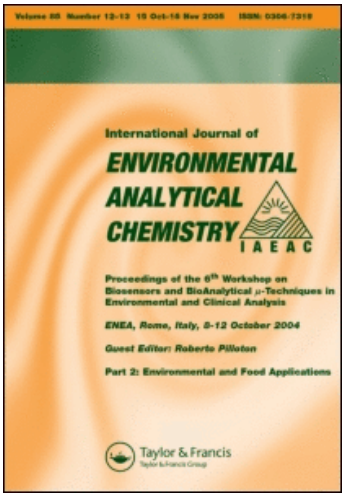

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A simple and rapid phosphorimetric method for the determination of the fungicide fuberidazole in water samples

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A simple and rapid phosphorimetric method for the determination of the fungicide fuberidazole in water samples

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The applicability of heavy-atom induced room-temperature phosphorescence to determine pesticides in real samples is demonstrated in this work. Thus a new, simple, rapid and selective phosphorimetric method for fuberidazole determination is proposed. The phosphorescence signals are a consequence of intermolecular protection when analytes are found exclusively in the presence of heavy atom salts and sodium sulphite when used as an oxygen scavenger to minimize RTP quenching, so protective media (such as cyclodextrines, micellar media, etc) are not necessary to use for obtaining phosphorescence in solution. The determination was performed in 0.4 M KI and 8 mM sodium sulphite at a measurement temperature of 20°C. The phosphorescence intensity was measured at 515 nm exciting at 308 nm. Phosphorescence was easily and rapidly obtained, showing a linear concentration range between 0 and 25 ng mL^{-1} with a detection limit of 95 ng L^{-1}. The method has been successfully applied to the analysis of fuberidazole in water.

Keywords: Pesticide analysis; Fuberidazole; Heavy atom induced; Room temperature phosphorescence; Water

1. Introduction

Pesticides are one of the major organic pollutants in the environment due to their massive use in agriculture. The tolerable concentrations demanded by regulatory authorities for potential access routes in tropic chains are becoming stricter and stricter. Therefore, it is essential to develop sensitive, selective, automatic and rapid analytical methodologies as real and practical alternatives to the robust and efficient chromatographic methods, which are time consuming, instrumentally expensive, ill-suited to real time analysis and usually require a pre-treatment of the samples.

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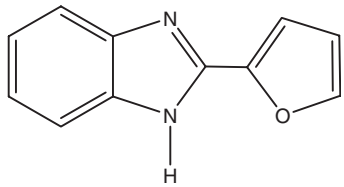

Figure 1. Chemical structure of fuberidazole.

2-Substituted benzimidazol is the most important class of benzimidazoles used in agriculture (see figure 1). Fuberidazole (2-(2′-furyl)benzimidazole, FBZ) has been applied as a fungicide [1–3], as an anthelmintic [4, 5] and against entero-viruses [6].

Several spectrofluorometric methods for the individual determination of FBZ [7, 8] or simultaneously [9–11] with other pesticides have been developed.

Phosphorimetry is more selective than photometry or fluorimetry for the analysis of many compounds. Thus micelle-stabilized RTP has permitted the determination of FBZ in different matrices in solution [12].

However, recent studies have demonstrated that RTP emission of naphthalene derivatives and heterocyclic compounds can be directly induced in aqueous solutions only with the addition of perturbed heavy atom and sodium sulphite as a chemical deoxygenator [13–16]. This methodology is called heavy-atom induced room-temperature phosphorescence (HAI-RTP) and has been applied to pharmaceutical analysis [17, 18] and some pesticides in vegetables matrices [19, 20]. The methodology offers many advantages compared to other RTP techniques, and allows the development of a very simple, fast and possibly automatic analytical method.

In this work a simple, selective and fast phosphorimetric method is proposed for fuberidazole determination in water.

2. Experimental

2.1 *Instrumentation*

A Varian Cary-Eclipse fluorescence spectrophosphorimeter (Varian Iberica, Madrid, Spain) was used to obtain the phosphorescence spectra and the relative phosphorescence intensity (R.P.I.) measurements. The spectrophosphorimeter was equipped with a xenon discharge lamp (peak power equivalent to 75 kW), Czerny-Turner monochromators, R-928 photomultiplier tube which is red sensitive (even 900 nm) with manual or automatic voltage controlled using the Cary Eclipse software for Windows 95/98/NT system.

2.2 *Reagent and solutions*

Analytical reagent-grade chemicals were used for preparing all the solutions. Thallium (I) nitrate, potassium iodide and anhydrous sodium sulphite were purchased from Sigma Chemical Co. (Spain) and were used as received. A two moles solution of potassium iodide and thallium nitrate solution at 0.25 M concentration was prepared. The 0.1 M sodium sulphite solutions were prepared daily and kept in tightly closed containers.

Standard stock solution (50 μg mL^{-1}) of fuberidazole (Sigma Chemical Co) was prepared in water, stored below 5°C and protected from the light.

The water used was doubly distilled and prepared with a Milli-Q system (Millipore, Bedford, MA, USA).

2.3 *General procedure*

Aliquots of fuberidazole stock solution in water with 2 mL of 2 M of potassium iodide, 3 mL acetonitrile and 800 μL of 0.1 M sodium sulphite were introduced into a 10 mL calibrated flask and made up to volume with doubly distilled water. Standard 10 mm quartz cells were used in all cases.

The relative phosphorescence intensities (R.P.I.) of the samples and the corresponding blanks were measured at the phosphorescence wavelength maxima of $\lambda_{ex}/\lambda_{em}$ 308/515 nm, $slits_{ex/em}$ 20/20 nm, decay time 0.10 ms, gate time 5.00 ms and detector voltage 950 V. Reagent blanks lacking fuberidazole were prepared and measured following the same procedure.

2.4 *Water sample procedure*

Drinking water samples from the city of Granada and mineral water samples were spiked at three different concentration levels to obtain final diluted samples containing 2.4, 10.0 and 20.0 ng mL^{-1} of pesticide. These three levels of pesticide concentrations are within the calibration graphs previously established for fuberidazole determination. The samples were measured as indicated in the General Procedure and no pre-treatment was necessary.

3. Results and discussion

3.1 *Phosphorescence properties*

Figure 2 shows the excitation and phosphorescence emission spectra of fuberidazole in aqueous solution in the presence of KI and sodium sulphite. Fuberidazole emits phosphorescence with a maximum excitation at 308 nm and a maximum emission at 515 nm. In these experimental conditions, the half life-time of the fuberidazole phosphorescence emission is 172 μs.

3.2 *Influence of heavy atom perturbers*

Various kinds and concentrations of heavy atoms affect the intensity of the HAI-RTP signal. We present the effects of two heavy atom salts, KI and $TlNO_3$ in this paper. Fuberidazole only emits phosphorescence when KI is used as a heavy-atom perturber.

As can be observed in figure 3, no phosphorescence response of the FBZ was obtained in the total absence of KI while, in general, the HAI-RTP intensity increased with increasing heavy atom concentration until a concentration of 0.4 M. This value was chosen as optimum for the rest of experimental work.

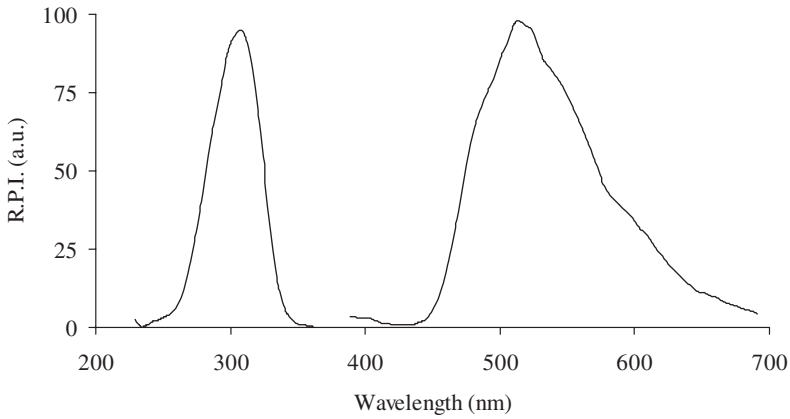

Figure 2. Spectrum of fuberidazole. [FBZ] = 20 ng mL^{-1}, [KI] = 0.4 M, [Na_2SO_3] = 8 mM. Excitation and emission wavelengths 250–375 nm and 400–700 nm respectively, slits$_{exc/em}$ 20/20 nm, $t_{d/g}$ 0.1/5 ms and detector voltage 950 V.

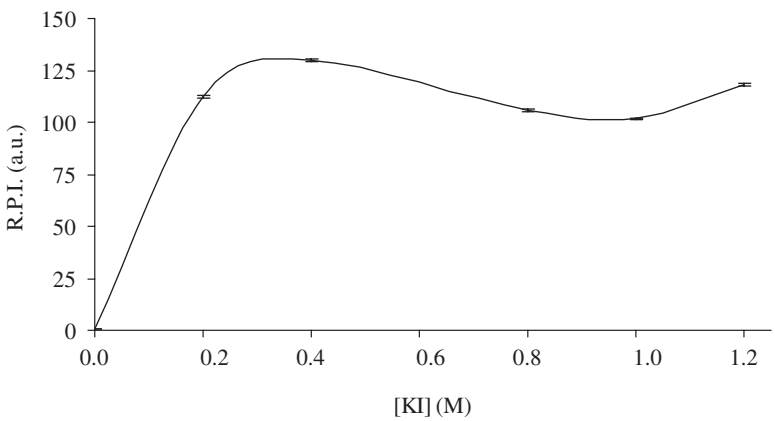

Figure 3. Influence of potassium iodide concentration on the relative phosphorescence intensity (R.P.I.) of fuberidazole. [FBZ] = 20 ng mL^{-1}, [Na_2SO_3] = 8 mM. $\lambda_{ex}/\lambda_{em}$ = 308/515 nm. The rest of instrumental parameters as in figure 1.

3.3 *Influence of deoxygenation*

Sodium sulphite was selected as the deoxygenation scavenger. In aqueous solution, the elimination of dissolved oxygen is practically immediate, although both the relative phosphorescence intensity and the stabilization time (time necessary for sample deoxygenation) can change with sodium sulphite concentration. This study was performed by monitoring the signal as a function of time until the HAI-RTP signal was stabilised for at least 2 min. To establish the optimum concentration of sodium sulphite, different amounts between 1.0 and 10.0 mM of oxygen scavenger were added to a solution with a fixed concentration of fuberidazole in the presence of potassium iodide at a concentration of 0.4 M. A concentration of 8.0 mM of sodium sulphite in the solution was selected as optimum (see figure 4) because the deoxygenating time of practically zero and the intensity shows a plateau at this value of Na_2SO_3.

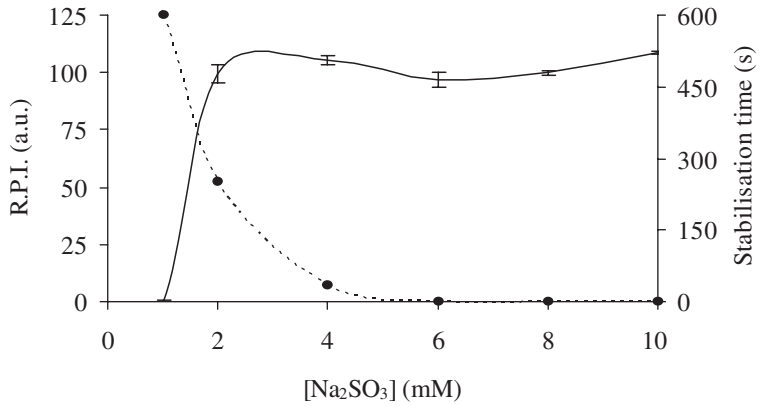

Figure 4. Influence of sodium sulphite concentration of R.P.I. (—) and stabilisation time (-----). [FBZ] = 20 ng mL^{-1} and [KI] = 0.4 M. $\lambda_{ex}/\lambda_{em}$ = 308/515 nm. The rest of instrumental parameters as in figure 1.

3.4 *Effect of organic solvents*

The effect of the different percentages of organic solvents (acetone, acetonitrile, ethanol and methanol) was studied in order to improve phosphorescent measurements and facilitate the solubilization of fuberidazole.

The study as carried out demonstrated that no changes were observed in relative phosphorescence intensity using ethanol up 20% (v/v). However, the presence of acetone and methanol produced notable phosphorescence quenching of the phosphorescence signal. The presence of acetonitrile increases the signal phosphorescence significantly and a percentage of 30% (v/v) was chosen as the optimum value.

3.5 *Stability*

Under these experimental conditions, phosphorescence signals of fuberidazole were obtained instantaneously and remained stable for at least one hour.

3.6 *Interference study*

In order to study the selectivity of the proposed method, the presence of other pesticides has been studied. Other pesticides such as carbendazin, warfarin, naptalam, quinomerac, imazalil, quinollamine, dithianon, denoxacar, diuron and linuron did not show interferences at the level of concentration of FBZ. Napropamide, thiabendazole and carbaryl interfered in the proposed determination at a molar relation of 1 : 1, however these products have different uses, and are not usually applied simultaneously with fuberidazole.

3.7 *Analytical performance characteristics*

Analytical performance characteristics of the proposed method were evaluated. A standard calibration graph was prepared according to recommended procedure. The wide linear range, small standard errors and correlation coefficient indicate excellent

Table 1. Analytical parameters.

Slope ($mL\,ng^{-1}$)	0.399
Intercept	4.370
Correlation coefficient	0.996
Linear range ($ng\,mL^{-1}$)	0–25
Detection limit ($ng\,L^{-1}$)	95
Quantification limit ($ng\,mL^{-1}$)	0.31
R.S.D. (%) $20\,ng\,mL^{-1}$	3.1

Table 2. Recovery study of spiked analytes in water samples.

	Added value ($ng\,mL^{-1}$)	Found value ($ng\,mL^{-1}$)	Recovery percentage (%)* (RSD %)
Tap 1	20	18.66	93.3 (1.7)
Tap 2	10	9.60	96.0 (3.9)
Tap 3	2.4	2.46	102.7 (8.0)
Mineral 1	20	18.10	90.5 (3.9)
Mineral 2	10	10.44	104.4 (3.3)
Mineral 3	2.4	2.60	108.3 (6.8)

*Seven replicates were analyzed.

calibration linearity. The detection and quantification limit have been calculated according to IUPAC [21]. Three replicates for the fuberidazole solution of 0, 5, 10, 15, 20 and $25\,ng\,mL^{-1}$ were taken in order to set up the calibration. All the features of the proposed method are summarised in table 1.

3.8 *Analytical applications*

Determination of pesticide levels in water is often needed to control environmental contamination.

Therefore rapid and simple analytical methods are always needed to provide a good knowledge of the distribution and bioavailability of pesticides in different water samples, which is important for the toxicity and mobility studies of pesticides in the environment.

Table 2 summarises the results at three spiked levels (2.4, 10, $20\,ng\,mL^{-1}$) for the two samples taken and the analysis of seven replicates. We can conclude that the methods show an acceptable accuracy and precision in the analysis of fuberidazole at these concentration levels.

4. Conclusions

We have shown that heavy atom-induced room-temperature phosphorimetry methodology enhances the sensitivity and selectivity for the analysis of small amounts of pesticide in water. But, on the other hand, all luminescence methodologies which work without selectivity on a extra separation step (chromatography, electrophoresis and so on) would be a risk to other luminescence compounds (phosphorescence in this case) or quenchers. For these reasons, the presented paper could be very useful for monitoring the environmental distribution or degradation of fuberidazole

at different locations or times after application of this fungicide and it also could be very helpful for routine laboratories as a first screening step.

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