

# LOW COST NITRATE SENSOR FOR AGRICULTURAL APPLICATIONS

Van Anh T. Dam and Marcel A.G. Zevenbergen  
Holst Centre / imec, 5656 AE Eindhoven, The Netherlands

## ABSTRACT

This work presents a flexible miniaturized sensor for quick nitrate detection for agricultural applications. The sensor was fabricated on a polyethylene terephthalate (PET) foil by using techniques which can enable large scale production to reduce manufacturing costs. The flexible sensor showed a good nitrate sensitivity in a concentration range, that is suitable for soil nutrient analysis.

## KEYWORDS

Nitrate, flex sensors, screen printing, agriculture

## INTRODUCTION

A high yield of crops requires monitoring of soil fertility by maintaining a balance between nutrient demand and fertilizer (nitrogen and phosphorus) application. A quick access of the nutrient level, such as nitrate content, directly in soil or in recirculating water in a greenhouse, is important for fertilizer use efficiency. This has the potential to reduce production cost and enables more sustainable agriculture [1].

Nowadays analysis of the nutrient level in soil is done by first extracting nitrate-nitrogen, phosphorus and potassium from the soil using an extractant followed by analysis. Concentration (or total concentration) of these compounds in the extract solution can be determined using spectrophotometric devices, conductivity sensor, or conventional ion-selective electrodes (ISEs) [2,3]. Among these devices, the ISEs are user friendly while providing relatively good sensitivity and selectivity thanks to their ion-selective membrane. The ISE is, however, relatively bulky and costly. It contains an internal electrolyte, which hampers the sensor miniaturization and integration. The aim of this work is to develop a low cost miniaturized, easy-to-use and integrable nitrate sensor for agricultural applications. To reduce manufacturing costs of the sensor, screen printing was used for electrode manufacturing, which allows large scale production of the sensors.

## EXPERIMENT

A cross-section of the flexible miniaturized nitrate-selective electrode developed in this work is schematically illustrated in Fig. 1. The fabrication process consists of several steps: first multiple AgCl electrodes were screen printed on an A4-format PET sheet using DuPont 5876 AgCl conducting paste. After each printing step, the AgCl layer was dried at 110°C for three minutes and a next AgCl layer was printed to get a thickness in the order of 50 µm.

Next, to protect the conducting paths and to form the reservoirs for the internal electrolytes, the foil was subsequently laminated with a 680 µm thick thermoplastic polyurethane (TPU) layer, which was patterned by laser cutting leaving wells with a diameter of 3 mm above the electrode area open (see Fig. 2). Subsequently, the cellulose gel layer, which contained 2% hydroxyethyl

cellulose (HEC) and 28% triethylene glycol (Sigma Aldrich) preloaded with 0.01 M NaNO<sub>3</sub>, was casted inside the wells on the AgCl electrode. Finally, after casting the cellulose gel layer, a nitrate-selective membrane was applied by drop casting of a polyvinylchloride-like nitrate-selective membrane solution containing nitrate exchanger [4,5] inside the reservoir on top of the cellulose gel layer. After drying overnight at room temperature, the miniaturized ion-selective electrodes were ready to test.

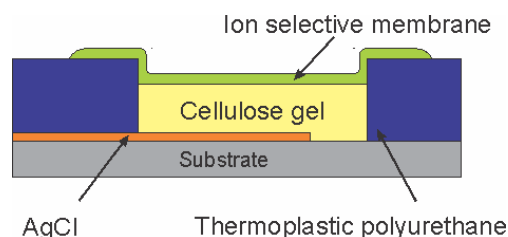


Figure 1: Illustration of cross section of a nitrate-selective electrode with a cellulose gel layer casted on screen printed AgCl electrode in a reservoir formed by a thermoplastic polyurethane layer. A nitrate-selective membrane was pipetted on top of the cellulose gel layer, which covered the TPU reservoir.

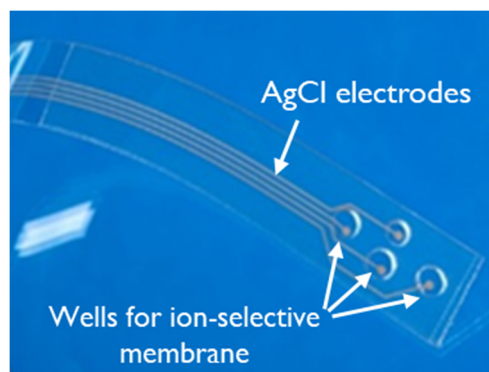


Figure 2: Top view photo of a half-fabricated sensor having AgCl electrodes and four wells for ion-selective membrane, which were created on a thermoplastic polyurethane layer laminated on the foil.

To compare the performance of the miniaturized nitrate-selective electrodes with conventional electrodes, a nitrate-selective electrode was constructed based on an ion-selective electrode body (Philips IS-561), which was filled with a 0.01 M NaNO<sub>3</sub> internal electrolyte. The nitrate-selective membrane was obtained by casting the nitrate-selective membrane solution on a Petri dish. After 48 hours drying, the membrane was punched out and mounted on the ion-selective electrode body, which was subsequently

filled with the 0.01 M  $\text{NaNO}_3$  internal electrolyte. The construction of this nitrate-selective electrode is similar to a conventional ion-selective electrode, that allows to independently and fast characterize performance of the nitrate-selective membrane.

Calibration of the nitrate-selective electrodes was performed with respect to a commercial 3 M potassium chloride reference electrode (Metrohm) in a series of test solutions containing  $10^{-6}$  - 0.1 M  $\text{NaNO}_3$ . In these test solutions, 0.01 M KCl was added as a supporting electrolyte. During the calibration, a commercial nitrate half-cell ion-selective electrode (HANNA Instruments HI 4013) was simultaneously measured in the same solution for comparison.

For determining nitrate content in soil, nitrate was extracted from the soil by using an extraction method with 0.05 M  $\text{K}_2\text{SO}_4$  solution described in [6]. First, 10 g soil was weighed and dissolved in 50 ml 0.05 M  $\text{K}_2\text{SO}_4$  (extractant). The mixture was stirred for approximately 30 minutes to dissolve the nitrate content in the soil. The slurry was filtered using standard Whatman filter paper (grade 42). The nitrate concentration in the extracts was analyzed using the screen-printed and commercial sensors.

All chemicals used in the experiment were of analytical grade.

## RESULTS

Figure 3 shows the potentials of the commercial nitrate-selective electrode (HANNA) and our nitrate-selective electrode made on the ion-selective electrode body, which were simultaneously measured as a function of time when the  $\text{NaNO}_3$  concentration changed from 0.1 to 50 mM.

As soon as the electrode was immersed in the solution, it showed a response immediately with a response time less than a minute. To calculate the nitrate sensitivity, the equilibrium potentials of the nitrate-selective electrodes measured in each  $\text{NaNO}_3$  solution were determined and plot as a function of the logarithm of the nitrate

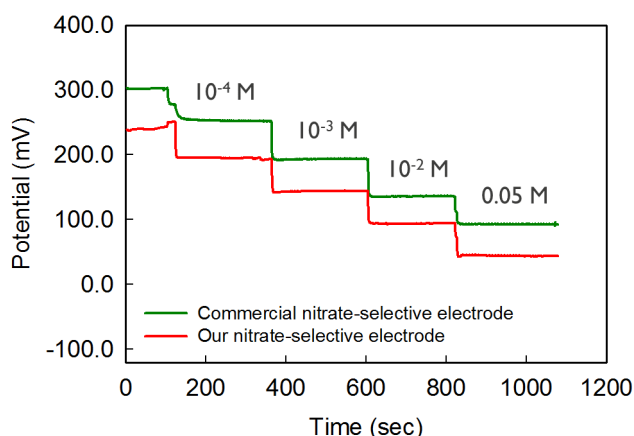


Figure 3: Change in the potential of commercial nitrate-selective electrode and our nitrate-selective electrode made on an ion-selective electrode body as a function of time when the  $\text{NaNO}_3$  concentration changes from 0.1 to 50 mM.

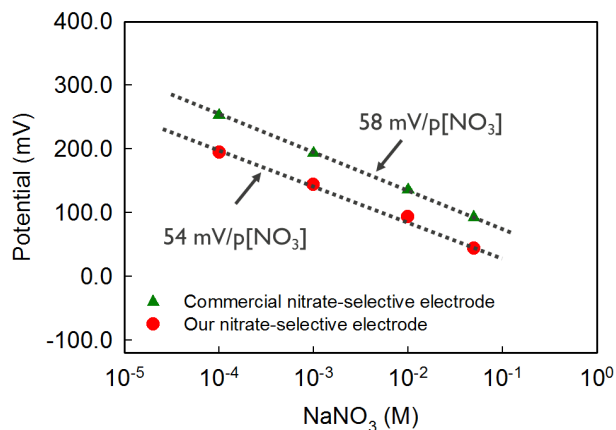


Figure 4: Linear dependence of the electrode potential extracted from Fig. 3 on the logarithm of the  $\text{NaNO}_3$  concentration. The solid line is a fit through the data of the commercial and our nitrate-selective electrodes with the slopes of 58 and 54 mV per decade, respectively.

concentration (see Fig. 4). Using a linear fit, as shown in Fig. 4, our nitrate-selective electrode showed a sensitivity of 54 mV per decade, which is a bit lower than that of the commercial sensor (58 mV/p[ $\text{NO}_3^-$ ]).

The cross sensitivity of our nitrate-selective electrode to other ions, which are commonly known in the agricultural applications such as  $\text{NO}_2^-$ ,  $\text{H}_2\text{PO}_4^-$ , etc. was characterized by measuring the electrode potential in solutions with various concentration of these ions and 1 mM  $\text{NaNO}_3$ . The sensor showed very low sensitivity of -1.7, -1.2 and 2.3 mV/dec to  $\text{H}_2\text{PO}_4^-$ ,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ , respectively (see Fig. 5). The sensor was cross sensitive to  $\text{NO}_2^-$  (with a sensitivity of 24 mV/p[ $\text{NO}_2^-$ ]) at a nitrite concentration above 1 mM. However, it should be mentioned that nitrate sensors are commonly known to be cross-sensitive to nitrite. The commercial nitrate sensor, which was used in this work, could exhibit cross sensitivity to nitrite when a ratio of  $\text{NO}_2^-$  to  $\text{NO}_3^-$  is larger than 2.

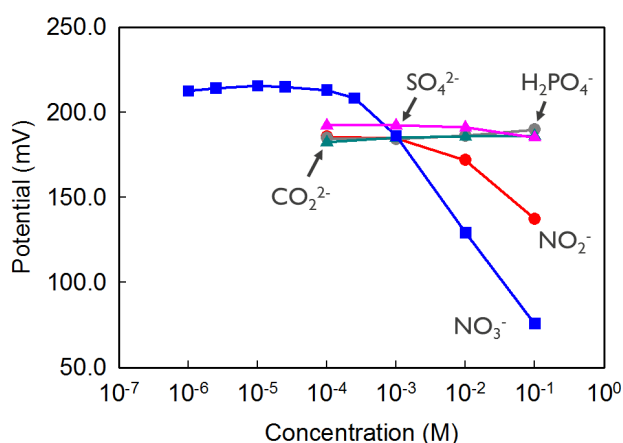


Figure 5: Response of our nitrate-selective electrode depends on concentration of interferent anions, which are commonly co-present with nitrate in the agricultural applications. In these measurements, 1 mM  $\text{NaNO}_3$  was added to the solution of interferent ions.

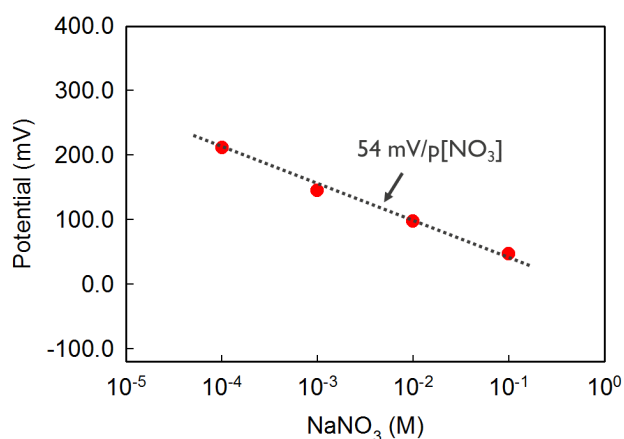


Figure 6: Linear dependence of the potential of a flexible nitrate-selective electrode on the logarithm of the  $\text{NaNO}_3$  concentration (0.1 – 100 mM). The solid line is a fit through the data with a slope of 54 mV per decade.

Calibration of the commercial sensor in the series of solutions containing varied  $\text{NO}_2^-$  concentration and fixed 1 mM  $\text{NaNO}_3$  showed that the sensor had a sensitivity of 26 mV/p[ $\text{NO}_2^-$ ] at nitrite concentrations above 1 mM, which was in the same order with our sensor. The sensitivity curve measured in a series of the nitrate solutions plotted in Fig. 5 showed that the sensor had a low limit of detection close to  $10^{-4}$  M. The same composition of the nitrate-selective membrane, which was measured on the ion-selective body (shown in Fig. 3 and 4) was used for the miniaturized flexible nitrate-selective electrode. The electrode was calibrated in a series of  $\text{NaNO}_3$  solutions and showed a sensitivity of 54 mV per decade in a concentration range of 0.1 – 100 mM (see Fig. 6).

The nitrate sensor was used to measured nitrate level in four different commercial soil types, in which nitrogen - phosphorus-potassium (NPK) fertilizers were added. These soils have different pH, conductivity and NPK contents as shown in table 1.

There are several solutions reported in literature for extraction of the nitrate from the soil [2,4,6]. Since the nitrate-selective electrode investigated in this work showed low sensitivity to sulphate, 0.05 M  $\text{K}_2\text{SO}_4$  solution was selected to extract the nitrate from the soil samples. After filtering out soil precipitation in the slurry, the nitrate concentration in the extract solution was measured by the nitrate-selective electrodes and presented in table 2. Table 2 shows that there is low difference between the nitrate content in the soil samples measured by the commercial and our sensors. Among all studied soil samples, soil sample 2 had the lowest nitrogen content, which could be caused of that only organic NPK was added to this soil. Comparing data on table 1 and 2, no clear relationship between the measured nitrate concentration and the NPK content in the soil samples could be established. This could be explained by the fact that the total nitrogen in the NPK content specified by the manufacturers comes in both nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ) forms. In this work, only nitrate content in the soil samples was measured while ammonium and other P and K contents in the soil samples were not analyzed.

Table 1: Summary of soil specifications provided by manufacturers.

	Soil 1	Soil 2	Soil 3	Soil 4
pH	5 - 6.5	3.5 - 5	5 - 6.5	*
Conductivity ( $\mu\text{S}/\text{cm}$ )	450	150	750	*
NPK organic	7-7-10 (3 $\text{kg}/\text{m}^3$ )	7-7-10 (1 $\text{kg}/\text{m}^3$ )	9-9-7 (1.5 $\text{kg}/\text{m}^3$ )	*
NPK non-organic	9-3-3 (2 $\text{kg}/\text{m}^3$ )	0	7-7-10 (1.5 $\text{kg}/\text{m}^3$ )	*

(\*) Manufacturer did not specify contents.

Table 2: Nitrate concentration in extracted solution of different soils, which was measured by using commercial and our nitrate sensors.

Sensor	Commercial sensor (mM/L)	Screen-printed sensor (mM/L)	Difference (mM/L)
Soil 1	6.3	7.2	-0.9
Soil 2	0.08	0.31	-0.23
Soil 3	5.6	5.6	0
Soil 4	4.1	3.8	0.3

## CONCLUSIONS

This work presents a feasibility study on development of the flexible miniaturized sensor with a nitrate-selective electrode for quick nitrate detection. The nitrate-selective electrode was made from a stack of AgCl electrode, which was screen printed on PET foil, internal electrolyte layer of cellulose gel loaded with  $\text{NaNO}_3$ , and nitrate-selective membrane casted directly on the cellulose gel layer. The flexible nitrate-selective electrode showed a sensitivity of 54 mV/p[ $\text{NO}_3^-$ ] in a nitrate concentration range from 0.1 to 100 mM, which is similar to that obtained with the same membrane composition measured on the ion-selective electrode body. The sensor showed the low cross-sensitivity to  $\text{H}_2\text{PO}_4^-$ ,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  (below 2.3 mV/dec). It, however, had cross-sensitivity to  $\text{NO}_2^-$ , which is commonly known cross-sensitivity for commercial nitrate sensors. In the real soil extracts with different interferences, the sensor studied in this work showed the nitrate concentration close to that measured by the commercial nitrate sensor (difference below 0.3 mM/L).

## REFERENCES

- [1] D. Tilman, K. G. Cassman, P. A. Matson, R. Naylor, S. Polasky, "Agricultural sustainability and intensive production practices, *Nature*, vol. 418, pp. 671-677, 2002.
- [2] V.I. Adamchuk, J.W. Hummel, M.T. Morgan, S.K. Upadhyay, "On-the-go soil sensors for precision agriculture", *Computers and Electronics in*

*Agriculture*, vol. 44, pp. 71–91, 2004.

- [3] S.J. Birrell a, J.W. Hummel, Real-time multi ISFET/FIA soil analysis system with automatic sample extraction, *Computers and Electronics in Agriculture*, vol. 32, 1, pp 45-67, 2001.
- [4] L. Campanella, C. Colapicchioni, G. Crescentini, M.P. Sammartino, Y. Su, M. Tomassetti, “Sensitive membrane ISFETs for nitrate analysis in waters”, *Sensors and Actuators B*, vol. 26-27, pp. 329 – 33, 1995.
- [5] W. Wróblewski, M. Chudy, A. Dybko, Nitrate-selective chemically modified field effect transistors for flow-cell applications, *Analytica Chimica Acta*, vol. 416, 1, pp. 97-104, 2000.
- [6] S. Ito, K. Baba, Y. Asano, H. Takesako, H. Wada, Development of a nitrate ion-selective electrode based on an Urushi matrix membrane and its application to the direct measurement of nitrate-nitrogen in upland soils, *Talanta*, vol. 43, 11, pp. 1869-1881, 1996.

## CONTACT

\*V.A.T. Dam, tel: +31-404-20-434;

Van.Anh.Dam@imec.nl