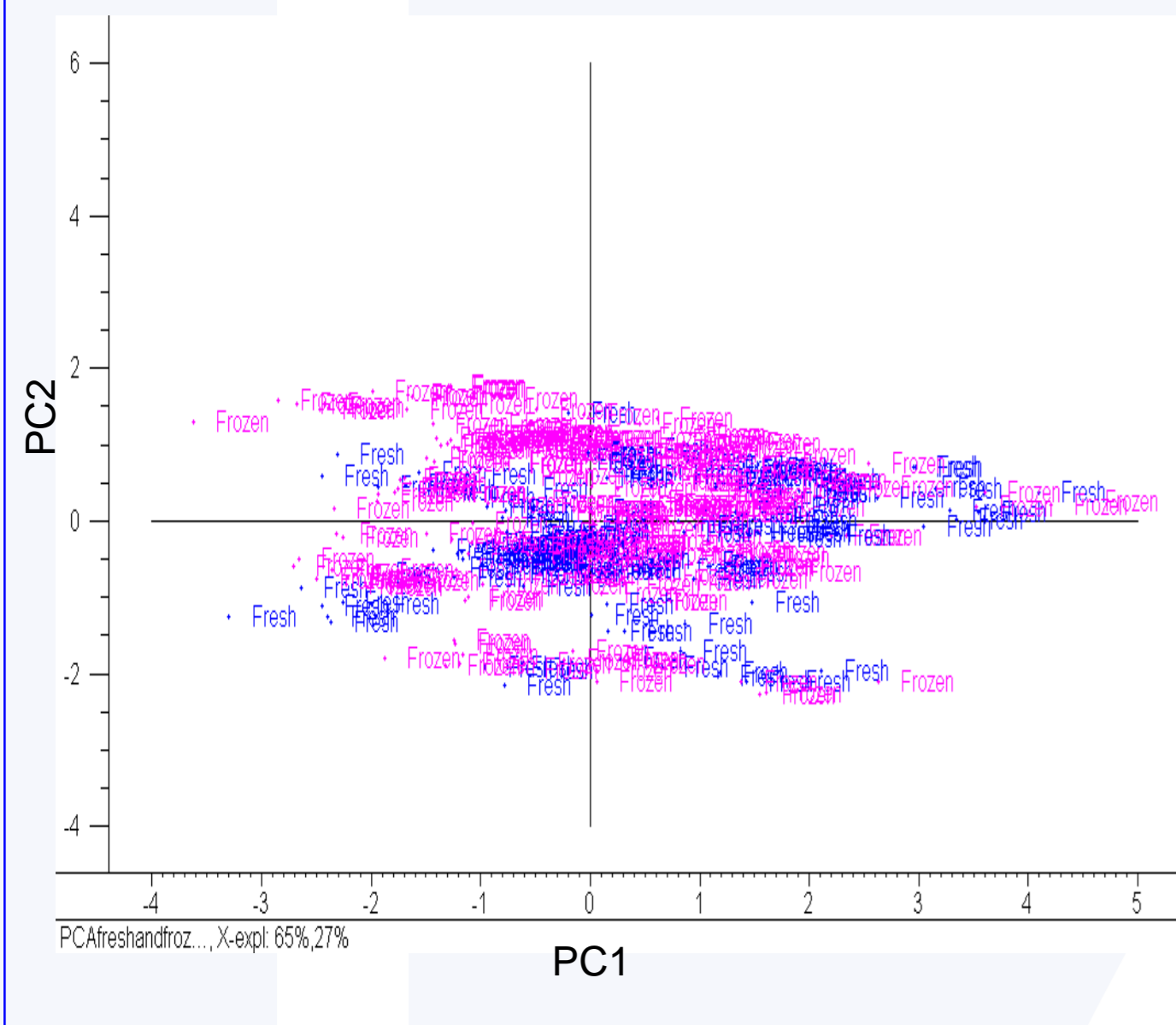




# Effect of freezing and frozen sample storage on visible and near infrared calibration for determination of total anthocyanins in red grapes

Daniel Cozzolino, Wies Cynkar, Les Janik, Bob Damberg, Leigh Francis and Mark Gishen  
The Australian Wine Research Institute, PO Box 197, Glen Osmond (Adelaide) SA 5064, Australia  
Cooperative Research Centre for Viticulture, PO Box 154, Glen Osmond (Adelaide) SA 5064, Australia  
Daniel.Cozzolino@awri.com.au

Figure 1. Score plot for the first two principal components (PC1 and PC2) marked according to sample storage.



### Introduction

The AWRI has previously demonstrated the potential of the use of visible (VIS) and near infrared (NIR) spectroscopy for the analysis of total anthocyanins (colour), total soluble solids (TSS) and pH in both red grape homogenates and whole grapes. The presentation of the sample is always a key factor in the robustness and accuracy of VIS-NIR analytical techniques. Although samples can be analysed either fresh or after storage in a frozen state, the effect of freezing and frozen storage on the VIS-NIR spectra has not been reported before. The objective of this study was to examine the effect of freezing and frozen storage on the VIS-NIR spectra of red grapes to measure the concentration of total anthocyanins.

### Materials and methods

Grape homogenates obtained from fresh and previously frozen berries were scanned in reflectance mode (400 – 2500 nm) using a monochromator instrument (FOSS NIRSystems6500). Spectral data collection and calibration were conducted using the WinISI software. Samples were scanned fresh, after freezing for 24 hours, and after 1, 3 and 6 months frozen storage. Calibrations were developed using modified partial least squares (MPLS) regression using cross validation.

### Results

The scores from the principal component analysis (PCA) for the VIS-NIR spectra showed no obvious differences between fresh and frozen (24 hours) samples (Figure 1).

Figures 2 and 3 show the calibration models for colour developed using either fresh or frozen samples alone, respectively. Since the residual predictive deviation (RPD), defined as the ratio between the standard deviation of the population and the standard error of cross validation (SECV), is greater than three, these calibration models are considered as acceptable for analytical purposes.

Figure 2. Calibration for fresh samples

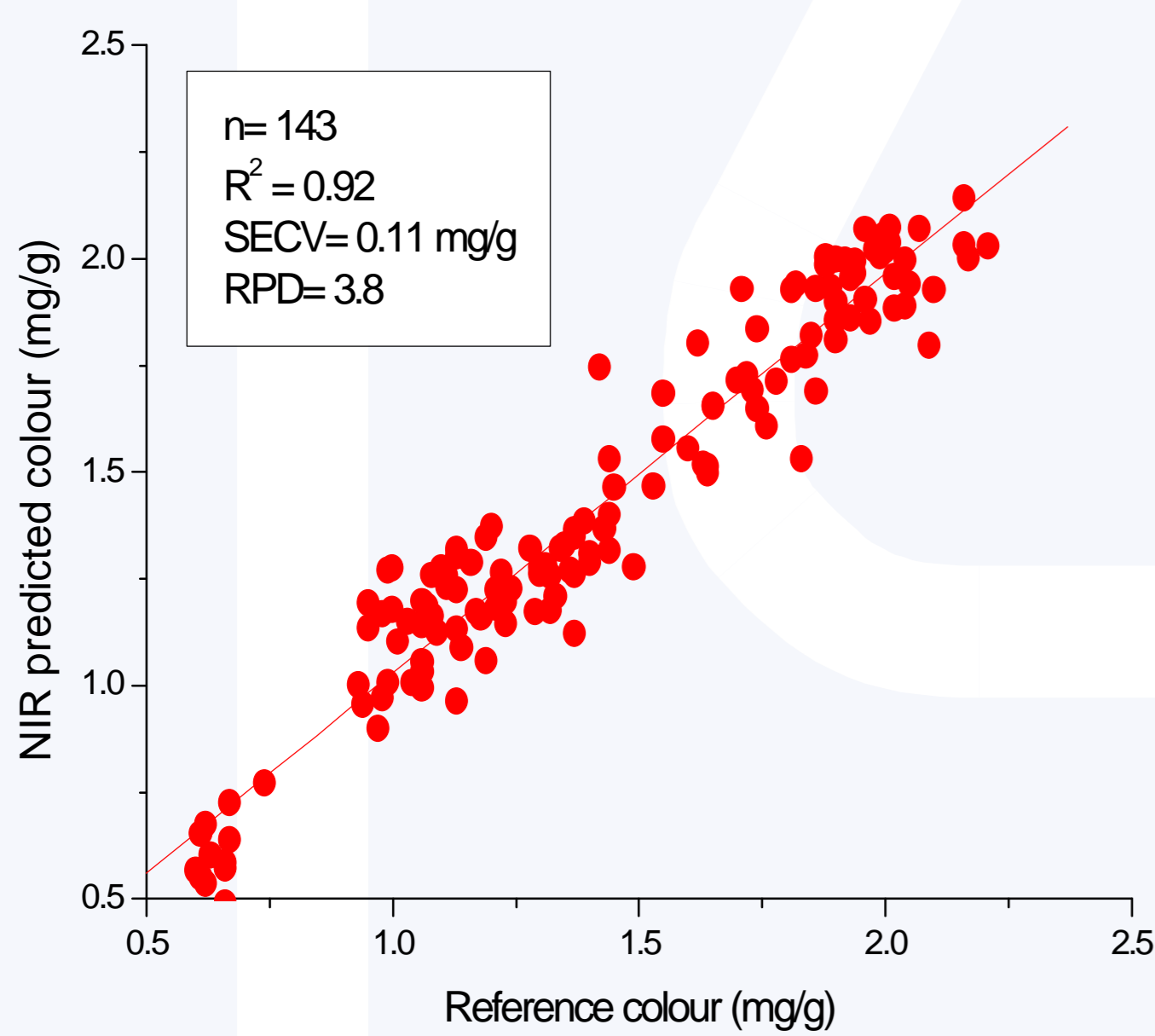
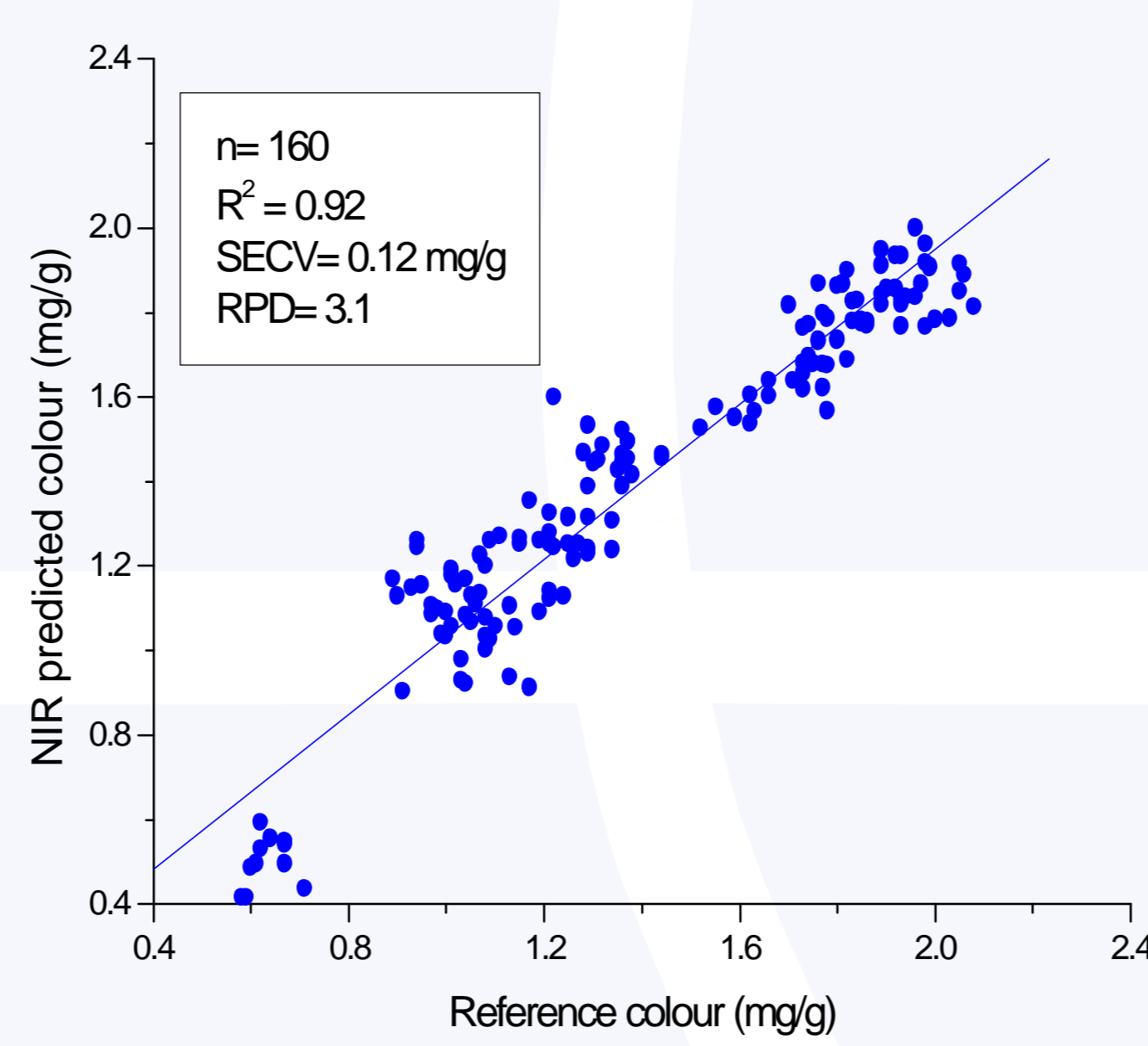


Figure 3. Calibration for frozen samples



Figures 4 and 5 show the relationship between the reference and NIR-predicted colour values for all samples when using a calibration developed on either fresh or frozen samples alone, respectively.

The SEP for total anthocyanins in all samples was slightly increased by freezing and storage when compared with calibrations developed on fresh or frozen samples alone.

### Conclusion

These results suggest that it might be possible to use NIR calibrations developed on fresh or frozen samples alone to measure the concentration of total anthocyanins in either fresh or frozen samples after appropriate slope and bias correction.

Figure 4. All samples predicted with the 'fresh' calibration

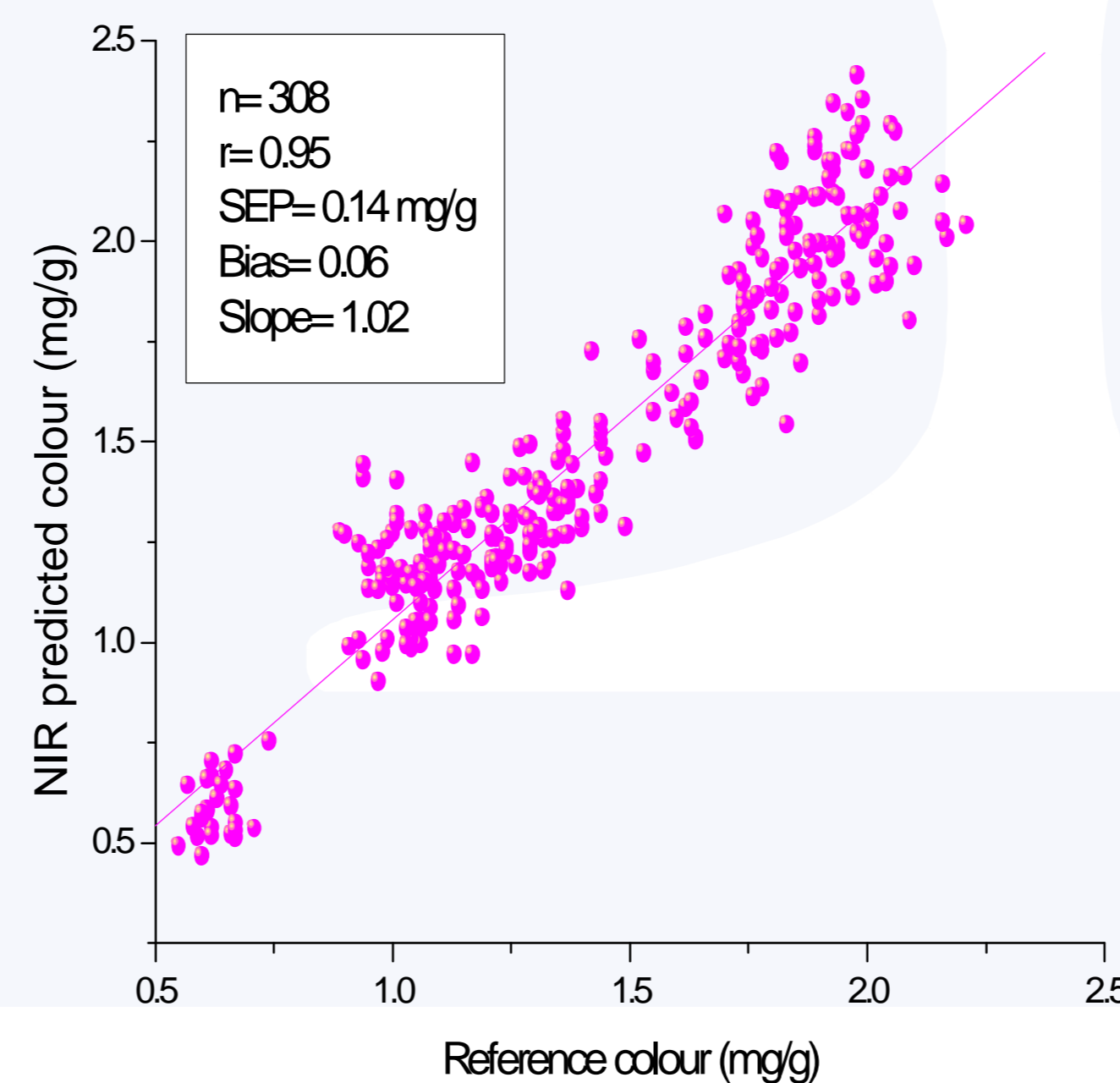


Figure 5. All samples predicted with the 'frozen' calibration

