

A Micelle Enhanced Fluorimetric Method for the Determination of Carbaryl

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Abstract

A simple, rapid and sensitive spectrofluorimetric method was developed for the determination of carbaryl. The use of surfactant sodium dodecyl sulfate (SDS) was investigated. The method is based on the enhancement of fluorescence intensity of carbaryl by the addition of SDS. Under the optimized experimental conditions, the enhanced fluorescence intensity was linearly proportional to the concentration of carbaryl in the range of 0.01-20 $\mu\text{g/mL}$ and the detection limit was found to be 2.3×10^{-3} $\mu\text{g/mL}$. The effect of the potential interfering substances was optimized. The method was successfully applied for the determination of carbaryl in tap water samples.

Keywords: Carbaryl, Micelle enhanced, SDS, Fluorescence

Introduction

Carbamate compounds belong to a group of the most widely used pesticides that have gained great attention in recent years due to their broad biological activity, high insecticidal activity and relatively low persistence [1]. It is a colorless white crystalline solid. Carbaryl (1 naphthyl methylcarbamate) (Fig. 1) is a chemical in the carbamate family and is used chiefly as an insecticide because of its effectiveness and low mammalian toxicity. It is a broad-spectrum insecticide which controls over 100 species of insects on various crops, poultry, and livestock as well as used as a molluscicide and an acaricide [2].

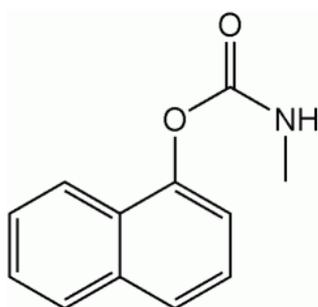


Figure 1. Structure of carbaryl.

Therefore, their residues may be found in fruits, vegetables and surface waters, which pose a potential hazard for its consumers. It can be toxic to humans with excessive exposure; though no known fatalities have been reported. It can have adverse effects in humans by inhalation, skin contact, or ingestion. Direct contact of the eye or skin with reasonable levels of this pesticide can potentially cause burns. Ingestion or inhalation of very large amounts can be toxic to the

nervous and respiratory systems, resulting in stomach cramps, nausea, and diarrhea [3]. It is found in almost all types of formulations including dusts, wet powder, granules, oil, molasses, aqueous dispersions, and suspensions [4]. Therefore, its acute toxicity is of great concern and it has become important to find a simple, sensitive and reliable technique for the determination of carbaryl in natural water, air, fruits, and crops. Since its commercial introduction in 1958, a variety of techniques have already been used for determining carbaryl in diverse matrices. These include; spectrophotometry coupled with flow injection [5-7], chromatographic techniques using different detection systems [8-12], immunoassay [13], electrochemical determination [2], biosensors [14-17] and chemiluminescence [4,18].

Fluorimetric techniques are becoming increasingly important for quantitative determination of organic compounds because of its high sensitivity and, to a lesser extent, its selectivity. Fluorimetric method for the determination of carbaryl has also been reported. Garcia *et. al.* [19] has reported a simple synchronous fluorimetric method for the determination of carbaryl in commercial formulation and human blood. Pacioni and co-worker [20] developed betacyclodextrin enhanced fluorimetric method for the quantification of carbaryl in fruits and tap water. Solid-phase laser-induced fluorescence method was published [21].

In this paper, a study of the fluorescence of carbaryl in micelle system has been carried out. Micelles are well-defined supramolecular organic structures, organized in aggregated systems. These compounds must present hydrophobic and hydrophilic regions at the same molecule; it suggests strong dipole moment and asymmetry in the structure, which allows the formation of micellar systems [22]. The ability of organized

media to provide an appropriate microenvironment by modifying the catalytic and luminescence properties of reactants and products are well known [23]. It was observed that the fluorescence signal of carbaryl can be greatly enhanced by the addition of sodium dodecyl sulfate (SDS) surfactant into the system. Based on this phenomenon, the sensitive quantitative determination of carbaryl in aqueous solution is established. This method has the advantages of high sensitivity and selectivity.

Experimental

Instruments

All the spectrofluorimetric measurements were conducted with a SPEX Fluorolog-2 spectrofluorometer. The spectrometer used a 450-W xenon lamp as the excitation light source and an R 928 photomultiplier tube powered at 950V (Hamamatsu Co.) as the detector. Excitation and emission monochromator slit, increment, and integration time were set at 1.25 mm, 1 nm and 1 second, respectively. All spectral data were obtained by SPEX DM 3000F spectroscopy computer. A pH meter (Model 520 A, Orion, USA) was employed for pH measurements.

Reagents

All reagents were of analytical grade and were used without any further purification. Carbaryl (Aldrich, USA) was used without any further purification. Carbaryl stock solution (1.0×10^{-2} M) was prepared in water followed by ultrasonication 6 hours at 20 to 40°C. Standard solutions were prepared daily by simple dilution. A solution of surfactant SDS (Aldrich, USA) (1.0×10^{-2} M) was prepared by dissolving SDS in deionized water. All the chemicals used were of analytical reagents grade and doubly deionized water

was used throughout. A series of Na_2HPO_4 - NaH_2PO_4 buffer solutions was used for the pH adjustment. A pH meter (Model 520 A, Orion, USA) was used for pH measurements.

Basic procedure

Apparent fluorescence excitation and emission spectra were measured at room temperature and optimum excitation and emission wavelengths were found from these spectra. 2.0 mL portion of 1×10^{-3} M carbaryl standard solution was transferred into a 10 ml standard flask. 2.0 mL of 0.01 M SDS and 0.5 ml Na_2HPO_4 - NaH_2PO_4 buffer (pH=5.0) were added successively. The solution was diluted to mark with DI water, mixed well and put into the quartz cell for measuring fluorescence spectra and intensities. The fluorescence intensity of the solution was measured at 349 nm with excitation at 281 nm.

Results and Discussion

Spectral characteristics

Carbaryl showed strong native fluorescence signals in aqueous solution. The fluorescent spectra showed a maximum excitation wavelength at 281 nm, while the maximum emission wavelength was detected at 349 nm. It is well-documented that the addition of a surfactant at a concentration above its critical micellar concentration (CMC) to a given fluorophore solution increases the molar absorptivity and or fluorescence quantum yield of fluorophore in many cases. This fact has been used to improve the performance of spectrofluorimetric methods for the determination of different compounds [24]. From the experimental results shown in Fig. 2, it was observed that the fluorescence spectra of carbaryl are greatly enhanced by the addition of SDS into the system.

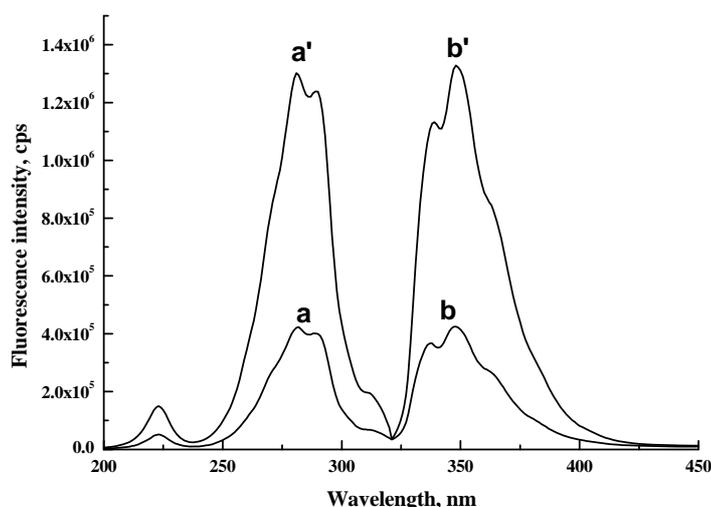


Figure 2. Fluorescence spectra (excitation and emission spectra) of carbaryl (a', b') in the presence of SDS and (a, b) in the absence of SDS. Conditions: Carbaryl 1×10^{-3} M; SDS 0.01 M.

Effect of pH

Influence of pH on the fluorescence intensity of carbaryl in micellar medium was studied. Three different buffers, namely acetate, phosphate and Britton-Robinson have been tested. Britton-Robinson consisted of a mixture of 0.04 M H₃BO₃, 0.04 M H₃PO₄ and 0.04 M CH₃COOH that has been titrated to the desired pH with 0.2 M NaOH. Among the three kind of buffer prepared, phosphate buffer solution was selected. Changes in the buffer concentration produced little variation in the observed fluorescence intensity. The effect of pH on the fluorescence intensity was studied over the range of 3.0–7.0. Without much difference, the highest intensity observed in pH 5. Hence pH 5 was chosen as optimum value for subsequent experimentation.

Effect of surfactant concentration

The employment of different surfactants in the fluorimetric system offered many advantages in comparison with those systems in the absence of surfactant, such as high sensitivity and high reaction speed [25-26]. In order to find the optimum concentration of SDS used for the FL system employed for the determination of carbaryl, the effect of SDS concentration on the FL signal was investigated. From the experimental results shown in Fig. 3, the maximum intensity reached at 0.01 M SDS. When the SDS concentration was above this level, the light intensity started to decrease. Hence, 0.01 M SDS was used for the determination of carbaryl.

Analytical Characteristics

Standard solutions of carbaryl were added into a series of colorimetric tubes. Under optimized experimental conditions, the fluorescence intensity was measured. The results showed that the fluorescence intensity was linear over a carbaryl concentration range of 0.01-20

µg/mL. The detection limit (3σ) was found to be 2.3×10⁻³ µg/mL. The values are compatible with the values reported by J.A.M. Pulgarín *et al.* [19], L. Alvarez-Rodríguez *et al.* and [6] B. Fernández-Band *et al.* [7]. The correlation coefficient found was 0.9996. The relative standard deviation calculated from a series of 11 standards each contains 10 µg/mL of carbaryl was found to be 1.64 %.

Interference studies

In a real sample, the analyte determination will be in the presence of interferents. They may suppress or enhance the fluorescence signal, although they have no significant effect on the intensity. In order to investigate the selectivity of the proposed method, a systematic study of the effects of various interferents on the fluorescence of the system was carried out under the optimum conditions. When the effect of the each foreign species on the peak height was less than 5.0 %, thus there was no interference on the determination of carbaryl. The obtained results are shown in Table 1 and under the optimized conditions, some ions only interfered with the signal at higher concentration ratio to carbaryl. So, this method can be suggested for the determination of carbaryl in natural water sample.

Table 1. Tolerance to interferences in the determination of 10.0 µg/mL carbaryl

Species added	Concentration ratio to carbaryl
Ca ²⁺ , Mg ²⁺ , K ²⁺ , Cu ²⁺ , Fe ³⁺	500
Fe ²⁺ , NH ⁴⁺ , Cl ⁻ , NO ³⁻	200
SO ₄ ²⁻ , PO ₄ ³⁻	50

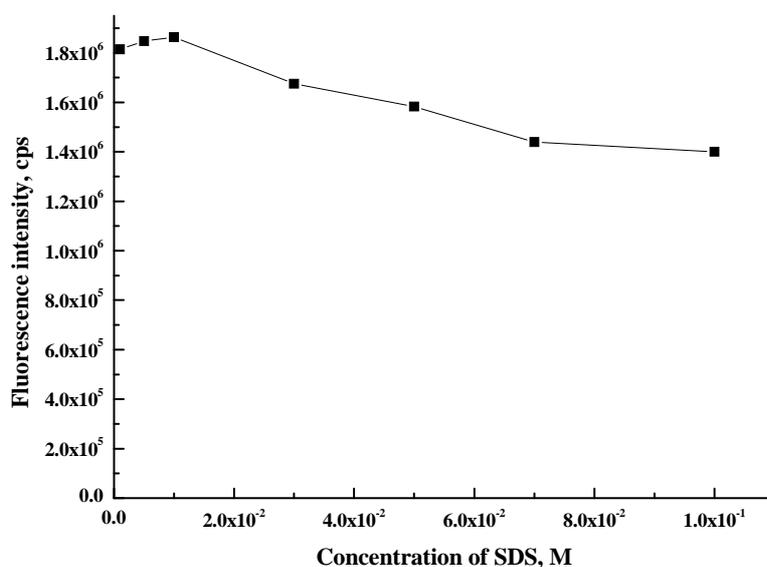


Figure 3. Effect of SDS concentration on fluorescence signal of carbaryl. Conditions: Carbaryl 1×10⁻³ M

Applications

Finally, the applicability of the proposed method was verified by determining carbaryl in spiked tap water samples. Tap water samples were collected into acid-washed (10%v/v HCl) high-density polyethylene (HDPE) bottles. Right after collection, the samples were filtered through a cellulose membrane filter and kept refrigerated in the dark at 4°C. All samples were free of carbaryl. A recovery study was, therefore, carried out with standard solutions of carbaryl. Table 2 summarizes the results obtained for the analyses of three replicates of the five water samples. The recoveries were quite consistent with the amounts added. S.-H. Zhu *et al.* [27] has reported the recoveries of carbaryl in tap water which is similar with results obtained in this work.

Table 2. Determination of carbaryl in tap water sample

Tap water sample	Carbaryl		
	Added ($\mu\text{g mL}^{-1}$)	Found ($\mu\text{g mL}^{-1}$) ^a	Recovery (%)
Sample 1	1.0	0.93 ± 3.1	93.0
Sample 2	2.0	1.97 ± 2.7	98.5
Sample 3	4.0	4.01 ± 1.9	100.2
Sample 4	6.0	5.94 ± 2.1	99.0
Sample 5	10.0	9.97 ± 2.2	99.7

^aAverage of three measurements.

Conclusion

The spectrofluorimetric method proposed for the determination of carbaryl in tap water samples has the advantages of simplicity, speed and the use of inexpensive instruments and reagents with wide linear dynamic range between 0.01-20 $\mu\text{g/mL}$ and the detection limit of 2.3×10^{-3} $\mu\text{g/mL}$. The fluorescent detection gives a special selectivity without interference from the common foreign species. The use of SDS micellar system provides a simple means to enhance the fluorescence of carbaryl. This phenomenon can be explained by protection of lowest excited state of fluorophore in micellar microenvironment from non-radiative or possible quenching processes that normally readily occur in bulk aqueous solutions. The method is thus suitable for routine analysis.

Acknowledgments:

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (KRF-C00565).

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