Product Introduction

Third Stage of the LAQUA Series!! LAQUA Series: Portable Water Quality Analysis Meters

Hisashi YAMANOUCHI

Manabu SHIBATA

As the new third stage of the LAQUA Series, the HORIBA Group has developed durable LAQUAact portable water quality analysis meters. Conventional pH meters have low alcohol resistance, and could not be used in places such as food factories, where they would need to be disinfected. There was also the problem that the pH electrodes had a short life time in hydrofluoric acid and alkali samples that dissolve pH responsive glass membrane. To solve these issues, HORIBA developed a pH meter that uses a polycarbonate chassis material with high resistance to alcohol and new pH responsive glass membrane with a strong frame structure containing rare earth elements. As a result, we were able to achieve a portable pH meter with higher durability against physical impact and improved chemical resistance compared to conventional models, and long-life time of pH electrodes for hydrofluoric acid and alkali solutions. This paper introduces these new products and the features and applications of pH electrode for low conductivity samples.

Introduction

The HORIBA Group developed the first pH meter made in Japan, and has maintained its top share of the pH meter market for 60 years. HORIBA has integrated the latest electronics with its proprietary sensing technology to develop accurate and highly reliable pH measurement technology. With the concept of being the best partner for water quality measurement, the water quality measurement brand LAQUA was launched in 2011. For the first stage of the series, HORIBA developed a table-top water quality analysis meter with a touch panel to be used in laboratorys. The second stage was the LAQUAtwin compact water quality meter that can easily measure pH anywhere. The third stage is the LAQUAact portable water quality analysis meter that can be used in both laboratorys and on site at production lines.

The main features of this device are high durability against physical impact and improved chemical durability. The portable pH meter has the advantages of having a shape that doesnit need much space and the convenience of portability, and can be used in laboratorys and on site at production lines. Conventional pH meters cannot be used in places where they have to be disinfected using alcohol, like food factories, because they use materials with low alcohol resistance (such as acrylonitrile butadiene styrene (ABS) and acrylic plastic) in their chassis materials and display windows. To solve this problem, the LAQUAact meter uses a new material with high alcohol resistance in its chassis material[1]. HORIBA also pursued durability for its pH electrodes, which are the most important of highly reliable pH measurement. Over the years, the HORIBA Group has developed pH electrodes with high durability against physical impact. The ToupH ('tough') Series pH electrode dramatically improved durability due to the development of thicker responsive glass membranes. In 2011, HORIBA developed pH electrodes with dome-shaped responsive glass membranes, which had improved strength in all directions. The LAQUAact line-up has pH electrodes whose new responsive glass membranes have improved chemical durability to hydrofluoric acid and alkali applications, and another LAQUAact pH electrode enable us to obtain quick response time of low conductivity samples such as tap water (Figure 1).

The life time of the pH electrode is short when used exposed to hydrofluoric acid and alkali solutions. To solve this issue, HORIBA developed responsive glass

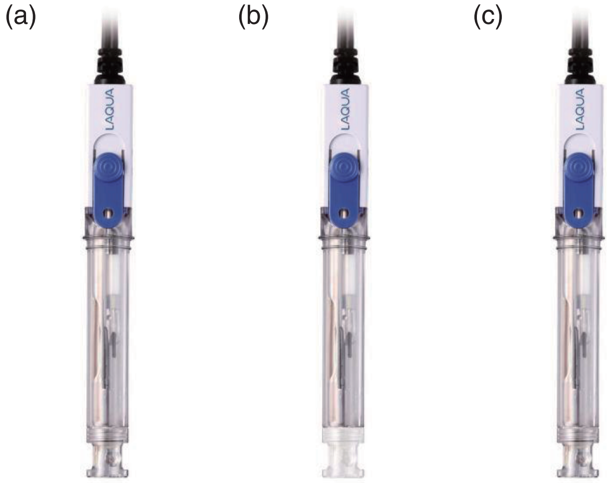

Figure 1 Appearance of new electrodes
(a) 9631-10D, (b) 9632-10D, (c) 9630-10D

membranes with strong glass frame structures due to the addition of rare earth elements in glass composition. It takes time for the measurement value to stabilize in low conductivity sample by use of conventional pH electrodes. The main reasons why the value doesn sample ment value toare because crock on the surface of the responsive glass membrane disturbs the electrode reactions and the diffusion potentials*2 of the ions in the hydration layer*1 doesn't stabilize. HORIBA developed new responsive glass membrane with higher purity of glass composition than conventional pH electrodes. New electrode enables us to obtain quick response time due to control the diffusion of ions in the hydration layer. This paper will start by explaining the fundamentals of pH measurement.

*1: Hydration layer: Area where glass compositions are hydrated, between the sample water and glass membrane.

*2: Diffusion potential: Potential that arises from the diffusion of ions between solutions when 2 different solutions come in contact

Fundamentals of Measuring pH

As shown in Figure 2, the pH in a solution is determined by the difference of cell voltage between two electrodes: the glass pH electrode and the reference electrode. The potential of the glass membrane in the glass pH electrode shifts corresponding with a change in pH of the sample solution. The reference electrode always generates the constant potential, even if the pH of the sample solution changes. When these two electrodes and a temperature compensation electrode are incorporated into a single unit, it is generally called a "3-in-1 pH electrode". Below, we will use "pH electrode" as a simplified term.

The pH meter measures the difference cell voltage above, and the pH value is calculated according to Equation 1

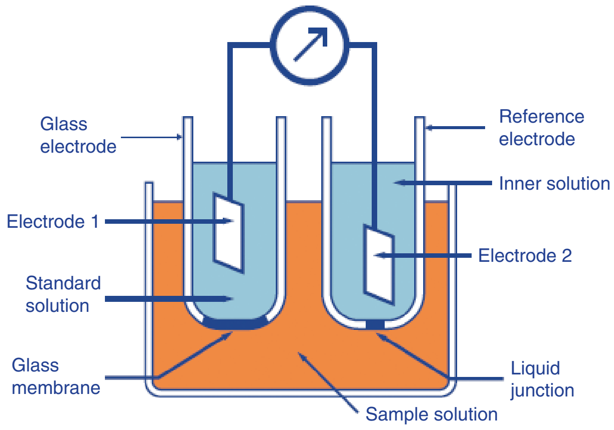

Figure 2 Diagram of pH measurement

based on the solution's temperature[2].

$$\mathrm{pH\,(X)} - \mathrm{pH\,(S)} = \frac{E_X - E_S}{2.3026RT/F} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

In this equation, pH(X) is the pH value of the sample, pH(S) is the pH value of the standard solution, E_X is the difference cell voltage measured in the sample, E_S is the difference cell voltage measured in the standard solution, R is the gas constant, T is the absolute temperature, and F is the Faraday constant. The glass membrane in the glass pH electrode has a high impedance of approximately 10^8 Ω, so an exclusive operational amplifier that can accurately measure the difference cell voltage is needed. The pH meter is composed of this operational amplifier, control circuitry, and the display area.

LAQUAact-Series pH Electrodes

This section will introduce the features and applications of the pH electrode for hydrofluoric acid, alkali, and low conductivity sample.

pH Electrode for Hydrofluoric Acid (Model 9631-10D)
The hydrofluoric acid used in glass etching solution and metal pre-processing solution dissolve glass, so the pH electrodes have shorter life time. The hexafluorosilicic acid (H_2SiF_6) that is produced by the reaction in Equation 2 is adsorbed on the surface of the responsive glass membrane and disturbs the electrode reactions, which decrease measurement reproducibility.

$$SiO_2 + 6HF \rightleftarrows H_2SiF_6 + 2H_2O \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

To solve this problem, HORIBA developed a responsive glass membrane that is highly chemical durability to hydrofluoric acid. Yttrium, which has a small ion radius and strong electron affinity, is filled into the mesh structure of the glass frame, which strengthens the glass frame and improves chemical durability[3]. Figure 3 shows the results of comparing the life time of a pH electrode for hydrofluoric acid and a standard pH electrode (9615-10D), when these electrodes are immersed in 1% hydrofluoric acid at 25°C. The horizontal axis denotes the immersion time in the 1% hydrofluoric acid, and the vertical axis denotes electrode sensitivity. Electrode sensitivity expresses the ratio of the actual measurement value to the theoretical value which the difference cell voltage shifts with a change in 1 pH of the sample. The theoretical values are calculated based on Equation 3.

$$\alpha = 2.3026RT/F \quad \cdots\cdots (3)$$

The actual measurement value was determined by difference cell voltages which are generated from potentials in standard solutions. The standard pH electrode was broken in approximately 350 minutes. However, the pH electrode for hydrofluoric acid was not broken even after 1,000 minutes, and there was no change in electrode sensitivity. The pH electrode for hydrofluoric acid has approximately 3 times longer life time than the standard pH electrode.

Next, we will introduce the measurements of a hydrofluoric acid. First, to remove the hexafluorosilicic acid produced in Equation 2, we wiped the responsive glass membrane using a soft cloth with ethanol on it. Second, we immersed the pH electrode in the sample for a few minutes, allowed the responsive glass membrane to react with hydrofluoric acid and stabilized the surface condition. Finally, we calibrated the pH electrode in the standard pH solutions, and started measurements. We repeated measurements of 1% hydrofluoric acid by 40 measurments. The results showed that the average pH value of it was 2.58, with a standard deviation of 0.042 pH, which was a good level of reproducibility. Also, to compare the measurement values with the calculation value, we used Equation 4 to determine the activity (a_{H+}) and pH value of 1% hydrofluoric acid .

$$pH = -\log a_{H+} \qquad a_{H+} = C_{H+} \times \gamma_{H+} \quad \cdots\cdots (4)$$

In this equation, C_{H+} is the hydrogen ion concentration (mol dm^{-3}), and γ_{H+} is the activity coefficient. We found the hydrogen ion concentration based on the dissociation constant of hydrofluoric acid (pKa=6.7×10^{-4}), and activity coefficient of 1% hydrofluoric acid (γ_{H+}=0.0249)[4]. As a result, pH value of 1% hydrofluoric acid was 2.56, and showed a good level of matching with the measurement value. Based on these results, this electrode eneble us to stable measurements of hydrofluoric acid over the long term.

pH Electrode for Alkali (Model 9632-10D)

The alkali solution used in plating solution also dissolves glass membrane and shortens the life time of the pH electrode. To solve this problem, HORIBA developed a new responsive membrane that contains scandium. Similar to yttrium, scandium strengthens the glass frame and improves the chemical durability to alkali[3]. In addition, this element also enable to reduces alkali errors that occur when measurements of strong alkali solution. This is possible to cause gaps in the glass frame due to addition of the small ion radius of scandium into it, and other substances such as lanthanum, which have large ion radius, fill the gaps. As a result, this controls the penetration of alkali metal ions into the glass frame, and reduces alkali errors.

pH electrodes that use pH responsive glass membranes containing scandium have approximately 5 times the electrode life time of standard pH electrodes. Figure 4 shows the results of comparing the life time of a pH electrode for alkali and a standard pH electrode, in a 0.1

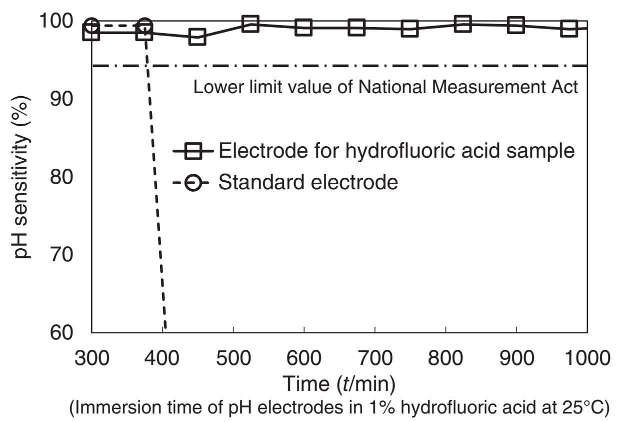

Figure 3 Comparison of lifetime of electrode with 9631-10D and 9615-10D

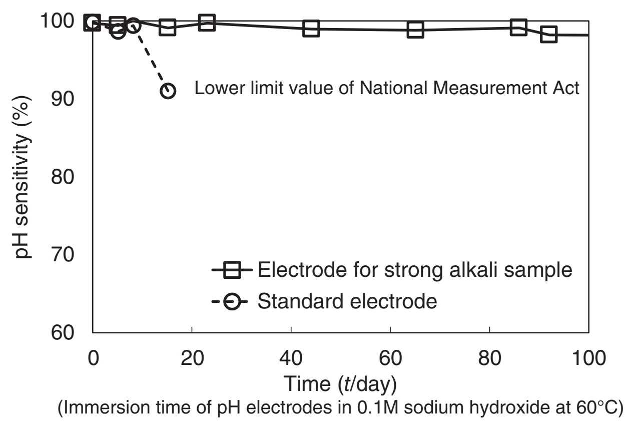

Figure 4 Comparison of lifetime of electrode with 9632-10D and 9615-10D

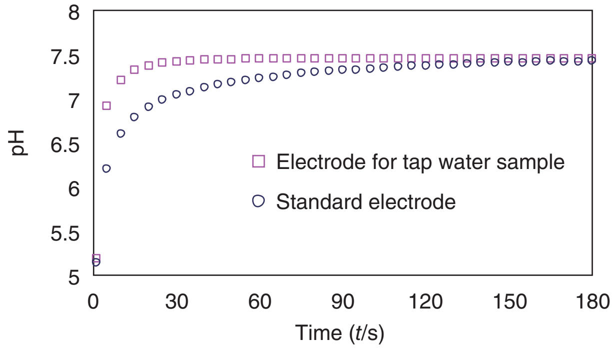

Figure 5 Comparison of response time of electrode with 9630-10D and 9615-10D

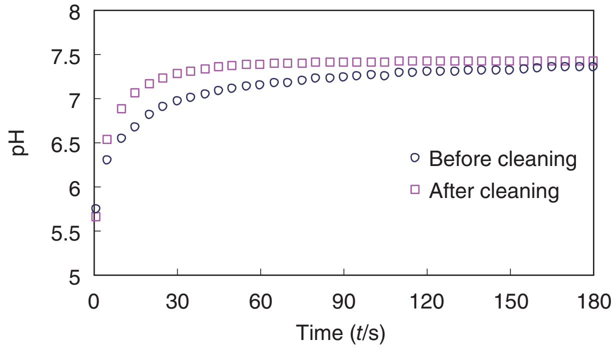

Figure 6 Comparison of responsetime of electrode with 9630-10D and 9615-10D

mol dm^{-3} NaOH solution at 60°C. The electrode sensitivity of the standard pH electrode degraded after approximately 15 days. Even after measurements for approximately 3 months, there was no change in electrode sensitivity of the pH electrode for alkali. We calculated the electrode sensitivity based on measurements of standard boric acid solution and standard phosphoric acid solution.

pH Electrode for Low Conductivity Sample (Model 9630-10D)

Tap water has low electrical conductivity and low buffer capacity. With this type of sample, it takes time to stabilize the ion diffusion in hydration layer of the responsive glass membrane. In addition, if metal ions enter the responsive glass membrane during the manufacturing process, the diffusion of these ions decrease in the response speed. To solve this issue, HORIBA improved the purity of the glass composition in the responsive glass membrane. Also, a cleaning solution for the pH electrodes (Type 230, cleaning solution A, 0.1 mol dm^{-3} NH_4FHF, cleaning solution B 0.01 mol dm^{-3} HCl) renews the responsive membrane surface, even if crock on the surface of the responsive glass membrane disturbs the electrode reactions.

Figure 5 shows the results of comparing the tap water response of the pH electrode for low conductivity sample (9630-10D) and a standard pH electrode. The response time of the pH electrode for low conductivity sample is shorter than that of the standard pH electrode. Figure 6 shows the change of response time in tap water before and after cleaning with a Type 230 cleaning solution to a pH electrode that had been used for about 3 months. Cleaning the electrode improves response time to like-new performance.

LAQUAact Portable Water Quality Analysis Meters

LAQUAact meters use a polycarbonate material with high alcohol resistance in the chassis and the display window, and use polyethylene terephthalate (PET) in the operating area (Figure 7a). These materials allow the unit to be spray-cleaned with alcohol, which means that they can be used on food factory plant floors, where disinfecting is required. Other disinfectants besides alcohol, such as sodium hypochlorite, can also be used, which increases the options for disinfecting methods. Also, these materials have high chemical durability, and the durability doesn't decrease even when immersed in acid with a pH of 1 or

(a)

(b)

Figure 7 Appearance of LAQUAact (pH meter)

Before cleaning   After cleaning

Figure 8 Appearance of LAQUAact (pH meter) with dipping into oil

an alkali solution with a pH of 13.

Furthermore, it consists of stain-resistant body. After the unit is immersed in oil, if it is cleaned with alcohol, it can be renewed to like-new condition without any oil sticking to it (Figure 8).

In addition, the instrument has been enhanced with features which a table-top water quality analysis has: e.g. a function for displaying 2 components simultaneously, 5 point calibration for pH and ions, and internal data memory of 1000 data items. When used with these functions, and combined with the stand accessory (Figure 7b), this meter can measure 2 components at the same time and make calibrations based on the sample pH, just like conventional table-top models.

Conclusion

The HORIBA Group developed the durable LAQUAact water quality analysis meter. LAQUAact meters can be used in any situation to measure pH with high reliability and easy convenience. Since the birth of the LAQUA brand in 2011, unique products have been developed to meet users' needs. As a result, the LAQUA brand has steadily been penetrating the market. In the future, HORIBA will pursue pH measurement technology with even higher reliability, and will continue to rise to the challenge of developing technological innovations that make HORIBA the best partner for application. The HORIBA Group will continue to provide technology with the aim of contributing to a safe, healthy, and abundant life.

References

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Hisashi YAMANOUCHI
Liquid and Water Quality R&D Dept.
Application R&D Center
Research & Development Division
HORIBA, Ltd.

Manabu SHIBATA
Liquid and Water Quality R&D Dept.
Application R&D Center
Research & Development Division
HORIBA, Ltd.
Ph. D