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Analytical Methods

Computer-operated analytical platform for the determination of nutrients in hydroponic systems

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ABSTRACT

Hydroponics is a water, energy, space, and cost efficient system for growing plants in constrained spaces or land exhausted areas. Precise control of hydroponic nutrients is essential for growing healthy plants and producing high yields. In this article we report for the first time on a new computer-operated analytical platform which can be readily used for the determination of essential nutrients in hydroponic growing systems. The liquid-handling system uses inexpensive components (i.e., peristaltic pump and solenoid valves), which are discretely computer-operated to automatically condition, calibrate and clean a multi-probe of solid-contact ion-selective electrodes (ISEs). These ISEs, which are based on carbon nanotubes, offer high portability, robustness and easy maintenance and storage. With this new computer-operated analytical platform we performed automatic measurements of K^+, Ca^{2+}, NO_3^- and Cl^- during tomato plants growth in order to assure optimal nutritional uptake and tomato production.

1. Introduction

Since 2009, for the first time in history, there are now more people living in cities than in rural areas, and in 2050 city populations are anticipated to reach 70% of an expected 9 billion-world population (FAO, 2009). These figures suggest future scenarios where urban water and food supplies will have to adapt: food is commonly produced far from cities and transportation costs are high in energy, time and personnel. As a result, initiatives such as km. Zero agriculture, which try to promote local sourcing, are becoming more important.

Hydroponics is a method of growing plants without soil, using a continuous water flow containing mineral nutrients. This system is water-, energy-, space-, and cost-efficient. It saves 5- to 10-times more water due to the recycling system, and produces up to 10-times more food than traditional soil methods (Winterborne, 2005). Hydroponic systems offer the modularity to be placed outdoors or indoors in any spatial configuration (e.g., vertical columns, walls, large tilted horizontal crops, etc.). Because they do not use soil, plants suffer from fewer diseases and, consequently, pesticides use is reduced. Considering 70% of fresh water use globally is for agriculture, hydroponics represents a great opportunity to increase the sustainability of present and future urban water and food supplies. Furthermore, significant plant production in urban areas would increase air quality and would connect people with nature.

Precise control of hydroponic nutrients is essential for growing healthy plants and producing high yields. This control also reduces costs related to fertilisers. Plant nutrients can be monitored using several ‘in-field’ analytical techniques such as colorimetry, photometry, conductimetry or potentiometry. However, the analytical instrumentation used is based on old technologies requiring recurrent liquid handling and provides only semi-quantitative information (e.g., colorimetry, photometry). The most commonly used instruments are pH meters and conductimeters, which provide pH and total ion concentration. With this information, farmers are able to roughly calculate fertiliser levels, but lack precise control of individual macronutrients (NO_3^-, K^+, HPO_4^{2-}, Ca^{2+}, Mg^{2+}, SO_4^{2-}) or micronutrients (Fe^{2+}, Mn^{2+}, BO_3^{3-}, Zn^{2+}, Cu^{2+} and Mo^{3+}).

Ion-selective electrodes (ISEs) are well established chemical sensors that can determine the concentration of a wide variety of ions in water solutions. Only recently, ISEs operational performance characteristics have been drastically improved with solid-contact configurations. New types of solid-contact ISEs offer technical advantage such as miniaturisation, cost-effective and robust fabrication, no maintenance, and choice of shape. In particular, nanostructured materials such as carbon nanotubes (CNT) show superior analytical and operational performance characteristics that make them ideal candidates for the fabrication of solid-contact ISEs in decentralised analysis (Düzgün et al., 2011). Solid-contact ISEs have already been proposed for nutrient solution monitoring (Gutiérrez et al., 2008) and there are commercially available CNT-based solid-contact ISEs specifically for industrial hydroponic farms. These are portable, require low maintenance,

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are easily stored, and offer in situ information about up to six nutrients simultaneously (NT Sensors, 2012).

In addition to established analytical advantages (i.e., high selectivity, high sensitivity, wide linear range), solid-contact ISEs have the same disadvantages (i.e., need for calibration, matrix effect) as conventional ISEs. The use of ISEs in hydroponic urban systems will depend on whether cost, access and skill barriers can be significantly reduced. Cost will soon be decreased since inexpensive fabrication onto paper, plastic or ceramic substrates is a reality (Novell, Parrilla, Crespo, Rius, & Andrade, 2012; Ping, Wang, Ying, & Wu, 2012; Rius-Ruiz et al., 2011). However, the specific knowledge and skills needed to access the analytical information are still a barrier.

In this article, for the first time, we integrate a computer-operated liquid handling system and a series of CNT-based solid-contact ISEs to monitor individual nutrient composition in a liquid-circulating hydroponic system to grow healthy and tasty tomatoes. Gutiérrez et al. demonstrated the application of a man-operated array of ISEs in hydroponic nutrient monitoring (Gutiérrez et al., 2008). This new analytical platform should reduce significantly current barriers for ISEs in hydroponic systems. The liquid-handling system uses inexpensive components (i.e., peristaltic pump and solenoid valves) that are discretely computer-operated (Feres, Fortes, Zagatto, Santos, & Lima, 2008). The deliberate choice of inexpensive and robust components means devices are low cost and reliable. To the best of our knowledge, this is the first report of a computer-operated analytical platform using solid-contact ISEs specifically built for the determination of individual nutrient composition in hydroponic systems. This new analytical platform is the first step towards a smart liquid handling system that would automatically control the optimum nutrient levels at each stage of the plant growth. Furthermore, it is envisaged the generalised use of hand-held computing devices (e. g., smartphones and tablets) with specifically designed sensing applications will facilitate the use of portable analytical platforms and allow access to the information necessary to make in situ decisions.

2. Experimental

2.1. Reagents

Analytical grade $Ca(NO_3)_2{\cdot}4H_2O$, KNO_3, $CaCl_2$ from Sigma–Aldrich were used to prepare calibration solutions. Reagent grade $Ca(NO_3)_2{\cdot}4H_2O$, KNO_3, $MgSO_4$, KH_2PO_4, $CaCl_2{\cdot}2H_2O$, $Fe(NO_3)_2{\cdot}9H_2O$, $MnSO_4{\cdot}H_2O$, $ZnSO_4{\cdot}7H_2O$, H_3BO_3, ethylendiaminetetraacetic acid from Fluka and Sigma–Aldrich were used to prepare hydroponic nutrient solutions. Distilled water was used to prepare all solutions.

2.2. Ion-selective electrodes

NO_3^- ISE (CNT ISE C62, NT Sensors), K^+ ISE (CNT ISE C39, NT Sensors) and a NO_3^-, K^+, Ca^{2+} and Cl^- four-ion ISE (CNT ISE M41, NT Sensors) were used to monitor the concentration of tomato nutrients. During the first 40 days, we monitored NO_3^- and K^+ concentrations with NO_3^- ISE and K^+ ISE respectively and during the following 80 days we monitored NO_3^-, K^+, Ca^{2+} and Cl^- with the four-ion combined ISE (see Fig. 1). Commercial reference electrodes were included together with commercial ISEs in the same body. Potentiometric signals (emf) were measured at room temperature (20 ± 2 °C) with an EM16 Lawson Laboratories, Inc. high-input (10^{13} Ω) impedance potentiometer.

A calibration solution containing simultaneously 603 ppm K^+, 200 ppm Cl^-, 551 ppm Ca^{2+}, 200 ppm Na^+, 2311 ppm $NO3^-$ was prepared according to NT Sensors formulation. This solution was subsequently 1:10 and 1:100 diluted to obtain three calibration solutions, which were used to calibrate the ISEs before the nutrient solution measurements. Discrete computer-operated nutrient measurements were performed once every 3–5 days. Before its use, ISEs were in-line conditioned for 10 min in 1:100 calibration solution to produce optimal analytical results. After measurements, ISEs were manually rinsed with distilled water and dry stored.

2.3. Computer-operated liquid-handling system

In all cases ISEs were calibrated and exposed to sample nutrient solutions using the computer-operated liquid-handling system. The liquid-handling system consisted of three 3-way solenoid valves (model 075T3MP, Biochem Fluydics) and a peristaltic pump (model WPX1, Welco) (Fig. 1). The solenoid valves were controlled with the CosDesigner PC software (BioTray) and the FlowTest hardware controller (Biochem Fluydics). A voltage of 10 V was applied to the peristaltic pump with a power supply (ISOTech IPS 1810H), producing a constant flow of 2 mL/min. When using two separate ISEs for two independent analytes, an in-series detection chamber (150 μL) was built within the ISEs distal ends. When using the 4-ion ISE, its distal end was capped so to be used as detecting chamber (500 μL).

2.4. Hydroponic system

We built a vertical hydroponic system following instructions from The Windowfarms Project (2011). A schematic representation of the vertical hydroponic system is shown in Fig. 1 (left part). The vertical structure was made with a 1.5 m wood stick and three recycled 2 L plastic bottles piled one on top of the other. Each plastic bottle held a 10 × 10 × 10 cm plant pot containing around 50 g coconut husk as solid support for plant roots. At the bottom of the structure, a 5 L recycled plastic bottle served as the structure base support and nutrient solution tank. Nutrient solution was distributed to the plant pots in a close loop using an air pump and plastic tubing.

The nutrient solutions were prepared following tomato plants hydroponic formulations (see Table S1 in Supplementary Material) (Hochmuth & Hochmuth, 2008). The nutrient solution contained all the recommended nutrients except for micronutrient Mo^{3+}, which was not available in our laboratories. Five different formulations were prepared and used depending on the plants growing stage. The growing stage was assessed according to the number of unripe tomato clusters produced by the tomato plants. We used Hydrobuddy free software (Hydrobuddy, 2011) to calculate the amount of each salt needed to prepare the nutrient and supplement solutions.

An autochthonous variety of tomato (*Solanum lycopersicum*) was grown from seedlings. We starting growing plants in December 2011 and collected the first fruits in April 2012. As plants grew, they were entangled with nearby air conditioning tubes, pruned and pollinated. No commercial pesticide or fertiliser was applied. We completely changed the tank nutrient solution only twice (every 60 days) in order to eliminate undesirable algae and flies larva.

2.5. Hydroponic solution measurements

We periodically (every 3–5 days) analysed the closed-loop hydroponic solution in order to monitor the concentration of the ions and to adjust the nutrients to its optimal values. The overall procedure was heavily computer-operated. We set a routine for the solenoid valves using the Biochem Fluydics software controller.