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MELLiSSA

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Evaluation of Ion Selective Field Effect Transistor (ISFET) Technology for their Suitability in the MELiSSA Loop

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INTRODUCTION

Currently there is a significant technology void with respect to ion control in closed hydroponics systems. Presently, nutrient levels are monitored using either electrical conductivity (EC) and pH meters or off line analysis. The EC and pH measurements are indiscriminate and provide only information for the entire nutrient solution. These measurements do not give any information about individual ions within the nutrient solution. Off line analysis, such as HPLC, allows for precise monitoring of individual ions, however since samples are taken off line and are then sent to a laboratory for analysis, there is a time lag between nutrient analysis and nutrient adjustment. This results in coarse ion control for closed hydroponics systems.

Ion-specific sensor development is expected to be an attractive means of controlling ionic balances in re-circulating hydroponics solutions used in higher plant culture. An exhaustive review and evaluation of commercially available technology and those in the research and development phase indicates that Ion Selective Field Effect Transistors (ISFETs) are the most promising of technologies. These sensors are expected to be relatively in-expensive (as compared to in-line HPLC) and are simple to operate. Further, preliminary results from a major greenhouse control systems firm, involved in the research and development of these sensors, indicate that these sensors will out-perform the commercially available ion-selective electrode variety. Unfortunately, ISFET sensors are not yet commercially available, but their future availability may have profound implications on nutrient solution management. The University of Guelph has secured a beta-test agreement with Sentron B.V. (De Lier, NL) for evaluation of these sensors. This project has evaluated newly developed ISFET sensors, for the purposes of assessing their susceptibility to contamination by other species, their susceptibility to electronic drift, their calibration requirements and their lifetime. A breadboard design and development phase has commenced following bench tests in order to demonstrate the feedback control concepts of interest to the advanced life support community and the commercial grower. The final phase of this project will be the inclusion of ISFETs into a model driven automated fertigation system. The ISFETs will monitor the nutrient levels and will control the ISFET actuated fertilizer injectors resulting in desired nutrient levels as specified by an independently developed crop nutrient model.

RESULTS OF SENSOR EFFICACY TRIALS

Initial work in beta testing the ISFET (ion selective field effect transistor), resulted in mixed success. The original model of ISFET included sensors for sodium (Na^+), potassium (K^+), and nitrate (NO_3^-). While working with these sensors, it was possible to calibrate the sodium ion sensor only. This is because during the beta-test period, Sentron replaced the ISFETs being studies with a new generation of sensors. As a result, work discontinued on the original sensors and work now continues on the new generation. Further it was believed that the performance of the sensor for sodium would lead insight into sensors for other monovalent cations such as potassium.

The calibration of the sodium ISFETs (Figure 1.) was done using a "bench-top" apparatus. The sensors were placed in 250 ml of a solution containing 0.1M of a secondary ion (i.e. for the sodium sensor, the solution contained 0.1M KCl). A solution with known amounts of the primary ion (NaCl) was the added. The concentration of the solution with respect to the primary ion ranged from $2.0*10^{-7}$ M to 0.01 M. For each addition of solution, the sensor potential (mV) was allowed to equilibrate and averaged over a period of 5 minutes using a CR7 measurement and control system. The result was a typical Nernstian response.

To date, a bench top calibration protocol has been developed. The sodium ion sensors have been calibrated over a sodium ion concentration range similar to that used in closed nutrient delivery systems and in the presence of varying potassium concentrations.

Although we were successful with the calibration of the sodium ISFETs, it was found that the sensors were problematic with respect to electrical interferences within the experimental set-up. In mid-February, 2001, Sentron B.V. discontinued production of the tested sensor model. Work is currently underway to examine the newly supplied sensor models with respect to their susceptibility to electrical interference. Work also is underway to determine whether interference is a result of problems with the sensors themselves, with signal conditioning or with the reference electrode.

Currently, the bench top testing apparatus is being upgraded. Data collection and sensor control will be achieved by using LabView software instead of the CR7. Designs have been produced for the bread -board sample by-pass loop that will be needed in order to incorporate the sensors into an automatic fertigation system. The by-pass sample loop is composed of two reservoirs, three two-way valves, one three-way valve, and electric pump and a sensor housing. The two reservoirs are for rinsing and calibrating solutions. The three two-way valves controls solutions flow from the reservoirs into the sensors. The three-way valve directs the solution back into the system or out to the waste. Also, we are in the initial phase of construction of an automatic fertigation system in our research greenhouse using the aforementioned design for the sample by-pass loop (Figure 2).

MEMBRANE FOULING AND SENSOR LIFE-TIME

It has been found that the Na^+ sensors would lose sensitivity and at the same time experience base line drift after 10 to 12 hours of use. This is normal and expected due to loss of sensor charge (leakage). The sensors are then recharged overnight in a solution containing 0.1M of the primary ion. Overtime, the sensors would experience the lose of sensitivity and base line drift at a faster rate (2 to 3 hrs). This, is believed to be due to membrane fouling. Membrane fouling can occur two ways: 1) the "clogging" of the ion selective membrane. This doesn't allow for maximum infiltration of the primary ion into the sensor, resulting in a smaller signal (however, it is possible that membrane fouling was not a significant factor in drift since the calibration solution was sterile., and; 2) loss of selectivity of the membrane. This allows for greater interference from "secondary" ions. While specific life-time profiles have not been established for each sensor (the magnitude of sensor drift was difficult to quantify since electrical interference problems confounding readings) it has been identified that capabilities for the recharging of the membrane is essential in in-line system development.

Under ideal conditions, it is possible to obtain a theoretical sensitivity of -56 mV/decade of solution change (i.e. for every 10 fold increase in concentration - 1 mM to 10mM - the signal will change -56 mV). When the system has been working we have observed signal changes from -54 mV to -60 mV. This corresponds to being able to detect changes of 0.4 ppm of sodium solution at the lower limit of the calibration range.

The amount of solution used in by the sensors should be less than 2.0 mL since that is the volume of the sensor cells. Further, we expect that the amount of calibration solution required will be less than 4.0 mL. These numbers have not been confirmed since the magnitude of matrix interference has not been quantified.

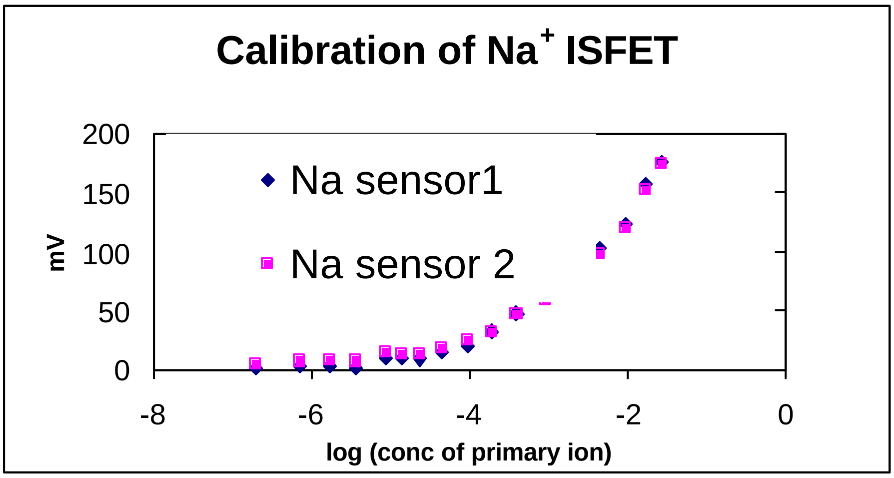

Figure 1. Calibration of Na^+ ISFET sensors. Sensor signal response was plotted against the concentration/activity of the primary ion of interest (Na^+) in the presence of an interfering ion, (K^+). Results indicate a typical Nernstian response even in the presence of an interfering ion.

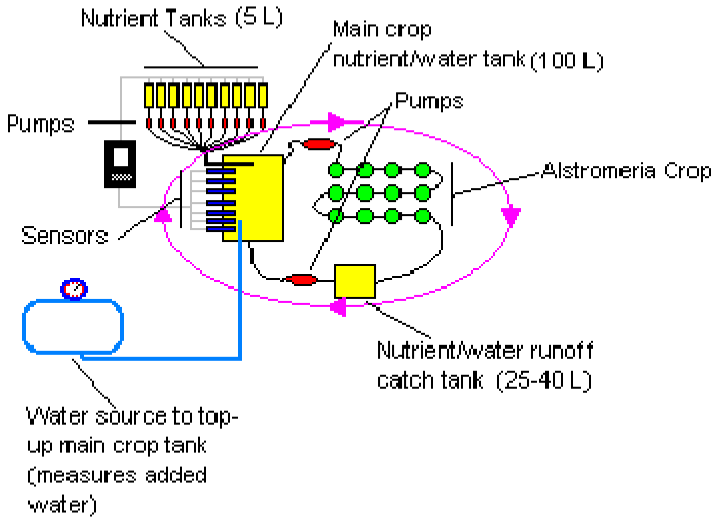

Figure 2. Automated sensor (ISFET) actuated fertigation system for greenhouse crop (*Alsteromeria*). ISFET sensors control the addition of required elements from eight nutrient tanks. The pH is also automatically adjusted as needed by addition of acid or base from one of two stock tanks

CONCLUSION

While our investigations have been limited to the sodium ion ISFET it is clear that a number of issues need to be overcome before ISFETs, in general, are sufficient technical maturity to be included in the MELiSSA loop. These include,

- reducing the effects of membrane fouling on cross and primary sensitivities
- establishing sensor systems with minimal susceptibility to drift
- increasing the operational life time of sensors, both in terms of the short term need for membrane re-charging and the long term effects of membrane deterioration
- the development of sophisticated sampling loops allowing for calibration, re-charging, rinsing and cleansing. It is expected that calibration will need to be performed after each re-charging of the sensor membrane (approximately 10 - 12 hours of use).

New ISFET models are in our possession at the University of Guelph and we will keep the MELiSSA community updated on their progress. We are, however, optimistic that significant progress will be made at improving sensor accuracy and precision to those desired within working ranges of typical hydroponics solutions.

While the ISFET sensors will continue to be evaluated, our immediate efforts will be on the development of a “black box” that will contain all of the algorithms and programming needed to accept an electronic signal (whether it be from an ISFET, ion selective electrode, or on-line HPLC). This system will be used to evaluate other technologies which may become available.

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