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# On-site Water Quality Monitoring Technology for Wastewater Treatment Plants†

MIYATA Jun[*1] NAKAHARA Keisuke[*2]

***Abstract:***

*JFE Engineering has been developing monitoring technology of the organic pollution load of wastewater as one of operation management technologies. During the development of noncontact on-site monitoring equipment, fluorescence of 340 nm wavelength was detected corresponding to the amount of soluble organic matters when the ultraviolet rays of 270–280 nm wavelength were irradiated at wastewater. A prototype was developed utilizing this characteristic and its actual plant test was performed by demonstrating potential applications.*

## 1. Introduction

The growing interest in environmental protection in recent years has led to a tightening of regulations on the quality of effluents discharged from factories and worksites. Moreover, the factories and worksites themselves are now recognized to bear full responsibility for monitoring their own compliance with environmental regulations. Operation control sorely needs to be rationalized, however, as enhanced effluent treatment in wastewater treatment plants generally increases operation costs.

Operations are rational in a wastewater treatment plant when the quality of the treated water is maintained stably at a minimum operation cost. Two control technologies are crucial for this purpose: (1) a technology to accurately grasp the pollution loads to be treated while reducing the power and chemicals used for treatment to requisite minimums (feedforward control), and (2) a technology to monitor the quality of the treated water and increasing the input of power and chemicals whenever the required quality cannot be maintained (feedback control).

The operation control technologies now being practically applied in wastewater treatment plants include a method to monitor the quality of the water using an ion sensor, a batch type device for measuring water quality, a method of charging coagulants, etc., when the target water quality is exceeded, and a method of the dissolved oxygen (DO) control to monitor DO concentration in an aeration tank with a sensor and to increase or decrease the volume of injected air to ensure that the DO concentration never falls below a specific value. There are challenges, of course, to applying these method effectively. In feedback control, the method of monitoring the quality of the treated water and adjusting operation conditions when the target water quality is exceeded, for example, the adjusted operation conditions are only useful if they improve the treatment condition immediately. This constraint limits the available methods for operating wastewater treatment plants, including the methods for the input of chemicals into the water to be treated.

Various devices to monitor the water quality are available. One type works with an electrode sensor, while another pumps up sample water and measures the absorption intensity while feeding the sample water through a flow cell. The conventional monitoring devices, contact-type devices which are often complicated to maintain, have been used only in the requisite minimum applications. When a contact-type device is used to treat wastewater that has not been treated in advance, biofilms quickly form on the contact portions and hinder correct measurement of water quality. For this reason, these contact-type devices have scarcely been put to practical use.

When a molecule is irradiated with light, the molecule absorbs the energy and may sometimes emit the energy as light, or "fluorescence." The properties and concentration of a molecule can be investigated by mea-

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[*1] Senior Researcher Staff Manager,
Aqua, Bio and Chemical Dept.,
JFE R&D

[*2] General Manager, Aqua, Bio and Chemical Dept.,
JFE R&D

suring the spectrum and intensity of its fluorescence. Several studies have been conducted to analyze the fluorescence emitted from water samples irradiated with light such as laser light and evaluate the concentrations of organic substances in the water based on the relationships between the intensity of the fluorescence and the concentrations of the organic substances in the water[1,2]. Our group has attempted to apply this fluorescence analysis method as a monitoring technique for the operation control of wastewater treatment plants. Specifically, the authors determined the wavelength regions suitable for the monitoring of organic substance concentrations, conducted fundamental tests with a fluorescence spectrophotometer, fabricated a noncontact-type monitoring device on a trial basis, and carried out monitoring tests in an actual sewage treatment plant. This paper describes the knowledge we obtained through these tests.

The fluorescence analysis method has following features: (1) the molecular species that emit fluorescence are relatively limited; (2) the intensity of fluorescence is often weak; (3) light amounts at zero level can be measured with high sensitivity when using a low-concentration sample (impossible with the absorption analysis method); and (4) fluorescence may be re-absorbed when using a high-concentration sample.

The direct measurement of pollutants in wastewater is generally impossible by this method, as only a limited portion of the pollutants actually emit fluorescence. When the information on pollution loads has at least one significant figure, however, it can be applied for the operational control of a wastewater treatment plant. For this reason, the fluorescence analysis method can conceivably be used as a technique for monitoring pollution loads when the pollution component ratio in wastewater is constant. Somiya et al[3,4]. reported that suspended solid pollutants in wastewater can be monitored by measuring Rayleigh scattered light and Raman scattered light, two types of light with higher intensity than fluorescence. In the same vein, the authors monitored the loads of solid organic substances by measuring the intensity of the Rayleigh scattered light. One important requirement for the effective operation control of wastewater treatment plants is to monitor the loads of soluble organic substances that oxidize and decompose quickly. When wastewater contains large amounts of suspended solid substances, however, the Rayleigh scattered light of the suspended solid substances rises to a high intensity which makes it difficult to monitor the concentrations of the soluble organic substances. As an alternative, the authors therefore decided to use the absorption intensity for monitoring in spite of its relative weakness.

Incidentally, the tests we report here were conducted on wastewater from urban sewage. In our view, this technique would be best applied for the monitoring of the inflow pollution loads and concentrations of organic substances in water treated at plants dedicated to the treatment of both organic industrial wastewaters and urban sewage.

## 2. Fundamental Test

### 2.1 Test Method

The test was performed by selecting inflow pollution loads in an urban sewage treatment plant and detecting the intensity of fluorescence emitted when the inflow sewage was irradiated with light. First, the authors identified the wavelength regions suitable for the monitoring of organic substances by verifying the relationship between the concentrations of the organic substances in sample sewage and the fluorescence intensity measured by a fluorescence spectrophotometer,.

An RF-1500 manufactured by Shimadzu Corp. was used as the fluorescence spectrophotometer. All of the samples tested were taken from a primary sedimentation tank effluent of a sewage treatment plant for urban sewage (an influent to a bioreactor). Some of the samples were untreated and others were liquid samples after filtration treatment with 5C filter paper (soluble samples). The water quality analysis was performed by the sewage testing method of the Japan Sewage Works Association[5]. All of the samples used were collected from May 11 to July 21. The samples were taken from a combined-sewerage treatment facility which treats rainwater and wastewater from the same sewer system. Large volumes of rainwater flow into the plant during periods of heavy rainfall.

### 2.2 Test Results

The fundamental test was conducted with eleven water samples collected from May to July. The chemical oxygen demand (CODcr), biological oxygen demand (BOD), and suspended solids (SS) concentration, i.e., the main indexes of the concentrations of organic polluting substances, were measured as water quality analysis items. **Figure 1** shows the results of the water quality analysis for the samples. The solid CODcr (or BOD) concentration was estimated by subtracting the soluble CODcr (or BOD) concentration from the total CODcr (or total BOD) concentration.

As the sample water was inflow sewage for a combined-sewerage type facility, large variations were observed in the total organic substance (CODcr and BOD) concentrations when the samples were collected. The total CODcr concentration ranged from 1 200 mg/*l* (maximum) to 160 mg/*l* (minimum), the total BOD concentration ranged from 420 mg/*l* (maximum) to 72 mg/*l* (minimum), and the suspended-solids (SS) concentration

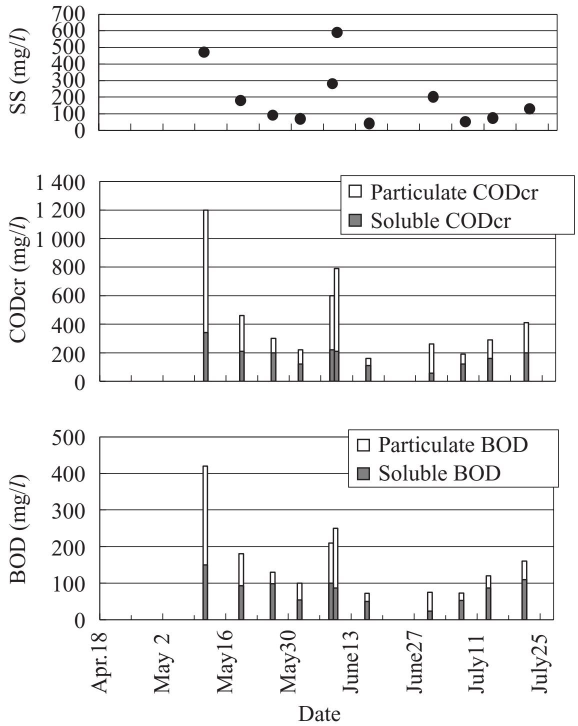



Fig. 1 Sample water quality with which the basic examination was presented

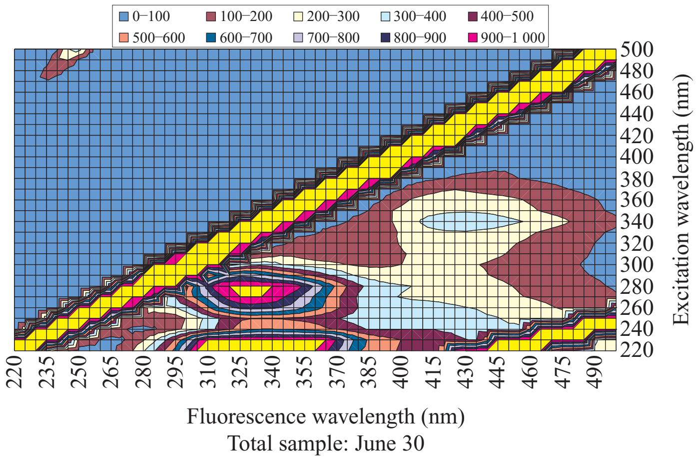



Fig. 2 The result of having measured the fluorescence intensity of sample wastewater

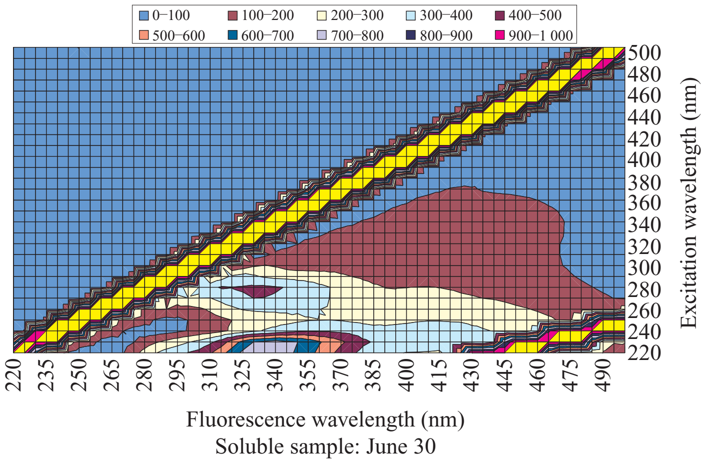



Fig. 3 The result of having measured the fluorescence intensity of sample wastewater (Soluble sample)

ranged from 590 mg/*l* (maximum) to 40 mg/*l*. The latter range was the greatest. The fluorescence spectrophotometer used in the test provided widely divergent results on the various samples tested.

**Figures 2** and **3** show the results of measurements of the fluorescence intensity of sample sewage by the fluorescence spectrophotometer. Figure 2 shows the results for all untreated samples; Fig. 3, the results for the soluble samples after filtration through filter paper. In the plotting of the scattered light intensity, the wavelength of the excitation light used to irradiate the samples is taken as the ordinate and the wavelength of the scattered light is taken as the abscissa.

In the measurement of the samples shown in Fig. 2 (samples with abundant suspended solids), the reflections are irregular the transmitted light decreases. On this basis, we speculate that the scattered light, including the fluorescence, rises to a high intensity overall. In Figs. 2 and 3, however, we observe fluorescence near 330 nm with excitation light of 270–280 nm, strong light near 300–380 nm with excitation light of 220 to 230 nm, and low-intensity fluorescence near 430 nm with excitation light of 340 nm. The fluorescence patterns are clearly similar, though they differ in intensity. The authors thus find that there is no fluorescence specific to solid organic substances, and that it might be possible to monitor the concentrations of the soluble organic substances or total organic substances by measuring the fluorescence intensity near 330 nm under irradiation with light of 270–280 nm or the fluorescence intensity near 300–380 nm under irradiation with light of 220 to 230 nm.

Organic substance are thought to show gentle light absorption in the whole ultraviolet ray region of 200 to 350 nm. It has also been reported[1)] that organic substances of unsaturated bonds absorb light in a wavelength range of 270–280 nm, and that fulvic acids, a family of organic substances, absorb light in a wavelength range of 340 to 360 nm. On this basis, we surmise that the organic substances present in abundant levels in sewage are the substances which emit the detected fluorescence. From Figs. 2 and 3 the authors clearly see that when light with wavelengths of 220–230 nm, 270–280 nm, and near 340 nm is absorbed, the absorbed energy is emitted as fluorescence.

Incidentally, we can attribute the opaque quality of the Raman scattered light of the water molecule (light with a wavelength about 1.12 times that of the excitation light) in Figs. 2 and 3 to the failure of the Raman scattered light to separate due to the high intensity of the Rayleigh scattered light (light with the same wavelength as the excitation light).

### 2.3 Summary of Results of Fundamental Test

In the wavelength region of 220–270 nm for excitation light, ultraviolet rays pass through glass at high rates of optical absorption and filters are of only limited use in filtering out specific wavelengths. Devices that generate short-wavelength light are costly to operate and consume considerable power. For the device to be applied in actual monitoring, the authors therefore decided to rely on longer wavelengths of 270 nm.

The authors measured the fluorescence intensity of the excitation light at the wavelength of 270 nm in each sample and investigated the correlations to the concentrations of organic substances. The relationship between the CODcr of soluble samples and fluorescence intensity is shown in **Fig. 4**.

The solid line in the figure indicates a primary regression line of the plotted data. The correlation is clear, albeit somewhat weak. Next, the authors determined the dispersion of the data based on the regression line to verify whether this relationship can be used in the monitoring of water quality. We used the following equation to determine the standard deviation when the distance from each measuring point to the regression line was regarded as a measurement error:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(S_i - \bar{S})^2}{n-1}} \quad \text{(1)}$$

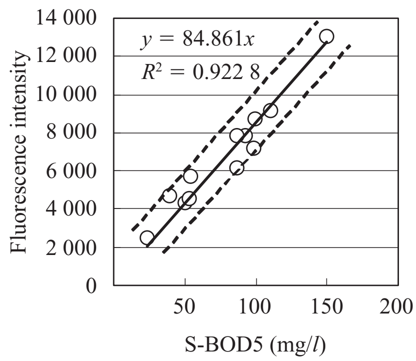
where $\sigma$: Standard deviation
$S_i$ : S-CODcr concentration of $i$-th data (mg/$l$)
$\bar{S}$ : S-CODcr concentration found from the regression line at the fluorescence intensity of $i$-th data (mg/$l$)
$n$ : Number of samples

In the measured data on the fluorescence intensity and soluble CODcr concentration at the excitation wavelength of 270 nm, $\sigma$ was about 15 mg/$l$. The dotted lines in Fig. 4 show the range of $2 \times \sigma$ (a 75% confidence interval) used to evaluate the error range of the data obtained in this test. When measuring a fluorescence intensity of 8 000, for example, the soluble CODcr concentration is thought to range from 173 to 233 mg/$l$. Though the measurements still lack adequate accuracy overall, it may be precise enough to monitor changes in the operation conditions of a wastewater treatment plant.

Similarly, the relationship between soluble CODcr and fluorescence intensity is shown in **Fig. 5**. The concentrations of CODcr and $BOD_5$ are correlated in urban sewage. For this reason, we also found a clear correlation between the $BOD_5$ concentration and fluorescence intensity. The standard deviation $\sigma$ was 9.4 mg/$l$, and the $BOD_5$ can be estimated to range from 75 to 113 mg/$l$ when a fluorescence intensity of 8 000 is assumed.

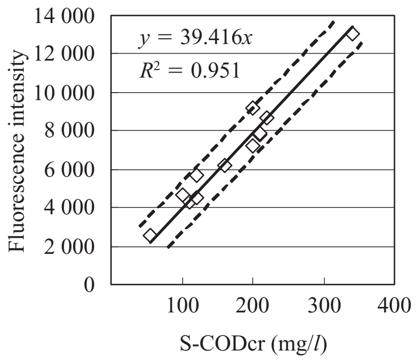
Next, **Fig. 6** shows the relationship between CODcr concentration and fluorescence intensity in the samples untreated by the filtration.

Judging from the correlation between the total CODcr concentration containing suspended solids and fluorescence intensity, the dispersion is clearly large



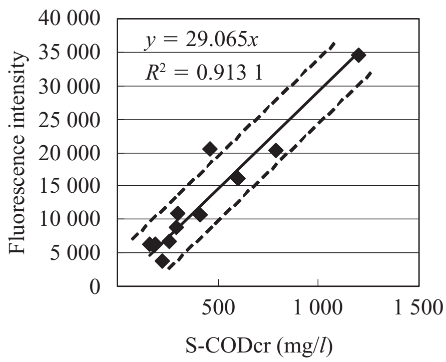

(Excitation wavelength: 270 nm
Detection fluorescence wavelength: 335 nm)

Fig. 5 Relationship between S-$BOD_5$ concentration and fluorescence intensity




(Excitation wavelength: 270 nm
Detection fluorescence wavelength: 335 nm)

Fig. 4 Relationship between S-COD concentration and fluorescence intensity




(Excitation wavelength: 270 nm
Detection fluorescence wavelength: 335 nm)

Fig. 6 Relationship between T-$COD_{cr}$ concentration and fluorescence intensity

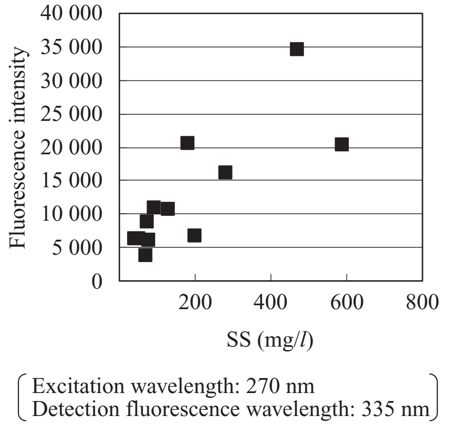



Fig. 7 Relationship between SS concentration and fluorescence intensity

compared to that from the data on the soluble samples. When $\sigma$ was determined by the same method used in the analysis of soluble samples, the value was 93 mg/*l*. This was about six-fold higher than the $\sigma$ of the soluble samples. And given that the total CODcr/soluble CODcr ratio is about 3, the authors can also surmise that the measurement error of the data increases. This increase of the measurement error might be attributable to the absence of fluorescence emission from the solid organic substances. Incidentally, the authors might also attribute the weak correlation to the relatively stable concentration ratio between the soluble and solid organic substances. The measurement data is plotted in **Fig. 7** for reference, with the suspended solids (SS) concentration as abscissa and the fluorescence intensity as ordinate.

Finding almost no correlation between the suspended solids (SS) and fluorescence intensity, we decided to separately determine the solid organic substances based on the intensity of the Rayleigh scattered light. In measuring the samples containing solid organic substances and soluble organic substances mixed together, a higher concentration of suspended solids (SS) might be expected to result in more irregular reflection and a higher overall intensity of irregularly scattered light. When monitoring soluble organic substances, it therefore might be necessary to correct the intensity of the irradiated light on the basis of a suspended solids (SS) concentration separately found.

## 3. Demonstration Test in a Sewage Treatment Plant

### 3.1 Makeup of the Trial Device

The authors conducted a demonstration test with a noncontact type on-site monitoring device for the operational control of wastewater treatment plants in an actual plant.

Results of the fundamental test identified excitation wavelengths of 270–280 nm and a detection fluorescence wavelength of 340 nm as the ideal conditions for monitoring the concentrations of soluble organic substances. The device was designed and fabricated on the basis of this result. As a noncontact type, the device had to be designed without a detecting element immersed in water or a pump to pump up samples (test water). The authors achieved this by making it installable at treatment plant sites based on the actual plant constructions. Device sensors detected scattered light generated by ultraviolet rays irradiated over the free water surface of a covered influent passage.

**Photo 1** shows the device used to detect the scattered light generated from the ultraviolet irradiation on a trial basis. Light from xenon mercury lamps (①, ②) is passed through multiple interference filters (③), and the light at the wavelength of 280 nm is selectively radiated. Mechanisms to remove the heat from the lamps are built into the system. Wastewater (sewage) is irradiated with the 280 nm light via a handle-type optical fiber (④). The scattered light from the wastewater is guided to detecting parts (⑥, ⑦) by another handle-type optical fiber (⑤). Interference filters in the detecting parts limit the detection to light of a specific wavelength. Light of other wavelengths can be detected simply by changing the filters, however, so the device can be easily accommodated to different types of wastewater. Each sensor is equipped with a set of high-sensitivity photomultiplier tubes. The sensor output is recorded in a data logger and used as data for control. The entire device is housed in a portable device that be easily carried by an operator.

The trial device radiates ultraviolet rays on the water surface and detects scattered light generated from the water surface. The irradiation part and detecting part must be kept at a constant distance from the water

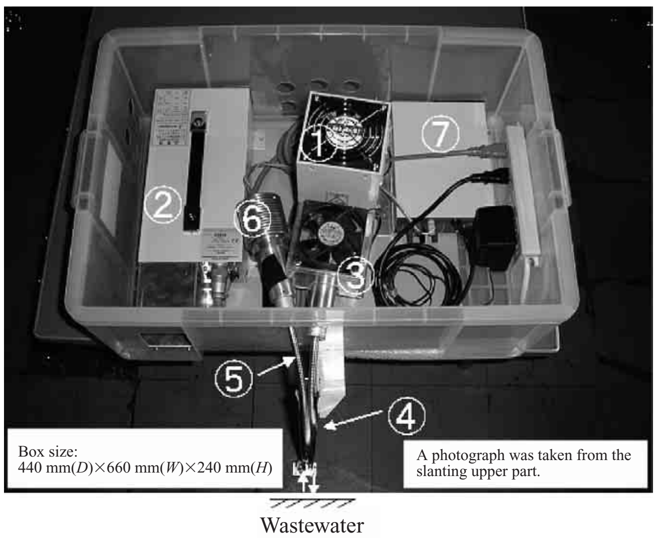



Photo 1 Examination equipment

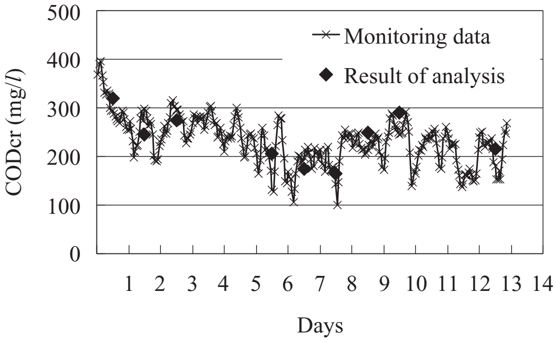



Fig. 8 The examination result in a real institution

surface to ensure that the radiation intensity remains constant and that the intensity of the scattered light is accurately detected. This presents a challenge, however, as the height of the water surface changes whenever the inflow volume changes in an actual influent passage. To cope with this, the device design allows the height of the irradiation part and detecting part to be freely changed by the use of optical fibers. The leading ends of the optical fibers are connected to the irradiation and detecting parts, and the irradiation and detecting parts are fitted with a mechanism to adjust the irradiation angle and thereby by control the intensity of the scattered light detected.

### 3.2 Test Results

Light at a wavelength of 280 nm was irradiated by this trial device. The concentrations of the suspended solids were found by measuring the intensity of the Rayleigh scattered light. The concentrations of the soluble organic substances were found by measuring the intensity of the fluorescence generated.

**Figure 8** shows the results of a test conducted for about two weeks. The figure also shows the results of the water quality analysis. The samples for the water quality analysis were selected as spot samples at a fixed time and used for comparison with the results of the continuous monitoring.

The analytical values of CODcr concentration changed between 165 and 320 mg/*l* during the test period. This tendency could be substantially monitored. In some data, errors exceeding negligible levels occurred. The average value of differences from the analytical values was 15.5 mg/*l*, however. This suggests that the trial device may be suitable for the monitoring of water quality for operational control.

## 4. Conclusions

In order to use the fluorescence analysis method as a monitoring technique for the operation control of wastewater treatment plants, we conducted a fundamental experiment based on the use of a fluorescence spectrophotometer, fabricated a noncontact-type monitoring device on a trial basis, and conducted a monitoring test in an actual sewage treatment plant. We obtained the following knowledge as a result:

(1) No fluorescence specific to solid organic substances was observed. The concentrations of solid organic substances had to be separately measured by the Rayleigh scattered light and the like.
(2) When urban sewage was irradiated with light at wavelengths of 220–230 nm or 270–280 nm, fluorescence was observed at 300–380 nm or near 330 nm.
(3) It may be possible to monitor the concentrations of soluble organic substances by irradiating urban sewage with ultraviolet rays and measuring the fluorescence.
(4) The changes in CODcr concentrations could be adequately monitored during a two-week test on a trial device in an actual plant.

The authors would like to extend their thanks to Dr. Yasunori Saito from Department of Information Engineering in Faculty of Engineering of Shinshu University for helpfully examining the specifications for the monitoring device and assisting us with the trial manufacture of the device.

### References

1) Kaiga, N. et al. Evaluation of tap water quality by spectrofluorometry. J. of Water and Environmental Technology. vol. 22, no. 1, 1999, p. 54–60.
2) Ohmi, Y. et al. Detection of organic chemical material using laser induced fluorescence. J. of Advanced Science. vol. 12, no. 1, 2, 2000.
3) Somiya, I. et al. Water quality determination by light scattering spectrophotometry. J. of Water and Environmental Technology. vol. 18, no. 3, 1995, p. 191–198.
4) Somiya, I. et al. Continuous determination of water quality by light scattering spectrophotometry. J. of Water and Environmental Technology. vol. 19, no. 1, 1996, p. 47–55.
5) American Water Works Association. Standard Methods for the Examination of Water and Wastewater. 21st Ed.