Non-destructive spectroscopy combined with chemometrics as a tool for Green Chemical Analysis of lignocellulose

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Abstract

The trend in the modern world is to replace fossil fuels with green energy sources in order to reduce their environmental impact. Lignocellulosic biomass is a highly abundant renewable resource that can be converted into several types of high-value-added products, including chemicals, biofuels and advanced materials. The biorefinery industry, within this premise, needs to establish quantitative and qualitative analytical methods to better understand lignocellulosic biomass composition and structure, thus analytical science plays crucial role in providing the biorefinery research with key information.

The classical "wet" chemistry methods are currently still preferred to yield accurate and precise results. However, chemical characterization of lignocellulose is a complex procedure involving several steps wherein wood components are isolated or degraded to monomeric fragments (Van Soest method [1], Klason method and their standardized procedures (ASTM D1106-96, NREL /TP-510-42618). These traditional wet laboratory methods are tedious, time consuming, require large sample sizes, involve a considerable consumption of energy and produce a significant amount of hazardous substances.

The advantage of using vibrational spectroscopic techniques, such as attenuated total reflectance Fourier transform mid infrared spectroscopy (ATR-FTIR), is the possibility of evaluating the composition of lignocellulosics by analysing small amounts of samples and developing non-destructive, simple, fast and direct determination methods. The use of this technique meets trends in wood analysis to develop green methods that generate fast responses with no consumption of reagents or solvents, and consequently less environmental impact. Moreover, non-destructive spectroscopy potentially enables the simultaneous analysis of several analytes in a single run, with a consequent saving of reagents and time.

Exploratory and quantitative methods employing vibration spectroscopic techniques require the joint use of chemometric tools. Among spectroscopic methods near-infrared spectroscopy (NIR) in combination with chemometric methods is being intensively applied for classification and quantitative characterization of pulp, wood and non-wood biomass [2-9].

So far, FTIR spectroscopy was mostly applied to qualitative identification and differentiation of woody matrixes by using multivariate statistical analysis including principal component analysis (PCA), hierarchical cluster analysis (HCA) or linear discrimination analysis (LDA) [10-13]. Applications of Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy for quantitative prediction of lignocellulose contents in wood samples are limited [14]. In comparison with FT-NIR spectroscopy it tends to have lower prediction accuracy and robustness [15, 16]. However, the performance of partial least squares regression (PLSR) models for quantitative prediction of wood components could be improved by application of interval variable selection algorithms to the spectral data [17]. Variable selection methods are useful for deleting irrelevant and noisy variables, improving the

performance and robustness of the method, increasing the signal-to-noise ratio, and reducing the model complexity [18]. The interval PLS (iPLS) method [19] is the most common continuous variable selection method based on the continuous screening of informative vectors estimated from multivariate models.

In present study 90 samples of three different wood species (pine, spruce and birch) grown in Estonia were characterized by wet chemistry analysis (acid-soluble and acid-insoluble lignin, metal and organic element contents, extractives) and ATR-FTIR spectroscopy. Obtained chemical and spectroscopic data was subjected for chemometric analysis. For estimation of the place of grow or the source of origin of unknown wood samples the discrimination of wood samples was achieved by using hierarchical cluster analysis (HCA), and principal component analysis (PCA). The linear discrimination analysis (LDA) was also used for classifying the unknown wood samples into the respective class.

Moreover, multivariate calibration was performed based on first derivative of the FTIR spectra for quantitative characterization of wood biomass. PLS multivariate calibration models allied to variable selection methods were developed and cross-validated to quantify the total and acid soluble lignin and the content of extractives. Although a wide range of input parameters (i.e., various wood species) was used, highly satisfactory results were obtained with the root-mean-square errors of 2-5 % for all parameters.

This study shows the potential of non-destructive IR spectroscopy combined with multivariate analysis methods for a quick identification, classification and evaluation of the chemical composition of lignocellulose, providing green alternative to classical “wet” chemical analysis.

References

1. Soest, P.V., *Use of detergents in the analysis of fibrous feeds. II. A rapid method for the determination of fiber and lignin.* Journal of the Association of official Agricultural Chemists, 1963. **46**(5): p. 829-835.
2. Liu, J., et al., *Rapid determination of lignocellulose in corn stover based on near-infrared reflectance spectroscopy and chemometrics methods.* Bioresource Technology, 2021. **321**: p. 124449.
3. Uddin, M.N., et al., *Development of chemometric model for characterization of non-wood by FT-NIR data.* Journal of Bioresources and Bioproducts, 2020. **5**(3): p. 196-203.
4. Pastore, T.C.M., et al., *Near infrared spectroscopy (NIRS) as a potential tool for monitoring trade of similar woods: Discrimination of true mahogany, cedar, andiroba, and curupixá.* Holzforschung, 2011. **65**(1): p. 73-80.
5. Xie, H. and Z.-G. Chen, *Application of genetic simulated annealing algorithm in detection of corn straw cellulose.* Chinese Journal of Analytical Chemistry, 2019. **47**(12): p. 1987-1994.
6. Alves, A., et al., *NIR PLSR model selection for Kappa number prediction of maritime pine Kraft pulps.* Wood Science and Technology, 2007. **41**(6): p. 491-499.
7. Kothiyal, V., et al., *Multi-species NIR calibration for estimating holocellulose in plantation timber.* Wood Science and Technology, 2015. **49**(4): p. 769-793.
8. Fišerová, M., et al., *Using niranalysis for determination of hardwood kraft pulp properties.* Wood Research, 2012. **57**(1): p. 121-130.
9. Poke, F.S. and C.A. Raymond, *Predicting Extractives, Lignin, and Cellulose Contents Using Near Infrared Spectroscopy on Solid Wood in Eucalyptus globulus.* Journal of Wood Chemistry and Technology, 2006. **26**(2): p. 187-199.
10. Sharma, V., et al., *On the rapid and non-destructive approach for wood identification using ATR-FTIR spectroscopy and chemometric methods.* Vibrational Spectroscopy, 2020. **110**: p. 103097.
11. Herrera, R., et al., *Non-destructive determination of core-transition-outer wood of Pinus nigra combining FTIR spectroscopy and prediction models.* Microchemical Journal, 2022. **179**: p. 107532.
12. Toscano, G., et al., *FTIR spectroscopy for determination of the raw materials used in wood pellet production.* Fuel, 2022. **313**: p. 123017.
13. Müller, G., et al., *FTIR-ATR spectroscopic analyses of changes in wood properties during particleand fibreboard production of hardand softwood trees.* BioResources, 2009. **4**(1): p. 49-71.

14. Zhou, C., et al., *Prediction of mixed hardwood lignin and carbohydrate content using ATR-FTIR and FT-NIR.* Carbohydrate Polymers, 2015. **121**: p. 336-341.
15. Chen, H., et al., *Qualitative and quantitative analysis of wood samples by Fourier transform infrared spectroscopy and multivariate analysis.* Carbohydrate Polymers, 2010. **82**(3): p. 772-778.
16. Schultz, T. and D. Burns, *Rapid secondary analysis of lignocellulose: comparison of near infrared (NIR) and Fourier transform infrared (FTIR).* Tappi journal, 1990. **73**(5): p. 209-212.
17. Miaw, C.S.W., et al., *Determination of main fruits in adulterated nectars by ATR-FTIR spectroscopy combined with multivariate calibration and variable selection methods.* Food Chemistry, 2018. **254**: p. 272-280.
18. Andersen, C.M. and R. Bro, *Variable selection in regression—a tutorial.* Journal of chemometrics, 2010. **24**(11-12): p. 728-737.
19. Norgaard, L., et al., *Interval partial least-squares regression (iPLS): A comparative chemometric study with an example from near-infrared spectroscopy.* Applied spectroscopy, 2000. **54**(3): p. 413-419.