

## *Evaluation of Three Flow Injection Analysis Methods for the Determination of Chemical Oxygen Demand*

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### Synopsis

Three methods for determining chemical oxygen demand (COD) by means of flow injection analysis (FIA) with potassium permanganate, potassium dichromate, or cerium(IV) sulfate as oxidant, developed in this laboratory, are described from the point of view of their operating properties. The permanganate method is the most sensitive and common, but forms manganese(IV) oxide precipitate which blocks the FIA lines and connectors. Addition of phosphoric acid in the reagent system is, however, effective to some extent in order to avoid blocking the flow system. The dichromate method is the most workable and stable, but produces toxic wastes containing chromium(VI). The cerium method is the most probable because cerium(IV) is the strongest oxidant of the three and less poisonous. The last method with cerium(IV) sulfate is therefore recommendable to apply to the continuous monitoring of COD in many situation.

### Introduction

Flow injection analysis (FIA) is a new method for automation of wet chemical analyses, developed by Ružička and Hansen in 1975.<sup>(1)</sup> In a

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decade, the method is widely spread over the world because of its simplicity, easiness, rapidity, and moderate price. Hence, the method is suitable to the modern times, calling upon us to save manpower, resources, and energy. The authors have been attracted by the FIA since 1978,<sup>(2)</sup> and applied the method to the monitoring of chemical oxygen demand (COD), required to reduce total loads of organic pollution in the water areas of closed character such as the Seto Inland Sea, the Bay of Tokyo, and the Ise Bay.<sup>(3)-(18)</sup>

Three oxidants such as potassium permanganate, potassium dichromate and cerium(IV) sulfate, have been examined as the oxidizing and spectrophotometric reagent in the two-lines FIA system by the authors. However, a potassium permanganate in 3.3 % sulfuric acid solution was first examined as a carrier solution of a one-line system,<sup>(3)</sup> but the system was then improved to a two-lines system which possessed a potassium permanganate-oxidizing reagent solution and a ca. 10 % sulfuric acid-carrier solution.<sup>(4)-(11)</sup> In this reagent system, to avoid precipitating manganese(IV) oxide, addition of ammonium sulfate<sup>(9)</sup> and ortho-phosphoric acid<sup>(11)</sup> were examined. Consequently, it was found that the mixture of sulfuric acid and phosphoric acid had to be used for the monitoring of COD as the acid carrier solution of the two-lines FIA system.

A potassium dichromate in sulfuric acid (1+2) solution was also examined as a carrier solution of a one-line system.<sup>(12)</sup> In the monitoring of COD, the system was then improved to the two-lines FIA system which possessed a potassium dichromate in sulfuric acid (1+1) solution and a water-carrier stream injecting sample solutions.<sup>(13)-(15)</sup>

A cerium(IV) sulfate in ca. 2 % sulfuric acid solution was recently examined as an oxidant and spectrophotometric reagent stream of the two-lines FIA system.<sup>(2), (16)-(18)</sup> The another stream was a water-carrier one in which sample solutions were injected. The system could, of course, be used to the continuous monitoring of COD in water pollution.

In this paper, three methods for the monitoring of COD mentioned above, are evaluated to their continuous operating properties. This paper also deals with practical values of the FIA apparatus for COD in the automatic measurement systems of water qualities.

## Experimental

### Reagents

Potassium permanganate solution: A stock solution is prepared by

dissolving 0.8g of potassium permanganate in about 1100 ml of distilled water. The solution is boiled for 1-2 h and allowed to stand overnight in the dark. It is then filtered through a glass filter, Type 3G4, and standardized by titration with n/40 standard sodium oxalate solution.<sup>(19)</sup> The solution is stored in an amber-glass bottle in a dark, cool place and diluted with distilled water before use to give an approximately 1 mM solution.

Potassium dichromate solution: Potassium dichromate (0.6g; previously dried at about 105 °C for 2 h<sup>(20)</sup>) is dissolved in 500 ml of distilled water and the solution is diluted with 500 ml of concentrated sulfuric acid. This solution is ca. 2 mM in dichromate and used as it is (having an absorbance of about 0.45 at 445 nm in the two-lines FIA system).

Cerium(IV) sulfate solution: Cerium(IV) sulfate tetrahydrate (0.2g; obtained from E. Merck A. G.) is dissolved in 800 ml of distilled water, and 20 ml of concentrated sulfuric acid is added into it. The solution is then diluted to 1 liter with distilled water. The resulting solution is stored in an amber-glass bottle in a refrigerator.

Acid carrier solution for a permanganate method: Ten per cent sulfuric acid solution containing 20 % ortho-phosphoric acid, is used.

Standard substance for COD: A mixture of L-glutamic acid and lactose (5:1) is used as standard in this work. Various concentrations of aqueous standard solutions, for which COD<sub>Mn</sub><sup>(19)</sup> values had been determined using the official method, are prepared.

All chemicals used were of analytical-reagent grade.

### Apparatus and procedure

A block diagram of the developed FIA system is shown in Fig. 1. The system is constructed of commercially available parts for high-performance liquid chromatography and poly(tetrafluoroethylene) (PTFE) tubings, selected to withstand continuous operation for long periods of time.

A Kyowa-seimitsu, Model KHU-W-52, double reciprocating micro-pump is used to pump the oxidant-reagent solution and the water-carrier stream separately at respective flow rates. Sample solutions are injected through a Kyowa-seimitsu, Model KAM-4V-2, automatic sampling valve into the stream of water. The streams merge at a Kyowa-seimitsu, Model KYU-1, PTFE joint. Reaction proceeds in a 10-m coil made of PTFE tubing (1-mm i.d., 3-mm o.d.) which is heated at 120 °C, in a Toyo, Model VC-250, thermostated bath containing silicone oil (accuracy  $\pm 0.5^{\circ}\text{C}$ ).

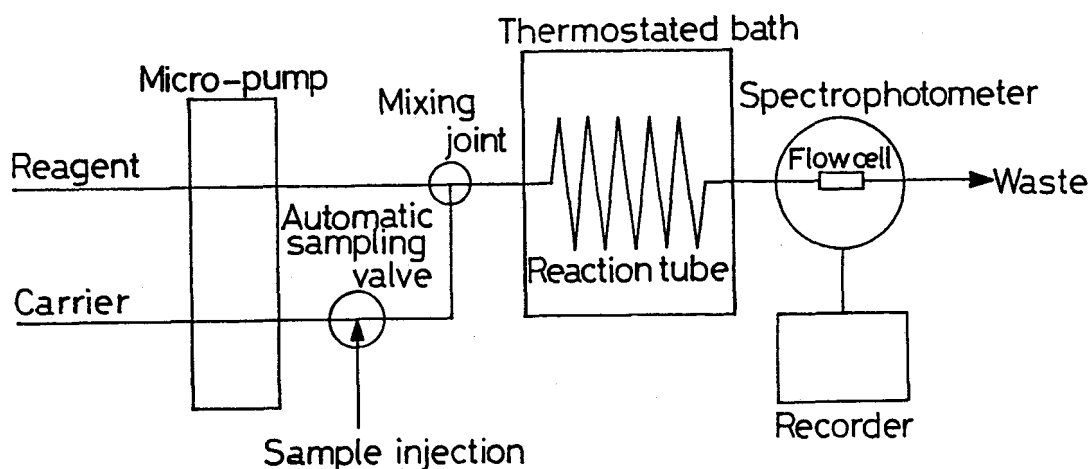


Fig. 1 Block diagram of the developed FIA apparatus for COD

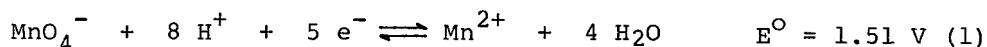
The reaction mixture then passes into a quartz tubular flow-through cell (10-mm pathlength, 18- $\mu$ l volume) in a Shimadzu, Model 150-02, double beam spectrophotometer. The absorbances measured at respective wavelengths, are recorded continuously using a Nippon-denshi-kagaku, Model U-228, multirange recorder. A calibration graph is prepared from the peak heights vs. the  $\text{COD}_{\text{Mn}}$  values of aqueous standard solutions.

## Results and discussion

### Property of oxidants

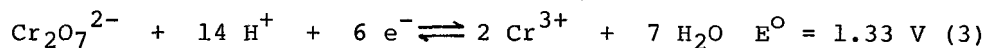
Oxidation-reduction potentials of the three oxidants dealt here, are as follows:<sup>(21)</sup>

Mn(VII)/Mn(II) system



$$E = 1.51 - 0.093 \text{ pH} + 0.012 \log \left( \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} \right) \quad (2)$$

Cr(VI)/Cr(III) system



$$E = 1.33 - 0.135 \text{ pH} + 0.0097 \log \left( \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{Cr}^{3+}]^2} \right) \quad (4)$$

Ce(IV)/Ce(III) system



$$E = 1.61 + 0.058 \log \left( \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} \right) \quad (6)$$

where E and  $E^{\circ}$  are the potential in the given system and the standard potential, respectively. Symbols in square brackets are the activities of oxidants or reductants in the given solutions.

Cerium(IV) ion has the strongest oxidizability of the three oxidants used in this work.

### Operating conditions

For application in continuous monitoring of COD in wastewater samples, the apparatus must be durable and reliable. The choice of pumping system is vital. The peristaltic pumps widely used in FIA are unsuitable because the present system is operated under at least 5 atm (measured by a Kyowa-seimitsu, Model KPG-50N, pressure gauge) by connecting a back-pressure PTFE coil (0.25-mm i.d., 3-m long) just after the flow cell. A double reciprocating micro-pump for HPLC was therefore used to pump both the acidic oxidant solution and the water carrier stream. The water carrier stream for samples avoided the blank peak formed when samples were injected directly into the oxidant reagent solution without the permanganate method.

For long reaction times, flow rates and tubing diameter and length are important parameters and must be chosen carefully to minimize peak broadening. In continuous monitoring, reagent consumption and the quantity of waste containing Mn, Cr, or Ce are also important. The micro-pump could be used reproducibly at total flow rates of about 0.6 ml/min when the rather viscous sulfuric acid solution and water pumped separately. Flow rates of 0.3 ml/min each were selected to maintain a constant 1:1 ratio. At these flow rates, a 10-m reaction coil of seamless 1.0-mm i.d. PTFE tubing was optimal for the reaction, giving a residence time of about 15 min and a reasonable compromise between reaction time and peak broadening. The quantity of waste was below 1 liter a day, causing few problem of waste treatment.

The effect of reaction temperature on the oxidation with the given oxidants was examined by using the present standard substance solutions containing L-glutamic acid and lactose. The results showed that a temperature of 120 °C was most suitable; temperature below 110 °C lowered

the sensitivity, and those between 120 and 140 °C gave constant peak-height values, but above 150 °C either bubbles were formed owing to vaporization of the solutions or the weakened PTFE tubing burst owing to the high back-pressure.

Attempts were made to improve the sensitivity by injecting large volume of sample solutions but broad peaks were then obtained; 200  $\mu$ l of sample occupied about 100 cm of the 0.5-mm i.d. coil used, so that complete mixing and reaction might not occur beyond 300  $\mu$ l of sample, even in the 10-m coil. Therefore, the optimum sample volume was less than 200  $\mu$ l, introduced via the automatic sampling valve having 50, 100, or 200  $\mu$ l loops of PTFE tubing.

The operating conditions in this work are listed in Table 1.

Table 1 Operating conditions of the FIA apparatus for COD

Oxidant	KMnO <sub>4</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Ce(SO <sub>4</sub> ) <sub>2</sub>
Reagent solution	1 mM in water	2 mM in H <sub>2</sub> SO <sub>4</sub> (1+1)	0.5 mM in 2% H <sub>2</sub> SO <sub>4</sub>
Carrier solution	10% H <sub>2</sub> SO <sub>4</sub> + 20% H <sub>3</sub> PO <sub>4</sub>	water	water
Temperature (°C)	120 °C	120 °C	120 °C
Reaction coil (mm)	1.0 $\phi$ x 10000	1.0 $\phi$ x 10000	1.0 $\phi$ x 10000
Flow rate (ml/min)	0.6	0.6	0.6
Reaction time (min)	15	15	15
Wavelength (nm)	525	445	320
Sampling rate (sample/h)	15	15	15
Detection limit (mg/l)	5 (50 $\mu$ l sample)	5 (100 $\mu$ l sample)	0.5 (200 $\mu$ l sample)
Std. deviation (%)	0.6	0.5	0.8
Chloride (mg/l)	200	100	Negligible

Under these operating conditions, the developed FIA system was satisfactorily operated for several days (i.e. one week). However, the permanganate method using a mixture of sulfuric acid and phosphoric acid, produces a few precipitates of manganese(IV) oxide in a long run. It was therefore found that the FIA method with potassium permanganate had not to be used in continuous monitoring of COD. The methods with potassium dichromate or cerium(IV) sulfate were found suitable for the COD monitoring without manpower over a week. However, the dichromate method seems unpractical because of the toxicity of chromium(VI).

### Calibration graph

Figure 2 shows a typical output from the present FIA system with cerium(IV) sulfate when different concentrations of aqueous standard solutions were injected. A plot of peak heights obtained under the recommended operating conditions for these standard solutions vs. the  $\text{COD}_{\text{Mn}}$  values determined by the official method,<sup>(19)</sup> was linear over the  $\text{COD}_{\text{Mn}}$  range 0-20 mg/l when 200  $\mu\text{l}$  sample solutions were injected.

The detection limit of the method is 0.5 mg/l  $\text{COD}_{\text{Mn}}$  when 200  $\mu\text{l}$  sample are injected; even lower values (0.2-0.3 mg/l) could be estimated if really necessary, because up to 300  $\mu\text{l}$  sample solutions were able to be injected in the system. This higher sensitivity compared to the other method with permanganate and dichromate, is achieved by relying on a strong oxidizability, and by increasing the sample volumes and the reaction temperature compared to the earlier works.<sup>(3)-(18)</sup>

As also shown in Fig. 2, the reproducibility of this COD measurement is good, reflecting the automatic character of the procedure. There is little opportunity for personal errors because of its automatic sampling, reaction, and detection based upon the principle of FIA. The precision of the method is good as is shown in Table 1; the standard deviation was 0.8 % in 10 determinations of 5 mg/l  $\text{COD}_{\text{Mn}}$  with aqueous standard solution.

About 15 samples can be measured per hour. Samples can be injected at 4-min intervals, although the residence time necessary for the oxidation reaction is at least 15 min at 120 °C.

### Application to continuous monitoring

In order to apply the present method to the continuous monitoring of COD in wastewaters, the effects of possible interfering ions must be known. Chloride ion, which present at levels of 10 mg/l in river water, was tested. As the results, it was found that chloride ion did not interfere with the COD measurement when cerium(IV) sulfate was used as an oxidant. Whereas the methods with permanganate and dichromate were interfered slightly by chloride ion as shown in Table 1.

The wastewater samples would require filtration with less than 100-meshed stainless filter, and this would require great care to avoid altering the composition of the oxidizable organic substances present.

For continuous monitoring of COD substances, the system can be fully automated by an automatic sampling valve. It allows direct

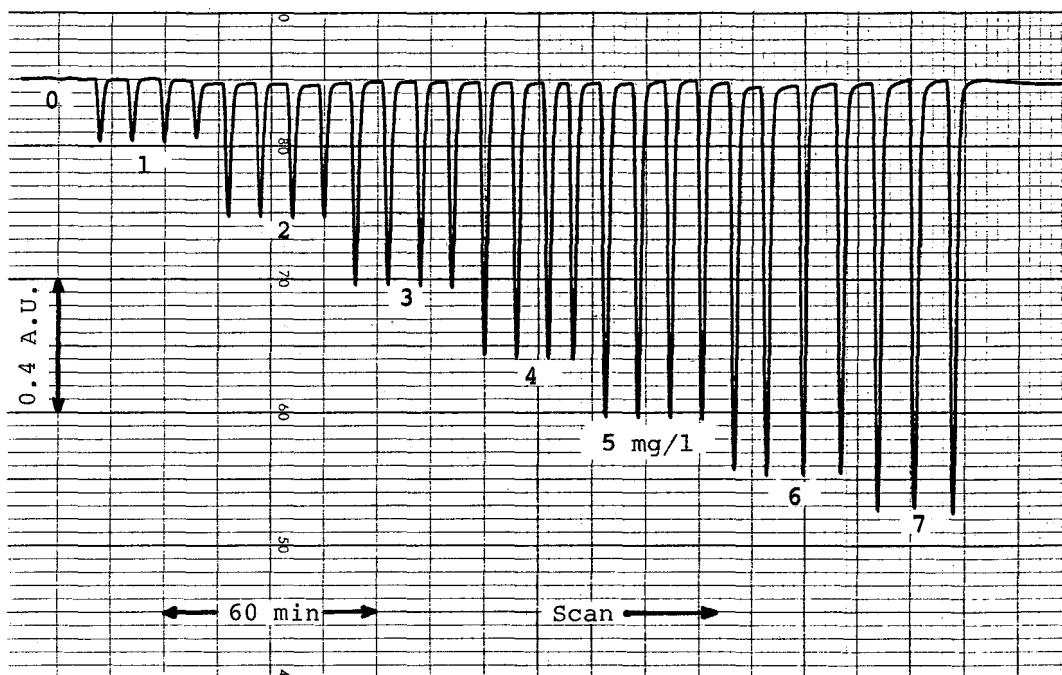


Fig. 2 Representative examples by the proposed FIA method with cerium(IV) sulfate for aqueous standard solutions

introduction of 200- $\mu$ l filtered samples into the water carrier stream at intervals of 4 min.<sup>(11)</sup>

Typical examples of results obtained in continuous monitoring of wastewater samples from the Center for Environmental Science and Technology, Okayama University, are given in Fig. 3, compared with the results from the official titration method.<sup>(19)</sup> The correlation coefficient between the FIA method with cerium (IV) and the official method with acidic permanganate, were found to be significant, though the values by the FIA method generally lie between the values obtained conventionally. It appears that COD substances in such wastewaters can be continuously monitored quite reliably in spite of prior filtration. Accordingly, the proposed instrumental method based upon FIA seems adequate for the continuous monitoring of COD.

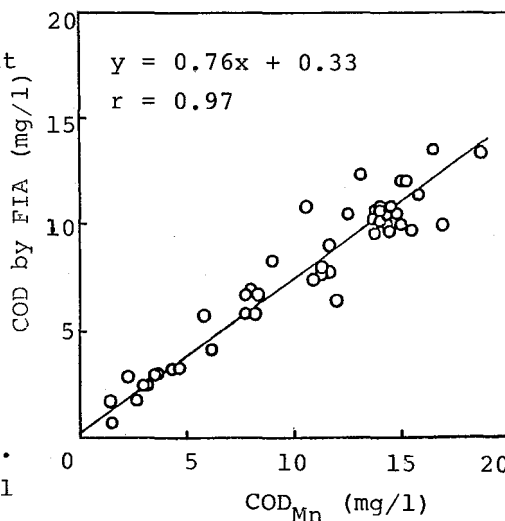


Fig. 3 Correlation of results



## Conclusion

This paper therefore described an evaluation of the three methods for the continuous monitoring of COD, based upon the FIA technique and developed by the authors. The improved points of the previous FIA methods<sup>(3)-(18)</sup> and the operating properties found in this work, are as follows:

1) Use of the cerium(IV) sulfate to oxidize the COD substances in wastewater samples enables the system to maintain continuous operation for a long time.

2) Redox reaction between cerium(IV) and COD substances is preferable to wastewaters because of its strong oxidizability.

3) Cerium is a non-toxic rare-earth metal, so that the waste causes no problem of water treatment.

4) In the cerium method, the interference caused by chloride ion is small enough to be ignored.

5) The method for COD monitoring with cerium(IV) is simple, flexible, robust, and inexpensive because a high-pressure micro-pump and an automatic sampling valve are effectively used in the system.

5) By comparison with other automatic methods, the proposed FIA system has the advantages of simplicity and continuity because of its flow analysis property.

7) The precision and reproducibility of the analytical results appears to be better than that attainable by other methods despite of the rapid sampling rate.

8) The cerium(IV) method is most suitable for continuous monitoring of wastewaters among the three methods using a mixture of L-glutamic acid and lactose as standard,<sup>(22)</sup> examined in this work.

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