In-Soil Potassium Sensor System

SHERLAN G. LEMOS,[†,‡] ANA RITA A. NOGUEIRA,*[,†] ANDRÉ TORRE-NETO,[§]
ALEIX PARRA,[#] JUDIT ARTIGAS,[#] AND JULIAN ALONSO[#]

Grupo de Análise Instrumental Aplicada, Embrapa Pecuária Sudeste, C.P. 339,
13.560-970 São Carlos, SP, Brazil; Departamento de Quimica, Universidade Federal de São Carlos,
São Carlos, SP, Brazil; Embrapa Instrumentação Agropecuária, São Carlos, SP, Brazil; and Grup de
Sensors i Biosensors, Departament de Química, Universitat Autònoma de Barcelona, Bellaterra, Spain

A potentiometric sensor system based on potassium ion-selective electrodes was developed for agricultural purposes. Sensors were built using PVC ion-selective membranes over an inner solid contact prepared with graphite−epoxy composites. A copper plate was used as a reference electrode. A two-stage electronic circuit composed of current and voltage amplifiers was designed to interface the sensors to a distributed data acquisition system. Three ion-selective sensors and three off-the-shelf temperature sensors and their associated circuits were mounted in a PVC tube to set up a soil probe. The electronic controls were placed in an airtight box fixed at the upper part of the probe. The system was evaluated in the field, where the sensors presented sensibility within the range of 69−71 mV dec^{-1}. Extracts of soil samples were analyzed by a current flame photometry approach, and the results, compared with the probe measurements, showed a linear relationship ($r^2 = 0.992$ and 0.995, respectively, to 5 and 20 cm depths), which implies viability and instrumentation reliability for agricultural applications.

KEYWORDS: Potassium; in-situ; soil analysis; soil fertility; potentiometric sensor

INTRODUCTION

Potassium is one of 16 nutrient elements needed by plants for healthy growth. It is the second one, surpassed by only nitrogen, in the amounts required by plants and is a key nutrient involved in many vegetal metabolic processes such as enzymatic activation, osmotic control of water economy, carbohydrate production, and cation/anion balance (*1*).

New agricultural practices have been focused on an economical and environmental point of view. These include the use of fertilization methods to optimize economical costs and to minimize negative environmental impacts. In this way, efforts dealing with concepts such as sustainable agriculture or precision agriculture (*2, 3*) have gained relevance.

Current agriculture demands continuous in-situ information of soil physical and chemical parameters, such as macro- and micronutrients, owing to modulation of the amounts of fertilizers to be added. Some commercial systems allow physical data to be obtained, but not much instrumentation has been developed to determine concentrations of key parameters such as nitrogen, phosphorus, and potassium in soil. These and other parameters are normally obtained by off-line methods (*4−8*); these methods provide some data of great accuracy and precision about the soil composition, but they do not allow the migration behavior of nutrients from soil surface application through the soil profile to be monitored, when submitted to different interaction processes such as sorption, leaching, bioaccumulation, and volatilization. Scarce examples of soil in-situ analysis (*9*) can be found in the literature.

The most promising analytical instrumentation developed belongs to the sensor field. In recent years, instrumentation based on direct contact or remote sensing performed in close proximity to the crop has been introduced. The advantages of sensors are their robustness, reduced size, versatility, and low mass-production costs. They are simple devices, compared with other analytical techniques such as chromatography or spectroscopy, and, moreover, they offer the possibility of designing in-situ analysis systems (*10*).

The aim of this work was to develope analytical instrumentation that permits potassium monitoring directly in soil, obtaining continuous and in-situ information for this nutrient. To accomplish this purpose, a K$^+$ soil probe containing three all-solid-state ISEs located at different probe heights was developed. Instrumentation capable of transmitting digital data signals via radio was coupled to the probe. The developed system was evaluated to provide an understanding of the relationship among free potassium in soil nutrients reserves, soil texture, and root growth, which could optimize fertilizer consumption. The results were compared by means of a standard method based on potassium extraction from soil with an ion-exchange resin and its subsequent determination by flame photometry (*11*).

* Author to whom correspondence should be addressed (fax 5516 3361 5754; telephone 5516 3361 5611; e-mail anarita@cppse.embrapa.br).
† Embrapa Pecuária Sudeste.
‡ Universidade Federal de São Carlos.
§ Embrapa Instrumentação Agropecuária.
# Universitat Autònoma de Barcelona.

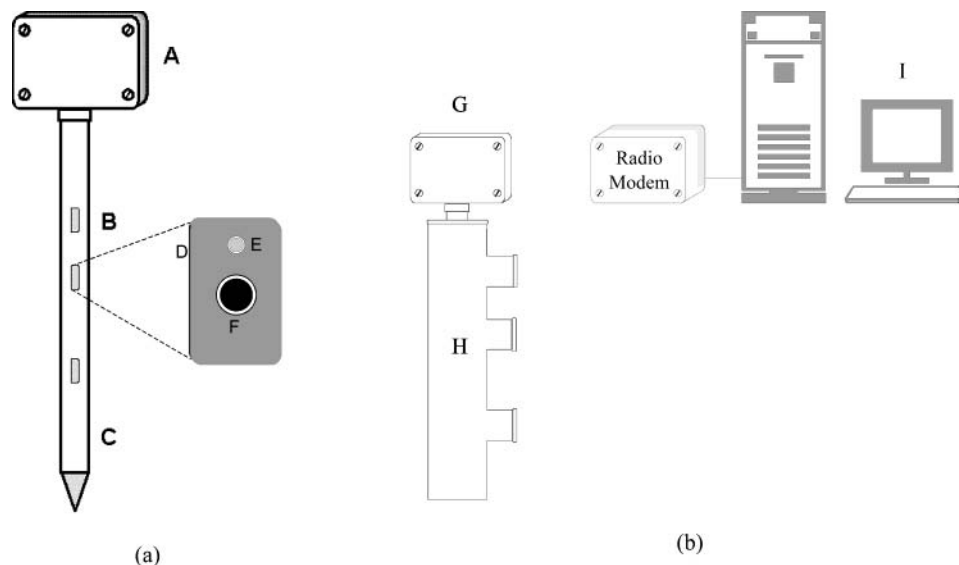In-Soil Potassium Sensor System

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Figure 1. Analytical probe: (**a**) A, upper part of the probe-containing amplifier, multiplexer, 8 bits A/D converter; B, PVC tube with sensors installed at 5, 20, and 50 cm depths; C, PVC plug; D, copper plate (reference electrode); E, polyethylene tube for addition of standard potassium solutions; F, frontal view of the sensor installed in the probe; (**b**) in-laboratory sensor system, G, analytical probe; H, PVC column filled with soil; I, radio receptor, converter, and PC for signal data acquisition, treatment, and storage.
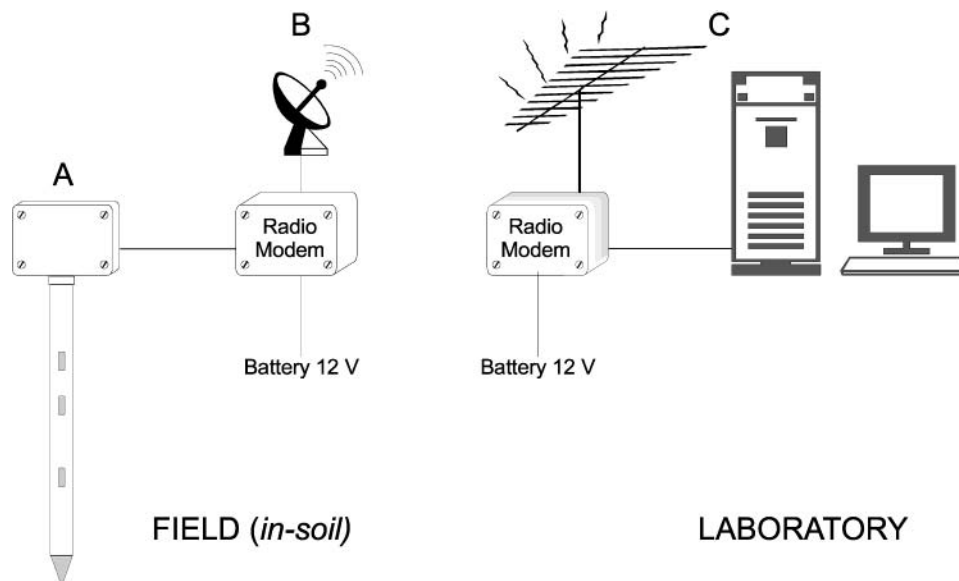

Figure 2. Assembly scheme for the in-field probe evaluation: (A) analysis probe; (B) data conversion and transmission; (C) data reception, acquisition, and treatment.

MATERIALS AND METHODS

All-Solid-State Potassium Sensor. Sensors were constructed using a 2 mm electrical connection welded to a circular copper plate. This set was inserted in a 6 mm i.d. and 18 mm length PVC tube, and its end was filled with a graphite−epoxy composite used as transducer. The epoxy resin was prepared by mixing Araldite M and the hardener HR (Ciba-Geigy) in a 1:0.4 weight ratio. This was also mixed with graphite powder (Merck) in a 1:1 weight ratio. The composite was cured at 40 °C for 24 h. After that, the surface was polished, a 0.3 mm depth cavity was obtained, and a polymeric membrane with sensor mixing was added, allowing the evaporation of tetrahydrofuran.

Polymeric membrane composition was as follows (w/w): 30% PVC, 67% plasticizer [bis(2-ethylhexyl)sebacate)], 2.5% potassium ionophore (Valinomycine), and 0.5% of an ionic additive [potassium tetrakis(4-chlorophenyl) borate]; 0.05 mL of tetrahydrofuran per milligram of PVC was used. All reagents were acquired from Fluka (Buchs, Switzerland).

Soil Potassium Probe. The soil potassium probe is depicted in **Figure 1**. Two main parts can be observed. The lower one comprises a PVC tube ($l = 1.2$ m, $\varnothing_{\text{ext}} = 9$ cm) with three potassium-selective electrodes and three off-the-shelf temperature sensors (LM35, National Semiconductors) located at 5, 20, and 50 cm depths related to soil surface. The ion-selective sensors are placed in the center of copper plates working as reference electrodes. Considering the type of sample, this reference electrode can maintain an intimate contact with the soil moisture, and maintenance problems could be avoided. Once a redox couple on the superficial surface was achieved, a constant and reproducible time-independent potential signal was provided. Moreover, this reference electrode has inherent advantages such as low cost, easy handling, and great in-soil stability (*9*).

The other part of the probe was composed of an airtight box, which holds necessary instrumentation for signal amplification and data transmission. At the top of each sensor, a small silicone tube, coming through the PVC tube from the upper airtight box, allowed in-situ calibration processes to be carried out when the apparatus was buried in-soil. Current amplifier circuits were mounted inside the PVC tube as close as possible to the sensors. A voltage amplifier was placed inside the airtight box located in the upper part of the probe. A data
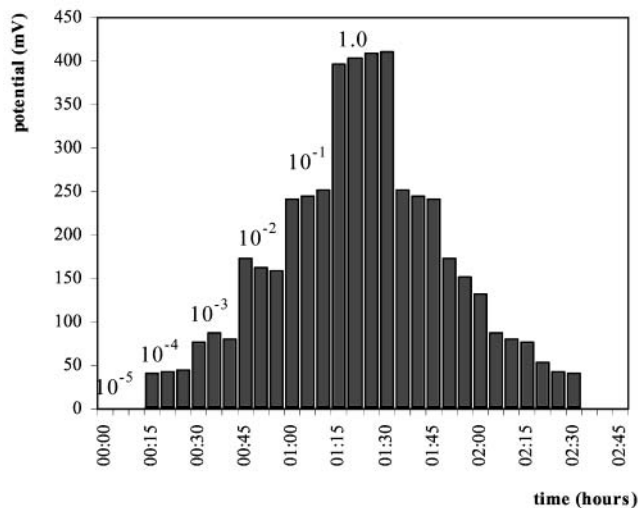
(a)
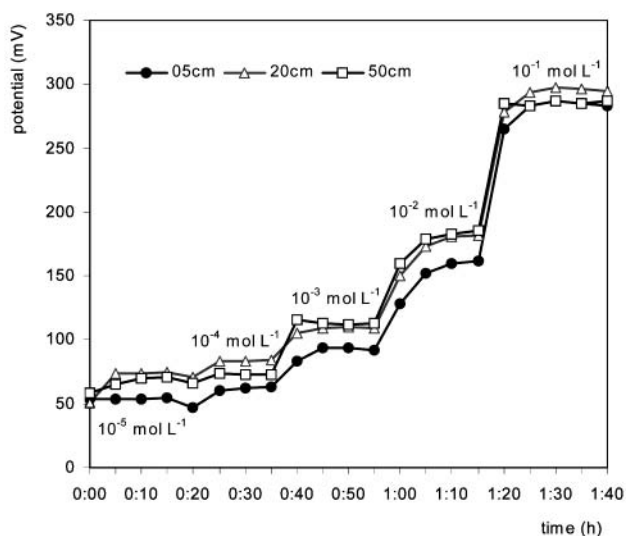
(b)

Figure 3. (a) Cyclic in-soil calibration using from 10^{-5} to 1.0 mol·L^{-1} analytical KCl solutions. (b) Potassium sensor calibration using 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} mol·L^{-1} analytical KCl solutions. Each bar or point corresponds to a 5 min average measurement.

Table 1. Analytical Curves Obtained by Addition of K$^+$ Standards through the Silicone Tubes ($n = 5$)[a]

sensor	equation
5 cm	$y = 69.4\,(\pm 10.9)^{b}x + 369.1\,(\pm 51.2)^{c}$
20 cm	$y = 70.9\,(\pm 8.2)^{b}x + 374.4\,(\pm 78.5)^{c}$
50 cm	$y = 71.2\,(\pm 10.6)^{b}x + 408.7\,(\pm 74.5)^{c}$

[a] y = potential (mV) and x = logarithm of potassium concentration (log [K$^+$]). Errors obtained with a 95% confidence level for [b]S_a and [c]S_b.

acquisition system developed by Torre Neto et al. (*12*) was used to collect temperature and potassium signals, convert them into digital data, and transmit them in real time via radio to a remote computer, where the data automatically fill out an electronic worksheet. The data acquisition system was programmed to obtain every 5 min temperature and potassium measurements. These experimental values were acquired as an average of 10 measurements obtained by the sensor system every 30 s.

Comparative Soil Potassium Determination. The comparative potassium method (*11*) used was based on a soil K$^+$ extraction with a
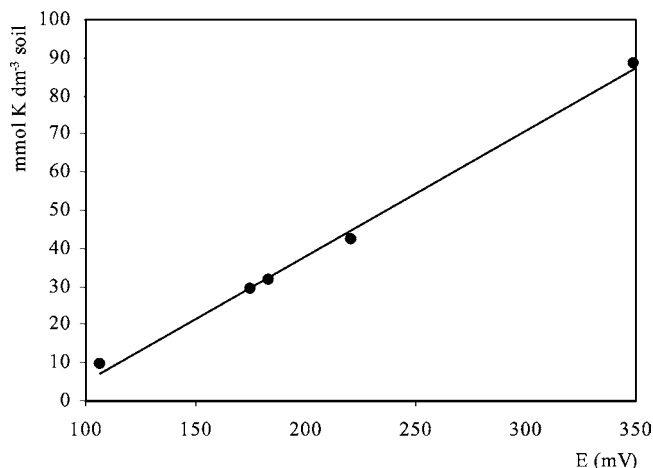

Figure 4. Extractable K$^+$ concentration versus potential plot (20 cm sensor).

Table 2. Calibration and Validation Sets for the in-Situ External Calibration[a]

		soil K concn (mmol K·dm^{-3} of soil)	
sample	potential (mV)	FP[b]	silicone tube calibration
1	96.7	6.85	4.16
2	106.5	9.82	7.36
3	183.6	31.7	32.6
4	221.2	42.4	44.9
5	349.1	88.5	86.8
6	104.0	8.16	6.56
7	217.8	39.1	43.8
8	175.3	27.4	29.9
9	133.3	19.6	16.2
10	129.9	18.9	15.0

[a] Samples 1–5 were used to construct the model, and samples 6–10 were used to model validation. [b] Flame photometry.

mixed cationic and anionic extraction resin followed by flame photometry determination.

In-Laboratory Studies. In this stage the electric signals provided by sensor probe were evaluated. The apparatus had to ensure their autonomous operation and the viability of the transmission via radio. The aim of these studies was also to determine the potassium sensor's performance under controlled conditions.

To perform sensor calibration when the probe is buried in soil, a setup constructed with a PVC tube ($\varnothing_{\text{i.d.}} = 12$ cm) filled with soil was assembled to simulate real conditions. The PVC setup had three lateral openings, corresponding to sensor depths in the probe (5, 20, and 50 cm), which were used to take soil samples. These samples were analyzed by the comparative procedure (*11*), and results were compared with those provided by the sensors.

With the probe inserted in the soil, 3 mL of potassium analytical solutions (10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}, and 1.0 mol L^{-1} KCl) was added through a silicone tube located in the inner part of the probe body with its outlet placed as close as possible to sensors, and the potential changes were set. Once the last standard solution was added, an excess of water was used to clean up the sensors and return to potential baseline. This experiment, called "in-situ external calibration", can cover 4 orders magnitude of K$^+$ concentration.

Another laboratory experiment was performed to evaluate the probe behavior after a potash fertilization. A mass of 1.27 g of KCl, corresponding to ~150 kg/ha K$^+$ as K$_2$O, was added at the top of the column, and the sensor signal evolution was monitored. Similarly to previous experiment, soil aliquots were collected at different levels and the exchangeable K$^+$ was determined by flame photometry, to compare the results. This experiment was called "soil-profile calibration".

In-Field Soil Studies. The potassium probe and its associated instrumentation were installed in a fertile soil close to the laboratory.
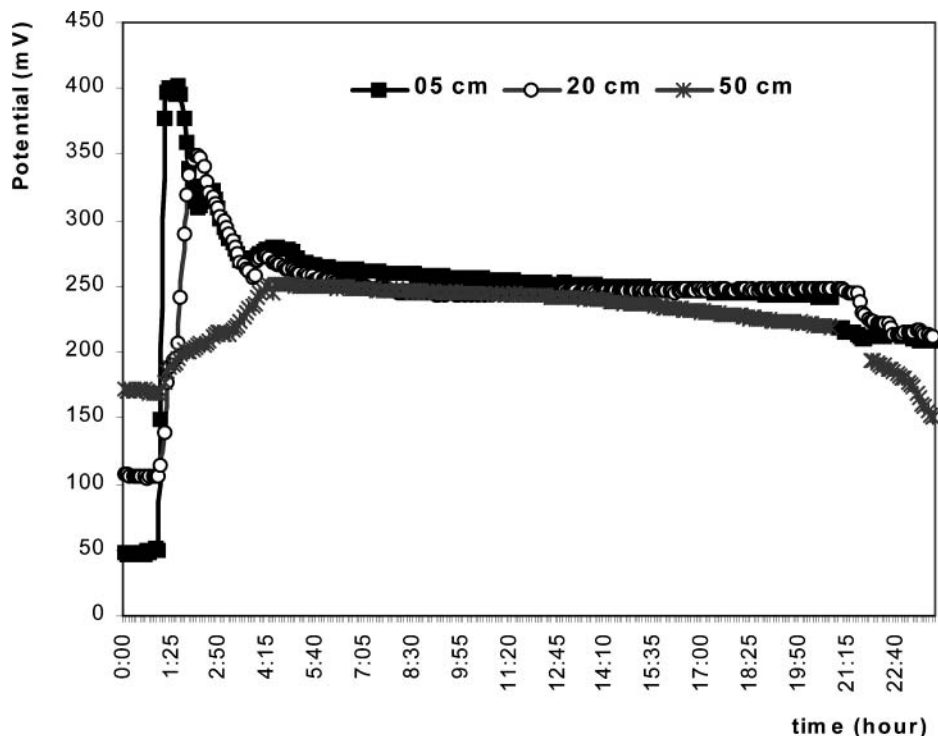
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Figure 5. Signal profiles after fertilizer addition.

All instrumental systems required to obtain and to transmit data were settled in field (**Figure 2**). First, an in-situ external calibration curve from 10^{-5} to 10^{-1} mol·L^{-1} was obtained by adding 3 mL of KCl standard analytical solutions through silicone inner tubes. A comparative in-field study was performed by collecting soil samples at three different depths, 0.5 m away from where the probe was installed. Potassium amounts were determined by flame photometry method and compared with the results obtained with the probe, after interpolation in the respective calibration curves.

RESULTS AND DISCUSSION

In-Laboratory Studies. External calibrations have been carried out previously to ensure potassium sensor's performance using potassium standard solutions at concentrations of $10^{-5}-10^{-1}$ mol·L^{-1}. Sensors presented a linear response from 10^{-4} to 10^{-1} mol L^{-1} and showed slightly super-Nernstian slopes of 72.1 ± 11.4, 70.9 ± 8.3, and 75.1 ± 8.7 mV·dec^{-1}, related to the sensors at 5, 20, and 50 cm depths, respectively. The super-Nernstian responses can be related with the experimental procedure employed, which is based only on the soil potassium diffusion, different from standard tests that are solution mixing dependent.

In-Situ Calibration. To verify possible memory effects on sensor response along the in-situ calibration tests, a cyclic calibration experiment with increasing and decreasing K$^+$ concentrations was performed. The cyclic behavior was obtained only when a higher amount of potassium solution was used in the decreasing concentration step, as could be expected due to the potassium behavior in-soil (*13*). This can be verified in **Figure 3a** by the softener decline response in that stage compared with the instantaneous response to the increasing concentration step using different KCl standard analytical solutions at the 20 cm depth K$^+$ in-soil sensor. This the developed instrumentation to be validated electronically.

Figure 3b shows one set of sensor calibration curves using 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} mol L^{-1} K$^+$ analytical solutions introduced by the inner silicone tubes when the probe was buried in-soil. As can be observed, sensor responses were similar and

independent of its depth. The equations of the in-soil analytical curves obtained for each sensor are described in the **Table 1**.

The results provided by this calibration approach are not the final information required to adjust a mathematical model, once the results produced are expressed as concentration in a liquid solution (mol·L^{-1}). Furthermore, by means of the data generated by the probe it is possible to find a value for potassium concentration in terms of moles per liter through the equations described in **Table 1**. Moreover, quantitative knowledge of the dilution caused by soil is unknown. Thus, the exchangeable K$^+$ amount is proportional to the generated potential and will always be smaller than the concentration added by the silicone tube. Besides, soil fertility monitoring programs usually generate results expressed in units of potassium concentration present in a solid matrix (mmol·dm^{-3} or mmol·g^{-1} of soil).

Therefore, previous in-situ external calibration was compared to results obtained by the FP methodology, obtaining a relationship between the generated potentials and the exchangeable K$^+$ soil concentration. Five samplings were accomplished for each depth fixed before and related to the K$^+$ amount determined by flame photometry comparative methodology. For each accomplished sampling, the respective potential was registered and related with the results obtained by the comparative procedure, obtaining new models. As an example, **Figure 4** shows the relationship between soil K$^+$ exchangeable amount and potential to the 20 cm sensor. The obtained equation was [K$^+$] (mmol·dm^{-3} of soil) $= 0.3272E$ (mV) $- 27.469$, $r^2 = 0.9952$.

Five more samples from the fixed depths were used as a validation set; that is, in each sampling the potential was registered and the exchangeable K$^+$ amount determined by its correspondent mathematical model. In **Table 2** is presented a comparison of the results obtained by the photometric methodology and using the calibration through the silicone tubes for the sensor at 20 cm. The first five results are referred to model construction and the five remaining to the validation.
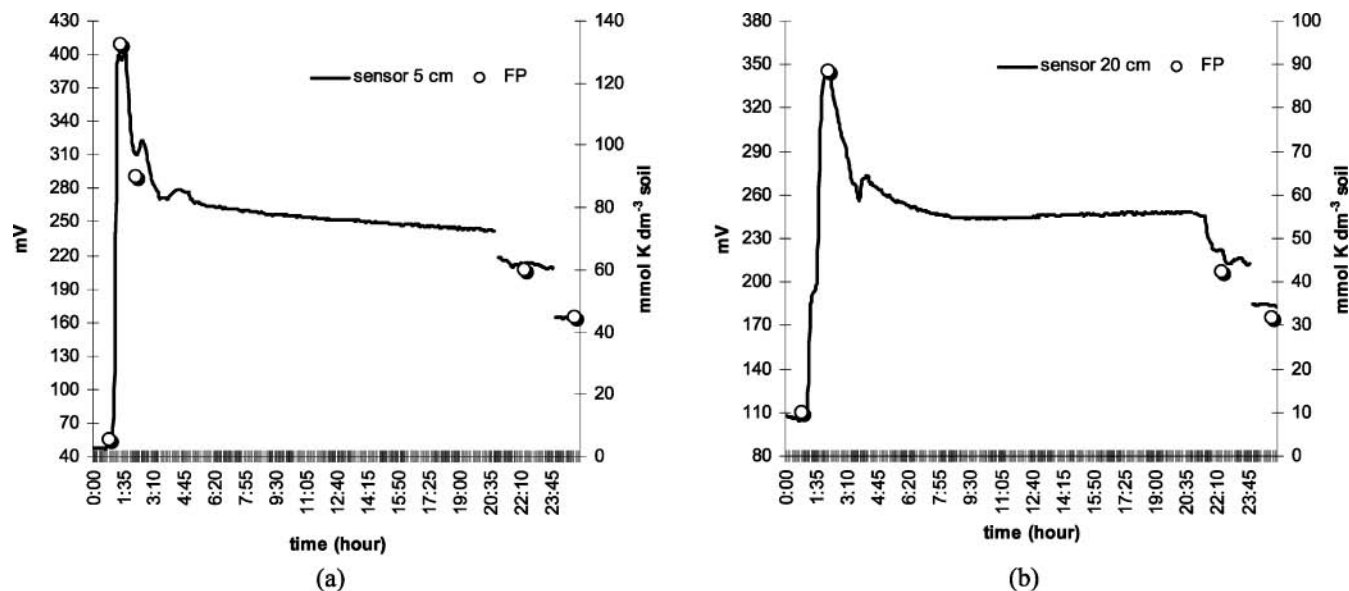
Figure 6. Sensor register in comparison with the results provided by the potassium soil analysis standard method: (**a**) 5 and (**b**) 20 cm.

Table 3. Linear Equations Obtained between the Potentials and the Flame Photometry Methodology[a]

sensor	equation	r^2
5 cm	$E_{(mV)} = 4.4\ (\pm1.6)^b[K_{FP}{}^d] + 41.7\ (\pm0.9)^c$	0.992
20 cm	$E_{(mV)} = 3.4\ (\pm0.4)^b[K_{FP}] + 77.4\ (\pm6.2)^c$	0.995

[a] Errors obtained with a 95% confidence level for ^bS_a and ^cS_b. [d] Flame photometry (mmol K·dm^{-3} of soil).

Using a paired *t* test, it was verified that the two data groups are not significantly different at a 95% confidence level.

Soil-Profile Calibration. System behavior was evaluated when the probe was buried in-soil and a fixed amount of potash fertilizer was added (**Figure 4**). Initially, sensors present a constant potential value. After fertilizer addition, three different potential curves can be observed. At a 5 cm depth, an abrupt potential increment, ~350 mV, and a no-return response to initial baseline were observed. The 20-cm depth sensor accomplished a similar response, but with a softer potential increment, ~250 mV. A wider peak for this sensor was expected; however, the fertilizer concentration used was overestimated and the 5 cm depth sensor area became saturated; consequently, almost the same amount of potassium was leaching to the 20 cm depth sensor area. At a 50 cm depth, a soil K^+ dilution occurred and the sensor set registered a lower increase, ~80 mV, and a broader behavior was observed due to soil dilution.

Different soil samples were taken along the previous experiment, and the results obtained by the photometric method were used in comparison to the potentiometric one. In **Figure 5**, the evolution of two sensor signals is presented and correlated with the results provided by the comparative FP procedure for soil samples taken during the experiment. Good agreement was observed in both procedures, and they can be used in soil sensor calibration.

An attempt had to be made to find a constant mathematical relationship among the generated potentials and the results obtained by the comparative methodology in order to obtain a calibration model when the sensor probe is installed in-soil. **Table 3** shows the linear equations and the relationships obtained between the two methodologies. Similar sensibilities with good correlation are observed among the sensors.

However, those models were generated in very specific conditions of temperature and moisture, with small changes in these properties. According to the Nernst law, the temperature is a relevant parameter in potential variations, and under normal harvest conditions, soil temperature can vary by >10 °C during the day. Therefore, such a parameter should be introduced as a variable in the calibration model to ensure confident in-field results. Indeed, whole measures were accomplished in the field capacity. These conditions facilitate the K^+ mobility, which is directly dependent on the total moisture content. To complete a calibration model, moisture and temperature variations have to be considered.

In-Field Soil Studies. The in-field monitoring system was accomplished in 15 days. The obtained potentials were similar to those obtained by the soil profile calibration step, presented in **Figure 6**. At a 50 cm depth, the sensor presented a higher sensibility and a lower detection limit compared to the former depths. This behavior can be explained by a proportional decrease of potassium concentration with soil depth. The calibration procedure designed during the laboratory step, based on additions through the silicone tubes, was used to determine K^+ concentration in the field, as described previously.

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