Feature Article

Innovations in Continuous pH Measurement Technology for Wastewater Treatment Processes

~Reduction of Maintenance Load: Industrial Self-Cleaning pH Electrode~

NISHIO Yuji

KOMI Takuhisa

In the pH measurement of industrial wastewater, contamination of the pH response glass by various organic compounds and microorganisms and clogging of the liquid junction of the reference electrode are problems because measurements are made continuously. Therefore, periodic cleaning and calibration are necessary to ensure stable and accurate measurements, which poses a significant burden on operators and a safety risk. To solve these problems, the authors commercialized pH electrode with a self-cleaning function. The electrode consists of a glass pH electrode coated with titanium dioxide (TiO_2), which is irradiated from a built-in UV-LED to the TiO_2 photocatalyst. The basic performance of the self-cleaning pH electrode is comparable to that of conventional pH electrodes, and in an implementation test in a microbial treatment tank, the self-cleaning pH electrode maintained sensitivity of more than 95% after more than 16 months of cleaning, while the current electrode required manual cleaning every month. In mounting tests at sites with large maintenance loads due to organic contamination, the self-cleaning pH electrode remained clean for a certain period of time, achieving no maintenance.

Keywords
pH, Glass electrode, Self –Cleaning, Maintenance free, TiO_2, Anti-fouling

Introduction

The world's population has exceeded 8 billion, and the impact of human activities on the global environment is increasing. While the population continues to grow, the amount of water available for drinking is 1% or less of the total water on the Earth. The conservation of the water environment becomes even more important in the future[1]. Therefore, it is important to measure and manage water quality for human beings to ensure the sustainable use of water resources. Sewage generated from daily life and various industrial activities is treated to protect the water environment of rivers and oceans before being returned to rivers. pH management is essential to optimize the process of purifying this sewage. For this purpose, in wastewater treatment facilities of general factories as well as sewage treatment plants, pH is measured and controlled at their many places. Among these places, organic matter with high concentration such as oil, sludge, and microorganisms are contained in raw water tanks, microbial treatment tanks, and final discharge tanks, which are for wastewater. Therefore, when pH electrodes are immersed in the above-mentioned samples for extended periods, contamination accumulates over time, making stable measurements difficult. The most common method for addressing contamination on electrodes is manual cleaning by operators, which places a heavy maintenance burden on operators and poses safety risks.

On the other hand, industrial pH electrodes are generally considered to be well established, and there has been little research and development on pH electrodes, leaving the above issue unresolved. Then, the authors developed a UV-LED-integrated pH electrode with a self-cleaning function that utilizes photocatalytic effects (photoinduced hydrophilicity and photodegradation) to address the fouling issue of pH electrodes. The reference electrode contains KCl granules in the internal solution and uses a water-insoluble gel with high UV transmittance. Additionally, a through-hole (open junction) was adopted in the liquid junction to eliminate clogging. The basic performance of the self-cleaning pH electrode is evaluated, and the results show that it has almost the same performance as the current product has although it is coated with titanium dioxide (TiO_2). Furthermore, field tests were conducted, and the results show that the electrode maintained surface cleanliness and performance in sites where organic fouling occur, such as the microbial treatment tanks, the raw water tanks, and the final discharge tanks, which are for domestic wastewater. This result indicates that the maintenance and calibration cycles can be extended significantly. This paper describes the development of the self-cleaning pH electrode that contributes to solving these maintenance burden issues.

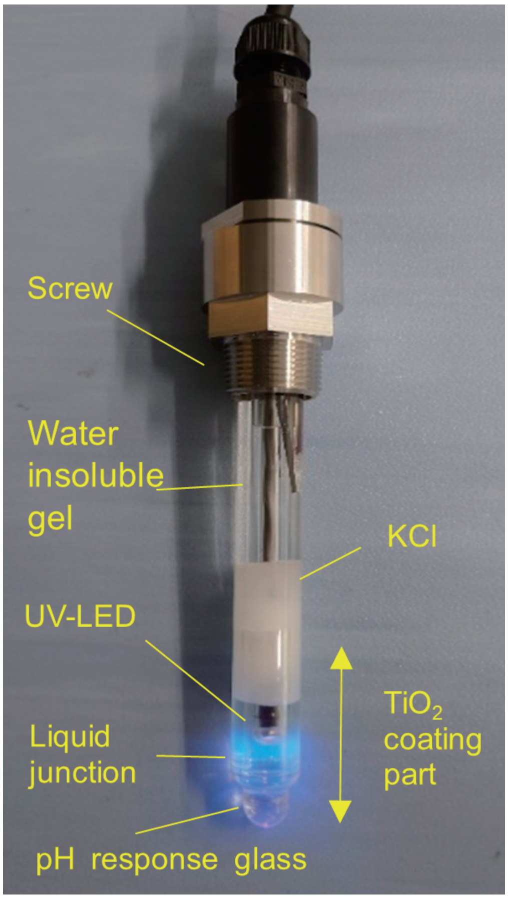

Figure 1 Picture of self-cleaning electrode 6122SA.

Electrode development and performance evaluation

Figure 1 shows the photograph of the newly developed UV-LED-integrated electrode with the self-cleaning function that utilizes photocatalytic effects (photoinduced hydrophilicity and photodegradation). Specifically, the electrode was structured so that the pH response glass membrane and the liquid junction were coated with TiO_2 and UV light was irradiated from the inside of the electrode. TiO_2 was coated approximately 30 mm from the tip of the electrode using the sol-gel method covering the pH response glass and liquid junction. Since titanium dioxide is an insulating material, the electrode does not respond when the pH response glass is covered completely. The reason why the sol-gel method was used is that the porosity film can be formed and its thickness can be controlled easily[2]-[4]. XRD (Smart Lab, manufactured by Rigaku) was used to check the presence of TiO_2 on the surface and a spectroscopic ellipsometer (UVISEL2, manufactured by HORIBA) was used to measure the film thickness. The transparent water-insoluble gel with low UV absorption was adopted as the internal solution of the reference electrode, eliminating the need for KCl solution replenishment[5]. In addition, the liquid junction was designed as an open junction that was not affected easily by

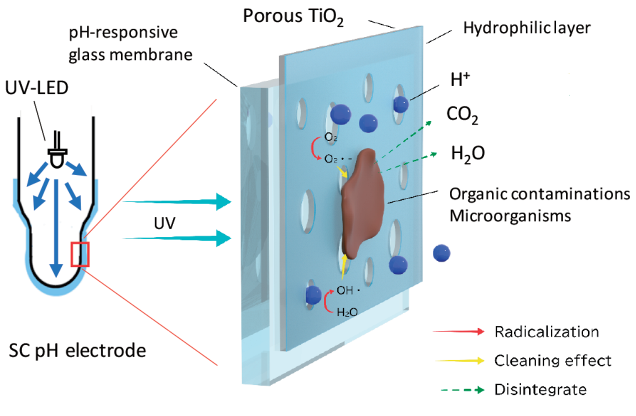

Figure 2 Schematic diagram of self-cleaning (SC) function.The rights to this illustration belong to HORIBA Advanced Techno,Co., Ltd.

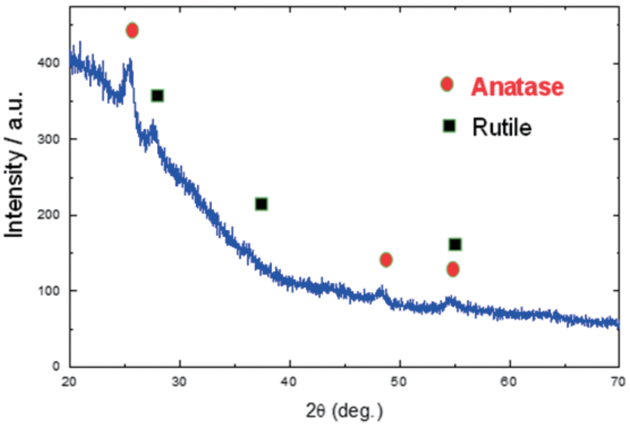

Figure 4 XRD Pattern of TiO$_2$ Coated Glass. Reprinted with permission from Ref. [1]. *Copyright 2018 EICA*

contamination[6]-[11]. The basic performance of the developed electrode was evaluated in terms of the asymmetric potential, the sensitivity, and the liquid junction potential by measuring the potential using the pH standard solutions.

Figure 2 shows a schematic diagram of the self-cleaning function of the electrode. The mechanism of the electrode is as follows. The surface of the pH response glass membrane was coated with porous TiO$_2$. UV light passed through the pH response glass membrane and irradiated TiO$_2$. Activated TiO$_2$ formed superoxide radical anions (O$_2^{\bullet -}$) and hydroxyl radicals (OH$^\bullet$) from oxygen (O$_2$) and water (H$_2$O) respectively. These active species decomposed organic matter. In addition, the photoinduced hydrophilic effect of photocatalyst washes away dirt, as this technology is used on the building exteriors. Hydrogen ions pass through the porous TiO$_2$ film and reach the pH response glass membrane.

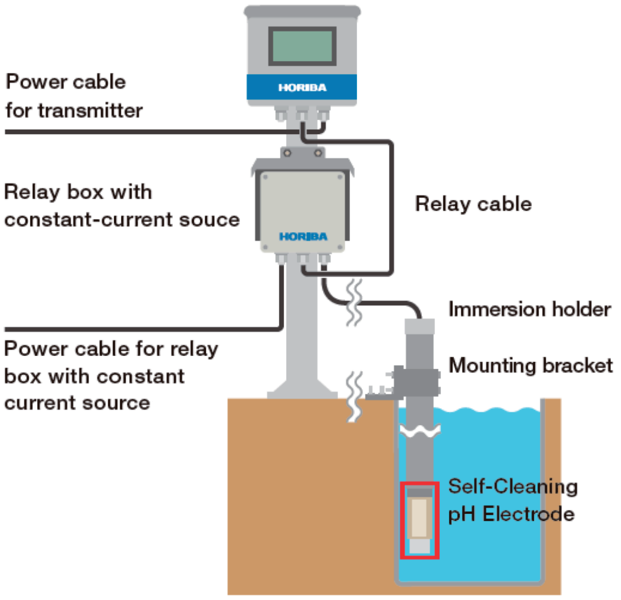

Figure 3 Schematic diagram of on-site installation (Immersion type). The rights to this illustration belong to HORIBA Advanced Techno, Co., Ltd.

Figure 3 shows a typical connection method from the pH meter to the electrode in this field test. Conventionally, the electrode cable was connected only to the transmitter. However, in the case of the self-cleaning pH electrode, a relay box with a constant current power supply was required to turn on the UV-LED. The anti-fouling effect was confirmed with the field test by immersing the electrodes continuously in a microbial treatment tank and in a raw water tank that are for domestic wastewater and are subject to the organic fouling.

Results and discussion

First, we checked that TiO$_2$, which was the photocatalyst, was formed as intended. TiO$_2$ was coated on commercially available glass plates using the sol-gel method. Figure 4 shows the result of XRD measurement on the coated surface. Diffraction patterns were observed including rutile-type and anatase-type. It was confirmed that the expected photocatalyst was formed as reported that the anatase-type TiO$_2$ was activated as a photocatalyst at wavelengths shorter than 388 nm. Next, the thickness of the TiO$_2$ film on the support tube was measured using the spectroscopic ellipsometer. The measurement point was set on the opposite side of the liquid junction through hole of the stem tube. Table 1 shows the results. The “roughness layer” in the table refers to the layer including surface irregularities. The average of the total value was 27.48 nm. Since the TiO$_2$ coating on the electrode contained a large amount of SiO$_2$, which was a component of the response glass membrane, the UV light emitted from

Table 1 Measurement of TiO$_2$ film thickness on stem tube using ellipsometer. Reprinted with permission from Ref.[9]. *Copyright 2024 Bunseki Kagaku.*

Sample number	1	2	3	average
Roughness layer (nm)	4.70	7.99	3.56	5.42
TiO$_2$ layer (nm)	23.86	19.99	22.33	22.06
Total (nm)	28.56	27.98	25.89	27.48

inside the stem tube passed through the pH response glass membrane and was irradiated onto the outer TiO_2 coating film. The UV intensity was measured using the UV irradiance meter (YK-35UV, manufactured by Kenis) showing that the UV irradiance near the liquid junction was approximately 2.0 $mWcm^{-2}$.

Next, eight electrodes were assembled as composite electrodes as shown in Figure 1 and their basic performance was evaluated[12]. Table 2 shows the results. As shown in Table 2, the self-cleaning pH composite electrode developed by the authors responded as nearly identical to the theoretical sensitivity, approximately 96% or higher, in the range between pH 4.01 and pH 9.18. The calibration range of the asymmetric potential is ±90 mV, and the liquid junction potential of the self-cleaning pH electrode was within approximately 6 mV (equivalent to 0.1 pH) although the gel-type internal liquids generally tend to generate liquid junction potentials. These results were comparable to those of commercially available products and were within a range that would not cause practical problems.

Field tests were conducted at more than 20 locations using these electrodes. The measurement results, out of these tests, are reported, which were conducted at a microbial treatment tank (an aeration tank) for domestic wastewater, an inflow special manhole at a sewage treatment plant, and a final discharge tank at an inorganic material manufacturing plant. These sites are heavily contaminated with organic matter, such as microorganisms and sludge, and manual cleaning are required for these sites once a month. Figure 5 shows the condition of the electrode during the implementation test at the site for 16 months. The current to the UV-LED for the test was set at the normal setting of 100 mA. The test began in December, and slight contamination was observed during the summer months of July to September. During the other periods, the self-cleaning pH electrodes maintained cleanliness with no contamination observed on the glass membrane or around the liquid junction. The performance of the electrodes was checked every two to three months. Figure 6 shows the change in the sensitivity over time calculated using the equation shown in *2 (the Nernst equation) with a pH standard solution. At six to nine months elapsed, which was the summer months, the sensitivity decreased to approximately 80%, but remained above 95% during other periods. The possible cause is the slight contamination on the electrodes in summer, as shown in Figure 5. When microbial activity is high in summer, it seems that the decomposition rate is slow compared to the contamination rate. It is desirable to increase the current.

In addition, during this 16-month period, the liquid junction potential of the reference electrode in each standard solution was maintained within ±3 mV, and no clogging

Table 2 Standard property of the Self-Cleaning pH electrodes. (n=8) Reprinted with permission from Ref.[9]. *Copyright 2024 Bunseki Kagaku.*

Asymmetry Potential (mV)	pH6.86*1	-24.1±4.1
	pH4.01	144.3±4.3
	pH9.18	-155.9±4.6
Sensitivity (%)*2	pH6.86-4.01	99.9±0.5
	pH6.86-9.18	96.0±0.1
	pH4.01-9.18	98.1±0.7
Liquid junction potential (mV)*3	pH6.86	3.9±1.2
	pH4.01	2.0±0.7
	pH9.18	1.5±0.7

*1 Asymmetry Potential

*2 Sensitivity was calculated by the following formula.

$$\text{Sensitivity (a - b) (\%)} = \frac{-100F(E_b - E_a)}{2.3026RT(pH_b - pH_a)}$$

E_a and E_b represent the electromotive forces generated in the respective test solutions a and b, with reference to the comparison electrode. Here, R denotes the universal gas constant (8.3145 $J \cdot K^{-1} \cdot mol^{-1}$), T is the absolute temperature (K), and F is the Faraday constant (96485 $C \cdot mol^{-1}$).

*3 Liquid junction potential was calculated by the following formula. Liquid junction potential(mV)=(Potential in each standard solution / mV) - (Potential in 3.33 mol L-1 KCl solution / mV)

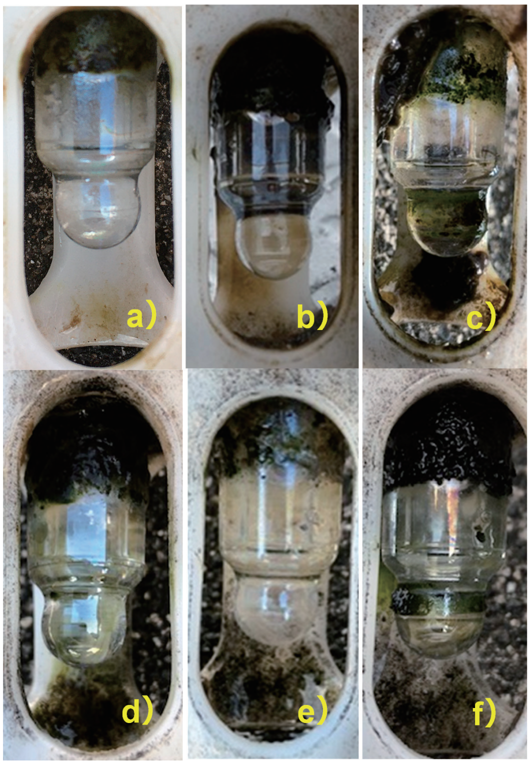

Figure 5 Photos of the change over time of the SC electrode in the microbial treatment tank : a) 5 months : b) 7 months : c) 9 months : d) 12 months : e) 14 months : f) 16 months. Reprinted with permission from Ref.[9]. *Copyright 2024 Bunseki Kagaku.*

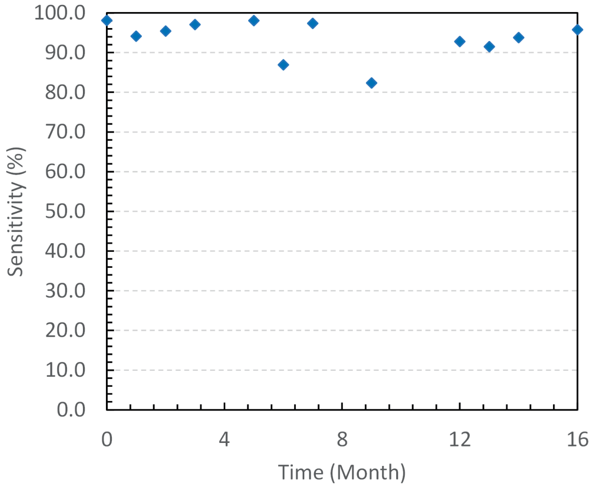

Figure 6 Change in sensitivity of Self-Cleaning pH electrode over time in microbial treatment tank. Reprinted with permission from Ref.[9]. *Copyright 2024 Bunseki Kagaku.*

occurred in the liquid junction. Although the KCl granules decreased gradually, some remained after 16 months. And the reference potential (potential difference in a 3.33 mol/L KCl solution between an Ag/AgCl electrode (#2565 of HORIBA Advanced Techno, Co., Ltd.) and the self-cleaning pH electrodes) maintained at 3 mV or less. These results suggest that the maintenance and calibration cycles can be extended.

In addition, it is confirmed that the life and performance of the reference electrode can be maintained for 16 months or more. Next, we report the results of continuous measurements at an inflow special manhole for domestic wastewater. This site is heavily contaminated with microorganisms and sludge as the same as the microbial treatment tank is, where the manual cleaning is required every two weeks. Figure 7 shows the condition of the self-cleaning pH electrodes by month. At this site, the self-cleaning pH electrodes under the continuous UV irradiation maintained cleanliness without any contamination on the pH response glass membrane or around the liquid junction that were coated with TiO_2 while the upper part of the stem tube was contaminated. Figure 8 shows the continuous measurement data for three months. The pH was stably measured at around 7 without any abnormal value. This electrode maintained the sensitivity of pH between 4.01 and 9.18 at approximately 98% even after three months. In addition, the measured value (asymmetry potential) of the pH 6.86 standard solution was pH 6.74. At this site, maintenance-free operation was achieved for more than six times longer than the conventional operations.

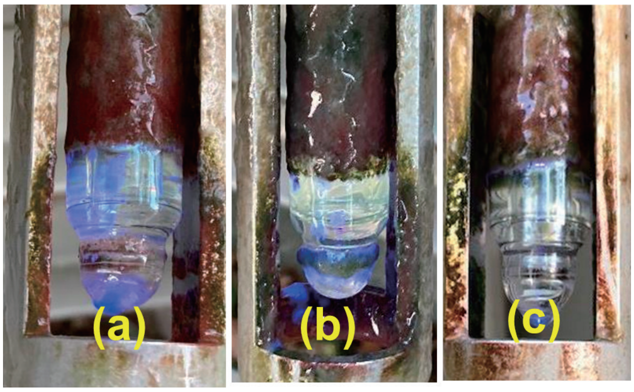

Figure 7 Results of continuous immersion tests in raw domestic wastewater tanks (a: 1 month, b: 2 months, c: 3 months)

Finally, the results of implementation tests are reported, which were conducted in a discharge tank at a chemical plant. The electrical conductivity of the tank was approximately 600 µS/cm, and the site was home to carp, resulting in a heavy microbial contamination on the electrodes. This site required manual cleaning every month. The continuous measurements were conducted immersing the self-cleaning pH electrodes set with the immersion holder as same as before. The test was conducted with the normal setting of the current to the UV-LED at 100 mA.

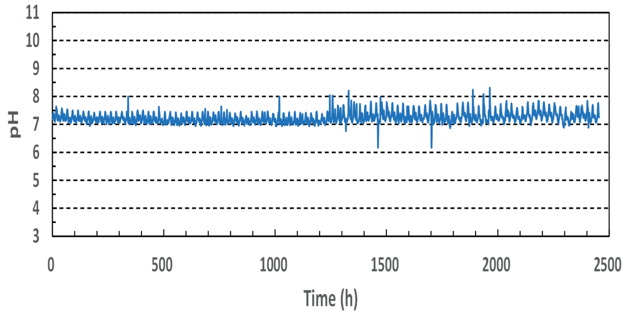

Figure 8 Continuous measurement data for raw domestic wastewater (inflow special manhole) Reprinted with permission from Ref.[8]. *Copyright 2023 Japan Sewage Association.*

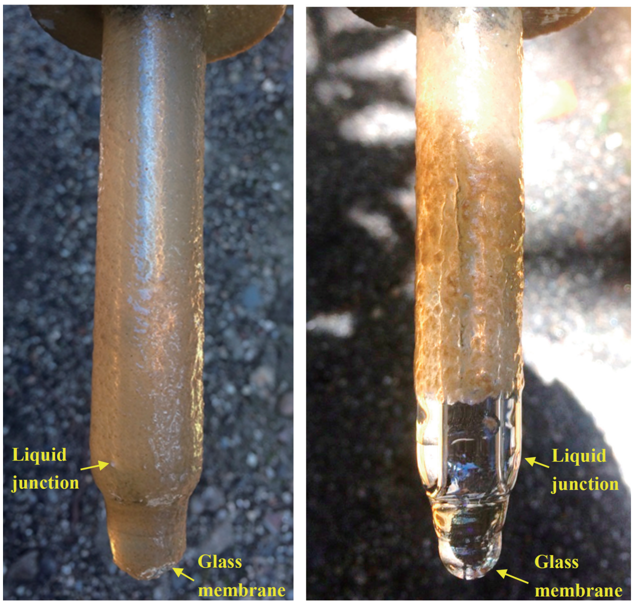

Figure 9 Change in sensitivity of Self-Cleanig pH electrode over time in microbial treatment tank. Reprinted with permission from Ref.[2]. *Copyright 2018 EICA.*

Figure 9 shows the photos comparing the conventional pH electrode with the self-cleaning pH electrode three months after the installation. The self-cleaning pH electrodes were coated three times with TiO_2 film before the test. At this site, the conventional pH electrode was covered with organic matter and biofilm. On the other hand, the self-cleaning pH electrode under the continuous UV irradiation maintained cleanliness without any contamination on the pH response glass or around the liquid junction[2].

Conclusion

In this paper, we have discussed the pH electrode designed to reduce the maintenance burden on users.
The self-cleaning pH electrode using TiO_2 photocatalyst demonstrated that TiO_2 photocatalyst could be applied to the pH glass electrode and that its basic performance was comparable to that of the conventional electrode. In addition, the maintenance-free operation is realized for a certain period of time with the anti-fouling effect in the implementation tests conducted in the sites where the continuous measurements are difficult due to the organic contamination such as microbial treatment tanks for domestic wastewater and return sludge tanks. Regarding the microbial treatment among these tests, it is possible to extend the calibration cycle up to approximately 16 times longer (maintenance frequency from once a month to once every 16 months). These results are expected to contribute significantly to the industry because the maintenance burden on users is greatly reduced. The electrode developed by the authors is applicable to sites with organic contamination but many issues remain unsolved such as anti-fouling to the inorganic contamination. In general, the pH electrode is considered as a matured device, but the authors will try to develop the pH electrode to satisfy the users because the authors believe that the pH electrode will have its potential.

Acknowledgment

We would like to express our sincere gratitude to Prof. Satoshi Kaneko (Mie University), Prof. Tadanori Hashimoto (Mie University), and other professors who provided guidance during this research, as well as to all the employees of our company who provided support.

* Editorial note: This content is based on HORIBA's investigation at the year of issue unless otherwise stated.

References

[1] L.A. Shiklomanov, John C. Rodda, World Water Resources at the Beginning of the Twenty-First Century, *Cambridge University Press*, 13 (2004)

[2] 西尾友志, 室賀樹興, 橋本忠範, 石原篤，EICA 環境システム計測制御学会, 23, 2/3, 69 (2018) (In Japanese)

[3] Y. Nishio, T. Muroga, T. Hashimoto, A. Ishihara: *ISA Analysis Division,* 2-(2), (2018)

[4] 西尾友志, 分析化学, 69, 7/8, 385 (2020) (In Japanese)

[5] 木下隆将, 伊東裕一, 西尾友志, 室賀樹興, EICA 環境システム計測制御学会, 25, 2/3, 59 (2020) (In Japanese)

[6] 西尾友志, 高味拓永, 橋本忠範, 石原篤, EICA 環境システム計測制御学会, 26, 2/3, 107 (2021) (In Japanese)

[7] 西尾友志, 橋本忠範, 月刊「計装」, 64, 9 (2021) (In Japanese)

[8] 西尾友志, 高味拓永, 橋本忠範, 石原篤, 日本下水道研究会，8，895 (2023) (In Japanese)

[9] 西尾友志, 髙味拓永, 橋本忠範, 石原篤，分析化学, 73, 4/5, 171 (2024) (In Japanese)

[10] 西尾友志，髙味拓永，e-Readout-014 Issued: June 4, 2024 (In Japanese)

[11] 髙味拓永，西尾友志，室賀樹興，橋本忠範，石原 篤，EICA環境システム計測制御学会，28, 2/3, 11 (2023) (In Japanese)

[12] JIS Z 8805 : 2011 pH 測定用ガラス電極 (In Japanese)

NISHIO Yuji

Advanced Technology Development Dept.,
Development Division,
HORIBA Advanced Techno, Co., Ltd.
Dr. Eng.

KOMI Takuhisa

Water Solutions R&D Dept.,
Development Division,
HORIBA Advanced Techno, Co., Ltd.