Selected Article

Introduction of the New H-1 Series Water Quality Instruments
工業用水質計H-1シリーズの特長

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We have developed the H-1 Series to provide a comprehensive water quality instrumentation product offering for a wide variety of applications. The measurement parameters include the 9 most commonly required parameters for monitoring water quality (pH, DO, ORP, F-, Conductivity, Resistively, MLSS, Turbidity, Residual Chlorine). Unique features incorporated in the design are a new glass membrane for pH, a MLSS sensor with high resistance to fouling, a low drift turbidity sensor with transmitted and scattered light detection at a 90° scattering angle, a changeable cathode electrode for residual chlorine analysis and a special purpose electrode for electrochemical cleaning. We targeted sensor enhancements to meet user demands for easy maintenance and longer sensor life as well as transmitter EMC improvements with wider temperature operating ranges and a more rugged environmental design. The H-1 Series instruments are available now.
We will introduce the features and characteristics of the H-1 series in detail.

工業用水質計H-1シリーズは，水質指標の基本9項目(pH／溶存酸素／酸化還元電位／フッ化物イオン濃度／電気伝導率／電気抵抗率／MLSS／濁度／遊離残留塩素)を測定対象としてフルラインアップした。新開発の応答ガラスを採用したpH電極，チップ交換と再生使用を両立した溶存酸素センサ，汚れが付着し難いMLSSセンサ，独自の2光源透過90度散乱法を採用した低ドリフトの濁度センサ，チップ交換式カソード極と電気化学洗浄専用極を備えた遊離残留塩素センサ，ノイズ耐性や環境性能を向上させた変換器など，センサの寿命改善やメンテナンス性の向上を目指した。各機種に搭載したHORIBAの独自性のある特長及びその効果について紹介する。

Introduction

With such importance being placed on conserving the global environment, we must remember that the conservation of the water environment is essential for the health and safety of human beings as well as meeting environmental regulations and industry profitability. Japan and some European countries introduced drainage regulations in the 1970s as part of efforts to combat environmental pollution. There has been an increase in management of water resources even on a private level following the development of industry over the past few years within Asia, particularly in countries such as China and India. Water management covers everything from industrial drainage to natural resources such as surface water and underground water, all as part of maintaining a safe level of water resources. This has led to a subsequent increase in demand for water quality -related environmental issues in each and every country. With these circumstances in mind, there is growing demand in the field of water quality measurement devices, especially those that are maintenance-free with long-term stable operation that comply with international standards such as IEC standards and RoHS regulations. These devices should also have a high level of reliability and minimal impact on the natural environment.
HORIBA and Horiba Advanced Techno have pooled their extensive experience and technical resources together for the release of the H-1 Series of industrial water quality meters. This is the first product series of the “Process &

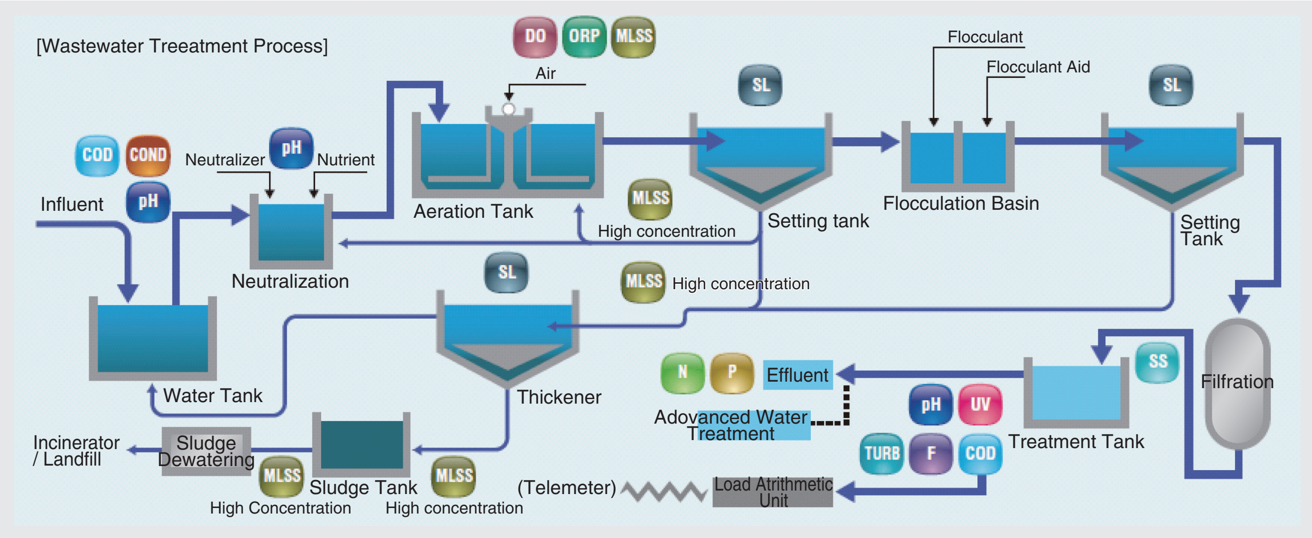


Figure 1 Example Usage of Water Quality Instruments in Wastewater Treatment Process

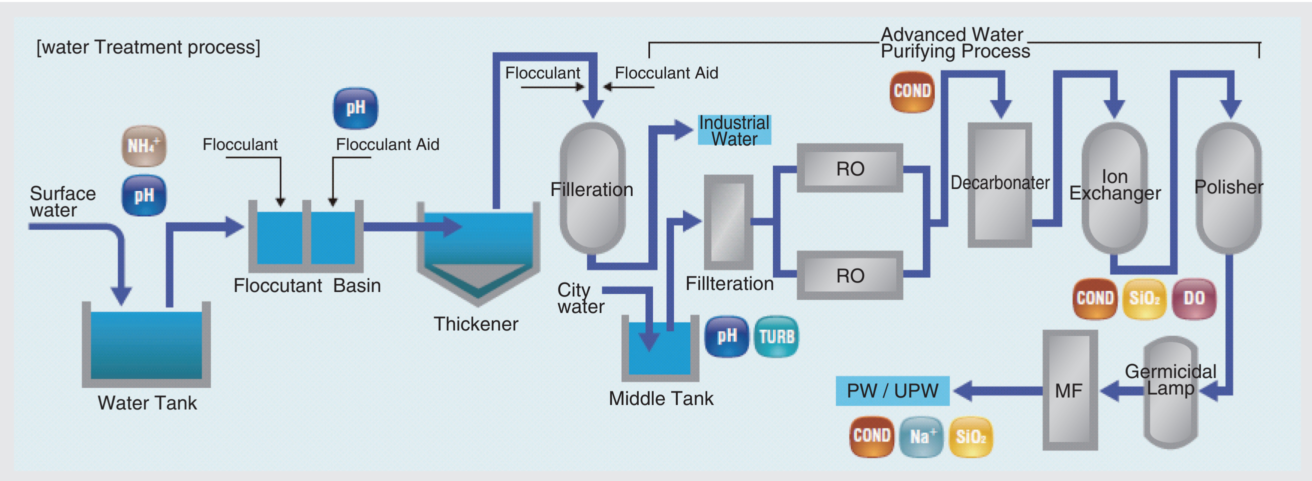


Figure 2 Example Usage of Water Quality Instruments in Wastewater Treatment Process

Environment" Division consisting of 16 models covering nine different parameters (pH, dissolved oxygen, oxidation-reduction potential, fluoride ion, electrical conductivity, electrical resistance, MLSS, turbidity, free residual chlorine). The H-1 Series has been developed by implementing the common concepts of tough, intelligence and ease of maintenance for all components - sensors, transmitters and cleaners for sensors - at all new levels. This document outlines in detail the technical features of the H-1 Series.

Overview of the H-1 Series: Analytical Instruments for Water Quality

Water treatment for drinking water, ultrapure water and waste water treatment processing of industrial drainage at sewage treatment plants requires constant monitoring of each water quality parameter listed previously. Treatment processes operated and managed appropriately ensures that draining complies with regulations. Figure 1 outlines the use of water quality meters in waste water treatment processing while Figure 2 outlines the use of water quality meters in water treatment processing. The measurement sensors of industrial water quality meters are prone to contamination and damage as they are often immersed in liquids that contain organic substances or chemicals for extended periods of time. While maintenance of these instruments is conducted daily, up to 60% of the maintenance time may be used to clean the measurement sensor or to replace the sensor itself. To reduce the time required for maintenance, instruments require sensors that do not become contaminated easily. Development of the H-1 Series thus focused on reducing the impact of contamination on the sensors as well as improving durability of the sensor itself.
Six models come with a 2-wire transmitter , while 10 come with a 4-wire transmitter and universal voltage power supply. Models with a 4-wire converter come standard with a transmission output (4 to 20 mA) for main

Figure 3 Extanal Appearece of the Transmitter

measurement items and water temperature as well as a digital communications output (RS-485). Figure 3 is an overview of the transmitter , while Figure 4 and 5 show an outline of the system design. The transmitter case is a tough aluminum die-cast version that meets protection class IP65 classification of water-proof and dust-proof. The instrument is designed with environmental impact in mind. It complies with IEC Standards for EMI and RoHS regulations for hazardous materials. Convenience for users has been improved as each sensor is equipped with a comprehensive self-diagnosis function. For example, the pH converter can automatically identify standard solutions, the instrument can be automatically calibrated with a single button, calibration history can be displayed and there is an output function to control pH levels.

HORIBA's Quest for Innovation

HORIBA has conducted development for products based on the concept of "Only one" as one of its keywords. Innovation has been sought as part of the H-1 Series,with

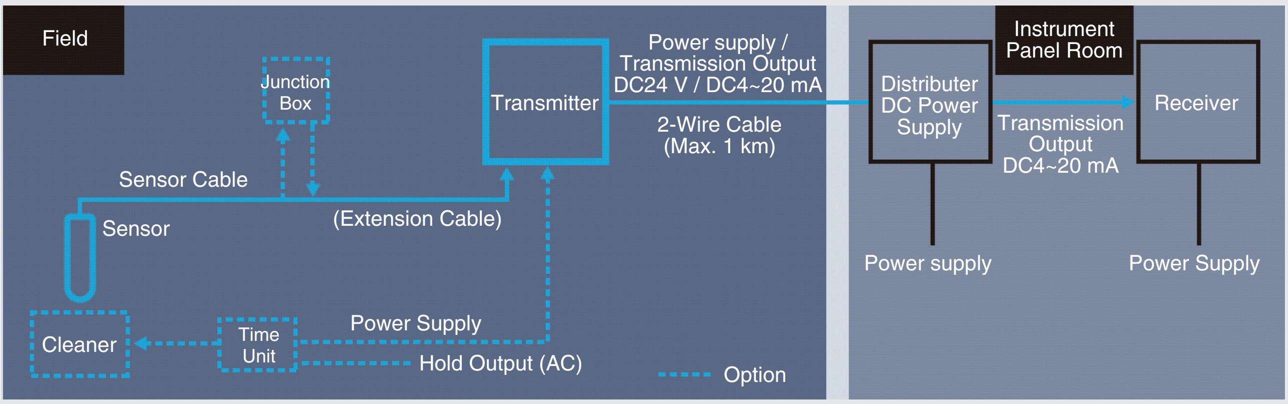


Figure 4 System Configurations for 2-Wire Transmitter

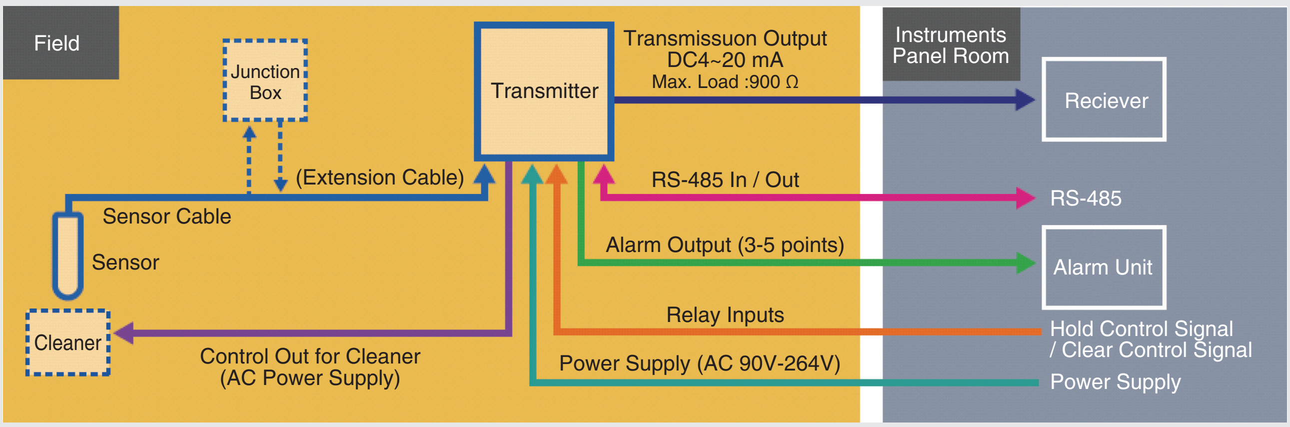


Figure 5 System Configurations for 4-Wire Transmitter

each and every model incorporating features that are useful for users. Major examples of these features are outlined below.

Features of the pH Electrode

HORIBA was one of the first in the world to use lead-free glass and has been selling electrodes with thicker glass membrane that is tough against shocks for many years. The composition of this responsive glass has been further improved with these models to create a lineup of pH electrodes to suit various sample conditions. Table 1 outlines the major specifications and features of each pH electrode.

In the past electrodes could only be manufactured with a thin tip. Development of the new tough responsive glass has enabled electrodes to be manufactured with a dome shape and thicker responsive glass. Shock resistance has been increased in all directions as a result and pressure resistance has been increased to 0.6 MPa. A smoother joint between the glass membrane and glass body is less prone to contamination and makes cleaning the tube much easier. The liquid junction that leaks trace amounts of the internal solution from the reference electrode features two zirconia ceramic pieces positioned facing each other to minimize the impact of contamination or clogging. Figure 6 shows a cross-sectional view of the responsive glass section of a domed pH electrode (6108-50B).

The pH electrodes used for drainage treatment at semiconductor plants requiring hydrofluoric acid processing or desulfurization and highly alkaline scrubbing liquids tend to show a drop in performance after just one month. This problem is due to the thickness of the glass gel layer, often called the hydration layer of

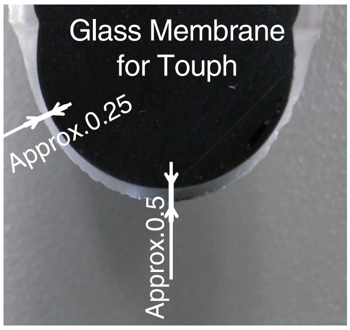


Figure 6 Cross section of Dome Type pH Electrode (6108-50B)

the pH sensitive glass.[1] A thicker hydration layer makes the glass react easier with the water and hence start dissolving easier. Deterioration of the responsive glass is prevalent when electrodes are used constantly in severe environments such as hydrofluoric acid solutions or highly alkaline solutions which can dissolve silicon dioxide, the major constituent of glass. HORIBA has worked to improve the durability of this glass by redesigning the very basic structure of the glass itself. To combat this, the electrodes are manufactured by blending several types of trace metals with the silicon dioxide, the major constituent of pH sensitive glass used in pH electrodes. The addition of trace metals is extremely important for determining the qualities of responsive glass. One example is the application of a metallic element called lanthanoid. Lanthanoid addition is known to reduce alkaline errors and it has been widely used. Although the ionic radius of lanthanoid is relatively large, its electron affinity becomes weaker and in turn is believed to increase the thickness of the hydration layer. The responsive glass has been improved in the new electrode

Table 1 Main Specifications and Features of the pH Electrode

Classification	General Purpose			Special Purpose					
Products Name	Dome Type	Fixed Sleeve Type	Replaceable pH Electrode Chip	HF-Resisting pH Electrode	High Alkali-Resisting pH Electrode	HF-Resisting pH Electrode (Replaceable pH Electrode Chip)	High Alkali-Resisting pH Electrode (Replaceable pH Electrode Chip)	Oil-resisting pH Electrode (Replaceable pH Electrode Chip)	Dome Type pH Electrode (Gel Type in inner Solution)
Model	6108-50B	6109-50B	6174-50B	6151-50B	6152-50B	6171-50B	6172-50B	6173-50B	6108G-50B
Appearnce									
Applicable Temperature range	-10~100 °C	-10~80 °C	-10~100 °C	-10~60 °C					-10~100 °C
Applicable Pressure range	0-0.6 MPa	0-0.03 MPa		0-0.2 MPa		0-0.03 MPa			0-0.6 MPa
Features	New TouphH electrode	New TouphH electrode	G.R Chip Replaceable	New TouphH electrode	High Alkali-Resisting pH Electrode	New TouphH electrode	G.R Chip Replaceable	New TouphH electrode	New TouphH electrode

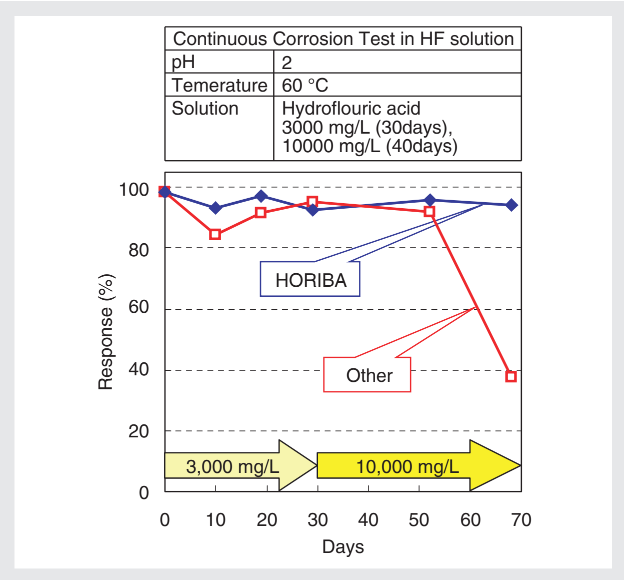


Figure 7 Reasults of the Life Test on HF-resisting pH Electrode

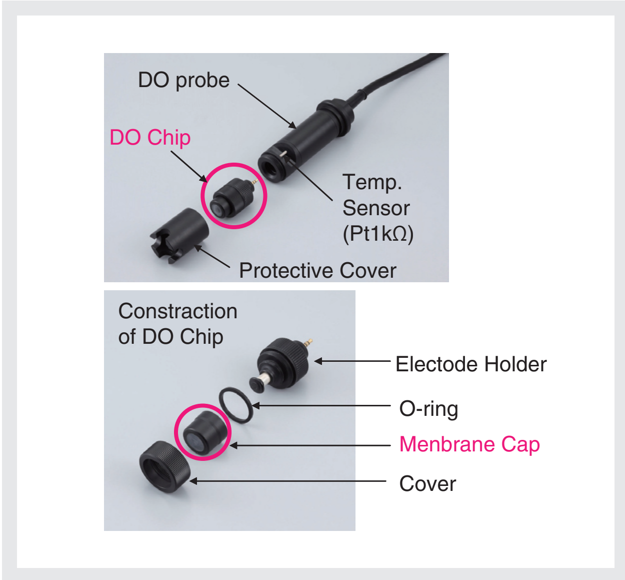


Figure 9 Structual Pictures of DO probe (D-1100) and DO Chip (5505)

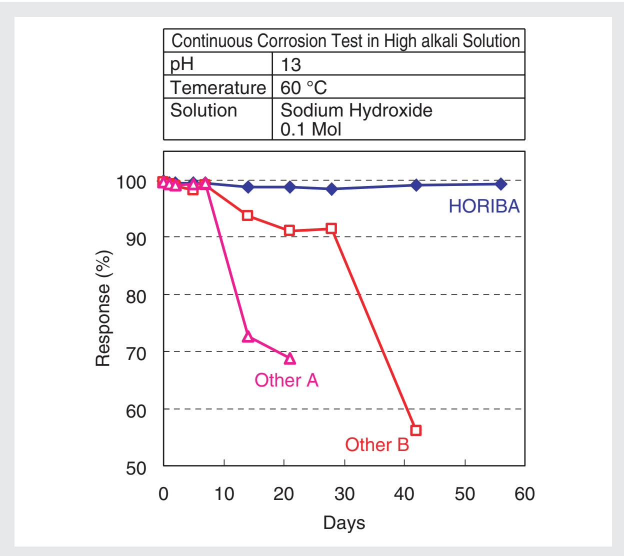


Figure 8 Continous Corrosion Test in High Alkali Solution

models by using other elements from group 3 metals of the periodic table with a smaller ionic radius providing a higher electron affinity than that of lanthanoid.[2] By adding metallic elements with a smaller ionic radius and higher electron affinity, the hydration layer becomes thinner. This results in durability that is twice as long as that of conventional electrodes when sampling hydrofluoric acid and highly alkaline solutions. The results of longevity testing of pH electrodes designed for hydrofluoric acid and highly alkaline solutions are shown in Figure 7 and 8.

Features of the Dissolved Oxygen (DO) Sensor

DO sensors are generally used for air flow control and DO concentration control in aeration tanks during drainage treatment as part of the activated sludge process. DO sensors consist of a DO probe (DO-1100) and DO chip (5505), and use a membrane type polarographic method for taking measurements. For the first time, this design now allows quick DO chip exchange for industrial sensors as well as sensor chips to be restored by replacing the internal liquid and membrane. This new innovation helps to reduce both the time required for maintenance out in the field and ongoing running costs. A structural overview of the DO-1100 and 5505 is shown in Figure 9. The cathode electrode is now made of plastic formed carbon which is electrochemically stable and tough. The membrane is made fo Perfluoroalkoxy Resin (PFA) which has excellent oxygen gas permeability. Membrane thicknesses come in two different models: 50 µm and 100 µm. The use of a thicker membrane helps to increase its durability when solids in the aeration tank strike the membrane minimizing any subsequent damage. The internal solution uses a safe, neutral solution (mixture of potassium chloride and phosphoric salt buffer solution). The use of a proprietary HORIBA cartridge-type membrane cap simplifies the sensor chip replacement for the user.. A sensor malfunction diagnosis function has also been installed to detect torn membranes or water leaking into probes, all of which help improve the precision of measurement values that have been obtained.

Features of the MLSS Sensor

MLSS sensors are generally used for activated sludge concentration control in aeration tanks during drainage treatment as part of the activated sludge process. The MLSS sensor (SS-90) makes measurements using the near-infrared light transmission method. This is the first model to use PFA, which exhibits excellent near-infrared light permeability and does not allow contamination to adhere easily. HORIBA's proprietary sensor head shape diminishes the impact of contamination on the measurement sensor. The light source used is a long-life near-infrared LED (with a wavelength of 860 nm) which employs a pulsating light to minimize the interference of static ambient light. An auto-correction function for fluctuations of the light source intensity, by the use of the reference light, has resulted in low drift over long periods of time. A structural overview of SS-90 is shown in Figure 10. Field tests have been conducted on batch tanks with standard activated sludge concentration (MLSS concentration of 2,000 to 4,000 mg/L) and aeration tanks for membrane separation bioreactors (MLSS concentration of 8,000 to 10,000 mg/L) that use high concentrations of activated sludge. Both tests were conducted continuously for six months without using cleaners and conducting any maintenance. The impact of sensor contamination on measurement values was favorable at less than 0.1% of full scale. Figure 11 shows the amount of sensor contamination after testing was complete. The sensor also incorporates a CPU so that certain data, such as correction data, can be sent to a converter digitally (via RS-485). This means the sensor does not need to be paired with a separate transmitter.

Features of the Turbidity Sensor

The turbidity sensor is generally used for turbidity control as part of treatment processes for treated wastewater, irrigation water and clean water. The turbidity sensor (SS-120) uses HORIBA's proprietary two-light source transmission 90° scattering method for its measurement principle. By alternating two pulsating light sources, comparing signals from two types of transmitted light and 90° scatteredlight, the geometric mean can be calculated to cancel out fluctuations in light source intensity and contamination in measurement cells. All this enables the sensor to measure low levels of turbidity reliably, and with low drift. The light source used is a long-life LED (with a wavelength of 660 nm). Figure 12 shows an overview of the measurement principles of the SS-120. The addition of an electric wiper cleaner enables extended periods of maintenance-free measurements. Both the sensor and cleaners have a CPU installed. This allows digital communications (via RS-485) with the transmitter for better communication of measurement data and operation of the cleaner.

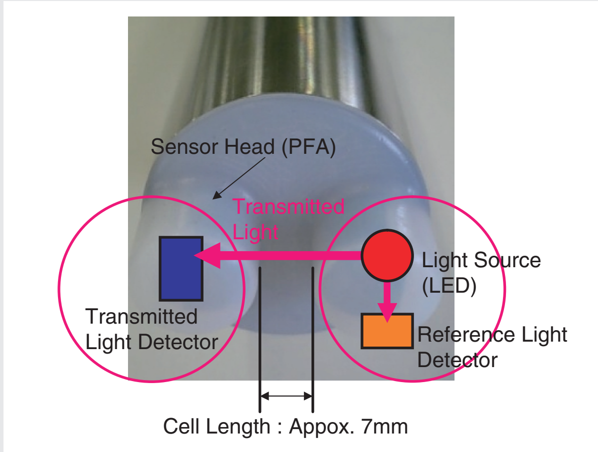


Figure 10 Structual Pictures of MLSS Sensor (SS-90)

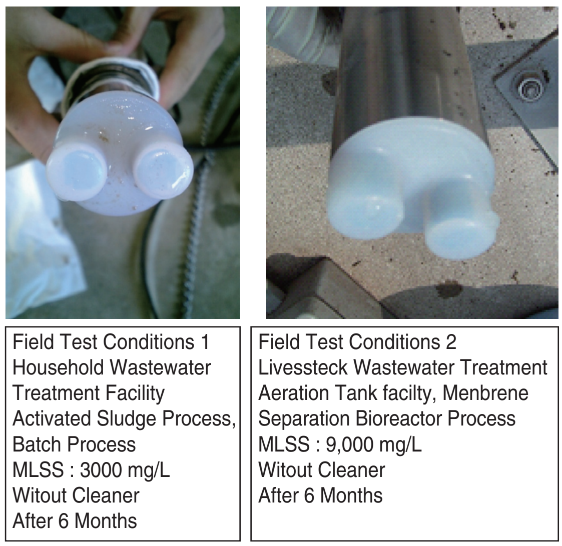


Figure 11 Examples of Adhesion of Dirt in Processes

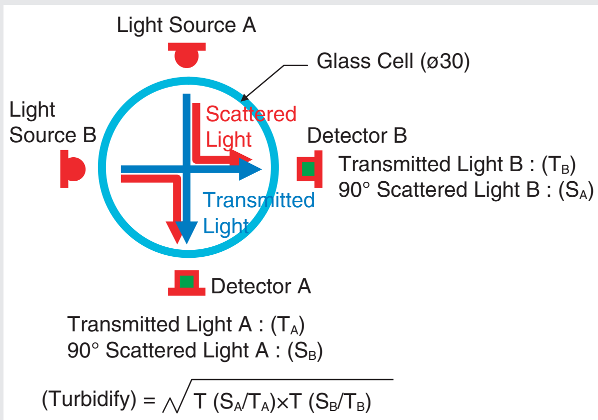


Figure 12 Measurement Principle of Turbidify Sensor

Features of the Free Residual Chlorine Sensor

The free residual chlorine sensor is generally used for control and management of sterilization treatment of water purification plants, pools and bathtub water using chlorine. The free residual chlorine sensor (RA-10) uses the 3-electrode polarographic method for taking measurements due to the minimal impact of sample properties. The cathode electrode is continuously kept clean with both physical cleaning using glass beads and electrochemical cleaning. Running costs have been reduced through the use of HORIBA's proprietary chip replacement cathode electrode. The structural overview of the RA-10 is shown in Figure 13. A special electrode only for the electrochemical cleaning has been installed to prevent any coating of the anode electrode. Figure 14 is an illustration of the electrochemical cleaning.
Table 2 provides an outline of the specifications of each sensor.

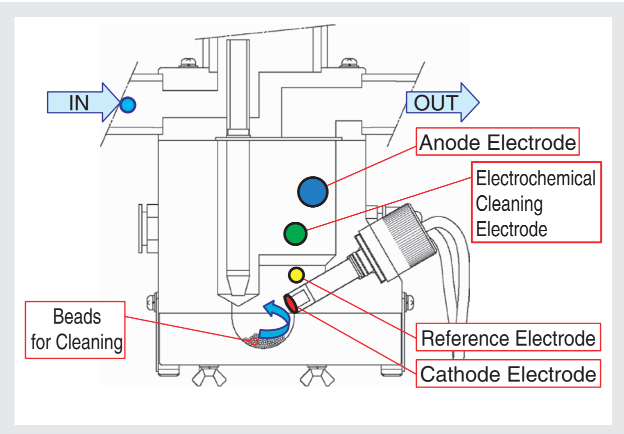


Figure 13 Structual Drowning of Residual Chlorine Seasor

Suitability Out in the Field

With so many installation environments and sample condition variations, industrial water quality meters require checks of their suitability in the area they are being used. Customers demand high quality for reliable operation over a long period of time while also asking for lower costs and maintenance-free operation. HORIBA has worked on promoting the benefits of proprietary technology and reducing costs. With the H-1 Series, an extra focus was placed on field tests. Suitability tests were performed in the field where measurements were taken and used as an important factor during the development process.. Continuous tests were conducted over a period of six months to a year in 30 different locations with various types of water treatment processes. This has allowed HORIBA to test its proprietary technologies outlined above as well as working on durability testing through repeated operations. One example is shown in Figure 15 which is a selection of test data taken from batch tanks at a municipal waste water treatment facility. This example obtained positive results without the use of a cleaner however a cleaner may be required depending on the condition of samples used. The H-1 Series comes with a full range of optional automatic cleaners, including ultrasonic cleaners, water and air jets, brushes and chemicals, all of which have been fully renewed. An example of a pH electrode equipped with a new ultrasonic cleaner is shown in Figure 16. The new ultrasonic cleaner uses an ultrasonic transducer to provide intermittent bursts of oscillation. This design prevents the standing waves generated by continuous oscillation of previous cleaners while also delivering a high level of cleaning.

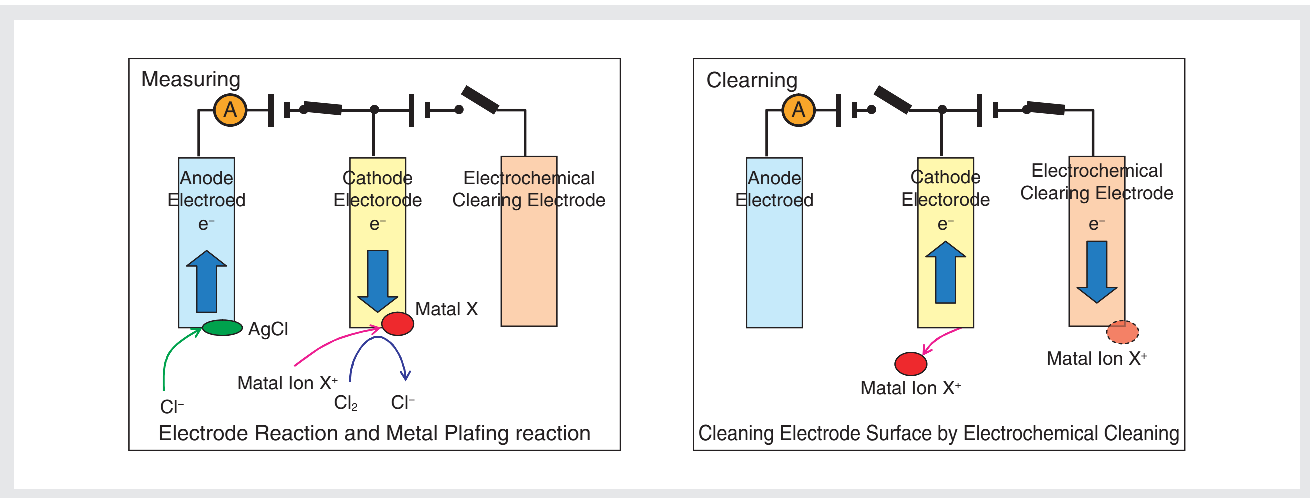
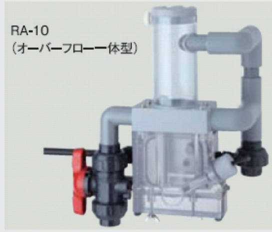


Figure 14 Explanation Drowing of Electrochemical Cleaning Principle

Table 2 Specicaton for DO, MLSS, Turbidity and Residual Chorine Sensor

Measurment Items	DO Sensor	MLSS Sensor	Torbidity Sensor	Residual Chorine Sonsor
Model	DO-1100, 5505, 5510	SS-90	SS-120	RA-10, RA-20
Appearance				
Measurment Principle	Membrene Type Potarogaghic Method	Near-Infrared Light Transmission Method	Two-Light Source Transmission 90° Scattering Method	The 3-Electrode Polaregraphic Method
Measuring Rang	0~20 mg/L	0~20,000 mg/L	Kaolin : 0~500 ° Formazine : 0~1,000 ° PSL : 0~100 °	0~3 mg/L
Sample Temp.	0~50 °C	5~50 °C	0~40 °C	0~45 °C
Sample Pressure	<0.5 MPa	<0.2 MPa	<0.3 MPa	<0.3 MPa

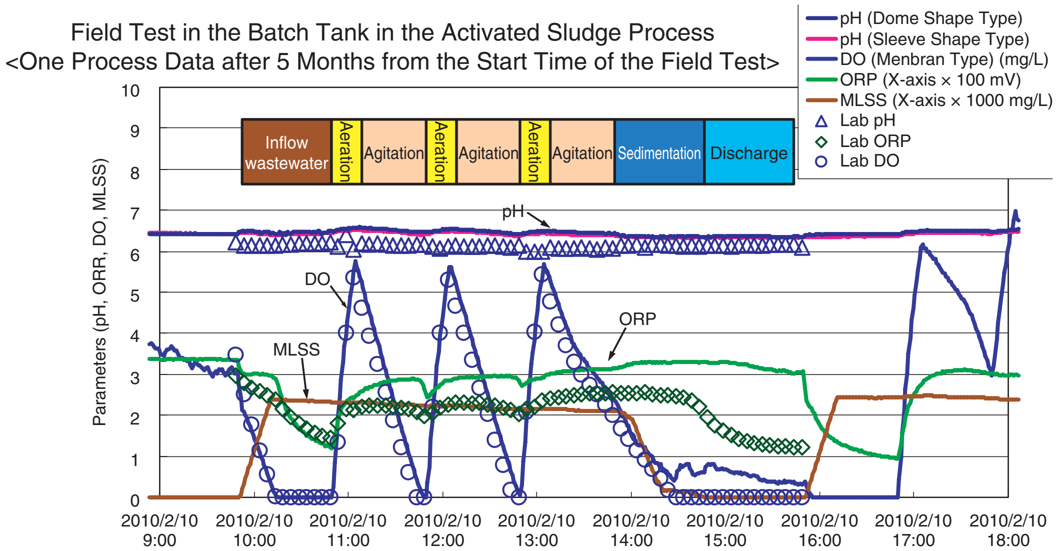
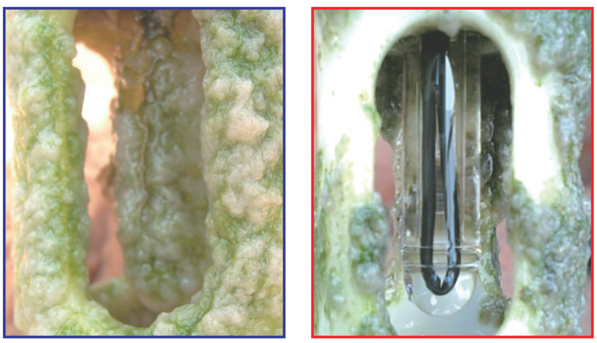


Figure 15 Field Test Date in the Batch Process

Without Cleaner | With Ultrasonic Cleaner



After 20 days
Electrode Covered with Algae

After 80 days
Electrode without Algae

Teat Conditions
Industrial Wastewater
Flocculation Process

Coagulation Agent (PAC)
Flocculation (Polymor)
Netralizer (NaOH)
Deforming Agent (Silicon oil)

Figure 16 Examples of Cleaning effect with the Ultrasonic Cleaner (UCH-101)

Conclusion

The most important factor of water quality meters installed in the field is a high rate of operation to combat the harsh environments where they are usually installed combined with the poor quality of samples being measured. The H-1 Series presented here has been tested out in the field and positively demonstrated to reduce maintenance costs. These tests also uncovered problematic application issues that can only be found out in the field. HORIBA is determined to continue focusing on product development out in the field to come up with more applications that are better suited for user's operations. There has been a marked reduction in the number of skilled technicians that can properly service these sensors due to changes in generation within the workplace and the cutting back of employees making reductions in time required for maintenance an important factor. HORIBA is currently developing maintenance support tools that connect wirelessly which will eventually form part of a new solution to save time further. Figure 17 is an overview of this new feature. HORIBA has a sense of pride and responsibility while at the same time playing a vital role in the efforts for maintaining and conserving precious water resources around the world. Products will continue to be designed so that users can benefit from the new features incorporated to promote ease of operation and their company's profitability..

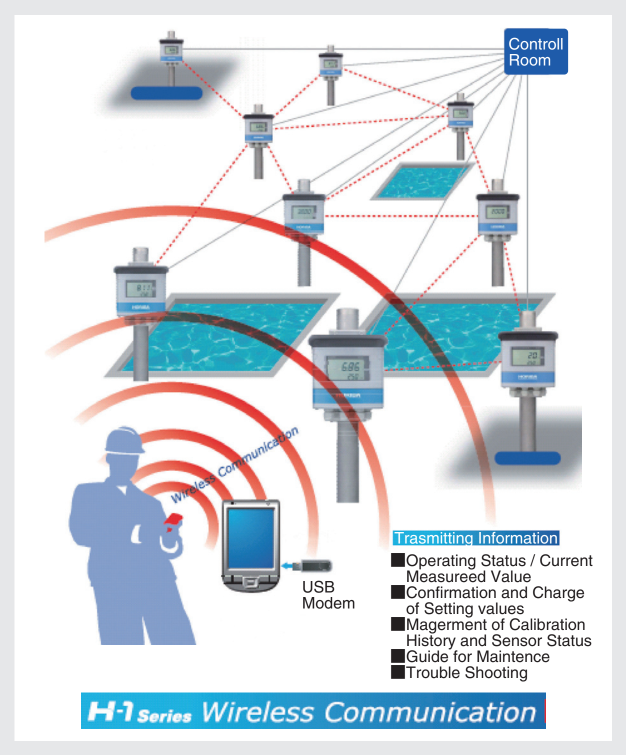


Figure 17 H-1 Series Wireless Communication

References

[1] Yuji Nishio. et al, Analysis of pH responsive glass using SIMS, 2006 Spring Meeting of the Electrochemical Society of Japan
[2] Patent publication number 2009-288117

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