Pollution Control of Nitrate-selective Membrane by the Inner Solution and On-site Monitoring of Nitrate Concentration in Soil

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A liquid-membrane type nitrate-selective electrode was improved to lower the influence of contaminants by modifying its inner electrode system from Ag|AgCl|Cl⁻ to Ag|Ag⁺. The NO₃⁻-selective electrode displayed a linear response to the concentration of NO₃⁻ with a Nernstian slope of -53 ± 1 mV decade⁻¹, in the concentration region between 10⁻⁵ and 2 mol dm⁻³ (M). The NO₃⁻ detection limit was about 10⁻⁵ M. The electrochemical response of this electrode was stable for more than 30 days. The deterioration in responding characteristics due to the coexistence of Cl⁻ was suppressed by use of the Ag|Ag⁺ redox couple in the absence of Cl⁻ inside the NO₃⁻-selective electrode.

Keywords Nitrate, tetraheptylammonium ion, ion-selective electrode, monitoring, soil

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Introduction

Fertilizers containing various elements are required for the cultivation of crops.¹⁻³ It is well known that 17 kinds of elements are essential for the growth of plants.⁴⁻⁶ Especially, the three elements of nitrogen, phosphorus and potassium are very significant from the viewpoint of the yield of crops, and they are called the three major elements of fertilizer. In agriculture, fertilization has been conducted to improve the yield of crops, but excessive fertilization causes adverse effects on the environment. Since it has become a social problem all over the world, it is necessary to control of fertilization from the standpoint of environmental protection.

Nitrogen is the most indispensable element in the growth period of plants and exists in the natural world as inorganic compounds, such as nitrate (NO₃⁻), nitrite (NO₂⁻), and ammonium ions (NH₄⁺), or organic compounds, such as amino acids, peptides, and proteins.⁷ Because plants mainly absorb NO₃⁻ and NH₄⁺, chemical fertilizers containing these ions are often used. It is realized that NO₃⁻ tends to escape from farmlands due to the negative charge of soil particles.^{8,9} Since excess NO₃⁻ is usually fertilized, eutrophication of the groundwater and water of rivers, lakes, marshes, and seas is a social problem worldwide. It is well known that methemoglobinemia, which is a neonatal disease, comes from NO₃⁻ in food and drink.¹⁰ Since the eutrophication and damage was caused by excessive fertilization of NO₃⁻ and/or NH₄⁺, improvement of monitoring methods to measure the concentration of NO₃⁻ in environmental water is required. In addition, the construction of a monitoring device of NO₃⁻ will help in the development of a hydroponic culture system used at plant factories furthermore.

Chromatography,¹¹ spectroscopy,¹² colorimetry,¹³ electroconductometry,¹⁴ and electrochemical measurements using an ion-selective electrode (ISE)¹⁵⁻¹⁸ and others are known as detection methods of nitrate. As for chromatography and spectroscopy, they need large-scale apparatus and pretreatment, such as sampling, filtration, and addition of a certain type of reagent. Accordingly, they are not suitable for *in-situ* analysis and/or monitoring for the concentration of NO₃⁻. Although an electroconductometer is inexpensive, portable, and easy to use, it is difficult to evaluate the concentration of NO₃⁻ exactly because of the coexistence of various ions in sample solutions. Electrochemical devices using ISE are inexpensive and portable, and do not require pretreatment. Although NO₃⁻-ISEs having good responding characteristics have been developed,¹⁵⁻¹⁷ it is difficult to apply them for practical use because of the change in function over time.

In the present study, a NO₃⁻-ISE using a PVC membrane immersed in an NPOE solution containing tetraheptylammonium (THA⁺) nitrate was improved. In the case of monitoring the environmental water (or soil), NO₃⁻ of the selective membrane is gradually replaced by coexisting anions (especially Cl⁻) around the sensor. This causes deterioration of the selectivity of the sensor. When the concentration of NO₃⁻ is measured in the range from 10⁻⁶ to 10⁻³ M, this effect is clearly observed.¹⁹ Since the inner solution of the NO₃⁻-ISE contained only nitrate salts in the present study, other anions distributed in the selective membrane were spontaneously replaced by NO₃⁻ within the inner solution. In addition, electrolyte species in the salt bridge between the reference electrode and the sample solution were examined to reduce the interference in measurements due to the existence of ions like K⁺ and Cl⁻.

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Fig. 1 Schematics of a) NO_3^- -ISE and b) a reference electrode.

Experimental

Chemicals

LiCl , LiNO_3 , Li_2SO_4 , NaCl , NaNO_3 , Na_2SO_4 , Na_2HPO_4 , NaH_2PO_4 , KCl , KNO_3 , K_2SO_4 , MgCl_2 , MgSO_4 , AgNO_3 , tetrahydrofuran (THF), and PVC were purchased from Wako Pure Chemical Ind., Ltd. The bromide salt of THA^+ (THABr) was bought from Tokyo Chemical Industry Co. Ltd. NPOE was obtained from Dojindo Molecular Technologies, Inc. GR reagent (Kishida Kagaku) was used for spectrophotometric determination of NO_3^- . The concentration of NO_3^- in soil was evaluated according to the conventional procedure using a UV-Vis spectrophotometer (Shimadzu, MultiSpec-1500).^{20,21} All chemicals were reagent grade and were used without further purification.

The nitrate salt of THA^+ (THANO_3) was produced by mixing an ethanol solution containing THABr with that containing excess AgNO_3 .¹⁹ Then AgBr precipitated from the solution was removed by filtration. By adding pure water to the filtrate containing THANO_3 while heating to about 70°C , THANO_3 precipitated in the filtrate. The white solid THANO_3 was separated from the solution *via* filtration, and it was washed with pure water several times to remove residual AgNO_3 . It was then dried under vacuum for several hours.

All the aqueous solutions were prepared using high-purity water ($\sigma = 18.2 \text{ M}\Omega \text{ cm}$).

Apparatus

The electrochemical cell utilized in this study is presented in Fig. S1a (Supporting Information), and it was also used as a hydroponic vessel. The potential between the NO_3^- -sensing electrode and the reference electrode was measured using a handmade electrometer using an instrumentation amplifier (Texas Instruments Inc., INA116) and an A/D converter (Graphtec Corp., Midi Logger GL 900).

All measurements were performed at $25 \pm 1^\circ\text{C}$.

Preparation of the nitrate-selective electrode

As a structural material for the NO_3^- -ISE, a urethane tube (inner diameter: 4 mm, outer diameter: 6 mm, length: about 10 cm) was used. A sensitive membrane was attached to one end of this tube. An aqueous solution containing 50 mM AgNO_3 and 50 mM $\text{Mg}(\text{NO}_3)_2$ was used as an internal solution. A Ag wire (diameter: 0.5 mm) was inserted into the internal solution and fixed with a paraffin film, as shown in Fig. 1a. The composition of the NO_3^- -sensitive membrane was made of the mass ratios of PVC, NPOE, and THANO_3 set to be 0.2:0.4:0.001,

respectively. These were dissolved in 2 mL of THF (1 mL per 0.1 g of PVC) and used to prepare the NO_3^- -sensitive membrane. Approximately 50 μL of the THF solution was dropped on a flat glass plate with a syringe, and THF evaporated day and night. After peeling the membrane off, the membrane was fixed to the end of the urethane tube with a small amount of the THF solution.

Preparation of the reference electrode

An overview of a reference electrode (RE) is indicated in Fig. 1b. The RE was prepared by fixing a porous ceramic block (diameter: 2.7 mm, length: 5 mm, ZR-11 Muff rod, Nikkato Co. Ltd.) to one end of a perfluoroalkoxyalkane (PFA) tube with a heat shrink tube. An aqueous solution containing 50 mM MgCl_2 and 2 M MgSO_4 was used as an internal solution and a silver wire coated with AgCl (hereinafter referred to as the $\text{Ag}|\text{AgCl}$ electrode) was inserted and fixed with a paraffin film.

Results and Discussion

Improvement of the reference electrode

Because it became clear that the potential response of the NO_3^- -selective membrane was inhibited by the presence of Cl^- concentrations of $>10^{-3} \text{ mol dm}^{-3}$, an aqueous solution saturated with MgSO_4 was used as a junction between the inner solution of the $\text{Ag}|\text{AgCl}$ electrode and a test solution. Here, MgSO_4 was utilized as an electrolyte because it is nontoxic and the liquid junction potential within the passage of the porous ceramic was almost constant. Although the potential of the double junction-type RE used in the previous study was very stable,¹⁹ the electrode structure was complicated and the Nafion membrane was often broken. The structure of the RE in the present study was very simple, and it is easy to make the electrodes. In addition, the potential shift of the RE was as small as the RE used in the previous study. The potential of the RE indicated about +10 mV to the calomel electrode, and its fluctuation was about several mV per day at maximum. The potential fluctuation of the RE was within $\pm 10 \text{ mV}$ during the first 30 days.

Characteristics of the NO_3^- -sensor

Electrochemical measurements were carried out using the aqueous solution of $5.0 \times 10^{-7} \text{ M}$ to 1 M $\text{Mg}(\text{NO}_3)_2$. The calibration curve of the NO_3^- -ISE was measured from the low-concentration side. After the sensor was washed with pure water and the surface was wiped off, each measurement was conducted. In the NO_3^- concentration region higher than 10^{-3} M , the response time was shorter than 10 s. Even when the concentration of NO_3^- was lower than 10^{-5} M , the response time was within 60 s. Measurement time was 120 s for each measurement and the average value of the potential (E) obtained from 60 to 120 s was finally recorded. Figure 2 shows the potential response of the NO_3^- -ISE. The NO_3^- -ISE indicated a linear response with a slope of $-49 \pm 1 \text{ mV dec}^{-1}$ to NO_3^- in the concentration range from 10^{-5} to 0.1 M . In addition, the NO_3^- -ISE showed a nearly linear response in the high concentration range up to 2 M , as shown in Fig. S2. The detection limit was experimentally estimated at about 10^{-5} M . The E value is expressed by Eq. (1).

$$E = (0.367 \pm 0.001) - (0.049 \pm 0.001) \log(c_{\text{NO}_3^-}/\text{mol L}^{-1}). \quad (1)$$

Here, $c_{\text{NO}_3^-}$ is the concentration of NO_3^- .

On the other hand, each ISE was found to actually respond to activity rather than concentration. Therefore, the activity of

Fig. 2 Calibration curve of the NO₃⁻-ISE. Electrolyte: NaNO₃. Fig. 3 Dependence of the potential of the NO₃⁻-ISE on the concentration of coexisting anions. Electrolytes: LiNO₃, LiCl, Li₂SO₄.

NO₃⁻ in each solution was calculated and the ISE potential was linearly changed with its logarithm. Here, using the activity constant of NO₃⁻, γ , the activity of NO₃⁻, $a_{\text{NO}_3^-}$, in the aqueous solution can be defined by the following equation,

$$a_{\text{NO}_3^-} = \gamma - c_{\text{NO}_3^-} \quad (2)$$

The mean activity coefficient, $\gamma_{\pm}$, is expressed by Eq. (3) based on the Debye-Hückel rule.²²

$$\log \gamma_{\pm} = \frac{Az_+z_-\sqrt{I}}{1+Bd\sqrt{I}} + bI \quad (3)$$

Here, $A = 0.509 \text{ mol}^{-1/2}$ (298 K), $B = 0.3291 \times 10^8 \text{ cm}^{-1} \text{ mol}^{-1/2} \text{ kg}^{1/2}$, $d = 3.78 \times 10^{-8} \text{ cm}$,²³ z_+ (charge number of Mg²⁺) = +2, z_- (charge number of NO₃⁻) = -1, I (ion strength of Mg(NO₃)₂ solution) = $1.5 c_{\text{NO}_3^-}$, $b = 0.055 \text{ mol}^{-1} \text{ kg}$. By use of $a_{\text{NO}_3^-}$ derived from Eqs. (2) and (3), the slope of Eq. (1) is $-53 \pm 1 \text{ mV dec}^{-1}$, which is more close to the theoretical value (-59 mV dec^{-1}). The potential responses of the NO₃⁻-ISE against the concentration and activity are shown in Fig. S1b. Since not only NO₃⁻ but also many kinds of cations and anions usually exist in the soil environment or culture solution, it is difficult to evaluate the accurate activity of NO₃⁻. Therefore, Eq. (1) is used for the evaluation of $c_{\text{NO}_3^-}$ in the sample solution.

Influence of coexisting ions

Figure 3 indicates the potential responses of the NO₃⁻-ISE to three anions (NO₃⁻, Cl⁻, and SO₄²⁻). As for Cl⁻, the negative shift of the potential of the NO₃⁻-ISE was observed in the

Fig. 4 Dependence of the potential of the NO₃⁻-ISE on the concentration of coexisting anions. Electrolytes: LiNO₃, Na₂CO₃, Na₂HPO₄, NaH₂PO₄. Fig. 5 Dependence of the potential of the NO₃⁻-ISE on the concentration of coexisting cations. Electrolytes: Na₂SO₄, K₂SO₄, MgSO₄, Li₂SO₄, Mg(NO₃)₂.

concentration region of more than 10⁻³ M. The potential response of the NO₃⁻-ISE was not affected by the existence of SO₄²⁻. Similarly, the potential responses of the NO₃⁻-ISE were not affected by the other three anions (CO₃²⁻, H₂PO₄⁻, and HPO₄²⁻), as shown in Fig. 4. On the other hand, the potential of the NO₃⁻-ISE responded to K⁺ in the presence of more than 10⁻³ M K⁺, as presented in Fig. 5. The influence of the coexisting ion on the resting potential of the NO₃⁻-ISE (E_{ISE}) is evaluated by the Nicolsky-Eisenman equation, as expressed by Eq. (4).²⁴

$$E_{\text{ISE}} = E_i^{\circ} + \frac{RT}{z_i F} \ln \left(a_i + \sum_{j \neq i} k_{ij}^{\text{pot}} a_j^{\frac{z_i}{z_j}} \right) \quad (4)$$

Here, E_i° is a constant value that depends on the properties of an objective ion i and on the cell composition, a_i and a_j are the activities of the ions i and j , z_i and z_j are the charge numbers of i and j , F is the Faraday constant, k_{ij}^{pot} is the selectivity coefficient of j , R is the gas constant, and T is the temperature. The $k_{\text{NO}_3/\text{Cl}}^{\text{pot}}$ values for Cl⁻, SO₄²⁻, HCO₃⁻ (at pH 7), H₂PO₄⁻ (at pH 6), and HPO₄²⁻ (at pH 8.5) previously reported by the author's research group are 0.01, 0.0009, 0.0007, 0.0005, and 0.0006, respectively.¹⁹ Figure 3 shows the potential responses of the NO₃⁻-ISE to Li⁺ salt of NO₃⁻, Cl⁻, and SO₄²⁻, respectively. Although SO₄²⁻ did not affect the NO₃⁻-ISE at all, the influence of Cl⁻ appeared around 10⁻³ M and above. Based on the Nikolsky-Eisenman equation, $k_{\text{NO}_3/\text{Cl}}^{\text{pot}}$ is evaluated with 0.01

Fig. 6 Time courses of the concentration of NO_3^- in the culture solution during hydroponic cultivation. Initial concentration of NO_3^- : 1.0 mM. Initial volume of the culture solution: 200 mL. Temperature: 25°C.

($i = \text{NO}_3^-$, $j = \text{Cl}^-$) and it is in good agreement with the previous value. In the present case, the $k_{\text{NO}_3^-\text{SO}_4^{2-}\text{pot}}$ value is less than 10^{-4} . Figure 4 indicates the potential response of the NO_3^- -ISE to the other anions such as CO_3^{2-} , HPO_4^{2-} , and H_2PO_4^- that often exist in the natural environment. Thus, these hydrophilic anions did not interfere with the NO_3^- -ISE. Figure 5 expresses the potential response of the NO_3^- -ISE to salts of SO_4^{2-} . It turned out that K^+ affected the NO_3^- -ISE around 10^{-2} M, while Mg^{2+} did not have an influence, similarly to Na^+ . That is, the $k_{\text{NO}_3^-\text{K}^+\text{pot}}$ value was estimated at about 10^{-3} . As for anion-selective electrodes, the selectivity is usually evaluated for coexisting anions, but it is suggested that some kinds of coexisting cations can also influence the liquid-membrane type ISE.

Real-time monitoring

The variation of the concentration of NO_3^- in the culture solution owing to the intake by a green plant, chrysanthemum coronarium (*Glebionis coronaria*), was monitored. The root of chrysanthemum coronarium was immersed in the culture solution (200 mL of tap water containing 1 mM KNO_3), and the NO_3^- -ISE and RE were inserted in the culture solution, as shown in Fig. S1b. The temperature was kept at 25°C using a plant incubator (Biotron LH200 NK system, Nippon Medical & Chemical Instruments Co., Ltd.), and the cultivation was carried out under illumination. A control experiment was carried out using the same container containing only tap water. The water volume of the control experiment was varied from 200 to 188 mL. After the cultivation, the volume of the culture solution changed from 200 to 123 mL. The difference seems to be caused by the stomatal transpiration. The weight of the green plant before and after the experiment was measured after wiping off drops of water on the surface. The plant weight increased from 5.14 to 7.68 g due to the culture. Figure 6 expresses the time-course of the concentration of NO_3^- in the culture solution during 48 h. In this case, the potential was recorded, as it was. The initial concentration was about 1 mM, and it decreased linearly with time. Since the concentration of NO_3^- rapidly decreased by the absorption and the NO_3^- concentration locally became heterogeneous, the culture solution was stirred during the real-time monitoring. It seems that the fluctuation of the NO_3^- concentration during the measurement was caused by the stirring and the absorption of NO_3^- . After 35 h, NO_3^- was almost exhausted. Thus, we succeeded in monitoring the concentration of NO_3^- in the culture solution in real time. It is thought that 2.5×10^{-3} g of nitrogen atoms in the culture solution was metabolized and converted to the plant body. The

Table 1 Comparison of the concentration ($c_{\text{NO}_3^-}$ /mM) of NO_3^- of soil samples 1–5 evaluated by the ISE method with that by spectrophotometric method

Method	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
ISE	17	43	21	43	17
Spectroscopy	20	48	22	37	11

Fig. 7 The concentration of NO_3^- in soil samples of which depth ranged from 0 to 10 cm. The concentration of NO_3^- was directly measured by the NO_3^- -ISE.

weight corresponds to 1.0% of the total weight change, and it matches with the percentage of nitrogen atoms in general plants.²⁵

Measurement of Nitrate Concentration in Soil

The dry soil sample was prepared as described in the SI. Soil samples were prepared by mixing the dry soil samples with tap water and adding a small amount of NaNO_3 . The water contents were prepared at about 20 wt%. The concentration of NO_3^- within the soil samples was directly measured using the NO_3^- -ISE and the reference electrode. About 30 g of a soil sample was measured and then dried at 200°C for 24 h. Then, 10 mL of distilled water was mixed with about 30 g of each dry soil sample, and the concentration of NO_3^- of the filtrate was spectrometrically determined by use of a GR reagent. Table 1 shows the concentration of NO_3^- of five soil samples. There was not a significant difference between the data obtained by the two measuring methods. Thus, the ISE method is very useful and powerful for practical use. The concentration of NO_3^- in the aqueous solution is often measured by a spectrophotometric method.^{21,26} Since this method requires a considerable amount of time and effort, an alternative method that can measure the concentration of NO_3^- easily and on-site is required. The ISE method seems to be optimum, because it does not need any pretreatment and the concentration can be directly evaluated.

Soil was filled into a cylindrical vessel (inner diameter: 10 cm, depth: 15 cm) that had multiple holes in the bottom, and 1 mM NaNO_3 was filled onto a saucer, as shown in Fig. S3. Since the soil usually contains NO_3^- and water easily evaporates at the surface, it is thought that the concentration of NO_3^- near the surface was 20–50 mM. Next, the depth dependence of the concentration of NO_3^- was estimated by use of the NO_3^- -ISE. Figure 7 indicates the depth dependence of the concentration of NO_3^- of 6 h later. Although the concentration of NO_3^- in soil samples with a depth of 9 and 10 cm is about 3 mM,

the concentration of NO_3^- around the surface increased. Since the dry soil sample contained NO_3^- derived from tap water, the NO_3^- in soil samples was concentrated around the bottom. It is considered that this behavior is caused by drawing water by capillary action and evaporation of water at the surface.

Conclusions

NO_3^- -ISE for detecting the concentration of NO_3^- in the region between 10^{-5} and 0.1 M was constructed. Although it is slightly affected by Cl^- and K^+ , no other ions coexisting in the usual environmental water affected the ISE, showing that the NO_3^- -ISE is applicable to real time monitoring. The direct measurement of soil was carried out with this ISE. As for the on-site analytical method, the measurement using optical sensors is well known.^{27,28} Since the concentration of nutrient ions on the soil surface is directly measured, it is very convenient to evaluate the concentration rapidly without needing pretreatment, as with the ISE method. It is thought that the fluctuation of the optical data is larger than those observed by use of the ISE. This might be because the surface condition significantly fluctuates with time.

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Supporting Information

This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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