091

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Determination of alpha and beta acid concentrations in type-90 hop pellets by near infrared (NIR) spectroscopy and chemometric analysis

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Abstract

Near Infrared (NIR) spectroscopy coupled with chemometric analysis offers the opportunity to eliminate much of the sample preparation and all solvent usage from the alpha and beta acid measurement of T-90 hop pellets. These facts combined with the increased speed of the measurement makes NIR a great potential tool for at-line analysis of hops pellets in the pelletizing plant, warehouse, or in the brewery.

Several Partial Least Squares (PLS) chemometric models were generated using both a dispersive NIR (dNIR) instrument and a Fourier Transform NIR (FT-NIR) instrument to gauge which technology would be the best fit. It was found that both instruments and a wide array of mathematical pre-treatments of the spectra generated prediction models for both alpha and beta acid with acceptable accuracy.

The careful choice of calibration standards such as to avoid spurious correlations resulted in more robust models than shown previously in the literature.[1]

Results: Sample distribution

The distribution of primary reference method values can greatly alter the quality of quantitative chemometric modelling.

For hops the interdependence of alpha and beta acid concentrations must be minimized.

This was accomplished by selecting cultivars of hops that have a wide range of alpha to beta acid ratios, as seen in the histogram in Figure 1.

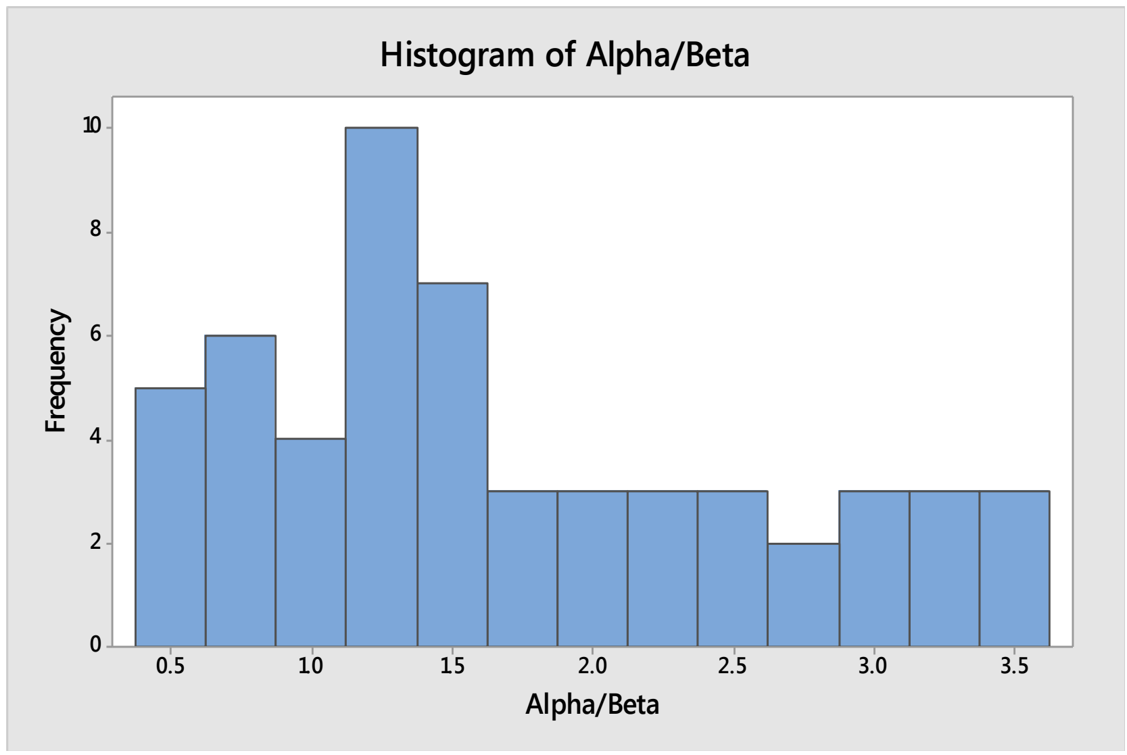


Figure 1: Histogram of alpha to beta acid ratios

57 samples of hops pellets
100 g per sample

Perkin Elmer Frontier FT-NIR

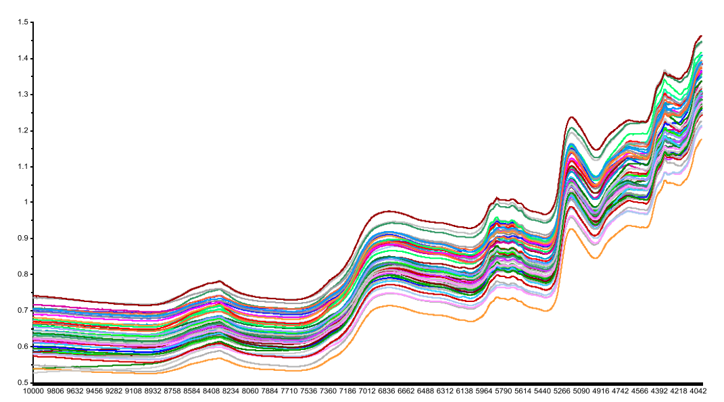
Perten DA7250 dNIR

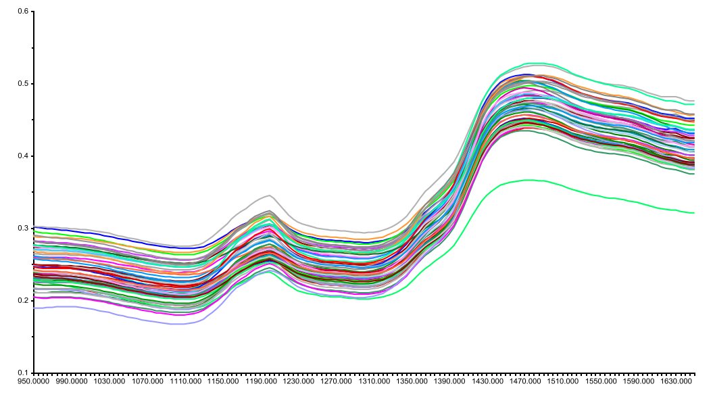
Grind
Extract in Hexane
Dilute in MeOH

4 avg/scan
3 scans

3 s/repack
3 repacks

Mod. Hops-6



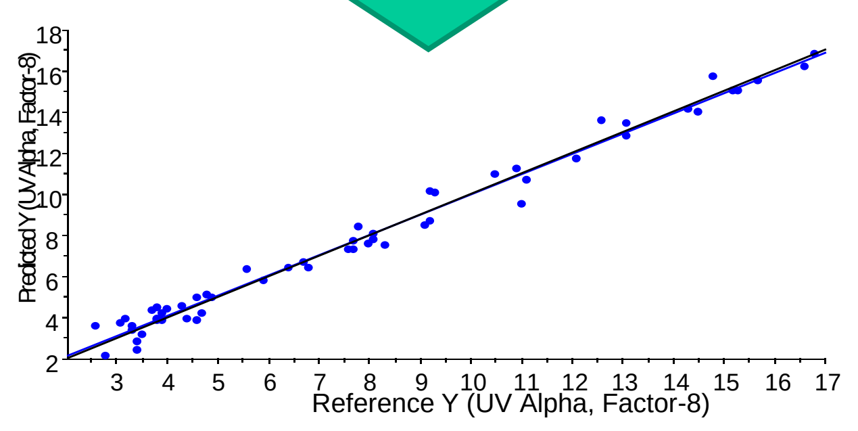


% alpha acid
% beta Acid

10,000-4,000 cm^{-1}
16 cm^{-1} resolution
(1,000-2,500 nm)

950-1,650 nm
5 nm step size

Chemometric Processing:
Mathematical Pretreatments
PLS-R analysis
Full Cross Validation (CV)



Results: FT-NIR

PLS chemometric models predicting the alpha and beta acid values determined by UV/Vis were generated in Unscrambler using many sets of mathematical pre-treatments and wavelength ranges.

Mathematical pre-treatments serve to correct for spectroscopic features associated with the presentation of the sample to the instrument, such as baseline corrections and signal normalizations. Examples of common pre-treatments include standard normal variate (SNV), multipicative scatter correction (MSC), and detrending.

A quality model will have low error (RMSECV), high correlation (R^2), a slope near unity, with as few factors as possible.

Table 1: Validation statistics for a variety of wavelength ranges and pretreatments for alpha acid determination by FT-NIR.

Frequency Range (cm^{-1})	Pretreatment 1	Pretreatment 2	RMSECV	R^2 (CV)	Slope (CV)	Factors
4000-10000	Detrend	SNV	0.726	0.970	0.979	7
4000-10000	Baseline	MSC	0.610	0.978	0.989	8
4000-10000	EMSC		0.706	0.972	0.979	7
4500-9000	Detrend	MSC	0.671	0.975	0.994	7
4500-7250	Detrend	MSC	0.684	0.974	0.991	5

Results: dNIR

Due to the narrower wavelength range available with the dNIR instrument, the entire wavelength range (950-1650 nm) was used for all calibrations.

Only the two most promising treatment strategies from the FT data were compared.

The errors found show that the dNIR instrument may offer a more cost effective option for determining alpha acid content with only modest accuracy losses.

Table 2: Validation statistics for two pretreatment strategies using the dNIR instrument for alpha acid determination.

Pretreatment 1	Pretreatment 2	RMSECV	R^2 (CV)	Slope (CV)	Factors
Detrend	SNV	0.824	0.962	0.966	7
Baseline	MSC	0.760	0.969	0.965	8

Results: beta acid

Chemometric calibrations for % beta acid content of hop pellets is more challenging due to the lower levels present in the sample. A higher number of samples would most likely improve the quality of the calibration.

Table 3: Validation statistics for beta acid determination by both instruments.

Instrument	Pretreatment 1	Pretreatment 2	RMSECV	R^2 (CV)	Slope (CV)	Factors	Outliers excluded
dNIR	Detrend	SNV	0.582	0.88	0.917	10	5
FT-NIR	Detrend	SNV	0.786	0.79	0.853	8	7

Conclusions

Both FT and dispersive instruments proved adequate, returning RMSECV values of 0.61 and 0.76 % alpha acid, respectively.

It is noted that a data set of 57 samples is still considered small for chemometric modeling. Also, due to the high absorptivity of water, it would be best to correct for water content for future development.

Since the accuracy of chemometric modelling is limited by the primary method, using HPLC determined values may improve the statistics of the model.

Beta acid modelling proved to be less robust, probably due to the lower concentrations. Sample choice can be key to the success or failure of a chemometric model.

Acknowledgements

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Reference:

1.) Killeen, D.P.; Anderson, D.H.; Beatson, R.A.; Gordon, K.C.; Perry, N.B. *J. Agri. And Food Chem.* **2014**, *62*, 12521