Soil macronutrient sensing for precision agriculture

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Accurate measurements of soil macronutrients (*i.e.*, nitrogen, phosphorus, and potassium) are needed for efficient agricultural production, including site-specific crop management (SSCM), where fertilizer nutrient application rates are adjusted spatially based on local requirements. Rapid, non-destructive quantification of soil properties, including nutrient levels, has been possible with optical diffuse reflectance sensing. Another approach, electrochemical sensing based on ion-selective electrodes or ion-selective field effect transistors, has been recognized as useful in real-time analysis because of its simplicity, portability, rapid response, and ability to directly measure the analyte with a wide range of sensitivity. Current sensor developments and related technologies that are applicable to the measurement of soil macronutrients for SSCM are comprehensively reviewed. Examples of optical and electrochemical sensors applied in soil analyses are given, while advantages and obstacles to their adoption are discussed. It is proposed that on-the-go vehicle-based sensing systems have potential for efficiently and rapidly characterizing variability of soil macronutrients within a field.

1. Introduction

The soil macronutrients, nitrogen (N), phosphorus (P), and potassium (K), are essential elements for crop growth. The application of commercial N, P, and K fertilizers has contributed to a tremendous increase in yields of agricultural crops that feed the world's population. However, excessive use of these fertilizers has been cited as a source of contamination of surface and groundwater.[1,2] Ideally, application rates should be adjusted based on estimates of the requirements for optimum production at each location because there is high spatial variability of N, P, and K within individual agricultural fields.[3,4]

Site-specific crop management (SSCM), also called precision agriculture, is a soil and crop management system that assesses variability in soil properties (*e.g.*, pH, organic matter, and soil nutrient levels), field (*e.g.*, slope and elevation) and crop parameters (*e.g.*, yield and biomass), to optimize inputs such as fertilizers and herbicides based on information obtained at within-field locations.[5] SSCM aims to improve profitability and to better protect soil and water resources as compared to conventional management practices.[6]

Soil nutrient testing is a management tool that can help accurately determine the available nutrient status of soils and guide the efficient use of fertilizers. With the increasing awareness of fertilizer effects on environmental and soil quality, soil tests have been instrumental in determining where insufficient or excess nutrient levels occur.[7] However, conventional soil testing methods, based on manual or mechanical soil sampling and colorimetric or atomic emission spectroscopy, are costly and time consuming. This expense limits the number of samples analyzed per field, making it difficult to characterize spatial or temporal variability in soil nutrient concentrations within fields.[8] In particular, accurate monitoring of soil nitrate has been limited by the relatively long turn-around time of laboratory analysis, because soil nitrate can be easily lost by leaching and denitrification between the time of testing and plant uptake.[9,10] Therefore, quantifying soil nitrate variability requires a fast on-site measurement at a high sampling intensity that will allow the variability to be mapped spatially and temporally with some degree of confidence.[5,11]

The time and cost required for the intensive sampling needed in SSCM, when using conventional sampling and analysis

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Environmental impact

Precision agriculture is an information-intensive management strategy where production inputs such as fertilizers are matched with site-specific needs of crops. Conventional soil sample collection and laboratory analysis for nutrient levels is costly and time consuming when applied spatially as is required in precision agriculture. Sensing soil macronutrient (nitrogen, potassium, and phosphorus) status in real time as a machine moves across a field would be more efficient. Sensing systems linked to variable-rate fertilizer application systems could target fertilizer to sub-field areas where it would be beneficial, reducing fertilizer application where nutrient levels are already sufficient. Such an approach could lower food production costs and reduce potential for negative environmental impacts to water supplies due to over-application of fertilizer nutrients.

techniques, may make implementation of a variable-rate fertilizer application system impractical.[12] In this situation, on-the-go real-time sensors could be useful to allow the collection of geographically referenced data on a much finer spatial resolution than is currently feasible with manual and/or laboratory methods. These automated sensor measurements can provide the benefits from the increased density of measurements at a relatively low cost.[13]

Soil fertility research has identified levels of macronutrient concentrations in the soil that are sufficient for field crop production without further additions. For example, Midwestern US Cornbelt research[9,10] suggested that soil with a residual nitrate level below 10 mg kg^{-1} would require a full-rate nitrogen application rate to achieve 100% corn yield goal. Residual nitrate levels above 30 mg kg^{-1} would require no additional fertilizer. Similarly, for corn production, soils having plant available phosphorus and exchangeable potassium levels of 27.5 mg kg^{-1} and 150 mg kg^{-1}, respectively, would be considered adequate to support crop production if the amounts removed by the crop each year were replaced.[14] Ideally, real-time sensors would be able to accurately sense macronutrient levels in these ranges, and allow perhaps six finite application rates over the range of zero to full rate. Also, since many of the present soil testing procedures use various solutions to extract different nutrients from soils, the identification of a multiple ion extractant that does not adversely affect the response of sensors, and that can extract representative amounts of soil macronutrients is needed for rapid, on-the-go soil analysis.

With recent advances in sensor technology, various techniques to quantify variability in soil nutrients have been developed and tested by many researchers. This paper describes sensor developments and related technologies that are applicable to the measurement of soil macronutrients in real-time for SSCM. First, various analytical techniques commonly used in soil N, P, and K analysis and the sensing principles of related laboratory instruments are discussed, along with considerations for the use of various soil extractants. Second, various types of soil macronutrient sensors, mainly based on optical and electrochemical methods, are reviewed. Finally, the development of on-the-go vehicle-based soil nutrient sensing is discussed.

2. Current laboratory methods of soil nutrient analysis

2.1 Analytical methods and instruments

In standard laboratory soil testing to measure macronutrients (N, P, and K), various automatic analyzers and extracting solutions have been used. The automated ion analyzer has been commonly used for simultaneously measuring nitrate-N and ammonium-N.[15,16] Phosphorus and K ions in soil extracts have been measured with a colorimetric spectrophotometer and an AAS (atomic absorption spectrophotometer) analyzer, respectively. The use of ICP (inductively coupled plasma) spectrometers in soil testing laboratories has expanded rapidly since the early 1990s due to the ability of the ICP to simultaneously measure multiple elements, including P and K, in one sample.[17,18]

In nitrate analysis using the automated ion analyzer in conjunction with FIA (flow injection analysis), nitrate (NO_3^-) is first reduced to nitrite (NO_2^-) using a copperized cadmium column in an NH_4Cl matrix. The nitrite is then determined by addition of a diazotizing reagent and a coupling reagent to form

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a reddish purple color in proportion to the concentration of nitrite. The sample absorbance is measured at a wavelength of 520 nm.[19–22]

The determination of P in solution with the colorimetric spectrophotometer, which measures the absorbance of a sample at a given wavelength, is achieved based on the reaction of P with a molybdate (Mo) ion to form a colored complex (ascorbic acid method). The resulting yellow color is intensified in the presence of vanadium (V). Alternately, the Mo can be reduced using ascorbic acid to form a characteristic blue color. The intensity of the yellow or blue color depends on the concentration of P in solution.[23] The determination of K in soil with the AAS analyzer is based on the passage of light at a wavelength specific for K through an atomic vapor of the element produced by a flame from an air-acetylene mixture.[24]

The measurement of both P and K with the ICP instrument is based on atomic emission spectroscopy that measures the intensity of light emitted at a specific wavelength when the excited electron returns to a lower energy state.[24] The ICP spectrometer, which uses an argon gas plasma as an energy source, is based on characteristic optical emission of atoms excited in a high-temperature (5000–8000 K) argon plasma.[17] Due to the high temperature of the plasma, chemical interferences are reduced, resulting in good linear responses to elements being tested. Soil analysis by ICP has recently become increasingly popular in soil-testing laboratories. This is due to the fact that compared to other instruments (*i.e.*, colorimetric and AAS spectrophotometers), the ICP spectrometer has many advantages, including: (1) minimum chemical interferences, (2) four to six orders of magnitude in linearity of intensity *vs.* concentration, (3) multi-element capabilities, (4) rapid analysis, and (5) better detection limits.[24]

2.2 Soil extractants

The first step in standard soil testing is extraction of the macronutrients in the soil sample. A 1M or 2M KCl solution is the commonly used extractant for soil inorganic N[16] and soil extractants commonly used in soil test laboratories for extracting P are Bray P_1 (0.025M HCl + 0.03M NH_4F),[25] Mehlich III (0.2M CH_3COOH + 0.015M NH_4F + 0.25M NH_4NO_3 + 0.013M HNO_3 + 0.001M EDTA),[26] and Olsen (0.5M $NaHCO_3$).[27] The Bray P_1 extractant is suitable for acid soils whereas the Olsen extractant is suitable for calcareous soils. The Mehlich III solution has been shown to provide good results for P over a wide soil pH range.[17,28,29] Extraction of total exchangeable K in soils containing other cations, such as Ca, Mg, and Na has typically been accomplished with 1M NH_4OAc, while the Mehlich III extractant has gained use more recently.[29,30] The Mehlich III solution has also been accepted as a simultaneous extracting solution for other cations including Ca, Mg, Na, and Zn, as well as P and K.[26,29] However, the Mehlich III solution is not useful for nitrate extraction because of the high concentration of nitrate in the extraction solution.

For the simultaneous detection of N, P, and K in automated on-the-go sensing, a universal extractant would be advantageous because its use would reduce the time and cost involved in the analysis, as less soil preparation would be required for detecting different nutrients, and a reduced number of calibration solutions would be needed. A search of the literature for such a universal extracting solution showed the Kelowna solution (0.25M CH_3COOH + 0.015M NH_4F) used in soil testing laboratories of British Columbia to be capable of simultaneous extraction of N, P, and K. Van Lierop[31] studied the applicability of the Kelowna extractant to soil nitrate determination by comparing the results obtained with nitrate ion-selective electrodes and the Kelowna extractant with those determined by steam distillation of 2M KCl extracts. He showed that nitrate ion-selective electrodes could determine nitrate in samples extracted using the Kelowna solution. However, since the electrode response was affected by chloride, the use of 0.05M Ag_2SO_4 solution was required to suppress the chloride interference.

Van Lierop[32] evaluated the Kelowna extractant by changing its chemical composition, soil to extractant ratios, and extraction times for determining available P in acidic and calcareous soils. For comparison to standard methods, reference P values were obtained with the Bray P_1 solution for acidic soils and the Olsen solution for calcareous soils. Results indicated that optimal extraction parameters for the Kelowna solution were a 5-min extraction time and a 1:10 soil-to-solution ratio.

A study of the simultaneous determination of K and Na in acidic and calcareous soils with the Kelowna solution was carried out by Van Lierop and Gough.[33] The study showed high coefficients of determination ($r^2 \geq 0.94$) when relating concentrations of K and Na extracted from soils by the Kelowna multiple extractant to those removed by 1M NH_4OAc. However, the Kelowna, on average, extracted 20% less K than did 1M NH_4OAc, although extracted Na levels were similar.

3. Nutrient sensing approaches

Broad reviews of various types of sensors to measure mechanical, physical and chemical soil properties were given by Sudduth *et al.*[5] and Adamchuk *et al.*[13] In this review, we focus on sensors for measuring macronutrients (N, P, and K) and pH levels in soils.

Although many sensing techniques are available, most of the soil nutrient sensors described in the literature involve one of two measurement methods:

• optical sensing that uses reflectance spectroscopy to detect the level of energy absorbed/reflected by soil particles and nutrient ions, or

• electrochemical sensing that uses ion-selective electrodes which generate a voltage or current output in response to the activity of selected ions.

3.1 Spectroscopy

Optical diffuse reflectance sensing in visible and near-infrared (NIR) wavelength ranges is one approach to rapidly quantify soil properties for SSCM. Such optical methods have been investigated by many researchers due to their attractive advantages over electrochemical technology, such as non-destructive measurement and no need to take a soil sample.[5,34,35] In principle, diffuse reflectance spectroscopy is based on the interaction between incident light and soil surface properties, such that the

characteristics of the reflected light vary due to the soil physical and chemical properties.[36]

Owing to the importance of soil N for crop growth, many researchers have investigated soil N sensing using optical methods. Upadhyaya et al.[37] used NIR absorbance data in conjunction with FFT (Fast Fourier Transform) and PLSR (partial least squares regression) analyses to determine soil NO_3–N over a concentration range of 0 to 300 mg/kg. The linear relationship between the NIR and standard methods was high ($r^2 > 0.9$). However, the standard error of prediction (SEP) was fairly high (6–38 mg kg^{-1} NO_3–N). This group conducted additional research on optical measurement of soil nitrate through laboratory and field experiments.[38] They were able to determine an optimal wavelength range (1800–2300 nm) for measuring soil nitrate, but a soil-specific calibration was needed to map nitrate variation over a large area due to the effect of soil type.

Linker et al.[39–41] used Fourier transform infrared (FTIR) attenuated total reflectance (ATR) spectroscopy in the mid-infrared range to measure nitrate content in soil solutions and pastes. They proposed a two-step approach, consisting of soil identification and a soil-dependent model, to improve accuracy. The soil identification was performed by comparing the so-called 'fingerprint' region of the spectrum (6400–12500 nm) to a reference spectral library, in conjunction with PCA (principal component analysis) decomposition and NN (neural network) classification techniques. Nitrate determination was achieved using PLSR models. Resulting errors ranged from 6.2 to 13.5 mg kg^{-1} N, smaller than the error obtained with a model for all soil types combined (19.1 mg kg^{-1} N).

Jahn et al.[42] used wavelet spectral analysis for the determination of soil nitrate based on mid-infrared FTIR-ATR spectroscopy. They tested two soil types (Yolo loam and Capay clay) treated with nitrate fertilizers by adding interfering compounds such as carbonate and humic acid. In the concentration range of 0 to 140 mg L^{-1} NO_3–N, the coefficient of determination (r^2) between the signal peak volume obtained and nitrate concentration was 0.93. However, the results were not satisfactory when attempting to measure low concentrations of soil nitrate or to obtain consistent predictive capabilities across a range of soils due to relatively high SEP (about 9.5 mg L^{-1} NO_3–N) and a significant effect of soil type. To investigate the feasibility of using wavelet analysis for nitrate determination in various soil types, Jahn et al.[43] applied wavelet analysis to soil FTIR-ATR spectra collected by Linker et al.[39] Coefficients of determination (r^2) as high as 0.96–0.99 and standard errors as low as 5–24 mg kg^{-1} NO_3–N were obtained in laboratory and field experiments when building site-specific calibration models for calcareous and non-calcareous soils. In addition, it was possible to use a single calibration equation and obtain standard errors as low as 3.6 mg kg^{-1} NO_3–N for 10 different soils using absorbance data in the 6500–7500 nm range.

Lee et al.[44] related spectral characteristics to chemical properties, including P and K, of soil samples from major soil orders in Florida, developing models to estimate pH, organic matter, P, K, Ca, and Mg concentrations. Their models accounted for more than 72% of the variation observed in the validation set for soil pH, P, Ca, and Mg, but less than 50% of the variation in K and soil organic matter. Bogrekci and Lee[45] focused on soil and vegetation P sensing using ultraviolet-visible-NIR spectroscopy.

Stepwise multiple linear regression (SMLR) and PLSR were used to relate spectral data to P concentrations. Overall, PLSR analysis results were better than SMLR results. Strong relationships ($r^2 = 0.78$–0.92) between absorbance and P concentration in soils were obtained with PLSR whereas a weak relationship ($r^2 = 0.42$) existed for vegetation samples. Follow-up studies investigated the effects of soil moisture content on the absorbance spectra of sandy soils with different P concentrations[46] and compared the prediction capabilities of three different spectral regions, i.e., ultraviolet (UV), visible and NIR in determining P contents in soil.[47] They found that removing the moisture effect by spectral signal processing improved P prediction in soils considerably, reducing root mean square error (RMSE) from 151 to 62 mg kg^{-1}. The NIR region produced better estimates than did the UV and visible regions, with a strong relationship ($r^2 = 0.95$) between reflectance and Mehlich I P concentration.

Other studies have simultaneously determined soil properties using optical methods. Dalal and Henry[48] used NIR reflectance spectroscopy to simultaneously estimate water content, total organic carbon, and total N in air-dried soils by multiple linear regression. They reported the partial correlation coefficients (r) for each of three wavelengths selected for the three measurement parameters were highly significant (>0.87). However, there was a significant difference in SEP between coarsely ground (<2 mm) and finely ground (<0.25 mm) soils. Also, at lower concentrations of organic carbon and total nitrogen, the estimation by NIR techniques was relatively poor.

Chang et al.[34] applied principal component regression (PCR) to relate 33 soil chemical, physical, and biochemical properties to NIR data obtained from 802 soil samples. They demonstrated the possibility of measuring diverse soil properties such as total C, total N, moisture content, cation exchange capacity (CEC), and extractable Ca with acceptable accuracy. Similarly, He et al.[49] used NIR spectroscopy to estimate nitrogen and organic matter in soils of a province in China using a total of 125 soil samples. They reported that the correlation coefficients (r) between measured and predicted soil nitrogen and organic matter were 0.92 and 0.93, respectively, and slopes of 0.59 and 0.71 were obtained for N and SOM measurements. More recently, the same authors applied NIR spectroscopy in conjunction with PLSR to the determination of P, K, and pH for 165 soil samples with a loamy mixed soil type.[50] Good estimates were obtained for soil pH (r = 0.91, SEP = 0.07). However, the results were not satisfactory for soil P and K, with correlation coefficients (r) of 0.47 and 0.68, and SEP of 33.7 and 26.5 mg kg^{-1}, respectively.

La et al. obtained good estimates of texture fractions, organic matter and CEC ($r^2 = 0.83$ to 0.92) for Missouri and Illinois surface soils whereas estimates of P and K were not as good ($r^2 < 0.7$) when PLSR was applied to develop calibrations between soil properties and reflectance spectra.[51] Similar estimates of P and K ($r^2 = 0.72$ and 0.74) were obtained for 14 distinct soil series of 42 Korean paddy fields.[52]

In summary, many authors have reported high correlations between reflectance techniques and standard methods when using diffuse reflectance spectroscopy in conjunction with various calibration and signal processing methods (i.e., PLSR, PCR, and FFT wavelet analysis) to estimate soil physical properties. However, results have most often not been satisfactory for

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soil macronutrinets in those ranges where fertilizer application decisions must be made, *i.e.*, 10–30 mg kg^{-1}, 10–27.5 mg kg^{-1}, and 50–150 mg kg^{-1} for N, P, and K, respectively. Although reflectance spectroscopy can respond to total nutrient concentrations in soil, calibration of the reflectance signal to the plant-available portion of the nutrient pool measured by standard soil tests is a considerable challenge. This challenge has contributed to the inability to obtain consistently good estimates across a range of soils, relatively high standard errors and significant effects of soil type.

3.2 Electrochemical sensing

Most of the electrochemical methods used to determine soil nutrient levels are based on the use of an ion-selective electrode (ISE), with glass or a polymer membrane, or an ion-selective field effect transistor (ISFET). The ISFET has the same theoretical basis as the ISE, *i.e.*, both ISEs and ISFETs respond selectively to a particular ion in solution according to a logarithmic relationship between the ionic activity and electric potential.[53]

The ISEs and ISFETs require recognition elements, *i.e.*, ion-selective membranes, which are integrated with a reference electrode and enable the chemical response (ion concentration) to be converted into a signal (electric potential).[54] Due to an increased demand for the measurement of new ions, and tremendous advances in the electronic technology required for producing multiple channel ISFETs, numerous ion-selective membranes have been developed in many areas of applied analytical chemistry, *e.g.*, in the analysis of clinical or environmental samples.[55,56] Ion-selective membranes are available for sensing most of the important soil nutrients, including NO_3, K, Na, Ca, Mg, and Cl.[57–64]

3.2.1 Nitrate ion-selective membranes and electrodes. Numerous reports on the development and application of nitrate ion-selective membranes (Table 1) have been described for various applications, such as food, plants, fertilizer, soil, and wastewater.[53,58,63–67] Nielson and Hansen[58] developed nitrate ISEs using various quaternary ammonium compounds and plasticizers in non-porous PVC-based membranes. A combination of tetradodecylammonium nitrate (TDDA) and dibutylphthalate (DBP) as the ligand and plasticizer, respectively, was found to show the best response to nitrate. The optimal membrane composition was proposed to be 29% PVC, 67% DBP, and 4% TDDA.

Birrell and Hummel[53] evaluated various PVC matrix membranes prepared with different combinations of ligand and plasticizer materials using an automated testing device. Membranes prepared with methyltridodecylammonium chloride (MTDA) or TDDA displayed an approximately Nernstian response to nitrates. The membranes based on the MTDA ligand showed slightly greater sensitivity to nitrate than did the TDDA membranes while the TDDA ligand gave superior selectivity for the nitrate ion. For best results in the presence of other interfering ions in soils, they developed multi-ISFET nitrate sensors using the TDDA-based nitrate membranes. The nitrate ISFETs were shown to effectively determine concentrations over a range of nitrates in soil with acceptable selectivity levels that were at least 40 times greater for nitrate than for chloride and bicarbonate.

Le Goff *et al.*[67] developed a rubbery membrane based on N,N,N-trially leucine betaine using a free radical initiated copolymerisation for use in measuring nitrate in agricultural drainage water over a 5-month period. Their goal was to provide reliable measurements without any deterioration in sensor performance over time due to leaching of chemicals from the membrane. In a concentration range of 0.47 to 16 mg L^{-1} NO_3–N, there was a significant linear relationship (r^2 = 0.99) between the new membrane-based ISE and laboratory methods. The system did not require re-calibration during a four-month test.

Gallardo *et al.*[64] used an artificial neural network to extract nitrate information from the cross-term responses to nitrate and chloride ions for quantifying nitrate in complex samples containing variable amounts of chloride. Three nitrate electrodes with different ionophores (*i.e.* tetraoctylammonium nitrate (TOAN), tridodecylmethylammonium nitrate (TDMAN), and tris (4,7-diphenyl-l,10-phenantroline nickel(II) nitrate (TDPNN)) and one chloride electrode were used in conjunction with a flow-injection system. This approach improved the accuracy of the determination of nitrate concentration over a range from 0.1 to 100 mg L^{-1} NO_3 without the need to eliminate chloride. However, they mentioned as a drawback that a large number of known samples were needed for training the system.

More recently, Kim *et al.*[68] investigated the responses of PVC membranes with tetradodecylammonium nitrate (TDDA) or methlytridodecylammonium chloride (MTDA) to nitrate ions in the Kelowna extracting solution. The TDDA-based nitrate membrane showed greater sensitivity and better selectivity for nitrate over interfering ions that may be present in soil than did the MTDA-based membrane. The TDDA-based membrane was capable of detecting low concentrations in soils to about 10 mg kg^{-1} NO_3 when a 1:10 soil-to-solution ratio was assumed.

Overall, the best results for sensing nitrate in soils were obtained with PVC ion-selective membranes prepared with quaternary ammonium compounds, such as TDDA or MTDA as the sensing element for nitrate (Table 1). These membranes were able to determine nitrate across the concentration range important for N fertilizer application management, *i.e.*, 10–30 mg/kg NO_3. They also maintained acceptable selectivity levels in mixed solutions, being at least 40 times more sensitive to nitrate than to chloride and bicarbonate.

3.2.2 Potassium ion-selective membranes and electrodes. Historically, a major interest for potassium (K) analysis came from clinical chemistry because changes in K concentration in human serum bring about the risk of acute cardiac arrhythmia.[69] Therefore, the majority of the research on the use of K ion-selective membranes has been focused on continuous monitoring of the human body during periods of rapidly changing K concentrations, such as during or after surgery.[69] From the results of numerous studies on ionophores for sensing K (Table 2) in analytical chemistry,[56,57,70–72] it is clear that valinomycin has been the most successful ionophore for sensing the ion because of its strong K selectivity.

Many researchers have attempted to expand the application of the valinomycin-based K membranes to monitoring of environmental samples, such as food, water and soil, by fabricating

Table 1 Comparison of nitrate ion-selective membranes

Composition	Characteristics[a]						Reference
	Sensitivity (mV/decade)	Linear range (M)	Detection limit (M)	Selectivity (log K_{ij})	Lifetime	Other	
15 wt% of tetradodecylammonium nitrate (TDDA); 40 wt% of 2-nitrophenyl octyl ether (NPOE); 45 wt% of high-molecular-weight polyvinyl chloride (PVC)	−63.4	10^{-4}–10^{-1}	—	$Cl^- = -2.40$; $HCO_3^- = -3.29$; $HPO_4^{2-} = -3.76$; $SO_4^{2-} = -3.76$; $Ac^- = -3.48$; $Br^- = -0.81$	—	—	53
4.0 wt% of TDDA; 67 wt% of dibutylphthalate (DBP); 29 wt% of PVC	−56.2	—	8.3×10^{-7}	$Cl^- = -2.30$; $NO_2^- = -1.15$; $F^- = -3.0$; $HCO_3^- \geq -3.30$	—	—	58
3.9 wt% of tetraoctylammonium nitrate (TOAN); 59.4 wt% of triooctyl phosphonate (TOP); 34.7 wt% of aliphatic urethane diacrylate Ebecryl 270 and hexanediol diacrylate (HDDA); 2.0 wt% of 2-2'-dimethoxyl phenylacetophenone (Irgacure 651)	−62.6	2.3×10^{-5}–6×10^{-2}	1×10^{-5}	$Cl^- = -2.0$	7 months	Photocurable membrane	63
3 wt% of tetraoctylammonium nitrate (TOAN); 67 wt% of DBP; 30 wt% of PVC	−54.0 ± 0.6	—	2.3×10^{-4}	—	—	Outputs from the three different membranes were combined for improved accuracy	64
4 wt% of tridodecylmethylammonium nitrate (TDMAN); 64 wt% of NPOE; 32 wt% of PVC	−56.1 ± 0.9	—	2.8×10^{-4}	—	—		
2 wt% of tris(4,7-diphenyl-1,10-phenanthroline) nickel(II) nitrate (TDPNN); 66 wt% of NPOE; 33 wt% of PVC	−55.8 ± 7.1	—	7.8×10^{-4}	—	—		
6 wt% of methyltridodecylammonium nitrate (MTDAN); 1 wt% of methyltriphenyl phosphonium bromide; 65 wt% of NPOE; 23 wt% of PVC	−55.6	10^{-4}–10^{-1}	—	$Cl^- = -1.45$; $HCO_3^- = -2.17$; $SO_4^{2-} = -2.74$	—		65
6.5 wt% of triallydecylammonium nitrate (TDDAN); 39.7 wt% of NPOE; 46.6 wt% of Krynac; 7.2 wt% of dicumyl peroxide (DCP)	−57.7	1.2×10^{-5}–10^{-1}	8.8×10^{-6}	$Cl^- = -4.0$; $HCO_3^- = -4.9$; $SO_4^{2-} = -5.0$	>6 months	Hot-pressing process used	66
6.5 wt% of N,N,N-triallyl leucine betaine; 40 wt% of NPOE; 43.5 wt% of polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) polymer; 10 wt% of dicumyl peroxide (DCP)		5×10^{-6}–10^{-1}	3.4×10^{-7}	$Cl^- = 2.47$	>5 months	Working pH range of 2–8; Response time of <1min	67
15 wt% of TDDA; 40 wt% of NPOE; 45 wt% of PVC	−54.9 ± 1.3	10^{-4}–10^{-1}	10^{-5}	$Cl^- = -2.07$; $HCO_3^- = -3.22$; $Br^- = -1.03$	—	Kelowna soil extractant as base solution	68

[a] Empty cells occur when data for that membrane characteristic were not provided in the reference. Distilled water was used as the base solution for all except ref. 68.

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Table 2 Comparison of potassium ion-selective membranes

Composition	Characteristics[a]				Lifetime	Other	Reference
	Sensitivity (mV/decade)	Linear range (M)	Detection limit (M)	Selectivity (log K_{ij})			
Valinomycin; Benzophenonetetracarboxylic acid tetra-n-undecyl ester (BTCU); High-molecular-weight polyvinyl chloride (PVC)[b]	51.7	10^{-4}–10^{-1}	—	$K^+ > NH_4^+ > H^+ >$ $Na^+ > Li^+ > Ca^{++}$	>2 months	—	59
2.0 wt% of valinomycin; 64.7 wt% of bis (2-ethylhexyl) sebacate (DOS); 32.80 wt% of PVC; 0.5 wt% of potassium tetrakis(4-chlorophenyl) borate (KTpClPB)	58	1.8×10^{-5}–10^{-1}	3×10^{-6}	$Na^+ = -4.2$ $Li^+ = -4.3$	>1 month	Double matrix type membrane; MFM (inert microfibre matrix) used	61
Upper: 3 wt% of valinomycin; 27 wt% of plasticizer; 70 wt% of polymer matrix Intermediate: 2.9 wt% of valinomycin; 3.2 wt% of EI; 26.1 wt% of plasticizer; 67.8 wt% of polymer matrix	58.8	3×10^{-5}–3×10^{-1}	—	$Na^+ = -2.7$ $NH_4^+ = -1.5$ $Mg^{2+} = -0.7$ $Ca^{2+} = -1.8$	—	Two-layer, photocurable membrane	62
2.3 wt% of valinomycin; 0.6 wt% of KTpClPB; 46.4% of DOS; 48.4% of Eb270 + HDDA	55.7	7×10^{-5}–0.1	4×10^{-5}	—	7 months	Working pH range: 3.5–8.0	63
2.0 wt% of valinomycin; 64.7 wt% of DOS; 32.80 wt% of PVC; 0.5 wt% of KTpClPB	51.5 ± 1.41	10^{-4}–10^{-1}	10^{-4}	$Na^+ = -2.57$ $NH_4^+ = -1.63$ $Mg^{2+} = -2.94$ $Ca^{2+} = -2.88$	—	Kelowna soil extractant as base solution	68
2 wt% of valinomycin; 64 wt% of dioctyl adipate; 34 wt% of PVC	54.88 ± 1.137	10^{-5}–10^{-1}	—	—	—	—	70
1 wt% of valinomycin; 66 wt% of dioctyl adipate; 24 wt% of PVC; 9 wt% of copolymer VAGH	53 ± 0.6	—	4×10^{-5}	$Na^+ = -4.0$	>28 days	Lifetime increased from ref. 70	71
1 wt% of cis-bis(15-crown-5 ether); 66 wt% of 2-nitrophenyl octyl ether (NPOE); 33 wt% of PVC	59	—	9.5×10^{-7}	$Na^+ = -3.69$ $NH_4^+ = -2.28$ $Li^+ = -4.07$ $Cs^+ = -2.25$	—	Base solution of 0.05M Tris-HCl (pH 7.2)	72
1 wt% of valinomycin; 33 wt% of dioctyl adipate; 66 wt% of PVC	58–59	—	—	—	—	Operating range: 10^{-5}–10^{-1}M; 15 s response time (95%)	73
1 wt% of valinomycin; 66 wt% of bis(2-ethylhexyl) adipate; 33 wt% of PVC	56–59	10^{-5}–10^{-1}	$\sim 10^{-6}$	$Na^+ = -3.56$	—	—	74

[a] Empty cells occur when data for that membrane characteristic were not provided in the reference. Distilled water was used as the base solution for all except ref. 68 and 72. [b] Percentage information for individual components not reported.

a sensor array with several different ion-selective membranes for multiple ion sensing.[59,61,63,73,74] In addition, most of these studies also included research on the adhesion of the PVC membrane to the gate region of ISFETs. The efforts were directed toward extending the consistent sensitivity period, and thus, the lifetime of the electrode.[59,63,71,75] Results demonstrated that the valinomycin-based K membranes were useful in measuring K in environmental samples containing various interfering ions.

Artigas et al.[63] reported on the fabrication of pH, Ca, NO_3, and K ISFETs with photo-curable polymeric membranes and their evaluation in aqueous soil solutions. The photo-curable polymeric membrane adhered better to the surface of the ISFET and had a longer life than PVC-based membranes. Sensor response characteristics were stable for two months. During that time no membrane damage occurred and no peel-off was observed in the laboratory.

Kim et al.[68] tested ion-selective membranes prepared with valinomycin as an ionophore and three different plasticizers (2-nitrophenyl octyl ether (NPOE), bis(2-ethylhexyl) sebacate (DOS), and bis(2-ethylhexyl) adipate (DOA)) for sensing Kelowna-extractable K. The DOS and DOA membranes showed satisfactory selectivity for measuring K in the presence of interfering cations such as Na, Mg, Ca, Al, and Li, and provided repeatable sensitivity slopes (1–2 mV/decade in terms of standard deviation) to different concentrations in the range of 10^{-4} to 10^{-1} M K. The sensitivity of these membranes to K in the Kelowna solution was high enough to measure the typical range in soil potassium at which additional K fertilizer is recommended.

As shown in Table 2, valinomycin has been the most commonly used ionophore for sensing potassium due to its remarkable K sensitivity and selectivity. Furthermore, with the high sensitivity of valinomycin-based membranes to potassium in soil extracts and their lifetimes of more than one month it seems reasonable that a K-ion sensor based on valinomycin would have high potential for commercialization.

3.2.3 Phosphate ion-selective membranes and electrodes.

Due to the importance of real-time monitoring of P in biological systems and living organisms, many researchers have tried to develop phosphate sensors in the form of ion-selective electrodes and biosensors. However, it has been reported that the design of an ionophore for selective recognition of phosphate is especially challenging for several reasons. Due to the very high hydration energy of phosphate, ion selective membranes have a very poor selectivity for phosphate.[69,76,77] According to the characterization by the Hofmeister series (perchlorate > thiocyanate > iodide > nitrate > bromide > chloride > acetate > sulfate ∼ phosphate), phosphate, being at the end of the series, shows the lowest selectivity response toward the anions.[76,78] The free energy of the phosphate species is very small and the large size of orthophosphate ions prohibits the use of size-exclusion principles for increased selectivity.[79]

According to an overall review of phosphate sensors,[69,80] phosphate sensors can be mainly classified into three types, i.e., polymer membranes based on organotin, cyclic polyamine, or uranyl salophene derivative; protein-based biosensors; and cobalt-based electrodes. Table 3 summarizes the composition and characteristics of recently reported phosphate ion-selective membranes and cobalt-based electrodes. In contrast to nitrate

and potassium, where researchers appear to have reached something of a consensus on membrane type, many more directions are being actively pursued for phosphate ion-selective membranes.

The use of organotin compounds was initiated by Glazier and Arnold.[81,82] They prepared various dibenzyltin dichloride derivatives, such as bis(p-chlorobenzyl)tin dichloride, dibenzyltin dichloride, and bis(p-methylbenzyl)tin dichloride. The bis(p-chlorobenzyl)tin dichloride showed the best selectivity for dibasic orthophosphate (HPO_4^{2-}) against various anions, such as nitrate, bromide, chloride, and acetate.

The sensitivity was satisfactory, yielding a detection limit of 3.2×10^{-5} M and a linear range of response from 2.2×10^{-4} to 1.2×10^{-2} M for dibasic phosphate activity, when tested in standard solutions at pH 7. More recently, numerous studies on the development of new ionophores based on tin compounds have been reported to enhance the performance, in terms of selectivity and durability, of the phosphate sensor that Glazier and Arnold developed.[76,79,83,84] Liu et al.[76] reported that a binuclear compound bis(tribenzyltin) oxide incorporated in a PVC membrane with 2-nitrophenyl octyl ether (NPOE) as the plasticizer yielded an improved linear response in the range of 5×10^{-6} to 10^{-1} M HPO_4^{2-} and a lifetime of one month. The direct use of a commercially available chemical as an ionophore for phosphate determination was reported by Sasaki et al.[84] The electrode membrane containing tributyltin chloride as the ionophore and 25 mol% NaTFPB exhibited high selectivity for $H_2PO_4^-$ with a slope of -60 mV/decade.

Carey and Riggan[85] tried four types of cyclic polyamines, N_3, N_4, N_5, and N_6-cyclic amines, as ionophores for sensing dibasic phosphate ions. The electrodes were tested in phosphate solutions at pH 7.2. The N_3-cyclic amine showed the greatest selectivity for HPO_4^{2-}, and a linear calibration curve was achieved between 10^{-6} and 10^{-1} M, with a slope of -28.9 mV/decade. Surprisingly, the lifetime of the electrode was about nine months.

Wroblewski et al.[86,87] developed a different type of PVC membrane based on uranyl salophene derivatives as ionophores for the determination of phosphate. The highest selectivity for $H_2PO_4^-$ over other ions tested in solutions of pH 4.5 was obtained when incorporating salophene III (with t-butyl substituents) and NPOE plasticizer in a PVC membrane containing 20 mol% of tetradecylammonium bromide (TDAB). This membrane had a sensitivity slope of -59 mV/decade and a maximum lifetime of two months.

Kubo[88] developed a biosensor based on phosphate-bind protein (PBP) from Escherichia coli. The PBP was immobilized on a sheet of nitrocellulose membrane by cross-linking. The response time was about 5 min in the concentration range of 10^{-4}–1.5×10^{-3} M and there was no change in electric potential when other anions such as sulfate, nitrate, and bromide were added at a concentration of 5×10^{-4} M.

Xiao et al.[89] introduced cobalt metal as a phosphate ion-selective electrode material. They reported that oxidized cobalt metal electrodes showed potentiometric sensitivity to phosphate in the concentration range of 10^{-5}–10^{-2} M in 0.025 M potassium hydrogen phthalate (KHP) solution at pH 4.0. The tested electrodes displayed good selectivity for $H_2PO_4^-$ over other anions, such as sulfate, chloride, nitrate, and acetate but responded to changes in the partial pressure of oxygen dissolved in solution. A

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Table 3 Comparison of phosphate ion-selective membranes and electrodes

Composition	Characteristics[a] Base solution	Sensitivity (mV/decade)	Linear range (M)	Detection limit (M)	Selectivity (log K_{ij})	Lifetime	Reference
Measured species: HPO_4^{2-}							
2 wt% of bis(tribenzyltin) oxide; 65 wt% of 2-nitrophenyl octyl ether (NPOE); 33 wt% of high-molecular-weight polyvinyl chloride (PVC)	KOH-H_2SO_4 solution (pH 7.2)	−30.1	5×10^{-6}–10^{-1}	10^{-6}	$HPO_4^{2-} > Br^- > NO_3^- > Cl^- > Ac^- > SO_4^{2-}$	15 days	76
1.0 wt% of bis(guanidinium); 100 mol% of HDTODAB (Relative to ionophore; 2:1 ratio of NPOE to PVC	0.01M HEPES-buffer (pH 7.10)	−32.1	—	10^{-6}	—	1 month	77
18 wt% of bis(p-chlorobenzyl)tin dichloride; 36 wt% of dibutyl sebacate; 34 wt% of PVC; 12 wt% of N, N-dimethylformamide	0.01M Tris-H_2SO_4 buffer (pH 7.0)	−33	2.2×10^{-4}–1.2×10^{-2}	3.3×10^{-5}	$HPO_4^{2-} > I^- > NO_3^- > Br^- > Cl^-$	28 days	81, 82
20 wt% of 3-decyl-1,5,8-triazacyclodecane-2,4-dione (N3-cyclic amine); 35 wt% of dibutyl sebacate; 45 wt% of PVC	KOH solution (pH 7.2)	−29	10^{-6}–10^{-2}	—	$HPO_4^{2-} > Cl^- > NO_3^- > SO_4^{2-}$	—	85
Measured species: $H_2PO_4^-$							
2 wt% of bidentate organic tin compound; 65 wt% of bis(2-ethylhexyl) sebacate (DOS); 33 wt% of PVC	0.01M MES buffer (pH 5.50)	−54.6	—	—	—	20 days	79, 83
1 wt% of trialkyl/aryl-tin chloride 66 wt% of NPOE; 33 wt% of PVC; 25 mol% of NaTFPB	0.01M Tris-H_2SO_4 buffer (pH 7.0)	−60	10^{-4}–10^{-1}	7×10^{-5}	—	—	84
1–2 wt% of uranyl salophene derivative; 65 wt% of NPOE 33 wt% of PVC; 20 mol% of tetradecylammonium bromide (TDAB)	0.01M MES buffer (pH 4.5)	−59	10^{-4}–10^{-1}	—	—	2 months	86, 87
20 mm cobalt rod (99.99%, 5 mm diameter) coated with Teflon	0.025M potassium acid phthalate buffer (pH 4)	−55	10^{-5}–10^{-2}	5×10^{-6}	$Br^- > Cl^- > SO_4^{2-} = AcO > NO_3^-$	—	89
40 mm cobalt wire (99.99%, 0.5 mm diameter) and 40 mm silver wire (99.99%, 0.5 mm diameter).	0.02M potassium acid phthalate (pH 4.5–5.0)	−38 ± 0.5	10^{-5}–10^{-3}	10^{-6}	$I^- > Br^- > Ac^- > Cl^- > NO_3^- > SO_4^{2-}$	—	91, 92, 93, 94
6 mm cobalt rod (99.95%, 5 mm diameter) coated with silicone and a plastic body	0.25M CH_3COOH + 0.015M NH_4F, titrated to pH 4.0 with NaOH	−32.9 ± 0.9	10^{-4}–10^{-1}	10^{-5}	$Ac^- > HCO_3^- > Cl^- > F^- > Br^- > NO_3^-$	—	96

[a] Empty cells occur when data for that membrane or electrode characteristic were not provided in the reference.

host–guest mechanism involving formation of a non-stochiometric cobalt oxide species on the electrode surface was proposed to explain the response characteristic. Further study of the response mechanism was carried out by Meruva and Meyerhoff.[90] They suggested a mixed potential mechanism involving a slow oxidation of cobalt, a simultaneous reduction of oxygen and the formation of $CO_3(PO_4)_2$ at the electrode surface. The mechanism could better explain various characteristics previously found in the cobalt electrode, such as the effects of sample stirring rate and pH on electrode response.

Chen *et al.*[91] investigated the applicability of cobalt wire as a phosphate electrode in FIA. The electrode showed a linear response with a slope of about −38 mV/decade change in phosphate when tested in a carrier of the FIA system containing 0.04 M KHP (pH 5). Additional research[92] was conducted to see if the system could be applied to the direct determination of phosphate in soil extract samples by spiking and diluting the soil samples with standard phosphate solutions. Spiked soil extracts showed good recoveries for phosphate in the concentration range of 10^{-4}–10^{-3} M.

The use of the cobalt wire-based FIA system designed by the above authors was expanded to the determinations of phosphate in wastewater and fertilizers, and in hydroponic nutrient solutions.[93,94] In the wastewater and fertilizer samples, the difference between data measured with the cobalt-based FIA system and with a standard spectrophotometer was generally ±5% (relative) when correcting for a chloride interference. In the hydroponic nutrient solutions, the FIA system showed a relative error of ±4.2–8.6% in the phosphate concentration range of 58–120 mg L^{-1} as compared to standard methods.

Engblom[95] studied the applicability of a cobalt rod electrode to the measurement of phosphate in soil extracts. Ammonium lactate-acetic acid (AL), commonly used in Sweden, was chosen as a soil extracting solution. He reported that the cobalt electrode was linearly sensitive to phosphate ranging from 10^{-4} to 10^{-3} M in the AL soil extractant with a sensitivity slope of −30 mV/decade. A five-soil study comparing cobalt wire electrode results with standard phosphate measurements including ICP and colorimetric analyses showed that the concentrations predicted by the cobalt electrode were the lowest among those obtained with the three different methods. He indicated that the effects of iron and organic matter in the soil extracts on electrode response resulted in a lower sensitivity than was expected.

Similarly, Kim *et al.*[96] evaluated cobalt rod-based electrodes for sensing phosphorus extracted from soils using the Kelowna soil extracting solution. The cobalt rod-based electrodes exhibited sensitive responses to $H_2PO_4^-$ over a range from 10^{-5} to 10^{-1} M total phosphate concentration with a detection limit of 10^{-5} M in the Kelowna solution at a pH of 3.2. It was expected that this detection range would encompass the typical range of soil phosphorus concentrations measured in agricultural fields.[14] The selectivity of the cobalt electrodes was also satisfactory for measuring phosphates in the presence of each of six interfering ions, *i.e.*, HCO_3^-, Cl^-, Br^-, NO_3^-, Ac^-, and F^-, with the electrodes being 47 to 1072 times more responsive to phosphate than to the tested interfering ions.

Parra *et al.*[97] developed a flow injection system using a tubular cobalt electrode for the determination of inositol phosphates in seeds and grains. Two different buffer solutions, 0.01M KHP

(pH = 4) and 0.01M Tris-HCl (pH = 8), were used for inorganic and organic phosphates, respectively. A comparison of the results to standard methods (ICP and colorimetric analyzers) was conducted using samples of seed and grain. They reported there were no significant differences among the results produced by the three different methods.

In contrast to the nitrate and potassium membrane studies previously mentioned, a wider range of compositions has been considered in research on the synthesis and characterization of phosphate-sensitive ionophores. However, despite this broad range of investigation and the technical progress made so far, a clearly superior P-sensitive ionphore has not been found. A key impediment that has not been overcome is the low selectivity response of such membranes toward many anions. At present, the best alternative for phosphate measurement in soil extracts appears to be the solid cobalt electrode, which has exhibited sufficient sensitivity, selectivity and durability to provide a quantitative measure of phosphates in soil extracts.

3.2.4. Application of ISEs and ISFETs in laboratory tests.
Ion selective electrodes have historically been used in soil testing laboratories to conduct standard chemical soil tests, especially soil pH measurement. Many researchers in the 1970's and 1980's concentrated on the suitability of ISEs as an alternative to routine soil nitrate testing.[98–108]

Dahnke[108] used an ISE for determination of nitrate in soil extracts while changing several factors, including interfering anions, extracting agents, soil-to-solution ratios, and reference electrodes. The results showed that the lowest detection limit of the NO_3 electrode was about 1–2 mg NO_3–N L^{-1} in solution. He reported this detection limit would be useful in measuring nitrate ions in routine soil testing.

Li and Smith[107] investigated the suitability of a commercial nitrate electrode for the determination of NO_3–N at low concentrations (<2 mg L^{-1}) in soil extracts obtained with saturated $CaSO_4$ solution, by comparing the results to standard methods (1M KCl and continuous flow analysis (CFA)). The nitrate levels measured with the electrode were highly correlated with those obtained with the CFA analyzer ($r^2 = 0.94$), showing an almost 1:1 relationship (slope = 0.93) between the two methods. Also, they found that the $CaSO_4$ solution was effective for the extraction of nitrates from air-dried soils, removing 95% of the extractable nitrates after a 5-min shake period.

Many researchers used K-selective electrodes to estimate soil K concentration.[109–113] Farrell and Scott[110] evaluated valinomycin-based and cationic glass ion-selective electrodes for the determination of exchangeable soil K in $BaCl_2$ and NH_4OAc extracts. The Ba-exchangeable K values measured with the valinomycin-based electrode were highly correlated with, and not significantly different from, those obtained by AAS. However, direct measurement of the NH_4^+-exchangeable K^+ values using the electrode was not feasible due to a high concentration of NH_4^+ in the extracts.

Adamchuk[111] conducted a preliminary test of nitrate and potassium ion-selective electrodes in soils as opposed to soil extracts. The laboratory test showed that it was feasible to determine soluble nitrate and K content of moist soil samples ($r^2 = 0.56$–0.94) if several limitations such as inconsistent contact

between soil and electrode and potential drift due to continuous measurements were addressed.

Brouder et al.[112] performed a correlation study between plant-available K of 32 agricultural soils determined by two ISEs (glass and PVC-based) and by AAS analysis. Results showed that the ISE-K readings in soil slurries were highly correlated with AAS-K values in filtrates when using DI water at a 1:1 soil:solution ratio for extraction (slope = 0.93, r^2 = 0.76). However, the PVC-based ISE was not usable for measurement in soil slurries due to durability problems. Also, the ISE-K values obtained using DI water for extracting K were not well correlated with those obtained with standard methods using 1M NH_4OAc solution and an AAS analyzer.

More recently, Ciesla et al.[114] and Grygolowicz-Pawlak et al.[115] used valinomycin-based K-selective electrodes to determine potassium in Egner-Rhiem, a soil extractant used in Poland, and $BaCl_2$ in soil extracts. The K electrodes could determine K in soil extracts, showing a strong linear relationship to standard methods (r^2 > 0.84).

Use of an ISFET chip combined with FIA for soil analysis was reported by several researchers.[12,53,63,116,117] According to the literature, ISFET technology offers inherent features such as fast response, small dimensions, low output impedance, high signal-to-noise ratio, low sample volumes, and the ability to integrate several sensors on a single electronic chip – all of which are desirable for a real-time sensor.[117]

Birrell and Hummel[53,116] investigated the use of a multi-ISFET sensor chip to measure soil nitrate in a FIA system using low flow rates, short injection times, and rapid rinsing (Fig. 1). The multi-ISFET/FIA system successfully estimated soil nitrate-N content in manually prepared soil extracts (r^2 > 0.90). The rapid response of the system allowed samples to be analyzed within 1.25 s with sample flow rates less than 0.2 mL s^{-1}. However, their prototype automated soil extraction system did not consistently provide soil extracts that could be analyzed by the ISFET/FIA, due to blockages in the filtration process. They suggested that considerable effort would be required to develop an automated soil extraction system that enabled the soil sample to be well mixed with extracting solution and the nutrients to be effectively extracted from the soil solution.

Price et al.[117] developed a rapid extraction system that might be used in the field for real-time measurement of soil nitrates using the ISFETs developed by Birrell and Hummel.[116] Several design parameters affecting the nitrate extraction from the soil cores and output data of the ISFETs were studied. The results showed nitrate concentration could be determined 2 to 5 s after injection of the extracting solution when using data descriptors based on the peak and slope of the ISFET nitrate response curve.

More recently, Kim et al.[118] evaluated a sensor array including three different ISEs, based on TDDA-NPOE and valinomycin-DOS membranes and cobalt rod, to simultaneously determine NO_3–N, available K, and available P in Kelowna-soil extracts. The nitrate ISE method used in conjunction with the Kelowna extractant provided results in close agreement with the standard method (Lachat analyzer and 1M KCl extractant). However, the Kelowna-K ISE concentrations were about 50% lower than those obtained with the standard method (Mehlich III extractant and ICP spectrophotometer) due to decreased K extraction by the Kelowna solution. Soil P concentrations obtained with the Kelowna extractant and cobalt P ISEs were about 64% lower than those obtained by the standard method (Mehlich III extractant and ICP spectrophotometer) due both to a lower P extraction by the Kelowna solution, and to lower estimates of P concentrations in the extract by the cobalt P ISEs. Although P and K concentrations were low in comparison to standard laboratory procedures, a calibration factor could address this issue because there was a strong linear relationship between ISE and standard methods (r^2 = 0.81 and 0.82 for P and K, respectively).

In general, laboratory tests using ISEs or ISFETs have shown it to be feasible to determine macronutrients in moist soils or soil extracts due to a strong linear relationship to standard methods. However, difficulties encountered with current systems included a slower-than-desired and not completely reliable extraction process, electrodes of limited durability, and the need for frequent recalibration due to signal drift. Efforts toward improved extraction systems, electrodes, and auto-calibration processes could significantly increase the potential for commercialization of such systems.

4. On-the-go soil macronutrient sensing

Because on-site, rapid measurements of soil nutrients are an ideal approach to variable-rate application of agricultural fertilizer, several researchers,[119–121] beginning in the early 1990s, have reported on real-time on-the-go soil nutrient sensing using custom-designed soil samplers and commercially available ion-selective electrodes for sensing nitrate and pH in soils.

Adsett et al.[119,121] designed a prototype tractor-mounted field monitoring system to measure soil nitrate levels in fields using ISEs because they had found that a nitrate ion-selective electrode gave reliable sensor readings and acceptable response times of less than 20 s.[122] The system, consisting of a soil sampler, an extraction unit, a flow cell, and a controller, was tested in the laboratory and field. The soil sampler was initially designed with a chain saw blade and belt-conveying unit to gather and transport samples of known volume and density to the extraction and analysis unit. Results from laboratory testing indicated that the actual nitrate level could be predicted with 95% accuracy after 6 s of measurement.
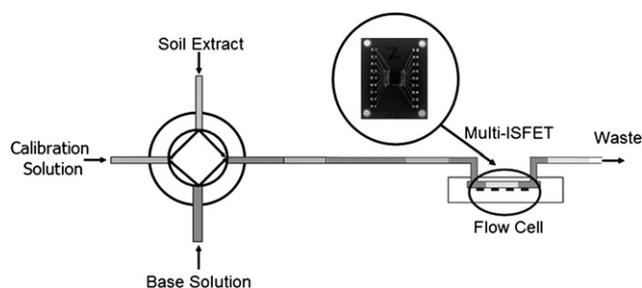
Fig. 1 Schematic of an ion-selective field effect transistor (ISFET) – flow injection analysis (FIA) system. The soil extract sample, calibration and base solutions are sequentially introduced through a flow injection line system with multiple inlets, and are transported to a multi-ISFET chip with outputs that continuously change due to the passage of the sample through the flow cell.

However, several mechanical and electrical problems were found during field testing, e.g., clogging of the extractor outlet with plant residue which resulted in unacceptable levels of noise in the electrode signal. Recently, it has been reported that the functionality of the automated soil sampler was improved and evaluated with comprehensive performance testing conducted in five fields. Soil samples with uniform bulk density were collected in a device of fixed volume, thereby providing precise estimates of the sample mass, as needed for accurate calculation of nitrate concentration.[123] Additional field-scale validation tests documented agreement between measurements of the soil nitrate by the extraction system and by standard laboratory instruments (slope = 1.0, r^2 = 0.94).[124]

Viscarra Rossel and Walter[125] built a soil analysis system comprising a batch-type mixing chamber with two inlets for 0.01M $CaCl_2$ solution and water. In the mixing chamber, there was a flat spinning disc ensuring efficient mixing of the solution and the soil. A pH ISFET was used to determine soil pH and estimate lime requirements. The system was tested in the laboratory using soil solutions of 91 Australian soils obtained by mixing 3 g of sieved soil and 15 ml of 0.01M $CaCl_2$ and tested in a 17-ha agricultural field to estimate lime requirements. The system produced an RMSE of 0.2 pH_{Ca} (r^2 = 0.66). However, the coefficient of determination for pH buffer estimates was not high (r^2 = 0.49).

Adamchuk et al.[120] developed an automated sampling system for soil pH based on direct soil measurement (DSM) by placing a flat-surface combination pH electrode in direct contact with moist soil collected by the sampling system. The system consisted of a lever situated below a soil tine, which collected a sample of soil and then rotated to press the soil slurry against the surface of the pH electrode. Tests showed a high correlation between the electrode voltage output and soil pH in the laboratory and field (r^2 = 0.92 and 0.83, respectively). The system could measure pH while taking soil samples at a pre-selected depth between 0 and 20 cm every 8 s.

As shown in Fig. 2, based on the results reported by Adamchuk et al.,[120] a commercial soil pH mapping system (Veris Technologies, Salina, Kansas, USA) was developed.[126] A soil sampling system consisting of a cutting shoe and a sampling trough was built to collect soil samples. The pH measurements were carried out with a flat-surface combination pH electrode, which was placed in contact with soil samples brought by the soil sampler. A microcontroller was used for controlling rinsing of the pH electrodes and communicating with a logging instrument. The accuracy of the system was evaluated by comparing collected pH data to laboratory analysis. The results showed a correlation coefficient of 0.79 between sensor readings and laboratory measurements. Afterwards, in a feasibility test of using the soil pH mapping system for the establishment of site-specific lime recommendations, Lund et al.[127] reported that on-the-go mapping of soil pH provided improved accuracy of lime prescription maps, showing a smaller lime estimation error of 1340 kg ha^{-1} than that obtained using 1 ha grid sampling (2109 kg ha^{-1}) when lime recommendations were calculated based on buffer pH laboratory tests. The feasibility of the on-the-go technology for soil pH mapping was studied by Adamchuk et al.,[128] who used the soil pH mapping system to plan variable-rate liming for eight production fields in six US states. The pH maps developed using the on-the-go system were compared with corresponding maps generated using conventional grid sampling. They reported that a field-specific bias in overall error estimates of 0.4 pH units or greater could be reduced to less than 0.3 pH units through site-specific calibration. Additionally, Staggenborg et al.[129] tested the feasibility of using the commercial mobile soil pH system on two fields in Kansas, one with a uniform soil and the other with six different soil types. Results showed that the real-time system provided more accurate estimates at the 0 to 7.5 cm depth (r^2 of 0.75–0.83) than at the 7.5 to 15 cm depth (r^2 of 0.53–0.79) In addition, the inclusion of soil electrical conductivity (EC) as a covariable improved pH estimates in the field with six different soil types, but not the uniform field.

Adamchuk et al.[130] investigated the suitability of the DSM approach for soil K, NO_3, and Na as well as pH. The r^2 of regressions between values determined by ion-selective electrodes and by corresponding reference methods were 0.93–0.96,
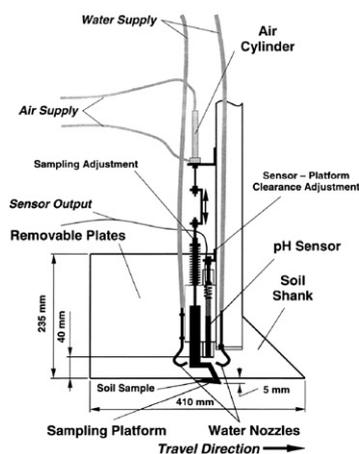
Fig. 2 A prototype pH-sensing shank and sampling mechanism (left, based on ref. 120 with permission) was a precursor of the commercial Veris Mobile Sensor Platform (right, Veris Technologies Inc., Salina, Kansas, USA). In the prototype system, a pneumatically-actuated sampling platform moves down to collect a small amount of soil and places it in contact with the pH electrode. Water is used to rinse the electrode between measurements. Although the implementation details are somewhat different in the commercial system, the general concept is the same.

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0.61–0.62, 0.41–0.51, and 0.1 for soil pH, K, NO_3–N, and Na, respectively. They mentioned that the reason for decreased accuracy for K, NO_3–N and Na was the difference in the level of variability of the soil properties in soil samples tested and stated that further research on integrated on-the-go mapping of soil chemical properties was needed.

Sethuramasamyraja et al.[131,132] developed an agitated soil measurement (ASM)-based integrated system that placed ion-selective electrodes into a suspension of soil and water. They investigated the effects of various measurement parameters, such as soil-water ratio and quality of water for electrode rinsing, on sensor performance and evaluated the system for on-the-go mapping of soil pH, soluble potassium and residual nitrate contents in 15 Nebraska soils under laboratory conditions. They reported that a 1:1 soil:water ratio and tap water for electrode rinsing were usable for simultaneous measurement of pH, K, and NO_3 with ion-selective electrodes. Calibration parameters were stable during each test for pH and K electrodes. However, significant drift was observed for the NO_3 electrode. Both accuracy and precision errors were low with good correlations to the reference measurements ($r^2 = 0.67$–0.98 for means).

Several researchers have used reflectance spectroscopy for in-situ monitoring of soil chemical properties in fields. Mouazen et al[133] developed a soil sensing system consisting of a soil penetration unit and an optical probe to measure soil carbon, moisture content, pH and P. Two different sets of VIS-NIR spectral data were collected in the laboratory and field. Calibration models were developed using the laboratory data, and the developed models were validated using the field measurement spectra. Estimation of moisture content was satisfactory ($r^2 = 0.89$) whereas the estimates of C, pH and P were not as well matched to the corresponding reference values ($r^2 = 0.73$, 0.71, and 0.69, respectively). Christy[134] evaluated NIR spectroscopy (920 to 1718 nm) for real-time, on-the-go measurement of soil chemical properties. Their system was evaluated in eight fields in central Kansas where spectral data were collected on transects, and calibration soil samples were obtained at multiple locations in each field. Of the soil properties evaluated, best estimates were obtained for organic matter (OM), with a RMSE of 0.52% and an r^2 of 0.67 between the laboratory measurements and NIR estimates. Soil P estimates were also fairly good (RMSE = 41 ppm, $r^2 = 0.65$), while K estimates were poor (RMSE = 146 ppm, $r^2 = 0.26$).

Overall, there has been much progress in on-the-go soil nutrient sensing based on ion-selective electrode technology. Notably, a soil pH mapping system is now commercially available after a sequence of research studies. Also, an automated field monitoring system with potential as a real-time soil NO_3–N analyzer has recently been improved with an automated sampler that provides precise estimates of the sample mass. On the other hand, on-the-go sensing of soil chemical properties using reflectance spectroscopy is somewhat less promising. Although good results have been reported in some cases, a number of calibration and accuracy issues remain to be addressed.

5. Conclusions

Growing concerns about environmental pollution by excessive use of fertilizers have led to increasing needs to monitor soil nutrients required for crop growth. Traditionally, such measurements have been carried out in a central laboratory, involving time-consuming sampling, transportation and storage steps. On-site monitoring of N, P, and K nutrients is preferable due to the potential for a higher density of measurements at a relatively low cost, allowing more efficient mapping of soil nutrient variability for variable–rate nutrient management. Optical diffuse reflectance in visible and near-infrared wavelength ranges has been used as a non-destructive method to rapidly quantify soil properties for site-specific management. However, application of optical sensor technology for on-site measurements of soil nutrients has been limited, primarily due to relatively poor estimates at critical macronutrient levels for soil fertility management, as well as strong effects of soil type. In principle, electrochemical sensing with ion-selective electrodes or ion-selective field effect transistors is a promising approach for real-time analysis because of rapid response, direct measurement of the analyte with a wide range of sensitivity, simplicity and portability. The disadvantage of on-the-go sensors based on ion-selective technology is that soil sampling and nutrient extraction are required, increasing the complexity of the system and the time required for a measurement. However, recent successful commercialization of a soil pH mapping system based on ion-selective technology shows there is potential to overcome these issues.

Improved on-the-go soil mancronutrient sensing leading to potentially commercial products will require additional research and development efforts. First of all, in the near future, further efforts are needed to improve the durability of current on-the-go sensing systems under harsh conditions found in the field. The adoption of a simple alarm monitor to signal the operator in the event of a system malfunction may be the first step toward commercial success. For practical use, future systems that allow continuous monitoring of soil nutrients will require further research to integrate soil sample collection, automated sample preparation, and nutrient analysis. These systems will likely rely on technical advances in electronics and mechanical engineering such as microelectromechanical systems (MEMS) and flow injection analysis (FIA) that may enable the system to be fully automated, thereby providing high reproducibility in sensor data. Since these miniaturization techniques will accommodate low-volume samples, resulting in a reduction in reagent consumption and waste generation, a feasible automated soil sampler and extraction system may be easier to develop. Furthermore, use of a sensor array capable of determining several analytes, such as soil macronutrients and pH, simultaneously would further reduce sample processing time, sample volume and reagent consumption. Integration of the multiple data streams available from such a multianalyte sensor array might provide improved estimates of the individual analytes through its ability to quantify and factor out any cross-channel responses.

Widespread adoption of on-the-go soil nutrient sensing may be somewhat limited by the degree to which precise sampling and rapid extraction of the macronutrients in the sample can be achieved in a real-time system. Because extraction efficiency is strongly affected by the extraction time and because the time required for complete extraction may not be feasible in a real-time system, this approach may provide different results as

compared to traditional soil testing methods. In this regard, research will be needed to calibrate sensor-based nutrient measurements against plant nutrient response, so that agronomists and growers gain confidence in the applicability of the new methods. Such a calibration might be implemented in the same way that past calibrations to standard laboratory measurements were developed. However, this process would require numerous field experiments with different crops and soil types. An alternative method, whereby sensor measurements were directly calibrated to laboratory nutrient measurements across a broad range of conditions, might be preferable. Although the calibration to plant response would be an indirect one with this approach, it would be considerably less costly and time-consuming.

Acknowledgements

6. References

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