Chemiluminescence detection of permanganate index (COD_{Mn}) by a luminol-KMnO$_4$ based reaction

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Abstract

A novel chemiluminescence (CL) system for determination of permanganate index (COD_{Mn}) combined with flow injection analysis has been proposed in this study. On the basis of the chemiluminescent reaction of luminol-KMnO$_4$ system, light emission caused by luminol-KMnO$_4$ system was detected by the photomultiplier tube, and its intensity caused by the appearance of KMnO$_4$ after sample digestion was inversely proportional to COD_{Mn}. Effects for COD_{Mn} determining such as pH, concentrations and interference were investigated in detail. A detection limit of 0.3 mg/L COD_{Mn} with a linear range of 0.3–200 mg/L for its theoretical COD_{Mn} was obtained under the optimized experimental conditions. The relative standard deviation was 4.3% for 5.0 mg/L COD_{Mn} ($n = 11$). This CL flow system for determining COD_{Mn} was simple, rapid, and suitable for automatic analysis. The data obtained by the present method were fairly in good agreement with those obtained by the standard titrimetric method. It has been applied to determine real samples with satisfactory results.

Key words: flow-injection; chemiluminescence; permanganate index (COD_{Mn}); luminol-KMnO$_4$

Introduction

Up to now, chemical oxygen demand (COD), which can indicate the level of pollution for water contaminated by reductive pollutants, is the main determinant used to assess organic pollution in aqueous systems and is one of the most important parameters in water monitoring (APHA, 1989). The standard reflux titrimetric method (APHA, 1992) for COD determination consists of oxidizing organic matter of the sample, adding a known amount of oxidant, reflexing at high temperature on open containers and titrating the excess oxidant. On the basis of the oxidizing agents used, the standard COD methods can be classified into either the dichromate method or the permanganate method. Due to its higher degradation degree toward a wide range of the organic pollutions, the standard dichromate method was widespread used and more popular than the latter. However, the standard dichromate method has several drawbacks: i.e., a time-consuming (2–4 h) reflux process, expensive and highly toxic reagents, and so on. Therefore, the standard dichromate method has been abandoned in Japan. In China, the standard dichromate method is designated as COD_{Cr} (GB 11914-89, 1990), and the permanganate method is designated as permanganate index (COD_{Mn}) (GB11892-89, 1990). The former is mainly used for assign the oxygen demand of organic pollutants in heavily polluted water bodies with oxygen demand of organic pollutants > 30 mg/L, such as industrial wastewater. The latter serves the purpose of monitoring organic pollution in surface water (GB 3838-2002, 2002) and ground water (GB/T 14848-93, 1994) with the range of the oxygen demand of organic pollutants from 1.0 to 15.0 mg/L. However, the conventional methodology suffers from a series of drawbacks: (1) the analysis time is too long; including digestion time and titration time; (2) handling is also considerable, thus increasing the probability of errors and the reproducibility of the results are dependent upon the operator skill; (3) there is a quite high consumption of chemicals; (4) several inorganic species cause interference on this method; (5) back-titration after sample digestion is an insensitive method of detection. Therefore, it is necessary to develop low-cost, simple, automated and easy to maintain COD_{Cr} and COD_{Mn} analytical instruments with higher sensitivity and broader linear range for quality control. These efforts mostly focus on the improvements over both digestion and analytical methods. For example, some reports have been published concerning the application of microwave radiation as a heat source for the determination of COD_{Cr}, and these methods have dramatically reduced the heating time (Cuesta *et al.*, 1996; Balconi *et al.*, 1992). On the other hand, some new analytical methods have been reported for determination of COD, including spectrophotometry (Jirka and Carter, 1975; Jones *et al.*, 1985),

atomic absorption spectrophotometry (Cuesta *et al*., 1998), photocatalytic degradation method (Kim *et al*., 2001) and photoelectrochemical method (Zhao *et al*., 2004; Zhang *et al*., 2006), etc. Among these analytical methods, spectrophotometry is the most common detector used in COD determination. However, some inherent problems of these systems with spectrophotometer measurements are presented: (1) to increase the oxidizing ability of reagents and decrease the digestion time, these systems are heated so as to produce bubble, and the signals are frequently unstable due to bubble formation (Balconi *et al*., 1992); (2) samples showing high turbidity are not suitable for this method due to serious interference (Jirka and Carter, 1975); (3) the systems lack enough sensitivity so that the systems need rather long digestion time and are not suitable for the samples with low COD; (4) the linear range of the systems is narrow, so the application of the systems is limited.

Flow injection chemiluminescence (CL) is known to be a powerful analytical technique that promises high sensitivity, fast response time, extensive dynamic range, and use of simple and inexpensive of instrumentation easy to set up a rapid reproducible means of detection. All these advantages have allowed the method that has been conveniently used in the determination of many inorganic and organic compounds in environmental samples. Recently, based on the high selectivity and sensitivity of chemiluminescent reaction of luminol-H_2O_2-Cr^{3+} system, a low cost chemiluminescence detector with a photodiode instead of photomultiplier tube (PMT) has been successfully developed for environmental monitoring of COD_{Cr} by measuring the appearance of Cr^{3+} after sample digestion using a laboratory-built portable photodiode luminometer, which was proportional to the chemical oxygen demand (Hu and Yang, 2004). Li *et al*. (2003) introduced a chemiluminescene system for automatic determination of chemical oxygen demand (the permanganate method) using flow injection analysis. In this system, potassium permanganate was reduced to Mn^{2+} which is first adsorbed on a strongly acid cation-exchange resin mini-column and concenreated during chemical oxidation of the organic compounds therein at room temperature, while excessive MnO_4^- passes through the mini-column to be waste, then the concentrated Mn^{2+} is eluted reversely and measured by the luminol-H_2O_2-Mn^{2+} CL system and photomultiplier tube.

In this study, the flow injection-CL method, based on the $KMnO_4$-luminol reaction instead of the luminol-H_2O_2-Mn^{2+} CL system, was developed for permanganate index analysis. The conditions of chemiluminescence detection of COD_{Mn} samples were optimized under flow injection-CL mode. This flow injection-CL system for determination of COD is highly accurate, simple, and fast, and easy to be automated. With this new method, results for real water samples are well correlated with COD_{Mn} values determined using the conventional titrimetric method (permanganate method).

1 Experiments

1.1 Chemicals and reagents

All the chemicals were of analytical reagent grade. All the solutions were prepared with distilled water.

Digestion solutions were prepared as described in the standard method (GB11892-89, 1990) for the titrimetric method, containing: $KMnO_4$ 0.01 mol/L; NaOH 1.0 mol/L; H_2SO_4 (H_2SO_4:H_2O = 1:3); $Na_2C_2O_4$ 0.01 mol/L. Furthermore, stock solutions of the chemiluminescence reagent such as 0.01 mol/L luminol (Fluka, Czech) (pH = 12.0) and 0.1 mol/L EDTA were prepared, respectively. Glucose (Shanghai Chemical Reagent Plant, China) was used as the COD_{Mn} standard substance (Westbroke and Temmerman, 2001). All the glucose standard solutions were prepared by appropriate dilution of the 10.3214 g/L (the theoretical COD_{Mn} value is 10 g/L) (Li *et al*., 2003).

1.2 COD_{Mn} determining procedure

Water samples were digested following the procedure of the standard method (GB11892-89, 1990) throughout the analysis. Solutions of $KMnO_4$, H_2SO_4 and water sample or glucose were mixed with appropriate ratio.

The oxidation reaction was carried out for 30 min. After digestion, 1.0 ml of water sample was diluted to 50 ml using distilled water for next experiments.

The home-made flow-injection (FI) system used for CL analysis is shown in Fig.1. Peristaltic pump and flow cell were purchased from Ruimai Company (Xi'an, China). Poly tetrafluoroethylene (PTFE) tube (0.8 mm i.d.) was used as connection material in the system. Injection was made using a six-way injection valve equipping a sample loop of 80 μl. Flow lines were inserted into the EDTA-NaOH, luminol, carrier (double-distilled water) and standard solution or sample solution, respectively. The pumps were started to wash the whole system, then, the luminol, EDTA-NaOH and carrier solution were pumped at a flow rate of 3.0 ml/min. The colorless glass coil (i.d. 2.0 mm, total diameter of the flow cell of 4 cm without gaps between loops) was placed in front of the photomultiplier tube (Binsong, China). The PMT was operated at –843 V and photocurrent was magnified by a signal magnifier (Nanjing University, China) and then recorded using a PC computer controlled by data acquisition software (Qianpu Software Ltd., Shanghai, China).

1.3 Methods

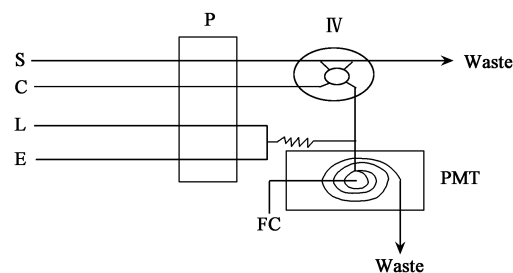It is clear that the digestion efficiency of organic material

Fig. 1 Schematic diagram of FI-CL system. S: sample; C: carrier (H_2O); L: lumimol; P: peristaltic pump; IV: injection valve; FC: flow cell; PMT: photomultiplier tube; E: EDTA-NaOH.

in samples mainly lie on the digestion process. To ensure organic material in samples digest completely and obtain the best reproducibility and accuracy, the standard digestion procedure is still chosen in the following experiments. Under these conditions, susceptible organic material is oxidized to carbon dioxide and water, and the $KMnO_4$ is reduced to Mn^{2+} ions:

$$4MnO_4^- + 5C + 12H^+ = 4Mn^{2+} + 5CO_2 + 6H_2O \qquad (1)$$

During the digestion process, we found that the manganous ions could react with MnO_4^- ions in the solution to form brown precipitate of manganic oxide (MnO_2):

$$2MnO_4^- + 3Mn^{2+} + 2H_2O = 5MnO_2 + 4H^+ \qquad (2)$$
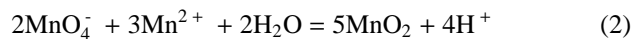
The total reaction is therefore given by:

$$4MnO_4^- + 3C + 4H^+ = 4MnO_2 + 3CO_2 + 2H_2O \qquad (3)$$

After oxidation, the excessive $KMnO_4$, which is reversely proportional to the COD_{Mn}, is determined by the home-made CL detection system:

$$MnO_4^- + luminol \longrightarrow h\nu + production \qquad (4)$$
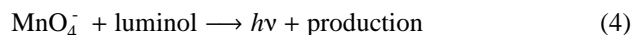
The signal of CL output of the PMT is amplified and recorded by a computer. It has been demonstrated by Westbroke and Temmerman (2001), that in a certain condition, the CL intensity of luminol-$KMnO_4$ reaction linearly increased with an increase of $KMnO_4$ concentration. Herein, the light intensity is proportional to the excessive MnO_4^- concentration, which is in reverse proportion to COD_{Mn} value of samples.

2 Results and discussion

2.1 Optimization of FI-CL systems

As mentioned above, the standard digestion procedure is chosen in the experiments. Obviously, the $KMnO_4$ concentration should appropriately increased with increasing the glucose concentration or the COD_{Mn} value of the samples, because it affected the digestion reaction. Higher concentration of $KMnO_4$ was also used to extend the linear range of COD_{Mn} detection. However, because of more brown precipitate of MnO_2 production for the samples with higher COD_{Mn} value, at the concentration $>8.0 \times 10^{-3}$ mol/L, the stability of CL signal was insufficient for precise determination of COD_{Mn}. Moreover, as shown in Fig.2, even though the digested sample 10 mg/L of COD_{Mn} was diluted 50 times, the CL was sensitive enough and suitable to perform a determination of COD_{Mn}. Therefore, a $KMnO_4$ concentration of 8.0×10^{-3} mol/L was chosen in this system.

For optimization, the standard glucose solution (the theoretical COD_{Mn} value is 10 mg/L) was used for investigating operating condition of the proposed system taking operational convenience. The concentration of luminol, EDTA and NaOH were all optimized for the sensitive and
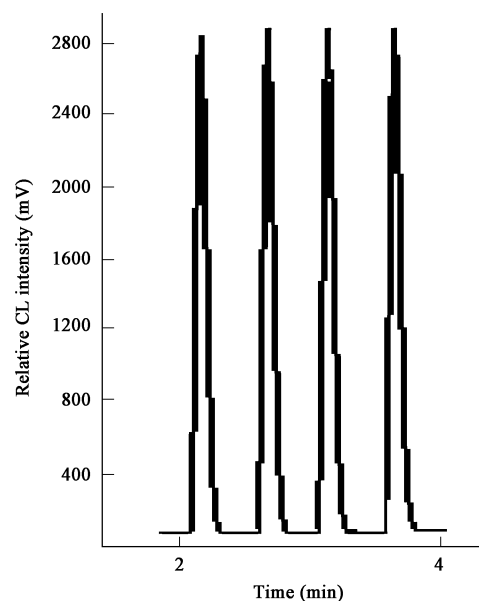

Fig. 2 CL signals of 10 mg/L COD_{Mn} standard sample. Condition: digested with standard method; dilution: 50 times; flow rate: 3.0 ml/min; $C_{luminol}=1.0\times10^{-3}$ mol/L (pH=12.0); $C_{EDTA}=1.0\times10^{-2}$ mol/L; $C_{NaOH}=0.1$ mol/L; $C_{COD_{Mn}}=10$ mg/L.

precise detection of COD_{Mn} value. The effect of luminol concentration on the COD_{Mn} detection was investigated. We found the CL intensity increased with the increasing luminol concentration until reached a maximum at about 3.0×10^{-3} mol/L. Because an increase in luminol concentration led to an increase in both the signal (S) and baseline noise (B), similar signal-to-noise ratio (S_{NR}) was achieved with the luminol concentration from 1.0×10^{-3} to 3.0×10^{-3} mol/L. The luminol concentration was set at 1.0×10^{-3} mol/L for further work, because of lower reagent consumption and enough CL sensitivity could be obtained as shown in Fig.2.

It is well known that luminol CL reaction depends on the reaction area pH. In the experiments, the final reaction area pH was controlled by adjusting the NaOH concentration. As shown in Fig.3a, the NaOH concentration that gave the greatest intensity for all COD_{Mn} studies was 0.1 mol/L. For convenience, EDTA solution was mixed with NaOH solution for the aim to avoid the effects caused by metal ions, and EDTA concentration should be as high as possible for practical application. Fig.3b shows the effect of the EDTA on the analytical signal. At the concentration < 0.01 mol/L, no obvious effect on the CL signal has been observed. The CL intensity began to decrease if the concentration become higher. Then, the EDTA concentration of 0.01 mol/L was chosen as optimum.

When equal molar luminol and $KMnO_4$ were mixed, the CL intensity increased with flow rate. For a good precision, low reagent consumption and high signal-to-noise ratio, flow rate of 3.0 ml/min was chosen to carry H_2O, luminol solution and EDTA-NaOH solution, respectively.

2.2 Interfering effects

When EDTA was adding into this system, the addition of the following metal ions: Na^+, K^+ (5×10^{-3} mol/L); Ag^+,

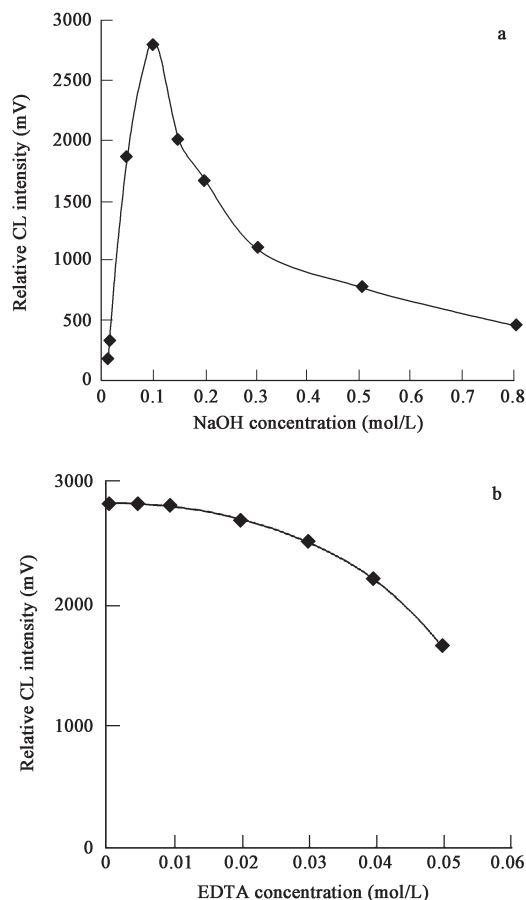**Fig. 3** Effects of the NaOH (a) and EDTA (b) concentration on CL intensity. Conditions: flow rate: 3.0 ml/min; $C_{luminol}$=1.0×10^{-3} mol/L (pH=12.0); $C_{COD_{Mn}}$=10 mg/L; C_{EDTA}=1.0×10^{-2} mol/L in (a); C_{NaOH} = 0.1 mol/L in (b).

Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Mg^{2+} and Ca^{2+} (2.5×10^{-3} mol/L); Fe^{3+}(1.0×10^{-3} mol/L); Cr^{3+}, Ni^{2+} (5×10^{-4} mol/L); Co^{2+} (2.0×10^{-3} mol/L); Mn^{2+}(1.0×10^{-3} mol/L) had no effect on the analysis of standard sample with 10 mg/L COD$_{Mn}$. Usually, the concentration of metal ions such as Co^{2+} and Cr^{3+} in surface water and ground water are lower than the interfering value in the above tested samples. So the interfering effects caused by metal ions could be avoided successfully by adding EDTA into this system. In this case, the cations in the water sample would not interfere with the determination of COD$_{Mn}$ for surface water and ground water analysis. Another important interference in the determination of COD$_{Mn}$ is chloride ion (Cl^{-}). For the standard sample (10 mg/L of COD$_{Mn}$), (5×10^{-3} mol/L Cl^{-} was found that to be tolerable concentration ration). Clearly, the CL method has a good selectivity, and ion-exchange resin mini-column and its procedure described in literature (Li *et al.*, 2003) have been eliminated successfully in our experiments, which therefore, made the COD$_{Mn}$ measuring device simpler and cheaper.

2.3 Linearity, detection limit and relative standard deviation

Using glucose as standard sample, as shown in Fig.4, under the optimum conditions described above, the cali-

bration graph of relative CL intensity (I, mV) vs. COD$_{Mn}$ was linear in the range of 0.3–200 mg/L with the regression equation of $I = -11.893COD_{Mn} + 3009.8$ ($r = 0.9953$). According to International Union of Pure and Applied Chemistry (IUPAC), the detection limit was determined for three times with the standard deviation of the blank signal as 0.3 mg/L. The relative standard deviation was 4.3% for 5.0 mg/L COD$_{Mn}$ ($n = 11$).
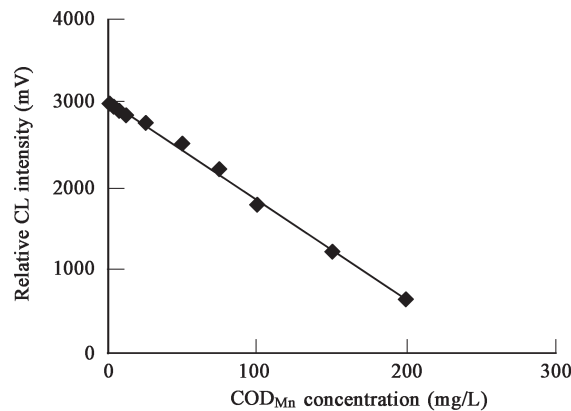

Fig. 4 Standard curve of COD$_{Mn}$. Conditions are the same as that in Fig.3 except for COD$_{Mn}$ concentration.

2.4 Analysis of real samples

Real water samples were collected from different surface water resources (Huazhong University of Science and Technology, China). All samples were taken at a depth of 50 cm and kept below 4°C until use. In Table 1, the COD value of the five real wastewater samples obtained using the proposed method and conventional titrimetric method (permanganate method) were compared. The COD$_{Mn}$ values of real samples determined by this method agreed well with the standard titrimetric method.

Table 1 Comparison of CL method and standard method for COD$_{Mn}$ determination

Sample No.	COD$_{Mn}$ (standard method) (mg/L)	COD$_{Mn}$ (CL method) (mg/L)	Difference* (%)
1	26.20	26.72	1.98
2	19.06	18.05	−5.30
3	10.08	10.26	1.79
4	7.93	7.44	−6.18
5	7.13	7.31	2.52

*(COD$_{Mn}$ (CL method)–COD$_{Mn}$ (standard method))/COD$_{Mn}$ (standard method)×100%.

3 Conclusions

A novel COD$_{Mn}$ analytical method has been proposed and experimentally valid. The developed method has also been successfully applied to determinate the COD$_{Mn}$ of real samples. The first advantage of this proposed method is that the filtering procedure (Hu and Yang, 2004), H$_2$O$_2$ and ion-exchange resin mini-column and its procedure (Li *et al.*, 2003) are eliminated successfully, therefore made the COD$_{Mn}$ measuring process and device simpler. The second

is that this method has high selectivity. Moreover, because water samples are digested following the procedure of the standard method, the principle of this proposed method for COD_{Mn} determination is therefore the same to the standard titrimetric method, then, the correlating procedure is unnecessary. Finally, the method is sensitive, which is capable of detecting as low as 0.3 mg/L. The linearity of this method covered the range of 1.0–10.0 mg/L and 2.0–15.0 mg/L COD_{Mn} from the first to fifth grade quality water for ground water analysis (GB/T 14848-93, 1994) and surface water analysis (Environmental GB 3838-2002, 2002), respectively, directed by the environment quality standard of China. The method is also environmentally friendly, robust, rapid, and easy to be automated.

Acknowledgements

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