Rapid Biomass Analysis: New Analytical Methods Supporting Biomass Pretreatment Research

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1. Abstract

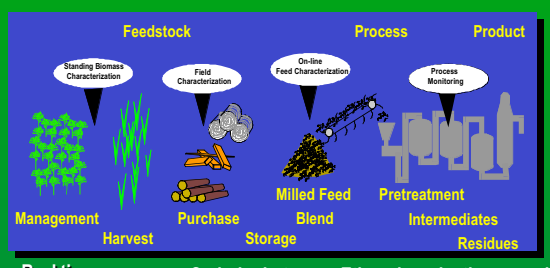
The ability to obtain an accurate chemical composition of biomass and biomass-derived samples using rapid and inexpensive methods is a key element supporting commercialization of processes that convert biomass to fuels and chemicals. New techniques are being developed at NREL that combine Near InfraRed (NIR) spectroscopy and Projection to Latent Structures (PLS) multivariate analysis for the rapid chemical characterization of corn stover and stover-derived solids. These rapid techniques can provide significant savings in time and money with precision and accuracy that matches traditional wet chemical methods. They also support and improve research by providing levels of information that would have been too costly to pursue using traditional methods.

Aspects of NIR/PLS method development are described including the collection of appropriate calibration samples, the development of robust spectroscopic methods, the importance of quality calibration data, the development and validation of multivariate analysis equations and the use of appropriate QA/QC techniques. Application of rapid analysis tools to the chemical characterization of dry solids, slurries and liquid samples produced during dilute acid pretreatment of corn stover are presented.

2. Why are Rapid Analysis Methods Needed?

- Faster
  - Minutes instead of days
  - Minimal sample preparation
- Cheaper
  - About $10 per sample
  - Compared to $800-$2,000 for wet analysis
- Better
  - Calibrated using best methods available
  - No loss of precision or accuracy relative to traditional methods
  - Less operator dependent (than traditional wet chemistry methods)
  - Provides levels of information not previously obtainable
- Useful in industrial applications

3. What are the Industrial Applications of Rapid Biomass Analysis?



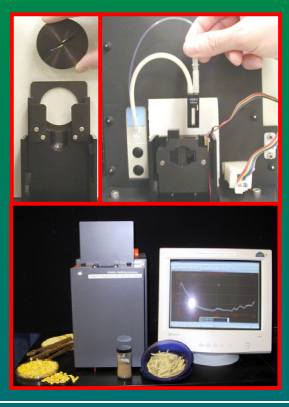
- Real time monitoring
- Carbohydrates
- Lignin
- Moisture
- Protein
- Cell mass
- Ethanol production capacity
- Heating value

Slide courtesy of B. Meglen

4. What are the Advantages of Using NIR Spectroscopy for Biomass Analysis?

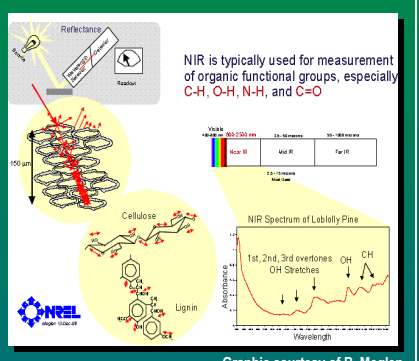
Advantages of NIR/PLS

- Minimal sample preparation
- Rugged instrument, adaptable to industrial environments, including on-line and at-line applications
- Scanning options, including reflectance, transmission, and transflectance
- Non-destructive technique
- Ability to analyze bulk samples



5. How Does NIR Spectroscopy Gather Biomass Constituent Information?

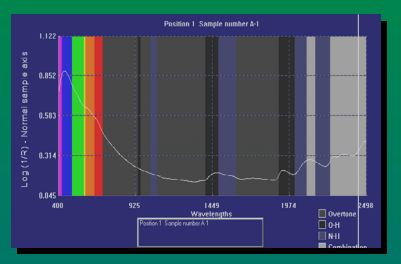
- Measures organic functional groups in the visible and near-infrared spectrum (400 nm–2500 nm)
- Spectra contains overtones and combinations from stretching and bending of bonds in molecules
- Contains all of the constituent information necessary to calibrate a biomass NIR/PLS method



Graphic courtesy of B. Meglen

6. How is a PLS Method Built from NIR Spectra?

- Multivariate model development software
  - Vision®
  - WinISI®
- Loading-score method
  - Loadings are spectral patterns
  - Scores are coefficients
  - Converts 2-dimensional spectra into multiple dimensional space by defining the "spectra to data" relationship in n-dimensional space



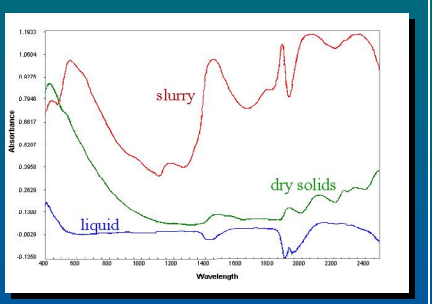
Sample Spectrum

7. What is Required to Develop a NIR/PLS Method?

- Calibration samples
  - Robust model requires approximately 100 samples
  - Should reflect the composition and variance expected in the unknowns
  - Concentration of major constituents must vary independently of one another
- Chemical characterization
  - Determines precision and accuracy of new method
  - Samples should be well characterized
  - Requires appropriate analytical methods
- Rapid technique
  - Determines speed and cost of new method
  - Should be robust, reproducible, sensitive to compositional differences
- Multivariate analysis tools
  - Translates spectroscopic data into compositional data
- QA/QC
  - Calibration checks (well characterized blind samples or standard reference materials)
  - Sample screening (use of outlier flags)

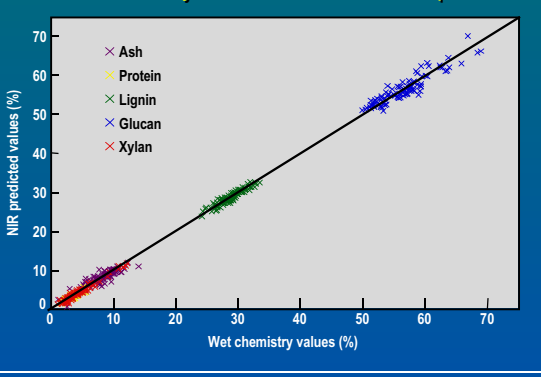
8. NIR Spectra and Math Treatments

- Math treatments used on raw spectra to minimize particle size effects, effective path length variation, and environmental fluctuations include:
  - First derivative: eliminates baseline offset
  - SNV (Standard Normal Variate): scatter correction
  - Detrend (1º polynomial): removes baseline offset and slope



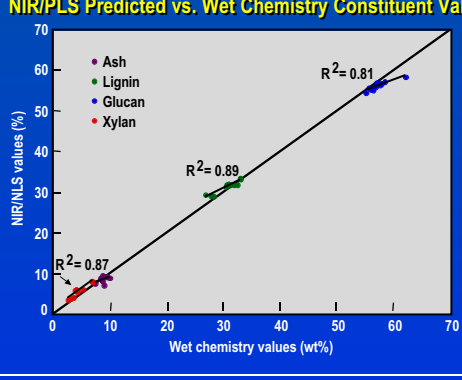
9. Predictive Quality using *Cross Validation* Predictions for Major Constituents in a Dry Solids Model

NIR/PLS Predicted vs Wet Chemistry Constituent Values for stovint5.eqa calibration samples



10. Predictive Quality using *Blind Validation* Samples Predicted on a Dry Solids Model

NIR/PLS Predicted vs. Wet Chemistry Constituent Values for Validation Samples

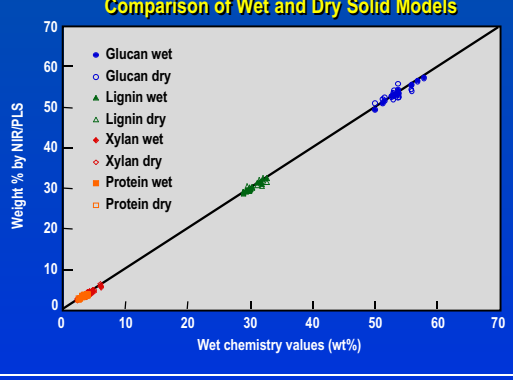


Actual % Difference for a Representative Blind Sample
Sample ID: P020502cs

% Ash	- 0.10
% Protein	0.10
% Lignin	0.57
% Glucan	1.08
% Xylan	- 0.22
% Galactan	0.13
% Arabinan	- 0.77
% Mannan	- 0.63
% Mass closure	0.16

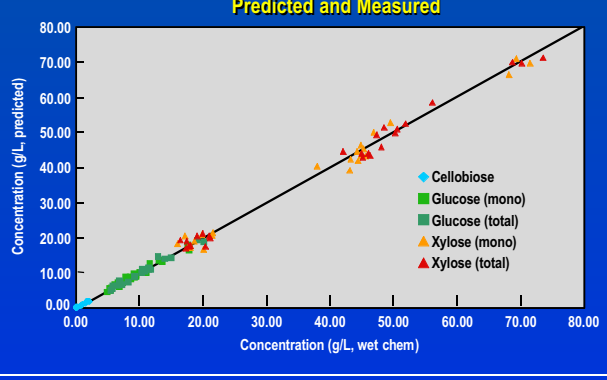
11. Comparison of Slurry Method and Dry Solids Method (Using Common Samples)

Comparison of Wet and Dry Solid Models



12. Predictive Quality using *Cross Validation* Predictions for Major Constituents in a Liquids Model

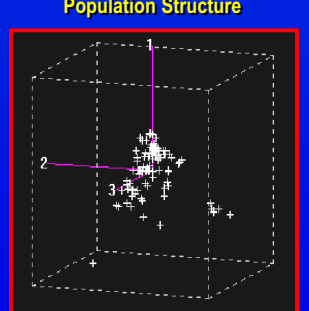
Predicted and Measured



13. How Is Method Performance Measured?

- Outlier flags
  - Predicted samples must fall within the calibration range
  - Mahalanobis Number (Global H) < 3.0
    - 2.5 standard deviations
    - 99.5% population inclusion
- Validated samples are occasionally run and the predictions are compared to historical values
- Method is expanded or improved if necessary

3-Dimensional Example of a Population Structure



14. Summary

- Rapid analysis of biomass with NIR/PLS
- Provides significant savings in time and money
- Maintains precision and accuracy of traditional methods
- Provides a level of information previously unobtainable
- Is an enabling technology for biomass utilization
- It is applicable to a wide variety of biomass and biomass-derived products
- Offers simple sample screening and method expansion
- Currently supports NREL research efforts
- Useful for interaction with industrial partners

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