

# Quantification of the degree of blockiness in pectins using $^1\text{H}$ NMR spectroscopy and chemometrics

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The gelling properties of pectins are known not only to be closely related to the degree of esterification (DE), but also to the distribution of the ester groups. In this study we have examined an experimentally designed series of pectins originating from the same mother pectin and deesterified using combinations of two different enzymatic mechanisms. The degree of esterification and distribution patterns of methyl ester groups have been analyzed using high-resolution (HR)  $^1\text{H}$  nuclear magnetic resonance (NMR) spectroscopy on pectin solutions. Quantitative calibration models using partial least squares (PLS) regression were developed with the ability to predict DE as well as the specific enzyme treatment, expressed as amount of ester groups removed with random and block enzyme, respectively. NMR spectroscopy was able to distinguish between enzyme treatments in simple classification by principal component analysis (PCA). This was due to the spatial structure of pectin together with the methyl ester distribution. Nuclear Overhauser effect spectroscopy (NOESY) experiments confirmed all the general assignments with the expected nuclear Overhauser effect (NOE) correlations. Degree of random deesterification (R) was better predicted than the degree of block deesterification (B). The calibration models for prediction of R obtained on extended inverted signal correction (EISC) processed data gave a root mean square error (RMSE) of cross-validation (CV) of 2 %p with 4 PLS components (latent variables, LV) and a correlation coefficient ( $r$ ) of 0.98. Spectral variable selection using interval PLS (iPLS) was shown to be valuable, as all the calibration models were improved.

**Keywords:** Pectin, NOESY, NMR, Chemometrics, Esterification, Blockiness, Block-enzyme, Random-enzyme