

Improved Method for the Flow Injection Analysis of Chemical Oxygen Demand Using Silver Nitrate

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Synopsis

On the flow injection analysis (FIA) of chemical oxygen demand (COD), silver salt was added as an oxidation catalyst for COD substances and a masking agent for halide to improve operating conditions of the FIA apparatus. Both of a proper concentration of potassium permanganate solution and 6.0 % sulfuric acid solution containing 0.1 % silver nitrate are individually pumped up with respective flow rates of 0.51 ml min⁻¹ and merged into a carrier stream. A 20 μ l of sample solution is injected into the flow of sulfuric acid solution at just before the merging place. The sample mixed with the carrier solutions in a reaction manifold (polytetrafluoroethylene tubing: 0.5 mm i.d. x 30 m), is passed through a thermostated bath at 100 °C and led to a flow cell for the absorbance measurements at 525 nm. The absorbances are continuously recorded with time. The peaks in the recordings showed good reproducibility and the calibration curve was obtained at a linear concentration range of 0 - 170 mg l⁻¹ COD with glucose as standard. The detection limit and precision confirmed with this method were 5 mg l⁻¹ and 0.8 %, respectively. Chloride ion up to 200 mg l⁻¹ did not interfere without elimination of a silver chloride precipitate. By the present FIA method, several industrial waste water samples were analyzed at a sampling rate of about 40 samples per hour, and their apparent COD values were compared with those found by the manual JIS method. Both of the methods gave the similar results within an error range from -35 to +5 %.

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1 Introduction

In recent papers(1-8), the authors have reported a simple and reliable method for the rapid and continuous determination of chemical oxygen demand (COD) based on the principle of flow injection analysis (FIA), which has been developed by Ružička and Hansen(9) and reviewed by Betteridge(10). The method has been applied to the COD measurements of aqueous environmental samples such as civil sewage and human waste(4), aqueous wastes from laboratories containing large amounts of organic COD substances(5,6), waste waters from university(7), and industrial waste waters(8) with reasonable results. The results found was then evaluated by comparing with a manual acidic permanganate method at 100 °C used officially in Japan(11). As the result of evaluation, it was found that the apparent COD values obtained by the proposed FIA method agreed with those obtained by the JIS method with a relatively large error of $\pm 30\%$ range.

On the other hand, high performance automatic COD analyzers have been desired for the rapid and continuous monitoring systems of COD, for the purpose of regulating total loads of organic pollutants in aqueous environmental media(12). In comparison with the commercially available automatic COD analyzers, the recommendable FIA apparatus reported by the authors(3-8) possessed the following advantages; (i) the volume of sample used was 20 μl , so large volume of sample taken might not be required, (ii) the redox reaction could smoothly occurred between potassium permanganate and organic pollutants, because the looped reaction manifold made of polytetrafluoroethylene (PTFE) tubing (0.5 mm i.d. x 40 m) was completely heated with a thermostated bath at 100 °C, (iii) the interference of chloride ion was scarcely observed because of its slow reactivity, since the residence time of each sample injected was about 9 min in the PTFE reaction manifold, (iv) the reproducibility and precision of the results were very good, for example the within-day precision was less than 1 %, (v) the popular and inexpensive spectrophotometer could be used for detection, so the maintenance of the FIA apparatus was easy, and (vi) the sampling rate could be achieved about 20 samples per hour since the continuous injections could be adopted to the flow system at each interval of about 3 min. With regard to this FIA apparatus for COD measurements, however, the cause of probable errors between the FIA and JIS methods should be find out in the case of utilizing glucose as a standard substance for COD(3-8), in order to use the FIA apparatus for the widely available techniques mentioned above.

In the present work, therefore, an improvement of the previous FIA method(3-8) and a trial of finding out the cause of errors are studied in detail by adding silver salt as an oxidation catalyst for organic pollutants and a masking agent for chloride in industrial waste water samples.

2 Experimental

2.1 Reagents

Potassium permanganate solution. Prepare a stock solution by dissolving 0.8 g of potassium permanganate in ca. 1.1 liter of distilled water(11). Boil the solution for 1 - 2 hr and let it stand over night at a dark and cool place. Then filter it with a Type 3G4 glass filter and standardize the resulting solution by titration with N/40 standard sodium oxalate solution. Store it in an amber glass bottle at a dark and cool place and dilute exactly with distilled water to give about 0.95 of absorbance at 525 nm with the present FIA apparatus (Fig. 1) before use.

Sulfuric acid solution. Prepare sulfuric acid (1+2) by adding 0.5 % potassium permanganate solution until a pink color appears(11). Dilute the solution exactly with distilled water to give a 6.0 % w/v solution and then add silver nitrate into it to become a final concentration of 0.1 % w/v.

Glucose as standard solution. Use glucose(13,14) of analytical reagent grade as a standard substance for COD to determine operating conditions of the present FIA apparatus. In this work, prepare various concentrations of aqueous glucose solutions, of which manual COD values are beforehand measured with the acidic permanganate procedure at 100 °C according to the JIS method(11).

2.2 Apparatus and procedure

A block diagram of the present FIA apparatus for measuring COD is shown in Fig. 1. The apparatus used in this work is made by modifying the previous FIA apparatus(3-8) as to the reaction manifold and thermostated bath.

Both of the potassium permanganate solution and the sulfuric acid (containing silver nitrate) solution are individually pumped up with a Kyowa-seimitsu Model KHU-W-52 double reciprocating micro-pump at respective flow rates of 0.51 ml min⁻¹. A 20 µl of sample solution is injected into the flow of sulfuric acid solution with a constant-volume sampling valve at just before a PTFE mixing joint. The sample is merged with the mixing joint and also with the carrier solutions in a reaction manifold made of PTFE tubing (0.5 mm i.d. x 30 m). The manifold is heated with a Toyo Model VC-250 thermostated bath using corn oil at 100 °C to accelerate and complete the redox reaction between potassium permanganate and organic COD substances in the sample. The reaction mixture is transferred to a quartz tubular flow cell (path length: 10 mm, inner volume: 18 µl) placed in a Shimadzu Model UV-100-01 spectrophotometer for the absorbance measurements at 525 nm. The absorbances are continuously recorded with time by using a Shimadzu Model R-11 recorder, which is modified to possess a multirange out-put unit.

The peaks in the recordings are reproducibly obtained and the calibration curve is then made between peak height (mm) and manual COD value (mg l^{-1}) with various concentrations of aqueous glucose solutions. Apparent COD values of the samples with this method are thus calibrated.

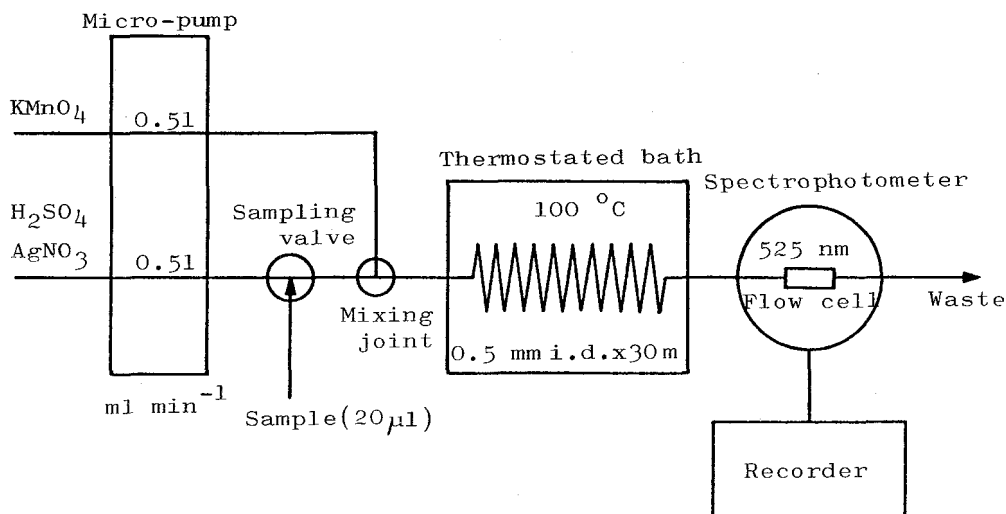


Fig. 1 Block diagram of the FIA apparatus for measuring COD

3 Results and Discussion

3.1 Choice of oxidation catalyst

As oxidation catalysts for organic COD substances, silver(I) (11,15,16) is known, and manganese(II) (17) and selenium, copper, iron, nickel, platinum (18) are also reported. In this work, however, only silver(I) salt was examined for the FIA measurement of COD with glucose (13,14) as the standard substance for COD, according to the recent information involved with the effectiveness on addition of silver salt in the FIA of COD (19).

When silver sulfate and nitrate were used as the silver(I) salt, both of the salts were found equally useful for the oxidation catalyst of the redox reaction between potassium permanganate and organic COD substances (e.g. glucose). Hence, silver nitrate was used because of its good solubility in this work.

3.2 Effect of amount on addition of silver nitrate

In a 6.0 % sulfuric acid solution, various amounts of silver nitrate were added and then examined about their catalytic effects. With a PTFE

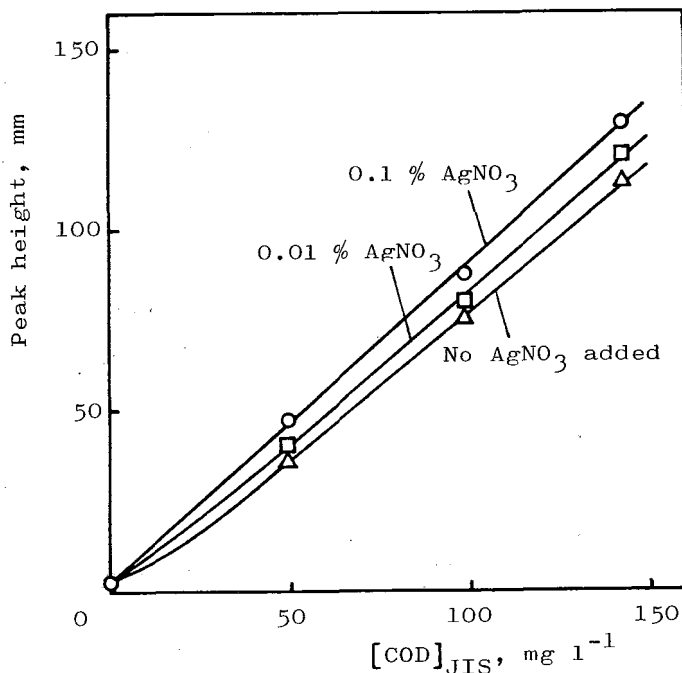


Fig. 2 Effect of amount of silver nitrate added in 6.0 % sulfuric acid solution

reaction manifold (0.5 mm i.d. x 30 m), the results obtained between potassium permanganate and glucose are shown in Fig. 2. When more than 0.05 % silver nitrate was added into the sulfuric acid solution, a linear calibration curve was obtained. However, more than 0.2 % silver nitrate could not completely be dissolved in a 6.0 % sulfuric acid solution. Therefore, the added amount of silver nitrate was fixed at 0.1 % in the sulfuric acid solution in this work. In that case, about 3.3×10^{-4} M potassium permanganate and about 2.9×10^{-4} M silver(I) nitrate were existed in the carrier stream (3.0 % sulfuric acid solution).

3.3 Effect of reaction manifold length

When a flow rate of the carrier stream after mixing was adjusted to about 1 ml min^{-1} , the effect of reaction manifold length was examined by connecting some 0.5 mm i.d. PTFE tubings. As shown in Fig. 3, the best sensitivity of peak height was obtained for 20 m, but its calibration curve was not straight and seriously bended in a low concentration range of COD. With the increasing manifold length, however, the dispersion also increased and so the shorter length was desirable to prevent dispersion. Even when 0.1 % silver nitrate was added into the present FIA system, the reactivity

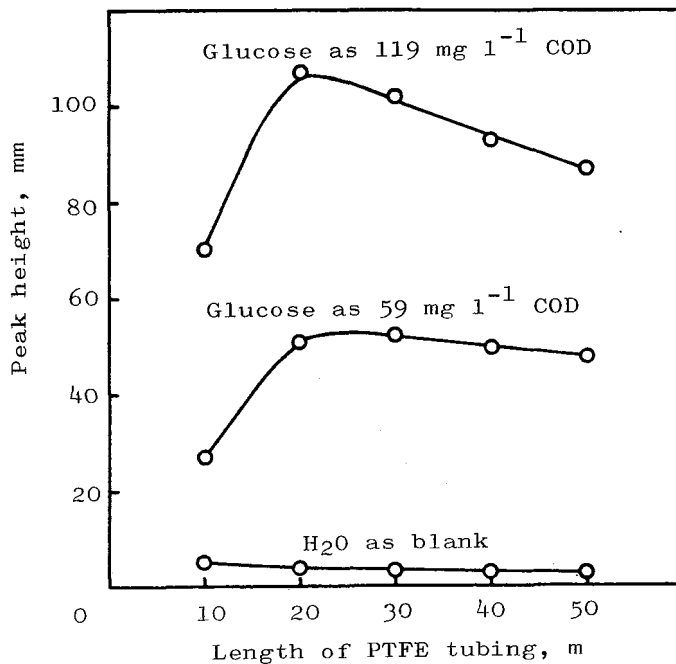


Fig. 3 Effect of length of reaction manifold of the improved FIA apparatus

of each organic COD substance was not yet sufficient and so the slow reaction between potassium permanganate and such organic COD substances required the longer reaction manifold to insure the reactivity. As shown in Fig. 3, with the increase in manifold length, the peak heights decreased according to the dispersion increasing of injected samples and the coefficient of variance also decreased to 40 m. Therefore, the best compromise length of reaction manifold was found 30 m on addition of 0.1 % silver nitrate in the 6.0 % sulfuric acid solution since the peak height was essentially constant at the manifold length of 30 m or longer. Accordingly, the sensitivity achieved with the present FIA method using silver nitrate was found higher than that with the previous method(3-8) using a 40-m length of PTFE reaction manifold (without silver nitrate).

3.4 Effect of flow rate of carrier stream

The effect of flow rate of the carrier solution was also examined in the 30-m length PTFE reaction manifold. When the ratio of pumping rates between the potassium permanganate solution and the sulfuric acid solution (containing silver nitrate) was fixed at about 1:1, the pumping rate of about 1 ml min⁻¹ was found suitable for the carrier stream after merging. Hence, both of the solutions were individually pumped up with the double

reciprocating micro-pump at respective flow rates of 0.51 ml min^{-1} in this work. It was also found that the dispersion was seldom observed with the decelerating flow rate in the 0.5 mm i.d. PTFE reaction manifold, since a constant peak height was obtained at the flow rate of less than 1 ml min^{-1} .

Under these conditions, the residence time of sample injected was about 7 min and the peak obtained in the recordings was very sharp and reproducible. For reference, although the flow of sample injected was stopped in the reaction manifold at 100°C for a while, the peak height of glucose sample solution was no longer changed at all with this longer residence time.

3.5 Effect of co-existing chloride ion

In the JIS method(11), 1 g of silver sulfate powder had to be added into the testing solution as a masking agent of co-existing chloride ion and an oxidation catalyst of organic COD substances. In the present FIA method, however, a precipitate of silver chloride formed has closed the flow lines such as a PTFE reaction manifold, PTFE connectors and a flow cell. Following the results of this examination, chloride ion up to 200 mg l^{-1} did not interfere with the COD determination without eliminating such a precipitate because chloride co-existed in the sample was diluted with the carrier solution (dispersion). Accordingly, common industrial waste waters from river or city waters (containing about 10 mg l^{-1} level of chloride ion) could be supplied to the newly proposed FIA apparatus using silver nitrate as a masking agent and an oxidation catalyst without any special care.

3.6 Calibration curve and precision

With the present FIA method, the peak heights were reproducibly obtained by using various COD concentrations of aqueous glucose solutions according to the recommended apparatus and procedure. The peak heights at 525 nm in the recordings were plotted against the manual COD values of aqueous glucose solutions. The linear relationship was obtained between 0 and 170 mg l^{-1} COD, and the limit of detection confirmed with the present method was about 5 mg l^{-1} whereas that with the previous FIA method without silver nitrate(3-8) was about 10 mg l^{-1} .

As all the reactions in this FIA apparatus could be automatically performed, the reproducibility of the method was good and the precision confirmed with the method was about 0.8 % in 12 determinations ($119 \text{ mg-COD l}^{-1}$ glucose solution).

Figure 4 serves as a representative example. Although a residence time of the injected sample was about 7 min, each injection of sample solution could be carried out with rapidity and continuance. Therefore, as each

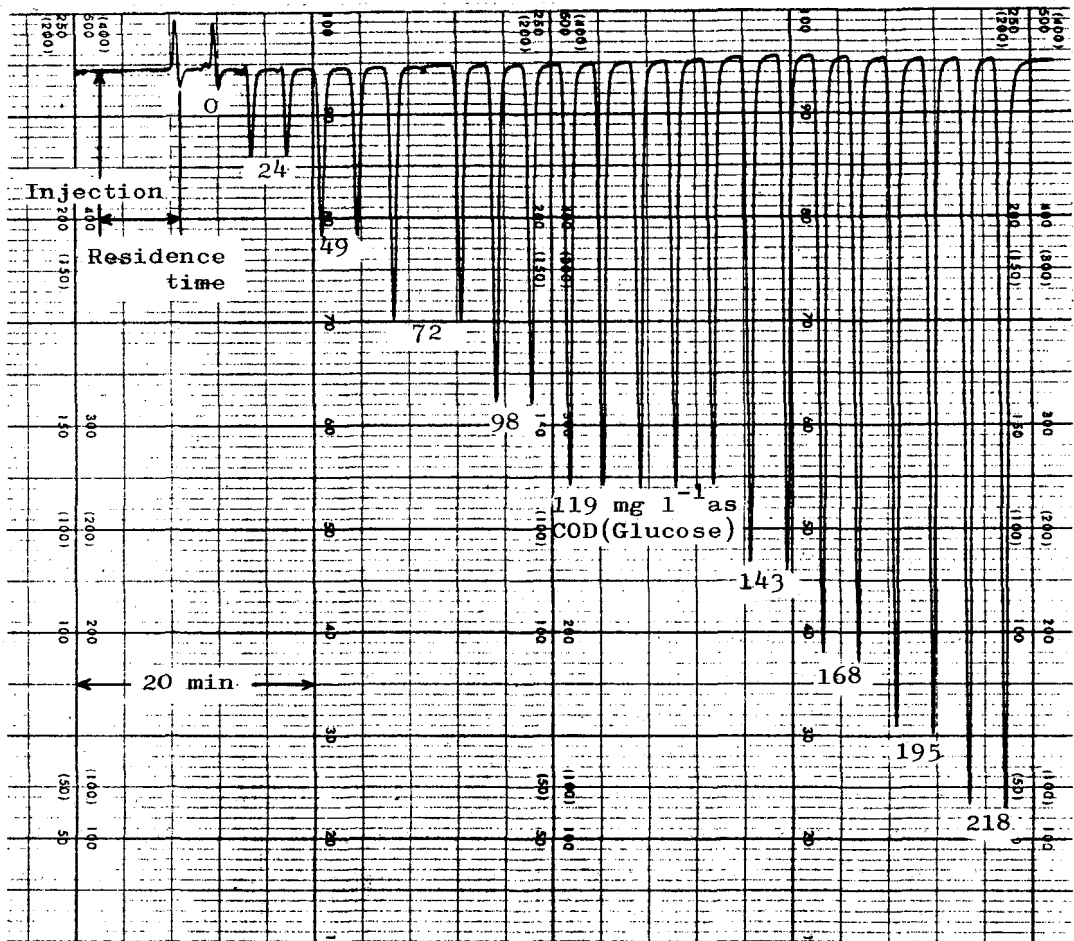


Fig. 4 Typical example of flow injection results for COD determination

injection interval could be easily achieved to be about 2 min, the apparent COD values with the present FIA method could be determined at the sampling rate of 30 - 40 samples per hour.

3.7 Application to industrial waste water samples

To apply to practical samples such as industrial waste waters, the effects of sample filtration and sample storage were also examined. As the results of first examination, the samples used in this work could be used as received since they were clear and had few suspended solid. However, the filtration of sample solutions are necessary if the samples are turbid. Because the operation of such a FIA apparatus will demand filtration of the sample which may affect the composition of oxidizable organic substances so that the experiment must be very carefully performed. In the second experiment, the sample solutions stored in a refrigerator (about 4 °C) was

found stable and their COD values were not changed for at least 2 weeks in polyethylene containers.

The analytical results were obtained for several industrial waste water samples by the present FIA method using silver nitrate without any prior treatment (Table 1). All the samples could be successfully supplied to the improved FIA apparatus proposed here, and their apparent COD values could be precisely analyzed according to the recommended apparatus and procedure using glucose as the standard substance for COD.

To check the results, the recovery of apparent COD value was examined by adding known amounts of glucose to the sample solutions. Consequently, the COD values were found to be measured by the present FIA method without loss and gain in the industrial waste water samples used in this work.

To evaluate the results obtained with this improved FIA apparatus, the manual COD values obtained with the Japanese official method based on the acidic permanganate value at 100 °C(11) are also given in Table 1. From Table 1, the apparent COD values with the present FIA method were found to correspond to those with the manual JIS method within an error range from -35 to +5 %. It was therefore considered that the results with this improved FIA method were more reasonable than those with the previous FIA method(3-8). However, as these results showed that organic pollutants in samples were less oxidizable with the acidic permanganate solution than glucose as the standard substance for COD, a more proper standard substance for COD should be found out in the FIA method for COD determination.

Table 1 Analytical results of industrial waste water samples

Sample	COD (mg l ⁻¹)		X/Y	
	FIA method(X)	JIS method(Y)		
Waste water from food industry	1	29	32	0.91
	2	133	190	0.70
textile industry	3	51	49	1.04
	4	27	31	0.87
chemical industry	5	86	116	0.74
	6	88	136	0.65
machinery industry	7	123	180	0.68
	8	97	146	0.66

4 Conclusion

This paper thus described an improved FIA method for the rapid and continuous determination of COD in industrial waste water samples by using silver nitrate as an oxidation catalyst and a masking agent. The improved points of the previous FIA method(3-8) achieved are as follows:

(i) The slow reaction between potassium permanganate and organic COD substances was accelerated by adding silver nitrate as an oxidation catalyst, so that the PTFE reaction manifold could be shortened from 40 m to 30 m in the present FIA system.

(ii) As the result of (i), the dispersion with the increasing in manifold length decreased, hence the sensitivity of the present FIA method was higher than that of the previous one (the limit of detection could be achieved to 5 mg l^{-1}).

(iii) As the results of (i), the sampling rate with this method could be achieved to about 40 samples per hour.

(iv) The interference of co-existing chloride ion was not affected up to 200 mg l^{-1} without elimination of a silver chloride precipitate even when 0.05 % silver nitrate was added in the present FIA system, so that common industrial waste water samples co-existing 10 mg l^{-1} level of chloride could be analyzed by this method without care.

(v) The probable errors between apparent COD values with the FIA method and manual COD values with the JIS method decreased in the present improvements, but a more proper standard substance for COD was found necessary in order to apply directly the present FIA apparatus to the continuous monitoring of COD in various waste water samples as the automatic COD analyzer.

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