Semiautomated Determination of COD
in Environmental Water Samples

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Synopsis

A new method based on the principle of flow injection
analysis is presented for the semiautomated determination
of chemical oxygen demand (COD) in environmental water
samples. The method is rapid and continuous, and suitable
for the monitoring of COD in wastewaters. The apparatus
used was simply constructed by parts commercially avail-
able for high performance liquid chromatography. Teflon
tubing heated with a boiling water was used as a reactor
and simultaneously used for mixing coils and transmission
lines. The operating conditions were examined to apply
the determination of COD in wastewaters by using glucose
as a standard COD substance. The procedures recommended
are as follows: Both 4.9×10^{-4} M potassium permanganate
and 6.7 % sulfuric acid solutions are individually pumped,
20 μl of a sample solution is injected into the flow of
the sulfuric acid solution, and then mixed with a mixing
joint. The mixed solution is transported to a flow cell
situated in a spectrophotometer fixed at a wavelength
of 525 nm, and decrements of absorbance are recorded.
The peaks were reproducibly obtained at a concentration
range of 10 - 200 mg-COD 1^{-1}. Chloride up to 1000 mg 1^{-1}
was not interfered at all. Various wastewater samples
were analyzed by the proposed method at a sampling rate
of 30 samples per hour, and the apparent COD values obtained
were compared with the manual COD ones obtained by JIS method.

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1. Introduction

To reduce water pollution due to organic substances, total loads of chemical oxygen demand (COD) are to be regulated from 1981 on June in the water areas of closed character such as the Seto Inland Sea, Bay of Tokyo and Ise Bay. For the purpose described above, the Water Pollution Control Law (WPC Law) and the Special Law for Conservation of the Environment of the Seto Inland Sea (CES Law) had been partly changed on June 13, 1978, and the changed Laws have been enforced on June 12, 1979. According to the WPC and CES Laws, continuous routine analyses of COD in wastewaters must be prepared for the law-abiding because of the measurements of the COD load (=[COD concentration] x [effluent volume of wastewater]).

Previously, Korenaga[1] had proposed the principle of measuring COD based on flow injection analysis (FIA). In that work, at room temperature, potassium permanganate solution dissolved in 3.3 % sulfuric acid was used as the reagent solution and sodium oxalate solution was used as the sample solution respectively, and the phenomena of FIA obtained were continuously recorded with a spectrophotometer fixed at a wavelength of 525 nm having a flow cell. The results showed that the method proposed could be successfully expanded into the rapid and continuous determination of COD in aqueous environmental samples. He recently reported the development of the apparatus for measuring COD based on the previously proposed method[1] using potassium permanganate and glucose as an oxidizing reagent and a standard COD substance respectively[2]. The apparatus was efficiently constructed by the parts commercially available for high performance liquid chromatography such as a double plangent micro-pump, a sampling valve, a flow cell, a spectrophotometer, and a recorder. Polytetrafluoroethylene (Teflon) tubing was used as a reactor and simultaneously used for mixing coils and transmission lines.

In this paper, the apparatus made is applied to the determination of COD in wastewaters. To adapt for use as a COD monitoring apparatus of wastewaters, operating conditions such as effects of temperature, Teflon tubing length and flow rates of potassium permanganate and sulfuric acid solutions, are examined by using aqueous glucose solutions as the standard COD substance in detail. An optimum oprating condition can be obtained, and an interference caused by sodium chloride was also examined. The apparatus is thus supplied for the measurements of COD in various wastewater samples of Okayama University, and the apparent COD values obtained by the proposed method are evaluated by comparing with the COD values obtained by JIS method[3].

2. Experimental

2.1. Reagents

Potassium permanganate solution, 4.9×10^{-4} M: Dissolve 0.8 g of potassium permanganate in ca. 1100 ml of distilled water. Boil the solution for 1 - 2 hr and stand the resulting solution over night in a dark place and then filter with a glass filter (Type 3G4). Transfer the solution in an amber glass bottle and store it in a dark place. Standardize the solution by titrating with N/40 standard sodium oxalate solution. Dilute exactly the potassium permanganate solution obtained to give a 4.9×10^{-4} M solution and use it as an oxidizing reagent for COD substances in wastewaters and also as a colorimetric reagent having a maximum absorption wavelength at 525 nm.
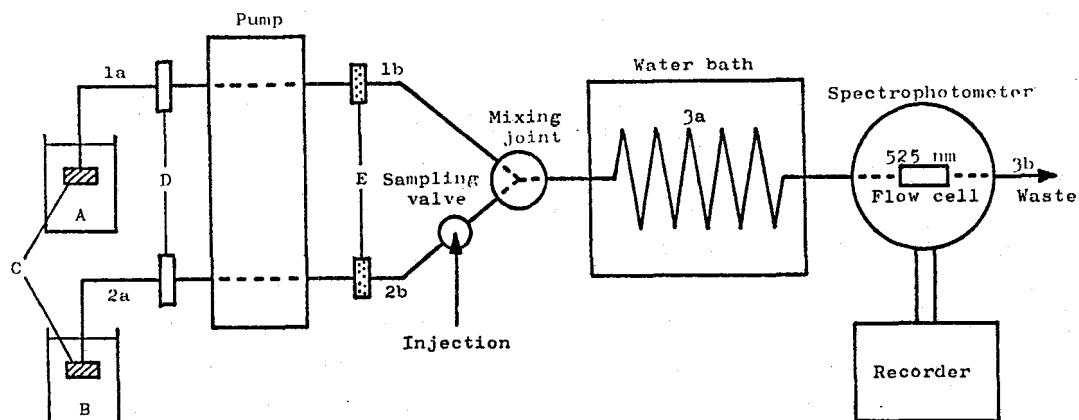
Sulfuric acid solution, 6.7 %: Add 0.5 w/v % potassium permanganate solution into a mixture of a part of concentrated sulfuric acid in two parts of distilled water until a pink color appears. Dilute the resulting solution with distilled water to give a 6.7 % solution.

Glucose solutions: Use glucose of analytical reagent grade as the standard COD substance according to the literatures[4 - 6]. Dissolve appropriate amounts of glucose weighed exactly in distilled water and dilute the solution with distilled water to give various concentrations of glucose solutions used in this work. Determine the manual COD values of the solutions according to the acidic permanganate method at 100 °C described in the testing methods for industrial wastewater of Japan Industrial Standard (JIS)[3].

2.2. Apparatus

A schematic diagram of the apparatus for measuring COD based on FIA used in this work, is shown in Fig. 1. As given in Fig. 1, the apparatus is simply composed by parts commercially available for high performance liquid chromatography and efficiently designed by using a double plangent micro-pump to yield the maximum flexibility.

When a Kyowaseimitsu Model KHU-W-104 double plangent micro-pump for inorganic aqueous solutions, of which parts in contact with the pumping solutions were made by acid-proof materials such as polytetrafluoroethylene (Teflon), sapphire and ruby, was used for pumping the reagent (A in Fig. 1) and acid (B in Fig. 1) solutions respectively. A pumping rate of a few ml per min was achieved by using this pump with good accuracy. The potassium permanganate (in A) and sulfuric acid (in B) solutions were pumped through lines (1a and 1b) and (2a and 2b) at respective rates of about 0.4 - 4.8 ml min^{-1} per line whereas the pumping

A: 4.9×10^{-4} M Potassium permanganate solution, B: 6.7 % sulfuric acid solution

C: Teflon porous membrane filter, D: glass degassor, E: line filter.

Fig. 1 Schematic diagram of the apparatus for measuring COD

rate in a line (3a and 3b) was about $0.4 - 9.0$ ml min^{-1}.

A Kusano micro-volume two-position sampling valve (10 or 20-μl volume) was arranged en route to a line (2b) and a position of 20-μl volume was preferably used as the sample injector in this work.

Both lines (1b) and (2b) were joined with a Kyowaseimitsu Model KYU-1 mixing joint and become. a line (3a) for reaction and simultaneous transmission.

A line (3a) was connected with a quartz tubular flow cell (10-mm light path and 18-μl volume) situated in a Shimadzu Model UV-100-01 spectrophotometer fixed at a wavelength of 525 nm and then heated with a Yamato Model BM-41 water bath at about 100 ^{o}C.

The spectrophotometer was joined with a Hitachi Model 056 multirange recorder and the signal obtained was continuously recorded with fast and precise response.

Of coils and lines, polytetrafluoroethylene (Teflon) tubings having various inner diameters and lengths were used in this work. Each of the reagent (in A) and acid (in B) solutions was passed through a Teflon porous membrane filter (C) and pumped into a 2.0-mm inner diameter Teflon tubing (1a and 2a, about 50-cm length), respectively. The solutions were then degassed with respective glass degassors (D) and again filtered with respective line filters (E). The solutions were thus introduced into a mixing joint via lines (1b) and (2b) (made by 0.5-mm inner diameter and about 50-cm length Teflon tubings). The mixed solution was then transported by a long-looped 0.5-mm inner diameter Teflon

tubing (3a) and simultaneously heated with a boiling water. After the solution was passed through the flow cell, a 0.25-mm inner diameter Teflon tubing (3b) of about 1-m length was used to prevent vaporizing the mixed solution in the line (3a).

2.3. Procedure

A 4.9×10^{-4} M aqueous potassium permanganate solution and a 6.7 % sulfuric acid solution were used as the reagent (in A) and acid (in B) solutions and separately pumped to the lines (1a) and (2a) at rates of 0.68 and 0.33 ml min^{-1}, respectively. A 20-μl volume of aqueous sample solution was injected into the flow of sulfuric acid solution in the line (2b) by using a sampling valve and a 1-ml volume of glass syringe. These solutions were separately introduced to the mixing joint and mixed. The mixed solution was then heated in the line (3a) and trans-ported to the flow cell. The absorbances measured at 525 nm were contin-uously recorded and the peak heights obtained from absorption decrements were used for the determination of COD in sample solutions.

3. Results and Discussions

According to the previous experiments[2], a ratio of pumping rates between the reagent (in A) and the acid (in B) solutions was proper to be adjusted to be of 2:1. Also, the Teflon tubing of the line (3a) was heated with a boiling water in order to accelerate the reaction between COD substances (e.g. glucose as the standard COD substance) and an acid-ic potassium permanganate solu-tion.

3.1. Effect of tubing length

When a 0.5-mm inner diame-ter Teflon tubing was used as a reactor and simultaneous mixing coils and transmission lines, the effect of length of Teflon tubing was examined. As shown in Fig. 2, a 40-m length of it was found to be suitable to detect COD of glucose with the highest sensitivity. A looped 40-m length Teflon tubing of 0.5-m inner diameter was therefore
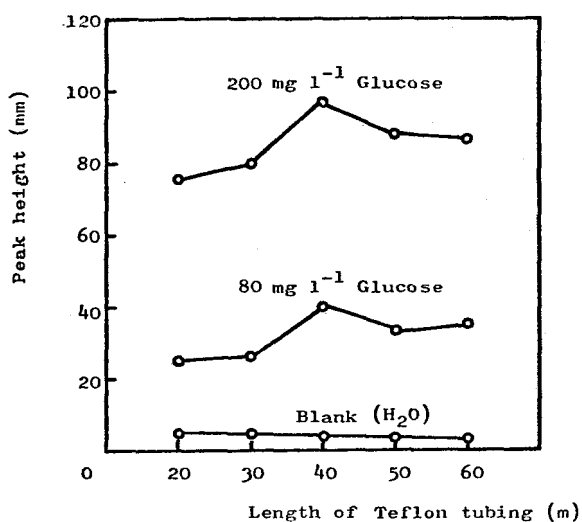

Fig. 2 Effect of length of Teflon tubing of the apparatus

used in the line (3a). It was immersed in the water bath and heated at about 100 $^{\circ}$C.

3.2. Effect of flow rate

The effect of flow rate of the mixed solution obtained after mixing was also examined by using the 40-m length and 0.5-mm inner diameter Teflon tubing (Fig. 3). When the ratio of flow rates between potassium permanganate and sulfuric acid solutions before mixing was constant and about 2:1, the flow rate of the mixed solution was varied from about 0.8 to 1.6 ml min^{-1}. From Fig. 3, a flow rate of

Fig. 3 Effect of flow rate of the mixed solution

about 1.0 ml min^{-1} was found to be the best for the COD detection with the highest sensitivity. Accordingly, the flow rates before mixing were fixed at 0.68 and 0.33 ml min^{-1} for the flows of potassium permanganate and sulfuric acid solutions respectively. The flow rate of the mixed solution was therefore fixed at 1.01 ml min^{-1} in this work.

3.3. Effect of chloride concentration

To evaluate an interference of chloride on the COD determination described in JIS[3], the effect of chloride concentration up to 1000 mg l^{-1} was examined for this semiautomated determination of COD in wastewaters. When 200 mg l^{-1} aqueous glucose solution was used and chloride up to 1000 mg l^{-1} was added, the peak heights obtained were found to be equal. Therefore, chloride up to 1000 mg l^{-1} being not interfered at all, COD in wastewaters containing chloride at the 10 p.p.m. level generally present in river and city waters could be analyzed without addition of silver sulfate or nitrate.

3.4. Precision and reproducibility

Two series of experiments were carried out in order to check the precision and reproducibility of determinations of COD by using various concentrations of aqueous glucose solutions. In the first experiment, the precision studies were made by determining the precision of peak
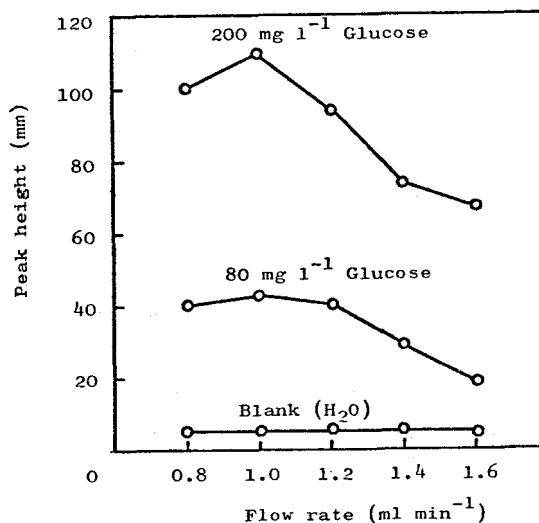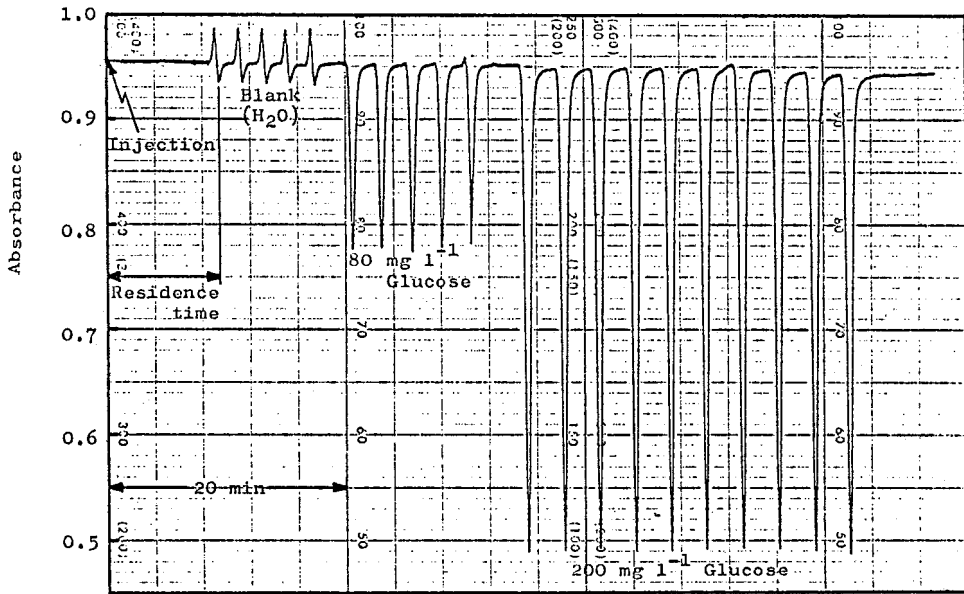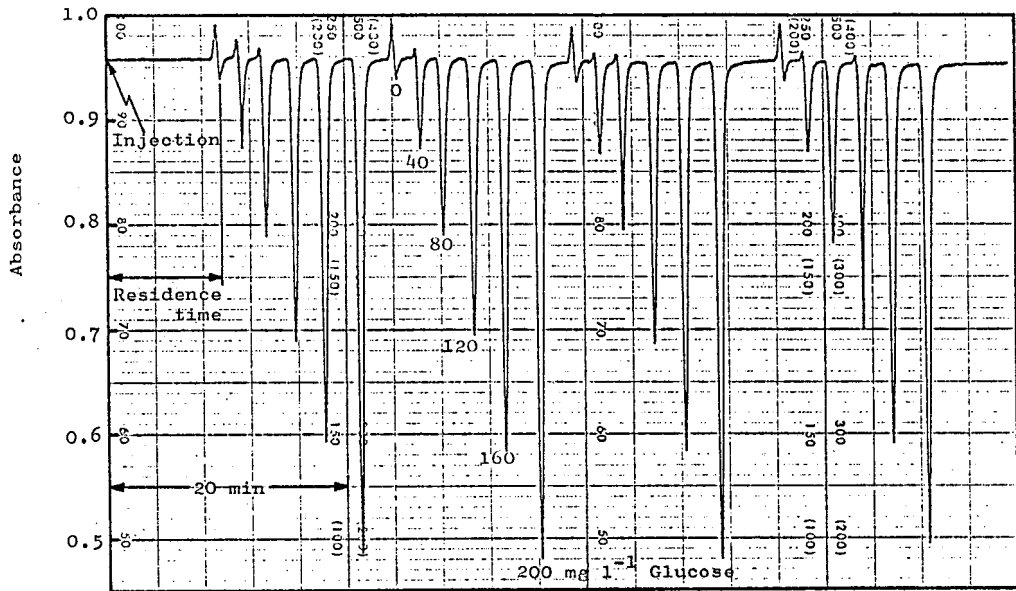
Fig. 4 Precision studies

Fig. 5 Reproducibility studies

heights as shown in Fig. 4. The mean value of the peak heights obtained from Fig. 4 was 97.9 mm for 200 mg l^{-1} glucose and its standard deviation was 0.52 mm in 10 determinations. The coefficient of variance was therefore 0.53 %. In the second experiment, the reproducibility studies were also made as shown in Fig. 5. The results reflect the reproducibility of the total FIA system, but show good reproducibility as shown in Fig. 5.

3.5. Calibration curve

According to the procedure mentioned above (2.3.), the calibretion curve using glucose as the standard COD substance was obtained as shown in Fig. 6. Although the calibration curve was not a straight line, the apparent COD values obtained by this method were precise and reproducible as described above. Therefore, the apparent COD values could be determined at a concentration range of about 10 - 200 mg-COD l^{-1} (corresponding to 20 - 340 mg l^{-1} aqueous glucose solutions).
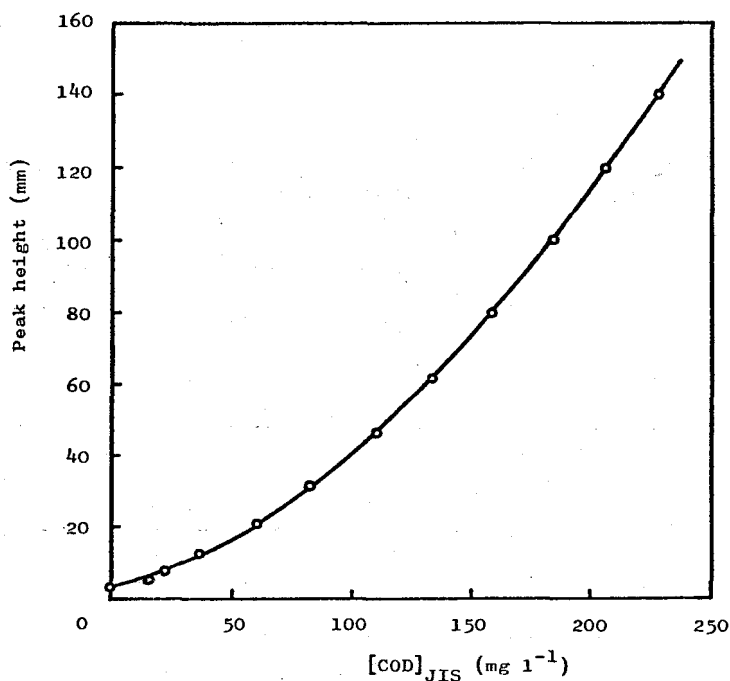

Fig. 6 Calibration curve

Table 1 Determination of COD in wastewaters

Sample[*]	Sampling date	COD (mg l^{-1})		FIA/JIS
		FIA method	JIS method	
A	December 17, 1979	48	40	1.20
B	December 17, 1979	119	151	0.79
C	December 18, 1979	131	182	0.72
D	December 19, 1979	103	102	1.01
E	December 19, 1979	85	104	0.82
F	December 19, 1979	112	146	0.77
G	December 20, 1979	54	48	1.13
H	December 20, 1979	120	154	0.78
I	December 20, 1979	78	70	1.11
J	December 21, 1979	112	146	0.77
K	December 21, 1979	140	193	0.73
L	December 22, 1979	79	83	0.95
M	December 24, 1979	13	9.9	1.31
N	December 24, 1979	111	133	0.83
O	December 25, 1979	20	15.3	1.31
P	December 25, 1979	22	16.8	1.31

[*] Wastewaters of Okayama University. The detection limit of the proposed FIA method being 10 mg l^{-1}, samples containing less than 10 mg l^{-1} COD were excepted in this work.

3.6. Application to wastewater

By use of the apparatus for measuring COD shown in Fig. 1, the analytical results obtained with the calibration curve are given for wastewater samples of Okayama University in Table 1. The samples were stored in a refrigerator as soon as they were sampled. No more pretreatment of water samples were needed, but samples of high turbidity had not better be injected into this apparatus. However, as the samples used in this work were clear, they could be used as received.

The COD values of these wastewater samples were measured by the manual JIS method and the results obtained are also given in Table 1. Thus, the apparent COD values obtained by the present method using the FIA apparatus were evaluated by comparing with the COD values obtained by JIS method. From Table 1, these results show that the values of COD found by the former method agree with those by the latter within an error range of ± 30 %.

Accordingly, the apparent COD values might be used as the rapid and continuous routine determination of COD in wastewater samples, since the COD values obtained by JIS method had a large error ranging at least $\pm$10 %.

4. Conclusion

The apparatus proposed in the previous work[2] could be successfully applied for the determination of COD in wastewaters. The method was very rapid and simple, and a sampling rate could be easily achieved to be 30 samples per hour. Various wastewater samples were analyzed by the proposed method, and the apparent COD values obtained agreed with the manual COD ones obtained by JIS method with permissible errors to the continuous monitoring of COD.

As described above, if this apparatus is further improved to be used as the COD monitoring one, COD concentrations of wastewaters can be continuously measured. Comparing with commercial automatic COD analyzers based on the manual JIS method, the apparatus proposed possesses the following advantages:

(1) The COD determination by using this method is much more rapid than by using the commercial automatic COD analyzer, because the sampling rate with the former is achieved to be 30 samples per hour, whereas the sampling rate with the latter is one sample per hour,

(2) The procedure is simple, that is, measurements can be carried out only by injecting 20 μl of aqueous sample solution,

(3) The permissible concentration of chloride ion is very high without adding silver sulfate, that is, chloride up to 1000 mg l^{-1} is not interfered in this method at all,

(4) The method is very precise and reproducible, that is, a standard deviation of only 0.5 % is typical in 10 determinations because of the semiautomated procedure.

From these conclusions, the apparatus can be expected to be supplied to the measurements of COD loads in industrial wastewaters as the COD monitoring one, for the purpose of abiding improved WPC and CES Laws.

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