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Automatic Management of Nutrient Solution for Hydroponics-Construction of multi-ion stat-

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Abstract

In order to improve plant factories, an appropriate control system on fertilization is urgently required. An automatic management system to control nutrient concentration was constructed using a programmable logic controller (PLC) and ion selective electrodes (ISEs) of nitrate, phosphate, and potassium ion. The concentration of nutrient components in a culture solution was monitored using these ISEs. When the concentration of nutrient components diminished to the threshold set as an optimum condition (0.1-2.0 mM), an appropriate amount of a concentrated solution of each nutrient component was added to the culture solution using solenoid valves connected with the PLC. The present cultivation system was simply constructed without any computers and pumps. Three kinds of automatic control systems simultaneously worked and did not influence each other.
Introduction

With the continuous growth of world population, an increase in food production is required in recent years. The world population is estimated to become 9.5 billion by 2050, and a serious food problem has arisen with resource depletion, environmental deterioration and global economic crisis.\textsuperscript{1,2} It is necessary for modern agriculture to obtain a high yield with high quality environment reusable friendliness in future.

As a modern precision farming, hydroponics has developed rapidly in past decades. Gericke proposed the concept of hydroponics as a plant cultivation in liquid media.\textsuperscript{3} By comparison with conventional agriculture using soil, hydroponics possesses a lot of advantages. It makes possible to produce crops in the land that is not suitable for agriculture such as dryland, saline land, cold regions, and urban area because the influence of the condition of landform, geology, and weather is little.\textsuperscript{4} In addition, it is easy to reduce damages of insects, wild animals, and disease. Besides, the recycling of the nutrient solution causes water-saving.\textsuperscript{5} Some research groups have reported that the yield and quality of fruits and vegetables can be improved by optimizing culture conditions (temperature, humidity, quantity, wavelengths of light, and concentration management of nutrient salts).\textsuperscript{6-8}

On the other hand, hydroponics has some problems in practical use. Since costs of facility, equipment, and daily maintenance and electric charge are higher than those of the conventional agriculture, the product costs become 2-20 times higher than the usual products.\textsuperscript{9} In order to improve a plant more efficiently, the culture conditions such as water level, temperature, humidity, concentration of CO\textsubscript{2}, pH, nutrient condition, and the intensity of illumination must be kept at optimum\textsuperscript{7,8}. This optimization raises product costs furthermore.
In recent years, several research groups have reported automatic control systems for hydroponic cultivation. An automated pH- and nutrient-control system was constructed based on the conductometry. As for the monitoring of nutrient components using several ion sensors, there are several papers. Although pH was successfully controlled, the automatic control of three nutrient species (N, P, and K) without any computers and pumps has not been realized until now. The use of nutrient-component sensors of which stability and reproducibility are poor causes the computer-programmed calibration.

We have been constructed the robust phosphate sensor and nitrate sensor in the previous works. These sensors are suitable for the monitoring the hydroponic systems. In the present study, we designed an automatic nutrient control system for a hydroponic system comprised by a programmable logic controller (PLC), potentiometers, a data logger and ion-selective electrodes without any computers and pumps.

Experimental

Reagents and chemicals

A Co wire (1 mmφ, 99.99%), a silver wire (1 mmφ, 99.99%), and a platinum wire (1 mmφ, 99.99%) was purchased from Nilaco Co., Ltd. Sodium dihydrogenphosphate (NaH₂PO₄, Wako Co., Ltd., Japan), silver nitrate (AgNO₃, Wako Co., Ltd., Japan), sodium nitrate (NaNO₃, Wako Co., Ltd., Japan), tetraheptylammonium chloride (THACl, Sigma-Aldrich Co. LLC, Japan), valinomycin (AG Scientific, Inc., USA), sodium tetraphenylborate (NaTPhB, Kanto Chemical Co., Inc., Japan), potassium chloride (KCl,
Wako Co., Ltd., Japan), potassium sulfate (K$_2$SO$_4$, Wako Co., Ltd., Japan), polyvinyl chloride (PVC, Wako Co., Ltd., Japan), 2-nitrophenyl octylether (NPOE, Dojindo Molecular Technologies Inc., Japan), tetrahydrofuran (THF, Wako Co., Ltd., Japan), and liquid nutrient solution (HYPONeX undiluted solution, HYPONeX Co., Ltd., Japan) were purchased. All chemicals were reagent grade and were used without further purification.

**Apparatus**

Electrochemical measurements were conducted by use of an electrometer (HE-106A, Hokuto Denko Co., Ltd., Japan), a potentiostat/galvanostat (HA1010mM1A, Hokuto Denko Co., Ltd., Japan), a function generator (HB305, Hokuto Denko Co., Ltd., Japan), and an A/D converter (GL900, Graphtec Co., Ltd., Japan). The pH value of the solution was measured using a pH meter (PH-230SD, Lutron Co., Ltd., Taiwan). The automatic management system was formed by a PLC (RS Pro PLC, RS Co., Ltd., UK), an infusion set (NEOfeed, TOP Co., Ltd., Japan), and a power supply unit for illumination (ISC-201-2, CCS Co., Ltd, Japan). A hydroponics device (Green Farm Cube, UING Co., Ltd., Japan) was utilized to grow plants. An air pump (Silent β-60, Marukan Co., Ltd., Japan) was used to homogenize and to maintain the culture solution in air saturation.

**Fabrication of ion selective electrodes**

Nitrate ion sensor (NO$_3^-$-ISE), phosphate ion sensor (H$_2$PO$_4^-$-ISE), and potassium ion sensor (K$^+$-ISE) were fabricated according to methods of previous reports.$^{20-22}$ The composition of each electrode is entered in Figs. 1-3 as an inset. A water-volume controller was also prepared in accordance with a previous study.$^{22}$ When a Pt wire
electrode was entirely exposed on the water surface, the resistance between the Pt electrode and the reference electrode becomes infinity and the reading of the apparatus becomes out of the measuring range. In the case that the potential difference was gotten over a threshold, 2.5 mL of water was added to the culture solution by use of the water-supply system (operation time: 1 s).

**Operation check of the automatic supply system**

The performance of the automatic supply system as a multi-ion stat was checked using a pump (Unimor UPS-112E, Nitto Kohki, Co., Ltd., Thailand). Since plants slowly take nutrient components, a water was injected into a Pyrex glass vessel of which volume was 2 L by the pump at a flow speed of 100 mL min\(^{-1}\) and the fluid was stirred to homogeneously decline the nutrient concentration. At the same time, the nutrient solution was emitted from the cultivation vessel at the same flow speed. The nutrient solution was artificially diluted until the concentration reached the threshold of each ISE. The threshold for the \(\text{NO}_3^-\)-ISE was 0.62 V and that for \(\text{K}^+\)-ISE was set at \(-0.03\) V. When the potentials of the \(\text{NO}_3^-\) and \(\text{K}^+\)-ISEs arrived at 0.62 V and \(-0.03\) V, 7.5 mL of 0.01 M \(\text{NO}_3^-\) and 7.5 mL of 0.01 M \(\text{K}^+\) solutions, respectively, were added to the cultivation vessel. In this case, the \(\text{H}_2\text{PO}_4^-\)-ISE was not used because the response time of the \(\text{H}_2\text{PO}_4^-\)-ISE is 10-20 times longer than those of the \(\text{NO}_3^-\) and \(\text{K}^+\)-ISEs.

**Construction of the automatic nutrient solution concentration management system**

The system was improved based on a system reported previously.\(^2\) The volume of the culture vessel made of acrylic was about 300 mL, and 250 mL of the culture solution was set in the vessel. An air pump was used to keep the concentration of dissolved oxygen at a constant value because the phosphate ion sensor is influenced by the
concentration of dissolved oxygen. HYPONeX liquid fertilizer was diluted to 500 times by tap water and it was used as an initial cultivation solution. The additive solutions of NO$_3^-$, H$_2$PO$_4^-$, and K$^+$ were prepared by dissolving NaNO$_3$, NaH$_2$PO$_4$, and K$_2$SO$_4$, respectively, to become 0.01 M. The thresholds of the potentials of nitrate, phosphate and potassium ion selective electrodes were set at 0.62 V, −0.43 V, and −0.05 V, respectively, in the PLC system. These values corresponded to the concentration of these ions at 1 mM. After each potential reached the threshold, periods adding the nutrient solution (NaNO$_3$, NaH$_2$PO$_4$, or K$_2$SO$_4$) through the respective valve were set at 3 s, 1 s, and 3 s, respectively. The flow rate of each additive solution was about 2.5 mL s$^{-1}$. Since there were variations in stable measurement of ISE potentials, the interval between the additive operations of one component and the next operation was fixed to 10 s (NO$_3^-$ and K$^+$) or 10 min (H$_2$PO$_4^-$). In the present system, three bundles of Brassica rapa were used as plants for cultivation.

Results and Discussion

Responding characteristics of ISEs

The response characteristics of the NO$_3^-$-ISE, H$_2$PO$_4^-$-ISE, and K$^+$-ISE were checked, respectively. Fig. 1a presents the response characteristics of the NO$_3^-$-ISE in the concentration range from 10$^{-6}$ M to 10$^{-1}$ M, the slope was about 57 mV dec$^{-1}$. The response time of the NO$_3^-$-ISE was within 5 s and it can be stably used for more than 30 d continuously. The H$_2$PO$_4^-$-ISE responded to the concentration of H$_2$PO$_4^-$ from 10$^{-5}$ M to 10$^{-1}$ M, as shown in Fig. 1b. Fig. 1c indicates that the K$^+$-ISE responded to potassium chloride from 10$^{-6}$ M to 10$^{-1}$ M. Responding all the ion sensors’ performance was agreed with previous reports.$^{18-20}$ So they were applied to the present automatic control.
system, and the concentration range between. Since most of plants need $10^{-4}$ to $2 \times 10^{-3}$ M of these ions, the present automatic system seems to be useful for hydroponic cultivation.

Operating characteristics of a multi-ion stat

Since the responding time of the $\text{H}_2\text{PO}_4^-$-ISE is $10 - 20$ times longer than those of the $\text{NO}_3^-$-ISE and $\text{K}^+$-ISE, we investigated the responding characteristics of the $\text{NO}_3^-$-ISE and $\text{K}^+$-ISE as a multi-ion stat. In order to shorten a measuring time for the performance check of the automatic management system, we used the artificial dilution device. Fig. 2 indicates that the potential response of the $\text{NO}_3^-$-ISE. In this case, the threshold was set at 0.27 V. Thus, the actual potential of the $\text{NO}_3^-$-ISE was 0.26 - 0.27 V. On the other hand, the threshold of the potential of the $\text{K}^+$-ISE was fixed at $-0.03$ V. The actual potential was observed at $-0.2$ - $-0.3$ V. Arrows mean the additive points of each nutrient solution. It is proved that the concentration of the respective nutrient component is kept at almost constant and that the concentration of the respective nutrient component can be independently evaluated.

Practical use of an automatic control system

At first, some seeds of *Brassica rapa* were cultivated in a dish filled with a tap water until they germinated. They had been then moved to an incubator for about 5 days in the cultivated solution containing HYPONeX. The temperature was fixed at 28°C to avoid the influence of temperature dependence on all ISEs and to make plant growing well. The pH of the nutrient solution was about 6.0 throughout the measurement. Therefore, the $\text{H}_2\text{PO}_4^-$-ISE can be stably used. The other two ISEs are not affected by pH.
As shown in Fig. 3, arrows indicate the moment automatically added of the respective nutrient component. The right vertical axes in Figs. 3a-c were indicated using the concentration (M). Relative sharp fluctuations were observed. These fluctuations are caused by the addition of the respective nutrient solution. The decrease in the concentration means an intake of the objective nutrient component by the plant. As shown in Fig. 3a, the potential decreased with increasing the concentration of NO$_3^-$.

When the concentration of NO$_3^-$ decreased by the intake of NO$_3^-$, the potential increased up to 0.62 V. Then the concentrated aqueous solution was added into the vessel. The concentration of NO$_3^-$ (the right vertical axis) rapidly increased and the potential (the left vertical axis) suddenly dropped. As for Fig. 3b, the potential increased to about $-0.43$ V when the concentration of H$_2$PO$_4^{2-}$ decreased to about 1 mM. After the addition of the concentrated solution of H$_2$PO$_4^{2-}$, the potential sharply decreased and the concentration of H$_2$PO$_4^{2-}$ rapidly rose. In Fig. 3c, when the concentration of K$^+$ decreased to about 1 mM, the potential decreased to about $-0.05$ V. Owing to the addition the concentrated solution of K$^+$ into the hydroponic solution, the potential and the concentration of K$^+$ sharply increased. By comparing these figures, the potential fluctuations caused by addition of other nutrient solution were about several mV. Although the plant took K$^+$ at the early stage, it intakes H$_2$PO$_4^-$ at the latter stage. Thus nutrient component absorbed by plants is changed according to the growth period. So all the three kinds of automatic control systems can work simultaneously and do not affect each other. The results show that the system would be feasible for the on-site monitoring of the concentrations of NO$_3^-$, H$_2$PO$_4^-$, and K$^+$ in hydroponic solutions.

**Conclusions**

As a step toward realizing artificially intelligent plant factories, an automatic
management system for three main nutrient concentrations without any computers and pumps was constructed. Comparing with the conventional automatic systems, the present system was much more simple and inexpensive. The concentrations of the objective nutrient component were kept almost constant during plant cultivation. All the three kinds of automatic control systems can work simultaneously and do not have obvious influence each other. This makes precise control of the eco-friendly hydroponic system possible. In the future, other several nutrient components in the hydroponic nutrient solution (Ca$^{2+}$, Mg$^{2+}$, and NH$_4^+$) will be controlled simultaneously. Since the sodium-potassium balance is important for the plant cultivation, the control system of Na$^+$ concentration using a Na$^+$-ISE seems to be especially required. In addition, pH, temperature, humidity, and illumination should be added to the automatic management system.

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Figure Captions

Fig. 1  Potential responses of nitrate ion sensor in NaNO₃ solution (a), phosphate ion sensor in NaH₂PO₄ solution at pH 4.0 (b), and potassium ion sensor in KCl solution (c).

Fig. 2  Operation check of multi-ion stat. a: Potential of the NO₃⁻-ISE; b: Potential of the K⁺-ISE. Arrows mean the additive points of each nutrient solution.

Fig. 3  Practical tests of the automatic management system for NO₃⁻ (a), H₂PO₄⁻ (b), ad K⁺ (c). a: Potential of the respective ISE; b: Concentration of the respective ion in the cell system. Arrows mean the additive points of each nutrient solution.
Fig. 1a

$E / V$ vs. Ag$_2$AgCl $|$ sat. KCl

$\log(c / M)$

$E / V$ vs. Ag$_2$AgCl $|$ sat. KCl

$\log(c / M)$

Ag $|$ 10 mM AgNO$_3$, 0.5 M Mg(NO$_3$)$_2$ $|$ THA$^+$NO$_3^-$, NPOE (PVC) $|$ sample
Fig. 1b
Ag | 0.1 M KCl | K⁺$^{\text{TPhB}^-}$, Valinomycin, NPOE (PVC) | sample

$E / V$ vs. Ag/AgCl/sat. KCl

$\log c_K / M$

Fig. 1c
Fig. 2
Fig. 3a
Fig. 3b
Fig. 3c

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