



Ontario Agricultural College
Department of Plant Agriculture
Division of Horticultural Science
Guelph, Ontario CANADA
N1G 2W1
Tel. (519) 824-4120
Fax. (519) 767-0755

MELiSSA

Memorandum of Understanding
ECT/FG/MMM/97.012

TECHNICAL NOTE: 40.4

Evaluation of Sensor Technologies for Automated Control of Nutrient Solutions in MELiSSA Based Life Support Systems Incorporating Higher Plant Chambers

Version: 1
Issue: 0

Cloutier G., Dixon M.A.,

December 1998

EVALUATION OF SENSOR TECHNOLOGIES FOR AUTOMATED CONTROL OF NUTRIENT SOLUTIONS IN MELISSA BASED LIFE SUPPORT SYSTEMS INCORPORATING HIGHER PLANT CHAMBERS

1.0 - INTRODUCTION 1

2.0 - ION ACCUMULATION AND UPTAKE PATTERNS IN EC/PH BASED SYSTEMS 2

3.0 - ION SELECTIVE ELECTRODE EVALUATION 4

 3.1 ACTIVITY COEFFICIENT AND ION CONCENTRATION- 5

 3.2 ISE SENSITIVITY- 5

 3.3 ISE STABILITY AND DRIFT- 7

 3.4 ISE TEMPERATURE DEPENDENCY- 9

 3.5 FURTHER CONSIDERATIONS FOR THE DESIGN OF ISE BASED NUTRIENT CONTROL SYSTEMS- 9

4.0 - ION SELECTIVE FIELD EFFECT TRANSISTORS 10

5.0 - OTHER CONTROL/SENSING TECHNOLOGIES: NANOFILTRATION 11

6.0 - REFERENCES 11

List of Figures

Figure 1. Ion accumulation and depletion patterns in a recirculating solution 3

Figure 2. Typical calibration profiles for four ISEs 6

Figure 3. Influence of Nitrate ISE drift on concentration estimates 8

List of Tables

Table 1. Regression analysis results for ISE calibrations 7

Evaluation of sensor technologies for automated control of nutrient solutions in melissa based life support systems incorporating higher plant chambers

1.0 - INTRODUCTION

Complete closure of life support systems using higher plants demands the development of low-mass hydroponic nutrient delivery systems in which all materials, including degraded human waste water and inedible plant biomass, are recycled. A key problem with low-mass nutrient systems is in the maintenance of the recycled nutrient solution composition and quality throughout single and multiple crop rotations.

It has been well documented that within the period of crop development from seed to senescence, there are marked changes in nutrient uptake and accumulation in re-circulating hydroponic solutions (Harper, 1971; McKeehen *et al*, 1996). The accumulation of salts in re-circulating nutrient solutions can have negative consequences on growth through the influences of ion interaction at the root zone. Induced deficiency of individual ions can result when more concentrated ions of the same physicochemical properties (valency and diameter) compete for binding sites at either the root cell wall or at the root plasma membrane. Such effects have been documented for Mg^{2+} and Mn^{2+} by Heenan and Campbell (1981), for NO_3^- and Cl^- by Glass and Siddiqi (1985) and for NH_4^+ and NO_3^- by Breteler and Siegerist (1984). Ion imbalances in re-circulating solutions owing to differential rates of uptake and accumulation may also be the cause of reduced individual plant Ca/P ratios, increased ash and reduced Fe, Cu and Zn concentrations (relative to field grown crops) of rice, wheat and potato grown in NASA's Biomass Production Chamber (McKeehen *et al*, 1996). In addition to their potential for reduced crop yield and quality, ion imbalances are also expected to have significant impacts on the nutritional quality of food derived from life support systems. These issues become even more troublesome as life support system engineers attempt to manage nutrient solutions supplemented with degraded human waste and inedible plant biomass materials, such as those derived from the European Space Agency's MELiSSA project (Lasseur, 1994) and NASA's Intermediate-Scale Aerobic Bioreactor (I-SAB) (Finger and Strayer, 1994).

At present there is a technology vacuum associated with the reliable application of various sensors to the in-line management of closed nutrient delivery systems. Control of nutrient solutions using electrical conductivity (EC) and pH is currently the most common approach in both commercial and research hydroponic installations. NASA's Biomass Production Chamber and our facility at the University of Guelph both use this control strategy to maintain a minimum concentration of ions in re-circulating solutions (Wheeler *et al*, 1996). In this method, solution quality is maintained through the automated injection of nutrient concentrates into the hydroponic solution reservoir in proportion to declining solution electrical conductivity arising from plant nutrient uptake. A serious disadvantage of this practice is that conductivity measures are indiscriminate, providing no information on the concentrations of individual ions. In commercial settings more precise control over individual ions is often achieved by off-line chemical analysis (usually HPLC, if available) every two to three weeks, followed by adjustment of the composition of the nutrient concentrates. This method provides only coarse control since

the uptake of individual ions varies with the stage of crop development (McKeehen *et al*, 1996).

In advanced life support systems there is also a desire to develop techniques which will enable system throttling and which will provide information to remote (earth based) support teams (Drysdale and Grysikiewicz, 1995). A solution control/monitoring system based on ion selective sensor technologies may therefore play an important role in fingerprinting normal and aberrant patterns in life support system development. For example, such technologies may generate continuous nutrient uptake signatures which can be interpreted in the context 'normal' system development patterns. These models may then be used to detect, in real time, senescence, delayed anthesis, significant increases in background micro-organism populations or used to control the rate of biomass production.

This paper will discuss work being conducted as part of the Sealed Life Support Systems Project at the University of Guelph, Canada in the evaluation of potential sensor technologies for the automated monitoring and control of re-circulating nutrient solutions. Two in-line approaches to management are currently being investigated; the traditional EC/pH based system and one which will be based on ion selective electrodes (ISEs). Also, the inclusion of semi-conductor based sensors, known as ion selective field effect transistors (ISFETs), is currently being considered in our program. Work presented here is a result of bench tests conducted at both the University of Guelph and AlliedSignal Aerospace Canada, and studies in our own sealed environment chambers. Reference to work done by other researchers in greenhouse settings will also provide evidence relevant to the inclusion of these sensors in flight-testable life support systems.

2.0 - ION ACCUMULATION AND UPTAKE PATTERNS IN EC/PH BASED SYSTEMS

An evaluation of an EC/pH based feedback (PID) control system was conducted in one of the sealed environment chambers at the University of Guelph (Dixon *et al*, 1997). A total of 150, two week old Soybean (*Glycine max.*) plants were transferred from the greenhouses at the University of Guelph to the sealed environment chamber and grown in a ½ strength modified Hoaglands solution using glass beads as a rooting media. The composition of the Hoaglands solution was as follows; 2.5 mM Ca(NO₃)₂, 2.5 mM KNO₃, 1 mM MgSO₄, 0.16 mM K₂HPO₄, 0.33 mM NH₄H₂PO₄, 25 µM KCl, 12.5 µM H₃BO₃, 9 µM Fe as sodium ferric diethylenetriamine pentaacetate, 2.5 µM CuSO₄, 2.5 µM MnSO₄, 1 µM ZnSO₄ and 0.0075 µM (NH₄)₆Mo₇O₂₄. Solution pH was maintained at 5.5 through the automated injection of 0.1 M stocks of HNO₃ or KHCO₃. Solution EC was maintained at 1100 µS cm⁻¹ through the automated injection of two separate nutrient solution injection stocks which were at a concentration of 20x that of the solution reservoir. Chamber temperature was maintained at 26°C/20°C and light intensity was kept between 850 and 1200 µmoles m⁻²s⁻¹ PAR with a 12 hour photoperiod. Supplemental inner-canopy lighting provided energy to lower portions of the canopy at an intensity of approximately 150 µmoles m⁻² s⁻¹ PAR.

Nutrient uptake and accumulation was quantified over the first 32 days following chamber

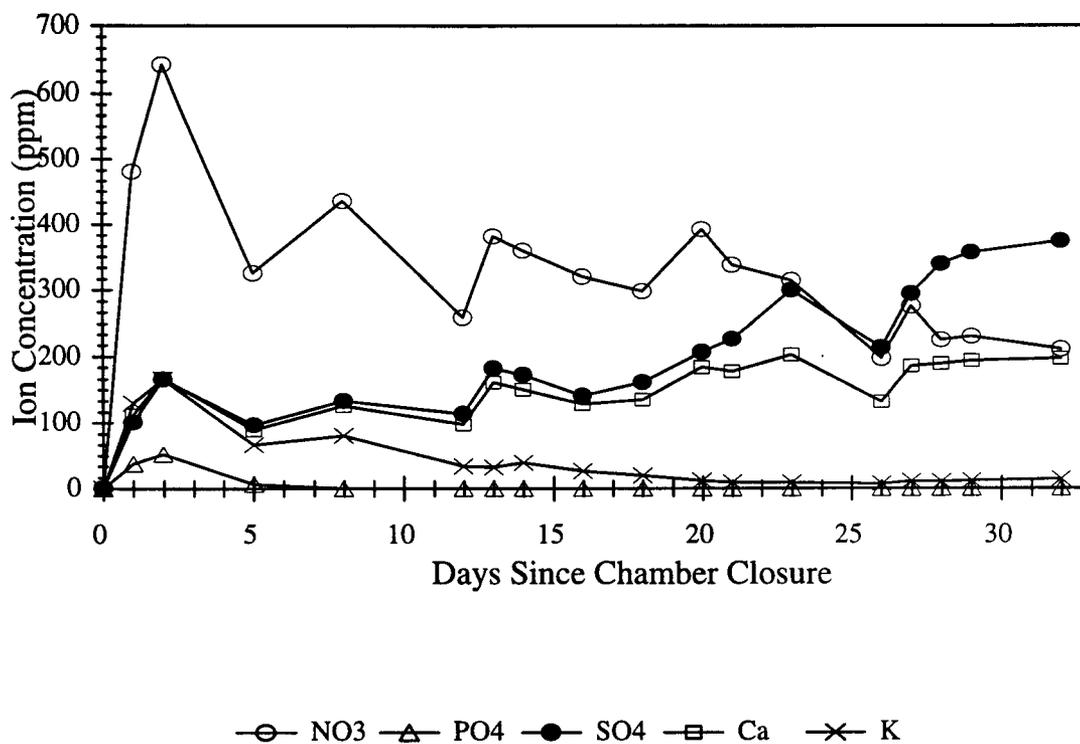


Figure 1. Ion accumulation and depletion patterns in a re-circulating nutrient solution in one of the sealed environment chambers. Concentration estimates were obtained using off-line HPLC with daily sample acquisition. Expected ion concentrations (in ppm) based on a 1/2 x Hoagland's solution are $\text{NO}_3^- = 310$, $\text{PO}_4^{3-} = 47$, $\text{SO}_4^{2-} = 97$, $\text{Ca}^{2+} = 100$, $\text{K}^+ = 111$. Stock injections were continuous.

closure using off-line HPLC (Dionex DX500) with daily (1 hr prior to dawn) sample acquisition. This period represented the most rapid vegetative production phase of the crop and was selected since it was

marked by the greatest frequency of nutrient concentrate injections. Cation and anion concentrations in the reservoir for some of the more important mineral nutrients are presented in Figure 2.

Profiles showed sharp decreases in phosphate concentrations during the first 5 days of the study. Concentrations of this ion remained close to zero throughout the remaining 27 days of the study. Potassium concentrations showed a slow general decrease during the first 22 days, and remained close to zero for the remaining 10 days. Nitrate concentrations also declined but remained within approximately 200 ppm of demand concentrations (465 ppm). Accumulations of sulphate and calcium were observed throughout the entire study period.

These results exemplify the problems with EC/pH based control systems. The accumulation of sulphate and calcium throughout the study period is undesirable and is a direct result of the indiscriminate analysis capabilities of EC/pH sensors. In response to declining solution EC complete Hoaglands concentrates were automatically injected into the hydroponic reservoir to bring EC back to demand levels. These repeated injections of stock included significant additions of sulphate and calcium despite their accumulation in solution. In one of our earlier studies the accumulation of sulphate reached levels which caused solution EC to become far in excess of demand levels. As a result, there were no further injections of nutrient stock and deficiency symptoms, due to declining concentrations of other ions, became evident. The fact that nitrate concentrations remained close to demand levels is the combined result of nutrient stock injections and injections of nitric acid. Automatic injections of nitric acid were in response to rising solution pH associated with mineral uptake. While these patterns in ion accumulation are crop specific, they do serve to illustrate the potential dangers of a control system based on EC/pH sensors alone.

3.0 - ION SELECTIVE ELECTRODE EVALUATION

Ion selective electrodes (ISEs) are electrochemical sensors that allow for the potentiometric determination of the activity of certain ions in the presence of other ions. Such an electrode constitutes a galvanic half-cell consisting of an ion-selective membrane (usually constructed of glass, or polyvinyl chloride), an internal contacting solution and an internal reference electrode. The other half cell is given by an external reference electrode which is in contact with the analyte. Modern ISEs ('combination' electrodes) have integrated the reference electrode with the sensing electrode in a single epoxy housing. The sensing electrode membrane potential (E_M , usually expressed in mV) results when target ions are transported across the membrane surface and for an electrode which is exclusively selective for ion of the sort I, is a measure of the respective activities in the contacting solutions on either side of the membrane. This potential can be given by;

$$E = E_i^o + s \log(a_i) \quad (1)$$

where a_i is the activity of ion I in the sample and s is identical to the Nernstian slope;

$$s = 2.303 \frac{RT}{z_i F} = 59.16 \frac{mV}{z_i} \quad (2)$$

and where R is the gas constant, T is the absolute temperature (value of slope in Eqn (2) is for 298 K), F is the Faraday equivalent and z_i is the charge of the ion.

A number of researchers have used ISEs for measuring the concentration of Ca^{2+} , Cl^- , Na^+ and NO_3^- ions and pH in re-circulating nutrient film (NFT) solutions in greenhouses (Clement *et al*, 1974, Bailey *et al*, 1988, Morimoto *et al*, 1992, Heinen and Harmanny, 1992). While there has been moderate success in the use of ISEs in controlling greenhouse based NFT systems there are potential limitations of their use in closed systems. These limitations will be highlighted with reference to short-term studies conducted at our facility and those of the researchers noted above.

3.1 Activity Coefficient and Ion Concentration

ISEs respond to ion activities (a measure of their effective concentration) in solution. If the composition of the nutrient solution is known, then ion concentration can be related to sensed activity according to;

$$a_i = \gamma_i c_i \quad (3)$$

where γ_i is the activity coefficient and c_i is the concentration of the ion.

The activity coefficient depends on the total ionic strength of the solution. In dilute solutions ($<10^{-4} \text{ mol L}^{-1}$) its value is close to unity, but as the total ionic strength of the solution increases so does the difference between individual ion activity and concentration. In practice a high concentration of an inert electrolyte (typically NaCl) is added to the sample to produce a solution of constant ionic strength from which direct concentration estimates can be determined from sensed activity and the activity coefficient. In a closed and non-destructive sampling system this is undesirable since an accumulation of salts in the hydroponic solution may ensue. In our studies of ISE performance and in those reported by Bailey *et al*, (1988), three complete Hoaglands calibration solutions spanning the range of the expected ion activities in the re-circulated solution were made and concentrations correlated with ISE output. The assumption was that the activity coefficients of the nutrient samples lay within or close to the range in the calibration solutions. An error in reported concentrations on the order of $\pm 6\%$ (for monovalent ions) is thus expected.

3.2 ISE Sensitivity

When electrodes are new, their sensitivities should be close to those predicted by Eqn (2), but their sensitivity decreases and/or becomes more erratic with age. Typical calibration curves having the form of Eqn (1) are presented in Figure 3. These calibration profiles were generated at 25°C in 5x, 0.5x and 0.05x normal strength Hoaglands solutions. The output of each of four electrodes for Ca^{2+} , K^+ , NH^+ and NO_3^- ions was plotted as a function of the log of the Hoaglands concentration.

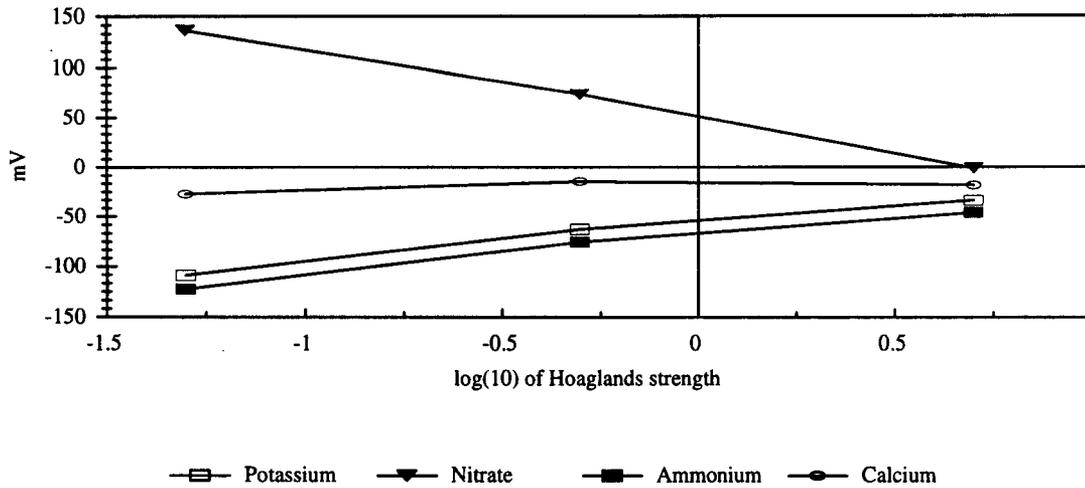


Figure 2. Typical calibration profiles for four ISEs. Electrode output was plotted against the log of the Hoaglands strength, according to Eqn (1). Regression analysis results are presented in Table 1.

Curves for K^+ , NH^+ and NO_3^- were consistently linear in the range of the calibration solutions. The NO_3^- electrode typically had slopes close to or higher than those predicted by Eqn (2) while K^+ and NH^+ electrodes had much lower sensitivities (Table 1). Curves generated for a number of Ca^{2+} electrodes repeatedly had poor co-efficients of determination and extremely low sensitivities (Table 1). Sensitivities lower than those predicted by Eqn (2) may be a result of the presence of interfering species, defective or aged electrodes or membrane contamination .

3.3 ISE Stability and Drift

To assess the short term stability of calibration slope and intercept estimates, calibrations were repeated for each of the four electrodes following 24 hours. Results of regression analysis performed on these calibrations are also presented in Table 1 (bracketed values). Over the 24 hour period electrode sensitivities for the Ca^{2+} , K^+ , NH^+ and NO_3^- electrodes varied by -134%, -20.2%, -26.5% and -12.0% respectively. Drifts in intercept (standard potential) estimates for the Ca^{2+} , K^+ , NH^+ and NO_3^- electrodes varied by -10.0%, -25.0%, -2.2% and -18.0% respectively. These estimates of drift are much higher than those reported by Bailey *et al*, (1988) and by Heinen and Harmanny (1992) who reported average daily drift in nitrate electrode potentials of about 3 mV decade⁻¹ day⁻¹ and 0.9 mV decade⁻¹ day⁻¹ respectively. The cause of these discrepancies is unknown but may be a result of differences in electrode age and construction.

Statistic	NO_3^-	NH^+	K^+	Ca^{2+}
r^2	99.8 (99.99)	98.2 (98.2)	98.2 (98.6)	48.5 (9.2)
s	-69.0 (-60.76)	38.4 (28.14)	37.7 (32.10)	4.49 (-1.54)
E^o_i	49.09 (-71.08)	-69.52 (-71.08)	-56.84 (-71.01)	18.58 (-20.50)

Table 1. Regression Analysis results for ISE calibrations.

The impact of electrode drift on concentration estimates of a solution of constant nitrate composition (465 ppm) is illustrated in Figure 4. Nitrate concentration estimates at the end of a 24 hour period were obtained using calibration curves generated at the start and end of the same period (days 1 and 2 respectively). Nitrate electrode output was continuously monitored for over a 1 hour period on each of the two days. Concentration estimates derived from the two calibration sets are plotted as a function of time (Figure 4). Electrode drift over this period was the same as that reported for the nitrate electrode in Table 1. As a result of this drift, concentration estimates (following a 40 minute equilibration period) differed by approximately 200 ppm (or 50%). Estimates were closest to actual concentrations when calibrations and analysis were from the same day (day 2). This implies the requirement for daily calibration since ISE utility is expected to decline within a 24 hour period. A drift in electrode sensitivity of 30% thus manifested itself in concentration estimate errors on the order of 50%, following the application of Eqn (1) to the raw data. Slight inflections in the concentration profiles, on the order of 25 ppm, are also evident. These inflections are attributed to electrical noise.

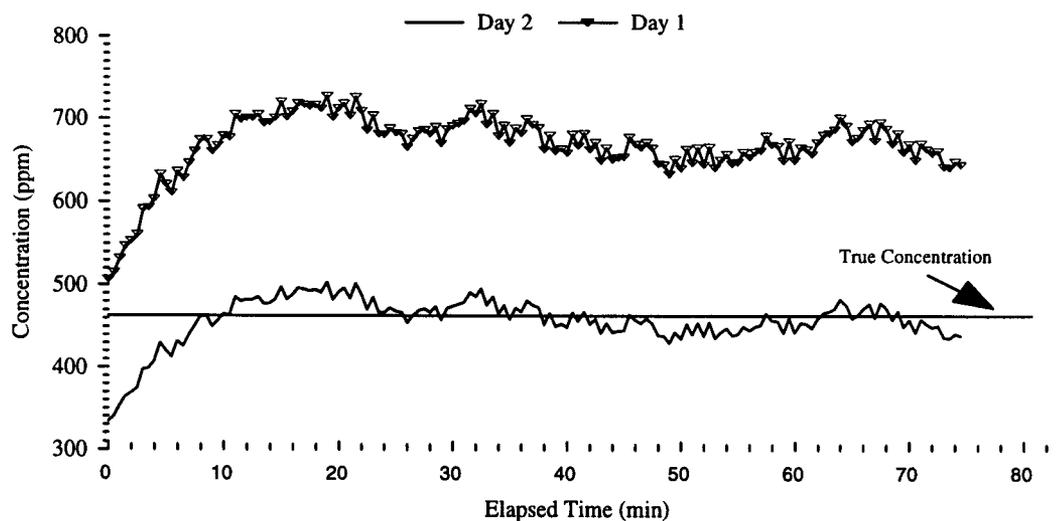


Figure 3. Influence of Nitrate ISE drift on concentration estimates. Nitrate concentration estimates at the end of a 24 hour period were obtained using calibration curves generated at the start and end of the same period (days 1 and 2 respectively). Nitrate electrode output was continuously monitored for over a 1 hour period on each of the two days. Concentration estimates derived from the two calibration sets is plotted as a function of time.

Figure 4 also illustrates that before electrode equilibration, which occurred approximately 25 minutes after immersion, there was an under estimation of solution nitrate concentration. Our studies have shown variable equilibration periods which were strongly dependent on the concentration of the analyte. In some cases equilibration took upwards of 90 minutes in dilute (1 ppm) solutions of KCl. Equilibration periods were also dependent on the concentration of solutions exposed to the electrode membrane surface immediately before analysis (ie: solution carry-over). Rigorous rinsing of the membrane surface with distilled water only partially relieved the problem.

3.4 ISE Temperature Dependency

As defined by the Nernstian response, electrode slope is dependent upon solution temperature and electrode body temperature. Sensitivities for ISEs sensing monovalent ions vary, theoretically, by approximately $0.5 \text{ mV } ^\circ\text{C}^{-1}$. In fact Heinen and Harmanny (1992) and our own studies have documented hysteresis loops between measured potential and temperature for NO_3^- and K^+ ISEs. Further, we have noted that a lack of isothermal conditions between solution and electrode body temperatures resulted in slow electrode responses and apparent drift. The large thermal capacitance of electrode epoxy housings greatly limits the rapid thermal equilibration between the electrode body and solution (Simpson, 1979). While temperature correction factors have been established based on Nernst's law, their utility in solutions of large thermal capacitance, such as those in hydroponic nutrient delivery systems, is limited. In fact, corrections applied by Heinen and Harmanny (1992) worsened temperature induced fluctuations in NO_3^- ISE output.

3.5 Further Considerations for the Design of ISE Based Nutrient Control Systems

The limitations of ISEs described above suggest that electrode drift is the most significant factor to be overcome in the design of automated solution control systems. Frequent, perhaps even daily, calibrations of ISEs will be required in order to derive reliable estimates of ion concentrations in re-circulating solutions. Of course, manual calibrations would place significant demands on crew time and are not guaranteed to give accurate results. The incorporation of automated calibration routines is therefore desirable.

In truly closed systems, calibration solutions would either be returned to reservoirs for re-use or incorporated into the nutrient delivery system stream. Daily calibrations spanning the range of anticipated ion concentrations would return significant volumes of calibration solution to the delivery stream. This, in light of the data presented in Figure 2, is undesirable since these volumes would likely contribute to the accumulation of ions such as SO_4^{3-} and Ca^{2+} . Instead, standard indirect analysis procedures incorporating both analysis and calibration in tandem are currently being explored in our system. These procedures involve the injection of dilute concentrations of calibration solutions into the analyte (Simpson, 1979). Electrode output before and after these injections is monitored and used to determine standard potentials and slopes at the time of analysis. While these techniques have significant automation requirements their

incorporation may mitigate the effects of ISE drift on concentration estimates.

Preliminary operational tests of ISEs in our sealed chambers provide evidence of their susceptibility to biofilm accumulation. Over a period of five days of continuous operation in our system, ISE membrane surfaces became occluded with a relatively thick (aprx. 1mm) mat of algae. Since automation requirements for the removal of biofilms is expected to be great, manual cleansing of membrane surfaces is likely to be the only practical alternative. Again, these maintenance procedures place significant demands on crew time.

In light of the potential limitations of ISE technology in individual ion based control systems, other advanced sensor types are being explored. One such sensor is known as the Ion Selective Field Effect Transistor (ISFET). Work done by other researchers in greenhouse environments will be briefly discussed here so as to highlight their potential application in life-support systems.

4.0 - ION SELECTIVE FIELD EFFECT TRANSISTORS

ISFETs are hybrids of ISEs and metal-oxide field effect transistors (MOSFETs). In ISE potentiometric measurements, the signal of an ISE is transmitted by wire to the input MOSFET of a voltmeter which modulates the current travelling between the MOSFET source and drain. In the ISFET, the metal gate of a MOSFET has been directly replaced by an ion-selective membrane. The surface field effect established by the transport of target ions across the membrane therefore modulates the drain current, and links the response of these sensors to current instead of potential (van den Vlekkert, 1992). These sensors are typically extremely small and thereby require very low solution volumes. While ISFETs have been used for nearly 20 years, their use in horticultural applications has just been recently recognised (ibid).

ISFETs for monitoring solution pH and K^+ in hydroponic solutions have been developed (van den Vlekkert *et al*, 1992). These sensors exhibited sensitivities on the order of 53 mVdecade^{-1} and remained stable over a 100 day test period. They also exhibited reduced sensitivities to noise and reproducibility of concentration estimates has been cited to be better than 10% (ibid).

Decreased performance of ISFETs and ISEs over time has been attributed to leakage of both the plasticizer and ionophore from the ion-selective membrane. Modifications to the bonding technique in which the ion-selective membrane is covalently bonded to the ISFET gate surface has been achieved (Reinhoudt *et al*, 1990). The incorporation of this type of bonding technology has greatly increased the life-time of ISFET sensors since leakage of the ionophore is reduced. While they are still very much in their research and development stages, these sensors have already exhibited stabilities which are greater than those found for ISEs. Their small size coupled with high reproducibility, long life times and ability for rapid, mass production make them very attractive alternatives to ISE technology. The incorporation of these sensors into the MELiSSA research program has been negotiated with a research and development company based in The Netherlands. While a beta-test agreement had been secured, the sensor's producer claims that they do not yet have a reliable prototype for our investigation at the University of Guelph. We

will continue to monitor the progress of these adolescent technologies for future developments and advances as well as those other technologies which may have application to the MELiSSA program.

5.0 - OTHER CONTROL/SENSING TECHNOLOGIES: NANOFILTRATION

In addition to the technologies described above, preliminary information has been gathered from the literature on nanofiltration as a solution control strategy.

Ohtani *et al* (1996) have investigated thirteen different nanofiltration (NF) membranes for the separation (rejection) of chemical components in nutrient solutions. Such membranes are reported to have ion rejection capabilities greater than reverse osmosis systems and operate at lower pressures similar to those required for ultrafiltration membranes. Using a nutrient solution composed of only potassium nitrate and ammonium di-hydrogen phosphate, observed rejection rates of phosphate and nitrate were quantified by Ohtani *et al* (1996). Within the range of 30 to 1000 ppm phosphate and 190 to 500 ppm nitrate (within the range of expected solution concentrations for $\frac{1}{2}$ x Hoaglands), the ion rejection ability of many of the NF membranes were independent of salt concentration. Rejection rates were reported to be between 60 and 100% for the phosphate ion and between 20 and 95% for the nitrate ion. For a given membrane type (UTC-20), the phosphate rejection rate was greater than that for nitrate (80% vs. 35% respectively). Thus, Ohtani *et al* (1996) concluded that an ion balance could be manipulated using a number of NF membranes placed in series, each having a selectivity for a different ion. While NF technologies seem to have application to hydroponics solution quality control, much of the work to date has been conducted on only a few specific membranes and in solutions not having the full compliment of ions required for plant growth. The progress of this technology will continue to be evaluated as new data and formal publications emerge.

Schlager (1996) has proposed the use of Hybrid Absorption Emission Spectrometry as an ion monitoring strategy. While the technique has been applied to the quantification of microbiological populations in solution, its application to ion monitoring has only been eluded to by Schlager (1996). Little information could be obtained at the time of the submission of this technical note on the results of bench tests, if any, for this application. This technology and others, will continue to be investigated.

6.0 - REFERENCES

Bailey, B.J., B.G.D. Haggett, A., Hunter, W.J. Albery and L.R. Svanberg, 1988. Monitoring nutrient film solutions using ion-selective electrodes, *J. Agric. Engng. Res.*, **40**, 129-142.

Breteler, H. and M., Siegerist, 1984. Effect of ammonium and nitrate utilization by roots of dwarf bean, *Plant Physiol.*, **75**, 1099-1103.

- Bugbee, B. and O. Monje, 1992. The limits of crop productivity: validating theoretical estimates and determining the factors that limit crop yields in optimal environments, *Bioscience*, **42**, 494-502.
- Clement, C.R., M.J. Hopper, R.J. Canaway and L.H.P. Jones, 1974. A system for measuring the uptake of ions by plants from flowing solutions of controlled composition, *J. Exp. Bot.*, **25**, 81-99.
- Dixon, M.A., B. Grodzinski, R. Cote and M. Stasiak, 1997. Sealed environment chamber for canopy light Interception and trace hydrocarbon analyses, *Advances in Space Research*, In press.
- Drysdale, A., and M. Grysikiewicz, 1995. Life Sciences Project Annual Report, McDonnell Douglas Space and Defense Systems, KSC Division.
- Finger, B.W., and R.F. Strayer, 1994. Development of an intermediate-scale aerobic bioreactor to regenerate nutrients from inedible crop residues, SAE Technical Paper Series 941501.
- Gitelson, I.I., I.A. Terskkov, B.G. Kovrov and L.S. Tirranen, 1989. Long-term experiments on man's stay in biological life-support system, *Advances in Space Research*, **9**, 865-871.
- Glass, A.D. and M.Y. Siddiqi, 1985. Nitrate inhibition of chloride influx in barley: implications for a proposed chloride homeostat, *J. Exp. Bot.*, **36**, 556-566.
- Harper, J.E., 1971. Seasonal nutrient uptake and accumulation patterns in soybeans, *Crop Science*, **11**, 347-350.
- Heenen, D.P. and L.C. Campbell, 1981. Influence of potassium and manganese on growth and uptake of magnesium by Soybeans, *Plant and Soil*, **61**, 447-456.
- Heinen, M., and K. Harmanny, 1992. Evaluation of the performance of ion-selective electrodes in an automated NFT system, *Acta Horticulturae*, **304**, 273-280.
- Lasseur, C., 1994. MELiSSA, Final Report for 1994 Activity, ESA.ESTEC, YCV/1626.CHL.
- McKeehen, J.D., C.A. Mitchell, R.M. Wheeler, B. Bugbee and S.S. Nielsen, 1996. Excess nutrients in hydroponic solutions alter nutrient content of rice, wheat and potato, *Advances in Space Research*, **18**, 73-83.
- Morimoto, T., H. Nishina, Y. Hashimoto, and H. Watake, 1992. Sensor for ion-control - an approach to control of nutrient solution in hydroponics, *Acta Horticulturae*, **304**, 301-308.
- Ohtani, T., Sase, S., Okushima, L. 1996. The control of chemical components of the nutrient solution in hydroponics with nanofiltration membranes, Proceedings of the International

Symposium on Plant Production in Closed Systems, *ActaHort*, 400, 217-222.

Reinhoudt, D.N. and E.J.R. Sudholter, 1990. The transduction of hostguest interactions into electronic signals by molecular systems, *Advanced Materials*, 2, 23.

Schaleger, K.J. 1996. Status and progress in on-line spectrometric monitoring and control of plant nutrient solutions, *Advances in Space Research*, 18, 113-124..

Simpson R.J., 1979. Practical techniques for ion-selective electrodes *In* Ion-selective electrode methodology, Vol. I, *Edited by* A.K. Covington CRC Press, West Palm Beach, Florida.

Van den Vlekkert, H.H., 1992. Ion-sensitive field effect transistors, *Acta Horticulturae*, 304, 113-126.

Van den Vlekkert, H.H., J.P.M. Kouwenhoven and A.A.M. van Wingerden, 1992. Application of ISFETs in closed-loop systems for horticulture, *Acta Horticulturae*, 304, 113-126.

Wheeler, R.M., 1992. Gas-exchange measurements in a large, closed plant growth chamber, *HortScience*, 27, 777-780.

Wheeler, R.M., C.L. Mackowiak, G.W. Stutte, J.C. Sager, N.C. Yorio, et al, 1996. NASA's biomass production chamber: A testbed for bioregenerative life support studies, *Advances in Space Research*, 18, 215-224.