

THE RELATION OF CHEMICAL OXYGEN DEMAND (COD) AND UV ABSORPTION OF RIVER WATERS IN KITAKYUSHU CITY

by

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SYNOPSIS

General discussion for COD and UV absorption was given at first. Effects of inorganic ions such as NO_3^- , NO_2^- , Cl^- and Br^- to UV absorption were investigated. Turbidity correction for UV absorbance was studied using kaolin standard suspension and the results were formulated for general use. Influences of volatile compounds such as benzene, chlorobenzene, acetone and pyridine to the values of COD were examined. It was found that volatile compounds, especially water insoluble compounds influence the COD and the apparent low oxidation degree of volatile pure compounds was partially explained by their volatility. The relation between COD and UV absorbance for surface water of rivers was investigated. COD vs. UV absorbance relation for sewage also was studied. The samples were collected from the rivers in Kitakyushu City and the neighborhood in Japan. Highest correlation was obtained at the wavelength of 260 nm in the present work. The UV spectrophotometry for the evaluation of the degree of organic pollution in water seems a useful method, especially combined with a COD measurement.

1. INTRODUCTION

When the pollution of the water in question is to be estimated, several particular characteristics in it must be picked up as indices of the water. Those indices might be pH, DO (Dissolved Oxygen), SS (Suspended Solid), BOD, COD, TOD (Total Oxygen Demand), TOC (Total Organic Carbon), color and turbidity. Indices only show the partial properties of water. So, the problem is "what kind of indices should be picked out". In the present work, a total amount of dissolved organic compounds was chosen as important factor for estimating the water pollution. Amount of organic compounds in contaminated water will approximately be estimated by the measurement of BOD, and/or COD. Especially, BOD test gives the important information to estimate the true natural oxygen demand and the extent of selfpurification by biochemical decomposition of the waste-water in nature. But there is delay because of its minimum five day incubation period. The more recently developed Chemical Oxygen Demand (COD) gives a fairly good approximation within several hours, although it does not give the true natural oxygen demand. These procedures are widely used today as an indication of industrial and municipal pollution. Unfortunately, it is difficult to conduct continuous monitoring or to measure automatically. On the while, organic compounds, in general, absorb light in the ultraviolet region. Therefore, a method of UV absorption measurement to estimate the amount of organic compounds in water was proposed, and many investigations were carried out, applied to river waters, lakes, industrial and municipal pollutions, and sea waters.¹⁻²⁹⁾ The works reported show wide range of correlations, low to high, between

COD and UV absorption owing to the characteristics of the water. Including this problem, water samples collected from the rivers in Kitakyushu city and the neighborhood, and sewage from the treatment plant were studied and discussed.

2. EXPERIMENTAL

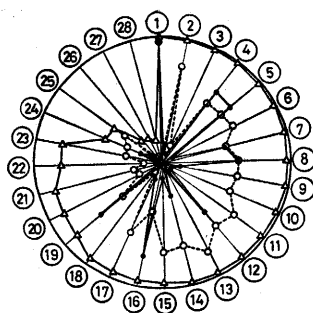
2.1. *Measurement.* The values of COD were determined according to the method in JIS (Japanese Industrial Standards) K0102 (1974). UV absorption spectra were determined on a Hitachi Model 200-20 type spectrophotometer using 1-cm cell.

2.2. *Water samples.* River waters were collected from the rivers in Kitakyushu City and the neighborhood, that is, from the Onga River, the Itabitsu River, the Murasaki River and the Ima River. Sewage was collected at sewage treatment plant in Kitakyushu City. River waters and sewage were filtered using glass filter (G4) before COD measurement, since these water contain suspended matter. However, sometimes fine particles pass through the filters. Therefore, turbidity corrections also were made on UV absorption measurement in the present study. Kaolin was used as turbidity standard and prepared according to JIS K0102 method.³⁰⁾

2.3. *Reagents.* All the reagents used were obtained commercially. That is, silver sulfate, mercury(II)sulfate, potassium permanganate, potassium dichromate, sodium oxalate, ammonium iron(II)sulfate, phenol, acetic acid, acetone, benzene, chlorobenzene, sodium nitrate, sodium nitrite, sodium chloride, sodium bromide, kaolin and active carbon were obtained from Wako Pure Chemical Industries Ltd., and 1, 10-phenanthroline was from Hayashi Pure Chemical Industries Ltd. All chemicals obtained, except kaolin and active carbon, were guaranteed reagents (G. R.) of the grade and used without further purification.

3. RESULTS AND DISCUSSION

3.1. *General discussion.* Generally speaking, organic compounds themselves are non-toxic and rather nourishing to living things. However, existence of large amount of them will in almost all cases, be the source of water pollution. Since they are oxidized by microbes to consume dissolved oxygen making the water anaerobic. The values of oxygen demands for decomposing the organic compounds have been attached importance as indices for water pollution, coming next to toxic substance. The amounts of oxygen consumption have been measured by several methods under various conditions. And these methods have their own characteristics. Familiar ones are $COD(M_n)$, $COD(C_r)$, BOD_5 and TOD . The methods which reflect the amount of dissolved organic compounds in water will be $TOD > COD(C_r) \geq BOD_5 \geq COD(M_n)$ in order. These relation will be depicted schematically in Fig. 1.³¹⁾ As the figure shows, $COD(C_r)$ method, in general, gives relatively high oxidation (decomposition) degree (80-100%) comparing with $COD(M_n)$ method. Straight chain aliphatic compounds, aromatic compounds and nitrogen contained heterocyclic compounds decompose very slowly. For straight chain aliphatics, addition of catalyzer such as silver sulfate elevate the decomposition degree greatly, but in vain to other compounds.³¹⁾ [It seems odd from the redox potential point of view that the values of $COD(C_r)$ is almost always greater than those of $COD(M_n)$, though the oxidation conditions are not the same to each other.] Of course, the values of TOD are greater than those of COD and BOD , presumably showing the total amount of organic compounds in water, in addition TOD is easy to operate and rapid to measure. But the problems of maintenance and high price of apparatuses prevent the popularizing



—△— COD(C_r), —●— COD(M_n), ---○--- BOD₅

Fig. 1 Schematic diagram for some methods of oxygen demand measurement.
 —△—: COD (C_r), —●—: COD (M_n), ---○---: BOD₅ Numbers ① to ⑳ represent the species of organic compounds. Lengths from the center along the radii represent the decomposition degree of organic compounds in percent, being each radius 100%.

- | | | | |
|--------------------|-----------------------|---------------------|-------------------|
| ① Formic acid | ⑧ Glycerine | ⑮ iso-Butyl acetate | ⑳ L-Glutamic acid |
| ② Acetic acid | ⑨ Formaldehyde | ⑯ Benzene | ㉑ Glycine |
| ③ Propionic acid | ⑩ Acetaldehyde | ⑰ Benzoic acid | ㉒ Glucose |
| ④ iso-Butyric acid | ⑪ Acetone | ⑱ Phenol | ㉓ Lactose |
| ⑤ Methanol | ⑫ Methyl ethyl ketone | ⑲ Toluene | ㉔ Saccharose |
| ⑥ Ethanol | ⑬ Diethyl ether | ㉐ Aniline | ㉕ Soluble starch |
| ⑦ n-Propanol | ⑭ Ethyl acetate | ㉑ Cresol | ㉖ Cellose |

of using them. Every compounds has its own property with respect to the chemical resistivity against oxidation. TOD (and TOC), however, neglect the such a difference. Thus, from the point of view of the natural purification, BOD₅ might be the best. As stated above, every method to obtain the amount of oxygen demand or organic carbon has its own characteristic and gives useful index for dissolved organic carbon in water. It is desirable that every component and its amount (probably trace amount) in dissolved organic matter is determined with high accuracy in short time and from the results obtained, prediction of TOC, TOD, COD and BOD is made if necessary. Such present day approaches are carried out by many researchers.³²⁻³⁸ However, detection of trace organic compounds requires much time and cost. Stillmore, the correlation of COD and the total amount of trace organic detected is not so good. The reason for it might be explained by the partial collection of the compounds within total dissolved organic matters in case of GC-MS technique using adsorbent much as XAD-2 resin, since the adsorbent in general can not adsorb polymer compounds. From the macroscopic point of view, measurement of COD to infer the total amount of organic compounds has useful meaning. UV absorption which has been reported to have good correlation with COD is easy to measure and requires short time to operate the apparatus, and continuous monitoring of water using UV method is possible. Comparison of COD and UV absorption seems significant. Correlation between COD and UV absorbance for general compounds is schematically shown in Fig. 2. In case of circled arrow conditions shown in Fig. 2, good correlation will be obtained as clearly known from the figure. It should be noted that as Fig. 2 shows, even if compounds are inorganic substances, they may contribute to both COD and UV absorbance. Thus to obtain the relation of COD vs. UV absorbance for true organic content, the components and amounts of inorganic compounds must be determined. Inorganic ions that exist relatively large amount in natural water are Cl⁻, SO₄²⁻, NO₃⁻, and NO₂⁻, and the effects of these ions to absorption spectra of natural waters

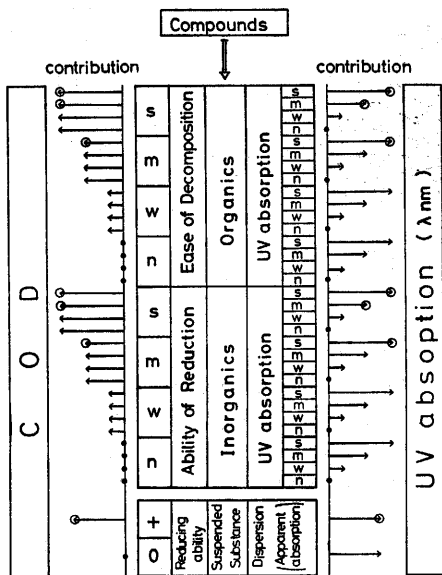


Fig. 2 Schematic representation for the correlation of COD and UV absorbance. s: strong, m: medium, w: weak, n: naught. (High correlation will be obtained in circled arrow cases in the figure.)

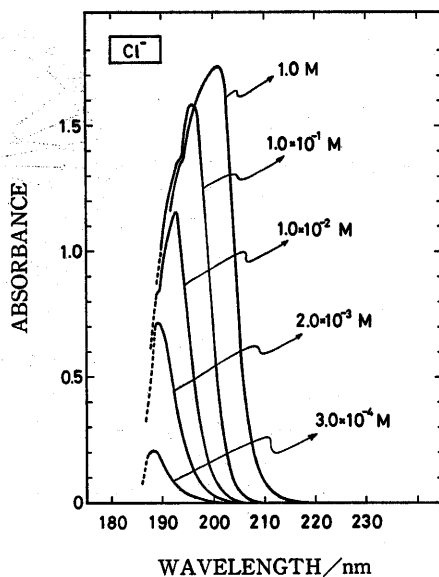


Fig. 3 Absorption spectra of Cl^- (NaCl) solution.

were studied by Ogura et al. extensively.^{5,15)} For sea water, Br^- contribute to the absorbance other than above stated ions. Some of these values of absorbances reported for these ions, however, might be unreliable, because the values listed in their studies are different to the same substances.^{5,15)}

Therefore, spectra for these ions were newly determined in the present investigation. Fig. 3 shows the absorption spectra of Cl^- (NaCl) solution. The spectra exhibit absorption maxima in fairly short wavelength region. The position of λ^{max} depend upon the Cl^- concentration. The absorption spectra show much deviation from Beer's law. They will be given as function of Cl^- concentration as follows.

$$\left(\begin{aligned} \lambda^{\text{max}}(\text{Cl}^-) &= 186.0 + 3.92420 \times 10^2 \times C^{1/5} - 4.82186 \times 10^3 \times C^{2/5} + 2.21846 \times 10^4 \times C^{3/5} \\ &\quad - 4.42004 \times 10^4 \times C^{4/5} + 3.25296 \times 10^4 \times C; \quad C = 0 \sim 1.0 \times 10^{-2} \text{ M} \\ \lambda^{\text{max}}(\text{Cl}^-) &= 186.0 + 2.54705 \times 10^2 \times C^{1/5} - 1.90680 \times 10^3 \times C^{2/5} + 5.69237 \times 10^3 \times C^{3/5} \\ &\quad - 7.48781 \times 10^3 \times C^{4/5} + 3.65282 \times 10^3 \times C; \quad C = 1.0 \times 10^{-2} \sim 1.0 \times 10^{-1} \text{ M} \end{aligned} \right.$$

$$\left(\begin{aligned} \text{Abs}(\lambda^{\text{max}}; \text{Cl}^-) &= 652 \times C; \quad C = 0 \sim 5.0 \times 10^{-4} \text{ M} \quad (\cong 18 \text{ ppm as } \text{Cl}^-) \\ \text{Abs}(\lambda^{\text{max}}; \text{Cl}^-) &= -2.494 \times C^{1/3} + 131.107 \times C^{2/3} - 592.500 \times C + 708.300 \times C^{4/3}; \\ &\quad C = 7.0 \times 10^{-4} \sim 1.0 \times 10^{-2} \text{ M} \\ \text{Abs}(\lambda^{\text{max}}; \text{Cl}^-) &= 11.664 \times C^{1/3} - 46.213 \times C^{2/3} + 94.667 \times C - 71.970 \times C^{4/3}; \\ &\quad C = 1.0 \times 10^{-2} \sim 1.0 \times 10^{-1} \text{ M} \end{aligned} \right.$$

Solution spectra of chloride ion show no absorbance in the region beyond wavelength of 220 nm. Since the solution spectra of Cl^- exhibit large concentration effect, the value of $\text{Abs}(220 \text{ nm}; \text{Cl}^- = 1 \text{ ppm}) = 4.3 \times 10^{-6}$ obtained by Ogura⁵⁾ seems meaningless for high concentration solution. Though solution spectra of bromide ion show similar spectra to those of chloride ion, absorption is relatively strong and exhibit in the long wavelength

region, and spectra of Br⁻ (NaBr) exhibit no absorption beyond 230 nm. For Br⁻, next relations were obtained.

$$\left(\begin{array}{l} \lambda^{\max}(\text{Br}^-) = 193.0 + 8.28783 \times 10^2 \times C^{1/6} - 1.84868 \times 10^4 \times C^{2/6} + 1.52922 \times 10^5 \times C^{3/6} \\ \quad - 5.554456 \times 10^5 \times C^{4/6} + 7.539978 \times 10^5 \times C^{5/6}; \quad C = 0 \sim 1.0 \times 10^{-4} \text{ M.} \\ \lambda^{\max}(\text{Br}^-) = 193.0 + 5.85100 \times 10^3 \times C^{1/7} - 7.76891 \times 10^4 \times C^{2/7} + 3.857359 \times 10^5 \times C^{3/7} \\ \quad - 8.472795 \times 10^5 \times C^{4/7} + 6.949171 \times 10^5 \times C^{5/7}; \\ C = 1.0 \times 10^{-4} \sim 5.0 \times 10^{-4} \text{ M.} \end{array} \right.$$

$$\left(\begin{array}{l} \text{Abs}(\lambda^{\max}; \text{Br}^-) = 1.129 \times 10^4 \times C; \quad C = 0 \sim 4.0 \times 10^{-5} \text{ M} (\cong 3.2 \text{ ppm as Br}^-) \\ \text{Abs}(\lambda^{\max}; \text{Br}^-) = -3.07983 \times 10^2 \times C^{1/6} + 6.01684 \times 10^3 \times C^{2/6} - 4.43278 \times 10^4 \times C^{3/6} \\ \quad + 1.460054 \times 10^5 \times C^{4/6} - 1.793023 \times 10^5 \times C^{5/6}; \\ \quad C = 4.0 \times 10^{-5} \sim 1.0 \times 10^{-4} \text{ M.} \\ \text{Abs}(\lambda^{\max}; \text{Br}^-) = 1.26441 \times 10^3 \times C^{1/9} - 1.31423 \times 10^4 \times C^{2/9} + 5.07824 \times 10^4 \times C^{3/9} \\ \quad - 8.63599 \times 10^4 \times C^{4/9} + 5.46324 \times 10^4 \times C^{5/9}; \\ C = 1.0 \times 10^{-4} \sim 5.0 \times 10^{-4} \text{ M.} \end{array} \right.$$

$$\varepsilon(\lambda = 210 \text{ nm}; \text{Br}^-) = 1.71 \times 10^3, \quad \varepsilon(\lambda = 220 \text{ nm}; \text{Br}^-) \cong 100;$$

$$C = 0 \sim 6 \times 10^{-5} \text{ M (4.8 ppm)}.$$

Solution spectra of nitrite ion follow Beer's law, through an absorbance of 1.5 (concentration of 3×10^{-4} M). Following values were obtained.

$$\varepsilon^{\max}(\lambda^{\max} = 208 \text{ nm}; \text{NO}_2^-) = 5.10 \times 10^3, \quad \varepsilon(\lambda = 220 \text{ nm}; \text{NO}_2^-) = 3.60 \times 10^3, \\ \varepsilon(\lambda = 230 \text{ nm}; \text{NO}_2^-) = 1.32 \times 10^3.$$

Solution spectra of nitrate ion also follow Beer's law through an absorbance of 1.6 ($C = 2.0 \times 10^{-4}$ M). Obtained values were

$$\varepsilon^{\max}(\lambda^{\max} = 200 \text{ nm}; \text{NO}_3^-) = 9.07 \times 10^3, \quad \varepsilon(\lambda = 210 \text{ nm}; \text{NO}_3^-) = 7.30 \times 10^3, \\ \varepsilon(\lambda = 220 \text{ nm}; \text{NO}_3^-) = 3.13 \times 10^3, \quad \varepsilon(\lambda = 230 \text{ nm}; \text{NO}_3^-) = 6.25 \times 10^2.$$

Solution spectra of NO₂⁻ and NO₃⁻ exhibit no absorbance beyond wavelength of about 250 nm and 245 nm, respectively. Existence of inorganic ions, as described above, influences UV absorption and sometimes COD. But if wavelength measured were set beyond 250 nm, the influence of those ions on UV absorbance will be neglected.

3.2. *Turbidity correction.* Suspended solid (SS) often interferes the reproducibility of COD and UV absorption determination. For small amount of suspension due to fine particles passed through the glass filter, turbidity corrections were carried out. The influence of turbidity to the absorption is illustrated in Fig. 4 using kaolin turbidity standard. Fig. 5 shows the good linearity between turbidity and absorbance for respective wavelength. In the following, turbidity correction for any wavelength using kaolin turbidity standard is discussed. The problem is the determination of $k(\lambda_1, \lambda_2; X)$, the parametric constant, in equation (1).

$$A(\lambda_1; X) = k(\lambda_1, \lambda_2; X) \cdot A(\lambda_2; X) \quad (1)$$

where, $A(\lambda_i; X)$ ($i=1, 2$) represents the absorbance of kaolin suspension with turbidity X (mg/l) at the wavelength λ_i . In the range of turbidity 0 to 500°, turbidity is proportional to absorbance in this work although the linearity become bad when the turbidity exceeds 500°.

$$A(\lambda; X) = \alpha(\lambda) \cdot X \quad (2)$$

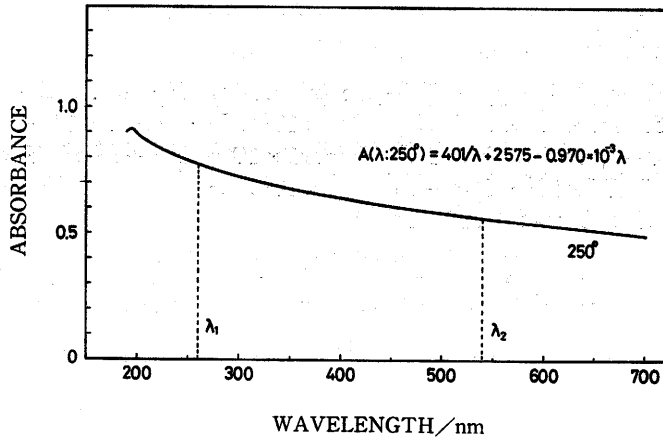


Fig. 4 Apparent absorption spectrum of Kaolin turbidity standard with turbidity 250°.

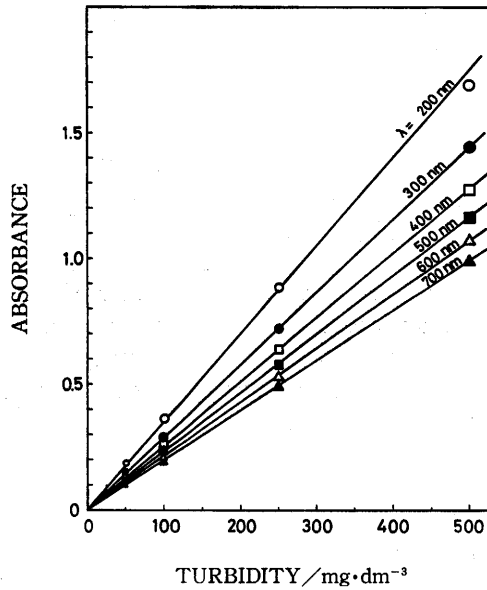


Fig. 5 The relation between absorbance and Kaolin turbidity standards for respective wavelength.

and $A(\lambda; X)$ was found to be expressed as

$$A(\lambda; X) = a'(X)/\lambda + b'(X) + c'(X) \cdot \lambda \quad (3)$$

using the Eq. (2), Eq. (3) is further expressed as

$$A(\lambda; X) = X \cdot [a/\lambda + b + c \cdot \lambda]. \quad (4)$$

From Eq. (4), $k(\lambda_1, \lambda_2; X)$ is obtained to be

$$\begin{aligned} k(\lambda_1, \lambda_2; X) &= (a/\lambda_1 + b + c \cdot \lambda_1) / (a/\lambda_2 + b + c \cdot \lambda_2) \\ &= k^0(\lambda_1; \lambda_2). \end{aligned} \quad (5)$$

Thus, we know the contribution to absorbance due to suspension at λ_1 , by measuring the absorbance $A_{(\lambda_2; X)}^{\text{turb}}$ at wavelength λ_2 .

$$A_{(\lambda_1; X)}^{\text{turb}} = k^\circ(\lambda_1; \lambda_2) \cdot A_{(\lambda_2; X)}^{\text{turb}}. \quad (6)$$

Concrete expression of Eq. (4) in this study is given as

$$A(\lambda; X) = X \cdot [1.604/\lambda + 0.0103 - (3.88 \times 10^{-6}) \cdot \lambda]. \quad (4')$$

If wavelength of λ_2 , at which sample materials dissolved does exhibit no absorption, were chosen, only apparent absorption due to suspension, $A_{(\lambda_2; X)}^{\text{turb}}$ will be obtained. Thus, turbidity correction at $\lambda_1 (\lambda_1 < \lambda_2)$ can be made.

$$A^{\text{correctd}}(\lambda_1) = A^{\text{measd}}(\lambda_1) - A^{\text{turb}}(\lambda_1)$$

$$A^{\text{correctd}}(\lambda_1) = A^{\text{measd}}(\lambda_1) - k^\circ(\lambda_1; \lambda_2) \cdot A^{\text{turb}}(\lambda_2). \quad (7)$$

For example, if $\lambda_1 = 260 \text{ nm}$, $\lambda_2 = 540 \text{ nm}$ were chosen, we obtain $k^\circ(\lambda_1; \lambda_2) = 1.38$ using Eq. (5) and Eq. (4)'.

$$A^{\text{correctd}}(260 \text{ nm}) = A^{\text{measd}}(260 \text{ nm}) - 1.38 \times A^{\text{measd}}(540 \text{ nm}). \quad (8)$$

3.3. COD and volatile compounds. The values of COD in general reflect the organic content in water. But normal chain aliphatic, aromatic, and nitrogen containing heterocyclic compounds such as pyridine are difficult to be oxidizingly decomposed under the usual conditions as described previously. The reason, of course, is that these compounds are chemically stable and have strong chemical bonds to give low decomposition degree. However, Tokuhira and Ui et al. pointed out another reason for the apparent low decomposition degree of these compounds that these compounds are very volatile and they might be vaporized during 30 minutes boiling in COD measurement.³¹⁾ Here, for acetone, pyridine, benzene and chlorobenzene,³¹⁾ the possibility was examined using UV spectrophotometric technique. Benzene and chlorobenzene are only slightly soluble in water, so dissolved in ethanol at first then successively diluted with water. Heating conditions were identical with COD measurement, except the oxidizing agent and acid. Absorption spectra of samples were measured before and after heating. Concentration of the samples were then determined using calibration curves. As shown in Fig. 6, when calibration curves exhibit deviation from the Beer's law, preferable curves that show approximately straight lines were chosen. (Ex. Peak of 2nd band was chosen in case of chlorobenzene.) Results were shown in Table 1. Although Table show some scatter, the trends are probably real. These results show that COD values are influenced by volatile compounds, es-

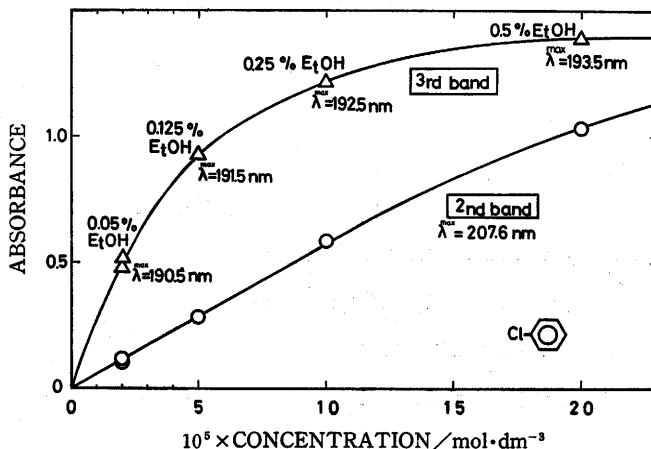


Fig. 6 Calibration curve of chlorobenzene in dilute ethanol solution.

—○—: 2nd absorption band, —△—: 3rd absorption band.

Table 1. Residual percent of volatile compounds after 30 min. boiling.

Compounds	Residual percent (Concentration of solute in ppm)				
	benzene		52% (10 ppm)	34% (50 ppm)	22% (100 ppm)
chloroform ^{a)}	15% (2.3 ppm)	32% (5.7 ppm)	15% (11.3 ppm)	15% (28 ppm)	4.2% (113 ppm)
pyridine ^{b)}	100% (1.6 ppm)	60% (4.0 ppm)	100% (7.9 ppm)	55% (19.8 ppm)	
acetone			92% (100 ppm)	92% (500 ppm)	87% (1000 ppm)

a) 11.3 ppm of chloroform is equivalent to 1.0×10^{-4} (mol/l).

b) 7.9 ppm of pyridine is equivalent to 1.0×10^{-4} (mol/l).

pecially by water insoluble matters. Therefore attention should be paid to pure volatile compounds in COD measurement although the effects are relatively small in case of water soluble compounds. In particular, for water soluble volatile compounds, when the ground-glass stoppers of Erlenmeyer flask were properly pressed during boiling, the effect of evaporation become very small. On the other hand, for water insoluble ones, pressing of stoppers during boiling become very difficult because of their strong volatility. Practically all the COD values are measured at open system and volatile compounds are usually neglected.

3.4. *COD and UV absorption for pure substances.* For pure substances, the relations between COD and UV absorbance were shown in Fig. 7(a), (b). Figures show that for both phenol and acetic acid, the correlation is very high. In both cases, COD(C_r) is higher than COD(M_n) at the same absorbance. Because the values of COD(C_r) give higher decomposition degree than those of COD(M_n). COD(M_n) are, however, widely used in this country and the values of COD(M_n) are used hereafter in the present work.

3.5. *COD vs. UV absorbance for surface waters of rivers.* Waters of the Onga River, the Itabitsu River, the Murasaki River, and the Ima River were chosen as actual water samples. Those samples were collected from Dec. 11, to Dec. 20, in 1979. Collected points are ranging from the upper reaches to the lower streams of the rivers, about 8 to 10 samples for each river. The collected points of surface water samples were depicted

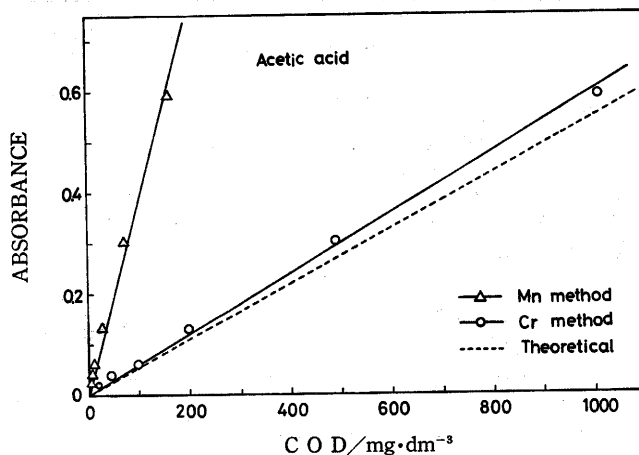


Fig. 7(a) Relation between COD and UV absorbance for acetic acid, being $\lambda=210$ nm.

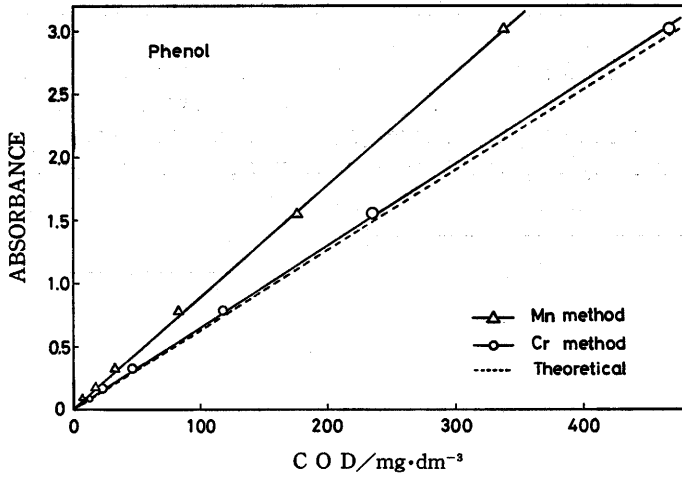


Fig. 7(b) Relation between COD and UV absorbance for phenol, being $\lambda = 270$ nm.

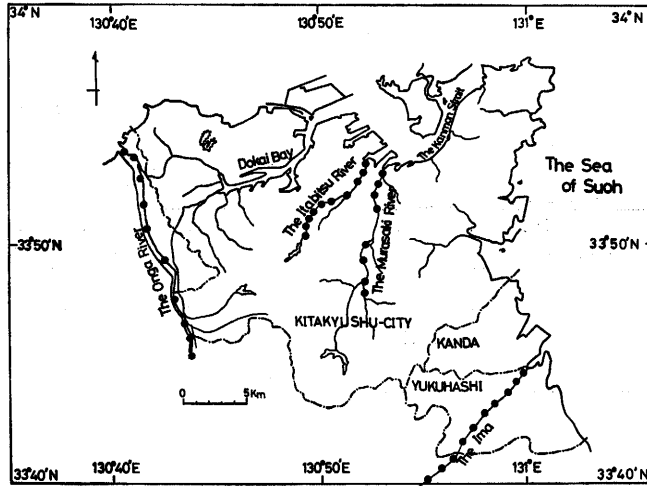


Fig. 8(a) Rivers in Kitakyushu-city and the neighbor
● : Sampling points along the rivers.

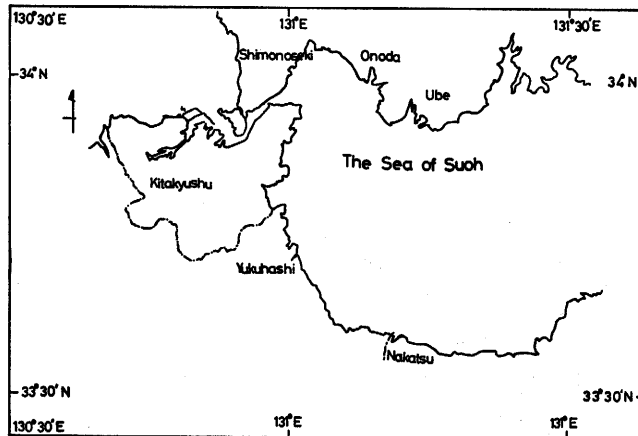


Fig. 8(b) Geographical position of Kitakyushu-city.

in Fig. 8(a), (b). Absorption spectra of rivers were shown in Fig. 9(a)-(d). Fig. 10 indicates the wavelength dependence of correlation coefficients determined from COD vs. absorbance relation for these river waters, including for sewage from the treatment plant. The results show no clear-cut dependence on wavelength. However, the wavelength of 260 nm might be the best one to give the highest correlation coefficients averaged under study. Turbidity corrections were made of all measurements about river waters.

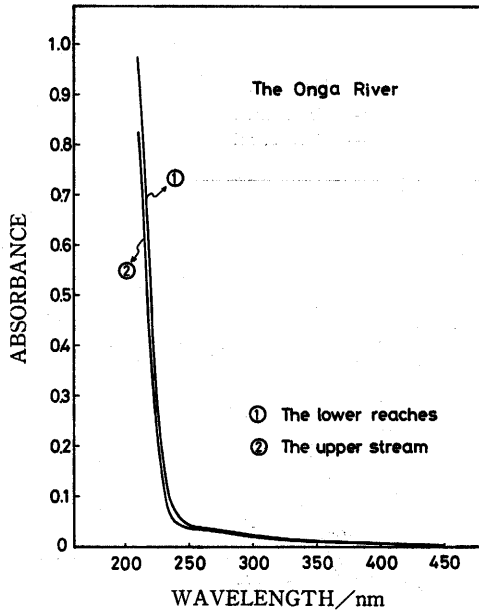


Fig. 9(a) Absorption spectra of the Onga River.
 ①: The lower reaches, ②: The upper reaches.

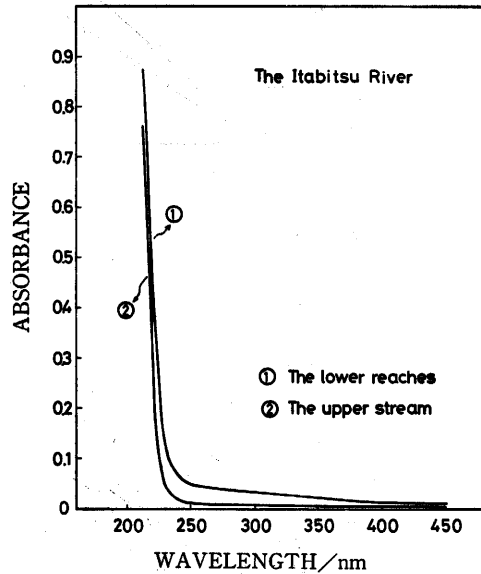


Fig. 9(b) Absorption spectra of the Itabitsu River.

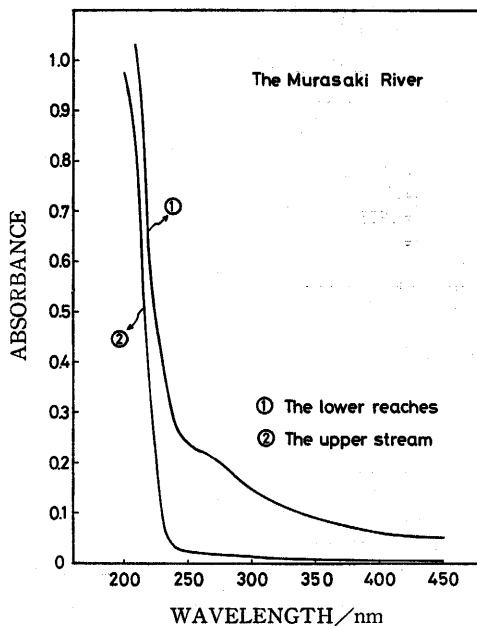


Fig. 9(c) Absorption spectra of the Murasaki River.

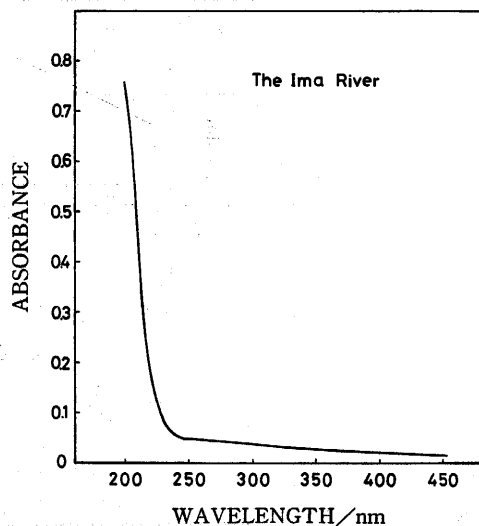


Fig. 9(d) Absorption spectrum of the Ima River.

The corrected values not always give higher correlation coefficients than those of uncorrected. Corrected values are slightly better than uncorrected on the average. These slight effects of turbidity may be explained by the fact that these water samples were filtrated through glass filter before measurement. The best straight lines for the data of river waters by the method of least squares with correlation coefficients, being corrected on turbidity ($\lambda_1 = 260 \text{ nm}$, $\lambda_2 = 546 \text{ nm}$), are shown in Fig. 11 and 12. For each river, two

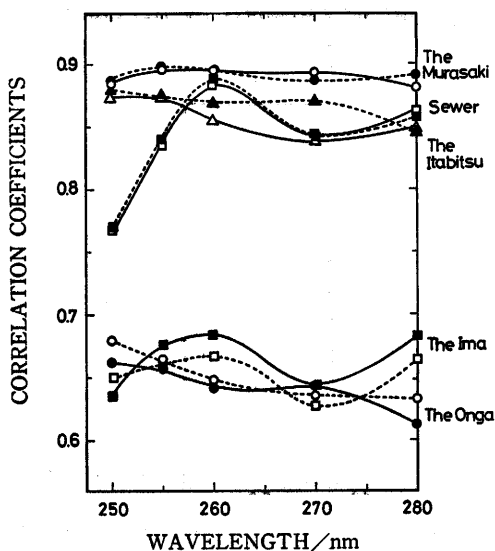


Fig. 10 Wavelength dependence of correlation coefficients, for respective rivers, and the sewer.

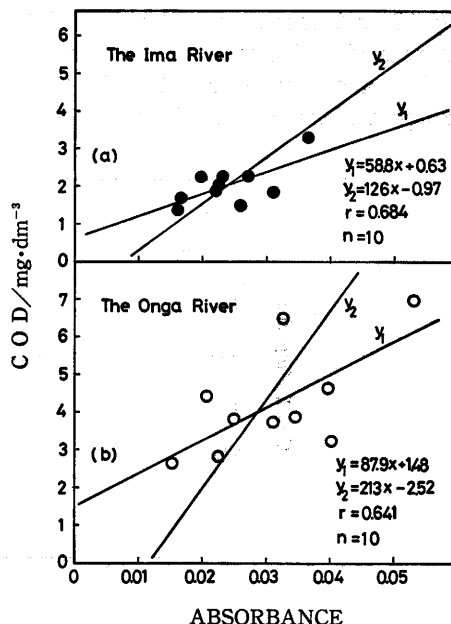


Fig. 11 Correlation of COD and UV absorbance for the Ima (a) and the Onga (b) Rivers.

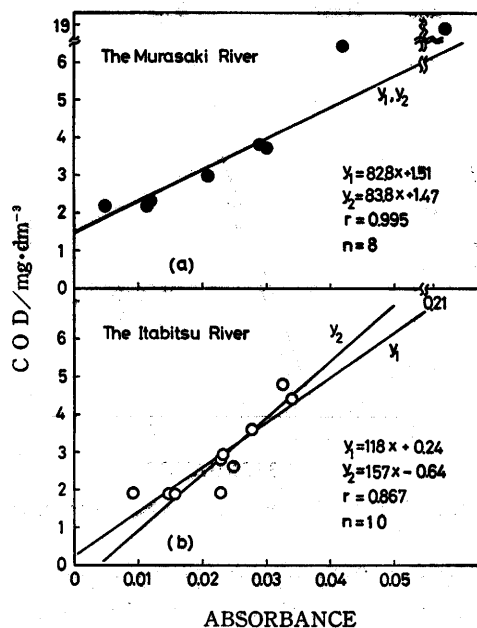


Fig. 12 Correlation of COD and UV absorbance for the Murasaki (a) and the Itabitsu (b) rivers.

straight lines are depicted. Because the method of least square gives different lines according to Y vs. X or X vs. Y relations. From the results obtained, it will be said that correlations of COD vs. UV absorbance for the Ima River and the Onga River are fairly good, and those for the Murasaki and the Itabitsu River are very good.

3.6. *COD vs. UV absorbance for sewage.* Fig. 13 shows the relation of COD and aeration time for a sewer. Fig. 14 was obtained from the respective value of COD in Fig. 13 and corresponding value of UV absorbance, and best straight lines also were determined. The sewer which was treated by aeration, gives a good correlation of COD vs. UV absorbance as shown in Fig. 14. This might be explained by the continuous changing of the contents by aeration.

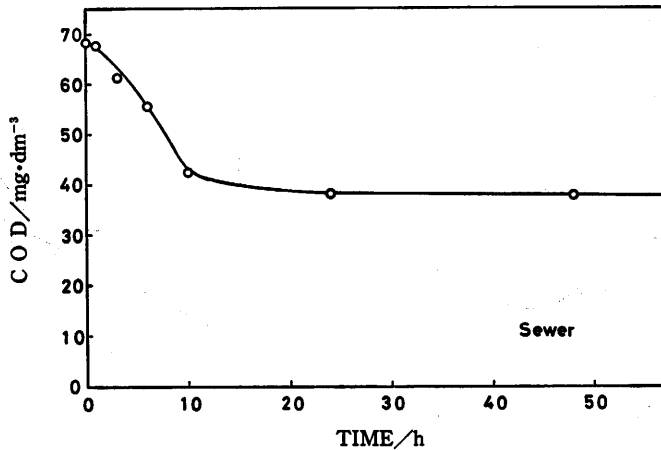


Fig. 13 The relation between COD and aeration time for the sewer.

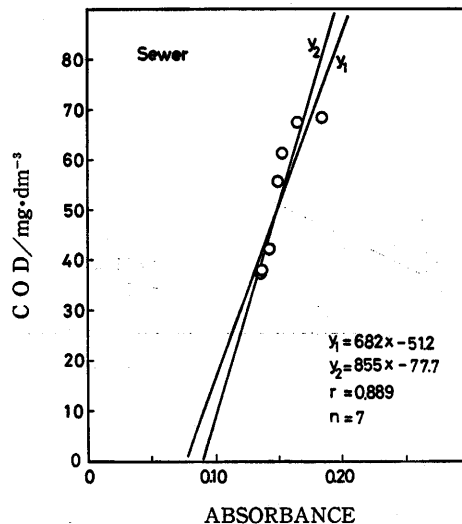


Fig. 14 Correlation of COD and UV absorbance for the sewer in Kitakyushu-city.

River waters in general absorb light strongly in the short wavelength region. Ogura et al. reported that absorbance of natural water at 220 nm shows good correlation with organic contents and Abs(220 nm) be the preferable index of organic contents in water.^{3,5)} Taking into account the absorption of inorganic compounds, however, absorbance

measured at beyond wavelength of 250 nm will give the higher correlation. Koga et al. obtained the correlation of COD and UV absorption using the samples collected from Dokai Bay in Kitakyushu City and discussed the results.²⁸⁾ They pointed out that inorganic ions such as nitrate and nitrite ions occupied the major parts of components of the water pollution and contribute the relatively great parts of the absorbance in their water samples. However, the correlation of COD and UV absorbance were not good, even though the corrections for inorganic ions were made. It should be noted that tedious operations for corrections give a counteract to the usefulness of the UV absorption method easily handled. The reasons why the correlation of COD vs. UV absorbance for the Onga River and the Ima River are not good comparing with those for the Murasaki and the Itabitsu River, are not obvious in the present stage. As shown in Fig. 2, coexistence of those kinds of compounds that show much contribution to COD and less to UV absorbance such as glucose, or show much contribution to UV absorbance and less to COD such as benzene evidently give low correlation coefficients. Continuous change of contaminants will show the good correlation of COD and UV absorbance, and contamination with many foreign substances will give bad ones, on the contrary.

4. CONCLUSION

From the results obtained, we may conclude that UV absorption method combined with COD measurements will give a useful technique for monitoring the quality and the change of the respective water such as river water, municipal and industrial water pollutions, although the simultaneous evaluation of many river waters, lakes and other water pollution using UV absorption method with COD values seems less important.⁹⁻¹⁶⁾ UV absorption method to be used independently as substitute for COD method appears not satisfactory at the present stage. In addition, measurement of UV absorption is useful for the COD measurement to estimate the volumes of COD samples without trial and error sampling.

5. ACKNOWLEDGEMENT

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