A METHOD FOR ESTIMATING K⁺ AND NO₃ UPTAKE RATE IN HYDROPONICS BY A FOUR-ELECTRODE CONDUCTIVITY SENSOR

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ABSTRACT


A four-electrode conductivity sensor and associated electronics were designed and applied to the continuous monitoring of conductivity and the rate of K⁺ and NO₃ uptake in a hydroponic system. The new device was successfully used to monitor continuously the depletion rate of K⁺ and NO₃ in a hydroponic solution in which tomato plants (Lycopersicon esculentum cultivar 'Naama') were cultivated. A model is proposed for estimating the rate of K⁺ and NO₃ uptake by the plant, and their total concentration, from conductivity measurements. Experimental results verify the proposed mathematical criterion for choosing the initial concentrations of K⁺ and NO₃, and validate the underlying assumption of the proposed model.

Keywords: four-electrode conductivity system; hydroponics; tomato.

INTRODUCTION

Continuous monitoring and knowledge of the relationship between the rates of ion absorption by plant roots and the concentration of the ions to the roots is important in plant nutrition studies and when growing plants in hydroponics.

In earlier studies, investigators and growers measured the electrical conductivity of the solution and used the results as an intuitive indication of the total amount of nutrients and salts (Cooper, 1977). This strategy was selected mainly because accurate determination of the nutritional environment of the roots by analytical methods is labour-intensive and time-consuming.

In the present study, we investigated the possibility of applying conductivity measurements not only for a rough estimation of total nutrient level in solution, but also for estimating the rate of K⁺ and NO₃ uptake.
The classical method of measuring electrical conductivity of a solution is based on a 2-electrode conductivity cell and associated electronics, which determine the resistivity (or conductivity) measured between the electrode leads. Long-term monitoring of solution conductivity by 2-electrode cells is subject to error drift due to accumulation of dirt and grit on the surface of the electrodes. This difficulty can be partly overcome by applying a 4-electrode conductivity sensor, which has found wide acceptance in geophysical research (Keller and Frischknecht, 1966) and in soil science (e.g. Kirkham and Taylor, 1950; Rhoades and Ingvalson, 1971; Gupta and Hanks, 1972; Rhoades and Van Schilfgaarde, 1976). The main advantage of the 4-electrode system, as compared to the 2-electrode approach, is the relative insensitivity of the former to the nature and form of the metal-to-solution interface. This makes the 4-electrode sensor more stable and hence more reliable for long-term monitoring. These characteristics have been used successfully by Dauphinee (1968) to construct a highly accurate and stable sensor for determining the conductivity of seawater.

It was then decided to apply this method in the present study. Here we describe the design of the new sensor and associated signal processing system, and assess the possibility of using the sensor for continuous monitoring of K⁺ and NO₃⁻ concentration and uptake rate in hydroponics.

**INSTRUMENT DESIGN**

Four tungsten rods of 3 mm OD were embedded in a PVC head of 25 mm OD in such a way that the spacing between the electrodes was 5 mm (Fig. 1). The electrodes were then connected to a shielded cable and the head assembly was potted into a PVC sleeve to form the complete sensor.

![Diagram of four-electrode sensor](image)

*Fig. 1. Four-electrode sensor used in the present study.*
An electronic system was designed to obtain a direct reading in conductivity units. This was accomplished by incorporating the 4-point sensor in a feed-back configuration around an operational amplifier (Amplifier A in Fig. 2). This configuration ensures a constant voltage between the inner (sensing) electrodes, so long as the amplitude of the oscillator is kept constant and the circuit's limits are not exceeded. The constant potential $V_s$ is, by Ohm's law, equal to the current $I_c$ times the equivalent resistivity $R_s$, seen between the inner electrodes.

$$V_s = I_c R_s \quad (1)$$

Consequently, the cell's current is proportional to the equivalent conductivity $G_s$ if $V_s$ is kept constant.

$$I_c = \frac{V_s}{R_s} = G_s V_s \quad (2)$$

The current was fed to a current-to-voltage converter (Graeme et al., 1971) built around an operational amplifier (B in Fig. 2). The amplified a.c. signal was then rectified by a synchronous detector driven by the main oscillator of the system. The rectified and filtered signal was then fed to the output via a galvanic isolator (Ben-Yakow and Sarandagi, 1979) to eliminate problems associated with ground loops.

![Fig. 2. Schematic diagram of electronic system used to read solution conductivity by the 4-electrode sensor of Fig. 1.](image)

*Electrical conductivity of hydroponic solutions.* — The evaluation of the rate of $K^+$ and $NO_3^-$ uptake from electrical conductivity is based on the assumption that the contribution of these ions to the total conductivity is independent on ionic strength, i.e. that the equivalent conductivity, $\lambda_i$, of these
ions is constant for the system under consideration. This assumption is justified on the basis of normal growing conditions, which do not permit large salinity (and hence conductivity) variations. Under these conditions, the equivalent conductivity of these ions remains constant to a first approximation. This can be inferred by examining published tables of the equivalent conductance of KNO₃, $\Lambda_{\text{KNO}_3}$, over the expected ionic strength range. The equivalent conductance of an electrolytic solution is related to the equivalent conductance of the ions by

$$\Lambda = \sum \lambda_i$$  \hspace{1cm} (3)

It is found (Harned and Owen, 1958) that at 25°C, $\Lambda_{\text{KNO}_3}$ varies between $144 \times 10^3$ and $120 \times 10^3$ dSm⁻¹ mol⁻¹ over the concentration range of zero to 0.1 mol l⁻¹. Consequently, the assumption of constant $\lambda$ for these ions is accurate to within ± 10% over this range. However, since the expected ionic strength variation of the hydroponic solution over the growing period is much smaller, $\lambda_{\text{NO}_3^−}$ and $\lambda_{\text{K}^+}$ can be considered constant for all practical purposes.

The total conductivity, $E$, of the hydroponic solution is given by

$$E = \sum i \lambda_i \| Z_i \| c_i$$  \hspace{1cm} (4)

where $c_i$ is the concentration and $Z_i$ is the valence of ion $i$, and the summation is over all the ions in solution. Assuming that $\lambda_i$ remains constant, the change in $E$ as a function of time is related to the change in the concentration of the ions by

$$\frac{dE}{dt} = \sum i \lambda_i | Z_i | \frac{dc_i}{dt}$$  \hspace{1cm} (5)

If $\text{K}^+$ and $\text{NO}_3^−$ are the major contributors to the conductivity changes, then

$$\frac{dE}{dt} \equiv \lambda_{\text{K}} \cdot \frac{dc_{\text{K}}}{dt} + \lambda_{\text{NO}_3^−} \cdot \frac{dc_{\text{NO}_3^−}}{dt}$$  \hspace{1cm} (6)

In eqn. 6, the unknowns are $\frac{dc_{\text{K}}}{dt}$ and $\frac{dc_{\text{NO}_3^−}}{dt}$. An approximate solution for these unknowns was recently derived by Bea-Asher et al. (1982). According to this study, at high ion concentration

$$\frac{dc_{\text{K}}}{dt} = F_{\text{max(K)}} \quad \text{and} \quad \frac{dc_{\text{NO}_3^−}}{dt} = F_{\text{max(NO}_3^−)}$$  \hspace{1cm} (7)

where $F_{\text{max}}$ is the maximum uptake rate of the subscribed ion. It follows from eqn. 7 that changes in concentration of one ion can be expressed in terms of time derivative of the other ion. For example

$$\frac{dc_{\text{NO}_3^−}}{dt} = \frac{F_{\text{max(NO}_3^−)}}{F_{\text{max(K)}}} \cdot \frac{dc_{\text{K}}}{dt}$$  \hspace{1cm} (8)
It should be noted that the ratio $F_{\text{max}(\text{K})}/F_{\text{max}(\text{NO}_3)}$ can be a priori and independently estimated from the N/K ratio in the dry plant tissue, assuming that the ratio of uptake rate for these nutrients remains almost constant over the growing period, which can be expressed in the forms

$$\frac{\delta E}{\delta t} = \lambda_{(\text{K})} \cdot \frac{\delta c_{(\text{K})}}{\delta t} + \frac{F_{\text{max}(\text{NO}_3)}}{F_{\text{max}(\text{K})}} \cdot \lambda_{(\text{NO}_3)} \cdot \frac{\delta c_{(\text{K})}}{\delta t}$$  \hspace{1cm} (9)$$

and

$$\frac{\delta E}{\delta t} = \lambda_{(\text{K})} \cdot \frac{F_{\text{max}(\text{K})}}{F_{\text{max}(\text{NO}_3)}} \cdot \frac{\delta c_{(\text{NO}_3)}}{\delta t} + \lambda_{(\text{NO}_3)} \cdot \frac{\delta c_{(\text{NO}_3)}}{\delta t}$$  \hspace{1cm} (10)$$

from which

$$\frac{\delta c_{(\text{K})}}{\delta t} = \frac{1}{\lambda_{(\text{K})} + \frac{F_{\text{max}(\text{NO}_3)}}{F_{\text{max}(\text{K})}} \cdot \lambda_{(\text{NO}_3)}} \cdot \frac{\delta E}{\delta t}$$  \hspace{1cm} (11)$$

and

$$\frac{\delta c_{(\text{NO}_3)}}{\delta t} = \frac{1}{\lambda_{(\text{K})} \cdot \frac{F_{\text{max}(\text{K})}}{F_{\text{max}(\text{NO}_3)}} + \lambda_{(\text{NO}_3)}} \cdot \frac{\delta E}{\delta t}$$  \hspace{1cm} (12)$$

For convenience we will now define the respective slopes of eqns. 11 and 12 as

$$A_{\text{K}} = \left[ \lambda_{(\text{K})} \cdot \frac{F_{\text{max}(\text{K})}}{F_{\text{max}(\text{NO}_3)}} + \lambda_{(\text{NO}_3)} \right]^{-1}$$

and

$$A_{\text{NO}_3} = \left[ \lambda_{(\text{K})} \cdot \frac{F_{\text{max}(\text{K})}}{F_{\text{max}(\text{NO}_3)}} \cdot \lambda_{(\text{NO}_3)} \right]^{-1}$$  \hspace{1cm} (13)$$

Equations 11 and 12 can be used to estimate directly the rate of K$^+$ and NO$_3^-$ uptake from the drop in the conductivity of the solution. It should be noted that the proposed method of estimation is independent of the total conductivity of the solution as long as $\lambda_{(\text{NO}_3)}$, $\lambda_{(\text{K})}$ and the ratio $F_{\text{max}(\text{K})}/F_{\text{max}(\text{NO}_3)}$ are assumed constant, and the concentrations of the other major ions are constant. However, analytical considerations might render the proposed method impractical when the background conductivity is very high, because of the difficulty of measuring small conductivity variations against a very high-conductivity background.

MATERIALS AND METHODS

The experimental set-up described by Ben-Asher et al. (1980) was used for this experiment. The primary aim of this hydroponic set-up was to
follow the nutritional environment in which large volumes of nutrients are employed. The indicator plant was tomato (*Lycopersicon esculentum* cultivar 'Naama'). Fertilizer was introduced all at once and rapidly distributed in the water. The salts used were according to Hoagland and Amon (1950); major nutrients were introduced as KNO₃, KH₂PO₄, Ca(NO₃)₂, MgSO₄ and NH₄H₂PO₄. Distilled water was added to the system automatically to keep a constant water level and to prevent any increase in electrical conductivity caused by water loss through transpiration. pH level was kept constant between 5 and 6. When plants were at their full activity, solution samples were taken periodically to follow depletion in concentration of 2 of the major nutrients (K⁺ and NO₃⁻) with time. Conductivity values were recorded on a multi-point recorder with the 4-electrode sensor, simultaneously with other parameters such as solution and air temperatures.

The 4-electrode conductivity sensor was incorporated into a flow-through cell through which the greenhouse water was circulated using a submersible centrifugal pump. The readings of the new system were calibrated against a commercial conductivity meter (Model TH27, EL-HAMA, Israel). Calibration and reading of the 4-electrode sensor were carried out when the sensor was installed in the flow-through cell to maintain a fixed cell constant.

The results of conductivity readings and the respective concentrations of K and NO₃ were then plotted and the correlation between the two was calculated using the least-squares technique.

\[ F_{\text{max}} = 1.5 \text{ and } 0.3 \, \text{mg} \, \text{L}^{-1} \, \text{d}^{-1} \text{ for NO}_3 \text{ and K, respectively.} \]

The initial concentration \( (c_0) \) was 700 and 140 mg L⁻¹ for the respective ions. The experiment was carried out on mature (109-day-old) plants to satisfy the model requirements for a fully developed root system. K was determined using a Combina flame photometer. NO₃ was determined using NAS reagent (diphenylamine sulfonic acid cromogene) and a colorimeter.

**RESULTS AND DISCUSSIONS**

Conductivity measurements during the present experiment reveal a correlation of K and NO₃ in solution. Complete depletion of K occurred after about 16 days, whereas NO₃ reached zero after 21 days. This would suggest that the K/N ratio in the feed solution (0.886 g/g on N-NO₃ basis) was too low and that a better choice would have been 0.886 × 21/16 = 1.16 g/g. Nonetheless, conductivity seems to follow the depletion of NO₃ and K, and levels off at about 0.400 dS m⁻¹, which represents the baseline conductivity due to the residual salinity in solution.

The slope of NO₃ concentration versus time (Fig. 3) shows a distinct break at about the 8th day, after which the rate of NO₃ uptake was significantly higher as judged from the slopes. This may indicate variations in the uptake rates \( (F_{\text{max}}) \) of the 2 ions.

The validity of the proposed model depends on the constancy of the ratio between \( F_{\text{max} (K)} \) and \( F_{\text{max} (NO_3)} \) and not on the constancy of their actual values. This ratio remained constant during the experiment, as re-
vealed from Fig. 4a and b in which the NO₃ and K concentrations during the experiment were plotted against E. Indeed, these figures seem to support a number of basic assumptions about the proposed model. They suggest that the ratio \( \frac{\delta C(K)}{\delta t} / \frac{\delta C(NO_3)}{\delta t} \) was kept constant during the experiment and that the ratio \( F_{max}(K)/F_{max}(NO_3) \) can be considered constant (eqn. 7). Secondly, Fig. 4a and b seems to support the assumption that \( \lambda_{(NO_3)} \) and \( \lambda_{(K)} \) can be considered constant, i.e. they validate eqns. 11 and 12. Furthermore, the ratio of the 2 slopes, as determined experimentally in these figures, is found to be 143/501 \( \approx \) 0.285 g/g or 1.26 g/g on N-NO₃ basis. This is well within the expected K/N ratio for tomato plant tissue, which was reported to be in the range 1–1.5 g/g (Schwarz, 1975).

The proposed model could further be tested by comparing the experimentally determined slopes of Fig. 4a and b with those calculated from the model (eqns. 11 and 12). Taking \( \lambda_{(K)} \) as \( 88 \times 10^{3} \) dSm⁻¹/equivalent and \( \lambda_{(NO_3)} \) as \( 85 \times 10^{3} \) dSm⁻¹/equivalent for a 35°C solution (Robinson and Stokes, 1959), the slopes are calculated from eqns. 11 and 12, after some dimensional adjustment, to be

\[
A_{(K)} = 141 \text{ mg l}^{-1}/\text{dSm}^{-1} \quad \text{and} \quad A_{(NO_3)} = 497 \text{ mg l}^{-1}/\text{dSm}^{-1}
\]

which is in excellent agreement with the slopes of the regression lines which were found to be 143 mg l⁻¹/dSm⁻¹ for K⁺ and 501 mg l⁻¹/dSm⁻¹ for NO₃. 
Fig. 4. Conductivity of hydroponic solution (from 4-electrode meter) as a function of NO\textsubscript{3}\textsuperscript{-} concentration (a) and K\textsuperscript{+} concentration (b). The solid lines are linear best fits to the data.
(Fig. 4a and b). Hence, the deviation of the calculated slopes from those experimentally determined is less than 1%. The calculated slopes are a function of the ratio $F_{\text{max}(K)} / F_{\text{max}(\text{NO}_3)}$, which were derived from the present experiment as already indicated above. However, if this ratio is not known, one can use as a first approximation the K/N ratio of the plant tissue. Assuming that this ratio is between 1 and 1.5 g/g (on N-NO$_3$ basis) $A_{(K)}$ and $A_{(\text{NO}_3)}$ are calculated to be in the range 120–159 mg l$^{-1}$/dSm$^{-1}$ and 531–467 mg l$^{-1}$/dSm$^{-1}$, respectively. These independently calculated slopes are also in good agreement with the experimentally determined slopes, to within ±10%.

The relative contribution of K$^+$ and NO$_3$ to the drop in $E$ are not equal, as can be evaluated from the ratio

$$\frac{F_{\text{max}(K)}}{F_{\text{max}(\text{NO}_3)}} = 0.47$$

which is taken from eqns. 6 and 7.

Although the proposed method is primarily intended for estimating K and NO$_3$ uptake rates from conductivity measurements, the latter can also be used to obtain a rough estimate of total nutrient level in solution by

$$c_{(K)} = A_{(K)} \cdot E + B_K$$

and

$$c_{(\text{NO}_3)} = A_{(\text{NO}_3)} \cdot E + B_{\text{NO}_3}$$

In eqns. 15 and 16, $B_K$ and $B_{\text{NO}_3}$ are the background conductivities. The method is especially attractive, and should yield accurate results, if the composition of feed solution is chosen to ensure complete absorption by the plant and if deionized water is used to replenish evaporation and water uptake by the plant. Under these conditions, the background conductivities $B_K$ and $B_{\text{NO}_3}$ should remain constant, enabling one to estimate $c_{(K)}$ and $c_{(\text{NO}_3)}$ from conductivity over relatively long periods of time.

If tap water is being used, then transpiration rate has to be taken into account, in a similar way to the work of Ben-Asher et al. (1982). This, however, was beyond the objectives of the presented study and is currently under investigation.

The ability of the proposed model to estimate the concentration and the uptake rate of K$^+$ and NO$_3$ is evaluated by comparing the calculated values (the solid lines in Fig. 4a and b) with the measured concentrations of these ions. The excellent agreement between the calculated values and the data points support our basic conjecture that the rate of NO$_3$ and K$^+$ uptake and their concentrations can indeed be estimated from conductivity measurements.

The proposed method seems to be valid as long as NO$_3$ and K$^+$ contribute appreciably to the total conductivity. This requirement was not met after the 16th day of the present experiment (Fig. 4), when K$^+$ and NO$_3$ dropped
to rather low levels. At these low levels, the assumption of zero-order kinetics may also not be valid, and one would expect that the proposed model would fail to yield accurate estimates of K⁺ and NO₃ uptake rates.

CONCLUDING REMARKS

The primary objective of this study was to develop a new technique for computerized monitoring, analysis and control of nutrient levels in hydroponic systems. This objective can be reached only after developing a mathematical model for the computer software based on sound physical principles, and using a simple reliable sensor for monitoring the model parameters. The present 4-electrode conductivity sensor was found to fulfill this requirement. By feeding the conductivity data to the computer, which has been programmed to follow the proposed model calculations, optimal nutritional conditions could be maintained automatically. Further studies are required to test the theoretical and practical aspects of this possibility.

REFERENCES


