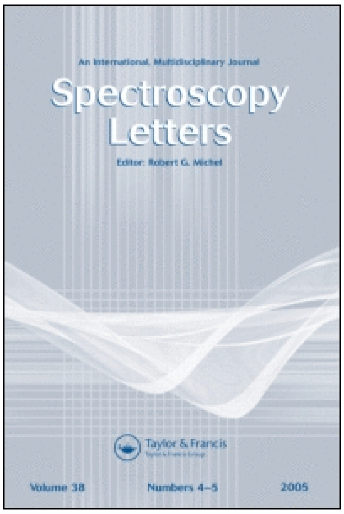

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Flow-Injection Chemiluminescence Study of Luminol-Hydrogen Peroxide-Carbendazim System

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Flow-Injection Chemiluminescence Study of Luminol–Hydrogen Peroxide–Carbendazim System

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Abstract: A new flow-injection chemiluminescence (CL) method is described for the determination of carbendazim. The method is based on the CL reaction of luminol and hydrogen peroxide (H_2O_2). Carbendazim can greatly enhance the chemiluminescence intensity in sodium hydroxide–sodium dihydrogen phosphate ($NaOH{-}NaH_2PO_4$) medium ($pH = 12.6$). Under the optimum conditions, the linear range for the determination of carbendazim is 2.00×10^{-8} to 2.00×10^{-6} g mL^{-1} with a detection limit ($S/N = 3$) of 7.24×10^{-9} g mL^{-1}. The relative standard deviation is 1.8% for 1.0×10^{-7} g mL^{-1} carbendazim ($n = 8$). The proposed method has been applied to the determination of carbendazim in tap-water samples. Furthermore, the possible enhanced CL mechanism is discussed by examining the CL spectra and fluorescence spectra.

Keywords: Carbendazim, chemiluminescence, flow-injection analysis

INTRODUCTION

Carbendazim (methyl 1H-benzimidazole-2-ylcarbamate; MBC) belongs to the group of the benzimidazole pesticides. It is a systemic fungicide used in

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agriculture for controlling a wide range of fungal pathogens on cereals, fruits, cotton, tobacco, turf, ornamental plants, and vegetables. It becomes a human-origin polluting compound that is usually present in water as a consequence of its massive use. Therefore, the residue determination of carbendazim in water is required.

The most often applied analytical technique to determine carbendazim is liquid chromatography (LC) coupled with mass spectrometry (MS) detection,[1–7] ultraviolet (UV) detection,[8,9] or diode array detection (DAD).[1,10] Other analytical techniques have been reported including fluorimetric methods,[11–13] electrochemical analysis,[14,15] enzyme-linked immunosorbent assay (ELISA),[16] and micellar electrokinetic chromatography (MEKC) with DAD.[17] Although some of the methods are sensitive and specific, they are also instrument-elaborate, time-consuming, and approach-complicated.

As a rapid, sensitive, and simple method with inexpensive instruments and wide linear range, chemiluminescence (CL) detection has recently attracted increased attention for the residue determination of polluting substances in water.[18,20,21,23,24] Agricultural use of pesticides has a major impact on water quality and leads to serious environmental consequences. However, in pesticide residue control, only a few contributions[19,21–26] have appeared using CL detection mode, and scarcely for the determination of benzimidazole pesticides.

In our experiment, carbendazim was found to enhance the CL emission intensity by the reaction of luminol with H_2O_2 in an alkaline medium. Based on this observation, a simple and fast flow-injection CL method has been developed for the determination of carbendazim, which has been satisfactorily applied in tap-water samples. The CL detection system can be further developed for appropriate chromatography. Furthermore, the possible CL reaction mechanism is also discussed in this paper. As far as we know, this is the first report on the chemiluminescence of carbendazim and the first report of determination of this pesticide in water samples by a CL procedure.

MATERIALS AND METHODS

Chemicals

All reagents were of analytical grade or better. Carbendazim was purchased from the National Institute for the Control Quality of Pesticide Products of China (Shenyang, China). Luminol was purchased from MERCK-Schuchardt (Hohenbrunn, Germany). The water used for the preparation of solutions was doubly distilled. A 0.01 $\mathrm{mol\,L^{-1}}$ luminol stock solution was prepared by dissolving 1.7710 g luminol in 0.1 $\mathrm{mol\,L^{-1}}$ sodium hydroxide solution and stocked at 4°C for at least 3 days to attain stability. The working solutions of luminol were prepared by diluting the stock solution with

$NaOH{-}NaH_2PO_4$ (pH 12.6) solution. Hydrogen peroxide (H_2O_2) 0.4% (v/v) was prepared by diluting 30% (v/v) H_2O_2 before use. A stock standard solution of carbendazim (1.0×10^{-4} g mL^{-1}) was prepared daily in 0.05 mol L^{-1} sulfuric solution and stored at about 4°C in brown bottles in order to avoid light decomposition. Working standard solutions of carbendazim were prepared daily by appropriate dilution of stock standard solution with 0.05 mol L^{-1} sulfuric solution.

Apparatus

The schematic diagram of the flow-injection chemiluminescence (FI-CL) system is shown in Fig. 1 (Procedure 1.1). A peristaltic pump (pump A) was used to pump luminol solution at a flow rate of 2.8 mL min^{-1}, and another (pump B, two channels) was used to carry carbendazim solution and H_2O_2 solution at a flow rate of 1.4 mL min^{-1}. Polytetrafluoroethylene (PTFE) tubing (0.8 mm i.d.) was used to connect all components in the flow system. Injection was operated using a six-way injection valve fitted with an 80-μL sample loop. The distance between this T-shaped piece and the flow cell is about 5.5 cm. The flow cell was made by coiling a 16-cm length of colorless glass tubing (1 mm i.d.) into a spiral disk shape and was placed close to the photomultiplier (Hamamatsu, Japan) of the type IFFM-D flow-injection chemiluminescence analyzer (ReiMai, Xi'an, China). The CL signal produced in the flow cell was collected with the photomultiplier and

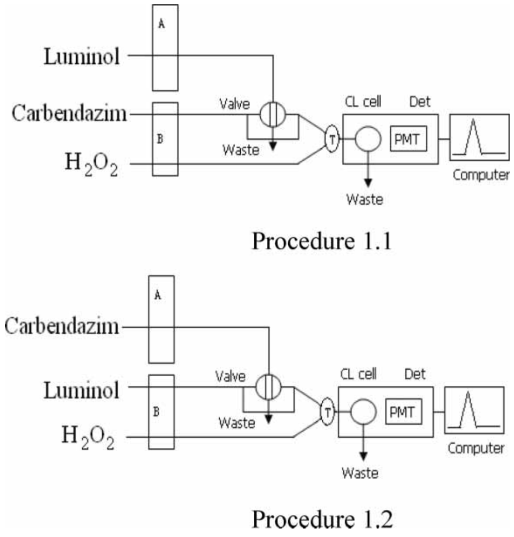

Figure 1. The flow-injection manifold. A, B, peristaltic pump; valve, injection valve; T, T-shaped piece; PMT, photomultiplier tube; Det, detector.

recorded with a computer using an REMEX software. The voltage in the photomultiplier tube was kept at −750 V. Fluorescence spectra were measured with a 970 CRT fluorescence spectrophotometer (Shanghai, China). Chemiluminescence spectra were measured with a 970 CRT fluorescence spectrophotometer (Shanghai, China) with the light source switched off. The pH values were measured with a precision pH meter, model pHS-3C (Shanghai, China).

RESULTS AND DISCUSSION

Analytical Procedure

Because carbendazim acts as enhancer of luminol–H_2O_2 chemiluminescent system, a study was necessary to choose between a reverse flow-injection analysis procedure (Fig. 1, Procedure 1.1) and flow-injection analysis procedure (Fig. 1, Procedure 1.2). Under same conditions, the effect of analytical procedures on CL emission intensity was studied. Higher signal-to-background ratio and better reproducibility were obtained in reverse flow-injection analysis. Therefore, the reverse flow-injection analysis was used subsequently in the study.

In reverse flow-injection analysis procedure, an aliquot of luminol solution was injected into the carrier stream of carbendazim sample solution by using the six-way valve with an 80 μL loop and then mixed with H_2O_2 solution in a T-shaped piece; the mixed solution was transferred into CL cell, and the CL signal was then recorded. The relative CL intensity ΔI (defined as the difference of CL intensity in the presence and in absence of carbendazim) was proportional to concentration of carbendazim. Calibration curve was prepared for the determination of the carbendazim.

Kinetic Curves of CL Reaction

The CL kinetic characteristics of the reaction of H_2O_2, luminol, and carbendazim in an alkaline medium were studied by a static injection method. The CL kinetic curves are shown in Fig. 2. Curve 1′ is the CL kinetic curve obtained when 0.4% (v/v) H_2O_2 was injected into pH 12.6 NaOH–NaH_2PO_4 solution containing 1.2×10^{-5} mol L^{-1} luminol. Curve 1 is the CL kinetic curve obtained when 0.4% (v/v) H_2O_2 was injected into pH 12.6 NaOH–NaH_2PO_4 solution containing 1.2×10^{-5} mol L^{-1} luminol and carbendazim 6.0×10^{-7} g mL^{-1}. It can be seen from curve 1 in Fig. 2 that this CL reaction was so rapid that the CL intensity reached a maximum at 5.5 s. Figure 2 also indicates that the CL intensity was enhanced in the presence of carbendazim (curves 1′ and 1).

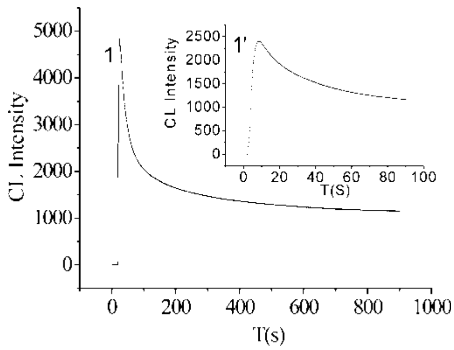

Figure 2. Kinetic curves of chemiluminescence systems. Insert (blank): Curve 1′: H_2O_2 0.4% (v/v); luminol 1.2×10^{-5} mol L^{-1}; NaOH–NaH_2PO_4, pH 12.6. Curve 1: Carbendazim 6.0×10^{-7} g mL^{-1}; H_2O_2 0.4% (v/v); lumiol 1.2×10^{-5} mol L^{-1}; NaOH–NaH_2PO_4, pH 12.6.

Optimization of Experimental Conditions

Effect of Surfactants

The effect of some surfactants [namely non-ionic surfactant Triton X-100, cationic surfactant cetyltrimethyl ammonium bromide (CTAB), and anionic surfactant sodium dodecyl sulfate (SDS)] on the present CL reaction was investigated. Although the three surfactants modify many CL reactions, there is no interesting effect on the present tested systems (Fig. 3). Therefore, these surfactants were not used for further work.

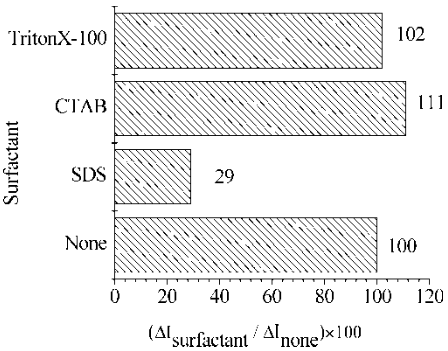

Figure 3. Effect of surfactant on CL intensity. ΔI: Relative CL intensity; ΔI_{none}: without surfactant. Experimental conditions: Sample volume 80 μL, flow rate main pump 1.4 mL min^{-1}, auxiliary pump 2.8 mL min^{-1}; H_2O_2 0.4% (v/v); luminol 1.2×10^{-5} mol L^{-1}; carbendazim 3.0×10^{-7} g mL^{-1} in various surfactants; CTAB 1.0×10^{-3} mol L^{-1}; SDS 8.0×10^{-3} mol L^{-1}; Triton X-100 10% (v/v).

Effect of pH of Luminol Solution

On account of the nature of luminol reaction, it is more favored in basic condition. Therefore, four kinds of media, 0.1 mol L^{-1} NaOH, 0.1 mol L^{-1} Na_2CO_3–NaOH, 0.1 mol L^{-1} Na_2CO_3–$NaHCO_3$, and 0.1 mol L^{-1} NaH_2PO_4–NaOH, were chosen to obtain the optimum condition for determination of carbendazim. The CL emission intensity of the 3.0 × 10^{-7} g mL^{-1} carbendazim–1.2 × 10^{-5} mol L^{-1} luminol–0.4% (v/v) H_2O_2 system in the presence of above media was investigated, respectively. It was found that the greatest relative CL intensity could be obtained in NaH_2PO_4–NaOH medium, while the maximum relative CL intensity achieved in NaOH, Na_2CO_3–NaOH, and Na_2CO_3–$NaHCO_3$ media were only 43%, 78%, and 61% of that obtained in NaH_2PO_4–NaOH medium, respectively. The effect of pH value of NaH_2PO_4–NaOH solution on the CL reaction was examined in the range of 12 to 13.2. As shown in Fig. 4, the relative CL intensity increased with an increase in the pH value from 12 to 12.6 and decreased with the pH value higher than 12.6. Thus, NaH_2PO_4–NaOH (pH 12.6) was finally chosen for further experiment.

Effect of Luminol Concentration

The effect of the concentration of luminol on the relative CL emission intensity was investigated in the range of 4.0 × 10^{-7} to 4.0 × 10^{-5} mol L^{-1}, and the results are shown in curve 1 of Fig. 5. As shown in curve 1, the relative CL intensity rapidly increased with an increase in the concentration of luminol from 4.0 × 10^{-7} to 1.2 × 10^{-5} mol L^{-1}. When the concentration of luminol exceeded 1.2 × 10^{-5} mol L^{-1}, the relative CL intensity slowly increased. However, a concentration of 1.2 × 10^{-5} mol L^{-1} luminol was selected, as higher concentrations gave rise to a high background signal, which reduces

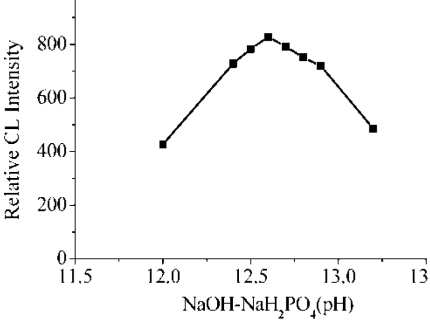

Figure 4. Effects of pH on CL intensity. Experimental conditions: Sample volume 80 μL, flow rate main pump 1.4 mL min^{-1}, auxiliary pump 2.8 mL min^{-1}; H_2O_2 0.4% (v/v); luminol 1.2 × 10^{-5} mol L^{-1}; carbendazim 3.0 × 10^{-7} g mL^{-1}.

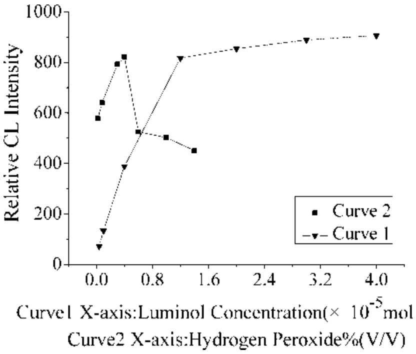

Figure 5. Experimental conditions: Sample volume 80 μL, flow rate main pump 1.4 mL min^{-1}, auxiliary pump 2.8 mL min^{-1}. Effect of luminol concentration on CL intensity: (▼) H_2O_2 0.4% (v/v); NaOH–NaH_2PO_4, pH 12.6; carbendazim 3.0×10^{-7} g mL^{-1}. Effect of hydrogen peroxide concentration on CL intensity: (■) Luminol 1.2×10^{-5} mol L^{-1} (in pH 12.6 NaOH–NaH_2PO_4); carbendazim 3.0×10^{-7} g mL^{-1}.

the application range of the method. Other reason for choosing the concentration of 1.2×10^{-5} mol L^{-1} was saving the reagent.

Effect of H_2O_2 Concentration

Concentration of hydrogen peroxide in the CL system is an important factor influencing signal intensity. The effect of the concentration of hydrogen peroxide on the relative CL intensity was examined in the range of 0.02% to 1.40% (v/v). As shown in curve 2 in Fig. 5, the maximum relative CL intensity was obtained at 0.4% (v/v) hydrogen peroxide. Therefore, 0.4% (v/v) hydrogen peroxide was chosen as the optimum concentration in the following experiments.

Interference Study

In order to assess the possible analytical application of the proposed method to water samples, the effect of the common substance in water on the determination of 5×10^{-7} g mL^{-1} carbendazim was investigated under the optimum conditions. The tolerance limit was taken as the maximum concentration of the foreign substances that caused an approximately ±10% relative error in the determination. No interference has been observed when including up to a 500-fold Na^+, Cl^-, K^+, NO_3^-, Ac^-, 200-fold NH_4^+, Ca^{2+}, Mg^{2+}, glucose, fenvalerate, 100-fold Ba^{2+}, Zn^{2+}, methamidophos, 50-fold phenol, and 5-fold Fe^{3+}, Cu^{2+}, Fe^{2+}, Cr^{3+}, or 2-fold Co^{2+}.

Because EDTA can be used to decrease the effect of metal ions on the luminol–hydrogen peroxide reaction based on its chelation with metal ions,[27] the effect of luminol solution contained NaOH–NaH_2PO_4

(pH 12.6) and 0.0 to 8.0 × 10^{-4} mol L^{-1} EDTA on CL reaction was examined. The experiment showed that no noticeable decrease in CL intensity was observed for a concentration of EDTA lower than 5.0 × 10^{-4} mol L^{-1}. But a concentration of EDTA higher than 5.0 × 10^{-4} mol L^{-1} resulted in a noticeable decrease in CL intensity. Therefore, 5.0 × 10^{-4} mol L^{-1} EDTA was added to luminol solution for further experiments in order to mask metal ions and improve the selectivity of the determination of carbendazim with the proposed method. The effect of the possible interference of metal ions in water on the determination of 5 × 10^{-7} g mL^{-1} carbendazim was investigated under the optimum conditions. The tolerance limit was taken as the maximum concentration of metal ions that caused an approximately ±10% relative error in the determination. No interference has been observed when including up to a 70-fold Cu^{2+}, 60-fold Fe^{3+}, Fe^{2+}, 45-fold Cr^{3+}, and 11-fold Co^{2+}.

Linear Response Range, Detection Limit, and RSD

Under the optimum conditions, the calibration curve (Fig. 6) shows that the CL intensity is linear with the concentration of carbendazim in the range of 2.0 × 10^{-8} to 2.0 × 10^{-6} g mL^{-1}. The linear regression equation is

$$\Delta I = 2725.4 \times C - 48.946 \quad r = 0.9952$$

where I is the CL intensity and C is the concentration of carbendazim (μg mL^{-1}). The detection limit of carbendazim (S/N = 3) is 7.24 × 10^{-9} g mL^{-1} and relative standard derivation (RSD) is 1.8% for 1.0 × 10^{-7} g mL^{-1} carbendazim (n = 8).

Analytical Application

The proposed method was applied to the determination of carbendazim residue in the tap-water samples, and the recoveries of carbendazim in

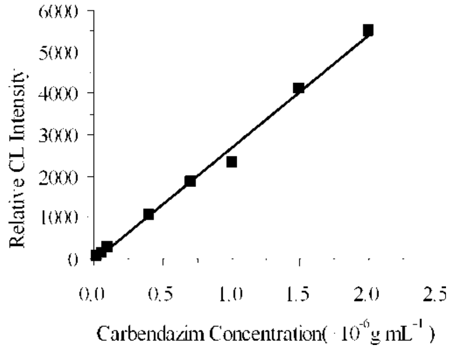

Figure 6. Calibration curve. Experiment conditions: Sample volume 80 μL, flow rate main pump 1.4 mL min^{-1}, auxiliary pump 2.8 mL min^{-1}; luminol 1.2 × 10^{-5} mol L^{-1} (in pH 12.6 NaOH–NaH_2PO_4); H_2O_2 0.4% (v/v).

Table 1. Determination of carbendazim in tap-water samples

Sample[a]	Initially present (μg mL^{-1})	Carbendazim added (μg mL^{-1})	Found (mean $\pm$ S.D., n = 4) (μg mL^{-1})	Recovery %
Tap water 1	0.000	0.100	0.104 $\pm$ 0.003	104.0
	0.000	0.500	0.444 $\pm$ 0.010	88.8
Tap water 2	0.000	0.100	0.107 $\pm$ 0.006	107.0
	0.000	0.500	0.468 $\pm$ 0.005	93.6

[a] Fuzhou, China.

tap-water samples were determined by the standard addition method. Under the optimum conditions, the results obtained are listed in Table 1. In pesticide residue analysis, the acceptable range for recovery in water is usually between 70% and 110% for routine analysis.[28] So the recovery of 88.8–107.0% obtained with the proposed method for the determination of carbendazim residue in water meets the current demands.

DISCUSSION

In order to obtain some ideas about the possible reaction mechanism, the following experiments were performed. The CL spectra are shown in Fig. 7.

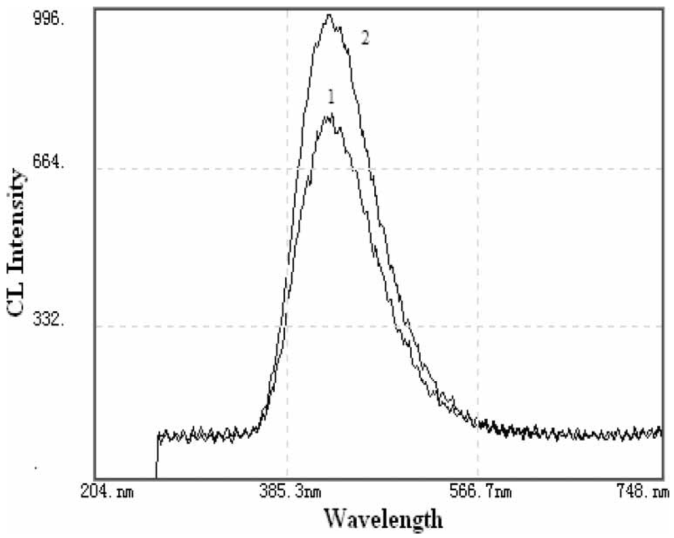

Figure 7. The CL spectra. Curve 1: Luminol 1.2×10^{-5} mol L^{-1} (in pH 12.6 NaOH–NaH$_2$PO$_4$), H$_2$O$_2$ 0.4% (v/v). Curve 2: Carbendazim 5.0×10^{-7} g mL^{-1}. Other conditions are the same as curve 1.

It was observed that CL spectrum of luminol in the presence of carbendazim was the same as that in the absence of carbendazim, and the maximum light emission was at 425 nm. The results also showed that the chemiluminescence intensity of the luminol–H_2O_2 system was enhanced in the presence of carbendazim. These suggested that the emitter could be 3-aminophthalate ($\lambda_{max} = 425$ nm),[29] the oxidization product of luminol.

Under the same excitation wavelength, the following experiments were also performed. The fluorescence spectra are shown in Fig. 8. The fluorescence emission spectra showed that the fluorescent intensity of carbendazim (neutral form $\lambda_{max} = 305$ nm, protonated form $\lambda_{max} = 393$ nm) after adding luminol and H_2O_2 was decreased. When the concentration of H_2O_2 was increased, the fluorescence peak of carbendazim was greatly decreased. The above experimental results also indicated that carbendazim was oxidized by H_2O_2.

These results also indicated that the emitter might be involved in the subsequent reactions. Intermediate radical products of oxidization of carbendazim may transfer the energy to the ground state of 3-aminophthalate ions that were the oxidization product of luminol, and then the excited 3-aminophthalate ions return to the ground state with enhanced CL phenomena. The possible enhanced CL mechanism of the reaction in the present work is as follows:

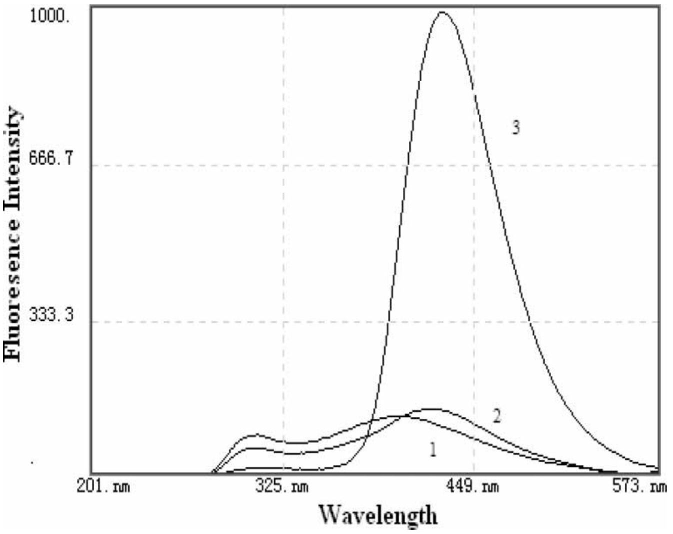

Figure 8. The fluorescence spectra ($\lambda_{ex} = 253$ nm). Curve 1: Carbendazim: 5.0×10^{-7} g mL^{-1}. Curve 2: Luminol 1.2×10^{-5} mol L^{-1} (in pH 12.6 NaOH–NaH_2PO_4), H_2O_2 0.2% (v/v); carbendazim 5.0×10^{-7} g mL^{-1}. Curve 3: Luminol 1.2×10^{-5} mol L^{-1} (in pH 12.6 NaOH–NaH_2PO_4), H_2O_2 0.4% (v/v); carbendazim 5.0×10^{-7} g mL^{-1}.

In alkaline medium,

$$HO_2^-(H_2O_2) - e \longrightarrow HO_2\bullet$$
$$HO_2\bullet \longrightarrow H_2O_2 + O_2\bullet$$
$$2O_2\bullet + \text{carbendazim}^{Red} \longrightarrow H_2O + \text{carbendazim}^{Ox^*}$$
$$\text{carbendazim}^{Ox^*} + \text{3-aminophthalate}$$
$$\longrightarrow \text{carbendazim}^{Ox} + \text{3-aminophthalate}^*$$
$$\text{3-aminophthalate}^* \longrightarrow \text{3-aminophthalate} + h\nu\ (\lambda_{max} = 425\,\text{nm})$$
$$(\text{Red} = \text{reduced form, Ox} = \text{oxidized form})$$

CONCLUSIONS

In this work, a new flow-injection CL method was described for the determination of carbendazim, based on the CL reaction of the studied carbendazim with luminol and H_2O_2 in $NaOH-NaH_2PO_4$ medium. This method has been successfully used in the determination of carbendazim in tap-water. Under the optimum conditions, the determination of sample can be performed within 4 min, including sampling and washing. Comparing to the present method for determination of carbendazim, the proposed method shows its advantages in simplicity, sensitivity, rapidity, and inexpensive instruments. The CL reaction mechanism is also proposed.

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