

Simultaneous Determination of Carbaryl and 1-Naphthol by First-Derivative Synchronous Non-Protected Room Temperature Phosphorescence

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The applicability of non-protected room temperature phosphorescence (NP-RTP) in real samples was demonstrated in the present work. In this methodology, only two reagents, potassium iodide and sodium sulfite, were used to obtain phosphorescent signals. Overlapping of the phosphorescence spectra was resolved by using first-derivative synchronous phosphorimetry. The synchronous first-derivative spectra of carbaryl and 1-naphthol in the mixture were completely separated by changing the synchronous wavelength interval; with 240 nm the first-derivative spectra of carbaryl were recorded, while with 200 nm those of 1-naphthol appeared. The intensities in the spectra were proportional to the concentration of carbaryl and 1-naphthol. The calibration graphs were linear up to at least 1.1×10^{-5} mol L⁻¹ for carbaryl and 1.3×10^{-5} mol L⁻¹ for 1-naphthol, and the correlation coefficients were 0.9971 and 0.9932, respectively. Carbaryl and 1-naphthol were successfully determined by the proposed method in a hydrolyzed sample of a commercial formulation.

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Introduction

Carbaryl (1-naphthyl methylcarbamate) is a chemical in the carbamate family used chiefly as an insecticide because of its effectiveness and low mammalian toxicity. It controls over 100 species of insects on citrus, fruit, cotton, forests, lawns, nuts, ornamentals, shade trees, and other crops, as well as on poultry, livestock, and pets. It is also used as a molluscicide and an acaricide. It is a colorless white crystalline solid. It is one of the most-utilized insecticides for home gardens, commercial agriculture, forestry and rangeland protection. Its safety is somewhat controversial. It is a cholinesterase inhibitor, and can be toxic to humans with excessive exposure, though no known fatalities have been reported. It can produce adverse effects in humans by skin contact, inhalation, or ingestion. The symptoms of acute toxicity are typical of other carbamates. Direct contact of the skin or eyes with moderate levels of this pesticide can cause burns. Inhalation or ingestion of very large amounts can be toxic to the nervous and respiratory systems, resulting in nausea, stomach cramps, diarrhoea, and excessive salivation. Other symptoms at high doses include sweating, blurring of vision, incoordination, and convulsions. When ingested by people, it is rapidly metabolized and excreted in the urine.

Different analytical methods have been developed for the quantitative determination of carbaryl. Most of them make use of chromatographic techniques;¹⁻⁶ others, in a lesser quantity, use spectrophotometry,⁷⁻¹⁰ and fluorometry¹¹ and some biosensors have also been developed.¹²⁻¹⁵ Simultaneous determinations of carbaryl and its hydrolysis product, 1-naphthol, have been reported by employing different methodologies.¹⁶⁻²² Phosphorescence

analysis for the determination of carbaryl has been proposed,²³⁻²⁶ but no phosphorimetric method was found for the analysis of mixtures of carbaryl and 1-naphthol.

The phosphorescence of different organic compounds has normally been observed at cryogenic temperatures (77 K), at room temperature using adequate solid supports (solid-phase phosphorescence, SPP),²⁷⁻³² and in some instances analytes could be made to phosphoresce in solution at room-temperature when the non-radiative pathways were minimized (room-temperature phosphorescence in the liquid state, RTPL).^{31,33,34} The addition of a heavy atom perturber is necessary to achieve room temperature phosphorescence. The heavy atom produces an effective S₁-T intersystem crossing with a subsequent enhancement of the phosphorescence emission.

In the present work we showed that first-derivative synchronous phosphorimetry coupled to room-temperature phosphorescence (NP-RTP) allows the determination of carbaryl and 1-naphthol without any previous separation. The method is based on non-protected NP-RTP in aqueous solution in the presence of potassium iodide as a heavy atom salt and sodium sulfite as an oxygen scavenger. As in traditional phosphorimetry, the problem associated with oxygen quenching also remains. Deoxygenating by sulfite has become a successful method.³⁵ Synchronous methodology has been proposed as a means for increasing the selectivity of phosphorimetry, due to its associated band-narrowing effect.³⁶ A synchronous phosphorescence scan gives a narrow and simpler spectrum compared to the conventional excitation/emission spectrum. Therefore it is more effective for separating two overlapping spectra. The parameters needed to optimize are the wavelength interval ($\Delta\lambda$) and the synchronous phosphorescence maximum ($\lambda_{s,max}$).

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Experimental

Apparatus

All recordings of uncorrected phosphorescence spectra and phosphorimetric measurements were carried out on a Perkin-Elmer LS-50B luminescence spectrometer (Beaconsfield, England) equipped with a pulsed xenon lamp (half peak height $<10 \mu\text{s}$, 60 Hz), an R928 photomultiplier tube and a computer working with FL Winlab software. All of the measurements took place in a standard 10 mm path-length quartz cell with a PTFE stopper so as to avoid contact with air and with band paths of 15 and 20 nm for the excitation and emission monochromators, respectively. A gate time of 3 ms and a delay time of 0.03 ms were used throughout. The synchronous phosphorescence spectra were recorded on an excitation scale in the range 250 – 350 nm.

Reagents

1-Naphthol (Carlo Erba, Milan, Italy) was sublimed and recrystallized once from a mixture of ethanol-water (50% v/v). Carbaryl (Chem Services, West Chester, PA) was used without any further purification. Potassium iodide (Mallinckrodt, NY, USA) and sodium sulfite (Merck, Darmstadt, Germany) were used as received. Ethanol was purified³⁷ and water was doubly distilled.

Procedure

A $6.6 \times 10^{-4} \text{ mol L}^{-1}$ working standard solution of carbaryl (33.1 mg dissolved in 10 mL of ethanol and diluted to 500 mL with water) was prepared. An $8.4 \times 10^{-4} \text{ mol L}^{-1}$ stock standard solution of 1-naphthol (30.3 mg dissolved in 10 mL of ethanol and diluted to 500 mL with water) was prepared. Stock standard solutions of 3.0 mol L^{-1} potassium iodide and 0.1 mol L^{-1} sodium sulfite solutions were prepared daily.

Aliquots of working standard solutions were transferred to 10.0 mL volumetric flasks. Then, 3.4 mL portions of 3.0 mol L^{-1} KI and 0.2 mL 0.1 mol L^{-1} sodium sulfite were successively added and made up to volume with water. Reagent blanks were prepared following the same procedure. After thorough mixing, the relative phosphorescence intensities of the samples and the blanks were measured at the stated instrumental conditions.

The conventional emission phosphorescence spectrum was recorded at each wavelength of maximum excitation, and the relative phosphorescence intensity was measured at the wavelength of the maximum emission. Three-dimensional spectra of each compound were obtained and presented as an isometric projection where the emission spectra at 20 nm stepped increments of the excitation wavelength were recorded. The three-dimensional spectra were transformed into a plot in two dimensions of excitation and emission wavelengths (contour plots) by joining points of equal intensity. Each optimum $\Delta\lambda$ for a synchronous scan is immediately evident.

Results and Discussion

Spectral characteristics and instrumental parameters

Figure 1 shows the NP-RTP emission spectra of two compounds studied in aqueous solution after adding KI as heavy atom reagent and deoxygenating by sodium sulfite. The phosphorescence spectral characteristics of the compounds under study are summarized as follows: $\lambda_{\text{ex}} = 284 \text{ nm}$, $\lambda_{\text{em}} = 490/525 \text{ nm}$ for carbaryl and $\lambda_{\text{ex}} = 293 \text{ nm}$, $\lambda_{\text{em}} = 492 \text{ nm}$ for 1-naphthol.

Figure 2 shows two-dimensional phosphorescence contour

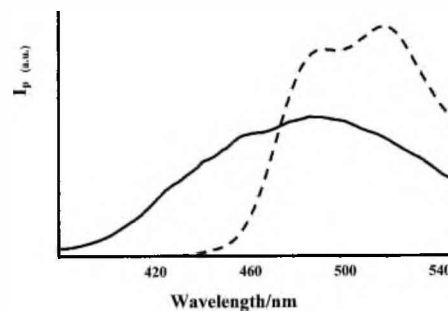


Fig. 1 NP-RTP emission spectra of (---) carbaryl, $\lambda_{\text{ex}} = 284 \text{ nm}$; (—) 1-naphthol, $\lambda_{\text{ex}} = 293 \text{ nm}$.

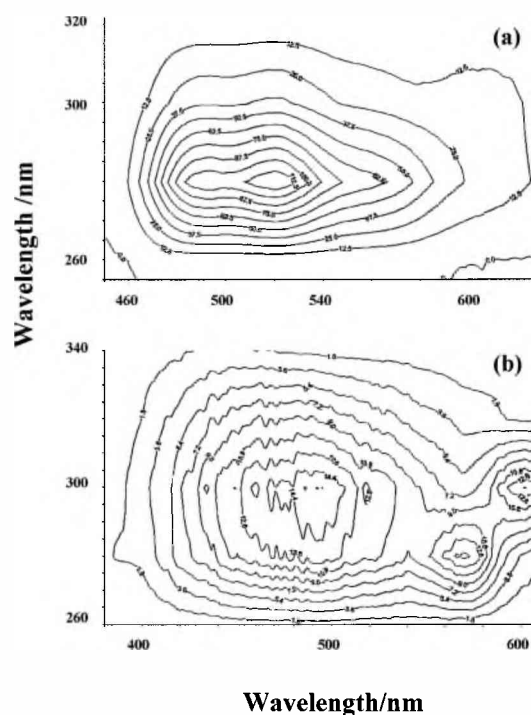


Fig. 2 NP-RTP contour plots of (a) carbaryl, (b) 1-naphthol.

plots for the two compounds studied. Each optimum $\Delta\lambda$ for synchronous scanning was selected from them. Figure 3 shows synchronous spectra obtained while maintaining the constant interval selected between the emission and excitation wavelengths.

Because of the large overlap of the spectra, the determinations of carbaryl and 1-naphthol by synchronous phosphorimetry are still not feasible. This overlap has been resolved by using first-derivative synchronous phosphorimetry. Figure 4 shows the first-derivative synchronous phosphorescent spectra of carbaryl and 1-naphthol. From an examination of this figure, suitable wavelengths to take the zero crossing measurements were found to be 287 and 282 nm. The height at 287 nm is proportional to the carbaryl concentration, and the height at 282 nm is proportional to the 1-naphthol concentration.

Two additional instrumental selectivity parameters are needed to obtain phosphorescence spectra: the delay time (t_d) and the gate time (t_g). The largest signals were obtained with a gate time of 3 ms, and a delay time of 0.03 ms was used in order to avoid interference from the lamp pulse.

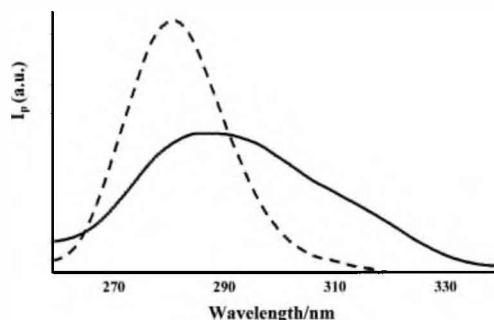


Fig. 3 NP-RTP synchronous spectra of (---) carbaryl, $\Delta\lambda = 240$ nm; (—) 1-naphthol, $\Delta\lambda = 200$ nm.

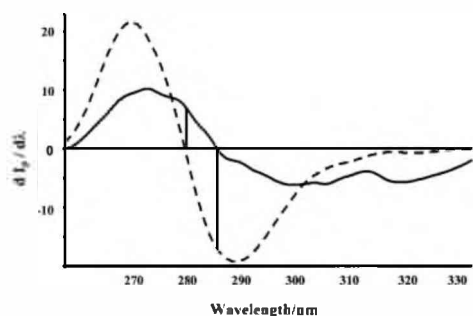


Fig. 4 First-derivative synchronous phosphorescence spectra of (---) carbaryl and (—) 1-naphthol.

Optimization of experimental variables

Two experimental variables were investigated to establish the optimum conditions for the analysis. The variables studied were potassium iodide and sodium sulfite. Because potassium iodide produces an effective spin-orbital coupling that favors the intersystem crossing between singlet and triplet states producing the phosphorescence emission, it is required to know the optimal concentration to be used. The effect of the potassium iodide concentration on the RTP signal was examined in the range of 0.0 – 1.6 mol L⁻¹. As the concentration of potassium iodide increased, a steep increment was observed until the concentration reached 1.0 mol L⁻¹ and a near constant value was maintained above this concentration. Therefore, 1.0 mol L⁻¹ potassium iodide was selected as the optimal value. The phosphorescent emission of 1-naphthol was not affected by the potassium iodide concentration.

The effect of the sodium sulfite concentration on the RTP signal was examined in the range of 0.0 – 2.2 × 10⁻³ mol L⁻¹. By using sodium sulfite at a concentration above 0.001 mol L⁻¹, the maximum RTP signal was obtained instantly, and remained stable for at least 1 h. A 0.002 mol L⁻¹ concentration was selected for the present work.

Analytical characteristics

Calibration graphs were obtained for each analyte. The analytical parameters for first-derivative synchronous phosphorimetry were estimated by applying a statistical model of linear regression,³⁸ and are shown in Table 1. The detection limits using the 3σB criterion (σB being the standard deviation of the blank) were evaluated. The linear range for carbaryl and 1-naphthol were 1.2 × 10⁻⁶ – 1.1 × 10⁻⁵ and 1.6 × 10⁻⁶ – 1.3 × 10⁻⁵ mol L⁻¹ with detection limits of 2.9 × 10⁻⁷ and 8.2 × 10⁻⁷ mol L⁻¹, respectively.

Table 1 Results of a least-squares regression analysis of the synchronous first-derivative phosphorescence intensity (a.u.) against the analyte concentration (mol L⁻¹)

Parameter	Carbaryl	1-Naphthol
<i>a</i> (intercept)	1.79	-0.24
<i>b</i> (slope)	3.11 × 10 ⁶	5.51 × 10 ⁵
<i>S_b</i> (standard deviation)	75694.8	20372.3
<i>S_{yx}</i> (regression deviation)	0.84	0.30
<i>r</i> (correlation coefficient)	0.9971	0.9932

N = 12 (number of calibration data points).

Application

The proposed method was applied to a commercial insecticide containing carbaryl. The contents of carbaryl and 1-naphthol in the commercial formulation were estimated by means of corresponding calibration plots. 1-Naphthol was not found, and the carbaryl assay result was 85.2 ± 0.9% w/w. This value agreed with the nominal content (85% w/w).

Heating produced a partial degradation of the insecticide. A solution of the commercial insecticide was prepared by dissolving 11.15 mg, and was made up to 100.0 mL with water. A portion of this solution was transferred into a glass-capped vial, and was heated in a thermostated water-bath at 100°C for 11 h. Afterwards, this solution was analyzed by the first-derivative synchronous non-protected room temperature phosphorescence methodology.

A nearly complete degradation was observed and concentrations of 3.01 × 10⁻⁴ mol L⁻¹ of 1-naphthol and 4.15 × 10⁻⁵ mol L⁻¹ of carbaryl were found. It is known that 1 mol carbaryl hydrolyzes to produce 1 mol 1-naphthol. Therefore, the sum of the molarity of the compounds should be invariable in the reaction process. In conclusion, the average sum of the molarity of the compounds during the reaction was in accordance with the carbaryl original concentration.

Conclusion

This study shows that synchronous phosphorimetry coupled to NP-RTP increases the sensitivity for the analysis of mixtures. The combination of both techniques allows a simultaneous determination of carbaryl and 1-naphthol at low levels in mixtures, without any previous preconcentration or separation.

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