Feature Article

Organic Pollutant Monitor OPSA-150

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The most important matter among water pollution indicators is organic pollutant. In Japan, since the first water quality total pollutant load control regulation was issued in 1979, organic pollutants have been continuously monitored, which has resulted in some improvement of water quality. On the other hand, Asian countries, especially China, rapid industrial growth has been accompanied by corresponding increases in water pollution. Thus, introduction of water quality regulations similar to the Japanese regulations are required. This article introduces the technology for measuring water pollutant levels and the OPSA-150, organic pollutant monitor manufactured by HORIBA. OPSA-150 is an ultraviolet absorptiometer (UV meter), which is a new version of the OPSA-120, common in the Japanese market for more than 20 years. While following the well-tried rotary cell length modulation method, wiper cleaning method, and turbidity compensating function by means of visible radiation, OPSA-150 also excels in measurement of both low and high concentrations. It can be used in diverse fields including extremely contaminated water discharge sites.

Introduction

In Japan, water quality total pollutant load control regulations have been in effect since 1979. These regulations aim to improve sewage systems, water-purifier tanks, and upgrade sewage processing. Under these regulations, the Minister of the Environment formulates basic policies for total amount reduction targeting the regions where drainage flows into closed water areas (Tokyo Bay, Ise Bay, and Seto Inland Sea). Among approximately 15,000 businesses located in the closed water areas, approximately 3,000 produce a drainage volume beyond 400 m^3, and restrictions are imposed on the total amount (drainage concentration x drainage volume). The drainage concentration control began from the organic pollutant regulations in which COD (chemical oxygen demand) was regarded as the indicator. From 2002, there was additional monitoring of nitrogen and phosphorous. COD indicates the amount of oxygen consumed during oxidization of oxidizable substances such as organic matter in water. In the Japanese official method, it is calculated by decomposition using potassium permanganate.

Devices that can continuously monitor organic pollutants include a COD meter, UV meter (ultraviolet absorptiometer), and TOC meter (total organic carbon meter) as shown in Table 1. In Japan, UV meters are used in approximately 70% of businesses. This is because UV meters are excellent in the correlation between the measurement principle taking advantage of ultraviolet absorption properties and COD, and no reagent is required, which facilitates maintenance.

Basic Measurement Principle of UV Meter

Most organic compounds show absorbance at approximately 253.7 nm of ultraviolet radiation. Using this property, absorbance of organic compounds is photoelectrically measured and the concentration of them is measured by means of the Lambert-Beer law[1].

$A = \log_{10}(Io / I)$

Io = Intensity of incident radiation

I = Intensity of transmitted light

Absorbance A is in proportion to the light path of the sample

Table 1 Features of Various Measuring Devices

	Principle	Advantages	Disadvantages	Japanese market share
COD meter	Sample is oxidized and decomposed by using reagent, and the amount of oxygen consumed is measured by potentiometric titration.	Correlated with official method.	Reagent is required. Waste solution is generated. Measurement must be performed hourly.	Approx. 20%
UV-photometer	Ultraviolet rays (UV) are applied to the sample and the UV absorbance is measured.	Maintenance is easy. Running cost is low. A high measurement frequency of 1 per second is possible.	Correlation with the official method cannot be obtained in some samples.	Approx. 70%
TOC meter	Sample is completely combusted and oxidized, and CO_2 generated is measured at the infrared gas detector section (NDIR).	Influence of coexistent substances is less.	It is necessary to exchange oxidation catalyst and combustion tube periodically, which increases the maintenance cost.	Approx. 10%

cell (L) and sample concentration (C), which can be expressed as follows.

$A = \alpha LC$

α = Absorption constant

By using this law, the sample concentration can be measured from the analytical curve.

In general, the absorption spectrum of organic compounds has the property shown in Figure 1. It is said that most of these peaks are the characteristics of unsaturated hydrocarbons (ex. Substance with benzene ring).

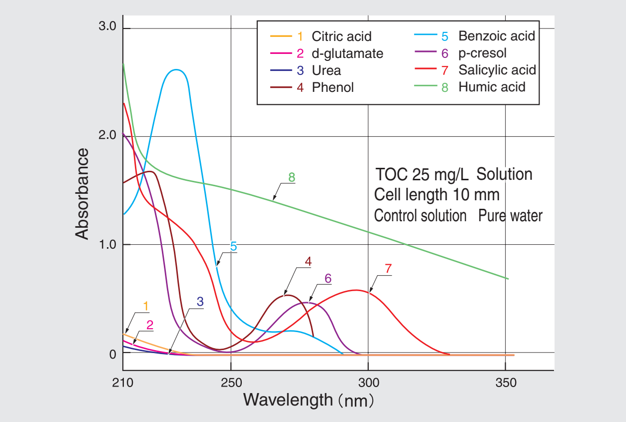

Figure 1 Absorption Spectrum of Organic Compound

Considering factories in general, drainage from various plants and part of waste water from miscellaneous sources are mixed and discharged to the effluent treatment facility. Such influent water contains lots of organic compounds. The ratio of organic compounds which have a complicated structure with benzene rings is frequently increased by performing effluent treatments such as activated sludge processing. Thus, UV meters are often applied to factory effluent.

Even in stream water, gently-sloping absorption properties are shown between 250 and 300 nm. This is because organic compounds with benzene rings such as humic acid, fulvic acid, lignin and tannin are present in drainage from sewage-treatment plants with activated sludge processing.

It is known that a correlation exists between COD and absorbance as shown in Figure 2. A UV meter is generally used by taking the correlation data between absorbance and COD as in Figure 2 and calculating the correlation coefficient.

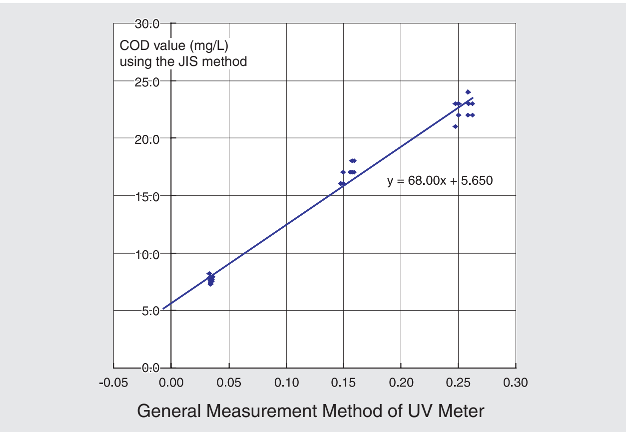

Figure 2 Correlation between Absorbance (Measurement Value of UV Meter) and COD

Usual Measurement Method of UV Meter

Figure 3 shows a typical constitution of absorbance measurement.

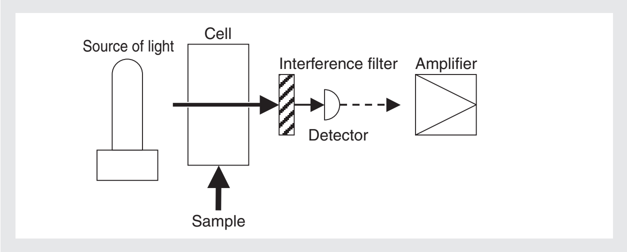

Figure 3 Typical Absorbance Detector Section

Though this basic method is simple, the following problems must be solved to perform continuous measurement.

- It is necessary to constantly compensate for the light intensity during measurement.
- If the measurement cell becomes soiled, some measurement errors occur.

To be more specific, the following measures are generally taken in combination in order to solve these mechanical problems so that continuous measurement can be performed:

(1) By providing an interference filter and detector, the light intensity compensation is performed without passing the measurement cell separately through the output side of the light source (Figure 4).

(2) A washing wiper is provided in the measurement cell to allow periodic cleaning (Figure 5).

However, there are still the following problems for stable long-term continuous measurement.

For (1), optical axes are different between the light intensity compensation and measurement and thus compensation becomes incomplete due to light source fluctuations and light source visual angle differences. In addition, the error factors cannot be eliminated because the measurement cell is not assessed alone. For (2), cleaning is intermittent, and thus contamination can still be an influence. Also, it is often difficult to remove dirt contamination once it has adhered.

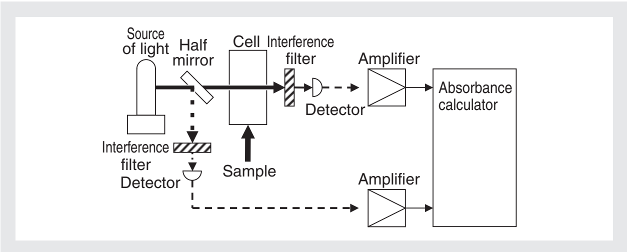

Figure 4 Absorbance Detector Section with the Light Intensity Compensation

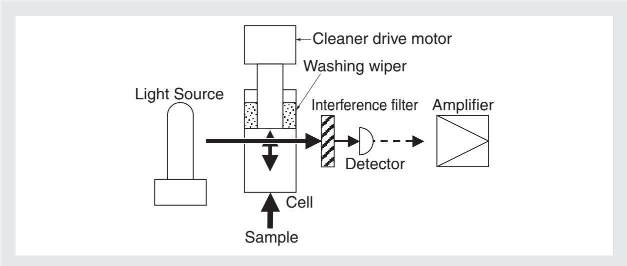

Figure 5 Absorbance Detector Section with Cell Cleaning Structure

Features of the OPSA-150

HORIBA has been a UV meter supplier since the first water quality total pollutant load control regulation was issued. We face-lifted the long seller UV meter which had established credibility over 20 years and developed a new product, the OPSA-150 (Figure 6).

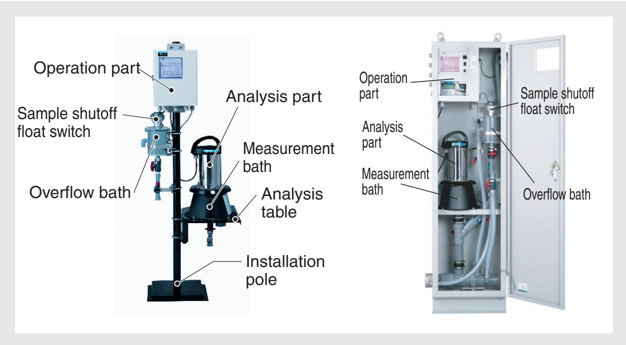

Figure 6 OPSA-150

This product adopted HORIBA's proprietary rotary cell length modulation method, which was a feature of the former model. This method is the landmark because cell length modulation and wiper cleaning are performed simultaneously. Using this method, stable data can be obtained constantly for long periods even in harsh drainage environments[2].

Figure 7 shows the Cell section of the OPSA-150.

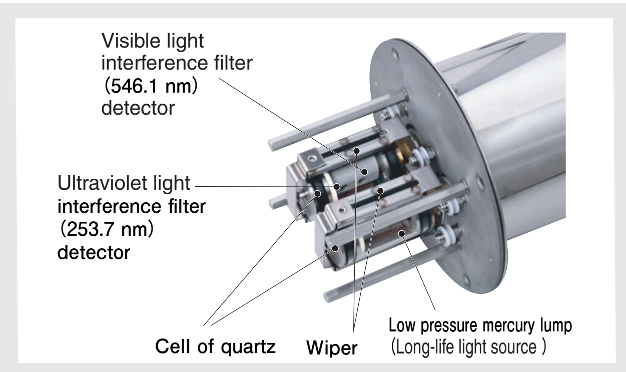

Figure 7 Cell section of the OPSA-150

In this product, the cell, which irradiates light of the low-pressure mercury lamp, and the cell which detects absorption of the ultraviolet light and visible light rotate respectively.

Figure 8 shows the relationship between the measurement cell length and output signal.

The cell length and output signal are changed by rotation of the two cells. Comparing the measurement value while the cells are closest to each other and the value while the cells are farthest apart from each other, compensates for the light source intensity. Because there exists one optical axis and the light intensity is compensated for through the measurement cell, error factors due to the measurement cell are also compensated for. Also, by taking advantage of constant rotation of the measurement cell, it is possible to clean the measurement cell continuously without interfering with measurement due to the cleaning wiper attached around the measurement cell. These allow continuous measurement with long term stability.

In the OPSA-150, while inheriting the merits of this rotary cell length modulation method, a wide measurement range was also achieved.

With conventional cell length modulation, only two points, the shortest point and the longest point are measured. In the OPSA-150, on the other hand, multiple points are measured while the cell length is modulating and the data is processed, which realizes the wide measurement range. Previously, the measurement range was fixed to either 0.5 or 1.0 at the full-scale value of absorbance (10 mm cell reduced absorbance*1) using the same analysis section. In this model, wide range variation from 0.1 to 5.0 was realized.

*1: Value expressed by $As \times 10/L$, where As is virtual absorbance obtained by the measuring device with the cell length of L mm (JIS K 0807).

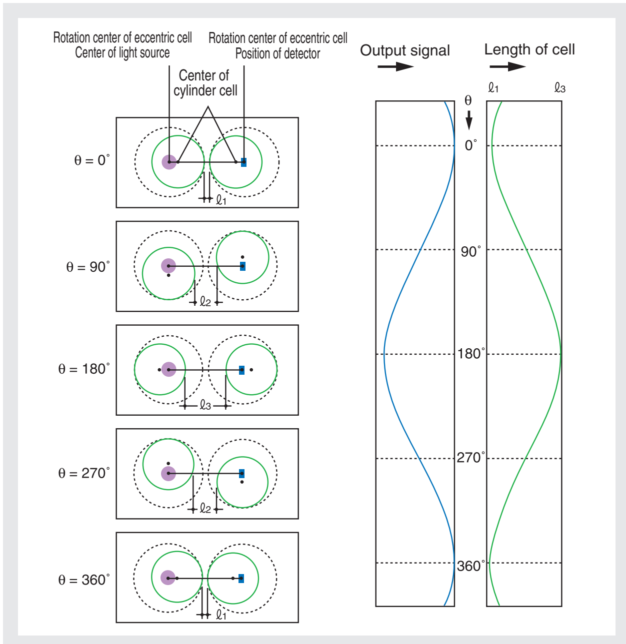

Figure 8 Cell Motion and Output Signal of OPSA-150

Furthermore, the OPSA-150 has the following features. (1) Samples with turbidity can be measured precisely by adopting a dual wavelength method and compensating for turbidity through simultaneous measurement of the UV value and absorption of visible light (VIS). (2) The open cell structure is adopted so that the measurement cell can be easily cleaned even if it becomes dirty. (3) Since calibration is performed using a special calibration sample solution, complicated preparation work is unnecessary, and UV and VIS can be calibrated at the same time. (4) A reduced COD value display function and reduced turbidity display function are provided. (5) A graphic touch panel is used for the display section as a user-friendly interface. (6) A data storage function is provided. Values acquired hourly can be stored consecutively up to a maximum accumulated period of a year. (7) The maximum resolution has been increased by a factor of ten over the former model, i.e., absorbance can be displayed in steps of 0.0001. As a consequence, measurement can be performed stably for long periods and the administrative and maintenance expenses can be minimized.

Applications Other than COD Measurement

UV meters are used for not only measurement of COD and environmental loads, but also other applications. Because the ultraviolet absorption method is used as the measurement principle, concentrations of samples which, show absorbance around ultraviolet radiation (253.7 nm) can theoretically be measured. For example, UV meters are used for phenol concentration control during industrial processes, control of antifreezing solution, control of dissolved ozone concentration, etc. Figure 9 shows the relationship between UV absorbance and phenol concentration as an example.

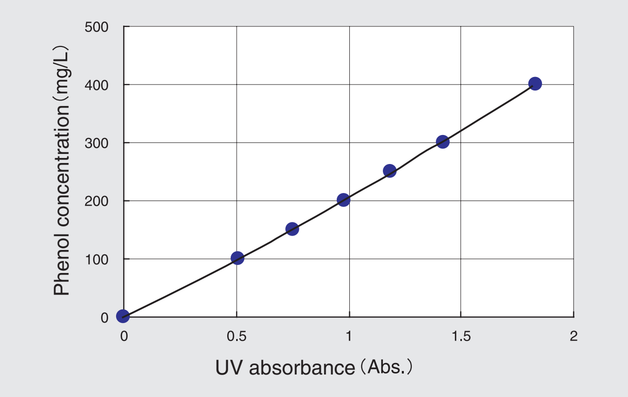

Figure 9 Relationship between UV Absorbance and Phenol Concentration

Also, trihalomethane contained in tap water, which is a cancer-causing substance, is perceived as a problem. It is considered that trihalomethane is generated during the chlorination process if organic matter is contained in untreated water to be used for tap water[3]. The trihalomethane generative capacity can be seen as an indicator by measuring the concentration of organic matter in untreated water by means of a UV meter. As a requirement for Japanese tap water, the annual average of the total amount of trihalomethane must not exceed 0.1 ppm. UV meters can be used as a continuous monitor for this.

Circumstances Abroad

Whereas UV meters have grown popular as a method for COD measurement in Japan, they have not yet spread overseas. It is likely that this is due to use of a dichromic acid method for COD measurement in most countries. Such countries use meters whose dichromic acid method has a strong correlation to manual analysis or TOC meters.

As described, COD meters and TOC meters are complex, use chemicals, and include lots of consumable parts for combustion. Thus, they seem not to be the best choice as analyzers. Especially in Asian countries where environmental problems will come under closer scrutiny in the future, popularization of analyzers takes top priority for the purpose of environmental improvement. The spread of UV meters, which can reduce cost and maintenance problems, is desirable.

With the cooperation of local firms in China, HORIBA is providing UV meters to Chinese factories, etc., and verifying a good correlation with COD. Also, HORIBA is verifying that even considerably dirty drainage can be measured stably for long periods without maintenance. While publicizing our achievements and experience gained over the years in Japan, we desire that UV meters be recognized as viable so are able to contribute to the improvement of water environments.

Conclusion

Thanks to UV meter measurement technologies, the water quality total pollutant load control regulations in Japan are being satisfied, and some successful results are being obtained. For example, going upstream of Ayu, sweetfish have been observed in the Yodo river system. Water quality is being improved step by step. On the other hand, environmental problems related to water quality are being taken seriously in countries such as China and which are experiencing remarkable industrial development. The importance of water quality monitoring technologies is now understood. Also in fields other than water environments, UV meters are low priced and of excellent stability during continuous monitoring. Thus, it is to be expected that UV meters will be also used for water quality control in industrial processes.

We are striving to make HORIBA's water quality monitoring technologies to be used by many around the world and in this way contribute to global environmental conservation and industrial development.

Reference

[1] JIS K0807-1997, Ultraviolet photometer for monitoring of water pollution, (2003).

[2] Shigeyuki Akiyama, Current states and future tasks of water quality analyzers, *Readout*,1,13-23 (1990).

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