

COMPARISON OF SOIL PHOSPHORUS MEASUREMENTS

G. Kweon, E. D. Lund, C. Maxton, W. S. Lee, D. B. Mengel

ABSTRACT. *This study evaluated four sensor technologies (near-infrared (NIR), Raman spectroscopy, electro-chemical, and colorimetry) to determine a feasible approach for an in-field soil phosphorus (available P) measurement system. The dataset consisted of 12 North American Proficiency Testing Program (NAPT) soils and 12 wet Kansas soils (P range of 5 to 156.0 mg kg⁻¹). An NIR spectrometer showed an R² ≥ 0.43 and a ratio of prediction to deviation (RPD) of 1.372, which did not reach the goal (RPD = 2 and R² ≥ 0.70). For a Raman spectrometer, a partial least squares (PLS) regression and a simple linear regression method of calibration were tested; however, both methods showed poor results (RPD = 1.21 and R² = 0.27 or lower). Customized cobalt ion-selective electrodes were tested in Mehlich 3 extraction solutions and resulted in poor results (R² = 0.44 and RPD = 1.33) for NAPT soils. A rapid colorimetric method was developed consisting of a shortened extraction (1 min), rapid filtration (syringe filter), and rapid color development (1 min with stirring at 50°C), which had an excellent R² of 0.98 for each change independently. The rapid colorimetric method was compared to the standard colorimetric analysis. This test resulted in an R² of 0.85 and an RPD of 1.94 for all NAPT samples, and soils with P < 80 mg kg⁻¹ had an R² of 0.95 and an RPD of 4.74. For field soils, the R² was 0.85 and the RPD was 1.91 for all ranges, and an R² of 0.83 and an RPD of 2.12 was found for soils with P < 80 mg kg⁻¹. Considering that it is not necessary to measure soil P contents precisely in areas where fertilizer does not need to be applied, this rapid colorimetric method would be used for in-field soil P measurement systems.*

Keywords. *Colorimetry, Ion-selective electrode, Near-infrared spectroscopy, Phosphorus, Precision agriculture, Raman spectroscopy, Soil sensing.*

Crop growers in the U.S. and in developed countries worldwide apply large amounts of phosphate fertilizers to their fields. In the U.S., for example, growers annually apply over 4,000,000 tons of P₂O₅ (USDA-ERS, 2008). Fertilizers are typically applied in excess of the crop requirements partially because the cost of fertilizer is relatively lower than the loss in crop yield, if a given nutrient is yield-limiting. Over-application of fertilizers can be harmful in some situations. For example, an increase in phosphorus may cause algae blooms in freshwater ecosystems. As algae die and decompose, the dissolved oxygen in the water decreases, which can harm fish and other aquatic organisms (Pierzynski, 2000). An excess of P in the soil can also increase the risk of P runoff and leaching. In addition, a high P availability can induce Zn deficiency in soils that are already marginally Zn deficient (Cornell, 2005).

Crops grown on P-deficient soils are susceptible to yield

reduction. University researchers have established recommendations for P levels based on crop-response research conducted in their own states. For example, the Kansas State University critical level for P is 20 ppm for Kansas field crops (KSU, 2009). The cost to rebuild soil test P levels once they drop to deficient levels is expensive; for a typical Kansas soil, 21 kg ha⁻¹ of P₂O₅ fertilizer are required to raise the soil test P level by 1 ppm. At current P₂O₅ prices, the application cost for phosphate fertilizer to raise a field from 10 ppm to 20 ppm would be over \$250 ha⁻¹ in total for several years. Phosphorus levels within a field often range from soils that are P-deficient to those that are significantly above the sufficiency threshold. The economic and environmental concerns of both extremes demonstrate the importance of keeping phosphorus levels within an optimal range.

In laboratory analyses, the phosphorus content of soils is typically determined using automated spectrophotometric or an inductively coupled plasma (ICP) atomic emission spectrometer, which provides fairly accurate results because of good linear sensitivity and relatively low interference from other ions (Watson and Isaac, 1990; Brown, 1998). However, such analytical methods cannot be adapted for field use because these instruments are quite expensive and they require complex sample pretreatment (Artigas et al., 2001).

Alternate methods, which may be feasible for field use, involve the use of various sensor technologies. These sensors are not as accurate as laboratory analysis, nor are the techniques involved subject to rigorous quality control procedures. However, sensor measurements are more rapid

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and feasible on a denser spatial scale than conventional lab-analyzed soil samples. The use of field sensors to stratify or predict variability patterns, in conjunction with follow-up laboratory calibrations, has the potential to improve the overall accuracy of field maps for various soil constituents. As compared to conventional sampling methods, the ability to obtain a large number of sensing points means that overall spatial estimation accuracy can increase even if the accuracy of individual measurements is lower (Sudduth and Kitchen, 2006). Gebbers et al. (2009) also reported that the quality of soil property maps was mostly influenced by sampling density, whereas other factors such as measurement errors are less important. Improvement of spatial predictions from soil sampling was made with grid sampling densities higher than 1 ha (McBratney et al., 1981; Laslett and McBratney, 1990). Therefore, a significant increase in sampling density and more rigorous geostatistical methods can significantly reduce the overall map error by accounting for sensor uncertainty and short-distance soil heterogeneity.

Field-deployable sensors, which are potentially helpful in identifying phosphate, can be divided into four basic approaches: near-infrared spectroscopic, Raman spectroscopic, electro-chemical, and colorimetric methods. Applications of near-infrared (NIR) spectroscopy began in the late 1950s (Goulden, 1957) and have increased in recent years. Phosphorus-containing compounds have several tentative wavelength assignments in the NIR. Despite the absorbances of P compounds in the NIR, most studies indicated that P concentrations in soil were generally poorly predicted by an NIR spectrometer (Roberts et al., 2004). In air-dried surface and subsurface soils with P concentrations ranging from 0.7 to 507.6 mg kg⁻¹, P measurements were predicted with a coefficient of determination (R²) of 0.40, a root mean square error of cross validation (RMSECV) of 32.3 mg kg⁻¹, and a ratio of prediction to deviation (RPD) of 1.18 (Chang et al., 2001). While not highly correlated to soil-test phosphorus, both NIR and mid-IR have shown the ability to distinguish P-deficient samples from high-P-content testing samples (Shepherd and Walsh, 2002; Jahn and Updadyaya, 2006).

Bogrekcı and Lee (2005) developed a portable Raman system and carried out initial laboratory tests with dry soil samples from a lake drainage basin. The results for P concentrations ranging from 1 to 2700 mg kg⁻¹ in this system were good, with an R² of 0.98 and an RMSE of 151 mg kg⁻¹. However, the P concentration range for this test was too broad compared to the actual ranges in agricultural fields (generally 95% of soil samples from Kansas fields have a P concentration lower than 200 mg kg⁻¹). A much weaker correlation was produced with this system when the P concentration upper limit was reduced to 200 mg kg⁻¹.

Ion-selective electrode (ISE) technology provides several advantages over current spectroscopic analytical methods, such as low cost, relatively simple methodology, direct measurement of the analyte, a wide range of sensitivity, and portability (Carey and Riggan, 1994). Xiao et al. (1995) introduced cobalt metal as a phosphate ion-selective electrode material and found a selective response for dihydrogen phosphate. Meruva and Meyerhoff (1996) later ex-

amined the detailed response mechanism for cobalt electrodes toward phosphate. Kim et al. (2007) implemented a soil phosphorus measurement test using a cobalt electrode and a Kelowna solution proposed to extract multiple elements in British Columbia, Canada (Van Lierop, 1986, 1988; Haby et al., 1990; Van Lierop and Tran, 1990). They reported that the P concentration measured by the cobalt electrode was much lower (about 63%) than the Mehlich 3 method analyzed by an inductively coupled plasma (ICP) mass spectrometer. This discrepancy was due to reduced P extraction by the Kelowna solution and lower P estimates in the extract by the cobalt P ISE.

Colorimetric methods are common in the analysis of environmental and agricultural samples such as phosphate, nitrate, ammonium, and chloride (Hurtado et al., 2008). The colorimetric measurement of phosphorus developed by Murphy and Riley in the early 1960s is still widely used in soil laboratories (Murphy and Riley, 1962; Hurtado et al., 2008). Colorimetric procedures are sensitive, reproducible, and lend themselves to automated analysis. In addition, these methods can accommodate water samples, digest solutions, and extracts (Pierzynski, 2000). The intensity of the blue color is proportional to the phosphate concentration in solution. The standard procedure in the north central region of the U.S. for P measurements with Mehlich 3 extractant is lengthy and can take 15 min just to process one sample; filtering adds additional 30 min (Brown, 1998). The implementation of this colorimetric method is laborious, costly, and time consuming, which limits the number of samples analyzed in the field. To our knowledge, there are no studies reporting accelerated extraction, filtering, and color reagent development.

The objectives of this study were to compare and evaluate four different sensor technologies with NIR spectroscopy, Raman spectroscopy, cobalt ISEs, and colorimetry for measurement of available P in soil samples, and to determine an optimum sensing technique for in-field measurements of soil phosphorus.

MATERIALS AND METHODS

SOIL SAMPLING AND ANALYSIS

To study the effectiveness of the four sensor technologies (NIR spectroscopy, Raman spectroscopy, cobalt electrodes, and colorimetry), two datasets were selected. The first dataset was composed of 12 dry soils obtained from the North American Proficiency Testing Program (NAPT) with a plant-available P range of 5.0 to 130.0 mg kg⁻¹ (in Mehlich 3 extractant). The second dataset consisted of 12 wet soil samples collected by a probe from three fields in Saline County, Kansas. These samples were a composite of a minimum of six 0 to 15 cm deep cores collected within a 2 m radius. To measure soil properties, these soils were dried at 104°C for 24 h, ground, sieved with 2 mm mesh, and tested by the standard procedure for the north central region in the soil-testing lab at Kansas State University as follows: measure 2 g of soil, add 20 mL of extraction solution, shake at 200 excursions per minute (EPM) for 5 min, gravity filter through Whatman No. 42 filter paper, transfer

Table 1. Soil test results for 12 North American Proficiency Testing Program (NAPT) soils.

Name	P_M3 ^[a] (mg kg ⁻¹)	P_M1 ^[b] (mg kg ⁻¹)	P_Bray ^[c] (mg kg ⁻¹)
Ade	76.0	59.8	73.5
Egan	98.1	143.0	95.5
Flock	26.1	13.5	24.2
Freehold	130.0	56.7	114.0
Immokalee	5.0	4.4	5.9
Ivan's	37.0	37.5	25.8
Lake_C	9.0	5.6	8.0
Marshall	54.0	24.5	53.7
Morrow	86.0	177.0	80.0
Oldham	16.0	6.6	3.1
Putnam	25.4	9.8	18.5
Warden	67.5	207.0	56.0

^[a] P_M3 = plant-available P concentration with Mehlich 3 extractant.

^[b] P_M1 = plant-available P concentration with Mehlich 1 extractant.

^[c] Bray = plant-available P concentration with Bray (1:10) extractant.

Table 2. Soil test results for 12 Kansas field samples.

Name	P_M3 (mg kg ⁻¹)	P_M1 (mg kg ⁻¹)	P_Bray (mg kg ⁻¹)	Moisture Content (%)
Q1	65.5	73.83	46	16.68
Q2	156.0	155.21	127	13.54
Q3	83.6	75.42	73	10.76
Q4	103.0	77.38	57	14.93
Q5	70.4	57.52	42	15.38
S1	20.6	25.92	14	13.11
S2	14.8	29.74	12	14.90
S3	19.0	47.26	16	16.41
W4	52.3	140.43	40	16.28
W5	24.2	16.46	13	12.99
W6	39.8	133.04	35	16.47
W7	44.7	52.45	38	12.47

2 mL of the filtered solution to a test tube, add 8 mL of color reagent, allow at least 10 min for color development, and then measure transmission at 882 nm (Brown, 1998). This test can take 15 min just to process one sample, plus filtering, which adds 0.5 h or more. The samples had a naturally occurring P range of 14.8 to 156.0 mg kg⁻¹ (in Mehlich 3 extractant). Standard deviations of plant-available P in Mehlich 3 were 39.54 and 41.52 for the NAPT and field soils, respectively. Tables 1 and 2 show soil testing results for the NAPT soils and field samples, respectively.

SPECTRA MEASUREMENT USING NIR SPECTROMETER

Each soil sample was measured using a spectrophotometer (AGL-2200, Veris Technologies, Salina, Kans.) including a charge-coupled device (CCD) array spectrometer, which measures spectra from 350 to 1020 nm (USB4000, Ocean Optics, Inc., Dunedin, Fla.) and an InGaAs photo-array spectrometer, which measures spectra from 1100 to 2225 nm (C9914GB, Hamamatsu Photonics K.K., Hamamatsu, Japan). Approximately 20 spectra per second were acquired from the spectrometers and transferred to a PC in continuous mode. The reflectance data for each sample were then averaged and transformed to absorbance for further analysis (Kweon and Maxton, 2013). In this study, each soil in the sample holder was scanned three times at different sample locations, and the average spectrum was used for P analysis in the range of 1150 to 2150 nm with 5 to 6 nm resolution after removing noisy data (fig. 1). Each dataset was mean-centered before a partial least squares



Figure 1. Soil P measurement using a spectrophotometer.

(PLS) regression was used to predict soil P concentrations. PLS calibrations were performed using Matlab and PLS Toolbox. In total, six pretreatments were applied (spectra only, standard normal variate (SNV), 1st derivative, 1st derivative + SNV, 2nd derivative, and 2nd derivative + SNV), and a leave-one-out cross validation was used to find the best performing calibration. Mean squared error (MSE) between lab-measured and estimated values was calculated for each treatment to see whether error estimates differed significantly at $\alpha = 0.05$. The data acquisition and analysis were implemented as described by Kweon et al. (2009). The technical objective of this method was to determine the feasibility of using an NIR spectrometer to measure soil phosphorus concentrations. The goal of each measurement was an RPD ≥ 2 and an $R^2 \geq 0.7$.

SPECTRA MEASUREMENT WITH RAMAN SPECTROMETER

Raman spectroscopy measurements were performed to analyze P concentrations in each soil sample (fig. 2). A portable Raman system was composed of a laser source, a fiber optic cable, a Raman spectrometer, a Raman probe, batteries, power supply circuitries, and a computer. A 785 nm laser beam was used to illuminate a soil sample, in the sample compartment, through a fiber optic cable and Raman probe. Reflected light was collected through the Raman probe and fiber optic cable by the spectrometer. The spectrometer measured the Raman spectrum between 13900 and 8600 cm⁻¹, and the Raman spectrum was transferred to a computer (Bogrekci and Lee, 2005). Every sample was measured three times at different sample locations in a sample holder, and then the measurements were averaged. Measurements were carried out using 20% laser output power and a 30,000 ms integration time. Two calibration methods were performed. First, a PLS calibration was used for wave numbers from 12500 to 8700 cm⁻¹, after removing noisy data. Second, a simple linear regression was done using the peak value for each spectra. Based on the previous investigations, the peak value of a Raman spectrum is proportional to the phosphorus concentration in the sample (Bogrekci and Lee, 2005).

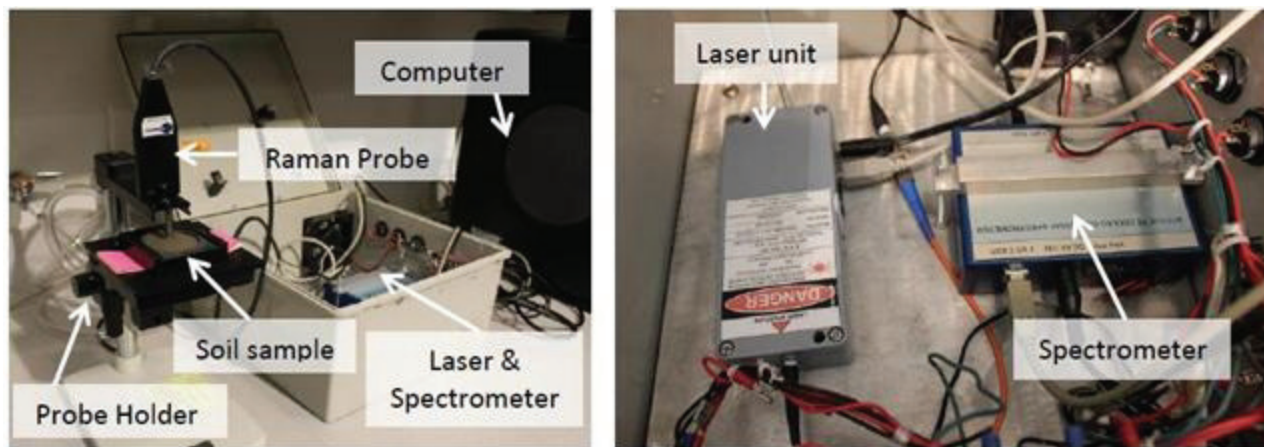


Figure 2. Soil P measurement using a Raman spectrometer.

COBALT ION-SELECTIVE ELECTRODES

Customized cobalt electrodes were sourced from an electrode manufacturer (Analytical Sensors & Instruments, Ltd., Sugar Land, Tex.). ISE data were measured with a Veris Technologies pH controller-meter, which was configured to record all ISE data in millivolts at a rate of 5 Hz. The following calibration equation was used to determine the slope and intercept for a P ion-selective electrode similar to nitrate and potassium electrodes (Adamchuck et al., 2002; Kweon et al., 2011):

$$mV = mV_{0pP} + mV_{pP} \cdot \log(P^+) \quad (1)$$

where

mV = electrode output (mV)

P^+ = phosphorus ion concentration (ppm)

mV_{0pP} = electrode output (intercept) at 1 ppm of P^+

mV_{pP} = mV output increase (slope) due to increase of P^+ by 10.

The tests were implemented in Mehlich 3 extractant with a ratio of 25 g of soil to 25 mL of solution. The mixture was stirred for 5 min with a magnetic stirrer, and then two cobalt ISEs were placed in the slurry. The outputs of the two ISEs were measured at 120 s for 1 s. This experiment was replicated two times, and all measurements for each soil were averaged. After each measurement, the electrodes were washed with distilled water. The pH levels of the tested solutions were adjusted to 4.0 to remove any pH effect, since cobalt ISEs respond to monobasic phosphate ($H_2PO_4^-$) (Lindsay, 1979).

COLORIMETRY

The colorimetric procedure could be divided into separate portions: extraction, filtering, and color development. Each portion of the standard method needs to be evaluated in order to reduce processing time. Mehlich 3 was evaluated to determine its sensitivity to reduced extraction times for soil samples. The standard colorimetric method with 200 EPM for a 5 min shaking time was compared to the rapid extraction method with a stirring rate of 500 rpm for 1 min. Stirring has sometimes been used in place of shaking for mixing soil with an extracting solution. Grava (1980) found a stirring rate of 500 rpm was acceptable. All

the other procedures followed standard laboratory practice. After extracting P from the soil, the standard procedure uses gravity filtration with Whatman No. 42 or similar filter paper. A rapid soil filtering method was also evaluated using a Whatman syringe filter (WH-FI-6783-2520, GE Healthcare Bio-Sciences, Pittsburgh, Pa.). A syringe pump was also used to control the elution speed (fig. 3). The standard colorimetric method with Whatman No. 42 filter paper was compared to the rapid filtering methods. The standard 5 min shake time and 10 min color development time remained the same for this test. The only variable that changed was the filtration method.

For the color development test, a magnetic stirrer was selected to speed up the color change. A hot plate stirrer with a temperature controller was used for the measurements at various temperatures. For simplicity, solutions containing 5, 10, 15, and 30 mg kg^{-1} of P were used for this test instead of extracted solutions of soil samples. The spiked solutions and reagents were maintained at three different temperatures in 24°C, 35°C, and 50°C baths. A stir stick and a mixing bowl were also preheated. The spiked solution (2 mL) and color reagent (8 mL) were added to a test tube and stirred on a hot plate. Transmittance was measured at 882 nm with a spectrometer (Spectronic 20D,



Figure 3. Syringe filter used to test the effects of rapid filtration.



Figure 4. Temperature control bath, stirring plate, and transmittance measurement equipment for the rapid color development method.

Table 3. Summary of four sensing technologies for soil P measurements in the research.

	NIR	Raman	ISEs	Colorimetry
Measurement	Spectra	Spectra	mV	Color intensity
Sensing ranges	1150 to 2150 nm	12,500 to 8700 cm ⁻¹	N/A	0% to 100%
Data acquisition	Three readings in sample holder and averaged	Three readings in sample holder and averaged	20 readings in 25 g soil to 25 mL solution and averaged	Three readings for transmittance at 882 nm and averaged
Data analysis	Mean centered and PLS	Linear regression and PLS	Linear regression	Linear regression
Comparisons	Estimated vs. lab-measured P	Estimated vs. lab-measured P	Estimated vs. lab-measured P	1 min vs. 5 min extraction, paper vs. syringe filter, color change by temp.

Milton Roy Co., Warminster, Pa.) every minute. This rapid color development method is shown in figure 4.

Comparison of P measurements by the standard and combined rapid methods were tested for field samples with Mehlich 3. In the combined rapid method, soil (2 g) in Mehlich 3 (20 mL) was blended at 500 rpm for 1 min and then filtered through a Whatman No. 42 syringe filter in 5 s. The color reagent (8 mL) at 50°C was added to the extracted solution (2 mL), stirred for 30 s, and color development was measured at 882 nm. Table 3 shows a summary of the four sensing technologies for measurement of soil P.

Table 4. Statistical results of the PLS model for NAPT soil P estimation by an NIR spectrometer.

Pretreatment	RMSECV ^[a]	RMSE	R ²	Slope	Offset	RPD
Spectra only	34.44	30.84	0.34	0.34	34.89	1.28
SNV	39.89	28.85	0.43	0.42	34.55	1.37
1st derivative	39.22	32.39	0.27	0.27	38.49	1.22
1st derivative + SNV	37.29	30.56	0.35	0.35	36.75	1.29
2nd derivative	39.75	33.49	0.22	0.22	41.14	1.28
2nd derivative + SNV	36.81	30.93	0.34	0.33	38.36	1.28

^[a] RMSECV = root mean square error of cross-validation; RMSE = root mean square error; SNV = standard normal variate.

Table 5. Statistical results of the PLS models for field soil P estimation by an NIR spectrometer.

Pretreatment	RMSECV	RMSE	R ²	Slope	Offset	RPD
Spectra only	40.07	27.72	0.51	0.51	28.12	1.50
SNV	40.56	26.62	0.58	0.55	19.79	1.56
1st derivative	42.05	27.68	0.52	0.52	28.03	1.50
1st derivative + SNV	35.45	26.89	0.56	0.54	21.94	1.54
2nd derivative	38.46	31.26	0.38	0.38	35.75	1.33
2nd derivative + SNV	34.17	25.63	0.60	0.58	19.09	1.62

RESULTS AND DISCUSSION

SOIL PHOSPHORUS ESTIMATION

BY NIR SPECTROMETER

The statistical results of the PLS model for NAPT soil P estimation by an NIR spectrometer are shown in table 4. The calibration with the spectra-only data set had the lowest RMSECV of 34.44; however, the R² and RPD values of 0.34 and 1.28, respectively, were not promising. The calibration with SNV showed the lowest RMSE (28.85) and the highest RPD (1.37) for the NAPT soils, although this did not reach our goal of an R² > 0.7 and an RPD > 2. The MSE values were not significantly different for different pretreatments for the NAPT soils. Table 5 shows the statistical results of the PLS model for the field soils. The calibration with preprocessing of the 2nd derivative and SNV was the best model, with an RMSECV of 34.17, an RMSE of 25.63, an R² of 0.60, and an RPD of 1.62. However, this model also did not meet the requirement. The slopes of all calibration models were lower than 0.6, and each model underestimated soil P concentrations. There was no significant difference among the different pretreatments for the field soils. In summary, a near-infrared spectrometer is an unsuitable candidate for in-field phosphorus analysis. Figure 5 shows scatter plots for P estimation, with the highest RPD by an NIR spectrometer for the NAPT soils and field samples, respectively.

SOIL PHOSPHORUS ESTIMATION

BY RAMAN SPECTROMETER

Figure 6 shows Raman spectra of the 12 NAPT soil

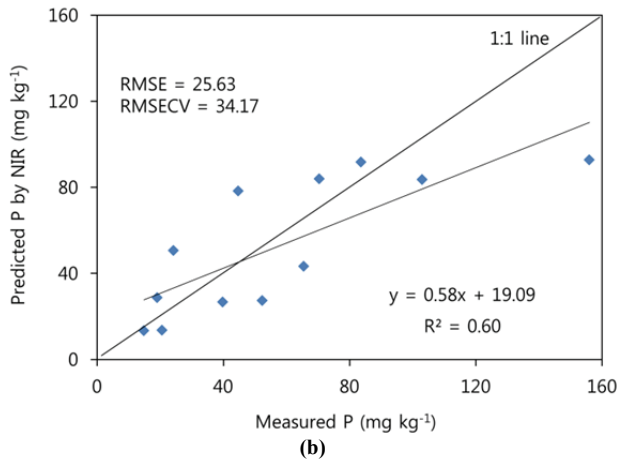
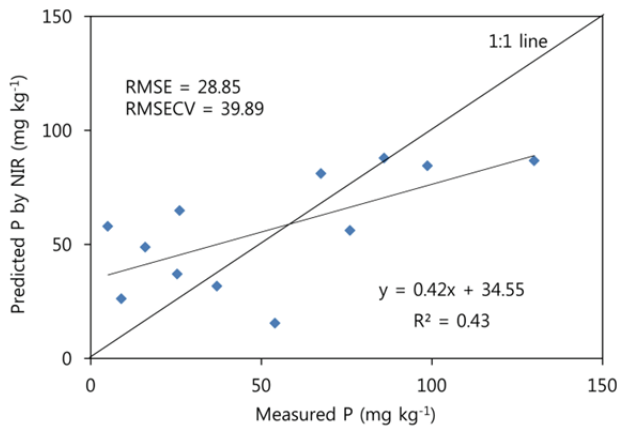


Figure 5. Measured soil P versus predicted P by a near-infrared spectrometer for (a) NAPT soils and (b) field soils.

samples with peak values observed around 12100 cm^{-1} . All PLS calibrations for NAPT soils provided poor results, with the highest R^2 of 0.27 and an RPD of 1.21 (table 6). The NAPT soil P estimations by linear regression using the peak values from the Raman measurements did not show promising results ($R^2 = 0.11$, $\text{RMSE} = 35.68$, and $\text{RPD} = 1.11$). The MSE values were not significantly different for different pretreatments for NAPT soils in Raman spectroscopy. The peak values varied from 33600 to 7500. The twelve field samples were also very poorly estimated by the Raman method because the spectral signature of each sample varied significantly due to uneven sample surfaces. In general, Raman spectroscopy measurements gave higher RMSECV values than the NIR method. Therefore, the Raman technology is an unlikely candidate for in-field phosphorus analysis.

SOIL PHOSPHORUS ESTIMATION BY COBALT ISES

Figure 7 shows the output measurements of cobalt ISES

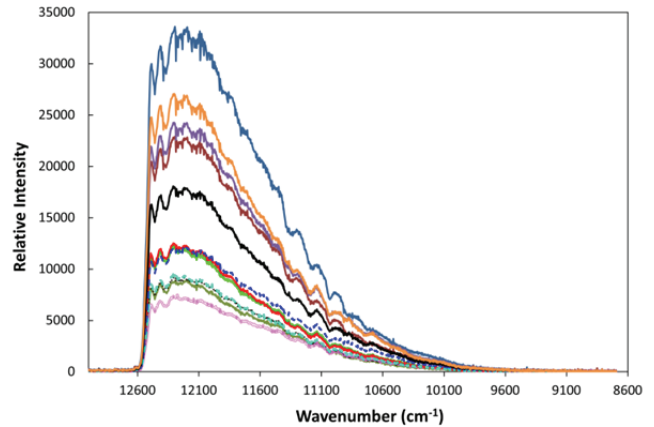


Figure 6. Raman spectra of 12 NAPT soil samples.

by time for the NAPT soils. Most soils showed a stable response after 60 s, and soils with lower concentrations of P required less time to reach a steady-state output signal.

Table 7 shows the average and standard deviation for each measurement by cobalt electrodes for the NAPT and field soil samples. Each measurement had 20 readings in total (two electrodes, five readings, and two repetitions). Ivan's and W6 had the highest standard deviation for NAPT and field samples, respectively. A scatter plot for NAPT soil P estimation using cobalt ISES is shown in figure 8. These results did not provide a good correlation ($R^2 = 0.44$, $\text{RMSE} = 29.66$, and $\text{RPD} = 1.33$). In addition, two samples exhibited large measurement errors using the cobalt ISES. One of these samples (Lake_C) had a lab-measured P concentration of 9 mg kg^{-1} , but the cobalt electrode measured value was approximately 50 mg kg^{-1} ; this discrepancy may have been caused by high levels of arsenic in the soil. The other sample (Freehold) with a lab-measured P concentration of 130 mg kg^{-1} was measured as 46 mg kg^{-1} ; however, the reason is unknown. There was no significant difference between two ISES in the estimations of NAPT and field soils.

In summary, P measurements using cobalt ISES for field samples did not afford promising results (fig. 8b). Results show a moderate coefficient of determination (0.79) but a very high RMSE of 29.70 and an RPD of 1.40. Poor results were found for soils with a P concentration lower than 80 mg kg^{-1} .

SOIL PHOSPHORUS ESTIMATION BY COLORIMETRY

Twelve wet field samples were analyzed in the rapid extraction test with a 1 min stirring time, and standard lab practice was followed. As shown in figure 9a, the rapid extraction method performed well, with an R^2 of 0.98 and an RMSE of 7.12, making this method a good candidate for

Table 6. Statistical results of the PLS model for NAPT soil P estimation by a Raman spectrometer.

Pretreatment	RMSECV	RMSE	R^2	Slope	Offset	RPD
Spectra only	42.97	35.66	0.11	0.11	46.65	1.11
SNV	38.93	33.00	0.25	0.24	43.04	1.20
1st derivative	42.65	35.54	0.12	0.12	46.33	1.11
1st derivative + SNV	39.33	32.94	0.25	0.24	43.47	1.20
2nd derivative	42.73	35.36	0.13	0.13	45.87	1.12
2nd derivative + SNV	39.26	32.62	0.27	0.26	42.62	1.21

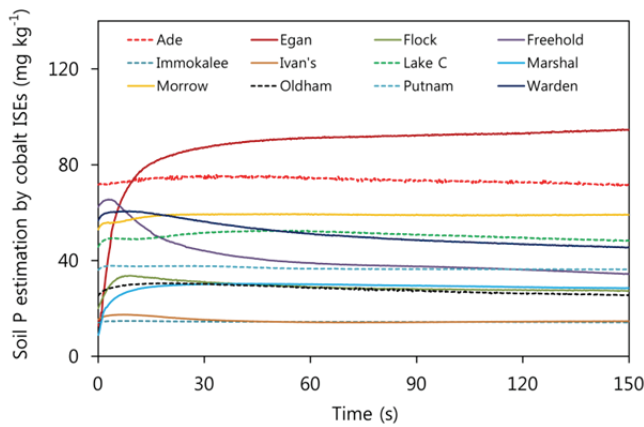


Figure 7. Output measurement of cobalt ISEs by time for NAPT soils.

Table 7. Cobalt ISE output (mV) for NAPT and field soil samples.

NAPT Soil Samples			Field Soil Samples		
Name	Average	SD	Name	Average	SD
Ade	-369.43	0.58	Q1	-352.82	2.13
Egan	-377.59	1.25	Q2	-366.79	0.75
Flock	-350.59	1.83	Q3	-356.29	1.12
Freehold	-360.30	0.90	Q4	-369.73	2.14
Immokalee	-360.69	1.16	Q5	-355.28	1.73
Ivan's	-342.10	3.29	S1	-335.34	6.90
Lake C	-363.35	2.60	S2	-347.40	1.40
Marshall	-353.68	3.28	S3	-339.30	5.32
Morrow	-364.36	2.81	W4	-340.30	2.93
Oldham	-350.57	2.04	W5	-364.88	3.91
Putnam	-354.99	1.72	W6	-347.23	7.71
Warden	-354.75	0.64	W7	-361.76	3.27

in-field measurements. Figure 9b shows a P measurement comparison of Whatman No. 42 paper filters (standard method) and syringe filters for field soils. The coefficient of determination was 0.98, and the RMSE was 12.93. Syringe filtration of samples was accomplished in 5 s, compared to 30 min required by the standard method. Based on these results, rapid filtration with a syringe filter did not affect P measurements significantly.

Figure 10 shows the color development in spiked solutions measured at 24°C, 35°C, and 50°C using a magnetic stirrer. At 24°C, at least 8 min was required for stable color development, and higher concentrations required more settling time. At 35°C, at least 3 min was required for color

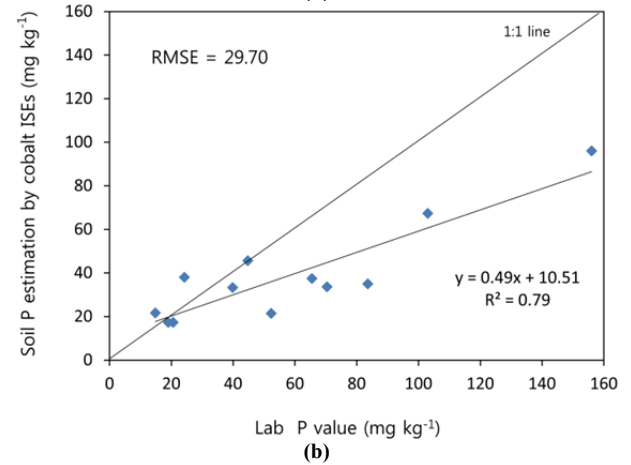
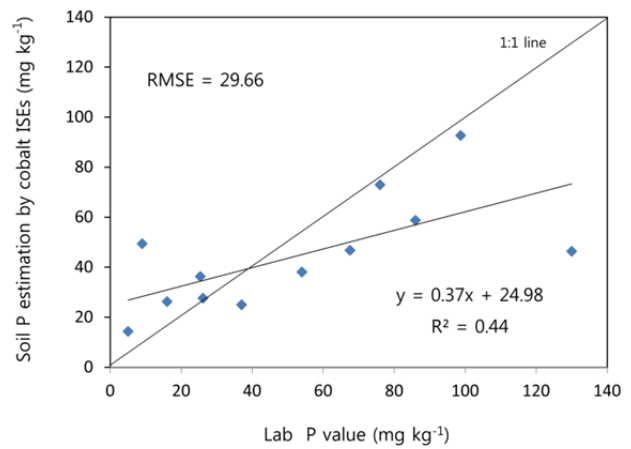


Figure 8. Soil P estimation by cobalt ISEs for (a) NAPT soils and (b) field soils.

development, and solutions with P concentrations of 15 and 30 mg kg⁻¹ had higher transmittance after 3 min. At 50°C, less than 1 min was sufficient for color development at all concentrations. Based on these results, a combination of higher temperatures and stirring resulted in quicker color changes with lower transmittance. For the measurement of rapid color development at 50°C, transmittance would be converted to concentration using a standard curve, which needs to be prepared from solutions of known concentration.

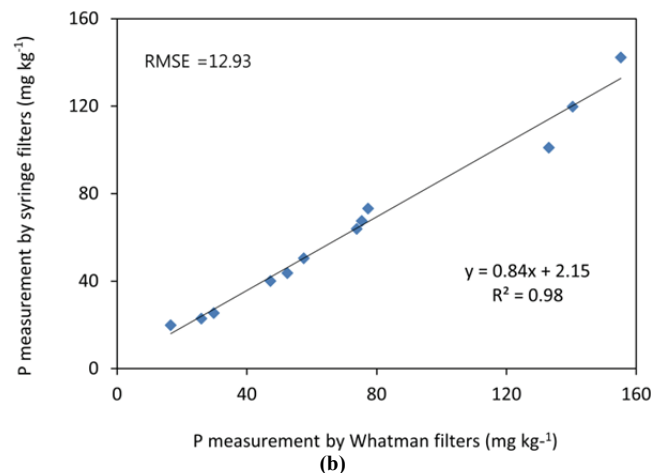
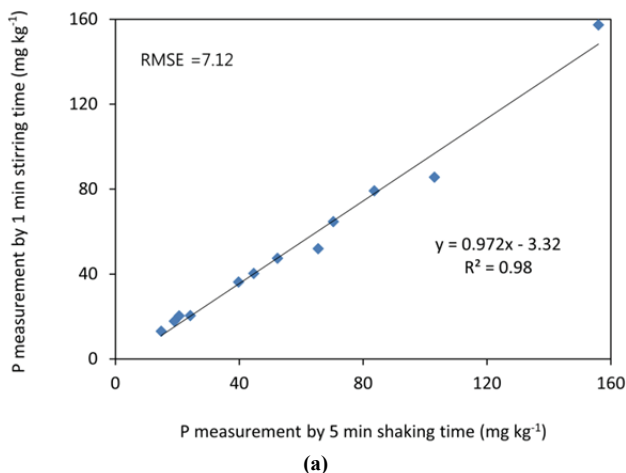


Figure 9. Comparison of P measurements by (a) extraction time and (b) filtration method for field soils.

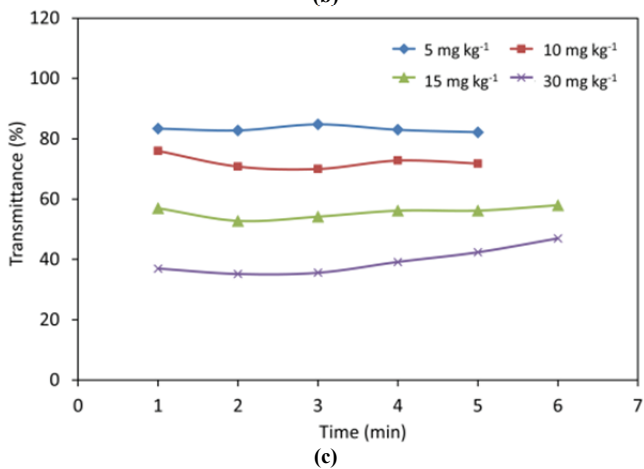
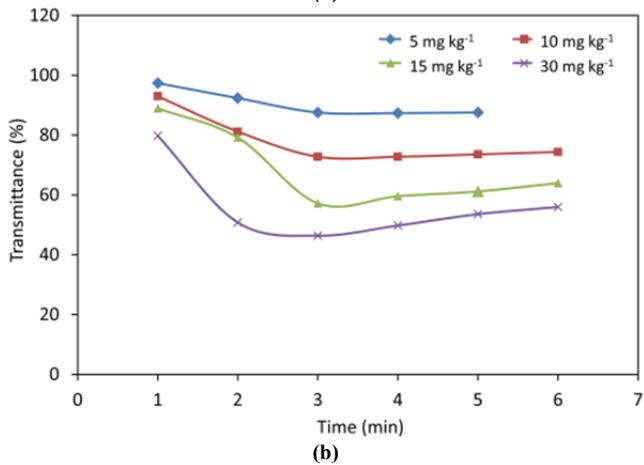
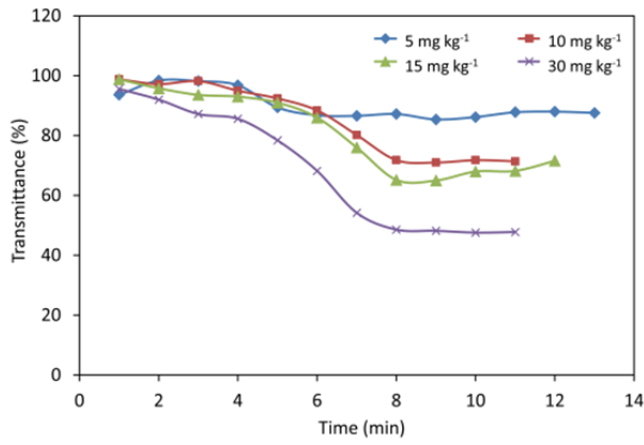


Figure 10. Color development by time at (a) 24°C, (b) 35°C, and (c) 50°C.

Each rapid method for extraction, filtering, and color development showed promising results; thus, the combined rapid method required further testing. Figure 11a shows a comparison of P measurements for the NAPT soils by the standard colorimetric method and combined rapid method. These results had a coefficient of determination of 0.85, an RMSE of 20.39, and an RPD of 1.94. As illustrated, soils with high P concentrations ($>80 \text{ mg kg}^{-1}$) were underestimated. However, NAPT soils with P concentrations lower than 80 mg kg^{-1} gave promising results ($R^2 = 0.95$, RMSE = 5.38, and RPD = 4.74). Figure 11b shows a comparison

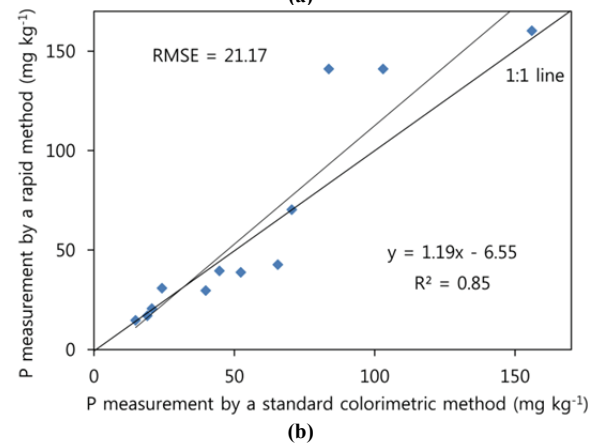
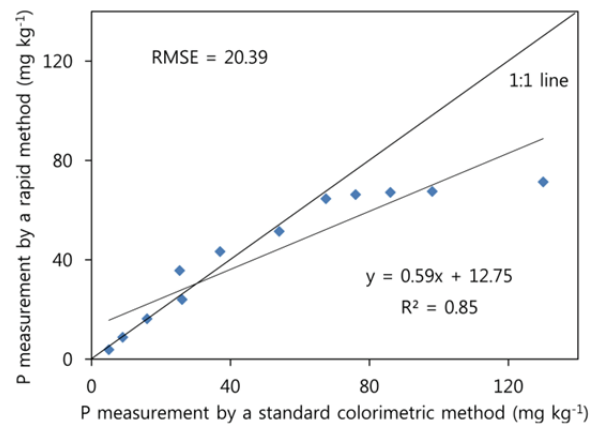


Figure 11. Comparison of P measurements by standard colorimetric and rapid methods for (a) NAPT and (b) field soils.

Table 8. Statistical results of rapid colorimetric methods for NAPT and field soils with Mehlich 3 extractant.

Statistic	P Ranges for NAPT Soils		P Ranges for Field Soils	
	All	$\leq 0 \text{ mg kg}^{-1}$	All	$\leq 80 \text{ mg kg}^{-1}$
RMSE	20.39	5.38	21.72	9.80
R^2	0.85	0.95	0.85	0.83
Slope	0.59	0.89	1.19	0.75
Offset	12.75	3.78	6.55	4.82
SD	39.54	25.52	41.52	20.74
RPD	1.94	4.74	1.91	2.12

of P measurements by the standard and combined rapid methods for the field soils. The rapid colorimetric method showed a moderate result ($R^2 = 0.85$, RMSE = 21.71, and RPD = 1.91). However, soils with P concentrations lower than 80 mg kg^{-1} were estimated quite well ($R^2 = 0.83$, RMSE = 9.8, and RPD = 2.12). Therefore, this rapid colorimetric method is a good candidate for in-field soil P measurements because precise determination of P concentration is not necessary in areas where fertilizer is not required. Table 8 shows a summary of the statistical results for the combined rapid colorimetric method.

CONCLUSION

To study the effectiveness of four sensor technologies (near-infrared spectroscopy, Raman spectroscopy, cobalt electrodes, and colorimetry), two datasets were selected.

The first dataset was composed of 12 dry soils obtained from the North American Proficiency Testing Program (NAPT) with a plant-available P range of 5.0 to 130.0 mg kg⁻¹ (in Mehlich 3 extractant). The second dataset consisted of 12 wet soil samples collected by a probe from three fields in Saline County, Kansas, with a naturally occurring phosphorus range of 14.8 to 156.0 mg kg⁻¹.

To evaluate the effectiveness of NIR spectroscopy, soil samples were measured using a Veris Technologies commercial Vis-NIR spectrometer for NIR (1150 to 2150 nm). Each soil was scanned three times, and the average spectrum was used for analysis. PLS calibrations were performed using Matlab and PLS Toolbox. NIR spectroscopy did not reach the goal of an RPD of 2 and an R² ≥ 0.70 on either sample set.

Raman spectroscopy measurements were performed to analyze P concentrations in the twelve NAPT soils. Two methods of calibration were performed. The first method used a PLS calibration for wave numbers from 12500 to 8700 cm⁻¹. The second method employed a simple linear regression using the peak value of each spectrum. A PLS calibration method did not show a promising result (RPD = 1.21 and R² = 0.27 or lower). Estimations of P concentrations by a Raman spectrometer for the NAPT soils by linear regression using the peak values resulted in an R² of 0.11 and an RPD of 1.11. The twelve field samples were also very poorly estimated by the Raman method.

Customized cobalt ion-selective electrodes were purchased, and the output was measured at 120 s for Mehlich 3 extraction solutions. The pH levels of the solutions tested were adjusted to a value of 4.0 to remove any pH effect. The results for the NAPT soils gave poor results (R² = 0.44 and RPD = 1.33). Phosphorus measurements by cobalt ISEs for the field samples did not show a promising result either. Results showed a moderate coefficient of determination (0.79) but a very high RMSE of 29.70 and thus a low RPD of 1.40. Poor results were found for soils with P concentrations lower than 80 mg kg⁻¹.

The colorimetric method met the objectives of this study and was determined as the most feasible for future commercialization. This method employs an optical measurement of extracted soil solutions with an added color reagent. The standard procedure for the colorimetric method has three stages: extraction, filtering, and color development. This test can take 15 min just to process one sample, and filtering adds 0.5 h or more. Our goal was to evaluate each portion of the standard method and find ways to reduce the time for each step.

A shortened extraction time of 1 min stirring instead of 5 min shaking with Mehlich 3 performed well, with an R² of 0.98, making this method a good candidate for rapid in-field measurements. A rapid soil filtering technique employing a syringe filter provided excellent filtering speed (5 s) and an R² of 0.98 for the field samples. The time required for color development was reduced significantly by heating the stirred solution to 50°C. At 50°C, less than 1 min was sufficient for color development. Each of these accelerated steps was tested independently, performing the other steps exactly according to standard lab procedures. All results were compared to the P measurement using the

complete standard analysis. As a final test, all accelerated methods were combined and compared to the standard lab analysis. This test resulted in an R² of 0.85 and an RPD of 1.94 for all NAPT samples, and soils with P concentrations lower than 80 mg kg⁻¹ were estimated quite well (R² = 0.95 and RPD = 4.74). For the field soils, the R² was 0.85 and the RPD was 1.91 for all ranges, and an R² of 0.83 and an RPD of 2.12 was found for soils with P concentrations lower than 80 mg kg⁻¹. Therefore, the rapid colorimetric method is a good candidate for in-field soil P measurements because precise determination of P concentration is not necessary in areas where fertilizer is not required.

The combination of a shortened extraction time, rapid filtering, and heating to speed up color development provided a reasonable P measurement in less than 2 min. While this time is too long for an on-the-go sensor, these are promising results for in-field P measurements using a colorimetric process. Future research will be implemented to compose an automated P processing system based on the rapid colorimetric method.

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