Article

An Alternative Spectrophotometric Determination of Carbaryl Insecticide Residues in Water Samples Using the Cerium-Catalyzed Belousov-Zhabotinsky Oscillating Reaction

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An alternative approach for carbaryl determination based on the change in the oscillation period of the Belousov-Zhabotinsky (BZ) reaction under the addition of carbaryl is demonstrated. The oscillations were observed by spectrophotometric measurement at 320 nm, corresponding to the maximum absorption wavelength of cerium(IV) catalyst. The oscillation periods increase with the carbaryl concentrations, which can be discussed based on the Field-Körös-Noyes (FKN) mechanism. The increase of oscillation periods is proportional to the concentration of carbaryl in the range of 0.1-200 mg L^{-1} with the regression coefficient of 0.9938. The limits of detection and quantification were 0.044 and 0.147 mg L^{-1}, respectively. The precisions in terms of intra-day and inter-day measurements were efficient with relative standard deviation (RSD) lower than 2.1%. Accuracy of carbaryl in different water samples was obtained with high recoveries in the range of 94-106% and also comparable to the results of high performance liquid chromatography (HPLC) analysis. The proposed method is precise, cost-effective and can be alternatively employed for the screening and determination of carbaryl residues in water samples.

Keywords: carbaryl, water samples, oscillations, Belousov-Zhabotinsky reaction, UV-Visible spectrophotometry

Introduction

Carbaryl (1-naphthyl methylcarbamate) is an active insecticide in the carbamate family used chiefly in agricultural fields.[1] It is a toxic substance for human beings by skin contact, inhalation or ingestion. There are many analytical methods for determining carbaryl, such as gas chromatography (GC) and high performance liquid chromatography (HPLC).[2-4] Despite those techniques are powerful, GC is suitable for analyzing volatile compounds without decomposition, whereas HPLC normally requires long analysis time and consumes large volume of mobile phases. Also, the experimental operation of such instruments is quite complicated and maintenance costs are relatively high. Therefore, simple, cost-effective and sensitive methods for the determination of carbaryl are of great importance and would be a challenge in this research field. When compared with the aforementioned complicated

techniques, spectrophotometry is considered as an alternative cost-effective method and has been developed for quantifying carbaryl in various types of samples.[1,5-11] However, most previous methods required the derivatization process of carbaryl and suitable coupling reagents (such as 2,4-dimethoxyaniline, 2,4,6-trimethylaniline, 2,6-dibromo-4-methylaniline, and 2-naphthylamine-1-sulfonic acid) to form color species prior to spectrophotometric detection.[6] In addition, some coupling reagents required preparation before use and carbaryl was also hydrolyzed in strong alkali condition to naphthol form (hydrolysis product) before derivatization. Therefore, a simple direct detection of carbaryl by using the spectrophotometric method based on the oscillating reaction is interesting to demonstrate in this work.

Over a decade, the application of the chemical oscillations for determining trace amounts of substances has opened a new outlook in analytical chemistry. The dynamics change of oscillations under an addition of target analytes has been employed as a tool for quantitative

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analysis.[12-14] This method has been successfully employed for the determination of various compounds such as ascorbic acid,[15] glutamic acid,[16] hydroquinone,[17] indium ion,[18] and 1-naphthylamine.[19] One of the most famous chemical oscillations is the Belousov-Zhabotinsky (BZ reaction), which involves the oxidation of malonic acid by acidified bromate under the presence of a catalyst, such as cerium.[20-23] Generally, the oscillation dynamics can be followed by using electrochemical setup with ion selective electrode. One important dynamical parameter of the BZ oscillation is the oscillation period. It is noted that the oscillation period of the BZ reaction remains the same for a particular reactant concentration, but it can be altered if the system is perturbed with other chemicals. Hence, if a small amount of analyte is introduced into the BZ system, the reaction is perturbed and the change of the oscillation period can be detected.[12-14]

Recently, an indirect detection method of carbaryl based on hydrolysis in alkaline medium to form 1-naphthol was successfully determined by the copper(II)-catalyzed oscillating reaction implemented in a continuous-flow stirred tank reactor (CSTR).[24] The electrochemical setup is quite complicated with the reagent inflow and product outflow system. Thus, the flow system needs to be carefully maintained constant throughout the experiments to ensure the stable oscillation dynamics. In our work, the oscillations were carried out with a simple manner without flow system to avoid the complication of experimental setup. The oscillation dynamics was observed by using an alternative way with UV-Visible spectrophotometric measurement.

To the best of our knowledge, a spectrophotometric method for the direct detection of carbaryl insecticide in water samples based on an exploitation of the oscillating signals as the analytical tool has not been reported. Herein, we demonstrate a relatively simpler and efficient approach for the quantification of carbaryl in water samples through the cerium catalyzed-BZ oscillating system. The experiments were simply set up and the oscillation dynamics were performed in a simple manner with UV-Vis spectrophotometric measurement. Under the perturbation effect of cabaryl, the oscillating characteristic of the BZ reaction was evaluated and the oscillation period was used as a key parameter to assess the carbaryl content in real water samples.

Experimental

Reagents

In this work, malonic acid ($CH_2(COOH)_2$, Sigma-Aldrich, Germany), sodium bromate (NaBrO$_3$, Sigma-

Aldrich, Germany), sulfuric acid (H_2SO_4, QRêC, India) and cerium(IV) sulfate tetrahydrate ($Ce(SO_4)_2.4H_2O$, Riedel-deHaën, Germany) were used to carry out the cerium catalyzed-BZ reaction. The stock solutions included 0.12 mol L^{-1} NaBrO$_3$ dissolved in deionized water, 0.4 mol L^{-1} $CH_2(COOH)_2$ dissolved in 2 mol L^{-1} H_2SO_4, 1.6×10^{-3} mol L^{-1} Ce^{IV} prepared by dissolving $Ce(SO_4)_2.4H_2O$ in 2 mol L^{-1} H_2SO_4. 2 mol L^{-1} H_2SO_4 solution was prepared by a dilution of conc. H_2SO_4 (96%, m/m). The cerium catalyst solution was kept in a polyethylene bottle and was covered with aluminium foil. Deionized water with resistivity of 18 MΩ cm from RCI Labscan (Thailand) was used throughout. Carbaryl was purchased from Sigma-Aldrich, Germany. The stock solution of carbaryl (250 mg L^{-1}) was prepared in acetronitrile. The working standard solutions were then prepared by diluting the stock solution to various concentrations of 0.1 to 200 mg L^{-1}. Formic acid and acetronitrile (Merck, Germany) were used as mobile phases in HPLC analysis.

Apparatus

The BZ reaction was studied in a closed batch reactor equipped with a quartz cuvette cell (path length 1 cm). A magnetic bar (1×2 mm) was put inside the cell. Then, it was placed on the temperature and stirring control units. The temperature and stirring rate were set by Agilent UV-Vis ChemStations software. The BZ solution was continuously stirred at a constant rate of 600 rpm. The temperature in the cell was kept constant at 25.0 ± 0.5 °C by using the Peltier temperature control unit. The experiments were conducted using Agilent 8453 (USA, wavelength range of 190-1100 nm) diode array spectrophotometer for the kinetic measurement of the BZ reaction. In this work, the HPLC coupled with a photo-diode array detector (Shimadzu, Japan) and an Inertsil C8 column (4.6×150 mm, 5.0 μm) connected to a guard C8 column (4.0×10 mm, 5.0 μm) (GL Science, Japan) were also used to determine carbaryl in water samples.

Generation of the BZ oscillating reaction

In order to generate the BZ oscillations, 0.75 mL of water, 0.75 mL of 0.12 mol L^{-1} sodium bromate, and 0.75 mL of 0.40 mol L^{-1} malonic acid were first mixed thoroughly in a cuvette cell. Then, the solution was bubbled with nitrogen gas for 15 min. Subsequently, 0.75 mL of 1.6×10^{-3} mol L^{-1} cerium(IV) sulfate tetrahydrate was rapidly added into the mixed solution. All experiments were carried out under constant temperature and stirring rate. The oscillations were followed by UV spectrophotometric measurement at 320 nm.

Calibration and analytical performance for determination of carbaryl

To study the effect of carbaryl concentration on the BZ oscillating reaction, 50 µL of each working solution of carbaryl (0.1-200 mg L^{-1}) were injected into the BZ system. Then, the change of the oscillation period under addition of carbaryl was investigated. In this work, the timing for an addition of cabaryl into the BZ system was fixed at the fifth oscillation cycle. The calibration curve was constructed by plotting the oscillation period against carbaryl concentrations. The limits of detection (LOD) and quantification (LOQ) were also determined by carrying out five experiments at an aforementioned BZ condition with an addition of 0.10 mg L^{-1} carbaryl.

Precision of the proposed method

In addition, the precision of the proposed method was evaluated. The experiments were carried out at five levels of carbaryl concentrations (1, 5, 10, 25 and 50 mg L^{-1}). The intra-day experiments were performed in triplicate (n = 3) in a day, while the inter-day experiments were conducted over three consecutive days (n = 3 × 3). The standard deviation (SD) and relative standard deviation (RSD, in percentage) of the oscillation period under addition of different concentrations of carbaryl were calculated and evaluated.

Analysis of carbaryl in water samples

Based on the calibration curve, the amount of carbaryl in real water samples was investigated by the proposed method. Three water samples were collected from the different sources including tap, swamp, and river. All water samples were filtered through Whatman filter papers (No. 1) and 0.45 µm nylon membranes prior to use. To prepare the fortified samples, water samples were spiked with cabaryl at three concentrations (0.5, 1.0 and 2.0 mg L^{-1}). After that, the content of cabaryl in these spiked samples was investigated by the presented method and also compared with the HPLC technique. In HPLC analysis, regarding their complexity and different matrices, only tap and river water samples were selected as the representative samples for evaluating accuracy in term of recover, as presented in previous work.[25] The water samples were spiked with 0.5 and 1.0 mg L^{-1} carbaryl before analysis. The HPLC analysis was achieved using reversed-phase system with 80:20 acetonitrile/0.1% (v/v) formic acid as isocratic elution mobile phase (flow rate of 1.0 mL min^{-1}) and sample injection volume of 20 µL. The chromatograms were recorded at 280 nm corresponding to the maximum absorption wavelength of carbaryl.

Results and Discussion

Dynamics of chemical oscillations

In this work, the optimized BZ condition was employed based on previous report.[26] The BZ solution was consisted of 0.1 mol L^{-1} malonic acid, 0.03 mol L^{-1} sodium bromate, 4.0 × 10^{-4} mol L^{-1} cerium(IV) sulfate tetrahydrate, and 1.0 mol L^{-1} sulfuric acid. The concentrations were fixed and used throughout the experiments since the oscillation dynamics of this oscillatory system was dependent on the reactant concentrations. The oscillation of the BZ reaction was reported in terms of the absorbance of cerium(IV) at 320 nm as a function of reaction time. A typical temporal trace of the BZ oscillations was shown in Figure 1. An oscillatory characteristic of the studied BZ system without the perturbation of carbaryl was presented in Figure 1a. When all the reactants of the BZ reaction were mixed and reacted, the absorbance was sharply decreased to a minimum value at point A. Then, the absorbance abruptly increased and decreased to point B. An interval from point A to point B represented the induction period, which was the characteristic found in the bromated-malonic acid-sulfuric acid-cerium catalyzed BZ oscillating reaction. In this period, the system required the accumulation of the brominated organic products, e.g., bromomalonic acid, to reach its crucial concentration for the onset of oscillations.[27,28] Thus, the oscillations were started after the induction period.

Another main characteristic parameter was the oscillation period (T$_u$), defined as the time interval between the two maximum consecutive oscillating peaks as labeled in Figure 1. It was noted that the interval between data points was 1 s, as shown in the inset of Figure 1a.

The average value of T$_u$ for the reaction condition without an addition of carbaryl was 85.7 ± 2.1 s. The deviation of two seconds is acceptable in the studied batch system.[26] Figure 1b presented an oscillation profile under the same BZ condition with an addition of 200 mg L^{-1} carbaryl. The perturbation point, where carbaryl was introduced into the system, was indicated by an arrow. It was found that the oscillation period before perturbation (T$_u$) was 86.0 ± 2.0 s, which was consistent with that of the unperturbed system displayed in Figure 1a.

However, the rise of the oscillating base line and the extension of the oscillation period after the perturbation (T$_p$) were observed. The average value of T$_p$ for this perturbed condition was 123.3 ± 2.9 s. In this work, the oscillation
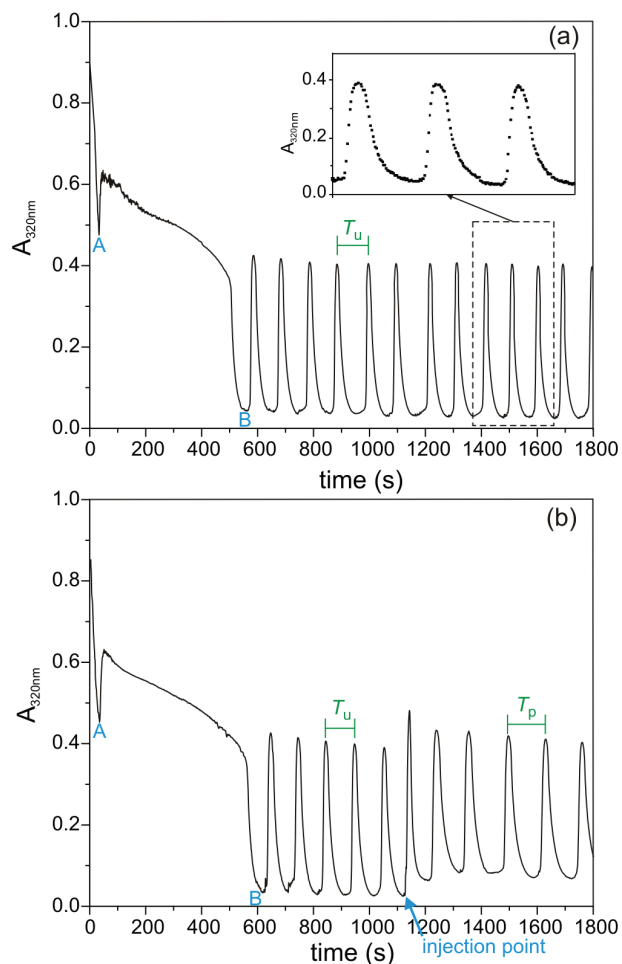
Figure 1. Temporal trace of oscillations in the BZ system at the condition (a) without and (b) with an addition of 200 mg L^{-1} carbaryl. The arrows indicate the instant of carbaryl addition. T_u and T_p are the oscillation period before and after the perturbation, respectively.

after perturbation (T_p) was employed as a key analytical parameter for the investigation of carbaryl.

Oscillations under addition of different concentrations of carbaryl and the calibration curve

Figures 2a-2e presented the oscillation profiles of the BZ reaction under an addition of different concentrations of carbaryl. Although the increase of oscillation periods with carbaryl concentrations was not obviously evidenced (Figures 2a-2e), the average value of T_p linearly increased with the increase of carbaryl concentrations as shown in Figure 2f. Figure 2f presented the calibration curve by plotting the T_p values against the concentrations of carbaryl in the range of 0.1-200 mg L^{-1}. It was noticed that the oscillation period was linearly proportional to the concentration of carbaryl as follows; $y = 0.2101x + 82.08$, where y was the T_p value in the unit of second and x was the concentration of carbaryl in the unit of mg L^{-1}, with

the correlation coefficient (R^2) of 0.9938. Hence, this established linear relationship was employed for further quantification of carbaryl in real water samples.

Mechanism under addition of carbaryl

Generally, an oscillation cycle of the BrO$_3^-$-malonic acid-cerium-catalyzed BZ reaction could be described by the three processes of the Field-Körös-Noyes (FKN) mechanism as depicted by a schematic representation in Figure 3.[20-23] Process A involved the decrease of the concentration of Br$^-$ and bromination of malonic acid to produce bromomalonic acid. Process B was the autocatalytic reaction of HBrO$_2$ and the catalyst was oxidized. Process C was the regeneration of Br$^-$ via the reduction of catalyst by malonic acid and bromomalonic acid. Although Br$^-$ and Ce^{III} were not initially added in the BZ reaction, the trace amount of Br$^-$ was obtained from bromate reactant as it was used without purification. Thus, process A of the BZ reaction could be initiated. However, it might take time in this process to reach crucial concentration of bromomalonic acid, which was an important reducing agent for changing Ce^{IV} catalyst to Ce^{III} as presented in the induction time of Figure 1 (point A to B). Then, the cycle of the BZ oscillations could start.[28]

For the BZ solution without carbaryl, the average oscillation period evaluated from the result in Figure 1a was 85.7 ± 2.1 s. When the BZ oscillating system was perturbed with carbaryl, the average oscillation period was increased. It was reported that carbaryl in the BZ system could be oxidized by bromine.[10] Furthermore, its oxidized product such as 1,4-naphthoquinone could also react with bromine.[29] Not only bromine, but also carbaryl could be oxidized by cerium(IV).[30] However, the experimental results showed that the amplitude of absorbance was unchanged under the increase of carbaryl concentrations as presented in Figures 2a-2e. These results suggested that Ce^{IV} catalyst was not strongly interfered by addition of carbaryl.

The BZ reaction was very sensitive to the change of bromide concentration as it was the bromide control system.[26-28] Bromine was another important compound, produced from the reaction between bromate and bromide in the process A. It was slowly reacted with malonic acid in enol form to generate bromomalonic acid, one of the most important products in the BZ reaction.[27] With the addition of carbaryl in the BZ system, carbaryl and its oxidized products were competitively reacted with bromine against malonic acid in process A. This might result in the extended time to complete the bromination of malonic acid for producing bromomalonic acid to reach its crucial
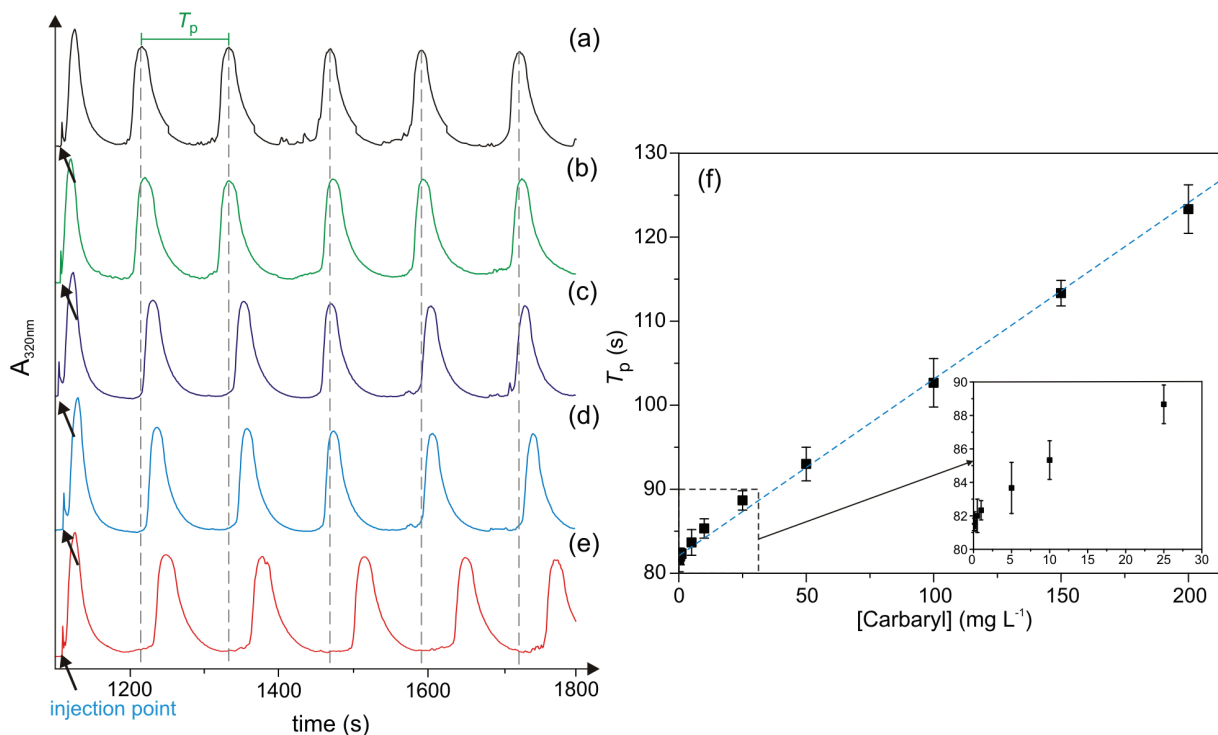
Figure 2. A representative temporal trace of oscillations for (a) 10, (b) 50, (c) 100, (d) 150, and (e) 200 mg L⁻¹ of carbaryl concentrations. An arrow indicates the instant of carbaryl addition. (f) Calibration curve plotted between the oscillation periods and the concentrations of carbaryl.
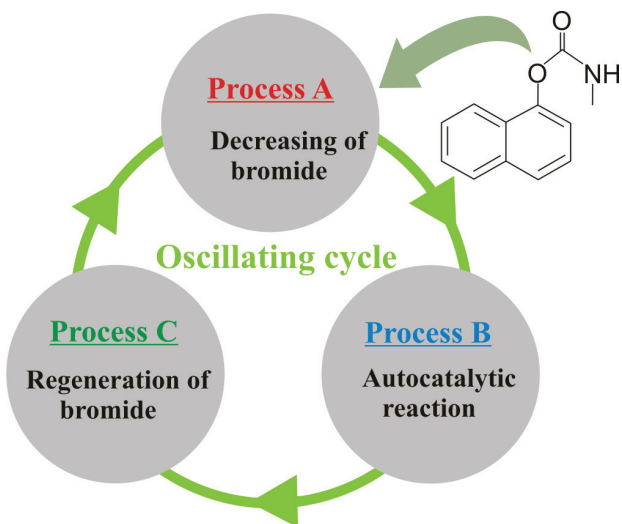

Figure 3. A schematic representation of the possible mechanism of the cerium-catalyzed BZ oscillating reaction under addition of carbaryl.

concentration, thereby increasing time to complete a cycle of oscillation. Therefore, the increase of the oscillation period was observed.

Analytical performance and precision of the proposed method

Analytical performance of the proposed method for carbaryl determination was presented as the limits of detection (LOD) and quantification (LOQ). These parameters were estimated by carrying out five experiments of the BZ condition without an addition of carbaryl. The value of LOD was estimated at 95% confidence level using 5 replicates (n = 5, ν = 4, t = 2.776),[31] n is the number of replications, ν is degrees of freedom (n − 1), and t is the critical *t*-values at 95% confidence level. LOQ was estimated using 3.3LOD. We found that the obtained values of LOD and LOQ were 0.044 ± 0.018 and 0.147 ± 0.059 mg L⁻¹, respectively.

The precisions of the proposed method were evaluated in terms of the intra-day and inter-day experiments. The relative standard deviation (RSD, in percentage) of T_p was then calculated. The precision results were summarized in Table 1. The RSD of intra-day repeatability was less than 1.6%, while the RSD of inter-day precisions was less than 2.1%. These results showed that the present approach based on the cerium-catalyzed BZ oscillating reaction had a good precision for the determination of carbaryl. All analytical parameters of the proposed method for determination of carbaryl were summarized in Table 2.

Effect of foreign species on the determination of carbaryl

To evaluate the analytical applicability of the proposed method, the influences of various common inorganic species as well as other pesticides (e.g., carbamates and

Table 1. Precision of the proposed method for the determination of carbaryl

Carbaryl$_{std}$ / (mg L^{-1})	Intra-day (n = 3)			Inter-day (n = 3 × 3)		
	T$_p$^{a} / s	SD	RSD / %	T$_p$^{a} / s	SD	RSD / %
1	82.8	0.8	0.9	82.8	1.8	2.1
5	84.1	1.2	1.5	83.2	1.3	1.6
10	85.7	0.5	0.5	84.9	1.2	1.4
25	88.4	0.7	0.8	88.0	1.5	1.7
50	94.2	1.5	1.6	93.3	1.8	1.9

^{a}Average oscillation period; SD: standard deviation; RSD: relative standard deviation.

Table 2. Analytical parameters of the proposed method for carbaryl determination

Parameter	Result
Linear range / (mg L^{-1})	0.1-200
Regression equation (y = mx + c)	$y = 0.2101x + 82.08$
Correlation coefficient	0.9938
Relative standard deviation / %	
Intra-day (n = 3)	0.5-1.6
Inter-day (n = 3 × 3)	1.4-2.1
LOD / (mg L^{-1})	0.044 ± 0.018
LOQ / (mg L^{-1})	0.147 ± 0.059

LOD: limit of detection; LOQ: limit of quantification.

Table 3. Effect of foreign species on the determination of carbaryl

Foreign species	Tolerance ratio^a / (mg L^{-1})
Inorganic ions	
Cl$^-$	50
S$_2$O$_3$$^{2-}$	500
Ca^{2+}, Mg^{2+}, Cu^{2+}, Ni^{2+}	1000
Carbamates	
Aldicarb	200
Methomyl	250
Organophosphates	
Fenitrothion	50
Malathion, Chloropyrifos	100

^{a}Tolerance ratio causing ± 5% variation in T$_p$.

organophosphates) that could be found in different water sources were investigated. They might interfere with the oscillations of the BZ reaction and changed the oscillating characteristics. Thus, the effect of some pesticides and ions on the detection of carbaryl was studied. With the presence of other foreign species, the determination of carbaryl at 0.1 mg L^{-1} was investigated and the studied range of interferences was 1.0-100.0 mg L^{-1}. The tolerance limit was referred to the tolerance ratio, and it could be calculated from the concentration ratio of [interferences]/[carbaryl]. In this work, the tolerance limit was obtained from the concentration of interferences that causes ± 5% variation in oscillation period. Table 3 presented the effect of other chemical species and the tolerance limit of each interferences. The results revealed that chloride ion and fenitrothion could strongly interfere with the detection of carbaryl. It was well known that chloride ion strongly changes the BZ oscillating dynamics, especially its high concentration could inhibit the BZ oscillation via competitive reaction with crucial bromide species in the BZ system.[32] Fenitrothion was another compound that strongly interferes in the detection of carbaryl. When considering the structure of all studied carbamate and organophosphate interferences, fenitrothion was the only compound containing aromatic ring in its structure (similar to carbaryl). Bromination on aromatic rings of such compound might be favorable and had a strong effect

on the oscillation period, whenever it was added in the BZ solution.

Application of the proposed method for determination of carbaryl in water samples

The applicability of this method was investigated for the determination of carbaryl in three different water samples matrices collected from the various sampling sources including tap, swamp, and river. In the investigation of the proposed method, the contaminations by carbaryl in all studied water samples were not detected. To determine the accuracy of the method, the recovery was performed by spiking known amounts of carbaryl (e.g., 0.5, 1.0, and 2.0 mg L^{-1}) into the real samples. The results were summarized in Table 4. The mean recoveries were in the range of 94-106% (n = 3), which were in the acceptable range. The RSD was less than 6.7% for tap water, 4.1% for swamp water, and 3.1% for river water. As presented in Table 4, the recovery assay was clearly tendentious with the results generally less than 100%. The matrix effect of different water samples was studied. The oscillation periods under addition of various concentration of carbaryl (0.5-3.0 mg L^{-1}) in different water

Table 4. Recoveries of carbaryl in spiked water samples obtained from the proposed method (n = 3)

Sample	Added / (mg L^{-1})	Amount found / (mg L^{-1})	Recovery / %	RSD / %
	0.5	0.53 ± 0.03	106	5.7
Tap	1.0	1.05 ± 0.07	105	6.7
	2.0	2.08 ± 0.05	104	2.4
	0.5	0.49 ± 0.02	98	4.1
Swamp	1.0	0.97 ± 0.03	97	3.1
	2.0	1.92 ± 0.06	96	3.1
	0.5	0.47 ± 0.01	94	2.1
River	1.0	0.96 ± 0.03	96	3.1
	2.0	1.95 ± 0.03	98	1.5

RSD: relative standard deviation.

samples was investigated. The linear relation between T_p and the concentration of carbaryl in different water samples were summarized (see Supplementary Information section). We found that the slope of the linear relation was nearly the same. This results suggested that low matrix effect of real water samples was obtained. The recovery in case of tap water was slightly greater than 100%. This might effect from a small amount of chloride ion in tap water that could increase the oscillation period, resulting in the increase of the calculated amount of carbaryl in the studied samples.

The determination of carbaryl residues was also investigated by the HPLC technique. It was found that carbaryl was not detected in all studied water samples. The calibration curve of carbaryl for HPLC analysis was $y = 42.27x - 951.9$ with R^2 of 0.9994. The linear range was obtained between 0.01 and 5.00 mg L^{-1}. The calculated values of LOD (signal-to-noise ratio of 3) and LOQ (signal-to-noise ratio of 10) evaluated by HPLC analysis were 0.01 and 0.05 mg L^{-1}, respectively. To evaluate recovery, tap and river water samples were selected as the representative samples. The water samples were spiked with 0.5 and 1.0 mg L^{-1} carbaryl. In water samples, mean recoveries were found to be 103-113% with RSD below 3.0%.

The proposed method was compared with the other spectrophotometric methods for the determination of carbaryl in water samples (Table 5). The proposed method provided wide linear range and high precision. However, all of the report works used preconcentration step in addition to the spectrometric method, therefore their sensitivities were increased (low LOD). Although the sensitivity of the proposed method was lower than the report works, it could be used for the determination of carbaryl in water samples as the obtained LOD was lower than some regulations such as 0.050 mg L^{-1} from Japan regulation and 0.090 mg L^{-1} from the maximum acceptable concentration (MAC) of Canadian water quality guideline.[33] Therefore, the proposed cerium-catalyzed BZ oscillating reaction coupled with spectrophotometric method has a potential to be employed as a screening strategy for the determination of carbaryl in water samples.

Conclusions

In summary, UV-Visible spectrophotometry based on the cerium-catalyzed BZ oscillating reaction could be successfully employed as an alternative approach for the

Table 5. Comparison of spectrophotometric methods for determination of carbaryl in water samples

The basis of detection	Preconcentration technique	Detection wavelength / reagents	Linear range / (mg L^{-1})	LOD / (mg L^{-1})	RSD	Reference
Acid-induced cloud-point extraction coupled to derivatizing reagents	CPE	480 nm / 2-naphtylamine-1-sulfonic acid	0.1-7.0	0.050	2.3	6
Solid phase extraction with flow analysis	SPE	280 nm / polyether type polyurethane foam	0.1-1.0	0.012	3.4	7
Ultrasound-assisted dispersive solid phase microextraction with molecular imprinted polymer	UA-DSPME	280 nm / meta acrylic acid (MMA)	0.1-1.2	0.033	4.3	11
Cerium-catalyzed BZ oscillating reaction	none	320 nm / bromate-malonic acid- cerium	0.1-200	0.044	2.1	this work

BZ: Belousov-Zhabotinsky; CPE: cloud-point extraction; SPE: solid phase extraction; UA-DSPME: ultrasound-assisted dispersive solid phase microextraction; LOD: limit of detection; RSD: relative standard deviation.

screening and determination of carbaryl residues in water samples. Without requirement of derivatizing reagents to form color species as a conventional spectrophotometric method, the proposed detection method is more successful and simpler based on the oscillating characteristics of the BZ system by carbaryl. The relationship between the oscillation period and carbaryl concentration was used as an efficient analytical tool. Moreover, the proposed method provides good precision with RSD less than 2.1%. When compared to the HPLC technique, the detection limit of the developed method is relatively higher and the selectivity needs to be taken into consideration. However, the proposed method is inexpensive and could be exploited as an alternative screening technique for the quantitative analysis of carbaryl in water samples.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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