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Improvement of chemiluminescence method for determination of chemical oxygen demand

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ABSTRACT

In our previous study, a low cost detector with a photodiode for chemical oxygen demand(COD) analysis using luminol-H2O2-Cr3^{+} chemiluminescence reaction and manual syringe injection mode had been proved. Herein, the previously method was improved applying a flow injection system. The effects caused by Br- and Ag^{+} ions were investigated in detail. Moreover, the conditions for COD determining such as pH, concentrations, flow rate, interference and sample proceeded procedures were also optimized. With the developed instrument, the practical detection limit of 2.1mg/L COD with the linear range of 2.1-600mg/L was achieved. The data for environmental monitoring of real water sample obtained by the present method was in good agreement with those obtained by the standard reflux titrimetric method. The flow injection-photodiode chemiluminescence detection system for COD determination was low cost, simple, and robust. In addition, the automation and maintenance of the system were easy.

KEYWORDS

Chemiluminescence;
Photodiode;
Chemical oxygen demand;
Flow injection.

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[1]. The standard reflux titrimetric method for COD determination[2] consists of oxidizing the organic matter of the sample, usually done by adding a known amount of oxidant, refluxing at high temperature on open containers and titrating the excess oxidant. This methodology suffers from a series of drawbacks: (i) the analysis time is too long; including digestion time and titration time; (ii) handling is also considerable, thus increasing the probability of errors and the reproducibility of the results are dependent upon the operator skill; (iii) there is a quite high consumption of chemicals; (iv) several inorganic species cause interference on this method. (vi) back-titration after sample digestion is an insensitive method of detection.

Many efforts have been made to circumvent drawbacks caused by standard reflux manual titration[2]. In recent years, several new principles have been proposed to develop rapid and environmentally friendly new methods for the determination of COD. For example, Naffrechoux et al. tried to determine the contents of organic matter in water samples by measuring the absorbance of the untreated sample in the UV region and correlating it with COD[3]. Electrocatalytic, photocatelytic and photoelectrochemica oxidation principles also have been developed for COD determination[4-12]. Although these methods mentioned above have demonstrated many advantages over the traditional COD methods such as the rapidity of the analysis, environment friendly, the directness in the acquisition of analytical signal, and being easy to be incorporated into on-line analysis monitoring system, due to the disadvantages that described by Zhao et al.[12], such as the narrow dynamic working range and inconvenience for the system operation, these new methods with new principles are still far from being satisfied for practical, and significant improvements are required before that can be practically used.

Because the standard methods for determination of COD have been in place for many years, and have been accepted as the national standard methods in many countries, another ideal scheme is to perfect the traditional COD methods. These efforts mostly focus on improvements over both digestion and analytical methods. Jirka and Smith[13]developed the so-called micro semi-automated method, this method was similar to the conventional one, and the only difference from that the digestion step was carried out in closed culture tubes. Jeris[14] suggested that a mixed solution of sulfuric acid and phosphoric acid be substituted for concentrated sulfuric acid as the digestion media, thus the oxidizing ability of dichromate greatly increased so as to shorten the reflux time. Some reports have been published concerning the application of microwave radiation as a heat source for the determination of COD, and these methods have dramatically reduced the heating time[15,18]. On the other hand, some new analytical methods have been reported for determination of COD, including spectrophotometry[13,19], atomic absorption spectrophotometry[18,20], polarography[21], etc. Among these analytical methods, spectrophotometry is the most common detector used in COD determination. However, some inherent problems of these systems with spctrophotometric measurements are presented: (i) in order 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[15] (ii) samples showing high turbidity are not suitable for this method due to serious interference[13]; (iii) the systems lack enough sensitivity so that the systems need rather long digestion time and are not suitable for the samples with low COD; (iv) the linear range of the systems is narrow, so the application of the systems is limited. Therefore, it is necessary to develop low-cost, simple, automated and easy to maintain COD analytical instruments with higher sensitivity and broader linear range for quality control.

Flow-injection chemiluminescence(CL) is known to be a powerful analytical technique that promises high sensitivity, fast response time, extensive dynamic range, use of simple, inexpensive instrumentation to easily set up, as well as 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 environment samples[22]. 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 chemical oxygen demand by measuring the appearance of Cr^{3+} after samples digestion using a laboratory-built portable photodiode luminometer, which is proportional to the chemical oxygen demand[23]. Such system has the advantages of simplicity, low cost and high sensitivity, but suffers from automatization and non-stop analysis difficulties. In addition, the portable photodiode luminometer system is not suit for high throughput and fast on-line analysis.

In this study, the flow-injection method was developed for the aim of continuous and large-scale environmental sample analysis, replacing the previously used manual syringe injection mode. The conditions of chemiluminescence detection of COD samples were optimized under flow injection-CL mode. It was demonstrated that the optimum conditions of COD determination were quite different from that of luminol-H_2O_2-Cr^{3+} CL reaction. This flow injection-CL system for determination of COD was highly accurate, simple, and fast, and was suitable for automatic and continuous analysis. With this new method, results for real water samples were well correlated with COD values determined using the conventional titrimetric method.

EXPERIMENTAL

Reagent

All used Chemicals were of analytical reagent grade. All solutions were prepared with distilled water. A 0.1mol/L H_2O_2 solution was used as the stock solution of chemiluminescence reagent. Furthermore, stock solutions of the chemiluminescence reagent, such as 0.01mol/L solution of luminol, solution of EDTA, 2.5mol/L solution of KBr, 2.0mol/L solution of NaOH and mixed solution of KBr(2.5mol/L)-EDTA(0.01mol/L) were prepared, respectively. Digestion solutions were prepared as described in (2) for the closed reflux titrimetric method, containing 0.250mol/L of $K_2Cr_2O_7$, 0.1mol/L of $(NH_4)_2FeSO_4$, 2.0824mmol/L of potassium hydrogen phthalate (KHP). Catalytic solution of Ag_2SO_4 was prepared by adding Ag_2SO_4(0.1g)to H_2SO_4 (100mL). Solution of $HgSO_4$(0.11mol/L) was used for eliminate the interference of Cl^- ion.

Chemical oxygen demand determining procedure

Water samples were digested following with the procedure of the standard method China NEPA, 1989), and Ag_2SO_4 was used as catalyst. After digestion, firstly, the water samples were diluted to 100ml using distilled water, then mixed 1.0mL of diluted water sample with 2.5mL of EDTA, and consequently, further diluted to 25.0mL, meantime adjusting the pH value to about 2.0.

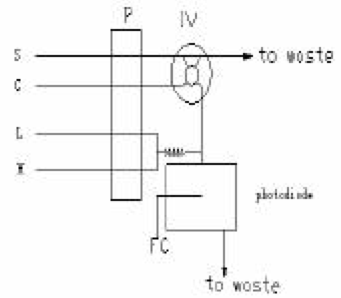
The home-made FI system used for CL analysis was shown in Figure1. Peristaltic pump and flow cell were purchased from Ruimai Company (Xian, China). PTFE tubing (0.8mm i.d.) was used as connection material in the system. Injection was made using a six-way injection valve equipping a sample loop of 80μL. the colorless glass coil(i.d.2.0mm, o.d. 3.5mm, length 15cm) was placed in front of the photodiode purchased from Department of Electronics of Wuhan University(China). Flow lines were inserted into the H_2O_2, luminol, carrier(double-distilled water) and standard solution or sample solution, respectively. The pumps were started to wash the whole system, and then, the luminol, H_2O_2 and carrier solution were pumped through at a flow rate of 2.5mL/min. The mixed solution was passed to the CL cell, and the light emitted from the CL reaction was detected with the photodiode and magnified by a signal magnifier (Nanjing University, Nanjing, China). Data acquisition and treatment were performed with commercially available software(Zhejiang University, Zhejiang, China) running under windows 98. All measurements were performed at room temperature.

RESULTS AND DISCUSSION

Preparation method of samples

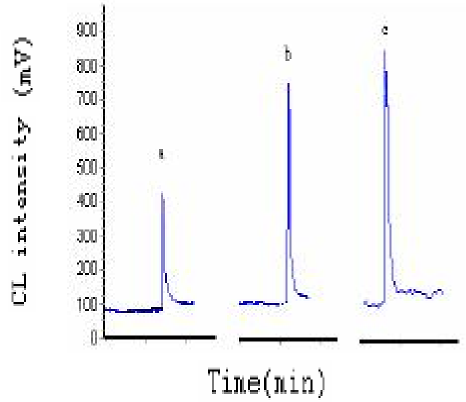
Recently, Zhang et al.[23] found a chemiluminescene system for automatic determination of chemical oxygen demand (the permanganate method) using flow injection analysis. In this system, potassium permanganate was reduced to Mn^{2+} which was first adsorbed on a strongly acid cation-exchange resin mini-column to concentration during chemical oxidation of the organic compounds therein at room temperature, while excessive MnO_4^- passeed through the mini-column to be waste, then the concentrated Mn^{2+} was eluted reversely and measured by the luminol-H_2O_2-Mn^{2+} CL system and photomultiplier tube(PMT), and a complete analysis could be performed in 1.5 minute. The interference of excessive MnO_4^- with the luminol CL system was eliminated by the separation with cation-exchange resin mini-column, at the same time Mn^{2+} was concentrated on the cation-exchange resin mini-column. It was well known, on the basis of the oxidizing agents used, that the standard COD method could be classified into either the dichromate method or the permanganate method. The former was more popular mainly due to its higher degradation degree toward a wide range of the organic pollutants. For this reason, the dichromate method but the permanganate method was chosen for search in our previous work[23,24]. In brief, according to the standard COD determination method(China NEPA, 1989), the samples oxidation by a known excess of potassium dichromate in hot acid, after oxidation, the appearance of Cr^{3+}, which is proportional to the chemical oxygen demand, was determined by the homemade portable photodiode(instead of PMT) luminometer system with Luminol-H_2O_2-Cr^{3+} CL reaction, and the chemiluminescence intensity was proportional to the Cr^{3+} concentration, therefore to the COD values of samples. The other advantage of Luminol-H_2O_2-Cr^{3+} CL reaction was that the specificity of this reaction for Cr(III) and COD analysis could be achieved in the presence of ethylencadiamine tetraacetic acid(EDTA)[23,24], and then, the cation-exchange resin mini-column and separation procedure described by zhang et al.[25] could be removed in our research.

It is clear that the digestion efficiency of organic material in samples mainly lies on the digestion process. As that described before[23,24], in order to ensure organic material in samples digested completely and obtain the best reproducibility and the accuracy, the standard digestion procedure was still chosen in next experiments. Following the procedure described in our previous experiments[23,24], under the optimum luminol-H_2O_2-Cr^{3+} CL reaction condition with Ag_2SO_4 solution as catalyst and Br^- ions as enhancer, AgBr floccules occurred, which could cause loss of samples during the filtering process and seriously affect the detection precision and accuracy. Therefore, the samples should be filtered to remove the precipitation of AgBr before using. In addition, with manual syringe injection mode and portable luminometer system, for the reason that higher dilution times could apparently affect the sensitivity of CL detection, the negative effect mentioned could be successfully overcome by filtering the dilution samples into 100 times. Obviously, preparation for samples was critical to avoid the filtering procedure and device, and to realize robust, automatic and continuous injection and analysis. However, filtering would apparently increase the cost of instrument. When the digested samples were diluted higher than 100 times, Ag^+ ions and Br^- reacted and produced AgBr colloid but floccules. Peak-to-peak signals shown in Figure2 indicated that addition of Br^- ions significantly enhanced COD detection signal. Furthermore, the fact that peak$_c$ was higher than peak$_b$ indicated that filtering procedure could cause Br^- ions, Cr^{3+} and signal loss. These results demonstrated that this colloid solution could be used for direct manual injection without signal degradation as well as the filtering step could be eliminated. Figure3 showed chemiluminescence signals of 250mg/L standard samples with addition of Br^- ions and 100 times dilution, injected by FI system without filtering procedure. Unfortunately, Compared to that obtained in figure 2(c), the signal was too low to determine low COD values. Furthermore, AgBr colloid caused CL signal fluctuation, probably due to the colloid particles absorbed on the conveyance piping, injection valve and flow cell, *etc*. Results indicated that the 100 times dilution samples, which were suitable for the manual injection mode, couldn't be used in the FI injection mode.



S: sample; C: H_2O carrier; L: lumimol; H: H_2O_2; P: peristaltic pump; IV: injection valve; FC: flow cell; photodiode.

Figure 1 : Schematic diagram of FIA-CL flow system



Condition: Digested with standard method; Dilution : 100 times; detected with potable photodiode system by manual injection method; a : Without Brions addition; b : With addition of Brions and filter procedure; c : With addition of Br ions and without filter procedure

Figure 2 : CL signals of 250mg/L COD standard sample

Results shown in figure 2 also indicated that the enhance efficiency of Br^- ions used for COD analysis, about 2 times, which was not as evident as that in luminol-H_2O_2-Cr^{3+} reaction described by Chang et al.(1980), probably due to reactions between Br^- ions and some metal ions, such as Ag^+ and Hg^{2+}, etc. Apparently, the addition of Br^- ions was eliminable, and the Cr^{3+} ions concentration in the digested samples with lower dilution times was enough for CL detection, which had been illustrated in figure 4. The addition of Br^- was therefore eliminated in subsequent experiments. Before CL analysis, the digested samples were diluted 25 times to achieve sensitive COD determination.

During the dilution procedure, the pH of digested samples was adjusted, and EDTA solution was added for the aim to avoid the effects caused by other metal ions. As that presented before, the best standard Cr^{3+} samples pH was adjusted to 3.0 to obtain the best CL reaction signal of luminol-H_2O_2-Cr^{3+}. However, precipitate of Ag_2O was observed when the pH of 3.0 caused fluctuation of detection signals if the test samples were injected without filtering procedure. Despite lower pH of test samples could cause some loss of CL signal, as shown in figure 4, when the test samples pH was adjusted to 2.0, the obtained CL signal was still higher enough for the necessary of sensitive COD determination. This problem was overcome by adjusting the test samples pH lower than 2.0.

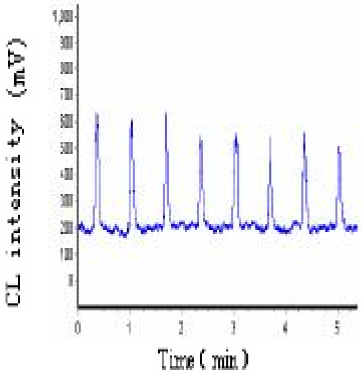
2. Optimization of FI-photodiode CL systems

When equal molar luminol and H_2O_2 were mixed, the CL intensity would increase with increasing flow rate. In order to obtain good precision, low reagent consumption and high signal-to-noise ratio, flow rates of 2.5mL/min were chosen for H_2O carrier, lumimol solution and H_2O_2 solution, respectively.

The H_2O_2 concentration was varied in order to maximize the CL signal. As shown in figure 5, CL intensity increased with the increasing H_2O_2 concentration until reached a maximum at about 8.0×10^{-2}mol/L. Further increasing H_2O_2 concentrations increased the background noise, reduced the CL intensity, and therefore reduced the signal-to-noise ratio (SNR). The effect of luminol concentration on the COD detection was also investigated and the results were presented in figure 6. An increase in luminol concentration led to an increase in both the signal (S) and baseline noise (B) until the optimum SNR was achieved with the luminol concentration of 1.0×10^{-3}mol/L. CL intensity was also significantly affected by pH of luminol. By varying the pH values from 10 to 14, the CL intensity was maximized with a pH value of 13.0.

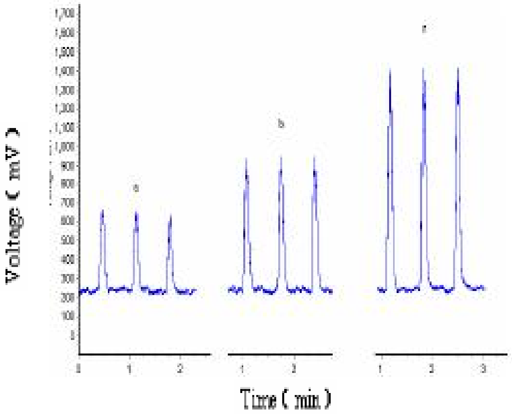
3. Interfering effects

The high selectivity of this chemiluminescence re-



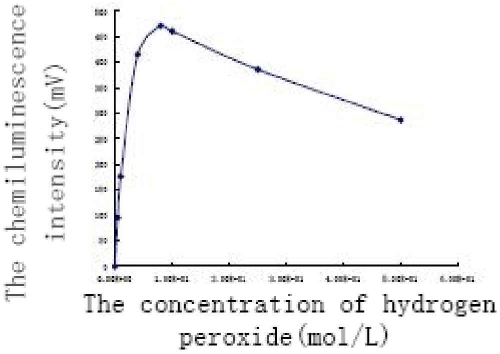
Condition: Digested with standard method; Dilution: 100 times; with addition of Brions and without filter procedure; $V_{luminol}=V_{H2O2}=2.5$ml/min; luminol: $1.0\times10^{?3}$mol/L; pH of luminol:13.0; H_2O_2: 8.0×10^{-2}mol/L; The pH of sample solution: 2.0. EDTA: 1.0×10^{-3}mol/L.

Figure 3 : CL signals of 250mg/L COD standard sample injected by FI system



Condition: $V_{luminol}=V_{H2O2}=2.5$ml/min; luminol: 1.0×10^{-3}mol/L; The pH of luminol:13.0; H_2O 8.0×10^{-2}mol/L; pH of sample solution: 2.0. EDTA: 1.0×10^{-3}mol/L; a: COD=150mg/L; b: COD=300mg/L; c: COD=500mg/L. Dilution: 25 times

Figure 4 : CL signals of standard samples with different COD value injected by FI system



COD=250mg/L; $V_{luminol}=V_{H2O2}=2.5$ml/min; Luminol: 1.0×10^{-4}mol/L; The pH of luminol: 12.0; The pH of sample solution : 2.0. EDTA: 1.0×10^{-3}mol/L.

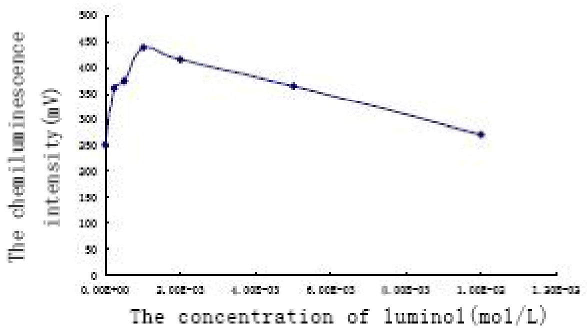
Figure 5 :The effect of the concentration of hydrogen peroxide on chemiluminescence intensity

action for COD determination was already proved in our previous works[23]. In brief, when EDTA was added into this system, the addition of 2000 times Cr^{3+} concentration of K^+, Na^+, Ca^{2+}, Mg^{2+}, and 100 times of Sr^+, Ba^{2+}, Th^{4+}, ZrO^{2+}, V^{2+}, MoO_4^{2-}, Wo^{2-}, CrO_4^{2-}, Mn^{2+}, Fe^{3+},Ni^{2+}, Rh^{3+}, pd^{2+}, OsO_4^{2-}, Ir^{4+}, Pt^{2+}, Cu^{2+}, Ag^+, Au^{3+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, SiO_3^{2-}, pb^{2+}, NO_3^-, NH_4^+, AsO_4^{3-}, SbO_2^-, Bi^{3+}, PO_4^{3-}, CO_3^{2-}, F^-, Cl^- and CN^- had no effect on the determination of Cr^{3+}. Co^{2+} with 0.5 times or higher concentrations as Cr^{3+} exhibited interference for Cr^{3+} and COD analysis, fortunately, as Cr^{3+} ions concentration in COD analysis solutions was above 10^{-5}mol/L level, and other metal ions such as Co^{2+} in real samples usually was far below this concentration level, thus the interference effects caused by metal could be negligible in our experiments. If the concentration of Co^{2+} would be higher than the interfering value, this interfering effect caused by Co^{2+} ions could be eliminated by adding 1,10-phenanthroline into the post-digestion samples.

Applications

Under the optimum conditions described above, the limit of detection, 2.1mg/L, was obtained as well as good linearity was observed between the light emission and the COD value, as shown in figure 7. The linear dynamic range covered from 2.1mg/L to 600mg/L for the standard potassium hydrogen phthalate sample prepared according to the standard method (China NEPA, 1989).

Reproducibility tests (n=6) showed the relative standard deviation of standard sample was 3.6% for 250mg/L COD of potassium hydrogen phthalate solution and 4.0% for 356.2mg/L COD (determined by standard method) of garbage-leakage-liquid wastewater sample solution. Furthermore, from TABLE 1, the recovery range from 7 wastewater samples was between 106.3% and 98.1%, with an average of 102.4%. In TABLE 2, the COD value of 22 real wastewater samples obtained using the proposed method and conventional titrimetric method was compared. The COD values of real samples determined by this method agreed well with the standard titrimetric method. The first advantage of this proposed method was that a low cost chemiluminescence detector with a photodiode instead of photo-multiplier tube (PMT) was used for detection of light emission. The second was that the filtering procedure and ion-exchange resin mini-column and its procedure[25] were eliminated successfully, which made the COD measuring device simpler and cheaper. The third was that this



COD=250mg/L; $V_{luminol}=V_{H2O2}$=2.5ml/min; The pH of luminol:12.0; The concentration of H_2O_2 : 8.0×10^{-2}mol/L; The pH of sample :2.0. The concentration of EDTA: 1.0×10^{-3}mol/L

Figure 6 : The effect of the concentration of luminol on chemiluminescence intensity

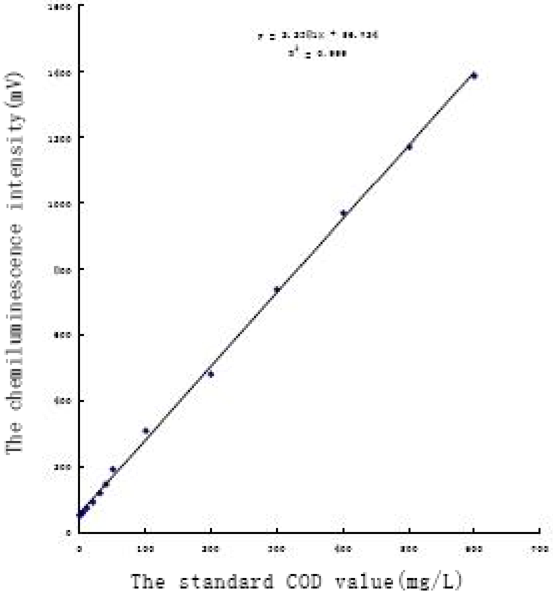


Figure 7 : The standard curve of COD

TABLE 1 : Comparison of test results of wastewater COD with standard method (COD, mg/L)

Wastewater samples	Samples COD	Adding COD*	COD found	Recovery COD	Recovery rate(%)
Dying wastewater 3	188.7	100	292.9	104.2	104.2
Oiliness wastewater 3	100.4	100	198.5	98.1	98.1
Garbage leakage liquid 1	389.2	300	709.4	320.2	106.7
Living wastewater 3	178.4	100	279.8	101.4	101.4
Organic wastewater 3	178.1	100	284.4	106.3	106.3
Saponin wastewarer 3	380.1	200	580.5	200.4	100.2
East lake water 3	28.6	20	48.9	20.3	100.2

*(B-A)A×100%

TABLE 2 : Comparison of test results of wastewater COD with standard method (COD, mg/L)

Samples	A,COD (standard method)	B,COD CLmethod	R.D* (%)
Dying wastewater 4	76.1	69.9	-8.14
Oiliness wastewater 4	128.1	130.2	1.63
Garbage leakage liquid 2	568.7	598.7	5.27
Living wastewater 4	228.1	210.6	-7.67
Organic wastewater 4	356.2	347.1	-2.55
Saponin wastewarer 4	403.1	380.6	-5.58
East lake water 4	30.9	32.6	-5.50
The inflowing wastewater of the sewage treatment plant	289.1	278.0	-3.8
The outflowing wastewater of the sewage treatment plant	125.5	121.7	-3.0
The cesspool wastewater	169.6	172.8	1.9
Wastewater of the Seng line garden 1	54.7	55.0	0.5
Wastewater of the Seng line LINE garden 2	608.0	604.0	-0.7
Wastewater of the HU XI river 1	15.2	14.5	-4.6
Wastewater of the HU XI river 2	38.0	36.3	-4.5
Wastewater of the Ling Jiao Lake 1	49.8	47.5	-4.6
Wastewater of the Ling Jiao Lake 2	42.0	39.6	-5.7
The outflowing wastewater of the soy bean plant	128.4	129.8	4.1
The wastewater of the dining-room	1251.0	1165.3	-6.8
The JING lake wastewater	33.4	36.5	9.3
The wastewater of the second chemical plant	640600.0	626000.0	-2.3
The wastewater of the fourth chemical plant	16400.0	15640.0	-4.6
The students' living wasterwater	330.3	358.4	8.5

*(B-A)A×100%

method had high selectivity. Moreover, because water samples were digested following with the procedure of the standard method and analyzed based on determination of Cr^{3+} ions, therefore the principle of this proposed method for COD determination was same to the standard titrimetric method, and the correlating procedure was unnecessary. Finally, the determination of concentration of Cr^{3+} and COD values in this method took only several minutes at most, thus it was suitable for large-scale environmental samples analysis with high analysis speed compared to the manual syringe injection mode[23]. As that described by Zhang et al.[25], the samples were oxidized and digested at room temperature with the permanganate method, and the interference of chloride ion with lower concentration was overcame, based on the short digestion reaction time, lower sulfuric acid concentration and not very strongly oxidizing ability of $KMnO_4$. Obviously, the application range of the presented FI-CL method was wider than that described by Zhang et al.[25], due to its higher degradation degree toward a wide range of the organic pollutants. So, it was easy to be accepted and widespread. Although the analysis of COD was still a time-consuming process(because the standard digestion process for COD was still used in batch mode, and the main step of limiting determination speed was digestion process), we believed the continuous analysis with short time was easy to resolve by combining this improved method with the digestion processes of automatic instrument, which were developed based on the principle of standard digestion method such as microwave digestion method [15-18] Furthermore, we had no doubt that the digestion procedures similar to the standard method without the use of Ag_2SO_4 solution as catalyst such as that was described in our previous work[23] could be directly used for continuous and on-line analysis, and further investigations were under way in our laboratory to perfect the presented method for that aim. Compared to other methods such as titrimetric, spectro-photometry, electrocatalytic, photocatelytic and photoelectrocatalytic detection, the presented method showed promising results including simplicity of instrument configuration, ease of maintenance, high precision and accuracy, fast response, low cost and high sensitivity.

CONCLUSION

This paper describes the fabrication of FI system based on the COD determination system reported in Talanta[23]. The advantage of this system is elimination of the filtration procedure and ion-exchange resin mini-column. The effect of important experimental parameters on analytical signal generation was systematically investigated, and the optimum conditions were obtained. Moreover, high selectivity of this system has been experimentally validated. The method was successfully applied to determine the COD of real water samples. The COD value of real samples determined by this method agreed with the standard titrimetric method.

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