Preliminary Study on Electrochemical Sensors for Ion Detection in Agriculture and Environment by Aerosol Jet Printing

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***Abstract*— The monitoring of potassium in agricultural and environmental contexts is crucial for sustainable farming practices and pollution control. This study explores a preliminary method for potassium ion sensing by exploiting electrochemical sensors enhanced by different interface materials, including Multi-Walled Carbon Nanotubes (MWCNTs), Single-Walled Carbon Nanotubes (SWCNTs), Poly(3,4-Ethylene DiOxyThiophene) (PEDOT), and Poly(3,4-Ethylene DiOxytThiophene): Poly(Syrene Sulfonic acid) (PEDOT:PSS). Fabrication was achieved using Aerosol Jet Printing (AJP), a state-of-the-art technique that enables precise, reproducible, and scalable deposition on flexible substrates. Profilometric and microscopic analyses verified the uniformity of the deposited layers, and potentiometric evaluations confirmed the sensors' effectiveness in detecting potassium ions, a critical nutrient in fertilizers but also a potential environmental pollutant in excessive concentrations. In addition, a PolyVinyl Chloride (PVC) membrane with a maximum height of 1.17 µm was preliminarily deposited in order to further optimize the sensitive layer. Through experimental evaluation, MWCNTs-based sensors showed superior sensitivity (74.63 mV/dec) and short-term stability, outperforming the other materials. These preliminary results highlight the potential of potassium sensors fabricated with AJP and optimized interface materials for real-time, in situ monitoring in soil and water systems. This research paves the way for advanced, field-ready sensors that can support precision agriculture, and environmental sustainability.**

Keywords—ion-selective sensors; potassium detection; printed electrochemical sensors; environmental applications.

I. Introduction

Electrochemical ion-selective sensors (ISS or ISE) are increasingly being recognized as essential tools for environmental monitoring, particularly for detecting and quantifying pollutants in soil [1]. The intensive use of fertilizers and agricultural inputs has led to elevated concentrations of specific ions, such as potassium and urea, in the soil, which can disrupt ecological balance and lead to long-term environmental degradation [2]. Potassium, a critical component of many fertilizers, is not only essential for plant growth but, in excessive concentrations, can act as a pollutant by altering soil chemistry and affecting nearby water bodies through runoff [3]. Understanding and managing these imbalances require reliable and precise monitoring tools capable of operating directly in the field.

Traditional methods for ion detection in soil, such as flame photometry [4], spectroscopy [2] and ion chromatography [5], are precise but resource-intensive, requiring laboratory facilities, skilled personnel, and significant time for sample preparation and analysis. Thereby, these limitations make them unsuitable for rapid, on-site applications. Potentiometric sensors [6], offer a promising alternative by enabling rapid, on-site detection of ions like potassium with minimal sample preparation [7]. Traditionally, these sensors have been made using standard fabrication methods that have limitations in terms of design flexibility, miniaturization, and scalability.

Recent studies have demonstrated the potential of potentiometric printed sensors for soil monitoring, showing their capability to achieve high sensitivity while maintaining portability [8]. Moreover, printed electronics is emerging as a transformative technology for the development of advanced soil sensing modes. This fabrication approach enables precise spatial modeling of a wide range of liquid electronic inks, which include conductive, semiconductive and insulating materials [9]. One of the key advantages of printed electronics is the ability to produce flexible and inexpensive components. These attributes make it particularly well-suited for soil sensing applications, where devices must overcome challenges such as soil heterogeneity, necessitating the analysis of representative areas, and the need for adaptable designs that can conform to non-flat surfaces, such as cylindrical rods. In addition, the scalability and cost-effectiveness of this fabrication approach enable the production of high-performance, efficient, and cost-effective sensors [10].

This study focuses on the fabrication of potentiometric sensors using Aerosol Jet Printing (AJP), an advanced printed electronics technology known for its precision and scalability. AJP enables high-resolution, non-contact deposition of functional materials on both 2D and 3D substrates by atomizing ink into fine microdroplets (1–5 µm) directed onto the substrate with an inert gas flow. This versatility supports a wide range of ink viscosities and materials, making AJP ideal for rapid prototyping and customization of electrochemical sensors [11], [12].

This study uses AJP to fabricate potassium ion sensors, leveraging its precise material deposition capabilities for robust performance and scalability. Potassium was selected for its dual role as an essential plant nutrient and potential environmental pollutant [13]. Sensors are built on circular commercial electrodes, incorporating materials identified through cyclic voltammetry as the most effective.
In this study, the printing of sensors with nanomaterials, including Carbon Nanotubes (CNTs, such as Single-Walled

Carbon Nanotubes (SWCNTs) [14] and Multi-Walled Carbon Nanotubes (MWCNTs) [15], Poly(3,4-Ethylene DiOxyThiophene) (PEDOT); [16] and Poly(3,4-Ethylene DiOxytThiophene): Poly(Syrene Sulfonic acid) (PEDOT:PSS) [17], showed significant potential in improving electrochemical performance due to their high conductivity, biocompatibility, and robustness and suitability for potassium detection. Carbon nanotubes, particularly MWCNTs, provide high surface area and outstanding electrochemical performance, making them ideal for signal transduction. PEDOT and its derivatives [18], known for their film-forming properties and conductivity, allow for the creation of uniform and stable sensing layers [19]. The preliminary studies focus on the comparative analysis of these materials to identify the most suitable one for final printing, evaluating parameters such as ion selectivity, sensitivity, and long-term stability.

This work marks a step toward next-generation ISE, combining AJP and advanced interface materials to enhance accuracy, reliability, and portability for soil monitoring. By addressing interference effects and expanding sensor applicability, this research supports sustainable agricultural practices and environmental conservation. Precision agriculture can optimize yields by monitoring agricultural conditions and integrating new knowledge to find sustainable solutions to these problems [20].

II. Materials and Methods

A. Electrode design with various interface materials

The adopted configuration is shown in Fig. 1, displaying a Working Electrode (WE), Counter Electrode (CE), and Reference Electrode (RE). The WE consists of several layers: carbon, interface material, and Ion Selective Membrane (ISM).

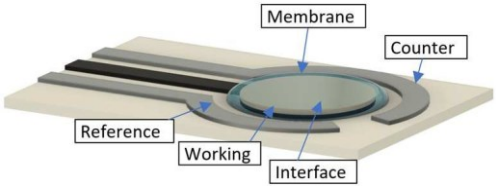

Fig. 1. Various layers of SPE electrode

For preliminary tests, screen printed electrodes (SPEs) (DropSens) were purchased from Metrohm, made of carbon (code 110). Carbon forms the WE and CE, while the RE is silver. Various interface materials were analyzed, including SWCNTs (1.5 nm diameter, from NanoLab, Inc., Waltham, USA, named Nink-1100, designed as ink with a viscosity of 3 cPs), MWCNTs (15 nm diameter, 2 g/liter in water, from NanoLab, Inc., viscosity of 3 cPs), PEDOT (from Sigma-Aldrich, containing dodecylbenzenesulfonic acid (DBSA) as a dopant), and PEDOT-PSS (300 S/cm conductivity, from Sigma-Aldrich, St. Louis, Missouri, USA). Each transduction material was applied to the WE and three preliminary sensors were fabricated.

The interface materials have different drying times. CNTs are dried at 37 °C for one hour to enhance adhesion. PEDOT and PEDOT:PSS are dried at 50 °C for 25 minutes before measurement. The deposition volume on the WE varies by material: 3 µL for MWCNTs, 2 µL for SWCNTs, 7 µL for PEDOT, and 5 µL for PEDOT:PSS, reflecting differences in wettability toward the substrate.

As reported in Fig.1, WE consists of three layers: carbon, transduction material, and PolyVinyl Chloride (PVC) membrane, designed specifically for potassium ion detection as described in [21].

The functionality of the potassium ISM is shown in Fig. 2. It contains 1% ionophore, 33% PVC, and 66% lipophilic plasticizer. Valinomycin, an ionophore, selectively transports alkali metal ions by forming a metal ion-peptide complex. The cavity size enables potassium ion trapping, while smaller ions like sodium and lithium are excluded. PVC provides mechanical stability and remains chemically inert with valinomycin. The lipophilic plasticizer makes the membrane permeable only to ions with the same sign as the target ion [22]. The membrane solution was preliminary deposited via dropcasting, depositing 20 µL of solution and dring at room temperature under a hood for three hours to evaporate the solvent (cyclohexanone).

After the deposition, the sensors underwent a preconditioning process, a preliminary step that prepares the sensor for its proper operation. The sensor is immersed in a solution with a concentration of 10 mM KCl, where potassium is the ion to be detected for a specified period of time. This process is necessary to increase the stability and sensitivity of the potentiometric measurement [23].

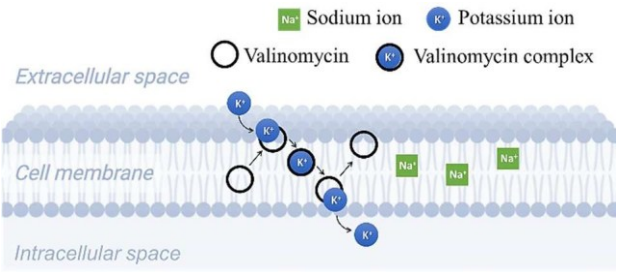

Fig. 2. Valinomycin ion transport and potassium binding.

B. AJP printing process

Preliminary evaluations of the PVC ISM printed by Aerosol Jet Printer AJ 300-UP (Optomec, Inc.) on a glass slide were performed in order to be able to morphologically characterize the membrane and be able to print it on the fully printed and functionalized sensor. Since the working electrode of the commercial sensor (Metrohm C110) has a diameter of 40 mm, a spiral was designed on 2D CAD software to cover the whole area. To print the spiral, the thickness of the trace is defined to ensure that the lines overlap. The geometry is transformed into instructions (coordinates) for the AJP printer. AJP uses two main methods for ink atomization: the ultrasonic and pneumatic systems [19] [29]. In the ultrasonic method, a piezoelectric membrane vibrates at ultrasonic frequencies, generating pressure waves that fragment the ink into aerosolized droplets. This approach is particularly effective for low-viscosity inks, generally between 1 and 10 cP, such as highly fluid liquid solutions. Since it is not necessary to use high pressures to force ink flow, the system is optimal for applications that require precision and uniformity in the deposition of liquid materials, such as nanoparticles or dilute solutions. The pneumatic system, on the other hand, relies on a pressurized gas flow, such as air or nitrogen, to force the ink through the nozzle and

atomize it. This method is distinguished by its ability to handle inks with significantly higher viscosities, up to about 1000 centipoise, making it suitable for denser materials, such as pastes or suspensions.

First printing test were realized with the ultrasonic method. Since for ultrasonic printing, 10 ml of membrane has high viscosity (120 cP), it was diluted: 100 µL of membrane was mixed with 900 µL of cyclohexanone to obtain a 10% concentration. The printing tests permitted to identify specific parameters reported in Table 1.

Tab.1. ISM process parameters.

Parameter	***Value***
Print speed (mm/s)	1
Sheat flow (SCCM)	80
Atomizer flow (SCCM)	50
Piezoelectric current (mA)	460
Refrigerator (°C)	21
Number of depositions	3

C. Cyclic Voltammetry Technique

To test the correct functioning of the proposed sensors different electrochemical analysis were executed. Cyclic voltammetry (CV) is an electrochemical technique used to study redox reactions and the behavior of chemical compounds. It is based on the application of a cyclic variable potential between the RE and WE, then the current flowing through the system is read on the CE. Such technique provides information on reaction kinetics, reversibility, and chemical mechanisms, and is particularly useful in the study of new materials and catalysts.

CV also requires the use of the auxiliary electrode, which is not the case in potentiometry, which we will see later. A variation of potential is performed between the RE and WE at a constant rate, starting from an initial potential to a final potential; subsequently, the potential is returned to the initial value, and the current between the auxiliary and working electrode is measured.

The peak current (i_p) is influenced by several parameters, including the potential scan rate (v), the active electrode area (A), and the concentration of the electroactive species (C). This relationship is described by Equation (1), which illustrates the dependency of the peak current on these parameters:

$$i_p = kn^{3/2}AD^{1/2}Cv^{1/2} \quad (1)$$

where k represents a proportionality constant, n the number of electrons transferred in the redox reaction, A the electrode's active surface area, D the diffusion coefficient of the electroactive species, C the concentration of the electroactive species solution, and v the scan rate of the applied potential.

This equation highlights the proportionality of the peak current to the square root of the scan rate ($v^{1/2}$), which is a characteristic feature of diffusion-controlled electrochemical processes. In practice, when plotting the peak current (i_p) against the square root of the scan rate ($v^{1/2}$), a linear relationship is observed, confirming the diffusion-controlled mechanism under ideal conditions.

The four transduction materials were tested, one for each sensor on the carbon WE, so a total of four different sensors were used. Thereafter, 60 µL of potassium ferrocyanide ($K_4[Fe(CN)_6]$) at the concentration of 5 mM diluted in PBS was added. PBS plays the role of supporting electrolyte; it is an inert salt that increases the conductivity of the electrolyte, decreasing the resistance of the solution. In fact, it ensures that the electrochemical process takes place by diffusion [24]. The ($K_4[Fe(CN)_6]$) was deposited as shown in Fig. 3, covering the whole area, and cyclic voltammetry was performed.

A single potential scan rate of 100 mV/s was set. The voltage range was defined from -0.6 V to 0.6 V with a sampling step of 0.01 V.

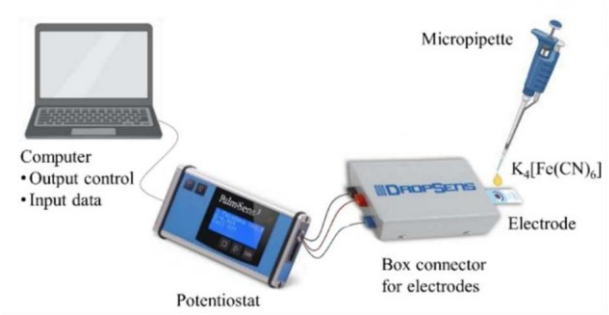

Fig. 3. Cyclic voltammetry measurement set up.

D. Potentiometric Technique

Potentiometry is an electrochemical technique for measuring the electrical potential of a solution, using only the two electrodes WE and RE without CE. It works in an open circuit, detecting the potential generated by the difference in chemical energy between the electrodes. Using Nernst Equation (2), it is possible to appreciate that this potential depends on the concentration of specific chemical species in solution, allowing precise analyses such as pH measurement or determination of specific ions [24]. Therefore, a change in potential is related to a change in concentration.

$$E = const - \frac{2.3\,RT}{zF} lnC \quad (2)$$

where E is the cell potential, R is the universal gas constant, T is the temperature in kelvins, z is the ionic charge (electron moles), F is the Faraday constant, C is the unknown concentration.

The twelve sensors described in Section IIA were used for potentiometric measurement, and for every three sensors, a single transduction material was deposited on the working electrode. After meeting the heating time for drying the material, the Ion Selective Membrane (ISM) was deposited.

The experimental measurement setup shown in Fig. 4 consists simply of the box connector and the PalmSens potentiostat, which is then connected to the PC. Inside a beaker 100 ml of distilled water is added, which is then placed on a magnetic stirrer at a speed of 200 rpm.

The sensor is inserted into the appropriate hole in the MetrOHM box and it is subsequently immersed in the solution. The box is attached with a rod and the box connectors are connected to the PalmSens3 Potentiostat and, through the use of this, device measurements are stored; therefore, the box acts as an interface between the electrode and the potentiostat. Every 100 seconds, potassium chloride (KCl) is added via a micropipette to the solution, which is mixed by the stirrer to accelerate the achievement of equilibrium. After each test, each sensor is rinsed with

distilled water for about 60 seconds and then dried at room temperature.

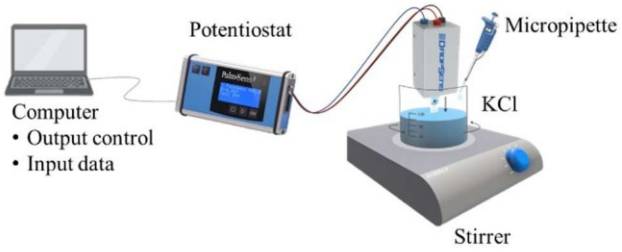

Fig. 4. Potentiometric measurement set up.

Table 2 shows the additions of KCl into the distilled water solution made with the micropipette every 100 seconds, for a total of five additions, or one addition every decade (range 10^{-6} – 10^{-2}) and thus an experiment lasting 600 seconds.

To calculate the additions, the classical formula for dilutions $C_iV_i=C_fV_f$ was used, where C_i and V_i are the initial concentration and initial volume in the micropipette, respectively, C_f is the final concentration desired to be obtained in the solution, and V_f is the sum of 100 ml of distilled water and the volume of KCl added with the micropipette.

Tab.2. KCl additions.

C_f [M]	C_i [M]	Micropipette volume (V_i) [µL]
10^{-6}	0.01	10
10^{-5}	0.01	90
10^{-4}	0.34	26
10^{-3}	0.34	266
10^{-2}	1	912

III. Results

A. Cyclic Voltammetry Evaluation

Fig. 5 shows the results obtained analyzing the four conducting materials (MWCNTs, SWCNTs, PEDOT and PEDOT:PSS) and it can be concluded that for this application, the material with the best performance in terms of conductivity and oxidation-reduction reactions is MWCNT.

This is because the material appears to have the highest peak current. Referring to Formula (1), no parameters have been changed for any material, and it can therefore be concluded that MWCNT has a greater active area.

B. ISM preconditioning and Potentiometric Evaluation

For the preconditioning analysis (Fig. 6), it is noted that 15 minutes is the best time, although for the other times the potential is higher. A better time of 15 minutes was determined because the signal is more stable than the other tests, as the other signals tend to decrease with the potential after addition.

A comparison of the four transduction materials is shown in Fig. 7, and the change in potential over time after KCl additions every 100 seconds is noted, as time is assumed to be sufficient to bring the signal to steady state and stabilize it. Indeed, it can be seen that with each addition of potassium, the potential increases and reaches a new steady state value. The change is more pronounced in the case of high concentrations.

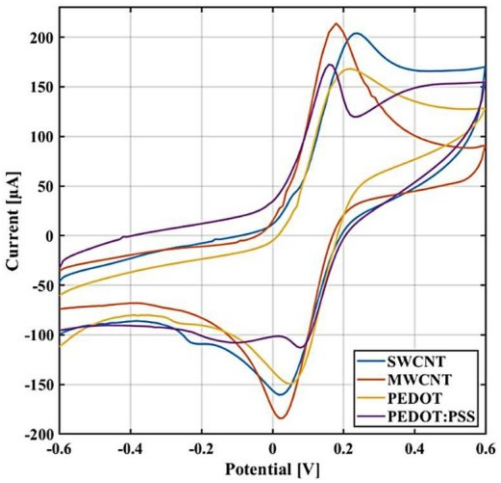

Fig. 5. Cyclovoltammetry comparison between the 4 different interface materials at 100 mV/s (current-time graph).

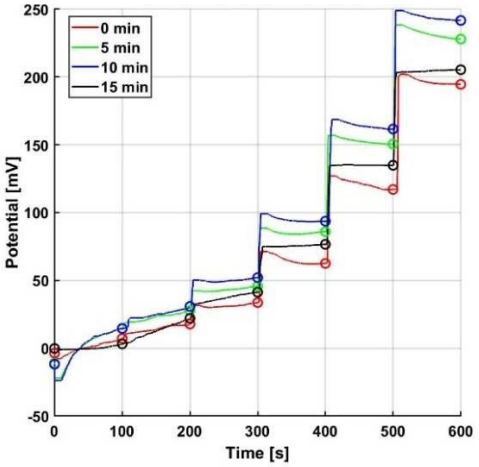

Fig. 6. Different preconditioning of ISM on a sensor.

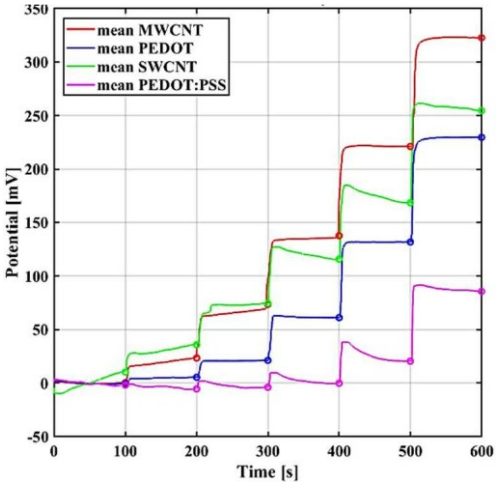

Fig. 7. Potentiometry signal comparison between the 4 different interface materials (potential-time graph).

An average of 3 tests was performed on the same sensor to have a comparison and potentially more reliable measurements. In addition, it was tested that the sensor after 3 tests no longer works, so at most only 3 tests can be done for comparison and therefore the sensor seems to have a not very high repeatability.

Sensitivity of the various sensors (Fig. 8) with the various interface materials was therefore subsequently calculated, always in the range from 10^{-6} to 10^{-2}, and the potential points

were recorded every 100 seconds and a graph was created in which the abscissae represent the logarithm of the concentration, and the ordinates the corresponding potential.

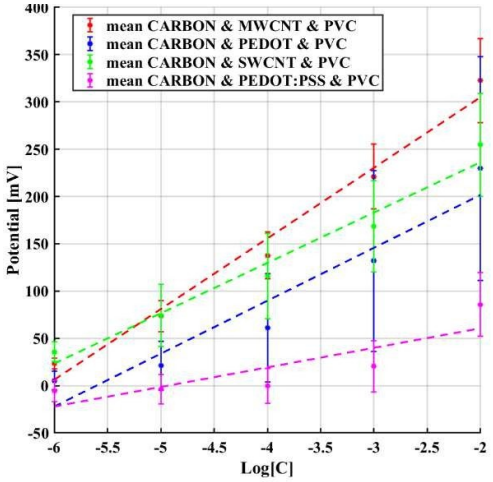

Fig. 8. Graph of calibration straight lines of various sensors with various interface materials.

From the various sensitivities obtained in Table 3, it can be seen that the sensor having MWCNT as the transduction material has the best performance in terms of sensitivity. The sensor with PEDOT has better sensitivity than that with SWCNT. Also, concerning the obtained results of R^2, it can be seen that the dots fit the line of the sensor having MWCNTs better. Therefore, the carbon nanotubes perform better than the sensors with the two conductive polymers.

Tab.3. Sensitivity and R^2 relative to the 12 sensors used. MW: commercial carbon sensor, then deposition of MWCNTs and then PVC; PEDOT: commercial carbon sensor, then deposition of PEDOT and then PVC; SW: commercial carbon sensor, then deposition of SWCNTs and then PVC; PSS: commercial carbon sensor, then deposition of PEDOT:PSS and then PVC.

Type of Sensor	***Sensitivity (mV/dec)***	***R^2***
MW	74.63	0.98
PEDOT	55.91	0.92
SW	53.19	0.97
PSS	20.65	0.72

C. Preliminary AJP tests on ISM

As a preliminary step towards fully-printed sensors, we used AJP to deposit the circular PVC membrane, after drying the membrane at room temperature for 3 hours, it was evaluated with an NB50T optical microscope (Orma Scientific, Sesto San Giovanni, Milan, Italy, trinocular zoom, 0.8), with its dedicated HDMI model MDH5 camera used to acquire images and to evaluate the accuracy of the printing process.

The ISM can be seen on Fig. 9. The transparency of the membrane facilitated an evaluation of the print geometry, which conformed to the specified design.

For morphological characterization, the thickness of the membrane was measured with a Profilm3D profilometer (Filmetrics, Inc.), obtaining after one pass a thickness of about 0.2 um, with 2 passes 0.6 um, with three 0.8 um and with 4 a maximum height of 1.17 µm is obtained (Fig. 10). Even with just two passes, complete deposition of a film is observed over the entire area and without the presence of holes or interruptions. Fig. 10 also illustrates the variation in thickness as a function of the number of passes. This value corresponds to a thin membrane according to the state of the art [25]. However, due to the profilometer's requirement for reflective substrates, thickness measurements on the matte ceramic substrate were not possible.

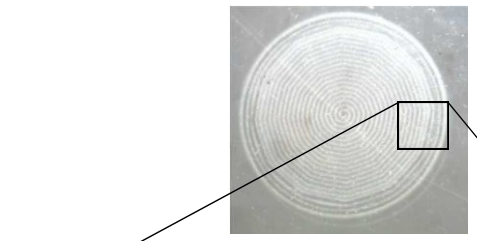

Fig. 9. Aerosol Jet Printed PVC membrane on glass slide.

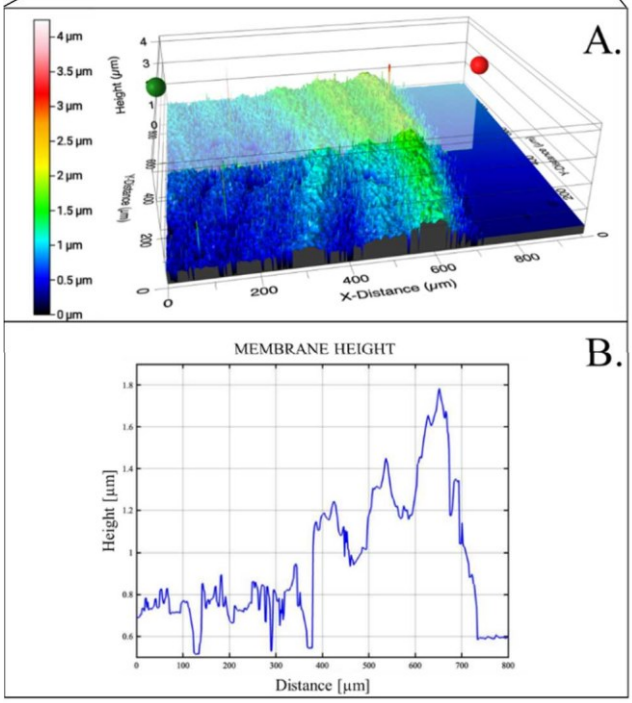

Fig. 10. Morphologic characterization. A. 3D Membrane height. B. 1D Membrane height.

IV. Conclusion and Future Developments

In this paper, novel electrochemical sensors for ion detection have been studied, fabricated and preliminary tested. Different transduction materials have been deposited and tested. It can be concluded that the sensor with MWCNT, as the transduction material, has the best performance in terms of sensitivity, as it reaches 74.63 mV/dec with an R^2 of 0.98. The sensor with PEDOT achieves a sensitivity of 55.91 mV/dec (R^2=0.92), which is better than the sensor with SWCNT that achieves 53.19 mV/dec (R^2=0.97). The sensor with the PEDOT:PSS, according to our tests, was the worst sensor in terms of sensitivity. In addition, regarding the AJP printing of the membrane, despite the ink dilution at 10%, the results obtained are promising. A study of the homogeneity and effectiveness of the deposition has been done. Based on this result, we will perform further tests in the future to evaluate its potassium sensitivity, with the goal of achieving optimal performance in terms of metrological characteristics.

These preliminary results from the interface material studies represent a first step toward fully printed sensors,

paving the way for new opportunities in soil monitoring and precision agriculture.

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