Rona Teknik Pertanian, 10(1)
April 2017

JURNAL RONA TEKNIK PERTANIAN

ISSN : 2085-2614; e-ISSN 2528 2654

JOURNAL HOMEPAGE : http://www.jurnal.unsyiah.ac.id/RTP

The Application Of Fourier Transform Infrared Photoacoustics Spectroscopy (FTIR-PAS) For Rapid Soil Quality Evaluation

Ichwana*[1)], Zulkifli Nasution[2], Agus A. Munawar[1],
[1]Department of Agricultural Engineering, Syiah Kuala University, Banda Aceh, Indonesia.
[2]North Sumatra University, Medan, Indonesia.
*E-mail: ichwana.ramli@unsyiah.ac.id

Abstract

The major function of soil is to provide fundamental natural resources for survival of plants, animals, and the human race. Soil functions depend on the balances of its structure and composition, well as the chemical, biological, and physical properties. It is become one important key aspect and routine activity in crop management system. To monitor and determine soil quality properties, several methods were already widely used in which most of them are based on solvent extraction followed by other laboratory procedures. However, these methods often require laborious and complicated processing for samples. They are time consuming and destructive. In last few decades, the application of infrared spectroscopy as non-destructive technique in determining soil quality properties (C, N, P and K) rapidly and simultaneously. Fourier transform infrared spectrum (FTIR) were acquired in wavelength range from 1000 to 2500 nm with applying photo-acoustic spectroscopy (PAS). Least square-support vector machine regression (LS-SVM) approach was then applied to predict soil quality properties. The results showed that C and N can be predicted accurately using FTIR-PAS whilst other parameters (P, K, Mg, Ca, S) can be predicted with maximum RPD index is 1.9. Moreover, soil clay, moisture and soil microbes were feasible to be detected by using FTIR-PAS combining with discriminant analysis (LS-DA) or cluster analysis (CA). It may conclude that FTIR-PAS technology can be used as a real time method in monitoring soil quality and fertility properties.

Keywords* : *infrared, soil, spectroscopy, photo-acoustic

Aplikasi Dari *Fourier Transform Infrared Photoacoustics Spectroscopy* (FTIR-PAS) Untuk Evaluasi Kualitas Tanah

Ichwana*[1)], Zulkifli Nasution[2], Agus A. Munawar[1],
[1]Program Studi Teknik Pertanian, Universitas Syiah Kuala, Banda Aceh, Indonesia.
[2]Universitas Sumatera Utara, Medan, Indonesia.
*E-mail: ichwana.ramli@unsyiah.ac.id

Abstrak

Tanah merupakan media tumbuh tanaman dan berperan dalam menjaga keseimbangan alam. Evaluasi kualitas dan kesuburan tanah menjadi hal penting dan merupakan pekerjaan rutin pada crop management system. Untuk memonitor dan menentukan kualitas tanah, beberapa metode telah diterapkan. Akan tetapi, metode tersebut berbasis pengukuran laboratorium yang melibatkan bahan kimia, memerlukan waktu yang lama dan kurang efektif pada aplikasinya. Infrared spectroscopy muncul sebagai salah satu teknologi yang cepat, simultan dan ramah lingkungan untuk digunakan dalam evaluasi kualitas dan kesuburan tanah dengan memprediksi nutrisi tanah yang utama berupa C, N, P dan K. Spektrum transmisi infrared (IR) diakuisisi pada panjang gelombang 1000-2500 nm dengan menerapkan metode photo-acoustic spectroscopy (PAS). Pendekatan metode Least square-support vector machine regression (LS-SVM) digunakan untuk memprediksi parameter nutrisi tanah. Hasil studi menemukan bahwa parameter C dan N pada tanah dapat diprediksi dengan sempurna karena C-N mengalami stretching akibat serapan gelombang IR. Sedangkan unsur nutrisi lain seperti P, K, Mg, Ca, S dapat diprediksi dengan maksimum residual predictive deviation (RPD) index maksimum 1.9. Lebih lanjut, lempung tanah, air tanah, dan mikroba tanah kemungkinan dapat diklasifikasi dengan baik dengan metode IR-PAS dan bantuan metode klasifikasi least-square discriminant analysis (LS-DA) dan cluster analysis (CA). Berdasarkan hasil studi, dapat disimpulkan bahwa teknologi FTIR-PAS dapat digunakan untuk real-time monitoring kualitas dan kesuburan tanah.

Kata kunci: infrared, tanah, *spectroscopy*, *photo-acoustic*

INTRODUCTION

As all we know that a major function of soil is to provide fundamental natural resources for survival of plants, animals, and the human race (Shi et al., 2014). The functions soil depend on the balances of its structure and composition, well as the chemical, biological, and physical properties. These balances are, however, being disrupted by highly accumulated heavy metals in soils, due to anthropogenic activities, such industrial pollutants, pesticides, livestock wastewater, mine drainage, and petroleum contamination (Khan et al., 2008; Salazar et al., 2012). Human activities, such as mining, transportation, sewage disposal and fertilizing, have been posing an ongoing threat to the soil health (Wang et al., 2014). Moreover, the consumption of metal-polluted crops (e.g., rice, corn and soybean) grown in agricultural soils greatly raises the potential risks of food security and human health (Zhuang et al., 2009).

Precision farming and similar modern approaches for efficient management of land resources require fast and accurate methods for soil characterization. Standard laboratory techniques for soil analysis are labor and time-consuming, and extensive research has been devoted to the development of new methods for rapid screening of large number of soil samples (Viscarra et al., 2008; McBratney et al., 2006). Among the approaches investigated, spectroscopy, both in the near-infrared (NIR) (Ben Dor et al., 2005; McCarty et al., 2002; Daniel et al., 2003) and mid-infrared ranges, has yield very promising results (Viscarra et al., 2006). While NIR spectra consist of non-specific overtones and tone combinations that are difficult to interpret, mid-infrared spectra consist of specific bands that can be directly associated with soil constituents.

During the last few decades, Fourier transform infrared (FTIR) spectroscopy has become one of the most promising and used non-destructive methods of analysis in many field areas including in agriculture due to its advantage; simple sample preparation, rapid, and environmental friendly since no chemicals are used. More importantly, it has the potential ability to determine multiple quality parameters simultaneously. Numerous studies have been carried out to investigate and apply FTIR in quality assessment of agricultural sectors. Since

FTIR itself cannot reveal chemical information in the spectra, chemometrics is required to extract the information about quality attributes buried on IR spectra through a process called multivariate calibration from which a mathematical relationship between IR spectra and the measured quality parameter will be revealed to determine desired quality attributes (Nicolai et al., 2007; Cozzolino et al., 2011).

Changwen et al. (2011) recently suggested the use of photo-acoustic (PAS) in combination with FTIR spectroscopy for soil identification and classification. Photo-acoustic spectroscopy is based on absorption induced heating of the sample, which produces pressure fluctuations in a surrounding gas. These fluctuations are recorded by a sensitive and particular microphone, and constitute the PAS signal. The major advantage of photo-acoustic spectroscopy is that it is suitable for highly absorbing samples, such as soils, without any special pre-treatment (McClelland et al., 2001).

Therefore, the objective of the present work is to systematically study the application of Fourier transform infrared technology combined with photo-acoustic (FTIR-PAS) as a non-destructive method for predicting C, N, P, K and other soil quality parameters. The models were established based on IR spectroscopic data after multiplicative scatter correction (MSC) using Least square-support vector machine regression (LS-SVM) approach.

MATERIALS AND METHODS

Spectra acquisition

The IR spectra of soil samples were collected as a bulk in form of transmittance spectra using self-developed FTIR instrument. Photo-acoustic was chosen as a basic IR acquisition. Soil samples, amounted 40 to 50 grams, were placed manually upon the cup (sample holder), multi-layered and piled with minimum air space among samples to minimize noises. This cup will set to rotates during spectra acquisition. Diffuse reflectance spectra in wavelength range of 1000 – 2500 nm with the increment of 2 nm resolution will be acquired 64 times and averaged.

FTIR-PAS spectra pre-processing

Prior to prediction model development, different spectra data pre-processing were applied to the spectra data. The spectra data acquired from the FTIR instrument contain spectra background information and noises which are interfered desired relevant attributes information. Interfering spectral parameters, such as light scattering, path length variations and random noise resulted from variable physical sample properties or instrumental effects need to be eliminated or reduced in order to obtain reliable, accurate and stable calibration models (Reich, 2005; Cen and He, 2007). Thus, it is very necessary to pre-process spectral data prior to modeling. This work presented prediction models to predict soil quality properties derived from untreated spectra (identified as none) and from six different pre-processing methods including Mean centering (MC), Mean normalization (MN), De-trending (DT), Multiplicative scatter correction (MSC), Standard normal variate (SNV), and Orthogonal signal correction (OSC) (Munawar et al., 2013; Munawar et al., 2016).

Calibration using SVMR models

Support vector machine regression (SVMR) approach was used to develop the prediction model (calibration) for selected quality parameters using soil samples spectra from calibration set. K-fold cross validation will be applied during calibration to quantify the model performance and to prevent over fitting. The optimum wavelengths for each quality attributes prediction will be selected based on regression coefficients curve derived from the calibration model (Cen and He, 2007; Sinelli et al., 2008). The capability of calibration models will be justified by predicting quality attributes using external samples from prediction dataset.

Prediction model performance evaluation

Predictive capabilities of these calibration models and their validation were evaluated by using several statistical parameters: (i) the coefficient of determination (R2) of calibration and validation representing the proportion of variance (fluctuation) of the response variable that is explained by the spectral features in the calibration or validation model. It also measure how certain one can be in making predictions from a certain models (Nicolai et al., 2007), (ii) the prediction error which is defined as the root mean square error of calibration (RMSEC), root mean square error of cross validation prediction (RMSECV) and the root mean square error prediction (RMSEP), (iii) the error difference between RMSEC and RMSECV or RMSEC and RMSEP (Jha, et al., 2006; Flores, et al., 2009), and (iv) the residual predictive deviation (RPD) providing the ratio between the standard deviation of the target variable and the standard error of prediction performance RMSECV or RMSEP. RPD is a commonly used to interpret and compare NIR calibration models (Fearn, 2002; Kapper, et al., 2012). The higher the RPD, the greater is the probability of the model to predict desired chemical constituent in samples set accurately (Sinelli et al., 2008). Finally, the number of factors or latent variables used in the prediction models wase also taken into account. Fewer latent variables are preferable to avoid modeling noise signal. Apparently, the ideal model should have a high R2 using a few latent variables, a high RPD, a low error prediction value (RMSEC, RMSECV or RMSEP) and small difference between RMSEC and RMSECV or RMSEC and RMSEP (Schmilovitch et al., 2000; Nicolai et al., 2007; Munawar et al., 2016).

Software

All spectra data processing and regression approaches were carried out using software packages namely The Unscrambler® X version 10.3 (CAMO software AS, Oslo-Norway).

RESULTS AND DISCUSSION

FTIR spectra features

Typical spectra and its spectra derivative after pre-processing for soil in IR region (1000-2500 nm) is shown in Fig.1. IR was sensitive to the concentrations of organic materials which involved the response of the molecular bonds of O-H, C-H, C-O and N-H. These bonds are subject to vibrational energy changes in which two vibration patterns exist in these bonds including stretch vibration and bend vibration. The presence of strong water absorbance bands were observed at around 1460 nm and 1930 nm because of O-H tone combination and first overtone of water. Absorption bands at around 1400 nm and 1900 nm were noted to be associated with water absorption (Workman & Weyer, 2008). Moreover, the absorption bands in the range of 2200 - 2300 nm is suggested to be related to C-H-O structures; whilst absorption bands at around 1400, 1800 and 2100 nm are associated with mineral content (Cen & He, 2007).

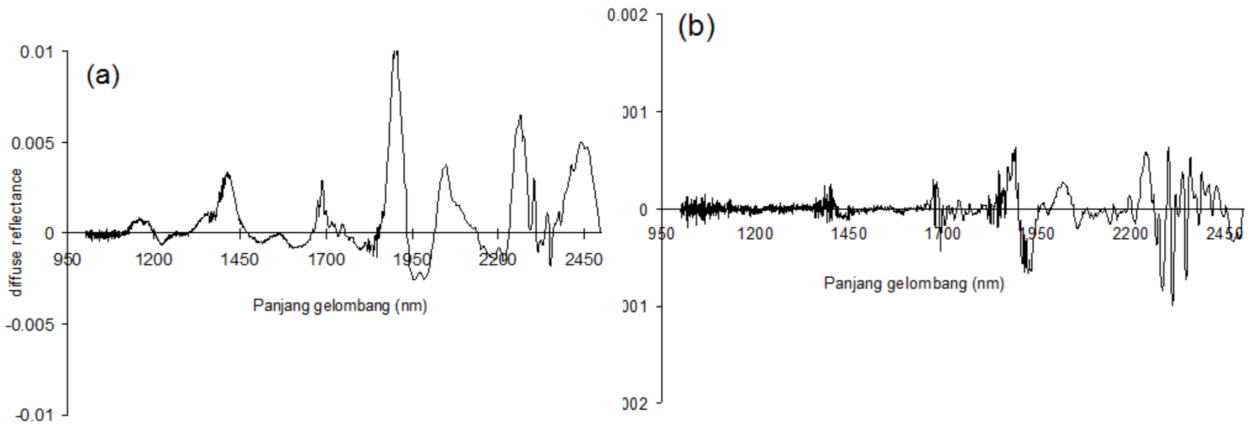

Fig.1. typical spectra of soil in wavelength range from 1000 to 2500 nm.

Calibration and prediction results SVMR approaches

A nonlinear regression approach for soil quality parameters was attempted by support vector machine regression (SVMR) method. It can map the complex and nonlinear data into a higher dimensional feature space, where the nonlinear problem could be solved. The input data subjected into SVMR approach was based on the principal component analysis (PCA) results of corrected spectra where the number of PCs that can explain all variance nearly to 99% or 100%. In this study, it is found that four principal components (4 PCs) of PCA are sufficient to represent maximum variance (99%) of both MSC and SNV spectroscopic data. Thus, score results of first 4 PCs were used as inputs for the SVMR.

SVMR provided superior results for soil quality prediction. The RPD index is above 3, we may argue that C can be predicted well by SVMR. On the other hand, other quality parameters such as P, K, Mg, Cu, S probably can be predicted with maximum RPD index result is 1.9.

It is obvious that soil is a biological object containing a great quantity of hydrogenous bonds. FTIR-PAS spectroscopy is based on overtone and combination of fundamental vibration from these bonds. Hence, the correlation between the spectra and soil quality attributes could be nonlinear. The source of nonlinearity may vary widely, and is difficult to identify. However, by contrast, some others source of nonlinearity requires the use of special nonlinear calibration approach. This means that classical regression methods are not always the most suitable option. Similar finding also reported by other researchers that nonlinear regression approach achieved optimal results compare to linear regression. It is clearly found from our present study that nonlinear regression approach, like SVMR can be used as a regression approach.

CONCLUSION

The overall calibration and prediction results sufficiently demonstrate that FTIR-PAS spectroscopy can be successfully used in determination soil quality parameters. The evaluation performance results of SVMR with respect to some selected quality parameters can be predicted with maximum RPD index is 3.1 for C prediction while for other quality parameters such as N, P, K, Cu, S can be predicted with maximum RPD index of 1.9. Nonetheless, the obtained results in this present study show the high potential of FTIR-PAS for determination and monitoring of soil quality parameters rapidly and simultaneously.

REFERENCES

Blanco, M., Coello, J., Iturriaga, H., Maspoch, S., & Pages, J. (2001). NIR calibration in non-linear systems: Different PLS approaches and artificial neural networks. *Chemometrics and Intelligent Laboratory System*, 50, 75-82.

Bobelyn, E., Serban, A. S., Nicu, M., Lammertyn, J., Nicolai, B. M., & Saeys, W. (2010). Postharvest quality of apple predicted by NIR-spectroscopy: Study of the effect of biological variability on spectra and model performance. *Postharvest Biology and Technology*, 55, 133-143.

Cen, H. Y., Bao, Y. D., He, Y., & Sun, D. W. (2007). Visible and near infrared spectroscopy for rapid detection of citric and tartaric acids in orange juice. *Journal of Food Engineering*, 82, 253–260.

Cen, H., & He, Y. (2007). Theory and application of near infrared reflectance spectroscopy in determination of food quality. *Trends in Food Science & Technology*, 18, 72-83.

Chang, C.W., Laird, D.A., Mausbach, M.J., Hurburgh Jr., C.R., 2001. Near-infrared reflectance spectroscopy-principal components regression analyses of soil properties. Soil Sci. Soc. Am. J. 65 (2), 480–490.

Chen, J. Y., Iyo, C., Terada, F., & Kawano, S. (2002). Effect of multiplicative scatter correction on wavelength selection for near infrared calibration to determine fat content in raw milk, *J. Near Infrared Spectrosc*. 10, 301-306.

Chen, L., Xue, X., Ye, Z., Zhou, J., Chen, F., & Zhao, J. (2011). Determination of Chinese honey adulterated with high fructose corn syrup by near infrared spectroscopy. *Food Chemistry*, 128, 1110–1114.

Clark, R. N. (1999). Spectroscopy of rocks and minerals and principles of spectroscopy. In Rencz, A. N (Ed.), *Manual of remote sensing*. (*Volume 3): Remote sensing for the earth sciences,* (pp. 3-58). New York: John Wiley and Sons, (Chapter 1).

Cozzolino, D., Cynkar, W. U., Shah, N., & Smith, P. (2011). Multivariate data analysis applied to spectroscopy: Potential application to juice and fruit quality. *Food Research International*, 44, 1888-1896.

Gomez, A. H., He, Y., & Pereira, A. G. (2006). Non-destructive measurement of acidity, soluble solids and firmness of Satsuma mandarin using Vis/NIR-spectroscopy techniques. *Journal of Food Engineering*, 77, 313–319.

Hue, C., Gunata, Z., Bergounhou, A., Assemat, S., Boulanger, R., Sauvage, F.X & Davrieux, F. (2013). Near Infrared Spectroscopy as a New Tool Determine Cocoa Fermentation Levels Through Ammonia Nitrogen Quantification. *Food Chemistry*, 240-245.

Jaiswal, P., Jha, S. N., & Bharadwaj, R. (2012). Non-destructive prediction of quality of banana using spectroscopy. *Scientia Horticulturae*, 135, 14-22.

Jha, S. N., Kingsly, A. R. P., & Chopra, S. (2006). Non-destructive determination of firmness and yellowness of mango during growth and storage using visual spectroscopy. *Biosystems Engineering*, 94, 397-402.

Kapper, C., Klont, R.E., Verdonk, J.M.A.J., & Urlings, H.A.P. (2012). Prediction of pork quality with near infrared spectroscopy (NIRS) 1.Feasibility and robustness of NIRS measurements at laboratory scale. *Meat Science*, 91, 294-299.

Kavdir, I., Lu, R., Ariana, D., & Ngouajio, M. (2007). Visible and near–infrared spectroscopy for nondestructive quality assessment of pickling cucumbers. *Postharvest Biology and Technology*, 44, 165–174.

Khan, S., Q. Cao, Y.M. Zheng, Y.Z. Huang, Y.G. Zhu, Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China, Environ. Pollut. 152 (2008) 686–692.

Kooistra, L., Wehrens, R., Leuven, R., Buydens, L., 2001. Possibilities of visible-near-infrared spectroscopy for the assessment of soil contamination in river floodplains. Anal. Chim. Acta. 446 (1–2), 97–105.

Munawar, A.A., Hoersten, D.v., Pawelzik, E., Wegener, J.K & Moerlein, D. (2016). Rapid and non-destructive prediction of inner quality attributes of intact mango using Fourier-transform infrared and chemometrics. J. Engineering in Agriculture, Environment and Food, 9 (1): 208 – 215.

Munawar, A.A., Hoersten, D.v., Pawelzik, E., Wegener, J.K & Moerlein, D. (2013). Prediction of quality attributes using near infrared spectroscopic data combined with multivariate analysis. Annual conference 33rd Gesselschaft Fuer Informatik (German Association of Informatics Engineer). Potsdam, 20-22 Ferbuary 2013.

Nicolai, B. M., Beullens, K., Bobelyn, E., Peirs, A., Saeys, W., Theron, K. I., & Lamertyn, J. (2007). Nondestructive measurement of fruit and vegetable quality by means of NIR spectroscopy: a review. *Postharvest Biology and Technology*, 46, 99-118.

Penchaiya, P., Bobelyn, E., Verlinden, B. E., Nicolai, B. M., & Saeys, W. (2009). Non-destructive measurement of firmness and soluble solids content in bell pepper using NIR spectroscopy. *Journal of Food Engineering*, 94, 267-273.

Reich, G. (2005). Near-infrared spectroscopy and imaging: Basic principles and pharmaceutical applications. *Advanced Drug Delivery Reviews*, 57, 1109-1143.

Rodriguez, J.H., A. Klumpp, A. Fangmeier, M.L. Pignata, Effects of elevated CO_2 concentrations and fly ash amended soils on trace element accumulation and translocation among roots, stems and seeds of Glycine max (L.) Merr, J. Hazard. Mater. 187 (2011) 58–66.

Salazar, M., J.H. Rodriguez, G.L. Nieto, M.L. Pignata, Effects of heavy metal concentrations (Cd, Zn and Pb) in agricultural soils near different emission sources on quality, accumulation and food safety in soybean, J. Hazard. Mater. (2012) 244–253.

Schmilovitch, Z., Mizrach, A., Hoffman, A., Egozi, H., & Fuchs, Y. (2000). Determination of mango physiological indices by near-infrared spectrometry. *Postharvest Biology and Technology*, 19, 245-252.

Schwartz, G., G. Eshel, E. Ben-Dor, Reflectance spectroscopy as a tool for monitoring contaminated soils, in: S. Pascucci (Ed.), Soil Contamination, InTech, Rijeka, 2011, pp. 67–90.

Shi, T., Yiyun, C., Yaolin, L., & Guofeng, L. (2014). Visible and near-infrared reflectance spectroscopy: An alternative for monitoring soil contamination by heavy metals. *Journal of Hazardous Materials*, 265, 166–176.

Siesler, H.W., Ozaki, Y., Kawata, S., & Heise, H. M. (2002). Near Infrared Reflectance Spectroscopy : Principles, Instrument and Application. Wiley VHC Verlag, GmbH, Weinheim.

Sinelli, N., Spinardi, A., Di Egidio, V., Mignani, I., & Casiraghi, E. (2008). Evaluation of quality and nutraceutical content of blueberries (*Vaccinium corymbosum* L.) by near and mid-infrared spectroscopy. *Postharvest Biology and Technology*, 50, 31-36.

Zhuang, P., McBride, M.B., Xia, H., Li, N., Li, Z., 2009. Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China. Sci. Total Environ. 407 (5), 1551–1561.