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Advancements in Instrumentation

Construction of an Automatic Nutrient Solution Management System for Hydroponics-Adjustment of the K⁺-Concentration and Volume of Water-

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Abstract

An automatic management system for nutrient solutions was constructed using a programmable logic controller (PLC) and a K⁺-ion selective electrode (K⁺-ISE). The concentration of K⁺ was monitored by the K⁺-ISE. When the concentration of K⁺ fell to the threshold limit, an appropriate amount of a concentrated K⁺ solution was added to the hydroponic solution. The volume was also maintained at a constant level by addition of water. This system can be constructed simply and inexpensively without any computers and pumps.

Keywords Hydroponics, K⁺-ISE, Nutrient solution, Automatic management, Ion stat.
Introduction

An increase in food production is necessary owing to the rapid global population growth in recent years. However, there are difficulties associated with the rapid increase in food production owing to the scarcity of land suitable for agriculture.\textsuperscript{1,2} In addition, it is hard to supply food at a constant rate owing to seasonal variations in weather and damage caused by blight, insects, and environmental conditions.\textsuperscript{3} Gericke first suggested hydroponics as a means of soil-free agricultural crop production by the use of nutrient solutions.\textsuperscript{4} Since then, many people have become interested in the cultivation of fresh vegetables and flowers without soil. Hydroponics has become significantly more widespread in commercial horticulture since Cooper invented the nutrient film technique (NFT), which exploits a flow system comprising a thin nutrient solution layer around the roots of the crop.\textsuperscript{5-7} In comparison with conventional soil-based agriculture, hydroponics presents many advantages. For instance, hydroponics does not depend on the features of land nor weather conditions. Furthermore, insect damage and the influence of disease seem to be lessened. Furthermore, it is easy to control the irradiation (period and strength) and temperature during cultivation. Since the nutrients can be reused, the culture media can be utilized without waste.\textsuperscript{8} Several research groups have reported that the yields and quality of fruits and vegetables can be improved by optimizing culture conditions.\textsuperscript{9-11}

Since hydroponic products are usually more expensive than those grown by conventional means owing to the higher running costs, the construction of more efficient systems is demanded. Accordingly, the optimum conditions for the growth of plants have been established.\textsuperscript{12} Although changes in the concentrations of nutrient components can be observed by methods such as spectroscopic, chromatographic, and electrochemical analysis, these are not suitable for real-time monitoring because they require pretreatments such as sampling and filtration.\textsuperscript{13,14}
It has been established that the electrical conductivity of a hydroponic nutrient solution generally depends on the total concentration of the major nutrient components.\textsuperscript{15,16} As for the monitoring of nutrient components using several ion sensors, there are some papers.\textsuperscript{17-22} Although the ion sensors are powerful tools to monitor the concentration of the objective components, it is generally known that the accurate monitoring of the concentration of phosphate ions and nitrate by use of the ion sensors is difficult. In recent years, several researchers have reported automatic control systems for nutrient components and automated pH and nutrient control systems that rely on conductometry have been developed.\textsuperscript{23-25} However, it is difficult to control of respective nutrient components by conductometry. Although pH can be successfully controlled to a certain level using a pH sensor system,\textsuperscript{26} the automatic control of various nutrient species (N, P, and K) without any computers and pumps has not been realized until now.

In the present study, based on the analytical chemical aspect of ion sensors which were used to measure the potential difference, we designed an automatic nutrient control system for a hydroponic system comprising a programmable logic controller (PLC) and a K\textsuperscript{+}-ion-selective electrode (K\textsuperscript{+}-ISE) without any computers and pumps. Here, K\textsuperscript{+}-ISE was utilized to detect the concentration of K\textsuperscript{+} as a typical nutrient. In addition, the volume of the nutrient solution is automatically maintained by a water supply system.

**Experimental**

**Reagents and chemicals**

Valinomycin (AG Scientific, Inc., USA), sodium tetraphenylborate (NaTPhB, Kanto Chemical Co., Inc., Japan), potassium chloride (KCl, Wako Co., Ltd., Japan), polyvinyl chloride (PVC, Wako Co., Ltd., Japan), 2-nitrophenyl octylether (NPOE, Dojindo Molecular
Technologies Inc., Japan), and tetrahydrofuran (THF, Wako Co., Ltd., Japan) were purchased. All chemicals were reagent grade and were used without further purification.

**Apparatus**

Electrochemical measurements were conducted using an HE-106A electrometer (Hokuto Denko Co., Ltd., Japan), an HA1010mM1A potentiostat/galvanostat (Hokuto Denko Co., Ltd., Japan), an HB305 function generator (Hokuto Denko Co., Ltd., Japan), and a GL900 A/D converter (Graphtec Co., Ltd., Japan). The pH value of the solution was measured using a PH-230SD pH meter (Lutron Co., Ltd., Taiwan). The automatic management system was constructed using an 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 used to grow vegetable seedlings. In order to check the mechanical function of the automatic nutrient control system, a pump (Unimor UPS-112E, Nitto Kohki, Co., Ltd., Thailand) was used to draw the culture solution.

**Fabrication of K⁺-ion selective electrodes**

Potassium tetraphenylborate (KTPhB) was synthesized by the following steps: First, 10 mL of 0.1 M NaTPhB was mixed with an aqueous solution containing excess KCl, and the mixture was stirred for 2 h. The precipitated KTPhB was isolated by filtration and washed with distilled water. The precipitate was dried at 50 °C under vacuum.

A liquid-membrane type K⁺-ISE was prepared as follows. A responsive membrane was prepared by drying a THF solution (1.5 mL) containing 0.04 g of valinomycin, 0.004 g of KTPhB, 0.152 g of PVC, and 0.304 g of o-NPOE. The end of a pipette tip (1 mL) was cut and the cross-sectional area was about 0.1 cm². Then, the top was soaked in the THF solution. After
vaporization, the PVC membrane was prepared at the end of the pipette tip. Then, 1.5 mL of 0.1 M KCl was placed into the pipette tip and an Ag|AgCl electrode was inserted. The pipette tip was then covered with a rubber stopper. The structure and appearance of the K⁺-ISE are shown in Fig. S1. A more detailed construction method is given in the SI. Fig. S2 shows the construction of the measurement system of the K⁺-ISE.

**Characteristics of the K⁺-ISE**

All electrometrical measurements were carried out with a two-electrode system using a reference electrode (Ag|AgCl|sat. KCl) and K⁺-ISEs (3 sets). The selectivity coefficient \( (k_{ij})_{pot} \) of the ion \( j \) was evaluated against the coexisting ion \( j \) based on the mixed-solution method. The potential of the K⁺-ISE is obtained from Eq. 1.

\[
E_{ISE} = E_i^o + \frac{RT}{z_i F} \ln \left( a_i + \sum_{j \neq i} k_{ij}^{pot} a_j^{z_j} \right),
\]

where \( E_i^o \) is a constant that depends on the property of the ion \( i \), \( z_i \) and \( z_j \) are the charge numbers of the ions \( i \) and \( j \), \( F \) is the Faraday constant, \( a_i \) and \( a_j \) are the activities of the ions \( i \) and \( j \), \( R \) is the gas constant, and \( T \) is the temperature. As for \( E_{ISE} \), the interpretation based on the ion transfer voltammetry at the interface between the aqueous and the NPOE solutions is noted using Fig. S3.

**Design of the automatic K⁺ concentration management system**

As shown in Fig. S4, the automatic management system comprises four units. In the cultivation unit, green plants are cultured in a container filled with a hydroponic solution. A K⁺-ISE, a reference electrode, a water volume sensor, and a temperature sensor are placed in the container. The hot-plate stirrer fitted with a thermostat is employed to homogenize the solution. An LED illumination device was set up to allow the growing of green plants.
In the monitoring unit, the potential difference between the K⁺-ISE and the reference electrode was recorded in a computer using a potentiometer and a logger. The temperature sensor was directly connected to the logger.

In the control unit, a programmable logic controller (PLC) is connected to the logger and the computer is used just as a recorder. Figure S5 shows PLC software interfaces of the nutrient supply system and the volume control system. When the potential of the K⁺-ISE drops beneath a certain level, an alarm from the logger is triggered. The signal reaches the PLC and the valve on the tank of the aqueous solution containing 0.5 M KCl is opened, delivering 1 mL of the solution to the system. Furthermore, a water level sensor made by a Pt wire was used to keep the volume of the nutrient solution constant. When the electric connection between the Pt wire and the reference electrode is broken due to the lowering of the water level, an alarm is triggered, similarly to the K⁺-ISE system. When this alarm is activated, 5 mL of water is added to the solution. In the present case, the computer was used to record the data. The actual operation using the present management system needs a logger and a PLC only.

In the supplying unit, the programmable logic controller was connected to the valve to supply 1 mL of the K⁺ solution, and the other valve was opened just after the signal was received. Similarly, 5 mL of water was added in the case of receiving the alarm due to the decrease of the volume of the nutrient solution.

Thus, the concentration of K⁺ in the nutrient solution is monitored during cultivation, and the volume of the nutrient solution is kept at an almost constant level.

Operation checking for the automatic supply system

Only to prove that the water supply system works according to the break in the electric connection between the nutrient solution and a platinum wire electrode, a pump (Unimor UPS-112E, Nitto Kohki, Co., Ltd., Thailand) was used. For performance checking, water was
injected into the cultivation device by the pump at a flow speed of 100 mL min\(^{-1}\). At the same time, the nutrient solution was flushed from the cultivation device at the same flow speed. The nutrient solution was artificially diluted until the concentration falls below the threshold (0.001 M), at which point 1 mL of 0.55 M K\(^+\) nutrient solution is added. In this way, the K\(^+\)-concentration of the nutrient solution was kept at a largely constant value. This time, 0.55 M K\(^+\) was added to easily recognize the control system. Therefore, it is appropriate to add the diluted solution (e.g. 0.01 M) to the culture solution.

Practical plant cultivation using the control system

*Brassica rapa* was cultivated in a commercial hydroponic nutrient solution for 20 days. The water level was controlled by the water volume sensor. The threshold of the potential was set at \(-0.028\) mV, which corresponded to 0.005 M. The concentration of the additive KCl solution was 0.5 M, and the volume of every addition was 1 mL.

Results and Discussion

Response characteristics of the K\(^+\)-ISE

The K\(^+\)-ISE shows a linear response to K\(^+\) in the concentration range \(10^{-6}–10^{-1}\) M with a slope of \(-59.7\) mV dec\(^{-1}\), as shown in Fig. 1. The practical response time was recorded by changing the concentration of K\(^+\) from \(1 \times 10^{-6}\) M to 1 M, as shown in the inset of Fig. 1. The potential reaches a constant value within 5 s of the addition of KCl into the cell system. The fluctuation of the potential at the same concentration is within ±2 mV over 24 h. The potential response of the K\(^+\)-selective electrode is very stable, as previously reported by several research groups.\(^{27,28}\) The selectivity coefficient \((k_{ij}^{pot})\) is usually given by Eq. 1. As shown in Table 1, the K\(^+\)-ISE exhibits excellent selectivity in the presence of other common cations. Thus, it was
successfully utilized as a potassium sensor in the present automatic management system.

**Monitoring of the K⁺ concentration during the plant cultivation and volume control of the nutrient solution**

Figure 2(a) shows the time-course of the potential change for the K⁺-ISE during plant cultivation. Arrows indicate the points at which water was automatically supplied by the water volume control system. Thus, the water volume is maintained around a certain level throughout plant cultivation. In addition, it was confirmed that the K⁺ is exhausted by *Brassica rapa* after two weeks.

As shown in Fig. 2(b), the potential value is maintained in the region between −0.040 and 0.005 V, and the fluctuation is within ±3 mV. It can be verified that the automatic control system maintains the concentration of the nutrient component within the 0.005–0.02 M range. If the amount of KCl added is decreased, this concentration region can be narrowed. In the present case, these conditions were selected to more clearly assess the management of nutrient control.

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

By combining the concentrated KCl solution supply system and the water supply system, an automatic nutrient management system was constructed. As indicated in Fig. 3, the concentration of K⁺ is controlled within a fixed value (0.0055 ± 0.0010 M). If the amount of KCl added is decreased, the concentration of K⁺ can be controlled around the threshold value more precisely.

**Conclusion**

As a step toward realizing artificially intelligent plant factories, an automatic management system for water volume and nutrient concentration without computer-control or pumps was
constructed. Comparing with the conventional automatic systems, the present system was much more simple and inexpensive. This is the first report of an automatic management system for both the volume of the nutrient solution and its concentration. Although the present equipment is very simple, the volume of the nutrient solution and the concentration of the objective nutrient component (K\textsuperscript{+}) were kept almost constant during plant cultivation. This makes precise control of the eco-friendly hydroponic system possible. In the future, several nutrient components in the hydroponic nutrient solution (potassium, phosphate, and nitrite) will be controlled simultaneously. In addition, pH, temperature, humidity, and illumination should be added to the automatic management system.

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**Supporting Information** (optional)

As for detailed construction methods, explanation is presented in the supporting information. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

**References**

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Graphical Index
Table 1 Selectivity coefficients of common cations

<table>
<thead>
<tr>
<th>Anion</th>
<th>log ($k_{ij}^{pot}$)</th>
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<tbody>
<tr>
<td>Na$^+$</td>
<td>$-5.5 \pm 0.2$</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>$-4.0 \pm 0.3$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>$-5.0 \pm 0.3$</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>$-3.1 \pm 0.2$</td>
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Figure captions

Fig. 1. Calibration plot of the K⁺-ISE, and response time curve of the K⁺-ISE (Inset).

Fig. 2. Monitoring of the concentration of K⁺ during the plant cultivation (a) and potential change of the K⁺-ISE under the simulation condition (b); Arrows indicate the points at which water (a) or 0.5 M KCl (b) is supplied. 1: concentration of K⁺; 2: potential of the K⁺-ISE.

Fig. 3. Practical testing of the automatic management system. 1: Concentration of K⁺ in the cell system; 2: Potential of the K⁺-ISE.
Fig. 1. K. Xu, et al.
Fig. 2. K. Xu, et al.
Fig. 3. K. Xu, et al.