

Technical Note – Calibration Transfer

A key aspect for NIR spectrophotometric method development involves the issue of calibration transfer. This is important if you are developing a calibration on a laboratory unit for use on a process unit, or if the original analyzer unit must be replaced for any reason. Multivariate calibrations are often a challenge to transfer since they can be sensitive to very small changes in a spectrum. For a successful calibration transfer, the two analyzers must be as close to identical as possible. The most important instrument parameters that can affect transferability are wavelength accuracy, bandwidth accuracy, absorbance accuracy, and noise levels. This note will describe the transfer of a hydrocarbon calibration from one analyzer unit to two other measurement channels on the same analyzer and to several other separate analyzers.

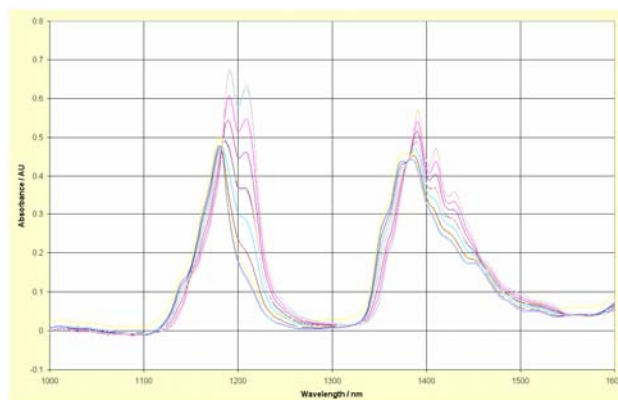
Background

Six Guided Wave Model 412 spectrophotometers were used in this study. These included both laboratory and process unit configurations. Units A through D have three measurement channels. Units E and F are single channel units. A calibration was developed using data from one channel on Unit A and transferred to the other two channels on that unit as well as to all channels on Units B through F.

Experimental

The NIR spectra of a set of 17 binary mixtures of hexane and ethyl acetate were measured between 1000 and 1600 nm using Guided Wave Model 412 Spectrophotometers as mentioned above. The sample mixtures for prediction were prepared independently on several occasions. Therefore prediction errors include a component from sample preparation variation as well as instrument variation. Figure 1 shows the absorbance spectrum of the initial samples. The concentration range of each component was from approximately 10% to 90% (volume percent). Data from channel 2 on Unit A were used in PLS (Partial Least Squares) calibrations for both analytes. These models were then used to predict samples measured on the other

Figure 1 NIR Spectra Calibration Mixtures



analyzer units as described. For a discussion of the principles of PLS and other multivariate calibration techniques see Martens & Naes¹ and ASTM E1655². Several different data pre-processing methods were used to explore the sensitivity of the calibration transfer to the pre-processing methods. Table 1 shows the calibration cross validation results with different pre-processing techniques. All give similar RMSEPCV values. The baseline correction was a 2-point linear correction. The derivative was a second order polynomial Savitsky-Golay 1st derivative.

Method	# of PCs	RMSEPCV Ethyl Acetate	RMSEPCV Hexane
None	3	0.1427	0.1427
Baseline	2	0.1492	0.1492
Derivative	2	0.1338	0.1338

Table 1 - Calibration RMSEP values in volume percent

The data measured on different channels from Unit A, and on all of the other analyzer units were then predicted using the original models. Figures 2-7 show the results for the different pre-processing methods for both ethyl acetate and hexane. It is clear

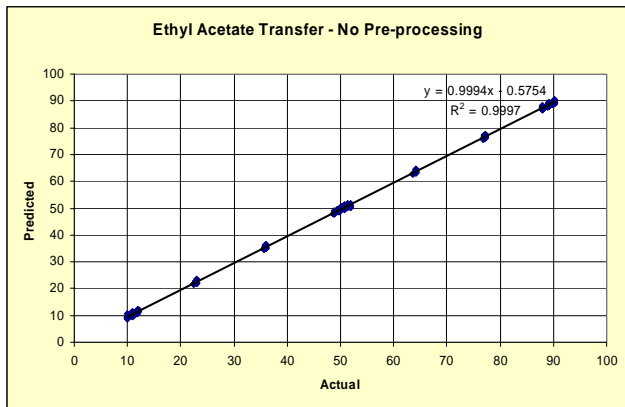


Figure 2 Ethyl Acetate Transfer - no pre-processing

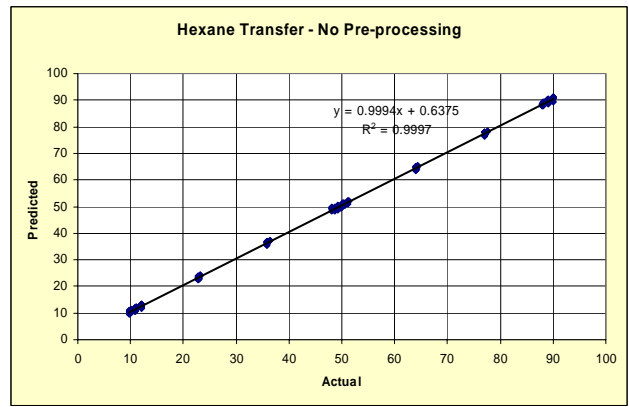


Figure 5 Hexane Transfer - no pre-processing

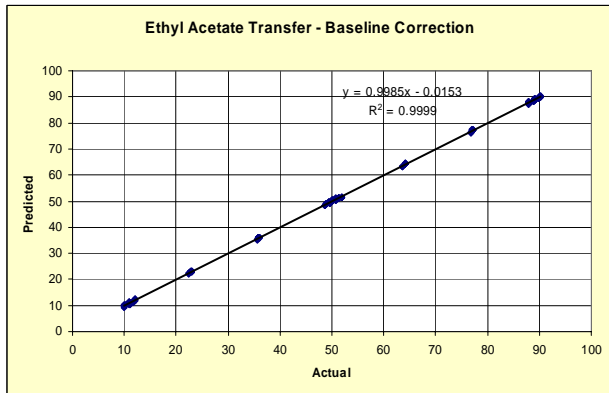


Figure 3 Ethyl Acetate Transfer - Baseline Correction

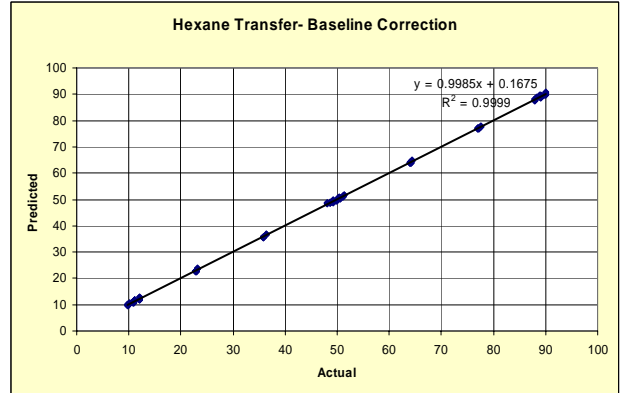


Figure 6 Hexane Transfer - Baseline Correction

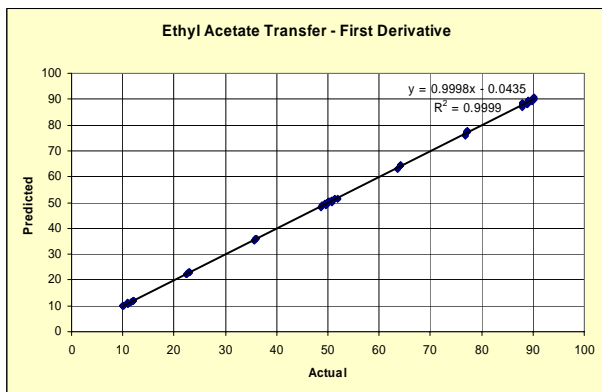


Figure 4 Ethyl Acetate Transfer 1st Derivative

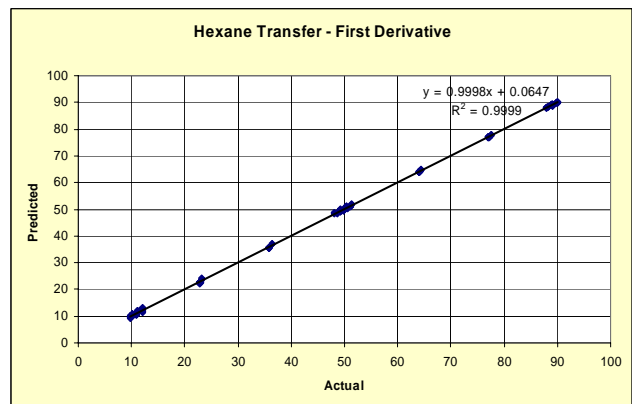


Figure 7 Hexane Transfer - 1st Derivative

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that the models transfer well for both constituents and for all three pre-processing options. Table 2 lists the SEP and bias values for the transfer predictions.

Conclusion

The ability to transfer multivariate calibration models between instruments is a key consideration when choosing an analyzer. The data presented here shows that calibrations developed on a

Guided Wave Model 412 spectrophotometer are easily transferred to other Model 412 units with no mathematical manipulation beyond the normal data pre-processing. This result is consistent with the success achieved in practical transfers in the field and provides a quantitative basis for the success. For more detailed information regarding system specifications please contact a Guided Wave sales or technical specialist.

Pre-processing	Ethyl Acetate (Unit – Channel)			Hexane (Unit – Channel)		
	A-1	A-3	B-1	A-1	A-3	B-1
None	0.18 / 0.35	0.17 / -0.66	0.16 / -0.79	0.18 / -0.35	0.17 / -0.66	0.16 / 0.79
Baseline	0.16 / -0.05	0.25 / -0.23	0.14 / 0.07	0.16 / 0.05	0.25 / 0.23	0.14 / -0.07
Derivative	0.16 / -0.10	0.20 / -0.17	0.30 / 0.28	0.16 / 0.10	0.20 / 0.17	0.30 / -0.28
	B-2	B-3	C-1	B-2	B-3	C-1
None	0.15 / -0.97	0.12 / -1.10	0.11 / -0.53	0.15 / 0.97	0.12 / 1.10	0.11 / 0.53
Baseline	0.14 / -0.10	0.12 / -0.15	0.15 / 0.17	0.14 / 0.10	0.12 / 0.15	0.15 / -0.17
Derivative	0.14 / -0.04	0.13 / -0.04	0.13 / 0.14	0.14 / 0.04	0.13 / 0.04	0.13 / -0.14
	C-2	C-3	D-1	C-2	C-3	D-1
None	0.11 / 0.09	0.14 / -0.03	0.17 / -0.96	0.11 / -0.09	0.14 / 0.03	0.17 / 0.96
Baseline	0.11 / 0.10	0.13 / -0.10	0.16 / -0.47	0.11 / -0.10	0.13 / 0.10	0.16 / 0.47
Derivative	0.14 / -0.11	0.21 / 0.08	0.36 / -0.71	0.14 / 0.11	0.21 / -0.08	0.36 / 0.71
	D-2	D-3	E-1	D-2	D-3	E-1
None	0.05 / -1.06	0.12 / -0.91	0.11 / -0.97	0.05 / 1.06	0.12 / 0.91	0.11 / 0.97
Baseline	0.07 / -0.65	0.12 / -0.291	0.10 / 0.09	0.07 / 0.65	0.12 / 0.291	0.10 / -0.09
Derivative	0.06 / -0.30	0.25 / -0.43	0.14 / 0.09	0.06 / 0.30	0.25 / 0.43	0.14 / -0.09
	F-1			F-1		
None	0.06 / -0.38			0.06 / 0.38		
Baseline	0.07 / 0.34			0.07 / -0.34		
Derivative	0.08 / 0.32			0.08 / -0.32		

Table 2 SEP (volume percent) and Bias values (SEP / BIAS) for transfer predictions

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References

1. H. Martens, T. Naes, Multivariate Calibration, John Wiley & Sons, 1989.
2. ASTM E1655 Standard Practices for Infrared, Multivariate, Quantitative Analysis.

GLOSSARY

Bias - The average error from a prediction.

PC – Principal Component. Each PC describes some combined variation in the spectral data and is then used in a regression model with the parameter of interest.

PLS - Partial Least Squares (PLS) is a quantitative spectral decomposition technique that is used to build a regression equation relating spectral data to a concentration or quality parameter.

RMSEP – Root Mean Square Error of Prediction, a measure of prediction accuracy on unknown samples not included in the model.

SEP – Standard Error of Prediction, a measure of prediction accuracy on unknown samples not included in the model with the bias removed.

RMSEPCV – Root Mean Square Error of Prediction during Cross Validation, a measure of prediction accuracy based on the calibration samples themselves.

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