

# Miniaturized biparametric probe for in-soil nutrients monitoring

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## Abstract

In this work, a miniaturized biparametric probe based on the green tape technology is presented. The probe includes two ion-selective electrodes for the simultaneous and direct determination of nitrate and potassium not only in aqueous solution but also in soil. Results obtained from calibration experiments performed in both media showed adequate analytical features. In-soil monitoring experiments demonstrated the viability of this probe to provide understanding information about soil processes in which  $K^+$  and  $NO_3^-$  ions are implied. Additionally, the green tape properties combined with the simplicity and reduced dimensions of the probe design, provide a way to develop wireless devices that integrate all the associated elements in the same substrate (sensors and electronics). These devices could be later applied to establish a wireless sensor network able to generate useful and complete information about long extensions of soil.

**Keywords:** nitrate, potassium, ion-selective electrodes, green tape technology, wireless sensor network.

## INTRODUCTION

Nowadays, grand efforts have been focused on the development of new agricultural practices that allow not only to optimize economical costs but also to minimize their negative environmental impact through appropriate and controlled fertilization processes. Current tendencies for precision agriculture point to obtaining continuous *in situ* information about soil physical and chemical parameters. Chemical sensors are one of the most promising fields for in-soil analysis systems.<sup>1</sup> They are simple devices, compared with other analytical techniques, do not require the use of extraction methodologies and provide a robust, versatile and low cost methodology. The miniaturization of this kind of system provides some advantages when compared with their counterparts in the macro scale

(portability, reduced costs and complexity, minor invasion of the medium of interest, among others). Analytical devices from the micrometer to the centimeter scale are usually fabricated using glass, silicon and polymers.<sup>2</sup> Silicon and glass present well-established fabrication processes that offer high precision and reliability. However, the integration of the different platforms associated to an analytical process implies high costs and long-term fabrication processes. On the other hand, polymers provide chemical inertness and low costs, which results in economical and disposable devices. Different polymers, such as polydimethylsiloxane (PDMS), polymethylmethacrylate (PMMA) and polycarbonate (PC), have been widely investigated for applications in microsystems fabrication.<sup>3</sup> Nevertheless, these materials present sealing problems when using the multilayer approach and

deficient adherence to printed tracks that are required in electrochemical detection systems. Recently, the low-temperature co-fired ceramics (LTCC), commonly used for electronic circuit fabrication, have been applied as novel substrates to fabricate micro analysis systems.<sup>4</sup> Unlike silicon, glass and polymers, this technology does not require clean rooms, allows easily developing three dimensional structures with perfect adhesion between layers and involves reduced prototyping times. Additionally, since this technology is perfectly compatible with screen-printing techniques, electronics and printed electrodes can be easily integrated within the same substrate, allowing the procurement of complete analytical devices.

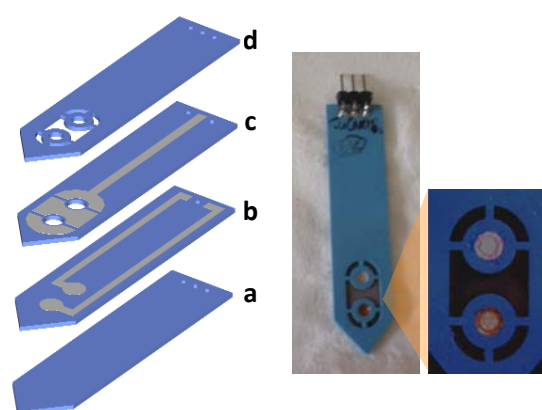
In this work, a miniaturized biparametric probe based on the green tape technology was developed to monitor two in-soil macro nutrients ( $K^+$ ,  $NO_3^-$ ).<sup>5-7</sup>

Taking advantage of the compatibility presented by the green tape technology with screen-printing techniques, both the polymeric-based ion-selective and the reference electrodes were embedded into the ceramic body using silver-based paste. This compatibility can be later profited to integrate all the electronics associated to signal conditioning and data acquisition in the same substrate. Further efforts are under development to obtain an autonomous device able to be applied in a wireless sensor network.

## EXPERIMENTAL

**Miniaturized biparametric probe fabrication.** The sensor probe was fabricated using Dupont 951 as substrate and applying the multilayer approach of the green tape technology, as described elsewhere.<sup>4</sup> A total amount of 6 layers were needed (250  $\mu\text{m}$  each). Conductive paths were screen-printed on layers *b* (ISEs) and *c* (reference electrode) to provide electrical contact between the chemical sensors and an external set-up. The three-dimensional approach of the

green tape technology allowed defining cavities for the later deposition of PVC-based ion-selective membranes for  $K^+$  and  $NO_3^-$  determination. These cavities were defined in layers *c* and *d*, this way, once the sensor cocktails were deposited into them, a direct contact between the membranes and the corresponding silver track printed on layer *b* was established. Layer *d* allowed defining a region surrounding the two ISEs, that exposes the printed track corresponding to the reference electrode.



**Figure 1.** Miniaturized biparametric probe for nutrients monitoring; **a:** bottom layer; **b:** silver paths over which the PVC membranes will be deposited; **c:** layer containing the reference electrode; **d:** top layer. The dark region surrounding the ISEs in the photo corresponds to the Cu/CuO reference electrode.

Once the device was burned-out, an anodization procedure was applied to the reference silver track to deposit Copper onto its surface. The anodization process consisted on immersing the probe in a  $\text{CuSO}_4$  1 M solution and applying a fixed potential of 0.5V during 10 minutes to the corresponding electrical terminal. Once the Cu was deposited, it was oxidized to form the pair Cu/CuO. The PVC-based ion-selective membranes were deposited by dripping the membrane cocktails into the previously defined cavities.

The composition of the nitrate membrane<sup>8-10</sup> consisted of 6 wt % tridodecylammonium nitrate

$[(C_{12}H_{25})_3(CH_3)N]^+NO_3^-$  (Fluka), 65 wt % TEHP (tris(2-ethyl)hexyl phosphate) (Fluka) and 29 wt % PVC (Fluka). The potassium membrane consisted of 1 wt % valinomicyn ( $C_{54}H_{90}N_6O_{18}$ ) (Fluka), 65.5 wt % Bis(2-ethylhexyl) sebacate  $((CH_2)_8(COOC_8H_{17})_2)$  (Fluka), 0.5 wt % potassium tetrakis(4-chlorophenyl)borate (Fluka) and 33 wt % PVC (Fluka). All the membrane components were weighed out and dissolved in THF.

**Experimental set-up.** Since the signals provided by both sensors can produce values in the range from -1 V, a signal conditioning circuit (SCC) was developed to adjust them to a new range between 0 and 2.5 V (input range of the data acquisition system). This SCC was implemented by means of instrumentation amplifiers that applied the expression:  $y=1.25(x+1)$  to the lecture. The data acquisition system consisted in a TMI potentiometer (Barcelona, Spain).

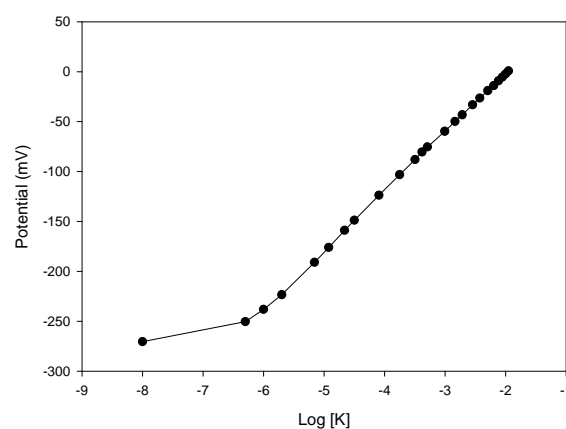
## RESULTS AND DISCUSSION

To ensure a proper analytical behavior of the microprobe (ISEs and reference electrode) a calibration process was performed in milli-Q water (Millipore, Bedford, MA). In this case, the evaluation was done using  $KNO_3$  standard solutions. Analytical features of the LTTC device, such as sensitivity and limit of detection were obtained from the calibration plots.

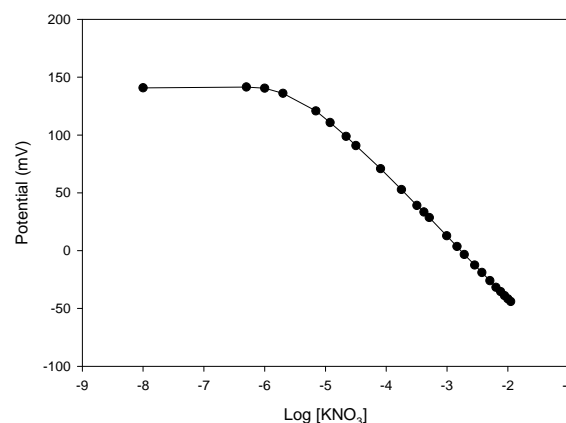
Figures 2 and 3 present the calibration plots obtained in solution for potassium and nitrate, respectively. In both cases, the sensors presented near-nernstian slopes, comparable with those found in the literature for conventional ion selective electrodes. According to these plots, a four-decade working range was obtained.

The limit of detection was found to be  $2.9 \times 10^{-7}$  M  $3.2 \times 10^{-6}$  M for potassium and nitrate, respectively. Moreover, the reference electrode employed (Cu/CuO) presented a stable signal without significant drift.

The response for both sensors is given by the expressions:  $P = -52.39 \cdot \log[NO_3^{-1}] - 145.59$  and  $P = 59.02 \cdot \log[K^{+1}] + 116.73$ , respectively.



**Figure 2.** Potassium calibration plot in an aqueous medium.

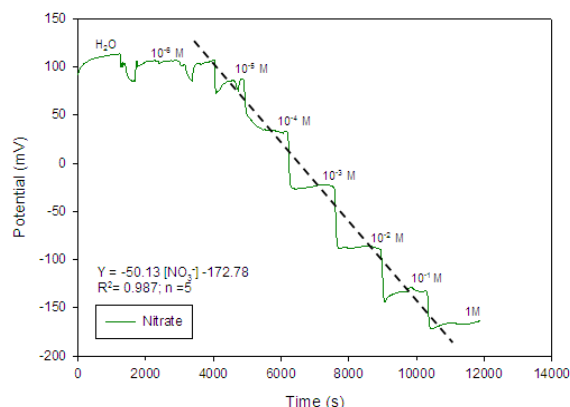


**Figure 3.** Nitrate calibration plot in an aqueous medium.

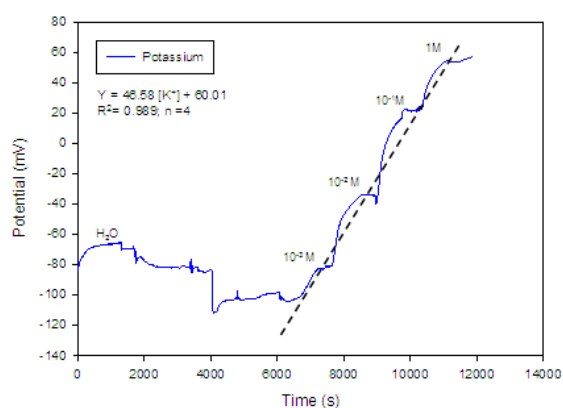
Once evaluated in solution, it was considered to apply the miniaturized probe to monitor nitrate and potassium in a fertile soil. To develop this study, fertile soil obtained from Verdtech S.A. (Lepe, Spain) was used.

In this case, previous to in-soil calibration, the soil was washed repeatedly using milliQ water. The calibration procedure consisted in adding 15 mL of  $KNO_3$  at concentrations in the range from  $10^{-6}$  to 1 M. This way, both ions could be calibrated simultaneously. Once the last standard solution was added, an excess of water was used to clean up the sensors and to return to the baseline potential. Figures 4 and 5

show the calibration plots obtained in these conditions. These figures allow clearly observing the signal variation as a new standard solution was added to the experimental set-up.



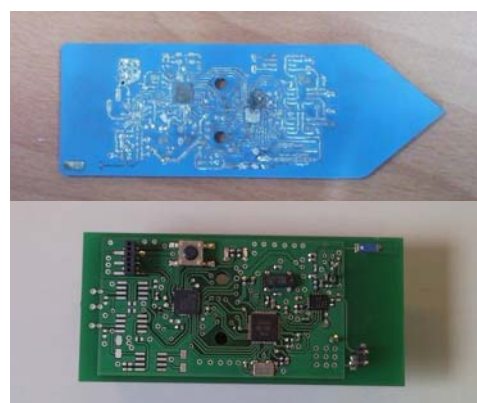
**Figure 4.** Nitrate in-soil calibration



**Figure 5.** Potassium in-soil calibration

Calibration curves were obtained by registering the potential provided by each sensor once the signals stabilized after each addition. In both cases, slightly sub-nernstian slopes were observed:  $-50.13$  mV/Dec ( $r^2=0.987$ ;  $n=5$ ) and  $46.58$  mV/Dec ( $r^2=0.989$ ;  $n=4$ ) for nitrate and potassium, respectively. The lower sensitivity observed for the cation when compared with that presented by the anion could be explained by the stronger electrostatic interaction between the soil and the  $K^+$  ion. This fact is also reflected by the curved shape steps obtained for potassium after each addition (less well-defined steps when compared with those obtained for nitrate).

Results obtained from both sensors demonstrate the potentiality presented by these miniaturized probes for their application for nutrients monitoring directly in soil. Further work is under development to build up the electronics associated to data acquisition and wireless communications in order to obtain an autonomous probe that enable to establish a wireless sensor network for monitoring longer extensions of soil (see figure 5).



**Figure 5.** Electronic prototype under development (up) fabricated on green tape and (down) fabricated using FR-4.

## CONCLUSIONS

The miniaturized biparametric LTCC-based probe developed in this work provides a robust, simpler and less invasive way to monitor the nitrate and potassium concentration in the water content of soil. This approach could be extended to monitor other interesting compounds, such as ammonium, calcium, pH, phosphate, heavy-metal ions, etc., allowing obtaining an exhaustive map regarding the soil behaviour for different crops during long periods of time.

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