



Automated sensing of hydroponic macronutrients using a computer-controlled system with an array of ion-selective electrodes



Hak-Jin Kim^{a,*}, Won-Kyung Kim^a, Mi-Young Roh^b, Chang-Ik Kang^c, Jong-Min Park^d, Kenneth A. Sudduth^e

^a Department of Biosystems Engineering and Biomaterials Science, Seoul National University, Seoul 151-921, Republic of Korea

^b Rural Development Administration, Suwon 441-707, Republic of Korea

^c Science Lab Center Co., Daejeon 305-509, Republic of Korea

^d Department of Bio-Industrial Machinery Engineering, Pusan National University, Miryang 627-706, Republic of Korea

^e Cropping Systems and Water Quality Research Unit, USDA-ARS, Columbia, MO 65211, USA

ARTICLE INFO

Article history:

Received 21 August 2012

Received in revised form 8 January 2013

Accepted 20 January 2013

Keywords:

Hydroponic nutrients

PVC ion-selective membrane

Sensor array

Greenhouse

Nitrate

Potassium

ABSTRACT

Automated sensing of macronutrients in hydroponic solutions would allow more efficient management of nutrients for crop growth in closed hydroponic systems. Ion-selective electrodes (ISEs) are a promising approach because they can directly measure the analyte with a wide range of sensitivity and are small and portable. However, signal drift and reduced accuracy over time are major concerns with an in-line management system based on continuous immersion of ISEs in a solution. An ISE-based, computer-controlled measurement system for automatic sampling, calibration, and electrode rinsing is a viable technique to improve accuracy and precision in the determination of nutrient concentration. This study reports on development and evaluation of such a system for direct measurement of macronutrients in recirculating hydroponic solutions. The sensitivity and selectivity of PVC membrane-based ISEs fabricated with TDDA–NPOE, valinomycin, and calcium ionophore II were satisfactory for measuring NO₃–N, K, and Ca concentrations in single-ion solutions over ranges typical of hydroponic solutions. However, an acceptable Mg membrane was not identified. An ISE array incorporating the selected membranes, in combination with a computer-controlled measurement system, was evaluated for the direct measurement of NO₃–N, K, and Ca concentration in paprika hydroponic nutrient solutions. Using previously developed baseline correction and two-point normalization methods, ISE-measured NO₃–N and K concentrations in spiked or diluted hydroponic nutrient samples were strongly related to those determined using standard laboratory instruments ($R^2 = 0.85$). However, the tested Ca electrode did not provide satisfactory results due to reduced sensitivity and poor selectivity in the hydroponic solution. The approach used in this research, where a base solution is used for both referencing the baseline and rinsing electrodes and two calibration solutions are injected to implement the two-point normalization method, could be used in an automated sensing system for hydroponic nutrients in greenhouses. Additional research is required to identify ion-selective membranes for Ca and Mg ions in hydroponic solutions.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Hydroponics, known as a soilless farming, is a method of growing plants using mineral nutrient solutions in water, without soil. The macronutrients, nitrogen (N), phosphorus (P), and potassium (K) in the hydroponic solution are essential for crop growth. These nutrients are generally taken into plants in various ionic forms, such as nitrate (NO₃⁻), orthophosphates (H₂PO₄⁻ or HPO₄²⁻), and potassium (K⁺) through a combination of root interception, mass

flow and diffusion processes (Havlin et al., 1999). Since the reserves of nutrients for the plants are limited in hydroponic greenhouse cultivation, an inaccurately balanced nutrient solution may result in an unbalanced nutrient composition in the root environment (Savvas, 2002). In closed hydroponic systems that reuse the drainage solution, it is important to determine the nutrient concentrations in the reused solution to regenerate a nutrient solution of optimal composition (Gutierrez et al., 2007).

Current practices for managing hydroponic nutrients in closed systems are usually based on automatic control of electrical conductivity (EC) of the nutrient solution. In this method, solution quality is maintained through the automated injection of nutrient concentrates into the hydroponic reservoir in proportion to declining solution EC arising from plant uptake (Bailey et al., 1988;

* Corresponding author. Tel.: +82 2 880 4604; fax: +82 2 873 2049.

E-mail addresses: kimhj69@snu.ac.kr (H.J. Kim), w-kyung@nate.com (W.K. Kim), rohmy17@korea.kr (M.Y. Roh), me-gane@hanmail.net (C.I. Kang), parkjssy@pusan.ac.kr (J.M. Park), ken.sudduth@ars.usda.gov (K.A. Sudduth).

Cloutier et al., 1997). A main problem with this practice is that EC measurements provide no information on the concentrations of individual ions, and therefore do not allow individual real-time corrections to each nutrient in response to the demand of the crop (Cloutier et al., 1997). Improved efficiency of fertilizer utilization may be possible through accurate measurement and control of the individual nutrients in the solution in real time.

The need for such fast, continuous monitoring has led to the application of ion-selective electrode (ISE) technology to measure hydroponic macronutrients (Bailey et al., 1988; Cloutier et al., 1997; Gutierrez et al., 2007). Advantages over standard analytical methods (spectroscopic techniques) include simple methodology, direct measurement of analyte, sensitivity over a wide concentration range, low cost, and portability (Hashimoto et al., 1989; Heinen and Harmanny, 1992). The key component of an ISE is the ion-selective membrane that responds selectively to one analyte in the presence of other ions in a solution. Recently, significant progress has been made toward the development of various ion-selective membranes in the area of analytical chemistry. There are currently ion-selective membranes available for most of the important hydroponic nutrients, including NO_3^- , K^+ , Ca^{2+} , and Mg^{2+} (Nielson and Hansen, 1976; Shen et al., 1998). Reliable phosphate sensing has been more difficult. Although several polymer membrane-based phosphate ISEs have been developed (Carey and Riggan, 1994; Glazier and Arnold, 1991), they have generally exhibited poor selectivity for phosphate and a limited lifetime. As an alternative, cobalt-based electrodes have been developed and have exhibited sensitive responses to phosphate and acceptable selectivity (Xiao et al., 1995; Kim et al., 2011).

There are several potential disadvantages of ion-selective electrodes, as compared to standard analytical methods. One is chemical interference by other ions because ion-selective electrodes are not truly specific but respond more or less to a variety of interfering ions. To overcome interference issues, various data processing methods have been used. For example, multivariate calibration models have been proposed to allow cross responses arising from primary and interfering ions to be decoupled, thus allowing accurate determination of individual ion concentrations within mixtures (Forster et al., 1991). In some cases, another compound can be added to suppress the interference effect. For example, Ag_2SO_4 can be used to suppress the chloride interference in nitrate sensing (Van Lierop, 1986).

Another disadvantage is reduced accuracy due to electrode response drift and biofilm accumulation caused by the presence of organic materials in hydroponic solutions (Carey and Riggan, 1994; Cloutier et al., 1997). In particular, signal drift and biofilm accumulation may be a major concern when considering an in-line management system that includes continuous immersion of ISEs in hydroponic solution. Bailey et al. (1988) investigated the performance of commercially available ISEs (NO_3^- , Ca^{2+} , K^+ , H^+ , and Cl^-) in conjunction with a flow cell installed in a nutrient film technique (NFT) system. They found a decrease in sensitivity over time for all of the tested electrodes, which they suggested could be addressed by regular calibration. Heinen and Harmanny (1992) investigated the use of membrane-based NO_3^- and Ca ISEs and a glass-based K ISE to measure hydroponic nutrients in an automated NFT system. They reported that the electrodes provided more accurate estimates when temperature of the nutrient solution was measured or maintained constant due to a temperature dependency of the electrode response and that frequent calibrations were needed to maintain usability over long periods. Additionally, the performance of the Ca electrode was not satisfactory for use in hydroponic solution due to its low sensitivity.

Successful application of ISE technology to real-time sensing of hydroponic nutrients requires continuous determination of individual nutrient concentrations with acceptable sensitivity and

stability. In general, stability and repeatability of response are a concern in the use of an array of multiple ISEs to measure ion concentrations in a series of samples because accuracy of the measurement may be limited by drift in electrode potential over time. The use of a computer-based automatic measurement system would improve accuracy and precision in the determination of nutrient concentration because consistent control of sample preparation, sensor calibration, and data collection can reduce variability among multiple electrodes during replicate measurements (Dorneanu et al., 2005; Kim et al., 2007, 2011). Ideally, an automated sensing system for hydroponic nutrients would be able to periodically calibrate and rinse the electrodes and continuously measure nutrients in the hydroponic solution, while automatically introducing solutions for calibration and rinsing as well as measurement.

In a previous study (Kim et al., 2007), we established the ability of ISEs and Kelowna extractant (pH = 4.0) to simultaneously quantify NO_3^- -N, P and K ions in a set of 37 soils. We developed methods (baseline correction and two-point normalization) that standardized ISE response and allowed application of a single calibration equation across multiple ISEs fabricated simultaneously. A test stand with an array of ISEs was constructed and used to analyze soil extracts obtained through a standard Kelowna-based extraction process in the laboratory.

The overall goal of this research was to modify and apply the ISE-based macronutrient sensing system of Kim et al. (2007) for real-time and direct measurement of macronutrients in recirculating hydroponic solutions based on automatic sampling and electrode rinsing. Specific objectives were to (1) identify ion-selective membranes suitable for measuring typical ranges of macronutrient concentrations in hydroponic solutions with respect to their sensitivity, lower detection limits, and selectivity against interferences of other ions, and (2) evaluate the ability of a sensor array consisting of the selected ion-selective membranes, in combination with a laboratory-made automated test stand, to directly estimate NO_3^- -N, K, and Ca concentrations in hydroponic nutrient solutions.

2. Materials and methods

2.1. Preparation of NO_3^- -K-Ca-Mg ion-selective electrodes

Five different PVC-based ion-selective membranes were prepared with different mixtures of chemicals for sensing nitrate (NO_3^-), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions (Table 1). The chemical compositions of the NO_3^- and K ion-selective membranes were the same as those reported by Kim et al. (2006). One and two chemical compositions for Ca and Mg ion-selective membranes, respectively, were prepared according to the procedures described in previous studies (Erne et al., 1980; Maj-Zurawsk et al., 1989; Müller et al., 1988; Schefer et al., 1986).

The membrane disks with a diameter of 2.5 mm were attached to the ends of laboratory-made plastic bodies of 44 mm length using tetrahydrofuran (THF) solvent. Each ISE was filled with an internal solution consisting of 0.01 M NaNO_3 + 0.01 M NaCl, 0.01 M KCl, 0.01 M CaCl_2 , and 0.01 M MgCl_2 , for NO_3^- , K, Ca, and Mg ions, respectively. An Ag/AgCl electrode prepared by coating silver wire (99%) with a diameter of 1 mm with Ag/AgCl ink (Model 01164, ALS, JAPAN) was immersed as the inner reference electrode. A double junction glass electrode (Orion 90-02, USA) was used as the reference electrode.

2.2. Development of computer-controlled test stand

A computer-controlled test apparatus (Fig. 1), based on automatic data collection and electrode rinsing, was developed for

Download English Version:

<https://daneshyari.com/en/article/6541037>

Download Persian Version:

<https://daneshyari.com/article/6541037>

[Daneshyari.com](https://daneshyari.com)