Product Introduction

Rotary Residual Chlorine Meter HR-200RT RA-30

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In Japan, you drink water straight from the tap, damage is not necessarily done to the body. That is because advanced water disposal is performed in the water treatment plant. The Water Treatment & Environment product of HORIBA including a rotary residual chlorine meter supports those water disposals. In the water treatment plant, the processing using chlorine is indispensable processing for sterilization. There are also some methods of measuring residual chlorine and each has the feature. In this paper, firstly, processing in a water treatment plant is introduced. Next, the measurement principle of residual chlorine and the feature of residual chlorine meters are introduced.

Introduction

If we consider all the countries in the world, there are relatively few countries where people can use the water that comes out of the faucet as drinking water as-is, as people can do in Japan. Developing countries have not achieved sufficient water treatment of their water supplies, and it is not rare to find countries where contaminated water is used as-is for daily use. More people die from unsanitary water than from wars, and treating water is an important global issue.

Water in Japan's domestic water supply is made at water purification plants and is distributed to general households. HORIBA's water products, such as the residual chlorine meter with rotating electrode, are essential for treating water in water purification plants, and support a safe water supply.

Water purification plants take river water, lake water, and ground water, etc., treat it, and distribute it to general households. Purified and treated water must meet the criteria stipulated in Japan's Water Supply Law. In order for water purification and treatment to be done under the optimal conditions, the water quality must be monitored during each treatment process using pH meters, conductivity meters, turbidity meters, and residual chlorine meters (see Figure 1 & Table 1). Many water purification plants install equipment that measures various required parameters such as pH, turbidity, and residual chlorine as units (see Figure 2) in rooms dedicated to that function. Before companies can enter the clean water market, they must have a full line-up of all the measuring equipment. Together, HORIBA's residual chlorine meter with rotating electrode and high-sensitivity turbidity meter for water purification plants form the line-up needed to be a comprehensive supplier in the clean water market.

General Flow of Water Purification and Treatment

First, water purification plants take in water at water intake sites from nearby rivers and dammed lakes. Water intake sites use oil film detectors to check whether or not there is oil in the water taken in from the river. Close to 80% of river water quality incidents involve oil getting into the water. When oil gets into the water, it causes water purification plants to have to stop taking in water, and also causes major damage to downstream ecosystems. If water that contains oil flows in from a river, a large amount of water will be necessary to treat that water. Oil film detectors are required at water intake sites where water flows in from rivers, in order to prevent oil films from getting inside water purification plants.

The water to be treated is sent from the water intake site to a grit tank. The water contains a large amount of suspended solids such as sand, debris, and bacteria. Large particles of sand, debris, etc. are removed using

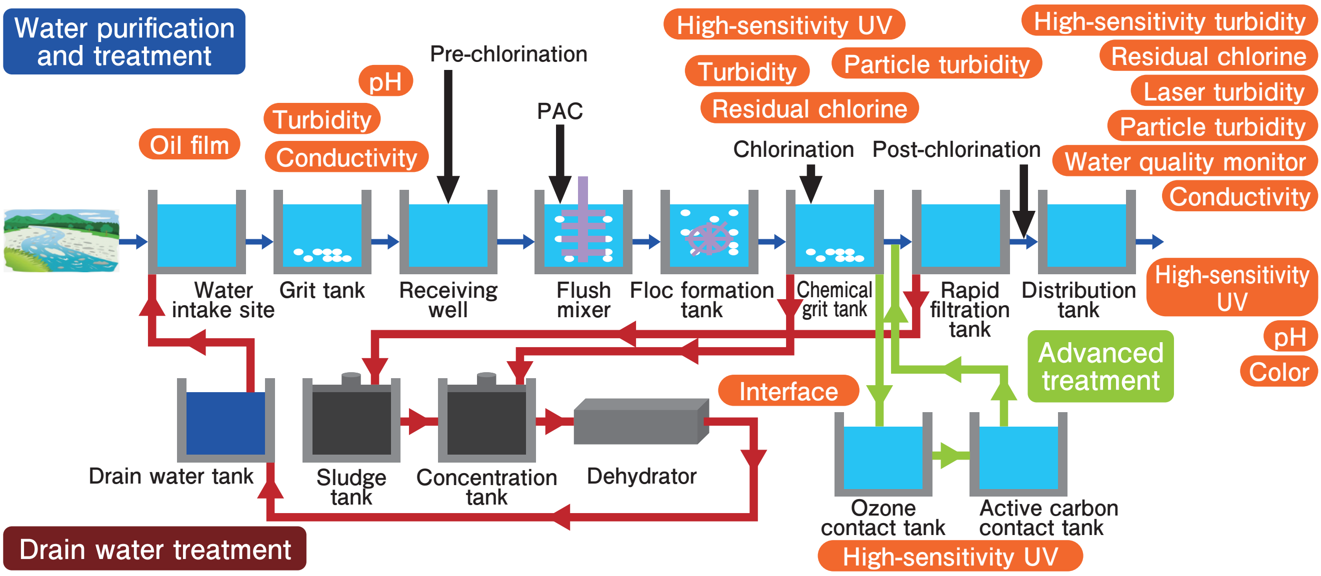


Figure 1 Water purification and treatment

Table 1 Meter specifications

Product	Oil film detection	pH	Electrical conductivity	Residual chlorine	Turbidity	Highsensitivity turbidity	Laser turbidity	Particle turbidity	Highsensitivity UV	Water quality monitor	Interface
Model	LO-200	HP-200	HE-200C	HR-200 HR-200RT	HE-200TB	HU-200TB-H	HU-200LT	HU-200LP	CW-150	TW-100	SL-200
Principle	Laser reflection type	Glass electrode method	2-electrode method	Electrical analysis method	Permeation/ 90-deg. scattering method	Permeation/ 90-deg. scattering method	Laser interference ridge counting	Laser interference ridge counting	Cell length modulation system	Based on measurement items	Ultrasonic wave reflection color
Range	Max. 3 m	pH 0-14	200 mS/m	3 mg/L	1000 deg.	10.00/2.000 deg.	2.0000 deg.	2.0000 deg.	5.0000 Abs	Residual chlorine, turbidity,	0-10 m
Resolution					0.01 deg.	0.001 deg.	0.0001 deg.	0.0001 deg.			
Application	Managing the inflowing oil film	Controlling PAC, monitoring water distribution	Monitoring raw water, monitoring water distribution	Managing treated water, managing water distribution	Monitoring raw water, monitoring treated water	Monitoring water distribution	Monitoring water distribution	Detecting broken film, monitoring cryptosporidium	Monitoring organic matter, adding activated carbon, managing YHM, managing	Water pipe end, water purification facilities	Primary settling sludge

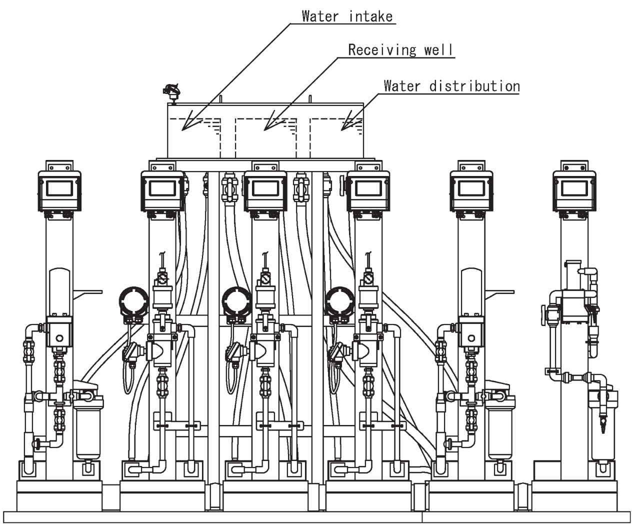


Figure 2 Unit

sedimentation treatment in the grit tank, which is the primary treatment tank. Then the water is sent to the receiving well. In the receiving well, various processes occur. Things such as iron, manganese, and ammonia are removed, microbial disinfection is performed, sodium hypochlorite is added to prevent the growth of algae, and activated carbon is added to remove bad odors from the raw water.

To treat suspended solids that couldn't be removed in the grit tank or receiving well, coagulants like Polyaluminum Chloride (PAC) and aluminum sulfate (sulfuric acid band) are added, which cause the small sand and debris particles, etc. to coagulate and become sediment. These clumps are called "floc", and the tank where this occurs is called the "floc sedimentation tank". These chemicals control the pH at the appropriate level, and maximize the coagulation effect. For this reason, each treatment plant stipulates a pH control value that is used to optimize water treatment.

Fine suspended solids that still could not be removed in the above stage are removed through filtration. The turbidity of the filtered water is measured using a turbidity meter, and the amount of coagulant is controlled. Then sodium hypochlorite is added, the water is disinfected, and the water is distributed to general households. The Water Supply Law stipulates that in Japan, the pH of water must be between 5.8 and 8.6 for it to be distributed as clean water. The law also stipulates that the water in fire hydrants must be disinfected with chlorine and that free residual chlorine must be maintained in the water at 0.1 mg/L or more. For that reason, the pH and residual chlorine concentrations in treated water are monitored, and pH meters and residual chlorine meters are installed in distribution tanks to ensure that treated water that doesn't meet the criteria doesn't get sent into homes.

Chlorine Treatment During Water Purification and Treatment

As mentioned above, there are 2 objectives in water purification and treatment for adding sodium hypochlorite. Also, the chlorine smell that arises in the summer is caused by chloramines, which are generated by a reaction between the ammonia nitrogen in the raw water and chlorine, and the level of odor can be reduced by adding the most appropriate amount of chlorine. For these reasons, water purification plants require that residual chlorine be measured. Also, in some areas, at facilities called simple water purification plants, sodium hypochlorite is added to clean pumped ground water, which is disinfected and sterilized, and this water is distributed to general households.

Methods of Measuring Residual Chlorine

There are 2 general types of methods for measuring residual chlorine. The first is the Diethyl Paraphenylene Diamine method (DPD method), and the second is absorptiometry, of which the iodometric titration method is a typical example. The electroanalysis method used in HORIBA's residual chlorine meter is the second type (see Figure 3: Trends). The DPD method is an inspection method stipulated in the Water Supply Law, but this method cannot take ongoing measurements. With the electroanalysis method, as long as water is flowing into the cell to be measured, ongoing measurements can be taken. Residual chlorine has no fluid that is set as a criteria like pH standard solution, so the most general usage method is to measure the on-site samples using the DPD method, match the readings from the ongoing measurement meters to that value, and then do calibration to make adjustments. Meters that use the DPD method may have variances in their values due to things such as the amount of reagent used, the effect of bubbles inside the cells, or cells being contaminated, so care needs to be taken with these instruments.

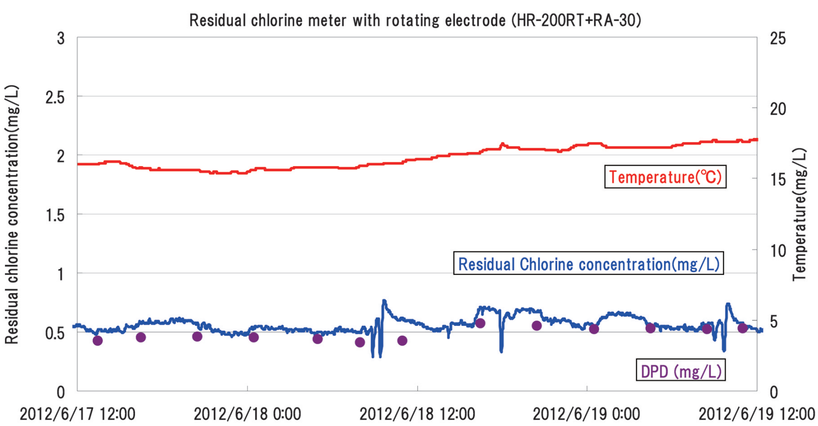


Figure 3 Trends

"Residual chlorine" refers to 2 basic types: free chlorine (chlorine gas, hypochlorite, hypochlorite ions) and combined chlorine (monochloramine, dichloramine, trichloramine). Combined, both types are called chlorine.

HORIBA's residual chlorine meter with rotating electrode and bead-type residual chlorine meter only measure free residual chlorine, so samples that contain a lot of combined chlorine tend to have higher readings. The bead type (HR-200+RA-10 or RA-20) has a cleaning mechanism that uses water flow. The rotating electrode type (HR-200RT+RA-30) cleans when the active electrode itself rotates. In Japan, these 2 types are mainstream, and the rotating electrode type is popular, particularly in the clean water market.

Measurement Principles

The electroanalysis method that uses a residual chlorine meter is called the 3-electrode polarographic method. The electroanalysis method measures the electrical current flowing between the electrodes, and converts it to concentration. With the HR-200RT+RA-30, metal is used for the active electrode, and silver or silver chloride is used for the opposite electrode and the reference electrode. There are different electroanalysis methods, such as the galvanic method and the 2-electrode polarographic method, but these methods are easily affected by the electrical conductivity of the water and the residual chlorine concentration. Using the 3-electrode polarographic method makes it possible to take measurements in a stable manner over the long term.

The 3-electrode polarographic method is

controlled so that the potential of the active electrode has a constant potential difference with the reference electrode. The following reactions occur on the surfaces of the active electrode and the opposite electrode.

Active electrode : $Cl_2+2e^- \rightarrow 2Cl^-$

Opposite electrode : $Ag+Cl^- \rightarrow AgCl+e^-$

When chlorine reaches the active electrode, it is immediately reduced, and becomes chloride ions. At this time, the electrical current flow rate flowing between the electrodes is proportional to the concentration, so measuring the current allows us to find the free chlorine concentration.

As mentioned above, in the electroanalysis method DC voltage is applied from the outside, but the potential difference differs based on the material to be measured and the material of the electrode, so the appropriate voltage is determined based on the item and material to be measured. However, it is difficult to take these measurements in a stable manner if the sample contains substances that contribute to the electrode reactions (oxidizers like ozone or hydrogen peroxide) or substances that change the state of the electrode (reductants like sodium thiosulfate). Also, if there has been a long period of exposure to sunlight, the surfaces of the opposite electrode and reference electrode change, so it is desirable to install the equipment in a way that avoids exposure to sunlight. The electroanalysis method acquires electrical current by consuming the item to be measured that exists on the surface of the electrode, so it is difficult to take measurements if samples have not been supplied or if the sample has low electrical conductivity.

Comparison with Conventional Products

There are 2 meters that use the electroanalysis method to take ongoing measurements of free residual chlorine: the HR-200+RA-10 or RA-20 (released in 2011), and the recently released HR-200RT+RA-30. The HR-200+RA-10 has integrated its overflow tank and measurement cells, and is set up so that a pH electrode can be attached to the overflow tank. The HR-200+RA-20 can take in-line measurements, and has a lower flow rate required to take measurements than the RA-10 has. Both products are the bead type that uses water flow, and require a higher flow rate than the residual chlorine meter with rotating electrode. Both the bead-type products have electrochemical cleaning functions derived from the beads. The HR-200RT+RA-30 model with the rotating electrode only uses beads to clean, and does not have an electrochemical cleaning function. The pH compensation function is a function that only the residual chlorine meter with rotating electrode has. As mentioned above, free

Table 2 Specification comparison table

	RA-10	RA-20	RA-30
	Bead type	Bead type	With rotating
Bead material	Glass/ceramic		Ceramic
Active electrode	Au	Au	Au
Reference electrode opposite electrode	Ag/AgCl	Ag/AgCl	Ag/AgCl
In-line measurement	No	Yes	No
Electrochemical cleaning	Yes	Yes	No
pH correction function	No	No	Yes
Flow rate (L/min)	1.3-2.0	0.6-1.0	0.1-0.5

residual chlorine exists in the form of chlorine gas, hypochlorite, and hypochlorite ions, and the ratios of those vary based on the pH. The more alkaline the pH is, the higher the percentage of hypochlorite ions will be. Hypochlorite ions have less of a contribution to reactions on the surface of the electrodes than hypochlorite does, so if the percentage of hypochlorite ions increases due to the pH being alkaline, the free residual chlorine readings will decrease. With the residual chlorine meter with rotating electrode, the pH or the sample's pH is entered using RS-485 communication, and is corrected to the residual chlorine concentration for a pH of 6.86 (see Table 2: Specification comparison table).

Features of the residual chlorine meter with rotating electrode

The residual chlorine meter with rotating electrode can take measurements with low flow rates. The active electrode rotates and acquires a relative flow velocity with the sample, which enables it to take measurements at low flow rates, such as 500 ml/min or less. Also, if metal ions or organic contaminants stick to the surface of the active electrode, this can cause the sensitivity to decrease. However, as mentioned above, in this meter, the active electrode is rotating inside an area with ceramic beads, and the beads have the effect of polishing the surface of the active electrode, which prevents contaminants from sticking (see Figure 4: Electrode Configuration Diagram). Also, the samples have a structure that allows overflow inside the measurement cells, and in-line measurements cannot be taken. In water purification plants, the water is distributed from a large overflow tank and is sent to various measuring equipment, so there are almost no instances of in-line measurements, and we used a cell release structure that is easy to maintain.

When the rotating electrode in the residual chlorine meter stops rotating, a value lower than the actual concentration is displayed. For this reason, there is a risk that excessive chlorine may be added. When the rotation stops, the device has a function that automatically detects that, and re-starts the device. The active electrode is connected to the motor's rotating shaft, and is always rotating while measurements are being taken. A detection plate attached to the motor shaft detects whether or not the active electrode is rotating. If the motor has stopped, it is restarted. If it isn't restarted, a warning will be issued regarding the abnormality. This design quickly notifies the operator of abnormal situations where the motor isn't rotating, and also prevents excessive amounts of chlorine reagents from being added (Figure 5: Motor detection).

With the electroanalysis method, the electrical current flowing to the active electrode and opposite electrode is measured and converted to concentration. For that reason, the meter with the rotating electrode needs to extract the electrical current from the rotating active electrode. The HR-200RT uses a small piece of silver that has low electrical resistance as the rotating contact point, and the signal is picked up by pushing a wire rod on the silver. The wire rod is made of a contact point alloy and spot-welded on the leaf spring. If wear progresses on the contact point, powder is generated by the wear, which can cause defects at the contact point. Silver is a relatively soft metal, and when it is pushed and contacted, pieces don't get shaved off, but instead it deforms along the wire material, and prevents wear. Wear caused by rotation is also prevented by applying conductive grease between the shaft and the plate spring. As such, this model makes it possible to take stable measurements over the long term.

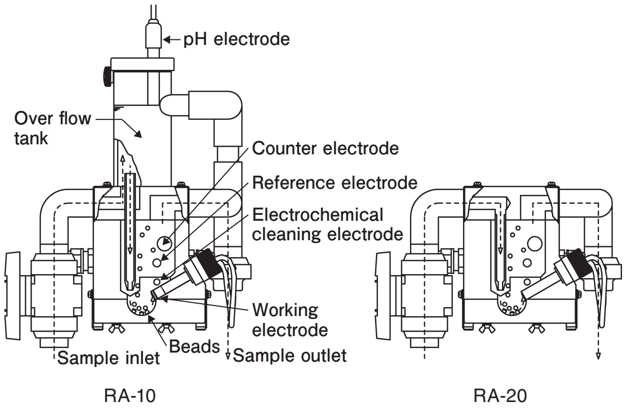


Figure 4 Electrode configuration diagram

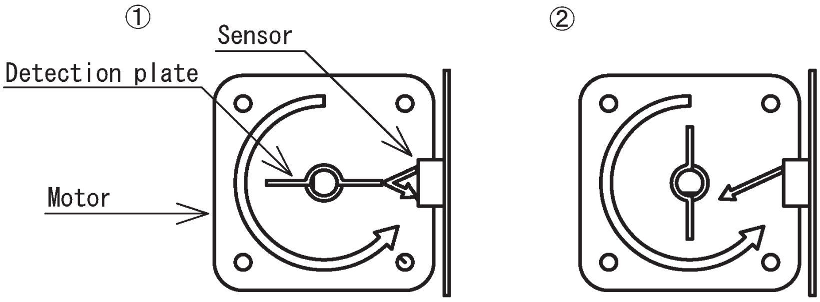
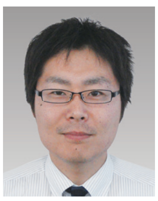


Figure 5 Rotation detection
During rotation, rotation is judged by repeatedly detecting states 1 and 2 above.
If there is no change and a state remains constant, the system judges that the device has stopped, and restarts.

Conclusion

HORIBA's residual chlorine meter with rotating electrode makes it into a comprehensive supplier for the clean water market. The electroanalysis method is not limited to measuring residual chlorine, and this technology can be used to measure various components in water. We would like to use our experience in developing this residual chlorine meter to make a positive contribution to society and water analysis in the future.



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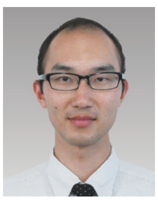

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