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HAI–RTP Determination of Carbaryl Pesticide in Different Irrigation Water Samples of South Spain

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In this work, a widely used pesticide named carbaryl, present in numerous water supplies, has been determined by the so-called heavy atom induced room-temperature phosphorescence (HAI–RTP) methodology. A detailed study of numerous instrumental variables such as sensitivity, slits, decay time, and gate time, and those of experimental type such as heavy atoms, oxygen scavenger, temperature, buffer solutions, and organic solvents, have been carried out. The detection limit was 2.8 ng mL^{-1} with a relative standard deviation of 2.12% at the 150 ng mL^{-1} level. Spiked irrigation water samples taken from different places near agricultural fields gave mean percentage recoveries of 95.7%. The results obtained in this study indicate that the proposed method is suitable for the determination of residues of carbaryl pesticide in water samples with good reproducibility and sensitivity for the analysis of this compound being rapid and very simple for routine analysis.

Keywords: *Carbaryl; pesticide analysis; phosphorescence*

INTRODUCTION

Recently, there has been an increased need for residue analytical methods of identification and quantification of numerous pesticides at trace levels in environmental water matrixes, such as surface, estuarine, and ground- and seawater (Miliadis, 1998).

Carbaryl, (1-naphthyl methylcarbamate, CBL) is a broad-spectrum carbamate class of nitrogen-containing organic insecticide (Quintero et al., 1988) whose toxic effects are due to the inhibition caused in the cholinesterase enzyme and its teratogenic character (Seifert and Casida, 1978). Because CBL is frequently spread in crops in large quantities, it may constitute an important entry route for residues into the human food chain and natural waters.

Although a great number of analytical methods have been proposed for its determination by different instrumental methods (Benson and Finocchiararo, 1965;

Argauer et al., 1970; Argauer and Bontoyan, 1970; Argauer and Warthen, 1975; Larkin and Day, 1979; Pieper, 1979; Deberardinis and Wargin, 1982; Appaiah et al., 1982; Krause, 1985), very few using phosphorescence methodology have been proposed (Yansheng et al., 1994; Panadero et al., 1994; Segura Carretero et al., 1996; Capitán-Vallvey et al., 1998). Most of these methodologies need to be improved for their simplicity, sensitivity, and reliability.

In the present work, a simple heavy atom induced room-temperature phosphorescence (HAI–RTP) methodology (Segura Carretero et al., 1998a; Segura Carretero et al., 1998b; Fernández Gutiérrez et al., 1999; Segura Carretero et al., 1999) has been proposed for the determination of CBL in different irrigation water samples.

This method describes the possibility to obtain room-temperature phosphorescent emission using only heavy atom perturber and sodium sulfite as deoxygenator with a series of advantages in contrast to other phosphorescent methodologies previously described such as micel-

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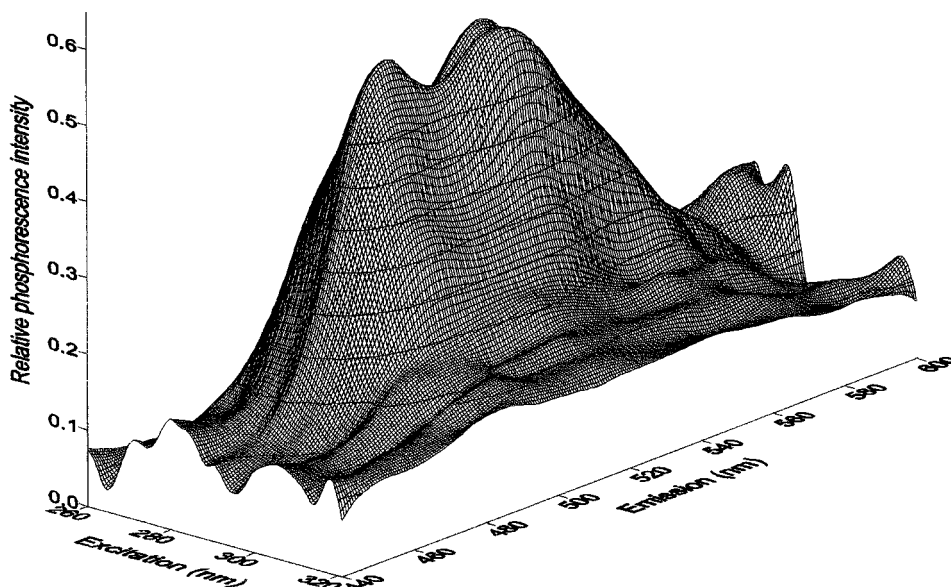


Figure 1. Projected three-dimensional spectrum of CBL. [CBL] = 100 ng mL⁻¹, [KI] = 1.4 mol L⁻¹, [Na₂SO₃] = 1.5 × 10⁻³ mol L⁻¹, and temperature = 15 °C. Emission = 440–600 nm, excitation = 260–320 nm, slits_{exc/em} = 16/16, *t*_d = 120 μs, *t*_g = 150 μs, detector voltage = 1100 V, and mpf = 5 ms.

lar stabilized-RTP (MS-RTP) (Scypinski and Cline Love, 1984) or cyclodextrin-RTP (CD-RTP) (Cline Love and Skrilec, 1981) which use micellar medium, micro-emulsion or cyclodextrin, respectively. This advantages are related to the fact that the system is a transparent and stable solution that no precipitate, such as occurs in CD-RTP (Scypinski and Cline Love, 1984) and no foams are formed, as occur in MS-RTP (Cline Love and Skrilec, 1981) with the possibility of combination with other analytical techniques such as liquid chromatography (LC), flow injection analysis (FIA), and automatic on-line analysis.

Due to the fact that numerous variables influence the phosphorescence emission of the analytes, we include a detailed selection to demonstrate the possibilities of the HAI-RTP methodology in the environmental field for a simple, sensitive, and reproducible determination of the insecticide carbaryl in different irrigation water samples of the South of Spain.

MATERIALS AND METHODS

Apparatus. All recording of uncorrected luminescence spectra and measurements of HAI-RTP intensities were carried out with an Aminco Bowman series 2 luminescence spectrometer equipped with a 7 W pulsed xenon lamp and a thermostated cell holder controlled by a personal computer. A Crison model 2001 pH meter with glass-saturated calomel combination electrode was used to measure the pH of solutions.

Reagents. Aqueous solutions were made with doubly distilled water. The different compounds employed as oxygen scavengers such as anhydrous sodium sulfite, sodium nitrite, metallic zinc, and anhydrous sodium carbonate were all obtained from Sigma Chemical Co.

All deoxygenated solutions were prepared in acid medium, except sodium sulfite; this solution was prepared daily and kept in tightly stopped containers. The heavy atom perturbers studied were reagent grade thallium(I) nitrate and potassium iodide (both from Sigma). Buffer solutions were prepared using glacial acetic acid, sodium acetate, sodium dihydrogen phosphate 1-hydrate, disodium hydrogen phosphate 12-hydrate, sodium tetraborate, and sodium hydroxide (all from Sigma).

Carbaryl (Labor Dr. Ehrenstorfer) was used without further purification. Stock solutions were prepared by dissolving 25 mg of CBL in 50 mL of double-distilled water.

Table 1. Influence of Excitation/Emission Slits in the Intensity and Standard Deviation of HAI-RTP

slit	carbaryl		blank	
	RPI	<i>s</i>	RPI	<i>s</i>
16/16	0.650	0.035	0.069	0.029
8/16	0.363	0.046	0.058	0.022
16/8	0.349	0.027	0.076	0.023
8/8	0.252	0.028	0.073	0.013
4/8	0.110	0.020	0.052	0.011
8/4	0.128	0.026	0.051	0.014
4/4	0.060	0.014	0.031	0.014

General Procedure. To prepare the calibration graph, different aliquots of the CBL stock solution, 7 mL of 2 mol L⁻¹ potassium iodide, and 150 μL of 0.1 mol L⁻¹ sodium sulfite were introduced into a 10 mL standard flask and made up to volume with water. Standard 10 mm fused-silica cells were filled with this analyte solution. Reagent blanks prepared without carbaryl were measured following the same procedure.

The instrument was set up as follow: $\lambda_{\text{ex}} = 288$ nm, $\lambda_{\text{em}} = 488$ nm (slits of 16 nm), detector voltage = 1100 V, select flash lamp in phosphorescence >200 μs (PMT masked) mode with delay after flash 120 μs and gate width 150 μs.

Sample Preparation. The present method has been applied to irrigation water samples from South Spain, with one taken from a stream located in the village of Atarfe (Granada, Spain) and two different well water samples from Vega de Granada (Spain). The water samples were filtered through Whatman no. 5 paper (pore size 2.5 μm) in order to eliminate the suspended organic matter, and a certain quantity of carbaryl was added to 10 mL of each sample in such a way that the final concentrations were included in the calibration graph. The basic procedure was applied to these solutions.

RESULTS AND DISCUSSION

Spectral Characteristics. Figure 1 shows the three-dimensional phosphorescent spectra of CBL in aqueous solution, obtained at 15 °C in the presence of sodium sulfite and potassium iodide. CBL emits strong phosphorescence with maximum excitation and emission intensities at 288 and 488/524 nm, respectively. These phosphorescence wavelength increase considerably the selectivity of carbaryl determination due to the fact that batocromic shifts of 200 and 151 nm are observed with

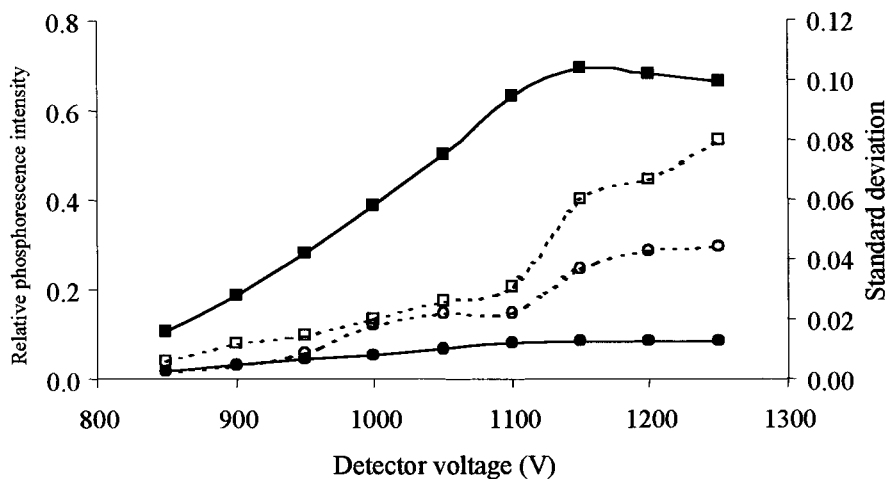


Figure 2. Influence of detector voltage on the relative phosphorescence intensity of CBL (—■—) and blank (—●—) and of standard deviation of CBL (---□---) and blank (---○---). Experimental conditions as in the caption to Figure 1. $\lambda_{exc} = 288$ nm, $\lambda_{em} = 488$ nm, $slits_{exc/em} = 16/16$, $t_d = 120$ μ s, $t_g = 150$ μ s, and mpf = 5 ms.

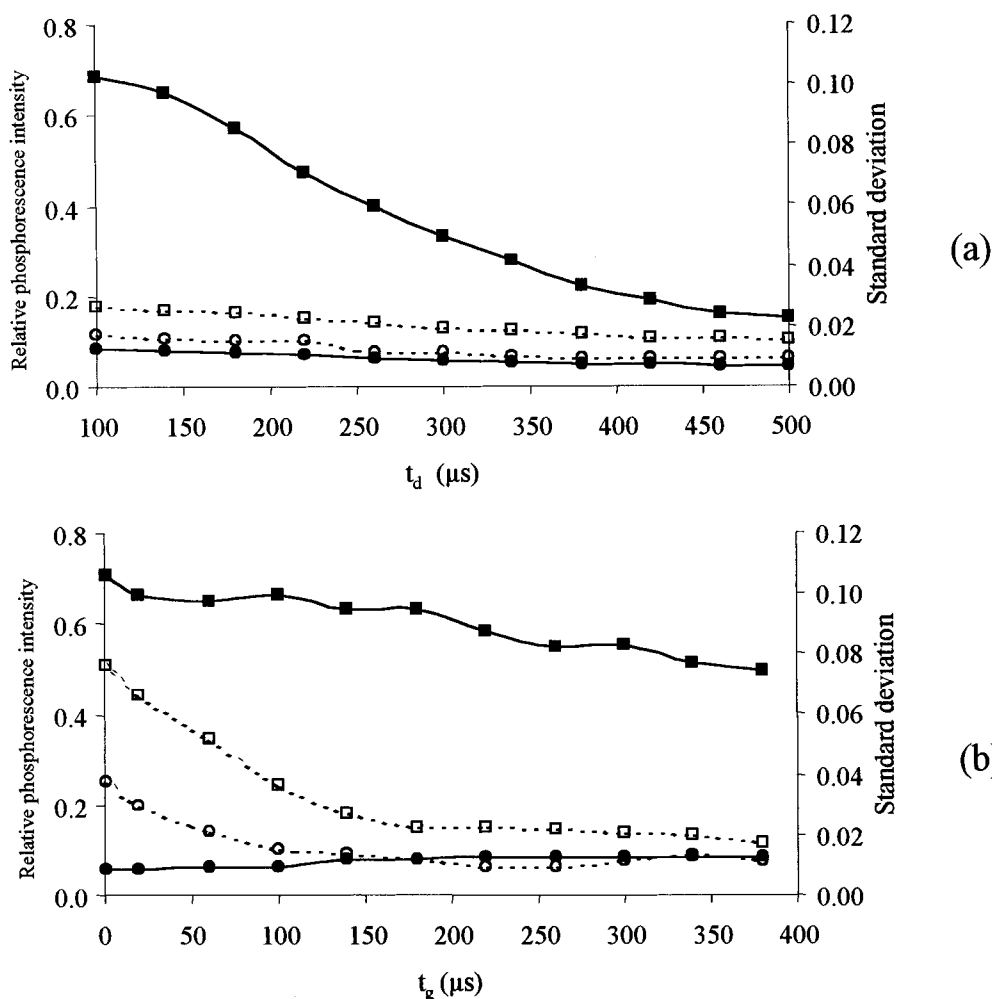


Figure 3. (a) Influence of decay time (t_d) and (b) influence of gate time (t_g) on the relative phosphorescence intensity of CBL (—■—) and blank (—●—) on standard deviation of CBL (---□---) and blank (---○---). Experimental conditions as in the caption to Figure 1. $\lambda_{exc} = 288$ nm, $\lambda_{em} = 488$ nm, $slits_{exc/em} = 16/16$, $t_d = 120$ μ s, $t_g = 150$ μ s, mpf = 5 ms, and detector voltage = 1100 V.

respect to the fluorescence wavelength of this compound. In this experimental conditions, a triplet lifetime (τ) of 180 μ s by the decay emission curve was determined.

Detector Voltage and Slits. An adequate optimization of instrumental parameters for the equipment used in this work was carried out to improve the sensitivity

of the determination. This is a general optimization that should be carried out each time the equipment is changed but the procedure would be always the same.

The selection of optimum values was carried out observing the changing phosphorescence intensity/noise ratio and the standard deviations of samples and blanks.

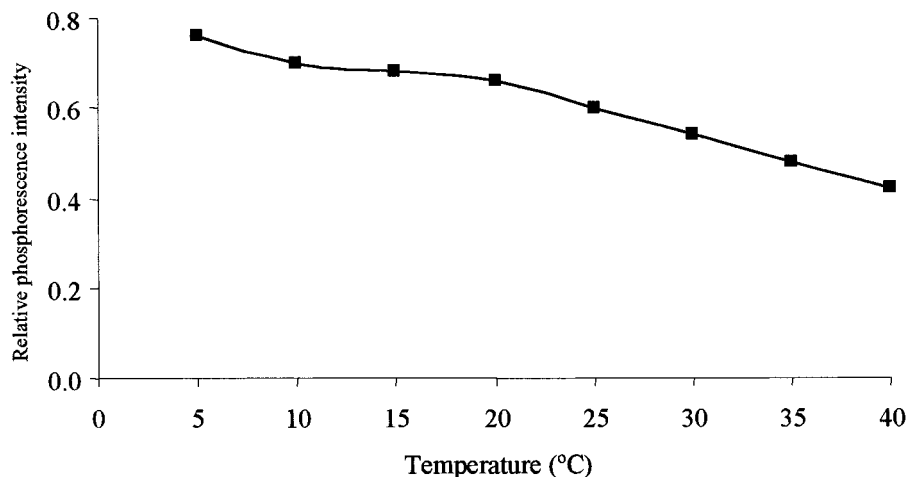


Figure 4. Influence of temperature on the relative phosphorescence intensity of CBL. [CBL] = 100 ng mL⁻¹, [KI] = 1.4 mol L⁻¹, [Na₂SO₃] = 1.5 × 10⁻³ mol L⁻¹. λ_{exc} = 288 nm, λ_{em} = 488 nm, slits_{exc/em} = 16/16, t_d = 120 μs, t_g = 150 μs, detector voltage = 1100 V, and mpf = 5 ms.

As it can be seen in Figure 2, the applied photomultiplier voltage directly influences both instrumental sensitivity and background. An increase on the detector voltage produces a linear increment of the CBL luminescence signal from 850 to 1150 V, being stable up to 1150 V. The blank signal and its standard deviation increases continuously until 1250 V, so an optimum value of 1100 V was chosen for the rest of experimental work.

The slits influence drastically the relative phosphorescence intensity (RPI) of CBL while they do not affect significantly the blank signal. The data obtained are summarized in Table 1. A 16/16 nm excitation/emission slits gave the best signal-to-noise ratio, so it was selected for the rest of the analytical determinations.

Effect of the Decay Time and Gate Time. Decay time (t_d) is the time between the flash and the start of data acquisition, whereas gate time (t_g) is the acquisition time. Both instrumental parameters present a great influence on phosphorescence emission and its optimum values depend on the analyte lifetime. Both variables must be studied and selected carefully for each compound to obtain the best signal/noise ratio.

As can be observed in Figure 3a, the CBL signal versus time curve corresponds to the decay emission curve, and it is possible to recalculate the lifetime parameters previous adjustment to exponential function (τ = 238 μs). Sample emission deviation slightly and noise deviation remains constant. A delay time of 120 μs after flash was selected because the best signal/noise ratio is obtained.

With respect to the gate time, the phosphorescence intensity diminishes slightly with the increase of this parameter while the noise value is increased (see Figure 3b). On the other hand, a strong diminution of the standard deviation occurs owing to the signal and noise. So, a gate time of 150 μs was chosen as more adequate for the rest of the experimental work.

Effect of Organic Solvent. The reduced application field of this methodology supposes an advantage due to intrinsic selectivity but also causes a limitation. This limitation is due to its impossibility to be applied to apolar compounds but this can easily be avoided using small percentages of organic solvents in the aqueous medium. This fact decrease the medium dielectric constant facilitating the solubilization of apolar com-

Table 2. Influence of Organic Solvents in the Intensity and Stabilization Time of HAI-RTP

organic solvent	percentage (%)	RPI	stabil. time (s)
acetone	0	0.600	0
	1	0.180	160
	1	0.560	70
	2	0.550	84
	3	0.560	99
acetonitrile	4	0.550	108
	5	0.550	120
	7	0.525	174
	1	0.540	0
	2	0.520	0
ethanol	3	0.540	0
	4	0.520	0
	10	0.540	0
<i>N,N</i> -dimethylformamide	1	0.523	402
	1	0.560	78
methanol	2	0.550	120
	3	0.560	99

pounds and, consequently, increasing the spread of the application fields of the HAI-RTP methodology.

The effect of five organic solvents miscible with water (acetone, ethanol, methanol, acetonitrile, and dimethylformamide) has been studied. Following the basic procedure, the aqueous solutions of CBL were mixed with different percentages of organic solvents, and the HAI-RTP emissions have been studied. The results are shown in Table 2. As it can be observed, the presence of 1% acetone clearly diminishes the phosphorescence emission and increases, considerably, the stabilization time. Also, the presence of small percentages of acetonitrile, *N,N*-dimethylformamide, and methanol does not influence the phosphorescence emission of the insecticide but clearly affects the stabilization time, which increases as the percentage of the organic solvent increases.

Although the presence of ethanol up to 10% is possible with no modification in the phosphorescence emission on the stabilization time, it clearly modifies the dielectric constant of the medium; thus, it could be selected for the experimental work.

Effect of Temperature and Stability. Temperature is an important parameter that affects the viscosity of the medium and deoxygenation kinetics of sulfite, so it needs to be carefully selected in HAI-RTP measurements.

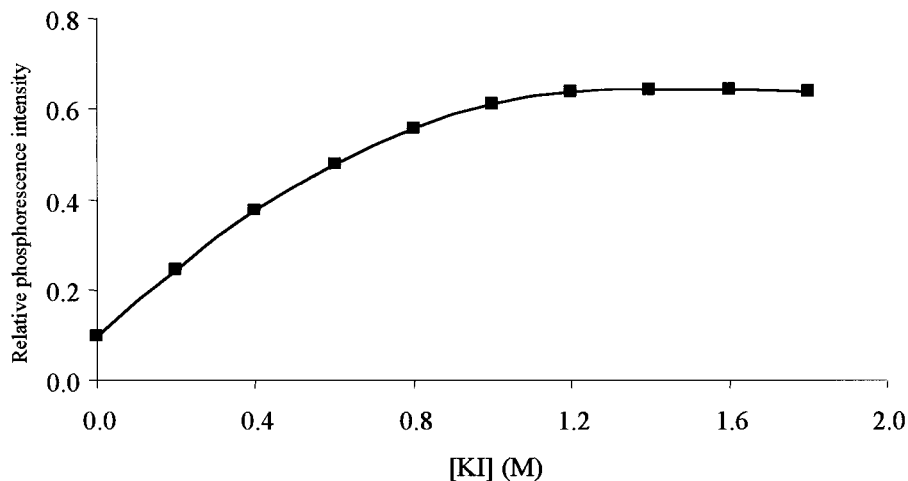


Figure 5. Influence of heavy atom concentration on the relative phosphorescence intensity of CBL. [CBL] = 100 ng mL⁻¹, [Na₂SO₃] = 1.5 × 10⁻³ mol L⁻¹. Instrumental conditions as in the caption to Figure 4.

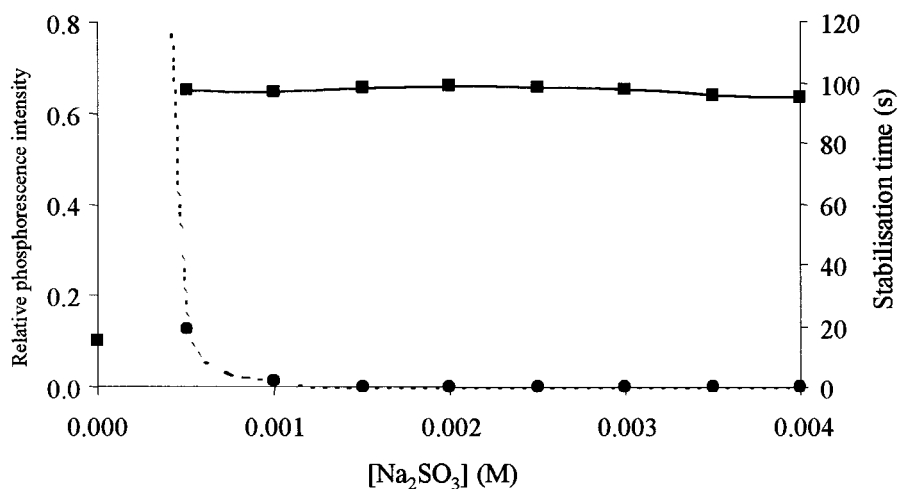


Figure 6. Influence of oxygen scavenger concentration on the relative phosphorescence intensity of CBL (—■—) and of stabilization time (---●---). [CBL] = 100 ng mL⁻¹, [KI] = 1.4 mol L⁻¹. Instrumental conditions as in the caption to Figure 4.

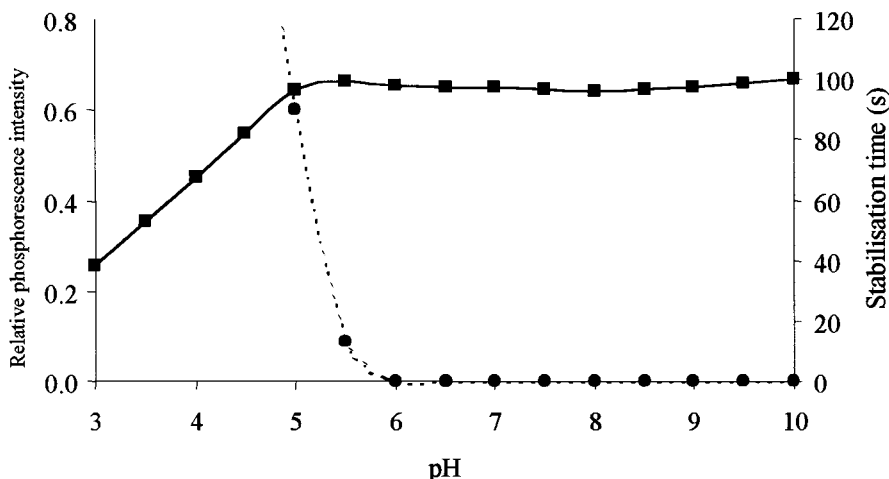


Figure 7. Influence of pH on the relative phosphorescence intensity of CBL (—■—) and of stabilization time (---●---). [CBL] = 100 ng mL⁻¹, [KI] = 1.4 mol L⁻¹, [Na₂SO₃] = 1.5 × 10⁻³ mol L⁻¹. Instrumental conditions as in the caption to Figure 4.

A detailed study of the phosphorescence emission of CBL at temperatures ranging from 5 to 40 °C was carried. As it can be seen in Figure 4, the evolution of the HAI-RTP was followed kinetically by monitoring at 488 nm with excitation at 288 nm.

Low temperatures increase the viscosity of aqueous medium and improve CBL RPI emission but slow the

deoxygenation kinetic, so the signal appears slower. Thus, a temperature of 15 ± 1 °C was selected for the rest of the experimental work.

The signal of the system reaches stability instantaneously under these experimental conditions and remain stable for at least 1 h.

Effect of Heavy Atom Perturbers. Previous stud-

ies indicated that the presence of different concentrations of heavy atoms in the measurement media affect significantly the phosphorescence emission in HAI-RTP of compounds such as naphthalene derivatives (Segura Carretero et al., 1998a; Segura Carretero et al., 1998b; Fernández Gutiérrez et al., 1999; Segura Carretero et al., 1999), for which a similar study has been carried out for CBL determination.

Aqueous solutions of CBL do not show phosphorescence emission in absence of heavy atom while, in general, the intensity improves as the heavy atom concentration increases. The selection of the kind of heavy atom perturber and optimum concentration range is necessary.

Different heavy atoms perturber, such as KI, NaI, KBr, NaBr, KCl, NaCl, TiNO_3 , CsCl, and RbCl, have been tested in the present work but CBL phosphorescent emission was only obtained when KI and TiNO_3 were used. Due to the high toxicity of Ti(I) which can replace potassium in various enzymes and thus inhibit enzyme activity (Clayton and Clayton, 1981), we chose KI as the heavy atom perturber for the rest of the experimental work.

The influence of its concentration on the phosphorescence emission of carbaryl was examined (see Figure 5), where it can be seen that an increase on KI concentration from 0 to 1.2 M causes a marked increase on the RPI to remain stable between 1.2 and 2 M. For such a reason, a concentration of 1.4 M KI was selected for the rest of the experimental work.

Effects of Oxygen Scavenger. In this report, different methods for oxygen elimination, such as SO_3^{2-} (Díaz-García and Sanz Medel, 1986), N_2 purging (Scypinski and Cline Love, 1984), $\text{Na}_2\text{CO}_3/\text{HCl}$ (Zang et al., 1997), Zn/HCl (Zang et al., 1997) and other reductor NO_2 assayed for their own research group have been tested. Only when SO_3^{2-} has been used has it been possible to obtain the basic vibrational structure of CBL HAI-RTP emission spectra. Other systems tested also eliminate the oxygen (deoxygenation verified with an oxymeter), but the phosphorescence signal does not appear due to molecular deactivation.

Among the different deoxygenation methods tested, only the sulfite ion permits one to obtain HAI-RTP signal from CBL in aqueous solutions in the presence of KI as heavy atom perturber, for which it has been selected for the present method.

Once it has been selected, the influence of its concentration on the phosphorescence emission and stabilization time is necessary. To carry out this experiment, the development of the HAI-RTP emission (phosphorescence signal) was followed kinetically by monitoring at 488 nm with excitation at 288 nm (see Figure 6). Various amounts of sulfite were added to a solution with a fixed amount of CBL and heavy atom salt while the concentration of sulfite was varied from 0 to 0.004 M. The concentration of CBL was 100 ng mL^{-1} , and the concentration of KI was 1.4 M.

As a result of this study, a concentration of 0.0015 M was selected for the rest of the experimental work.

Effect of pH. The pH affects the dissociation of the different compounds and the deoxygenation kinetics of the different oxygen scavengers (Weijun et al., 1994) because it affects the reaction speed of the deoxygenation systems. As it has been previously studied, when SO_3^{2-} is used, the pH must be higher than 5.6 to deoxygenate the system.

Table 3. Determination of Carbaryl in Irrigation Water

irrigation water sample	carbaryl spiked (ng mL^{-1})	percentage recovery ^a	RSD (%)
Atarfe village stream	50	98.2	3.1
	100	99.3	3.7
	150	100.1	3.2
Cortijo de San Matias well	50	84.7	2.9
	100	85.5	2.5
	150	86.3	2.7
Huerta de Santa Maria well	50	101.3	3.1
	100	102.2	3.2
	150	102.8	3.0

^a Mean of seven determinations.

Figure 7 shows the effect of the pH on the RTP emission from CBL in the presence of KI as the heavy atom perturber and sulfite as the oxygen scavenger at a temperature of 15 °C, with these variables being selected as optimum for its determination.

Different pHs ranging from 3.6 to 10.2 were studied with a solution of fixed amounts of CBL (100 ng mL^{-1}), heavy atom salt (1.4 M), and sulfite (0.0015 M). The development of the HAI-RTP emission was followed kinetically by monitoring at 488 nm with excitation at 288 nm.

Under these experimental conditions, an increase on the phosphorescence emission and a decrease on the stabilization time occurs from pH 5.5, with no changes up to pH 10, being the optimum pH interval for the analytical determination.

Because the system prepared as indicated presents a fixed pH of 8.12, no buffering is necessary. Despite this circumstance, different buffer solutions such as $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ and $\text{B}_4\text{O}_7^{2-}/\text{HCl}$ have been assayed, and similar phosphorescent intensities were obtained. So, no buffer has been used for the rest of the work.

Validation of the Method. The method was tested for linearity, precision, reproducibility, and specificity. The RPI was linear for CBL over the concentration range of 0–200 ng mL^{-1} , calculated in the final solution. The correlation coefficient obtained, $r = 0.998$ ($n = 15$), indicates good linearity. The detection limit was 2.8 ng mL^{-1} according to IUPAC (Long and Winefordner, 1983). The precision of the method was determined at two concentrations (100 and 200 ng mL^{-1}) giving a relative standard deviation (RSD) ($n = 15$) of 2.99 and 1.75%, respectively.

Application to Fortified Irrigation Water Samples. Determination of pesticide levels in surrounding soils and waters is often needed to control environmental contamination after their foliar application. Therefore, the availability of rapid and simple analytical methods is always desirable.

The present HAI-RTP procedure has permitted us to establish a simple, rapid, and sensitive method to determine the insecticide carbaryl added to irrigation water samples taken from three different places of South Spain.

Table 3 summarizes the results at three spiked levels (50, 100, and 150 ng mL^{-1}) of carbaryl added to three different water samples. It can be concluded that acceptable accuracy and precision can be obtained in the analysis of samples at these concentration levels of carbaryl and that HAI-RTP can be an elegant alternative for the determination of numerous pesticides with a selective technique such as phosphorescence in solution.

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