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Exploring the use of near infrared reflectance spectroscopy to predict minerals in straw

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ABSTRACT

The use of near infrared reflectance spectroscopy (NIRS) to predict minerals concentration (K, Na, Ca, Mg, Fe) in straw samples was investigated in this study. A total of 222 straw samples were collected in rural area of most provinces in China. Two types of straw samples were prepared, directly cut specimens and oven-dried, milled specimens. The spectra of two kinds of samples were employed to correlate with minerals concentration. Different spectral pre-treatments and regression methods were trialled to optimize the calibration. Coefficient of determination in prediction (R_v^2) and standard error of prediction (SEP) were 0.69, 0.54, 0.73, 0.79, 0.41 and 3.77 mg g^{-1}, 0.69 mg g^{-1}, 0.58 mg g^{-1}, 0.31 mg g^{-1}, 0.11 mg g^{-1} for directly cut straw; 0.85, 0.70, 0.82, 0.85, 0.63 and 2.35 mg g^{-1}, 1.46 mg g^{-1}, 0.47 mg g^{-1}, 0.27 mg g^{-1}, 0.13 mg g^{-1} for dried milled samples, respectively.

1. Introduction

Utilization of straw resources for energy production was proved to be one of the rational choices in terms of economic, energetic and environmental impact. However, experiences have shown that straw is rather problematic as a fuel for heat and power production. Comparing with coal, straw has a high percentage of potassium, chlorine, and silicon as well as minor amounts of Ca, Mg, Fe and Na [1]. Utilization of straw and straw derived pellet fuels was hampered by corrosion, fouling and slagging problems during combustion, gasification and pyrolysis [2,3]. Particularly for directly fired combined cycle, alkali metals in gas phase may lead to serious corrosion of gas turbine.

Acquisition of characteristics of straw prior to chemical/biochemical conversion is essential for equipment design and process simulation. Procedures for sample preparation and determination of major and minor elements in straw have been specified in the European Committee for Standardization (CEN) standards for solid biofuel. Grinding and chemical analyses are labour intensive and time consuming and result in high cost. From engineering practice point of view, a rapid analysis approach is indispensable for immediate determination of relevant components such as potassium.

Near infrared reflectance spectroscopy, which is based on correlation between chemical properties and absorption of light at different wavelength from 780 nm to 2500 nm, is a rapid, non-destructive, cost-effective predictive technique [4]. Extensively used for quantitative and qualitative analysis of organic matter in the fields of agriculture, petrochemicals, food and pharmaceuticals, NIRS is beginning to be applied to the analysis of minerals along with the advancement of chemometrics. From theoretical aspect, since minerals do not absorb in near infrared region, correlations between spectra and minerals contents are not reliable. However, researches found that NIRS had become more and more popular and suited for detecting minerals in plant tissue.

Earlier works reporting NIRS measurement of minerals were mainly focused on analysis of hay samples [5–8] and natural grass [9]. Ciavarella and Batten [10] reported NIRS calibrations for potassium in grape petioles, grape leaves, rice shoots and orange leaves. When tested on validation set of samples the NIRS calibrations accounted for 96%, 89%, 93%, and 85% of the concentration of Hallett et al. [11] evaluated the effectiveness of NIRS at predicting Al, Ca, Fe, K, Mg, and Mn concentrations in white pine and red oak foliage. Predictions were satisfactory for all these minerals except for Fe. Cozzolino and Moron [12] analyzed Na, S, Cu, Fe, Mn, Zn and B in two types of legumes. Good results were also obtained in prediction of minerals in tobacco leaves [13,14]. Although the accuracy was not high enough for routine analysis, calibration and validation statistics showed the potential of NIRS to predict trace minerals in legumes, particularly B, Na and S.

The first objective of this study was to examine whether NIRS can predict minerals in straw samples. Then equations based on directly cut samples and those based on dried milled samples were compared in precision and robustness.

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2. Materials and methods

2.1. Straw samples

During 2004 and 2006, a total of 222 straw samples (including 172 rice straw samples and 50 wheat straw samples), which varied in locations, varieties, soil characteristics, growing climates, harvest methods and farm managements, were collected from 24 provinces of China (as shown in Fig. 1). Number of samples harvested in 2004, 2005 and 2006 were 4, 7 and 211, respectively. From the time of sampling, samples were cut to about 5 cm long, blended, and divided into three parts. While one part of the samples were subjected to spectral analysis, other two were oven-dried for 24 h at 70 °C and ground using a ZM100 mill (1 mm sieve, Retsch GmbH & Co., KG) for spectral analysis and reference analysis, respectively. Before the time of analysis, all samples were stored in airtight ziplock bags at shady area. Arranged form the lowest to the highest by actual minerals contents, every fourth samples were selected for validation tests and remainder kept for calibration.

2.2. Reference analysis

Straw samples were digested using Ethos Touch Control advanced microwave labstation (Milestone Italy, equipped with HPR 1000/6S rotor) with 1200 W microwave oven. As recommended by the manufacturer, the microwave-assisted acid digestion of straw was performed according to the Milestone research report (code 18). About 0.5 g of dried milled straw sample was digested with 6 ml of concentrated nitric acid and 1 ml of concentrated hydrogen peroxide in a closed reactor in microwave oven. The resulting solution was quantitatively transferred into a 100 ml calibrated flask, where it was diluted to volume with ultra pure deionized water. Blanks were prepared with the same reagents undergoing a similar treatment. Finally, all solutions were stored in polyethylene bottles at 4 °C.

For K, Na, Ca, Mg and Fe quantification, 0.5 ml, 1 ml, 5 ml, 2 ml and 5 ml of the resulting solutions were diluted in a 50 ml calibrated flask, and analyzed by flame atomic absorption spectrometry (AAS Vario6, Analytik Jena AG Germany). In Ca and Mg quantification, 1 ml of lanthanum chloride solution was added to the calibrated flask as releasing agent.

2.3. NIRS analysis

Spectral analysis was conducted on a NIRSystem 6500 monochromator in reflectance mode, which is able to collect spectra from 400 to 1098 nm (visible to short-wave near infrared regions) with a silicon detector and from 1100 to 2500 nm (long-wave near infrared region) with a PbS detector. The directly cut samples were placed into a natural product cup and scanned in five replicates. The dried milled samples were placed into a quarter sample cup, scanned in three replicates. Room where the monochromator work was kept unventilated and temperature was controlled between 20 °C and 23 °C by an air conditioner. Spectra were recorded in Log (1/R) from 400 nm to 2500 nm with 2 nm intervals. The repetitious spectra from a sample were averaged before calibration.

2.4. Calibration development and validation

WinISI 1.5 software was used for data analysis of calibration and validation. Five scatter correction methods were provided, Standard Normal Variate (SNV), Detrending (DT), Combination of SNV and DT (SNVD), Standard multiple scatter correction (SMSC) and weighted multiple scatter correction (WMSC) [15]. Derivative treatment includes (0,0,1,1), (1,4,4,1) and (2,4,4,1), where the first number indicates the order of derivative, the second number is the gap in data points over which the derivative is calculated, the third and the fourth number refer to the number of the data points used in first and second smoothing, respectively. Principal component regression (PCR), partial least square (PLS) and modified partial least square (MPLS) were performed to develop the calibration equations. The PLS methods performed a principal component analysis decomposition in such a way that reference data is used for an optimal decomposition of NIR data and then performs regression equations; Modified PLS (MPLS) method standardizes residuals values before calculate next regression term; While PCR uses only spectral information in constructing principle compo-

Fig. 1. Provinces involved in straw sampling.