Feature Article

HORIBA Water Quality Products Approach to China and Asian Countries
中国・アジアへのHORIBA水質製品の展開

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Accompanied by water pollution in China and other Asian countries, Asian water quality regulations have become stricter every year. HORIBA tries to share and apply the products developed in Japan and know-how gained through the engagement in the Fifth Water Total Quality Regulation, for China and other Asian countries. This report describes an expanding movement of total quality controls in Asian countries, and the vision of product development in HORIBA group for these Asian water quality regulations.

中国及びアジア地域における水質汚染にともなって，アジア各国の水質規制は年々厳しくなっている。現在進行形で拡大するアジア各国における総量規制の動向と，HORIBAグループが日本で培った製品群や日本における第五次水質総量規制で得たノウハウ，の2点を中国およびアジア地域に生かしていきたい。本稿では，HORIBAグループ製品のアジア地域水質総量規制における展望について述べる。

Introduction

Along with the economic development of China and other Asian countries, water pollution in these areas is becoming more serious issue. As a countermeasure, quality control of drainage water is being on progress at high pace. HORIBA group has been engaged in all of the Water Total Quality Regulations from the First to the Fifth in Japan and mainly worked on providing measurement instruments. For the prospective water quality regulations in Asian countries, HORIBA group will create new products and suggest solutions to contribute to these countries.

Water Quality Regulations in China and Other Asian Countries

Surface Water Quality Regulation in China

Surface water is the water on the land surface such as rivers and lakes. Surface water and groundwater are highly precious for our daily life and it is essential to observe the quality of surface water. Although the average annual rainfall in Japan is about 1,700 millimeters, which is in abundance, many regions in Japan suffer from the shortage of water because of lack of rainfall or rapid population increase. The annual rainfall in China is about 660 millimeters, which is about 30% of that of Japan. Chinese government categorizes the types of surface water according to the purposes of water utilization as in Table 1 below. Water contamination has been a growing problem in China following an increase of its industrial and domestic wastewater. In China, water districts are sorted by the water usage purposes and conservation objectives. They are ranked from Category I: Drinking water source areas and national nature reserves to Category V: Agricultural use and for general sightseeing. For each category, environmental criterion is given to show the ideal water quality environment. The water quality measurement from 2001 targeting China's seven major river systems showed that 44% of 752

Table 1 Classification of water quality in China

Category	Main Purpose	Intended Use (Functional Division)
Category I	Drinking water	Mainly for drinking water source areas and national nature reserves
Category II	Drinking water	Mainly for primary domestic noncommercial water areas, rare fish habitats, and areas designated for the spawning of fish or shrimp
Category III	Drinking water	Mainly for secondary domestic noncommercial water areas, general fishery areas, and swimming areas
Category IV	Industry	Mainly for general industrial use and entertainment use, not involving direct human contact
Category V	Agriculture	Mainly for agricultural use and general sightseeing
Inferior to category V		Water inappropriate for usage above

monitoring spots belonged to the worst category and did not even meet the existing water environmental criteria: Category I to V. Especially in three major river systems of Hai, Huai and Liao Rivers where pollution is the severest, more than 60% of the spots showed its water quality below Category V. As for in Taihu, Chao and Dian Lakes, the quality of every spot was worse than Category V. These results have made a measure against eutrophication as a priority issue that needs to be solved. For this reason, against the three rivers and three lakes above, water pollution prevention measures had been intensively in effect by the Ninth Five Year Plan for State Environment Protection (1996 to 2000) and the subsequent Tenth Five Year Plan for State Environment Protection (2001 to 2005).

Specifically, total volume controls against COD (Chemical Oxygen Demand) and ammoniac nitrogen had been implemented, wastewater treatment plants had been rapidly constructed, and smaller factories (i.e., xiangzhen companies) with old production equipments that discharge a huge amount of polluted water contamination had been forced to be shut down and closed. However, the problem of the water contamination has not been improved, because of not only rapidly increasing industrial wastewater but also human sewage. Also, the regions other than except the three rivers and three lakes have a serious water contamination problem. Hereafter, it is expected that a water shortage may occur caused by the progress of this water contamination.

Environmental criteria for surface water in China are presented in Table 2-1. Table 2-2 shows Japanese water quality regulations. Compared to Japan, it is obvious that more checkpoints are used to monitor the water quality in China. The purpose of monitoring the surface water quality is to check if water is suitable for its use. In particular, in Asian countries, the sewage-treated water runs back into rivers and lakes and is reprocessed in the downstream to be used for potable or industrial water, marine products industry or agriculture.

pH is used as a significant factor for regulating the surface water quality in countries such as China and Japan. As pH, BOD (Biochemical Oxygen Demand) is also used. BOD is the amount of dissolved oxygen needed by

Table 2-1 Environmental criteria for surface water in China (mg/L)

		Category I	Category II	Category III	Category IV	Category V
1	Water temperature	Limits of artificial changes of water temperature The maximum range of temperature increase is ≤ 1 °C.				
2	pH	6-9				
3	Dissolved oxygen ≤	7.5	6	5	3	2
4	Total manganese salt rating ≤	2	4	6	10	15
5	COD ≤	15	15	20	30	40
6	BOD5 ≤	3	3	4	6	10
7	Ammoniac nitrogen ≤	0.15	0.5	1.0	1.5	2.0
8	Total phosphorus (TP) ≤	0.02 (0.01 for lakes and dams)	0.1 (0.025 for lakes and dams)	0.2 (0.05 for lakes and dams)	0.3 (0.1 for lakes and dams)	0.4 (0.2 for lakes and dams)
9	Nitrogen (N) ≤	0.2	0.5	1.0	1.5	2.0
10	Total copper ≤	0.01	1.0	1.0	1.0	1.0
11	Total zinc ≤	0.05	1.0	1.0	2.0	2.0
12	Fluoride ≤	1.0	1.0	1.0	1.5	1.5
13	Selenium ≤	0.01	0.01	0.01	0.02	0.02
14	Total arsenic ≤	0.05	0.05	0.05	0.1	0.1
15	Total mercury ≤	0.00005	0.00005	0.0001	0.001	0.001
16	Total cadmium ≤	0.001	0.005	0.005	0.005	0.01
17	Hexavalent chromium ≤	0.01	0.05	0.05	0.05	0.1
18	Lead ≤	0.01	0.01	0.05	0.05	0.1
19	Total cyanide ≤	0.005	0.05	0.2	0.2	0.2
20	Phenol ≤	0..002	0.002	0.005	0.01	0.01
21	Petroleum or petroleum-like substance ≤	0.05	0.05	0.05	0.5	1.0
22	Ion activator ≤	0.2	0.2	0.2	0.3	0.3
23	Sulfide ≤	0.05	0.1	0.2	0.5	1.0
24	Total coliform ≤	200	2,000	10,000	20,000	40,000

Table 2-2 Classification of water quality in Japan

Type	Main Purpose	Intended Use (Functional Division)	Water Quality Criteria
AA	Drinking water	First-class water Nature conservation	pH 6.5-8.5, BOD 1 mg/L or lower, SS 25 mg/L or lower DO 7.5 mg/L or more, Coliform 500 MPH/100 ml or lower
A	Drinking water	Second-class water Second-class fishery	pH 6.5-8.5, BOD 2 mg/L or lower, SS 25 mg/L or lower DO 7.5 mg/L or more, Coliform 1,000 MPH/100 ml or lower
B	Drinking water	Third-class water Second-class fishery	pH 6.5-8.5, BOD 3 mg/L or lower, SS 25 mg/L or lower DO 5 mg/L or more
C	Industry	Third-class water First-class industrial water	pH 6.5-8.5, BOD 5 mg/L or lower, SS 50 mg/L or lower DO 5 mg/L or more
D	Industry	Second-class industrial water Agricultural water	pH 6.0-8.5, BOD 8 mg/L or lower, SS 100 mg/L or lower DO 2 mg/L or more
E	Industry	Third-class industrial water environment conservation	pH 6.0-8.5, BOD 10 mg/L or lower, DO 2 mg/L or more

microorganisms to oxidize organic material present in water. In general, dissolved oxygen tends to fail as BOD value becomes higher, and rancid generates at the value more than 10 mg/L.

DO (Dissolved Oxygen) is replenished through phytoplankton photosynthesis and consumed by respiration in aerobic organisms. DO can be also used as a gauge of contamination level of the water. When the eutrophication is advanced to the degree that the nature cannot purify by itself, DO is reduced and only anaerobic microorganisms can live in a body of water. Although decomposition is carried on by anaerobic fermentation, the organic material does not have enough power to decompose the organic nitrogen compound, and this leads to the progress of eutrophication.

Effluent Standard Established by Chinese Government

Table 3 shows effluent standard values of the first contamination category in China compared to the corresponding standard values of Japan. The given values are almost equivalent. As shown in Table 3, it is only in China and Japan that the value of alkyl mercury must not be detected. The secondary standard values of Chemical Oxygen Demand (COD Cr) are determined in the range of 120 mg/L to 300 mg/L depending on categories. These values require attention when selected as a monitoring method, because its oxidative condition differs from that for Japanese standard value COD Mn 160 mg/L. To measure COD, there are four methods: COD Mn, COD

Table 3 Effluent standard values (mg/L) of the first contamination category

	Contamination	Chinese Maximum Allowable Concentration of Discharge	Japanese Uniform Standard
1	Total mercury	0.05	0.005
2	Alkyl mercury	Not to be detected	Not to be detected
3	Total cadmium	0.1	0.1
4	Total chromium	1.5	2
5	Hexavalent chromium	0.5	0.5
6	Total arsenicum	0.5	0.1
7	Total lead	1	0.1
8	Total nickel	1	–
9	3,4 benzo (a) pyrene	0.00003	–
10	Total beryllium	0.005	–
11	Total silver	0.5	–
12	Total α radiation	1 Bq/L	–
13	Total β radiation	10 Bq/L	–

Cr, UV and TOC (The last two need to gain correlations when used.) In Japan, the method of COD Mn is applied for COD measurement while COD Cr using hazardous hexavalent chromium or mercury is not adopted. In the UV method, unlike the COD Mn, running cost can be lower because no reagent is needed and the maintenance is easier. That's why it is applied in many measuring places. In China, the method of COD Cr is used for controlling industrial effluent, and the COD Mn is for measuring COD of surface water.

Present Situation of Monitoring Water Quality

As industrial effluent monitoring by the environmental administration organization, three methods are taken: regular monitoring, irregular monitoring and online monitoring. Generally, regular monitoring, and, irregular monitoring which is carried out without prior notice are performed once a year respectively.

Online monitoring was performed in many places between 2006 and 2008, which was one of the concrete ways to reduce COD emissions by 10% as recommended in the Eleventh Five Year Plan since 2006. COD is monitored basically by the COD Cr method in China, and a number of online monitoring equipments such as COD Cr and pH meters, turbidity meters and flowmeters are installed under the management of the Environment Protection Agency of provinces and cities.

There is a lot of concern about environmental pollution that can be caused by the use of the COD Cr method applied for COD monitoring in China. The reason for this is that the mercury used in the COD Cr method is directly drained downriver without being collected to a drain tank. Besides, with the COD Cr method, measurements

Table 4 Advantages and disadvantages of COD online monitoring

	Online Monitoring in Japan	Advantage	Disadvantage
COD-Mn method	For rivers, used when no correlation can be obtained with UV method (10-20%)	The correlated data do not need to be created at monitoring.	Reagent is required. Maintenance is necessary.
COD-Cr method	Not used	The correlated data do not need to be created at monitoring.	Reagents such as mercury are used. Maintenance is necessary.
UV method	Used mainly for fixed sources (70-80%)	No reagent is required. No hazardous substance is emitted. Maintenance is easy. Running cost is low.	The data correlated between UV and COD methods need to be created at monitoring. For a device that a cell is not automatically cleaned, drift tends to be extreme.
TOC method	Used mainly for fixed sources with low concentration (10%)	No reagent is required. No hazardous substance is emitted.	The data correlated between UV and COD methods need to be created at monitoring.

can be performed only once an hour, which makes the unexpected factory effluent unable to be measured. From this, the UV method which is popular in Japan is now admitted by the Environment Protection Agencies in Shandong and Canton provinces. Table 4 shows the characters of COD monitoring methods.

In China, continuous monitoring for total phosphorus and total nitrogen is considered to be enforced for controlling eutrophication under the Twelfth Five Year Plan starting in 2011. This regulation against total phosphorus and nitrogen has been already started in Japan since 2002. Eutrophication has been steadily controlled in Japan, by monitoring the total phosphorus and nitrogen conducted in the Water Total Quality Regulation. This achievement promises a success in solving the eutrophication phenomenon in Taihu and Dian Lakes in China, too.

Water Quality Regulations in Other Asian Countries

It is also being under consideration to start regulating the water quality in other Asian countries, as operated in Japan.

In Korea, the water total quality regulations have started in 2006. The values of COD Mn, total phosphorus and total nitrogen, pH, turbidity and flow are measured on approximately 600 spots of fixed sources (including sewage treatment plants) in Korea, and the data is transferred to the local Environmental Management Bureaus by data loggers. Surface water contamination has been improved with these water total quality regulations.

In Thailand, it is considered to start regulating the water total quality from 2010 on approximately 200 spots of fixed sources (including sewage treatment plants). Monitoring items or the contents of regulations are being discussed. To respond to this movement, some Japanese companies in Thailand have been quick to purchase water quality meters and started re-examining sewage treatment systems and self-monitoring, to be prepared for the upcoming regulations.

In Asian countries such as Malaysia, Vietnam, the Philippines, Indonesia and India, the surface water quality monitoring has started, and in some areas online monitoring has been adopted.

Link between Water Total Quality Regulations and Measuring Devices

The Example of Automatic Total Nitrogen/ Phosphorus Monitoring System <TPNA-300> for the Japanese Fifth Water Total Quality Regulation

In Japan, to control eutrophication of lakes and ocean areas, the Water Total Quality Regulations targeting the COD of the drainage from business institutions have been implemented on 4 occasions since 1979, in enclosed water area inland seas such as Tokyo Bay, Seto Inland Sea and Ise Bay.

However, those regulations did not lead to a complete settlement of the issues caused by the eutrophication, e.g., red and blue tides. Based on this situation, the Central Environment Council's Water Quality Subcommittee-Total Water Quality Standard Board established total quality regulations standards and methods for measuring pollution loads in October 2000. Since then, the business institutions, which drain the water volume more than 400 m^3/day, have become obliged to be equipped with automatic total nitrogen/phosphorus monitoring system. HORIBA group provides TPNA-300 as our product lineup for Automatic Total Nitrogen/Phosphorus Monitoring System. The features of the product are described below.

1. A small footprint makes it possible to store in a case designed for outdoor use. UV monitor (OPSA-150) can also be stored with it.
2. Features a built-in payload operation function that makes it possible to calculate the payload from the flow-volume signal.

3. Possible to make continuous measurements of two components, total nitrogen and total phosphorus, at the same time on one monitoring system.
4. Using a heating method and an ultraviolet oxidation decomposition method makes it possible to perform preprocessing at ambient temperatures and atmospheric pressure, which enables much easier maintenance than with traditional autoclave methods.
5. High correlation with manual analysis methods.
6. Offers a user-friendly, wide variety of functions, such as automated zero-point adjustment and calibration.
7. Reducing reagent consumption realized lower running costs.

- Reduction of reagent consumption: reduced the amount of the used sample reagent to 1 milliliter, which is a tenth of former models.
- Reduction of pure water consumption: reduced pure water used, to 50 liters a month compared to 700 liters for former models.
- Decrease of the number of replacement parts: adopts a decomposition/measurement cell integrated architecture to decrease the number of replacement parts to half of those for former models.
- Smaller amount of waste solution: emits only 15-liter waste solution per month, which is a one-fifth of that with former models.
- Lower power consumption: consumes 400 VA of the electricity, which is about half of that former models consumed.

This product retained 40% share of the Japan market in 2004, in the year when the Water Total Quality Regulation for the total phosphorus and nitrogen was enforced.

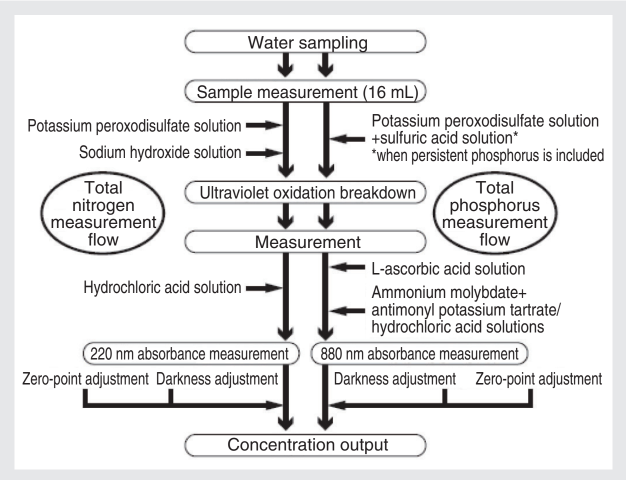

Figure 1 Measurement flow forTPNA-300

The Example of Organic Pollutant Monitor <OPSA-150>

In Japan, drainage concentration was first controlled with organic pollutants using COD as a criterion. Since 2002, total nitrogen and phosphorous have been added to measurement items.

The kinds of continuous measuring monitors for organic pollutants are COD monitoring system, UV meter, and TOC (Total Organic Carbon) meter. In Japan, UV meters are used in approximately 70% of business establishments. The reasons for this are: highly compatible correlation between COD values and ultraviolet absorption degrees, which are used as a principal method of UV meter easy maintenance due to the non necessity of reagents. To maintain stable continuous monitoring, it is necessary to correct the light intensity constantly during monitoring, and to wash a cell in order to prevent it from being polluted.

OPSA-150 adopts the rotary cell length modulation method, which is the only technique this model has. This is a breakthrough method that the cell length modulation and wiper cleaning are performed simultaneously. This method is effective to continuously obtain the, stable data for long periods of time even for the drainage with much contamination. Figure 2 shows the relation between output signal and measurement cell length.

The cell length and output signal change corresponding to

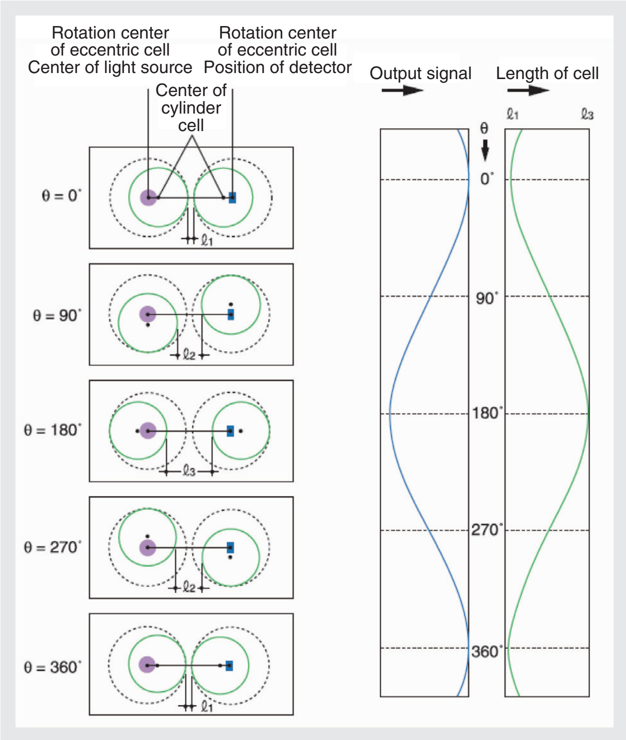

Figure 2 Cell motion and output signal of OPSA-150

Table 5 Service system in Asian countries

	HORIBA Office Location	Service System	Water Monitoring Product for Sale
Korea	Seoul, Ulsan, Suwon	Services supported by HORIBA Korea	All products
China	Beijing, Shanghai, Guangzhou, Chongqing	Services supported by HORIBA China	All products
India	New Delhi, Pune	Services supported by HORIBA India	OCMA, U-50/W-20, OPSA, CODA, TPNA, pH
Vietnam	Hanoi	The first services by HORIBA Hanoi office The second services by HORIBA Singapore	All products
Southeast Asia and other countries	Singapore	The first services by sales company office in each country The second services by HORIBA Singapore	All products

the rotation of the two cells. Based on the amount of light that each cell approach with the closest distance, check the difference of the light amounts between the based point and other ones to gain the absorption data of each cell length compensating the source light. In addition, using the function of rotation of the measurement cell, it is possible to clean the cell constantly by the wiper attached around the cell, without any influence on measurements. This function allows continuous and stable measurements for a long period.

The Example of COD Monitoring System <CODA-211/212>

CODA-211/212 are available to monitor COD values of samples from factory wastewater, rivers and harbors. The systems can calculate payload values by combining a payload calculation system, and offer measurements suitable for drainage total quality controls. CODA-211 is a system applied with an acid potassium permanganate method, which complies with testing methods for industrial wastewater in JIS, making the method automatically to function with the system. Mounting the enriched self-diagnostic function besides unique measuring and pumping sample liquid systems, more accurate measurements can be obtained with CODA-211. For samples including chlorine ion, e.g. seawater, CODA-212 is available for its adoption of an alkaline potassium permanganate method. The product features are shown below:

1. Automatic calibration (zero/span) is standard application. Contributes to enhancing the reliability of measurement values and saving time for regular maintenance.
2. Reagent replacement cycle for one month.
3. Chemical cleaning is optionally available (to solve and remove silver chloride inside a reaction tank).
4. Large and clear LCD display. Enables to indicate and confirm each data and setting conditions necessary for COD monitoring promptly.
5. The printer device fitted as standard equipment print out titration data graphically in addition to the display of time and COD setting value.
6. Store measuring datas for one month. Enables the data to be checked easily.

In recent years in particular, this systems have achieved sales over 30 units per year in response to the stricter water total quality regulations in Korea and China.

Supports and Services of HORIBA in Asia

In Table 5, the service system of HORIBA group in Asian countries is shown. Over the next five years, HORIBA/HAT plan to share products and human resources for each other “one company” and obtain an important position in the market, holding the international competitive strength.

Conclusion

In this report, market trends of Asia, and the approach by HORIBA group have been introduced. HORIBA group has provided the measuring devices equipped with technologies and functions, such as mainly TPNA-300, OPSA-150 and COD-211/212, especially to respond to the water total quality regulations in Asian market. We will keep on making efforts for contributions to environmental conservation and industrial development by having HORIBA’s water monitoring products to be used not only in Japan but also in other Asian countries.

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