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〈Research Article〉

Suggestion for deep learning approach to solve the interference effect of ammonium ion on potassium ion-selective electrode

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Abstract

An ammonium ion with a size and charge similar to that of potassium can bind to valinomycin, which is used as an ion carrier for potassium, and cause a meaningful interference effect on the detection of potassium ions. Currently, there are few ion sensors that correct the interference effect of ammonium ions, and there are few studies that specifically suggest the mechanism of the interference effect. By fabricating a SPCE-based potassium ion-selective electrode, the electromotive force was measured in the concentration range of potassium in the nutrient solution, and the linear range was measured to be 10^{-5} to 10^{-2} M, and the detection limit was $10^{-5.19}$ M. And the interference phenomenon of the potassium sensor was investigated in the concentration range of ammonium ions present in the nutrient solution. Therefore, a data-based analysis strategy using deep learning was presented as a method to minimize the interference effect.

Keywords : K ion detection; ion-selective electrode; NH_4^+ interference behavior; K^+ sensor; deep learning.

1. Introduction

From precision agriculture, environmental monitoring, industrial sites, to point-of-care diagnostic bio-signal analysis, there has been a continuous have required for powerful analytical tools for prompt ion measurement. Recently, to advances in nanomaterials science and technology, solid-state contact ion-selective electrodes (SC-ISE) with ultra-compact structures that enable in-situ measurements have shown great potential for portable ion detection [1]. This portable ion sensor technology is essential for crop growth monitoring in precision agriculture, which is rapidly growing due to the recent development of IoT technology.

Due to climate change, the aging of the agricultural population, and the global food shortage, precision agricultural technology that can maximize yield with minimal input is rapidly emerging [2]. In the hydroponics system, which accounts for the largest proportion of them, the fertilizer monitoring is important because it is directly related to the input cost and the yield. Since the demand for these ions

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differs depending on the type of plant and the growth stage, optimal nutrient input through their monitoring can effectively reduce costs and environmental pollution caused by waste nutrient solution discharge. Moreover, the real-time monitoring technology of ions in the waste nutrient solution is essential for the zero emission system for reuse of the nutrient solution [3].

As a method for analyzing the nutrient composition of crops, there is a traditional analytical method such as inductively coupled plasma (ICP) or ion chromatography (IC) analysis. However, they have disadvantages in that expensive analysis equipment, complex pre-processing, and professional operators are required. In addition, these traditional analysis methods are difficult to miniaturize, which limits real-time monitoring. On the other hand, the electrochemical measurement method has advantages of simple operation, low cost, and miniaturization. In particular, among the electrochemical measurement methods, the ion-selective electrode (ISE) is widely used in various fields such as environment, pharmaceuticals, the water and food because it can be measured in real time in the field without pretreatment [4]. The conventional ion-selective membrane-based ion-selective electrode is a liquid-contact type ISE with an internal filling solution in an electrode designed as a glass membrane. Liquid contact type ISE shows relatively stable potential in the research environment and has already been commercialized. However, it is difficult to maintain and miniaturization is difficult because of the presence of liquid inside. On the other hand, solid contact type ISE has no internal liquid, so it is easy to miniaturize and simple to manufacture [5]. ISE is manufactured by attaching an ion-selective membrane prepared by mixing an ionophore that selectively reacts with a specific ion with a polymer to an electrode. The fabricated ISE can measure the ion concentration by using the potential difference generated by the binding of the target ion with the ionophore in the selective membrane [6].

The potassium ion-selective electrode shows high sensitivity to K ions, but is affected by interference by other ions in the nutrient solution. Valinomycin is a natural peptidic macrocycle and is a key element in the design of ionophores for ion-selective electrodes because of its excellent cation binding and transport ability across hydrophobic environments. Metal cations are encapsulated by binding to a C3 symmetric backbone conformation with a network of ring structures formed by C=O···HN bonds [7]. In particular, Valinomycin is a representative ionophore of K+ and shows the best performance for selective detection of K^+. However, compared to other ions, NH_4^+ may interfere with K^+ detection because the charge-to-radius ratio of K^+ (ionic radii of K^+ is 0.133 nm) and NH_4^+ (ionic radii of NH_4^+ is 0.143 nm) is similar. Interestingly, the ammonium ion binds with a moderate distortion of the C3 configuration adopted in the complex of valinomycin and the metal cation, unlike the ionic bonding method of potassium [7]. The concentration range of potassium in the nutrient solution is 100 ~ 450 mg L^{-1}, and the error in the concentration of potassium due to interfering ions is mainly caused by NH_4^+ ions. Currently, there are few ion sensors that correct the interference effect of ammonium ions, and there are few studies that specifically suggest the mechanism of the interference effect. Therefore, deep insight is required to solve this issue.

An artificial neural network, one of the artificial intelligence technologies, is a data analysis algorithm similar to the structure of the human brain. Deep learning is the application of big data technology to artificial neural networks, and this technology is being applied to analysis methods that predict the future or predict results due to the accumulation of a large amount of data. Analysis of the interference behavior of ammonium ions in potassium detection using artificial intelligence deep learning is expected to yield optimal values for interference behavior.

In this study, a screen printed carbon electrode (SPCE) based a potassium sensor was developed, the linear range and limit of detection (LOD) of the potassium ion-selective electrode were measured by an open circuit potential (OCP) method, and the effect of K^+ monitoring due to the interference effect of ammonium ions was evaluated. In addition, the function and algorithm that can remove the interference effect of multiple ions were investigated using an artificial neural network that can consider the nonlinear process of different ions and a multiple regression model that can understand the correlation between two or more independent variables. Based on these results, we proposed a method for improving the ion-selective sensing performance of ion-selective electrodes in the future.

2. Experimental

2.1. Regents and instruments

Valinomycin, bis (2-ethylhexyl) sebacate (DOS), potassium tetrakis (4-chlorophenyl) borate (KTpClPB), Poly (vinyl chloride) (PVC), tetrahydrofuran (THF), potassium chloride (KCl), ammonium chloride (NH_4Cl), used in potassium ion-selective membrane (ISM) fabrication and performance evaluation of ion-selective electrodes were purchased from Sigma Aldrich with high purity reagents and were used without purification. For the preparation of all standard solutions, ultrapure tertiary distilled water prepared using a Milli-Q water purifying system (18 MΩ cm) was used. A screen printed carbon electrode (SPCE) used as an ion-selective electrode was manufactured by BTI (Korea). Electromotive force (EMF) measurements for performance evaluation of ion-selective electrodes were performed using a Gamry instrument (USA).

2.2. Fabrication of K ion-selective electrode

Figure 1 shows the overall schematic of the ion-selective electrode based SPCE. And the inset image is an SEM image showing the side view of the electrode. For

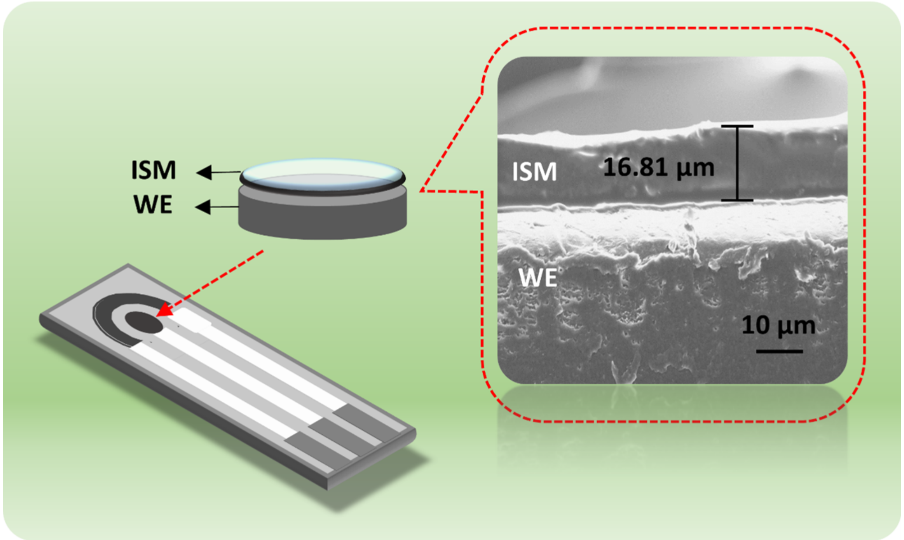


Fig. 1. Schematic illustration of a SPCE-based a potassium sensor

Table 1. Compositions of K ion-selective membranes

	K^+ ISM_Composition (wt. %)	
Ionophore	Valinomycin	2
Plasticizer	DOS	64.7
Additive	KTpClPB	0.5
Matrix	PVC	32.8

potassium ion-selective membrane cocktail, 100 mg of ionophore, plasticizer, additive, and PVC are weighed in a constant mass ratio as shown in Table 1. Their chemical structures are shown in Figure 2, 100 mg of the mixture prepared above was mixed with THF (1 mL) as a solvent, and ultrasonicated for 30 minutes to prepare a homogeneous cocktail [8]. And drop-casting 1 μL to the working electrode and drying in air for 2 h. In the SPCE electrode, the working electrode was composed of carbon (dia. 2 mm) and the reference electrode was composed of Ag, and 0.1M $FeCl_3$ was dropped on the Ag layer and reacted for 10 minutes to prepare an Ag/AgCl layer. Drop-casting 2 μL of the homogeneously mixed cocktail on the working electrode of SPCE and dry it in the air for 24 h.

3. Results and discussion

As shown in Table 2, considering the K ion concentration in the nutrient solution for hydroponics, the potassium concentration was about 156 mg L^{-1} (4×10^{-3} M) to 312 mg L^{-1} (8×10^{-3} M), therefore the electromotive force was measured in the concentration range of 0.0039 mg L^{-1} (10^{-7} M) to 390 mg L^{-1} (10^{-2} M). As shown in Figure 3, it can be seen that the electromotive force value increases as the concentration of potassium ions in the potassium ion-selective electrode increases (black line). The sensitivity to the potassium ion concentration change was 61.04 mV/decade. This value was measured similarly to the value of 59.12 mV/decade, which is the theoretical Nernstian slope at room temperature [9]. The same concentration

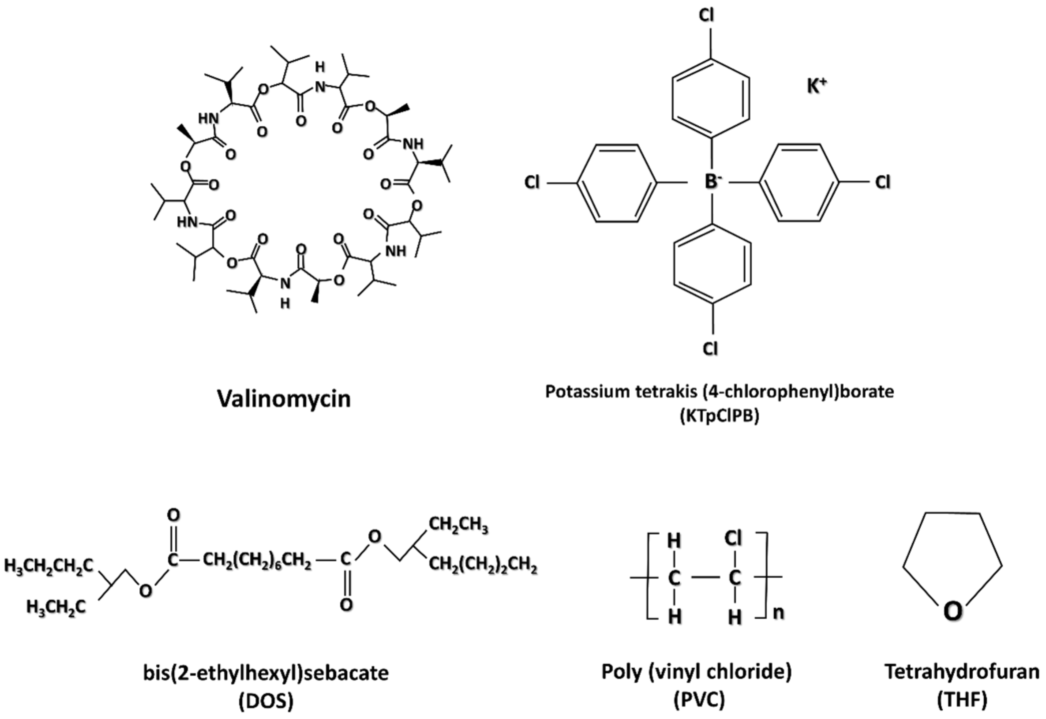


Fig. 2. Chemical structure of K^+ selective membrane composition material

Table 2. Concentration table of commonly used Yamazaki lettuce and Enshi strawberry nutrient solutions [3].

Element	Yamazaki Conc. (mg L^{-1})	Enshi Conc. (mg L^{-1})
Nitrogen	92.2	245.8
Potassium	156.2	312.5
Phosphorus	15.4	41.8
Calcium	40.1	161.3
Magnesium	12.1	49.3
Sulfur	16.1	65.4
Iron	2.4	3.8
Sodium	1.0	1.6
Boron	2.8	0.52
Manganese	0.14	0.46
Zinc	0.02	0.05
Copper	0.01	0.012
Molybdenum	0.0052	0.008

range was repeated 5 times, and the coefficient of determination (R^2) > 0.99 showed a highly linear regression equation. However, in the potassium sensor, the electromotive force was changed according to the concentration of ammonium ions (red line). The sensitivity to ammonium ion concentration change was 29.19mV/decade, which was 52.21% lower than that of potassium.

The NH_4^+ interference to the K^+ sensor is determined by the selection coefficient. A low value of the selection coefficient indicates a strong selectivity of the electrode for the target ion. The selectivity coefficient for the interference ions$\left(K_{A,B}^{pot}\right)$ were calculated using the Fixed Interference Method (FIM) with Eq. (1) [8].

$$LogK_{A,B}^{pot} = Log\frac{a_A}{a_B^{Z_A/Z_B}} \qquad \text{(Eq. 1)}$$

where α_A is the primary ion activity obtained at the intersection of the extrapolated portion of the linear part of the response curve, and α_B is the interfering ion activity in the solution background. Z_A and Z_B are the charges of the two targeted ions.

Potassium and ammonium ions activities were calculated at the intersection of the linear part shown in Figure 3 with the extrapolated part. The selectivity coefficient of the potassium sensor was

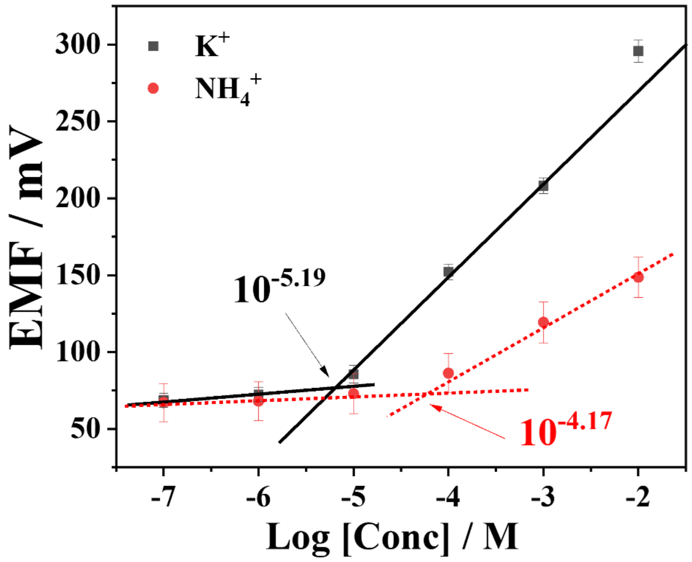
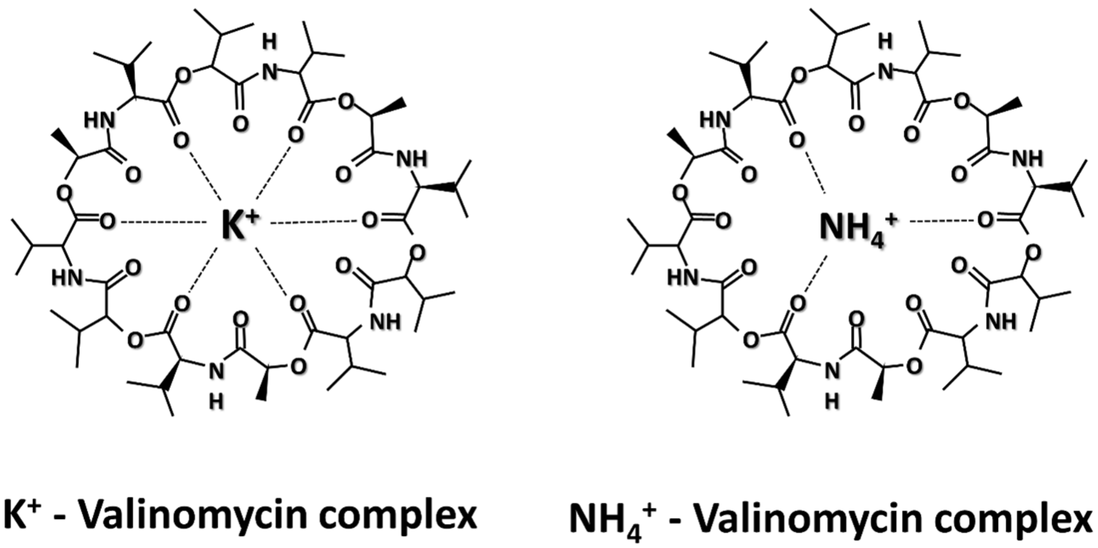


Fig. 3. Calibration curve of graphene-based K^+-ISEs, measured with a voltmeter; K^+ solution (black) and NH_4^+ solution (red).



K$^+$ - Valinomycin complex **NH$_4^+$ - Valinomycin complex**

Fig 4. The chemical structure of K$^+$-Valinomycin complex and NH$_4^+$-Valinomycin complex

determined to be -1.02 under ammonium interference. Moreover, as shown in Figure 4, Valinomycin has a macrocyclic structure, and through internal interactions, potassium ions in the valinomycin-potassium complex form 6 bonds with the carbonyl group, and ammonium ions in the valinomycin-ammonium complex form 3 bonds. These results can be expected to meaningful interfere with ammonium in the potassium sensor.

In general, since 10 % of the nitrogen component in the nutrient solution is supplied in the form of ammonium, the interference effect of potassium monitoring was investigated within the ammonium ion concentration of 5 to 30 mg L^{-1} in relation to the nitrogen concentration in Table 2. The change in the electromotive force with respect to the concentration of potassium in a solution in which 1.8 mg L^{-1} (10^{-4} M), 18 mg L^{-1} (10^{-3} M), and 180 mg L^{-1} (10^{-2} M) of ammonium ions were present was measured, respectively. As can be seen in Figure 5, it was confirmed that the higher the concentration of ammonium ions, the higher the electromotive force according to the potassium concentration and the lower

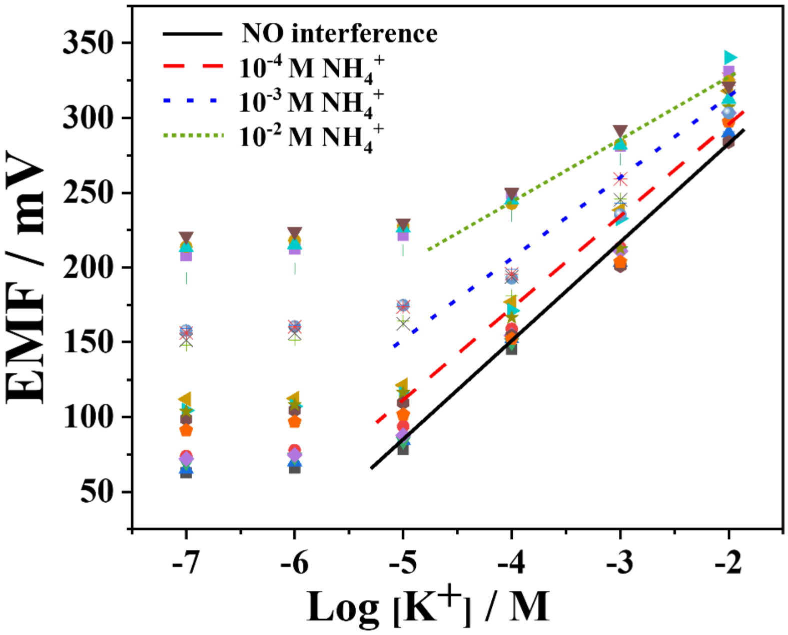


Fig. 5. The EMF (mV) response of the K$^+$-ISE sensor at six concentrations of K$^+$ (10^{-7} - 10^{-2} M) with three concentrations of NH$_4^+$ (10^{-4}, 10^{-3}, 10^{-2} M).

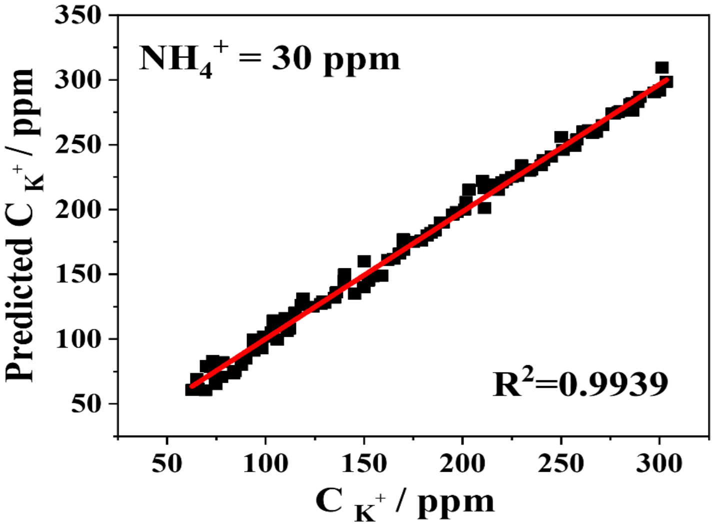


Fig. 6. K^+ concentration prediction in containing 30 ppm NH_4^+ using neural network model.

the slope. Each experiment was repeated 10 times, and showed a highly linear regression equation with a coefficient of determination (R^2) > 0.99. These results suggest that ammonium ions have a significant interfering effect on the monitoring of potassium ions. And investigation of their tendency can be utilized to derive the results of optimal values using artificial intelligence deep learning to remove the interference effect of ammonium ions later. Therefore, in order to investigate the possibility of deriving an optimal value using deep learning, a data input unit and a data learning unit were built, and the correlation between the ion concentration and the potential value was investigated by repeating learning 20,000 times. An open source software library was used for machine learning deep learning, and the stochastic gradient descent (SGD) algorithm method that finds the optimal value for each step was applied. As shown in Figure 6, the optimum value of the electromotive force value according to the potassium ion concentration under constant ammonium ion (30 ppm) interference was analyzed. After deep learning, an electromotive force value similar to the result of the potential difference without interference effect was derived in a potassium solution containing ammonium (R^2=0.9939). These preliminary research results suggest new possibilities for improving the selectivity of ion-selective electrodes using artificial intelligence deep learning.

4. Conclusion

In this study, a SPCE-based a potassium sensor was developed, the linear range and LOD of the potassium ion-selective electrode were measured by an OCP method, and the correlation of K^+ monitoring due to the interference effect of NH_4^+ was investigated. Ammonium ions showed an interference effect on selective detection of potassium ions, and a method using artificial intelligence deep learning was proposed as an alternative to solve this problem. The accumulated data was repeated 20,000 times, and the correlation between the effect of ammonium ion and the optimal value was analyzed to prediction a value in which the interference effect was removed. These results are expected to contribute greatly to the advancement of the ion-selective electrode as an optimal method for improving the selectivity of sensing ions in the ion-selective electrode. However, in this study, only results related to the monitoring of potassium at constant ammonium concentrations were investigated. There are various ions in the actual nutrient solution, and the concentration of ammonium ions also varies. Therefore, further research on the accumulated data on the interference effect according to the concentration of ammonium ions and other ions in the nutrient solution is needed in the future.

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