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.

Keywords: ion-selective electrodes, computer-operated, automated calibration, plant growth

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. 0 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 fertilizers. 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 fertilizer 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 miniaturization, 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 decentralized 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, are easily stored, and offer in-situ information about up to six nutrients simultaneously (NTSensors, 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 on to paper, plastic or ceramic substrates is a reality (Novell et al., 2012; Rius-Ruiz et al., 2011; Ping et al., 2012). 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 et al., 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 generalized 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 Section

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 Figure 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) (Figure 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 Figure 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 10x10x10 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 fertilizer 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) analyzed 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. Lawson Laboratories, Inc. software recorded the ISEs voltage versus time values. An excel spreadsheet readily transformed the voltage values obtained from the ISEs into K^+, NO_3^-, Ca^{2+} and Cl^- concentrations in the nutrient solution by using standard calibration lines (see Supplementary Material). Excess or shortage of each specific nutrient was computer calculated using an excel spreadsheet and immediately adjusted to optimal values by manual addition of nutrient solutions. Various supplement solutions containing high concentrations of ions were used to adjust any deficiency. We also obtained the concentration standard deviations (three measurements with the same electrode in conditions of repeatability), and the ISEs' sensitivity, stability and response time. The standard deviations, the sensors sensitivity, stability and time of response were also valuable data to assess the ISE's performance.

3. Results and Discussion

We built a simple computer-operated analytical platform (see Figure 1) as the first step towards general use of portable analytical tools for solid-contact ISEs in hydroponic systems. The cost of the analytical platform (excluding computer and ISEs) was around 2755 euros (3-way solenoid valves: around 110 euros each, peristaltic pump: around 70 euros, FlowTest hardware controller: around 1890 euros, power supply: around 465 euros). We deliberately chose commercially-available solid-contact ISEs, and simple liquid-handling system components in order to work with analytical tools with high flexibility and the potential to make future improvements. Commercial CNT-based ISEs are solid-contact ISEs with an inner CNT ion-to-electron transduction layer in close contact with the outer crystalline or polymeric selective recognition layer (NTSensors, 2012). The cost of the ISEs was around 400 euros (NO_3^- or K^+ ISE, including in both cases the reference electrode) or around 1100 euros (four-ion ISE including the reference electrode). Next steps will include the use of state-of-the-art low-cost screen-printed miniaturized CNT-based ISEs, which we have shown can be used in real sample measurements (Rius-Ruiz et al., 2011), or the use of other low-cost and low-energy consumer components such as micro-pumps substituting solenoid valves.

3.1 Computer-Operated Analytical System Development

Our first goal was to test the reliability of the new analytical platform for the determination of the target nutrients. We assessed the repeatability of the system on simultaneous calibration of K^+ and NO_3^- ISEs and subsequent analysis of sensitivity and standard potential (E_0) values (three measurements with the same electrode in conditions of repeatability). As shown in Figure 2, signal noise was negligible and a complete cleaning of the detecting cell was attained in 3 min after each calibration. Standard deviations were satisfactorily low for K^+ ISE and significantly higher for NO_3^- ISE (Figure 2). We considered these values to be suitable for computer-aided monitoring of hydroponic nutrient solutions. Batch tests showed that K^+ ISE stability was higher than NO_3^- ISE stability, consequently producing higher standard deviations for NO_3^- ISE. These initial results show that the liquid-handling system was producing good results for K^+ ISE and acceptable results for NO_3^- due to the NO_3^- ISE inferior stability. In the light of these results, we always calibrated the ISEs before a sample measurement.

3.2 Hydroponic Nutrients Monitoring

We applied the new computer-operated analytical platform for the monitoring of key nutrients in a hydroponic system. We grew 5 tomato plants in a vertical hydroponic system installed in a corner of an office. Reportedly, NO_3^- and K^+ are the most relevant nutrients to be managed in first stages of tomato growth (Hochmuth & Hochmuth, 2008). Therefore, we started monitoring these two nutrients in the hydroponic nutrient solution using two individual electrodes integrated in the computer-operated analytical platform. Apart from NO_3^- and K^+, there are other nutrients which are essential for tomato plants optimum development. For instance, low Ca^{2+} values provoke low blossoming and tomato production and Cl^- excess may stunt the plant growth or burn the plant leaves. We decided to monitor NO_3^-, K^+, Ca^{2+} and Cl^- by simultaneously using a 4-ion ISE probe from the 40th day of installation, when the first flowers started blossoming. The liquid-handling system was not altered regardless of whether we were using two electrodes or one 4-ion ISE probe, and only the detection chamber was adapted to the shape of each sensor.

First observations showed that NO_3^- and K^+ concentration values did not vary much during the first two weeks. This was an expected outcome since there were few roots and 4 L nutrient solution was circulating in a close-loop cycle. Figure 3 shows that NO_3^- significantly decreased after 15 days and K^+ started decreasing after 20 days. Every time we detected a deficiency or excess of any nutrient, we calculated the amount of each nutrient to be added or reduced in the hydroponic solution reservoir comparing the experimental obtained values with the optimal ones (listed in Table S1 Supplementary Material). Calculations were performed automatically using an Excel spreadsheet (see Supplementary Material). Excess of nutrients was corrected by dilution. Excess of Cl^- was corrected changing the whole nutrient solution (4 L). On 28th day, we tested whether the analytical platform was capable of detecting an abnormal increase in NO_3^-, which at this stage of growth could be poisonous for the plant. We added a supplementary solution containing far more NO_3^- (1000 ppm) than K^+ (100 ppm), and detected the imbalance effectively. Immediately afterwards, we restored normal levels by dilution with a NO_3^- poor hydroponic solution.

We started monitoring NO_3^-, K^+, Ca^{2+} and Cl^- values using a 4-ion ISE from day 40 the hydroponic system had been installed. By then, the tomato plants were significantly bigger and first flowers had started blossoming, provoking a higher variability in nutrient values. Figure 3 shows the values obtained for NO_3^-, K^+, Ca^{2+} and Cl^- measurements every 2 to 5 days. Dashed lines indicate the proposed optimal values for each nutrient (Hochmuth & Hochmuth, 2008). Note that after each measurement a supplementary nutrition solution was added so to reach optimal values, as explained above. Only the measurements on days 7, 27 and 43 ions were performed just after the supplementary solution addition to check that optimal values were reached.

Regarding NO_3^- values, it was usual to find them in the range from 120 to 50 ppm. These values are clearly lower than the proposed optimal ones, so we periodically added the extra NO_3^- necessary to reach optimal values (Table S1 Supplementary Material). A similar scenario was observed for K^+, with values significantly lower (70 to 10 ppm) to the optimal ones, and periodic addition of extra K^+ was needed. Concerning Ca^{2+}, observed values were more stable than NO_3^- or K^+ and only slightly below the optimal value of 150 ppm. Cl^- was commonly found in slight excess (>100 ppm compared with optimal 50 ppm) (University of Arizona, 1998). Supplementary nutrients were easily added thanks to the automatic calculations performed using the excel spreadsheet.

Experimentally, we observed that NO_3^- and K^+ were the most difficult to equilibrate and adjust to optimal values in a nutrient solution of 4 L. The NO_3^-/K^+ ratio shown in Figure 4 illustrates the constant variability of NO_3^- or K^+ values; although NO_3^-/K^+ ratio was generally 2-4.5, there were three occasions when the ratio far exceeded 5 and once the ratio was less than one. At the same time, NO_3^- and K^+ concentration values are the most relevant ones for the correct growth of the plant and they have to change significantly with the growth of the plant (see Table S1 Supplementary Material) (Hochmuth & Hochmuth, 2008). Thanks to the information provided by the computer-operated analytical platform, we could effectively take all the necessary in-situ decisions to balance any undesirable nutritional situation. Consequently, plants grew healthy and produced tasty tomatoes after 120 days. Figure 5 illustrates the tomato plants growth over a total of 120 days. The plants did not get direct sunlight due to their location in a corner of an office. This most probably stunted the plant growth and tomato production. Nonetheless, after 40 days, the first flowers started appearing, and only after 120 days we started collecting the first ripen red tomatoes. Note that conventional periods for total growing of tomato plants range between 95 to 115 days (Stephens, 1994). Long periods without nutrient monitoring (between days 86 and 112) provoked flowers shriveling and the appearance of algae, fungus and flies as a consequence of inadequate nutrient control.

3.3 Assessment of the ISEs' Analytical Performance

The data provided by the accumulated calibration plots can be used to assess the evolution of the ISEs, thus assessing the analytical reliability of the automated nutrient monitoring system and envisaging ways to optimize the analytical procedure.

K^+ ISEs showed moderate precision of the slope and excellent slope stability within the 120 days of study. K^+ ISEs' E_0 values showed low precision and good stability along time. NO_3^- ISEs showed low slope and E_0 precision and an important potential drift (-1.8 and -2.3 mV/day). Ca^{2+} ISE showed excellent slope precision and stability along the 120 days of study. Cl^- ISE showed low slope precision and an important change in slope from day to day. Table 1 summarizes all the results (graphically represented in Figures S1 and S2 in Supplementary Material).

Overall, the results show the higher stability of K^+ and Ca^{2+} ISEs in comparison with NO_3^- and Cl^- ISEs. In light of these results, K^+ and Ca^{2+} ISE response should be regarded as sufficiently stable to produce meaningful results with a calibration protocol of only one point (Rius-Ruiz et al., 2011). In other words, ISEs could provide a preset slope value and one calibration solution could be used to standardize E_0 values. However, NO_3^- ISE slope variability and NO_3^- and Cl^- ISEs constant E_0 drift (see graphics S1 and S2 in Supplementary Material) require calibration with a minimum two solutions before each sample measurement. A single point calibration would decrease the number of standard solution and valves needed in the analytical system. However, it would increase the uncertainty of the analytical results. When using a single multi-parametric probe (highly desirable in hydroponic nutrient solution measurements), our results suggest using a minimum of two standard solutions for calibration.

4. Conclusions

This article reports on a new computer-operated analytical platform consisting of commercially available CNT-based ISEs and a simple liquid-handling system. Analytical results showed the correct functioning of the whole computer-operated analytical platform. This integrated system reduces manual operations by automatically performing the conditioning, calibration, measurement and cleaning steps. Thus, this new and simple computer-operated analytical platform makes it easier for the final user to access the necessary nutritional information needed to grow a healthy hydroponic system.

The computer-operated analytical platform has been used to monitor K^+, NO_3^-, Ca^{2+} and Cl^- in hydroponic growing system during a long period of time (3 months). We have efficiently grown tomato plants from seedlings to harvesting healthy tomatoes with the assistance of the computer-operated analytical platform in a university office. Since the nutritional needs of the plant vary with every growth stage, we used the analytical platform to precisely determine the nutrient levels at each stage and immediately added the necessary nutrients to the nutrition solution. We observed that it is difficult to maintain optimal K^+ and NO_3^- values in mature plant growth stages, thus the analytical platform readily provided the necessary information to manage the nutrient solution for plant growth. In the light of the experimental results, we should have measured the nutrients more often to better control the ions concentrations, especially for NO_3^- and K^+, which are consumed quickly by adult plants.

Furthermore, we studied over time the evolution of ISEs sensitivity and E_0, statistically. Results suggest the suitability of ISE calibration before sample measurement to obtain more accurate results, although one solution calibration could be feasible for K^+ and Ca^{2+} ISEs.

The main limitations of the studied computer-operated analytical platform were its relatively big size (40 cm x 30 cm x 30 cm) and the lack of a feedback protocol unit. Future work will include the use of miniaturized components (i.e., valves, pump, ISEs) in an integrated platform, and feedback instructions and communication components, so the computer-operated system can maintain optimal nutritional values continuously and communicate remotely with any necessary human input.

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TABLES

Table 1. Slope and standard potential evolution of SC ISEs during the 120 days of experimental work. The uncertainty is expressed as standard deviation (n=13) in intermediate precision conditions.

	Single electrodes			
	Slope (mV/dec)	**Slope stability (mV/dec/day)**	**E_0 (mV)**	**E_0 stability (mV/day)**
K^+	54.6 ± 1.4	-0.035	216.9 ± 6.9	-0.1
NO_3^-	-57.3 ± 3.3	-0.010	154.6 ± 30.6	-1.8
	4-ion ISE probe			
	Slope (mV/dec)	**Slope stability (mV/dec/day)**	**E_0 (mV)**	**E_0 stability (mV/day)**
K^+	50.4 ± 2.3	-0.039	384.7 ± 14.2	-0.4
NO_3^-	-54.4 ± 3.2	0.130	170.9 ± 37.9	-2.3
Ca^{2+}	19.8 ± 0.8	-0.001	321.0 ± 8.6	-0.3
Cl^-	-47.9 ± 2.8	0.120	157.2 ± 6.3	-0.2

FIGURES

Figure 1. Photographs and scheme of all the elements composing the computer-operated analytical platform for the determination of nutrients in hydroponic systems.

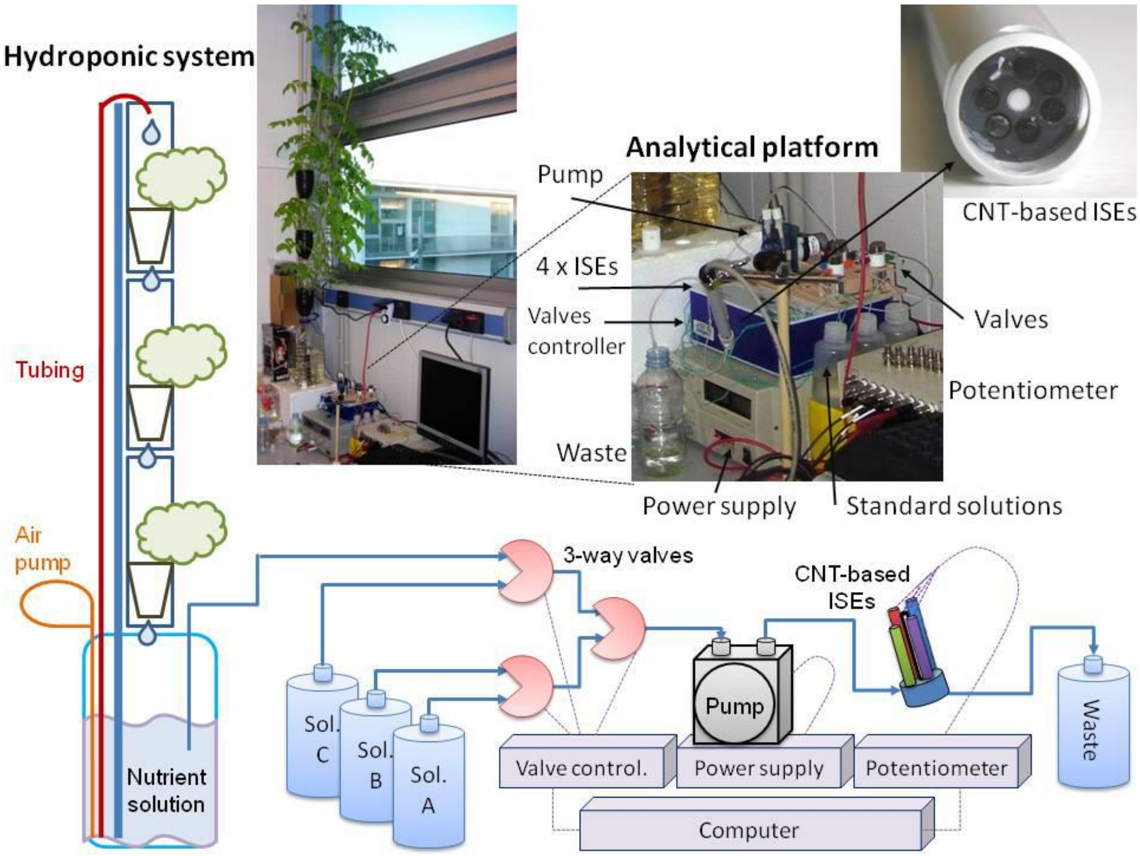
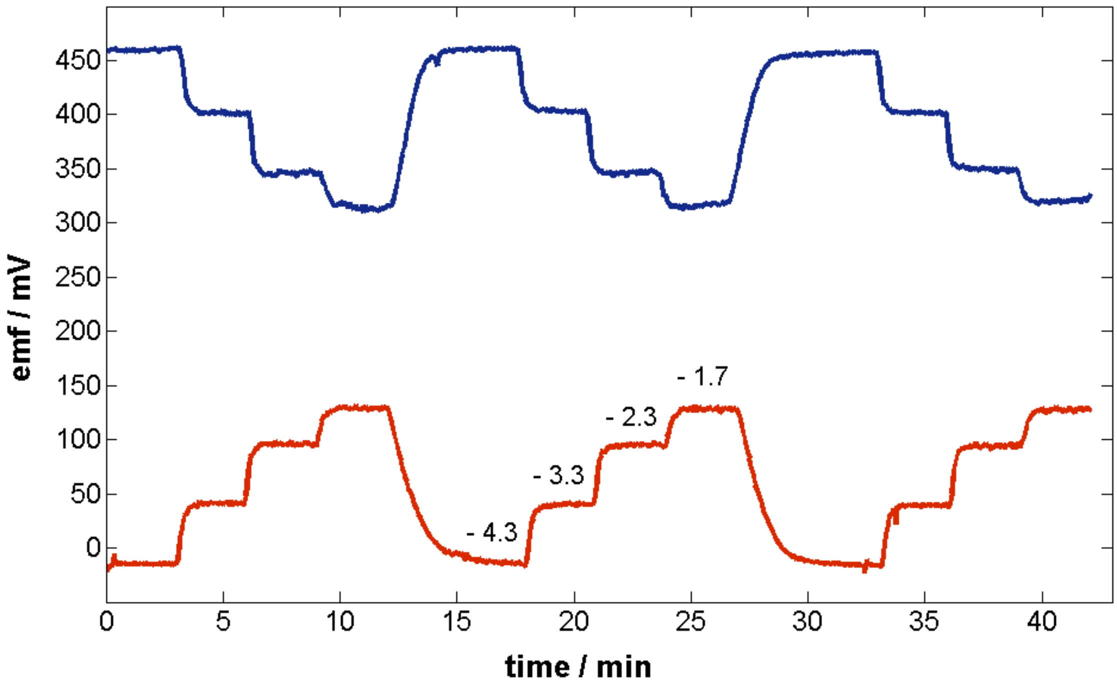


Figure 2. Potential response of simultaneous calibration of NO_3^- and K^+ ISEs using calibration standards. Values in the graphic indicated the log aI for both NO_3^- (blue line) and K^+ ions (red line). The uncertainty is expressed as standard deviation of three measurements using the same electrode in repeatability conditions.



	K^+ ISE	NO_3^- ISE
Sensitivity (mV/dec)	57.2 ± 0.4	-55.2 ± 2.3
E_0 (mV)	215.0 ± 1.3	237.5 ± 6.7

Figure 3. A) Evolution of NO_3^- (blue dots), K^+ (red dots), Ca^{2+} (green dots) and Cl^- (purple dots) values during 120 days from seedlings to tomato harvesting. Dashed lines show optimal values (Hochmuth & Hochmuth, 2008). B) Zoom in the 0-250 ppm concentration range.

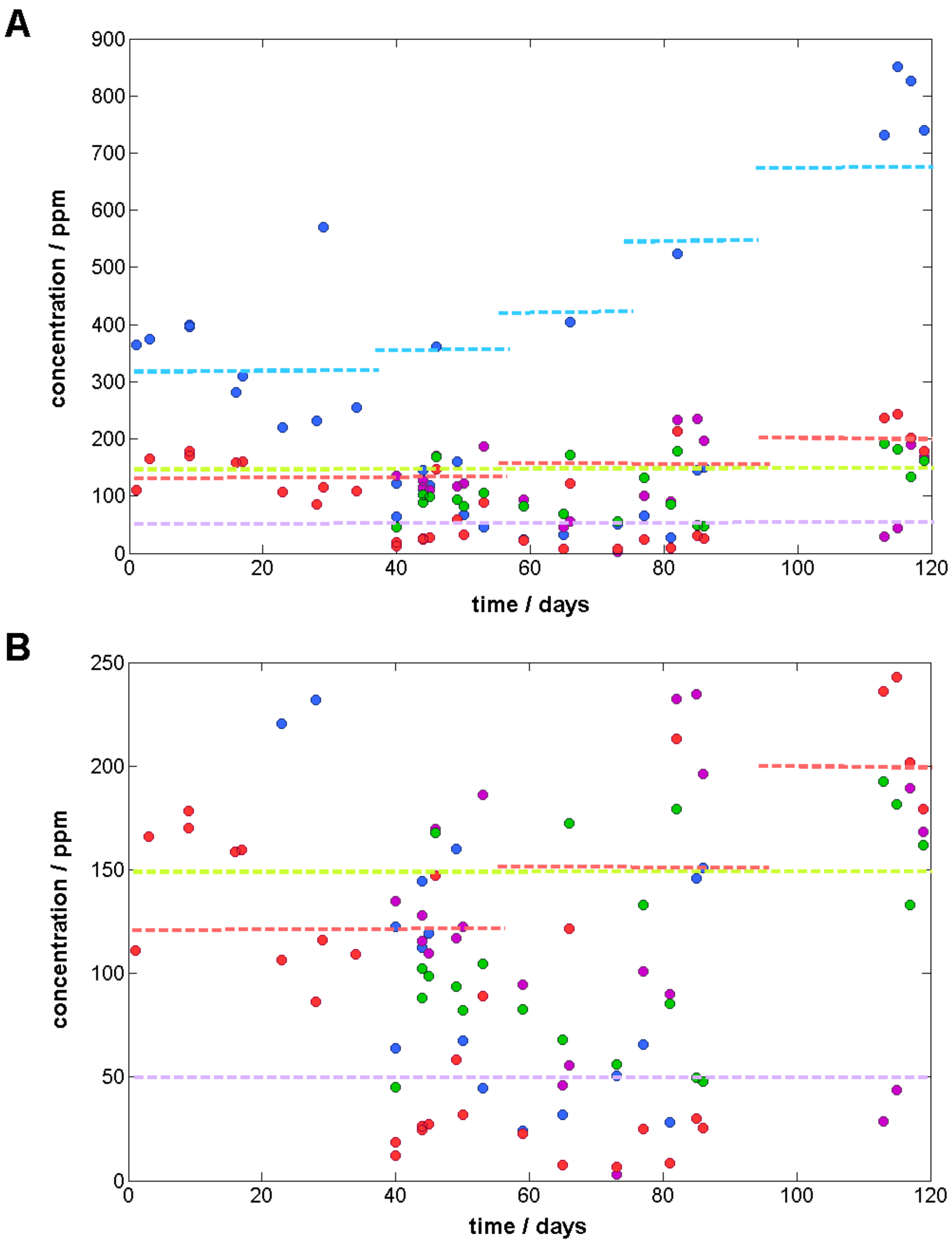


Figure 4. NO_3^-/K^+ ratio evolution during the total growth of the plant. Dashed lines show optimal values (Hochmuth & Hochmuth, 2008).

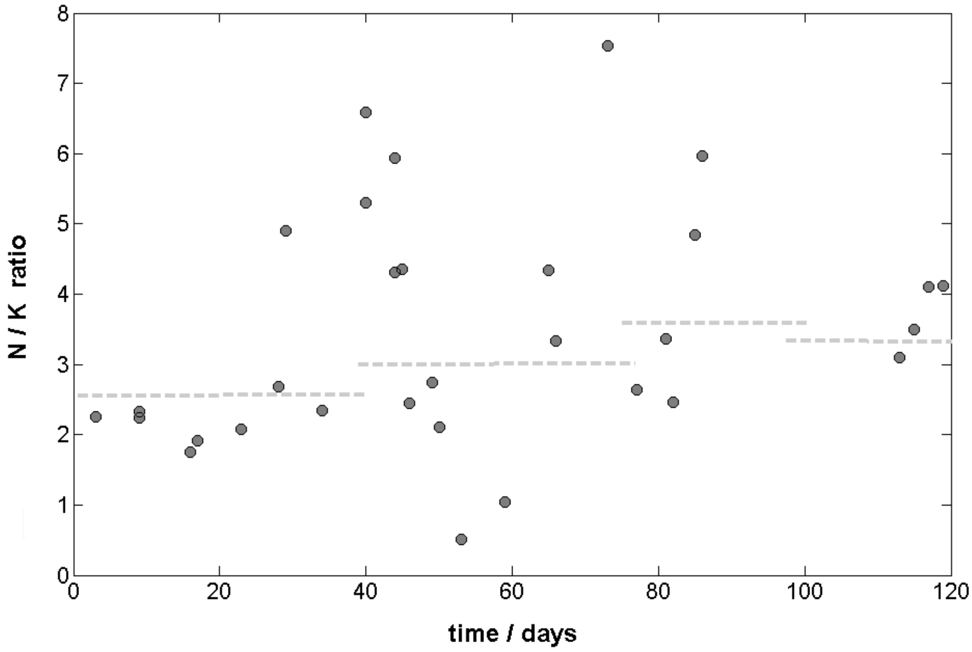


Figure 5. Evolution of the vertical hydroponic system (The Windowfarms Project, 2011) Right down corner, detail of tomatoes collected from the hydroponic system.