Use of NIR Technique for Determination of Total Phosphorus and Available Phosphorus in Korean Soils

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NIR spectroscopy is newly developed tools determining the soil properties. Phosphorus in soil is one of the most difficult and time consuming elements to assess for plant needs. The calibration coefficient(R) of NIR method for total phosphorus by HClO$_4$ and Na$_2$CO$_3$ P was 0.91 and 0.88, and available phosphorus by Lancaster and Bray 1. extractant was 0.88 and 0.82. According to Williams guidelines for the calibration coefficient, NIR method could also be used estimating total and available phosphorus if one performed optimal calibration for predicting soil properties. Applicability of NIR spectra, if improved accuracy, may allow for the use of soil testing.

Key words : NIR, Raw spectrum, Standard Error of Estimation, Standard Error of Prediction

Introduction

Phosphorus compounds in soils are mostly unavailable for plant uptake and had difficulty in assessing for plant needs(Kuo, 1996). Soil reactions that fix phosphorus to relatively unavailable forms are closely related to soil characteristics. In acid soil this reactions predominantly involve Al, Fe and Mn either as dissolved ion, oxides, hydrous oxides or silicate minerals which the most korean soils contain(Hong and Hong, 1977). Some of the added phosphorus to the soil may be changed to an organic form which it would be temporarily unavailable. Total phosphorus are determined by the Na$_2$CO$_3$ fusion, H$_2$SO$_4$ and HClO$_4$ digestion, and NaOBr oxidation(Kuo, 1996). The phosphorus availability indices are evaluated by the water, diluted weak acid and diluted strong acid dissolution extractant methods. These indices value depends on both test methods and soil characteristics.

Davies(1998) mentioned the potential of NIR technique and this has been a useful tools in determining soil properties(Ryu et al. 2000). Krischenko(1992) and Ryu et al.(2002) measured soil phosphorus using the NIR technique. Williams(2001) provided a scale of values of R(r^2) used to evaluate NIR performance for analyzing crops, commodities, food and feed. Guidelines for interpretation of R value showing that lower than 0.49 is poor correlation, 0.50 to 0.81 is OK for screening and higher than 0.83 is usable for most application including research. This study was investigated to determine the total and available phosphorus in the Korean soils using the NIR technique.

Materials and methods

Soils Total 148 soil samples from paddy, upland, orchard and others over the Kyong book province in Korea were collected. Soil samples were air-dried and prepared to pass 2.0mm sieve openings.

Determination of soil phosphorus Total phosphorus in soil samples was determined by ICP after digestion with 60% HClO$_4$ and conc. HNO$_3$ for 4 hours, and Na$_2$CO$_3$ fusion for 30 minutes. Available phosphorus was also determined by ICP after extraction with Bray 1 extractant for 1 minute, and the mixture of acetic acid, latic acid, NH$_4$F, ammonium sulfate and NaOH extractant (Lancaster extractant) for 10 minutes respectively. All results were expressed on the basis of dry weight.

Measurement of NIR spectra The NIR reflectance spectra of soils were measured using NIR spectrometer (Foss, NIR5000) ranging 1100 to 2500nm. The NIR reflectance spectra for the functional group of Ca, Fe and Al bounded phosphates were compared with after adding Ca, Fe and Al phosphate powder as 3% of P to a soil. The NIR spectral bands for the functional groups of the remaining phosphate in the soil after extraction by Bray 1

and Lancaster extractant were also compared. A total of 99 soil samples were used for calibration equation and 49 samples were used for prediction. The multiple linear regression was adopted for making the calibration.

Result and discussion

The data in table 1 shows the total and available phosphorus in the soils. Average total phosphorus by $HClO_4$ digestion used for calibration was 1,385 mg kg^{-1} ranged from 227 to 3,676 mg kg^{-1} of the soil and that used for prediction was 1,376 mg k^{-1} ranged from 326 to 511 mg kg^{-1} of the soil. Average total phosphorus by Na_2CO_3 fusion used for calibration was 1,713 mg kg^{-1} ranged from 419 to 3,544 mg kg^{-1} of the soil and that used for prediction was 1,713 mg kg^{-1} ranged from 473 to 3,829 mg kg^{-1} of the soil. Total phosphorus determined by the Na_2CO_3 fusion was greater than by the $HClO_4$ digestion. This seemed that the $HClO_4$ digestion was known not readily dissolve phosphorus in silicate mineral and therefore underestimate total phosphorus in the soils.(Kuo, 1996)

An available phosphorus data in soils used for calibration and prediction by Bray 1 and Lancaster extractant showed big difference as shown in table 1. This seemed mainly due to the different extractant and time of extraction which extracted different types of phosphate. Shin et al.(1990) showed the composition rate of Ca-P, Al-P and Fe-P for the Korean soil. Ca-P was far below average when soil pH was less than 5.5. It was far higher than average when soil pH was more than 5.5. Al-P was increased slightly with the decrease of soil pH and Fe-P was the smallest value when soil pH was below 4.5 and above 6.5. The difference in Al-P and Fe-P to soil pH was smaller to compare to Ca-P. After a soil was mixed with Ca, Fe and Al phosphate solution(3% as phosphorus), the change in NIR reflectance spectra to the functional group for Ca, Fe and Al bounded phosphates was not clear as shown in the above Fig 1. The minor change on raw and 2nd derivatives of the spectrum to these group was able to barely identified, therefore it is difficult to interpret exactly what were composed in the multitude of complicated

Table 1. Total and available phosphorus(mg/kg of soil) determined by various extractants of the soil used for statistics in the soil.

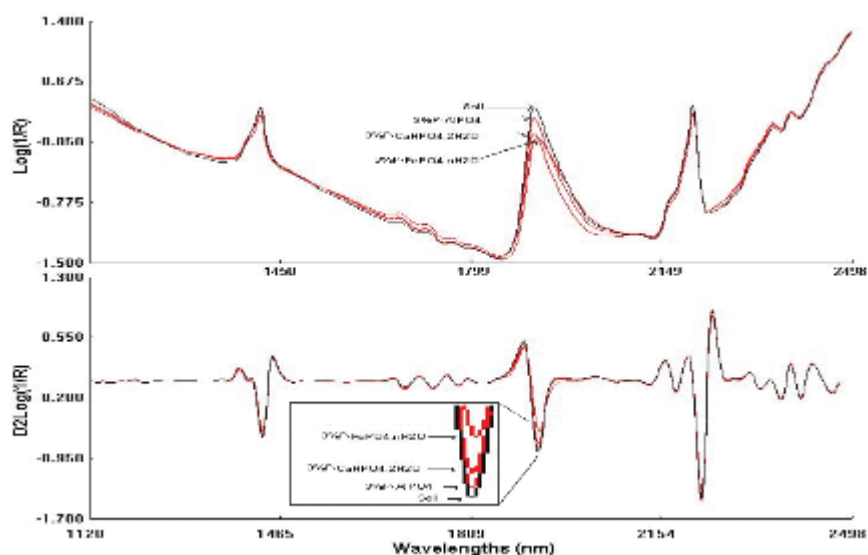| Type of phosphorus		Calibration(n=99)		Prediction(n=49)	
		Mean	Range	Mean	Range
		mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Total P	$HClO_4$	1,385	227~3,676	1,376	326~3,511
	Na_2CO_3	1,713	419~3,544	1,713	473~3,829
Available P	Bray 1	214	17~912	206	8~888
	Lancaster	414	37~1,490	390	8~1,131

Fig 1. Raw and corresponding 2nd derivative spectra after adding various phosphate(as 3% of phosphorus) compound solution to a soil and mixed through.
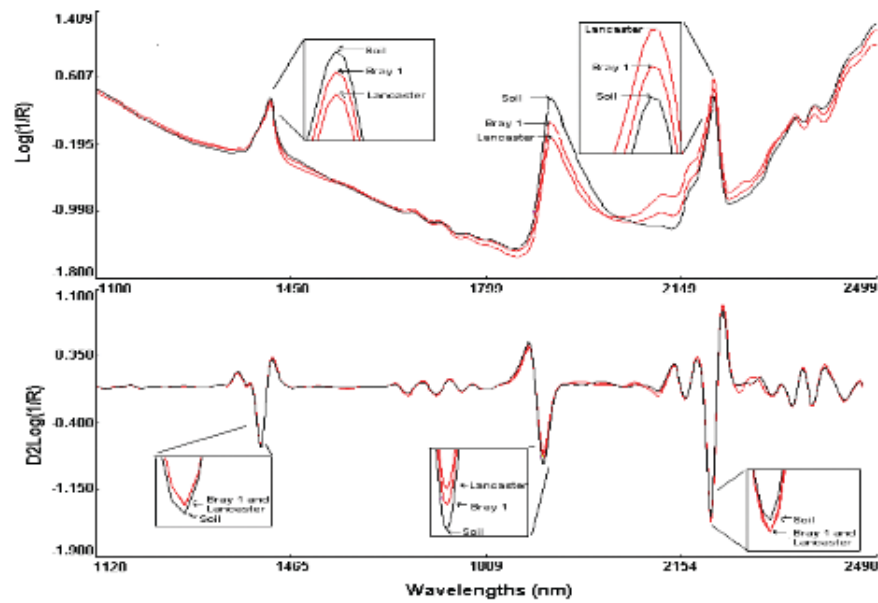
Fig 2. Raw and corresponding 2nd derivative spectra of a soil after extraction by different extractants and washing with distilled water.

bands.. After the soil was extracted by Olsen, Bray 1 and Truog extractant, minor change in NIR reflectance spectra for these functional group shown in Fig 2. was the same order with the functional group of Al, Ca and Fe bounded phosphate but the magnitude was different near at 1930 nm range. Diluted strong acid solution such as Bray 1extractant solubilized Ca, Al bounded phosphate and to a lesser extent of Fe phosphate and Al bounded phosphate was the primary soil P fraction by Bray 1 test. Olsen test extracted less p than Bray 1 test and well correlated with
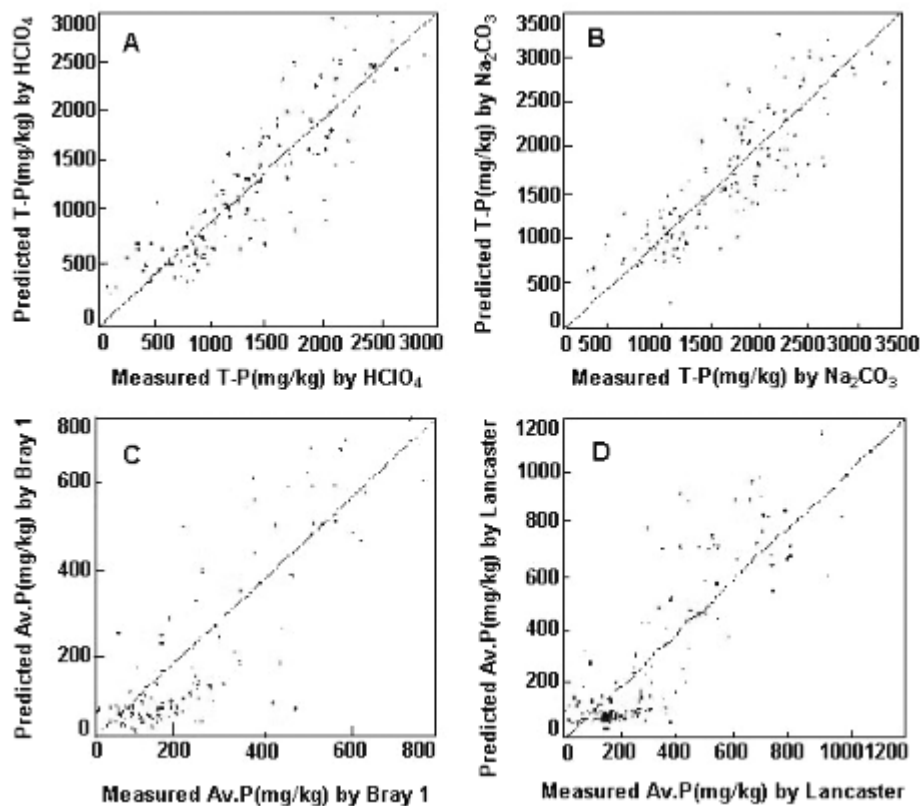

Fig 3. Relationship between measured phosphorus by HClO$_4$ digested total phosphorus(A), and Bray 1(B), Olsen(C) and Truog(D) available phosphorus, and predicted value by NIR in soils.

Table 2. Calibration and prediction statistics of multiple linear regression for total and available phosphorus(mg kg^{-1} of soil) by the various extractants.

Extractant	Spectrum	Terms	R	SEE	SEP	Bands used for calibration
						nm
HClO$_4$ P	Raw	9	0.91	329.0	429.7	1100, 1920, 1978, 2160, 2172, 2284, 2300, 2308, 2464
Na$_2$CO$_3$ P	Raw	9	0.88	400.4	530.5	1100, 1736, 1750, 1872, 1934 1980, 2158, 2172, 2498
Bray 1	2D	9	0.82	146.4	162.3	1242, 1252, 1330, 1742, 1962, 1990, 2140, 2252, 2344
Lancaster	1D	9	0.88	170.5	247.6	1196, 1292, 1310, 1838, 1928, 2166, 2294, 23.04, 2414

Al bounded P as Kuo(1966) mentioned. Ryu et. al(2002) mentioned that mean available phosphate was in the order of Bray 1, Olsen or, and Truog extractant phosphate but the range of these phosphate was in the order of Bray 1, Truog and Olsen extractant phosphate. Fig 3 shows the actually measured phosphorus by wet chemistry used for calibration and prediction and predicted value by NIR on 1:1 line.

Scattering of each measurement and prediction on 1:1 line seemed to be a function of complicated effects of phosphorus compounds and various extractants and time of extraction to various soil characteristics. As seen the figure actually measured values showed relatively good agreement with predicted value in spite of the complicated soil phosphorus analyses. The calibration developed for total phosphorus by HClO$_4$ and available phosphorus by Lancaster extractant were the best in estimating phosphorus with R(r^2) of 0.91, and with R of 0.88 respectively. The poorest one was Bray 1 P with R of 0.82. However Malley et al.(2004) mentioned the Williams' guidelines for interpretation of R during calibration that R value higher than 0.81 is usable with caution for most application, including research.

Terms represents number of wavelengths used for calibration, R(r^2) represents multiple correlation coefficient, Raw represents raw spectrum, 1D represents 1st derivative spectrum, 2D represents 2nd derivative spectrum, SEE represents standard Error of Estimation, SEP represents standard Error of Prediction.

Conclusions

NIR spectroscopy is increasingly used as a means of rapid and accurate determination of the properties and qualities of food and agricultural products. However NIR technique may not exceed the referenced laboratory analytical method in accuracy due to the calibration equation based on the referenced analytical data. Phosphorus in soil is one of the most difficult elements to assess for plant needs mainly duo to the difference in soil characteristics. According to Williams' guideline for correlation coefficient(R) as shown in table 2, NIR method could also be used as a routine method to estimate total phosphorus, and Bray 1 and lancaster extractant type of available phosphorus because of easiness of analyses operation as far as calibration was performed for optimal prediction of the soil . Often research side requires more accurate soil data for fertilizer recommendation than present data obtained by NIR. Applicability of NIR spectra, if improved accuracy, may allow for the use of soil testing.

Acknowledgements

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토양의 총인산과 유효인산함량을 측정하기 위한 근적외 기술의 이용

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근적외선스펙트로메타는 토양의 성분을 측정하는 새로운 기술로 발전하고 있다. 작물이 요구하는 토양의 인산 함량을 측정하는 데는 시간이 많이 소요되며, 침출액과 침출조건에 따라서 다르기 때문에 어려운 성분이다. 그러나 근적외선 방법을 이용하여 표준곡선을 정확하게만 만들어, 표준곡선 작성 시 Wiliams의 상관계수안내를 이용하면 상관계수의 수치에 따라서 토양의 총인산과 유효인산을 측정하는데 간편하게 이용할 수 있다. 또한 근적외 기술은 정밀도를 향상하면 포장 현지에서의 토양검정에도 쉽게 이용할 수 있는 쉬운 기술로 생각된다.