

Analysis and Measurement Technologies that Contribute to the Formation of a Water Recycling Society

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In recent years, the pattern of water resources has changed significantly. Securing water for daily life as the population increases and for industrial use as industry develops have become major social issues. However, the water that exists in rivers, lakes and ponds that are easily accessible to people accounts for only about 0.01% of the water on Earth, and this limited water resource is reused by purifying and circulating it. This paper describes the changes and issues in water resources, and the measurement technologies that contribute to a water-recycling society.

Introduction

Approximately two-thirds of the earth is covered with water, but only about 0.01% of Earth's water is available for human use. This limited resource is used for drinking water, industrial water, and irrigation water in the water cycle. However, population growth and climate change are causing imbalances in the supply of water resources.

According to “the United Nations World Population Prospects 1960-2060, revised in 2015”, the world population was approximately 7.35 billion in 2015 and is projected to reach approximately 9.73 billion by 2050. According to the Organization for Economic Co-operation and Development (OECD) “Environmental Outlook to 2050 (2012)”, water demand is expected to increase by 55% between 2000 and 2050, mainly due to increases in industrial water use in manufacturing (+400%), in power generation (+140%), and in water for daily life (+30%). By 2050, the population living in river basins and facing severe water shortages could reach 3.9 billion (more than 40% of the world's population). (Figure 1)

The amount of water available as a water resource is constantly changing due to variability in precipitation. For this reason, climate change caused by global warming, which is believed to be causing extreme weather such as heavy rains and droughts, has a significant impact on the amount of water available for use. According to the Centre for Research on the Epidemiology of Disasters (CRED), floods and droughts are occurring frequently around the world. In 2015, there were 152 national-level floods and 32 national-level droughts, affecting approximately 30 million people and 50 million people, respectively.

Measurement technologies used in a water cycle society

People use limited water resources for drinking, industrial water, and irrigation, and after purification, discharge it into rivers and oceans, forming a water cycle. In order to produce water for specific purposes, it is necessary to accurately measure the quality of raw water and appropriately treat it. For example, in order to produce ultrapure water used in semiconductor manufacturing processes, the pH, hardness, electrical conductivity, turbidity, and other properties of the raw water are continuously monitored. At the point of use, the electrical resistivity of the

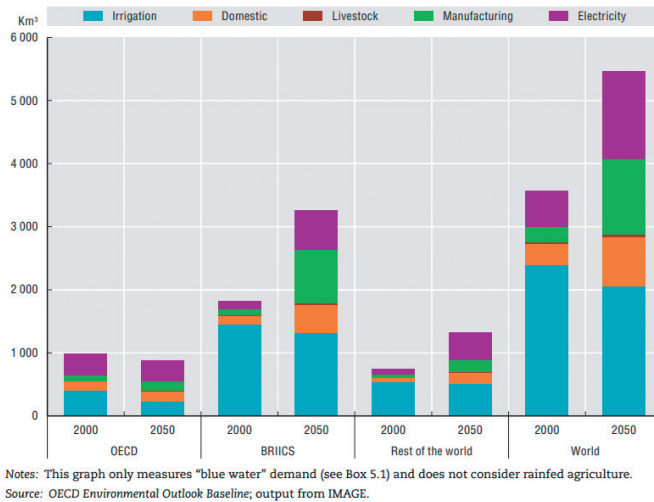


Figure 1 OECD's 2012 graph of projected global water demand to 2050

water must always be 18.20 MΩ·cm or higher, compared to the theoretical resistivity of the pure water, which is 18.24 MΩ·cm. Therefore, continuous monitoring of the electrical resistivity is used to ensure the water quality. In addition, with advances in semiconductor technologies, higher accuracy is required year by year as the water quality standards required for the ultrapure water. For example, with the miniaturization of semiconductors, it is necessary to measure even finer particle sizes. Wastewater generated in the semiconductor manufacturing process may contain hydrofluoric acid in the inorganic wastewater line. If discharged directly into rivers, it cannot be naturally purified, leading to environmental pollution and stagnation of the water cycle. Calcium chemicals are added to reduce the concentration of the hydrofluoric acid. To properly carry out this treatment, the concentration of the fluoride ions in the wastewater must be measured to determine the amount of the calcium chemicals to be added. Measuring the calcium concentration also helps to prevent excessive addition of the chemicals. After that, biological treatment improves the water quality to a level that can be naturally purified, and then the water is discharged into rivers and the ocean.

On-site industrial water quality meters, such as the H-1 series manufactured by HORIBA Advanced Techno Co., Ltd., are used for the water quality management described above (Figure 2). This measuring device is a field-installable water quality meter that can measure all the parameters necessary for comprehensive water quality measurement and management, and is used not only in the semiconductor industry but also for water quality management in water supply and sewage systems. It is used not only in the semiconductor industry, but also for water quality management in water supply and sewage systems. In addition, portable pH and water quality analyzers such as the WQ-300 series are used for water quality management in locations where installation is difficult and in rivers (Figure 3). This analyzer enables immediate measurement on site, supporting water quality management at any location.

As described above, water quality measurement is necessary throughout the water cycle and supports it globally. On the other hand, measurement technologies that contribute to food safety and security are also in demand. The following section introduces measurement technologies necessary for hygiene management in food processes.



Figure 2 On-site industrial water quality meters, H-1 series
<https://www.horiba.com/jpn/water-liquid/products/se-ries/h-1-series-field-installation-type/>



Figure 3 Portable pH and water quality analyzers WQ-300 series
<https://www.horiba.com/jpn/water-quality/handheld-meters/>

Residual chlorine concentration monitor using diamond electrodes UP-400CL

Aim of developing a residual chlorine concentration monitor and on-site needs

Food hygiene management in food processing plants and related facilities is required to be more stringent under the international HACCP (Hazard Analysis and Critical Control Point) system^{*1}. For example, in the process control of cut vegetable washing, the type and amount of vegetables, the temperature and pH of the washing solution, and the residual chlorine concentration must be recorded. Among these parameters, the concentration of residual chlorine decreases during washing, so it is necessary to frequently sample the washing solution to perform measurement and recording using the colorimetric method or the test paper, and to adjust the concentration as necessary. This requires considerable labor, and there is also concern about measurement errors, measurement omissions, and recording mistakes by workers. Furthermore, the current manual operations are not suitable for the rapid adoption of IoT in process control. As a means of overcoming these issues, we have developed the Residual Chlorine Concentration Monitor (UP-400CL), which can automate measurement tasks and enable data communication. We believe that this monitor contributes to food safety and security by not only improving the on-site environment, but also helping to prevent food poisoning and enhance food taste. Figure 4 shows the photo and the configuration of the residual chlorine concentration monitor.

This monitor is the world's first^{*2} residual chlorine concentration monitor designed to perform measurement during vegetable washing by using a diamond electrode. Since the main unit is compact and waterproof with a built-in pump, measuring 125 mm wide × 125 mm deep × 100 mm high, just installing the monitor near the washing tank enables the measurement. The residual chlorine concentration can be also checked in real time on the screen of the monitor. In addition, data can be stored on an SD card and transmitted to an external device.

*1 Refer to the Ministry of Health, Labour and Welfare (Japan) website.
https://www.mhlw.go.jp/stf/seisakunitsuite/bunya/kenkou_iryuu/shokuhin/haccp/index.html

*2 According to our research in August 2022.

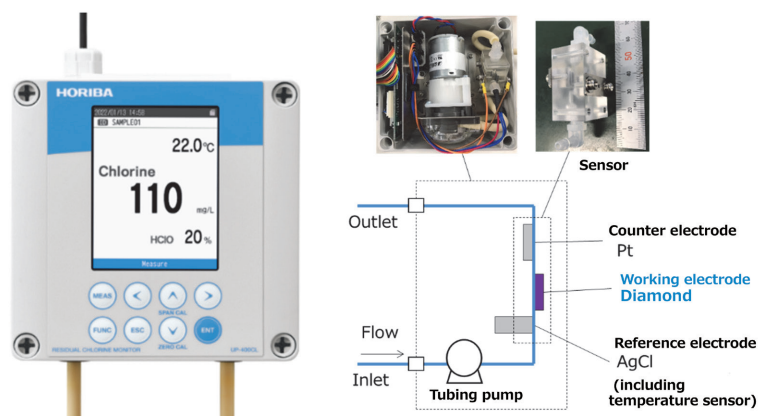


Figure 4 Photo and device configuration of residual chlorine concentration monitor.



Figure 5 Example of residual chlorine concentration monitor operation at a vegetable processing factory.

Core technology that enables measurement even during food washing

The polarography method using platinum or gold electrodes has been used for continuous measurement of residual chlorine. However, it is difficult to accurately measure the residual chlorine concentration during the vegetable washing.

This is because the reaction on the electrode surface is inhibited by organic matter eluting from the vegetables, causing the indicated value to drop rapidly. Therefore, we adopted a boron-doped diamond electrode (BDD: Boron-Doped Diamond)^[1] developed by professor Yasuaki Einaga of Keio University and developed a unique measurement sequence^[2] that is less susceptible to the effects of organic matter.

Compared to conventional electrode materials, BDD has a wide potential window, low noise, and high durability. Taking advantage of these characteristics, we have developed new technologies, such as a powerful electrolytic cleaning method to remove organic contaminants from the electrode, and a new measurement method capable of measuring both hypochlorous acid and hypochlorite ions with reduced influence from pH. In addition, we have developed a unique measurement sequence that reduces the influence of organic matter by applying a negative voltage immediately before measurement to remove negatively charged anionic organic matter from the electrode surface and then measuring the hypochlorous acid ion concentration immediately after (this technology is patent pending).

The function of this product is realized through these measurement methods and flow control of the pump built into the monitor.

Example of use in cut vegetable washing

Figure 5 shows an example of use in a cut vegetable washing line^{*3}. The monitor is installed next to the washing line and automatically samples the washing liquid through a stainless steel filter to prevent vegetable residues from entering. This allows the concentration of the residual chlorine to be checked in real time during washing. In addition, pH and liquid temperature are measured simultaneously when necessary. The data is stored in the cloud via a separately installed gateway, enabling monitoring on-site or remotely via tablets, PCs, and other devices.

Figure 6 shows the concentration measurement and its control during vegetable washing. By pre-setting operational limits and acceptable limits, alerts are triggered before these values fall below the limits, enabling appropriate process control. Furthermore, in the event that the measured values fall below the acceptable limits, alerts can be notified with warning lights or emails.

*3 <https://www.horiba.com/jpn/water-liquid/products/detail/action/show/Product/up-400cl-5075/>

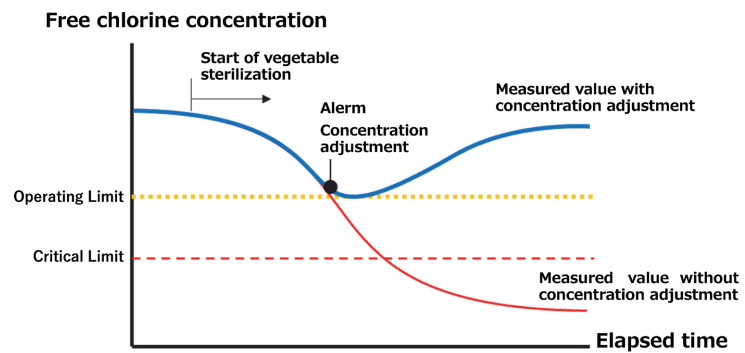


Figure 6 Image of concentration measurement and control during vegetable washing

Future challenges and prospects

Caution is required when the measurement method is switched from the conventional colorimetric method to the monitor, as the control values may not match. This is because the monitor measures free residual chlorine, whereas the colorimetric method measures total residual chlorine, which includes both free and combined residual chlorine. However, from the perspective of sterilization effectiveness, which should be the appropriate control indicator, the sterilizing power of combined residual chlorine is said to be less than one-tenth that of free residual chlorine. Accordingly, relying on colorimetric values when the concentration of the combined residual chlorine is increased may result in a significant and unintended reduction in disinfection performance. This concern stems from the previous lack of analytical method for continuously measuring the free chlorine during the vegetable washing, but the introduction of this monitor may change management practices in the future.

This monitor can be easily installed in washing tanks used for vegetable cleaning or in washing liquid supply tanks. It also supports SD card data storage and communication functions. Therefore, it is expected to play a key role in the IoT-based hygiene management and in improving on-site working environments in the future. Although this paper focuses on the washing of cut vegetables, the technology is also applicable to washing eggs and fish. In the future, since real-time measurement and automatic recording are possible, the measured concentration of residual chlorine could be considered as a monitoring item for CCP (Critical Control Point). We hope to contribute further to the food safety and security by developing technologies that meet user needs.

Conclusion

Appropriate water treatment is necessary for the efficient and effective use of limited water resources. This requires accurate and stable measurement of water quality. However, maintaining accurate measurements requires sensor maintenance, which is a significant burden for users. In order to reduce the burden of the sensor maintenance, it will be important to develop the sensors that are not affected by contamination and are highly durable. In addition, contactless measurement will be also the important technology that is conducted without any contact with liquids in the first place. Moreover, the measurement method with the multivariate analysis using multi-point measurements and multiple component measurements will be also important technologies to solve problems in measurement samples and in measurement environments that were difficult to be measured with conventional methods. We hope to contribute to the water cycle society, to support the prosperity of humankind, and to contribute to the industrial develop-

ment through the development of the liquid measurement technologies.

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

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