

# On-site Water Nitrate Monitoring System based on Automatic Sampling and Direct Measurement with Ion-Selective Electrodes

Dong-Wook Kim<sup>1</sup>, Dae-Hyun Jung<sup>1</sup>, Woo-Jae Cho<sup>1</sup>, Kwang-Cheol Sim<sup>2</sup>, Hak-Jin Kim<sup>1,3\*</sup>

<sup>1</sup>Dept. of Biosystems and Biomaterials Engineering, College of Agriculture and Life Sciences, Seoul National University, Seoul, 08826, Korea

<sup>2</sup>Scientec Lab Center co., LTD, Daejeon, 34016, Korea

<sup>3</sup>Research Institute of Agriculture and Life Sciences, College of Agriculture and Life Sciences, Seoul National University, Seoul, 08826, Korea

Received: September 28<sup>th</sup>, 2017; Revised: November 20<sup>th</sup>, 2017; Accepted: November 28<sup>th</sup>, 2017

## Abstract

**Purpose:** *In-situ* monitoring of water quality is fundamental to most environmental applications. The high cost and long delays of conventional laboratory methods used to determine water quality, including on-site sampling and chemical analysis, have limited their use in efficiently managing water sources while preventing environmental pollution. The objective of this study was to develop an on-site water monitoring system consisting mainly of an Arduino board and a sensor array of multiple ion selective electrodes (ISEs) to measure the concentration of NO<sub>3</sub> ions. **Methods:** The developed system includes a combination of three ISEs, double-junction reference electrode, solution container, sampling system consisting of three pumps and solenoid valves, signal processing circuit, and an Arduino board for data acquisition and system control. Prior to each sample measurement, a two-point normalization method was applied for a sensitivity adjustment followed by an offset adjustment to minimize the potential drift that could occur during continuous measurement and standardize the response of multiple electrodes. To investigate its utility in on-site nitrate monitoring, the prototype was tested in a facility where drinking water was collected from a water supply source. **Results:** Differences in the electric potentials of the NO<sub>3</sub> ISEs between 10 and 100 mg · L<sup>-1</sup> NO<sub>3</sub> concentration levels were nearly constant with negative sensitivities of 58 to 62 mV during the period of sample measurement, which is representative of a stable electrode response. The NO<sub>3</sub> concentrations determined by the ISEs were almost comparable to those obtained with standard instruments within 15% relative errors. **Conclusions:** The use of the developed on-site nitrate monitoring system based on automatic sampling and two-point normalization was feasible for detecting abrupt changes in nitrate concentration at various water supply sites, showing a maximum difference of 4.2 mg · L<sup>-1</sup> from an actual concentration of 14 mg · L<sup>-1</sup>.

**Keywords:** Arduino, Ion-selective electrode, Nitrate, Two-point normalization, Water quality monitoring

## Introduction

Recently, due to growing concerns about environmental pollution, the need for physical and chemical sensors used for *in-situ* water quality monitoring in agricultural and aquatic systems has risen (Bourgeois et al., 2003). Accurate measurement of ionic concentrations can provide useful

information toward the understanding of biogeochemistry in aquatic ecosystems. In particular, nitrate and ammonium contents are indicators of undesirable water contaminants. Nitrate contamination of ground and surface water can cause a severe problem where intensive agricultural practices occur (Schwarz et al., 2000). Since groundwater contamination due to the leaching of nitrates poses the most immediate health risk, the maximum permissible level for this ion in drinking water supplies is often regulated. As a consequence, the monitoring of water quality in aquifers and rivers is essential to preserve

\*Corresponding author: Hak-Jin Kim

Tel: +82-2-880-4604; Fax: +82-2-873-2049

E-mail: kimhj69@snu.ac.kr



public health (Capella et al., 2013).

Methods of determining nitrate concentrations have received consistent attention from the scientific community over the years. Several review articles have been published on the topic (Moorcroft et al., 2001; Yilong et al., 2015). The authors summarized various detection techniques and discussed the advantages and limitations of each. Recent studies focus on performing the measurements at the location of interest with electronic devices. The major advantages of on-line analysis over classical off-line procedures are: (a) elimination of contaminants due to sample handling, i.e., no or minimal sample transformation; and (b) minimization of the overall cost of data acquisition due to a reduction of sampling, handling, and analysis times (Rosca et al., 2009). According to Capella et al. (2013), conventional measurement techniques based on the use of handled samplers still suffered several drawbacks. For example, the requirement for a human employee to move to the sampling location increases the cost and limits the number of samples taken, thereby complicating the accurate characterization of the variability of nitrate concentrations during field testing. In addition, because this method does not employ real-time acquisition system, it is incapable of detecting rapid changes in nitrate concentrations. The need for quick, on-site monitoring of nitrates has led to the use of ion-selective electrodes (ISEs) due to their advantages such as rapid response, direct measurement of the analyte, low cost, and simplicity.

Solvent polymeric membranes based ISEs for the determination of anions and cations have become routine tools in electro-analysis. These potentiometric sensors are used in a wide range of applications in clinical, environmental, and food analysis (Oehme, 1991; Mikhelson, 1994; Bakker et al., 1999; Jung et al., 2015; Kim et al., 2013). Electroanalytical determinations of ions with the ISEs can often be carried out *in-situ* using field measurements and, in many cases, offers useful and inexpensive alternatives to photometric and chromatographic methods necessitating considerably more time and ionophores dissolved in a lipophilic solvent (Schwarz et al., 2000). However, since one of the major disadvantages of ISE technology compared to standard spectroscopy-based analyzers is a possible limitation in the accuracy of the measurement due to signal drift and reduced sensitivity over time (Carey and Riggan, 1994; Domingues et al., 2012). When using an on-site ion analyzer that requires frequent immersions of the ISEs in solution, accuracy in

the determination of nutrient concentrations can be more strongly affected by this signal drift (Bamsey et al., 2012; Gutierrez et al., 2007; Kim et al., 2013). A two-point normalization method that involves a sensitivity adjustment followed by an offset adjustment can be implemented to minimize the drift that might occur during continuous measurement (Jung et al., 2015; Kim et al., 2013).

The objectives of this research were (1) to develop an on-site water monitoring system mainly consisting of an Arduino board as a micro-control unit (MCU) and a sensor array of multiple ISEs that can measure the concentrations of nitrate ions in water and, (2) investigate the feasibility of using the developed system for the *in-situ* measurement of nitrate ions in a water supply.

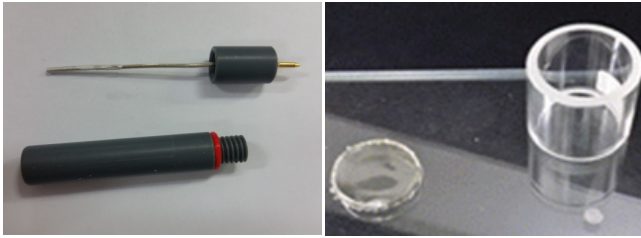
## Materials and Methods

### Preparation of ISEs

PVC-based ion-selective electrodes (ISEs) for the direct measurement of  $\text{NO}_3$  ions in water were prepared based on the membrane compositions shown in Table 1. The  $\text{NO}_3$  PVC-based membrane consists of quaternary ammonium compounds, as reported in previous studies (Birrel and Hummel, 2000; Kim et al., 2006). A ligand (tetradodecyl ammonium nitrate, TDDA) and a plasticizer (nitrophenyl octyl ether, NPOE) were used for producing the nitrate ion-selective membrane by dissolving the mixtures in 2 mL of tetrahydrofuran (THF) and evaporating for 24 hours in a 23 mm glass ring. The ISEs consisted of a PVC-based membrane, electrode body, and Ag/AgCl electrode. The Ag/AgCl electrode prepared by coating a 99% silver wire with a diameter of 1 mm with Ag/AgCl ink (Model 01164, ALS, JAPAN) was immersed in the ISE body as the inner reference electrode. Figure 1 shows an ISE body and the  $\text{NO}_3$  PVC membrane prepared in our laboratory. The  $\text{NO}_3$  ISEs were filled with an inner solution of 0.01 M  $\text{NaNO}_3$  +

**Table 1.** Chemical compositions of the  $\text{NO}_3$  ISE membrane used in study

|                | $\text{NO}_3$                                 | Composition (wt %) |
|----------------|---|--------------------|
| Ionophore      | TDDA<br>(Tetradodecylammonium nitrate)        | 4.0                |
| Plasticizer    | NPOE (2-nitrophenyl octylether)               | 67.75              |
| Matrix         | PVC (poly vinyl chloride)                     | 28.25              |
| Inner solution | 0.01 M $\text{NaNO}_3$ + 0.01 M $\text{NaCl}$ |                    |



**Figure 1.** Views of the ISE (left) and the NO<sub>3</sub> membrane (right) prepared in the laboratory.

0.01 M NaCl and were conditioned in 0.01 M NaNO<sub>3</sub> for 24 hours. A double junction electrode (Orion 900200, USA) was used as the reference electrode of the ISEs.

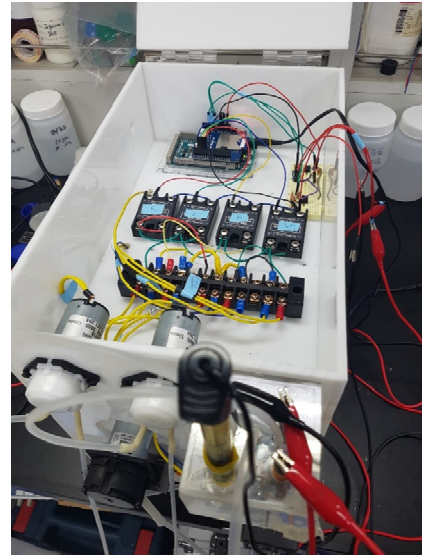
## Development of on-site water monitoring system

### Hardware

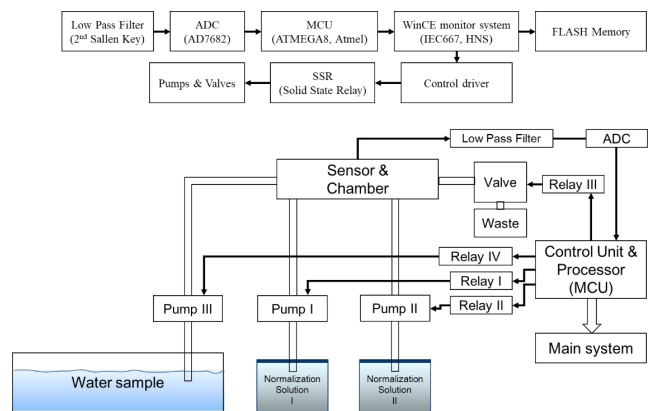
A prototype of an on-site water monitoring system was developed using a combination of three ISEs and a double-junction reference electrode, solution container, sampling system containing three pumps and solenoid valves, signal processing circuit, and an Arduino board for data acquisition and system control (Fig. 2). 220-VAC was converted to 12 VDC for supplying the electric power to the system. The system was assembled in a 40 cm × 25 cm × 30 cm plastic case and weighed a total of 7 kg. A block diagram showing the components and connection of the system is shown in Figure 3. The system consisted of several pumps and relays to perform automatic sampling in a water source. The system controlled the pumps and valves to fill and empty the container with normalization samples and water samples. The ISE analog input signals were obtained through a differential amplification circuit consisting of operational amplifiers for voltage following and Sallen-Key low-pass filter (Fig. 4). The voltage follower removed the influence of instrument loads by transforming the input and output impedances of the ISE signals and the differential amplifier outputted differences in the electrical potentials between the ISEs and the double junction reference electrode. Data were stored on an SD memory card installed in the Arduino main board.

### Software

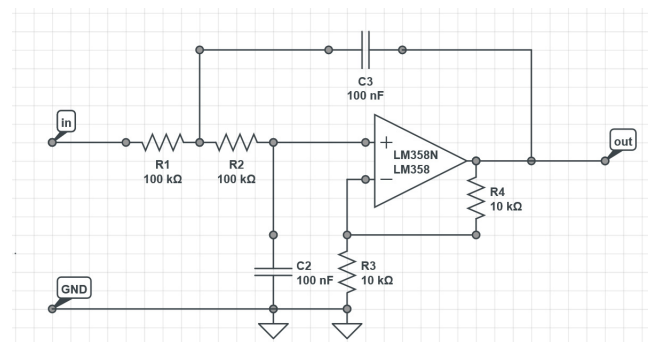
Figure 5 shows both the sequence of the on-site water monitoring system and the compensation method. The sequence contains two components: a two-point normal-



**Figure 2.** The prototype on-site water monitoring system developed in the study.



**Figure 3.** Block diagram of the on-site water monitoring system that shows the connectivity of each sub-system.



**Figure 4.** Signal processing circuit for ISE signal.

ization and water quality monitoring (Fig. 5 (left)), which includes rinsing, sampling using pumps, a drainage using a solenoid valve, and measurement using ISEs. In principle,

during the operation of ‘Two-point normalization’, the device fills the container controlling the pumps with normalization solution. After 30 s, the Arduino controls the solenoid valve to empty the container for rinsing. Finally, an EMF measurement is conducted using the ISEs within 60 s after re-filling the normalization solution in the container. The operation of ‘Water quality monitoring’ is identical to that of the previous step, but the water solution differs. As a result, three EMFs are obtained for two-point normalization and water quality is monitored during one step of the overall algorithm.

As reported in our previous studies (Jung et al., 2015; Kim et al., 2013), a two-point normalization method was implemented for a sensitivity adjustment followed by an offset adjustment to minimize the potential drift that could occur during continuous measurement and to standardize the response of multiple electrodes using calibration equations of the  $\text{NO}_3$  ion (Eq. 1).

$$\text{EMF} = -44.36 \times \log_{10} \text{NO}_3 + 257.29 \quad (1)$$

where EMF is the electro-motive force of the ISE input

signal (mV), and  $\text{NO}_3$  is the concentration of  $\text{NO}_3$  ions ( $\text{mg} \cdot \text{L}^{-1}$ ). The algorithm of the two-point normalization is shown in Figure 5 (right). Details of the two-point normalization method were described in a previous study (Jung et al., 2015).

### Sample tests

Laboratory tests were conducted to investigate the feasibility of using the on-site water monitoring system for monitoring the  $\text{NO}_3$  ion concentrations of several water solutions. Prior to sample measurement, the two-point normalization was performed using two normalization solutions with different concentrations of nitrate (10 and 100  $\text{mg} \cdot \text{L}^{-1}$  of  $\text{NO}_3$ ) to determine the slope and offset values to sample measurement. The EMFs measured with all individual ISEs were normalized. After this normalization, the calibration equation (Eq. 1) was applied to EMFs obtained with the ISEs to estimate the concentrations of nitrate in samples without requiring additional electrode calibration. The stability of the measurements obtained using the developed system was assessed by investigating the changes in the EMFs of the

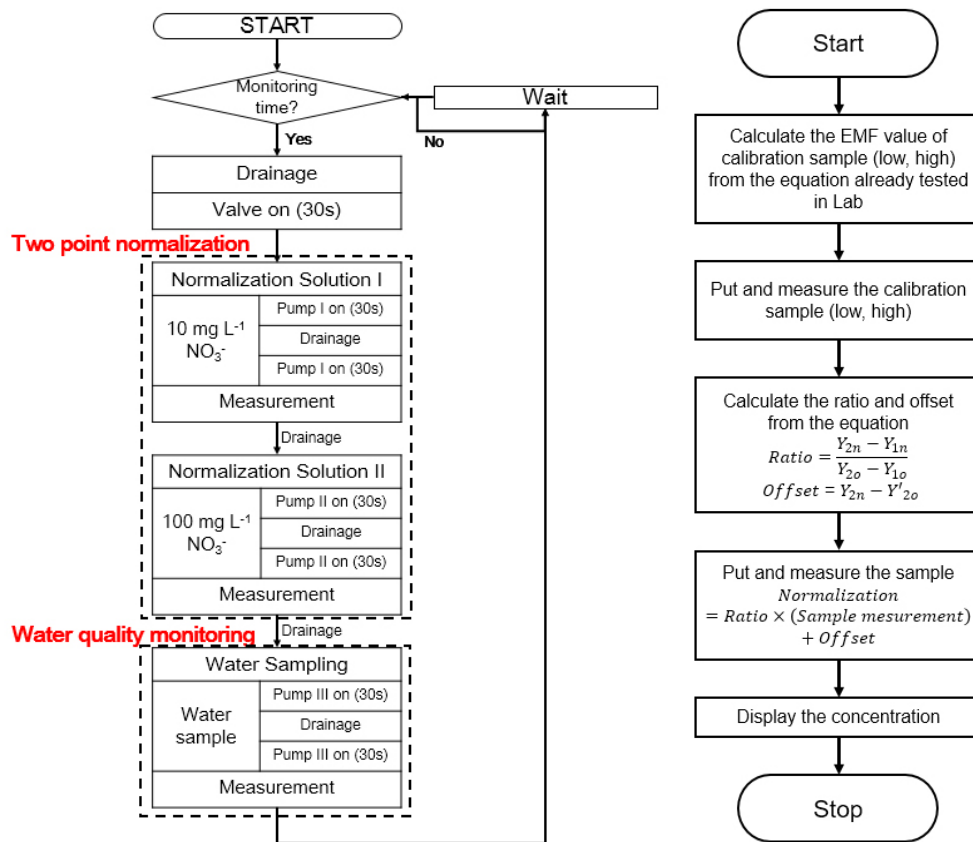


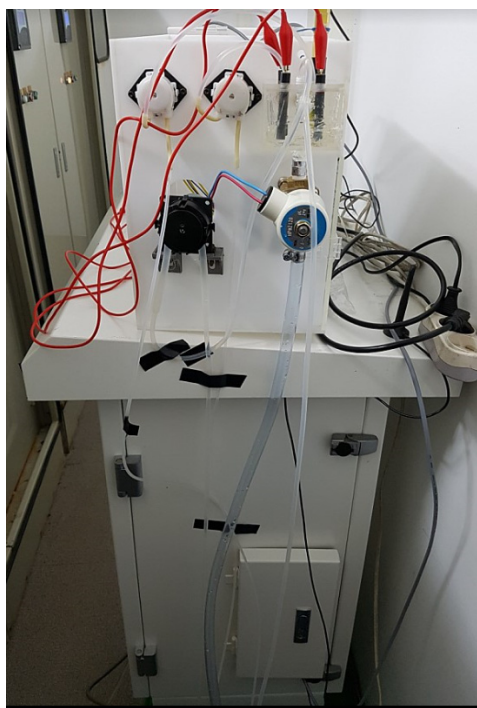
Figure 5. Flow chart for the sequence of the on-site water monitoring system (left) and flow chart for the two-point normalization algorithm (right).



ISEs measured in normalized samples with two different concentrations.

Prior to a field test, three water samples, (one from Gwanak, a valley stream of a Korean mountain, one from a drinking water supply in Jeongseon, and one from the Han river in Korea) were used to estimate the  $\text{NO}_3$  ion concentrations using the developed system. The actual  $\text{NO}_3$  concentrations for the three tested solutions were determined in a standard testing laboratory (National Instrumentation for Environmental Management (NICEM), Seoul, Korea) following standard analytical procedures. Three iterations of each sequence were conducted.

The prototype of the automatic nitrate monitoring system was installed in a facility that collects water in a Jeongseon water supply to investigate its potential for use in on-site nitrate monitoring (Fig. 6). The concentrations of the nitrate ion in water were repeatedly monitored three times per day at 4:00, 12:00, and 20:00 for 8 days. The water sample was automatically pumped into the solution container of the monitoring system. Prior to electrode normalization and sample measurement, each test sequence began by rinsing the electrodes twice with the lowest concentration of normalization solution, i.e.,  $10 \text{ mg} \cdot \text{L}^{-1}$ , which was used to begin each electrode normalization. The EMFs which measured  $\text{NO}_3$  ISEs



**Figure 6.** On-site installation of the developed system on the source of drinking water supply in Jeongseon.

relative to the reference electrode were collected at a sampling rate of 1 kHz using the Arduino with the signal buffering circuit module. Each test began when the desired volume of sample had been delivered to the solution container. After 60 s, one hundred EMF measurements were averaged to represent a single EMF output response at each concentration level.

## Results and Discussion

### Study on electrode sensitivity and water sample measurement

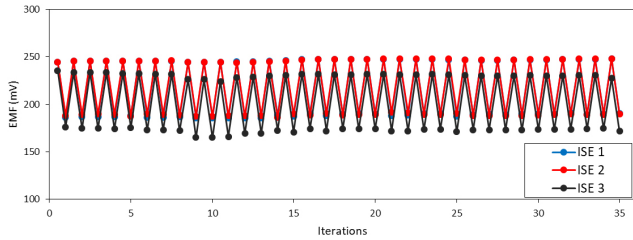
Figure 7 shows the changes in EMF between the low- and high-concentration normalization solutions, i.e.,  $10$  and  $100 \text{ mg} \cdot \text{L}^{-1}$ , which were repeatedly measured using three different  $\text{NO}_3$  ISEs. For each ISE, 35 replicates were performed at intervals of 5 minutes. The differences in EMF between the low- and high-concentration levels were nearly constant with negative sensitivities of  $58\sim 62 \text{ mV}$  during the measurement period of the three water samples, which was almost identical with the theoretical Nernstian slope, implying that the sensitivity responses of the electrodes was constant over the period of the sample measurement. Figure 8 compares the  $\text{NO}_3$  concentrations determined by the ISEs and the standard instruments for the tested real water samples. The  $\text{NO}_3$  concentrations determined by the ISEs and the standard analysis ranged from  $10.0$  to  $39.7 \text{ mg} \cdot \text{L}^{-1}$  and  $8.6$  to  $43.5 \text{ mg} \cdot \text{L}^{-1}$ , respectively. The differences between the actual and estimated concentrations were  $1.4$ ,  $1.4$ , and  $3.7 \text{ mg} \cdot \text{L}^{-1}$ , and the relative errors were  $7.7\%$ ,  $16.5\%$ , and  $8.7\%$  for the water samples from Jeongseon, Mt. Gwanak, and the Han river, respectively, implying that there was little difference in the nitrate amounts estimated by the two methods.

### Application to on-site water monitoring

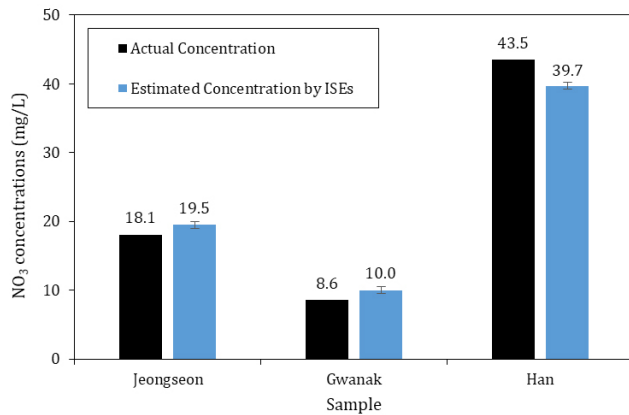
Figure 9 shows changes in EMF between the low- and high-concentration normalization solutions, i.e.,  $10$  and  $100 \text{ mg} \cdot \text{L}^{-1}$ , repeatedly measured using the three different  $\text{NO}_3$  ISEs in the source of drinking water supply for 8 days. The EMF differences between the solutions were  $\sim 50 \text{ mV}$  for 8 days, which were  $10 \text{ mV}$  lower than those measured in the laboratory test (Fig. 7). The difference could be attributed to a decrease in temperature, which was measured at the on-site environment. The

ISE1 provided a relatively high difference in EMF after the 6<sup>th</sup> day. This could be caused by the generation of air bubbles on the surface of the ISE1 membrane during the filling and emptying of solutions in the sensor chamber using the pumps.

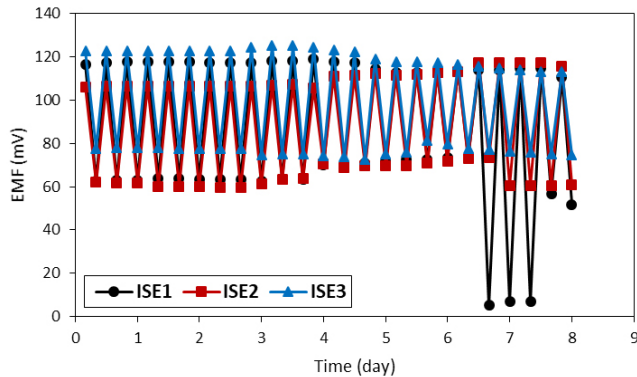
Figure 10 shows the performance of the NO<sub>3</sub> concentration estimation of the developed on-site water monitoring system tested at a source of drinking water.



**Figure 7.** Responses of the three NO<sub>3</sub> ISEs to the low- and high-NO<sub>3</sub> normalization solutions.

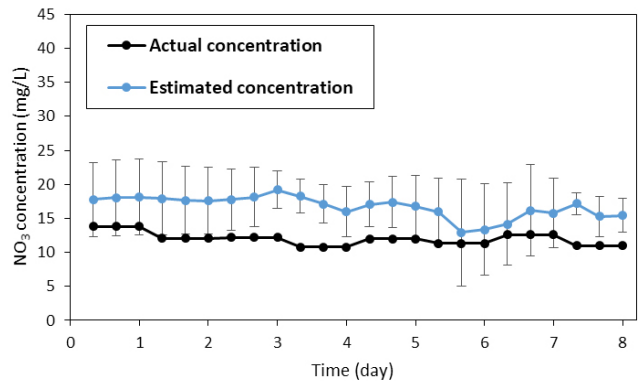


**Figure 8.** Comparison of the NO<sub>3</sub> concentrations for the three water samples estimated by the automatic nitrate monitoring system and by standard ion chromatography.

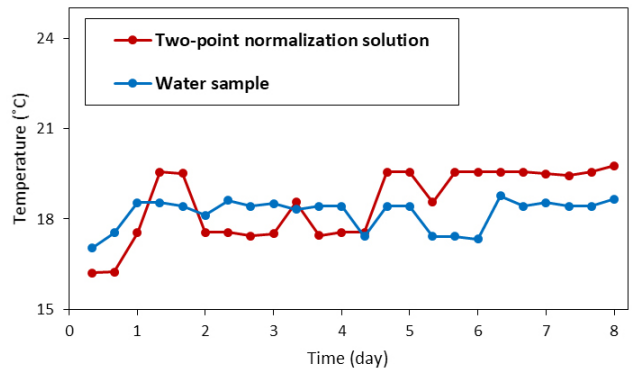


**Figure 9.** Changes in EMF of the three NO<sub>3</sub> ISEs installed in the prototype on-site monitoring system for the low- and high-concentration normalization solutions over time when tested in the source of drinking water supply for 8 days.

Overall, there was a higher difference in nitrate amount estimated by the two methods as compared to those measured at the three water samples in the lab (Fig. 8) because the sensitivities of the electrodes were affected by a difference in the solution temperatures between the normalization solutions and the water sample taken from the water supply (Fig. 11). That the effect of temperature on ISE measurement would be theoretically neglected if the normalization solutions and the water sample were maintained at a same temperature. Nevertheless, the changes in the pattern of the estimated concentration over time (see Fig. 10) were similar to those of the actual concentration, implying the use of one point normalization could offset the difference. In addition, it was thought that a maximum difference of 4.2 mg · L<sup>-1</sup> obtained between the two methods would show the potential of the developed system for use in on-site nitrate monitoring if the developed system is used for detecting and alerting the user to abrupt changes in nitrate concentration at various water supply sites.



**Figure 10.** The NO<sub>3</sub> concentration estimation performance of the on-site water monitoring system in the source of drinking water supply during eight-day period.



**Figure 11.** The temperature of the samples in the source of drinking water supply during the period of eight-day.

## Conclusions

In this study, an on-site water monitoring system consisting of an Arduino and a sensor array of multiple ISEs was developed to measure the concentrations of NO<sub>3</sub> ions in water samples with the two-point normalization method. The feasibility of the on-site water monitoring system was validated through a laboratory test of measuring NO<sub>3</sub> with known water samples and an on-site test installed in the site of a drinking water supply source.

The EMF differences between the low- and high-concentration normalization solutions during repeated measurement using the on-site water monitoring system were maintained at an almost constant level with negative sensitivities of 58~62 mV. The NO<sub>3</sub> ion concentrations estimated by the system were almost comparable to those obtained with standard instruments within 15% relative error. The small maximum difference of 4.2 mg · L<sup>-1</sup> obtained between the two methods in the field test demonstrates the potential of the developed system for use in on-site nitrate monitoring if the developed system is intended for detection and to alert users to abrupt changes in nitrate concentrations at various water supply sites.

## Conflict of Interest

The authors have no conflicting financial or other interests.

## Acknowledgement

This research was supported by the R&D center for Green Patrol Technologies, for KEITI (Korea Environmental Industry & Technology Institute), Republic of Korea. (E614-00184-0401-1)

## References

Bakker, E., P. Bühlmann and E. Pretsch. 1999. Polymer Membrane Ion-Selective Electrodes-What are the Limits? *Electroanalysis* 11(13): 915-933.  
Bamsey, M., T. Graham, C. Thompson, A. Berinstain, A. Scott and M. Dixon. 2012. Ion-specific nutrient

management in closed systems: the necessity for ion-selective sensors in terrestrial and space-based agriculture and water management systems. *Sensors* 12(10):13349-13392.

- Birrell, S. J. and J. W. Hummel. 2000. Membrane selection and ISFET configuration evaluation for soil nitrate sensing. *Transactions of the ASAE* 43(2):197.
- Bourgeois, W., A.-C. Romain, J. Nicolas and R. M. Stuetz. 2003. The use of sensor arrays for environmental monitoring: interests and limitations. *Journal of Environmental Monitoring* 5(6):852-860.
- Capella, J. V., A. Bonastre, R. Ors and M. Peris. 2013. In line river monitoring of nitrate concentration by means of a Wireless Sensor Network with energy harvesting. *Sensors and Actuators B: Chemical* 177:419-427.
- Carey, C. M. and W. B. Riggan Jr. 1994. Cyclic polyamine ionophore for use in a dibasic phosphate-selective electrode. *Analytical Chemistry* 66(21):3587-3591.
- Domingues, D. S., H. W. Takahashi, C. A. Camara and S. L. Nixdorf. 2012. Automated system developed to control pH and concentration of nutrient solution evaluated in hydroponic lettuce production. *Computers and Electronics in Agriculture* 84:53-61.
- Gutierrez, M., S. Alegret, R. Caceres, J. Casadesús, O. Marfa and M. Del Valle. 2007. Application of a potentiometric electronic tongue to fertigation strategy in greenhouse cultivation. *Computers and Electronics in Agriculture* 57(1):12-22.
- Jung, D. H., H.-J. Kim, G. L. Choi, T.-I. Ahn, J.-E. Son and K. A. Sudduth. 2015. Automated lettuce nutrient solution management using an array of ion-selective electrodes. *Transactions of the ASABE* 58(5):1309-1319.
- Kim, H.-J., J. W. Hummel and S. J. Birrell. 2006. Evaluation of nitrate and potassium ion-selective membranes for soil macronutrient sensing. *Transactions of the ASABE* 49(3):597-606.
- Kim, H.-J., W.-K. Kim, M.-Y. Roh, C.-I. Kang, J.-M. Park and K. A. Sudduth. 2013. Automated sensing of hydroponic macronutrients using a computer-controlled system with an array of ion-selective electrodes. *Computers and Electronics in Agriculture* 93:46-54.
- Mikhelson, K. 1994. Ion-selective electrodes in PVC matrix. *Sensors and Actuators B: Chemical* 18(1-3):31-37.
- Moorcroft, M. J., J. Davis and R. G. Compton. 2001. Detection and determination of nitrate and nitrite: a review. *Talanta* 54(5):785-803.
- Oehme, F. 1991. *Ionenselektive Elektroden*: Huthig Heidelberg.

Rosca, V., M. Duca, M. T. de Groot and M. T. Koper. 2009. Nitrogen cycle electrocatalysis. *Chemical Reviews* 109(6):2209-2244.

Schwarz, J., H. Kaden and G. Pausch. 2000. Development of miniaturized potentiometric nitrate-and ammonium selective electrodes for applications in water monitoring.

*Fresenius' Journal of Analytical Chemistry* 367(4): 396-398.

Yilong, Z., Z. Dean and L. Daoliang. 2015. Electrochemical and other methods for detection and determination of dissolved nitrite: a review. *International Journal of Electrochemical Science* 10:1144-1168.