JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Development of a Single Fluorescence-Based Optosensor for Rapid Simultaneous Determination of Fungicides Benomyl and Thiabendazole in Waters and Commercial Formulations

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A novel, sensitive, and straightforward spectrofluorimetric flow injection method is proposed in this work for the resolution of a binary mixture of two widely used fungicides (thiabendazole and benomyl). The continuous flow methodology is based on the implementation of on-line solid phase extraction (SPE), preconcentration, and separation of both analytes on a surface of C_{18} silica gel beads placed just in the flow cell, with solid surface fluorescence detection. A 45- and 25-fold sensitivity enhancement was obtained for benomyl and thiabendazole, respectively (in relation to the liquid phase measurements in the absence of solid support). The separation of the pesticides was performed because of the different retention−desorption kinetics in their interaction with the solid support, in the zone where the stream impinges the solid material. No previous separation of the analytes before they reach the flow cell is needed, simplifying extraordinarily both the procedure and the manifold. Using a sample volume of 3200 μL, the system was calibrated in the range of 0.4−20 and 20−400 ng mL^{-1} with detection limits of 0.06 and 3.6 ng mL^{-1} for thiabendazole and benomyl, respectively, and RSD values ($n = 10$) smaller than 0.8% for both analytes. The RSD values obtained replacing the solid support in each measurement were lower than 3%, and the day-to-day reproducibility RSD value was also lower than 5%. Sampling frequencies of 10 and 18 h^{-1} were obtained with 600 and 3200 μL of sample volume. Recovery studies carried out on natural water samples spiked with known amounts of both analytes at concentration levels in the range of 1−10 and 25−200 ng mL^{-1} provided mean recovery percentages ranging from 98.8 to 102% and from 98 to 103% for thiabendazole and benomyl, respectively. The proposed methodology was also applied to pesticide formulations.

KEYWORDS: Fluorescence; flow-injection; environmental analysis; pesticides; benomyl; thiabendazole

INTRODUCTION

The presence of pollutants in the environment poses risks for human health. Important contaminants include heavy metals, PAHs, flame retardants, chlorinated solvents, endocrine disrupters, biocides, and many others (*1*). Unavoidably, pesticides are one of the major environmental pollutants nowadays, because of their massive use in agriculture. Both thiabendazole [2-(4-thiazolyl-1H-benzimidazole] and benomyl [methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate] are systemic benzimidazolic fungicides used for the preharvest treatment of fruits and vegetables. They are also used in postharvest treatment of seed fruits to avoid rotting during storage (*2*). Taking into account their possible toxic effects, widespread use, and insufficient data, reliable analytical methods for the continuous monitoring of these compounds are of great interest.

Several chromatographic methods have been described in the literature for the determination of benomyl and thiabendazole (*3*−*6*). Because of the instability of benomyl in water and organic solvents (*7*), most of the chromatographic methods developed for this analyte are based in the prior quantitative conversion of benomyl into its major degradation product (carbendazim). The major pitfall associated with this methodology is that initial carbendazim present in the sample cannot be distinguished from carbendazim, which is produced from benomyl as its degradation product during the analysis. Furthermore, because carbendazim is also fungitoxic and its biological activity is different from that of benomyl, analytical determination of benomyl as carbendazim has only limited applications (*3*).

Luminescence spectroscopy is considered as a sensitive and relatively selective analytical technique. Therefore, it offers remarkable analytical features for the determination of organic pollutants (*8*). Different methods have been proposed for the spectrofluorimetric determination of both thiabendazole (*9*−*12*) and benomyl (*13*). However, the simultaneous determination of pesticide mixtures sometimes cannot be successfully achieved by classical fluorescence spectroscopy, because of overlapping

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10.1021/jf0353279 CCC: $27.50
Published on Web 03/27/2004

of excitation/emission spectra. To increase selectivity in fluorimetric methods, several authors have suggested the application of techniques such as variable angle scanning fluorescence (*10*), synchronous fluorescence (*14*), and polarization fluorescence (*15*) for the improvement of selectivity in pesticide mixtures analysis without separation steps as an attempt to reduce some of the drawbacks observed with common separation techniques.

Solid phase spectrometry (SPS) can be also considered as a reliable methodology to increase sensitivity and selectivity in spectrometric measurements. It is based on the retention and preconcentration of the target species on an active solid support combined with the direct spectrometric measurement on the solid phase (*16*). This methodology (batch mode) has been successfully applied to the sensitive fluorimetric determination of thiabendazole (*11*) and benomyl (*13*) residues in waters. However, a low overall sampling throughput is obtained, making this technique unsuitable for routine analysis. The use of SPS implemented with continuous flow system (CFS) (SPS−CFS) has been recently employed to determine low concentrations of various chemical species (*17*). In SPS−CFS, the solid support is placed in the flow-through cell, and the detection is performed during the retention step in the irradiated area of the active solid support (*17*). These kinds of systems based on the interaction of the radiation with the solid surface integrated in the detector have been called flow-through optosensors.

In this paper, a novel concept for obtaining on-line continuous flow separation without involving additional devices in the manifold is reported. The use of an extra amount of solid support, in relation to conventional flow-through sensors (*17*), placed just above the detection area, can be used as a simple and robust approach for the resolution of mixtures. This simplifies both the manifold and the procedure. This option has been chosen in this work, as the separation achieved by the solid support in the cell made possible the simultaneous determination of both analytes (only one injection is used) based on the measurement of their native fluorescence.

The above-mentioned methodology implemented with dual wavelength fluorescence detection is applied in this work to the simultaneous monitoring of two widely used pesticides (thiabendazole and benomyl) in environmental water samples and commercial formulations. By using a strongly acid aqueous medium, benomyl remains stable, making possible its determination in its present form (without degradation). Enhancement in selectivity is achieved by the separation step, which is carried out just before the detection step. To the best of our knowledge, a nonchromatographic continuous method has never been reported for the simultaneous determination of these two benzimidazolic fungicides. Therefore, this work represents a contribution to the field of fluorescence-based multiparameter methodologies, providing a simple, automatic, inexpensive, moderately selective and sensitive methodology for the simultaneous determination of thiabendazole and benomyl. The proposed method was applied to commercial pesticide formulations and different types of environmental water samples.

EXPERIMENTAL PROCEDURES

Apparatus and Instruments. The manifold used is outlined in **Figure 1**. It was built using a four-channel Gilson Minipuls-3 peristaltic pump (Villiers le Bel, France) fitted with a rate selector and two Rheodyne type 5041 six-port rotary injection valves (Cotati, U.S.A.), one of them used as carrier/eluting solutions selecting valve. PTFE tubing of 0.8 mm i.d. was also used.

A Varian Cary-Eclipse Fluorescence Spectrofluorimeter (Varian Inc, Mulgrave, Australia), equipped with a Hellma (Jamaica, NY) 176.052-QS quartz flow-through cell (25 μL of inner volume and a light path length of 1.5 mm) was used to perform all of the relative fluorescence intensity measurements. The spectrofluorimeter was connected to a computer with a Cary Eclipse software package for data collection. The flow cell was filled with C_{18} silica gel beads, as a slurry suspension in methanol, with the aid of a syringe. The flow-through cell was blocked at the outlet with glass wool, to avoid displacements of the C_{18} gel beads. A complete study of the optimal amount of the gel sensing material in the flow-cell was carried out.

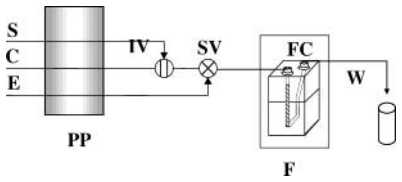

Figure 1. Flow injection manifold: S, sample; C, carrier; E, eluting solution; PP, peristaltic pump; IV, injection valve; SV, selection valve; F, spectrofluorimeter; FC, flow cell; and W, waste.

Reagents and Solutions. All standard solutions both for optimization studies and for calibration were prepared from analytical reagent grade chemicals by using doubly distilled water. Thiabendazole (Sigma) stock solutions of 200 μg mL^{-1} were prepared by dissolution of 20 mg in 100 mL of absolute ethanol (Panreac). This solution remained stable for at least 1 month when stored under refrigeration at 4 °C. Taking into account that benomyl (Riedel-de-Haën) is unstable in organic solvents because it decomposes into its major breakdown product carbendazim (*7*), its stock solutions of 200 μg mL^{-1} were prepared by dissolution of the appropriate amount in 5 M HCl solution. This solution remained stable for at least 2 weeks when stored under refrigeration at 4 °C. Working solutions containing both benomyl and thiabendazole were prepared by suitable dilution of the stock solution with a 1.5 M HCl (Panreac) solution, conditions in which benomyl remained stable for at least 24 h.

Commercial pesticide formulations were obtained from the Spanish market. Methanol (Panreac) was used, as a carrier solution [20% MeOH (v/v)] and as an eluting solution [65% MeOH (v/v)]. C_{18} bonded phase silica gel beads (Waters, Milford, U.S.A.) with average particle sizes of 55−105 μm were also used as an active solid support.

Continuous Flow Procedure. The working flow injection assembly is outlined in **Figure 1**. A volume of 600 or 3200 μL of sample solution was inserted into the carrier stream [MeOH 20% (v/v)] and pumped through the flow system at a flow rate of 1.16 mL min^{-1} to the flow-through cell, where the sample plug reached the integrated separation−detection unit, in which an on-line SPE−preconcentration−separation process was followed by the subsequent sequential fluorescence detection of both analytes.

The separation of the pesticides was performed because of the different retention−desorption kinetics in their interaction with the solid support. Thiabendazole, which showed a weaker retention, was detected first, performing its transient signal recorded at 305/358 ($\lambda_{exc}/\lambda_{em}$). Benomyl, meanwhile, was strongly fixed just above the detection area. When thiabendazole was totally eluted from the detection microzone by the carrier solution stream [MeOH 20% (v/v)] and its transient fluorescence signal was obtained, by turning the selection valve, a MeOH 65% (v/v) solution was used then as a eluting solution for benomyl, carrying it to the detection area where its analytical signal was recorded at 293/398 ($\lambda_{exc}/\lambda_{em}$). Then, by turning again the selection valve, the baselines were restored and it became possible to make another sample injection. Samples and calibration standards were analyzed by triplicate.

Sample Treatment. Water samples were filtered through a cellulose acetate filter [0.45 μm pore size, Millipore (Bedford, MA)]. The samples were stored at 4 °C until analysis, which was performed with the minimum possible delay. Formulation A (22.5% m/v thiabendazole, 7.5% m/v imazalil) was dissolved in absolute ethanol. Formulation B (50% m/m benomyl) was dissolved in 5 M HCl. Appropriate dilutions were made.

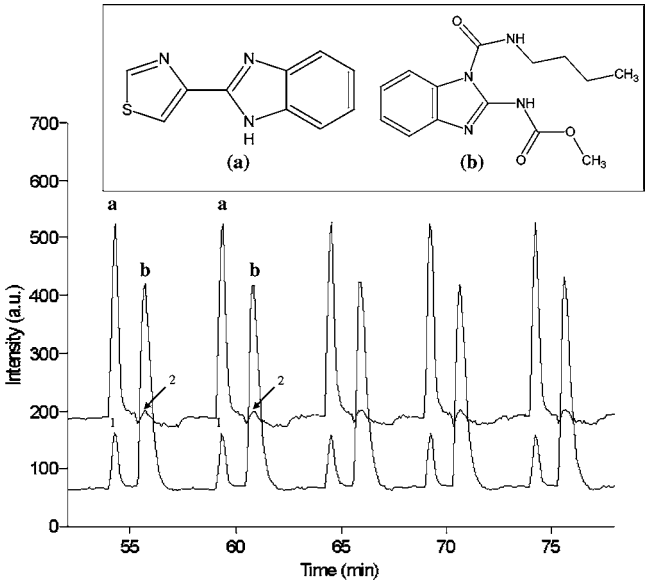

Figure 2. Determination of 0.030 and 1.3 μg mL^{-1} of thiabendazole (**a**) and benomyl (**b**), respectively, with a sample volume of 600 μL. Signal corresponding to thiabendazole on the baseline of benomyl (1) and vice versa (2). Inset: chemical structures of thiabendazole (**a**) and benomyl (**b**).

RESULTS AND DISCUSSION

Preliminary Studies. The spectral features of thiabendazole and benomyl were recorded in both gel phase and aqueous solution media. The fluorescence spectra in acidified aqueous solution showed maxima excitation/emission wavelengths at 280/400 and 301/360, for benomyl and thiabendazole, respectively. The spectra of the analytes sorbed on C_{18} silica gel beads showed maximum excitation/emission wavelengths at 305/358 for thiabendazole and 293/398 for benomyl.

Taking into account the wide profiles of excitation and emission spectra of both analytes, interference in the measurement of benomyl arose in the presence of thiabendazole, due to the strong overlapping shown by excitation and emission spectra of both analytes. Hence, it was impossible to perform the simultaneous determination without significant errors. A neat proof of the spectra overlapping was the small peaks, which appeared in the diagram, corresponding to thiabendazole in the baseline of benomyl. It can be seen in **Figure 2**. Therefore, the separation achieved by the solid support made easily possible the simultaneous measurement of both analytes. The maximum fluorescence excitation/emission wavelengths on gel phase were chosen for data collection for both analytes. A dual wavelength fluorescence detection mode was employed, making possible that two pairs of excitation/emission wavelengths could be simultaneously recorded. Therefore, the simultaneous monitoring at two different pairs of wavelengths could be achieved in this apparatus configuration, providing remarkable sensitivity and selectivity increases. Hence, the diagrams were composed by two different baselines, one for each pair of excitation/emission wavelengths.

Instrumental Variables. Relative fluorescence intensity measurements carried out in gel phase media are usually affected by background signal levels higher than those found in homogeneous solution, obviously because of the presence of the solid material in the irradiated zone. Therefore, instrumental parameters and conditions of measurement were carefully investigated in order to achieve the best possible signal-to-background ratio.

A study of the photomultiplier tube voltage was carried out in the range of 400−800 V, because this variable has an important influence on both background and analyte signals. As a compromise between sensitivity and signal-to-background ratio, the photomultiplier tube voltage was set at 725 V. The instrument excitation and emission slits widths were studied in the range from 1 to 20 nm width. Values of 5 and 20 nm width were established for excitation and emission slit width respectively, to obtain an optimum value of the ratio analyte signal/C_{18} background signal at both pairs of excitation/emission wavelengths.

Study of Retention−Separation−Detection Unit. Taking into account the structure of both benzimidazolic compounds, which presented potentially protonable nitrogen atoms, two types of suitable active solid phases were studied for the proposed method: a cation exchanger on dextran (Sephadex SP C-25) and a nonpolar sorbent (C_{18} silica gel). From the results obtained, C_{18} bonded silica gel beads proved to be the most suitable sensing material since it provided a higher signal enhancement than that provided by the cationic exchanger (1.5-fold the signal obtained with Sephadex SP C-25). Furthermore, the mixture resolution only could be achieved with C_{18} silica gel, because of the substantial differences shown by the analytes in the retention/desorption process. The solid support performance remained stable in the strongly acid experimental conditions for at least 2 weeks without any kind of problems such as deactivation or deterioration.

The optimal amount of C_{18} silica gel beads in the flow cell was carefully studied. The flow cell was filled with different amounts of C_{18} gel beads, as a slurry suspension in methanol, until the irradiated zone of the cell was filled. As the separation was performed by a temporary sequencing of the arrival of the analytes to the irradiated zone by an on-line separation process performed on the solid support area placed just above the detection zone, the optimization of the resolution was achieved by varying the amount of C_{18} bonded phase silica beads placed in the flow-through cell. A study was carried out in the range from 41.3 to 58.0 mg of C_{18} silica gel beads packed in the flow cell. An optimal resolution was obtained with 58.0 mg [20 mm height (h) above the irradiated zone]. The experience is schematically represented in **Figure 3**.

Chemical Variables. *Stability of Benomyl Solutions.* A study of sample media conditions as well as the nature of carrier and eluting solutions was performed. Because of the instability of benomyl in water and organic solvents, chromatographic methods usually rely on the prior quantitative conversion of benomyl into its major degradation product, carbendazim. A complete study of the stability of benomyl solutions was carried out by comparison of series of UV as well as excitation and emission fluorescence spectra of a solution of benomyl at different concentration levels of HCl. The series of spectra were collected in intervals of time of 4 h. The results obtained were in agreement with those provided by Singh et al. (*7*). At concentration levels lower than 0.1 M HCl, benomyl was converted progressively into carbendazim. Nevertheless, at values higher than 1 M HCl, benomyl solutions remained stable for at least 24 h. Therefore, stock solutions of benomyl were prepared in 5 M HCl, and working solutions and samples were acidified at 1.5 M HCl.

Nature and Concentration of Carrier and Eluting Solutions. Taking into account the nonpolar nature of C_{18} silica gel beads, several carrier solutions were prepared containing methanol and water in different proportions. Optimization of the carrier and eluting solution was carried out individually for each analyte,

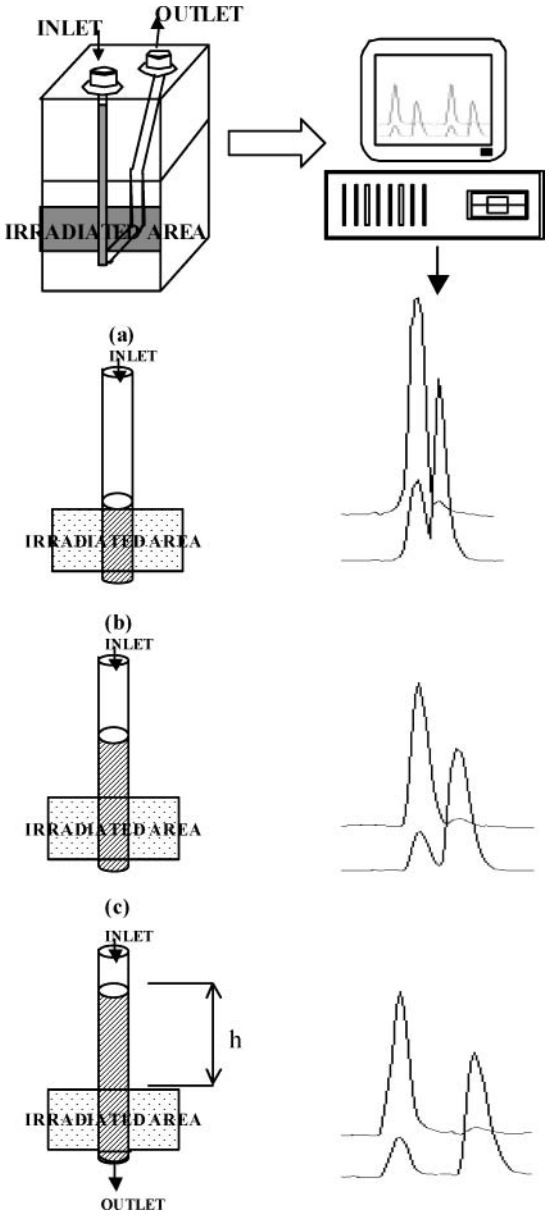

Figure 3. Optimization of the preconcentation–separation–detection device: (**a**) 41.3 mg of C_{18}; (**b**) 47.2 mg of C_{18}; (**c**) 58.0 mg of C_{18} [20 mm height (h) above the irradiated area]. Carrier, 20% MeOH; eluent, 65% MeOH; [TBZ] = 0.030 μg mL^{-1}; [BNM] = 1.0 μg mL^{-1} (600 μL sample volume).

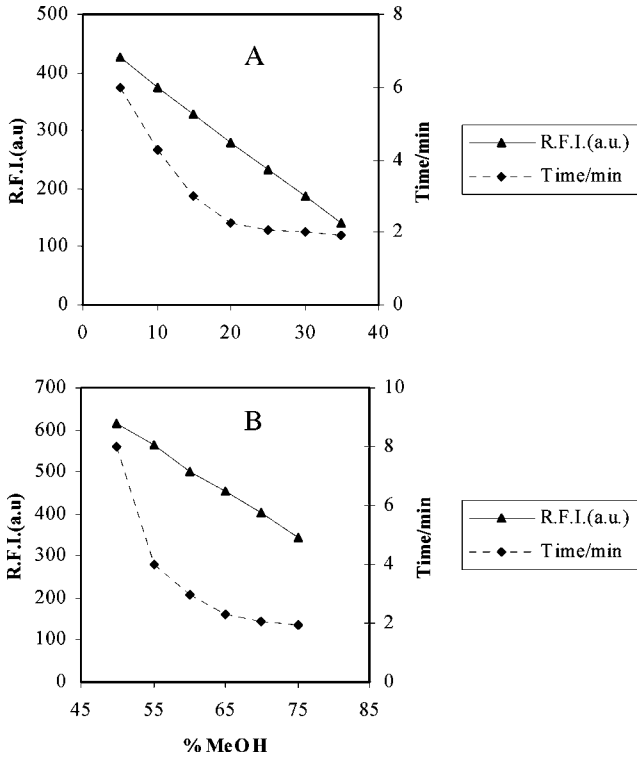

Figure 4. Optimization of chemical variables: study of carrier (**A**) and eluting (**B**) solution. Influence on both relative fluorescence intensity and total signal time. [TBZ] = 0.025 μg mL^{-1}; [BNM] = 1.75 μg mL^{-1} (600 μL sample volume).

with the optimum solid support level in the flow-through cell. The carrier solution was studied with methanol solutions with proportions in the range from 5 to 35% MeOH (v/v). A 20% MeOH (v/v) solution was the optimum value for a complete desorption, high signal peak, and low signal time for thiabendazole. The eluting solution was studied with methanol solutions with proportions in the range from 50 to 75% MeOH (v/v). Results obtained are shown in **Figure 4**. The higher the concentration of methanol, the lower the signal and the higher the signal time. Taking into account the experimental data provided in **Figure 4**, a 65% MeOH (v/v) eluting solution was chosen as a compromise between sensitivity and low elution time for benomyl.

Flow Injection Variables. *Flow Rate.* The effect of the flow rate and the sample volume was investigated. The flow rate was studied from 0.60 to 1.46 mL min^{-1}. The higher the flow rate was, the lower the analytical signal, and also, the elution time progressively decreased for both analytes while the sampling frequency increased. By increasing the flow rate from 0.60 to 1.16 mL min^{-1}, the signal decreased 29 and 23.5% for thiabendazole and benomyl, respectively. Nevertheless, an increase of about 75% in sampling frequency was achieved by using 1.16 mL min^{-1} of flow rate instead of 0.6 mL min^{-1}. As a compromise between sensitivity and total signal time, a 1.16 mL min^{-1} flow rate was chosen. Higher values involved a substantial loss of sensitivity with a scarce increase in sampling frequency. Furthermore, flow rates higher than 1.16 mL min^{-1} could not be used as a consequence of overpressure problems in the flow system.

Effect of Sample Volume. A remarkable advantage of SPS is the potential to improve the sensitivity by increasing the sample volume from which the analyte is concentrated in the solid support (*16*). A linear relationship was observed between the fluorescence signal and the sample volume injected in the volume range of 0.2−2.0 mL (thiabendazole: RFI = 15.0 + 230.41 V; r = 0.9977; benomyl: RFI = −1.1 + 244.9 V; r = 0.9982; V, mL). Therefore, the use of different sample loops makes the proposed method suitable for determining both analytes in a wide concentration range.

Analytical Features. Under optimized working conditions, calibration graphs were established, according to the proposed method, with different standard solutions containing both analytes for two different injection volumes: 600 and 3200 μL. **Table 1** summarizes the analytical figure of merit for the two injection volumes chosen. Detection and quantification limits were also evaluated according to the IUPAC criteria. The analytical performance of the proposed method compares well with other previously reported spectrofluorimetric methods (*9*, *11*, *12*). A 45-fold sensitivity enhancement in relation to the calibration graph slope values obtained in homogeneous solution measurements under the same flow injection conditions was

Table 1. Analytical Parameters

	thiabendazole		benomyl	
	volume of sample loop (μL)			
parameter	600	3200	600	3200
linear dynamic range (ng mL^{-1})	1.0–50.0	0.4–20.0	50–2000	20–400
calibration graph				
intercept	7.2	14.6	6.9	6.9
slope (mL ng^{-1})	11.03	39.35	0.258	1.334
correlation coefficient	0.9998	0.9996	0.9992	0.9997
detection limit (ng mL^{-1})	0.31	0.08	11.5	4.6
quantification limit (ng mL^{-1})	0.8	0.2	30	12
RSD (%; $n = 10$)	0.77 (0.03)[a]	0.59 (0.01)[a]	0.62 (1.5)[a]	0.65 (0.30)[a]
sampling frequency (h^{-1})	18	10	18	10

[a] Concentration level, μg ml^{-1}.

obtained for benomyl using a sample volume of 3200 μL. The enrichment factor obtained for thiabendazole in these conditions was 25. The different enhancing effects of the solid sensing zone for each analyte are due to the stronger sorption performed by benomyl on the C_{18} solid support. Both the repeatability and the reproducibility of the proposed method were also evaluated. Using the same solid phase, RSD values below 1% were obtained for both analytes. The repeatability of the filling process of the solid support was also evaluated. Values lower than 3% were obtained, replacing the solid phase in each measurement. Day-to-day reproducibility values were lower than 5% for both analytes. Sampling frequency was also evaluated. Values obtained are included in **Table 1**.

Study of Interferences. Foreign species were added to solutions containing both analytes, and their influence on the analytical signal was investigated, to assess the possible analytical applications of the proposed method. The study was carried out with 0.01 and 0.25 μg mL^{-1} of thiabendazole and benomyl, respectively (using a 3200 μL sample volume). A 1000 μg mL^{-1} level of each ionic species was tested first, and if interference occurs, the concentration was gradually reduced until the interference ceased. Other common pesticides, which are widely used and are even formulated together with the analytes (viz. imazalil), were also investigated, taking into account their respective solubility in water. As can be seen in **Table 2**, it can be concluded that both benomyl and thiabendazole can be determined in the presence of higher concentrations of potentially interfering compounds, which would be present in real samples.

Determination of Thiabendazole and Benomyl in Waters and Commercial Formulations. The proposed method was evaluated by applying it to the determination of benomyl and thiabendazole in two commercial pesticide formulations and three different environmental water samples in order to demonstrate its usefulness. Natural water samples analyzed were found to be free from both benomyl and thiabendazole residues. Therefore, spiked samples were prepared by adding known amounts of both pesticides at different levels in the range of 1−10 and 25−200 ng mL^{-1} for thiabendazole and benomyl, respectively. As can be seen in **Table 3**, the proposed methodology (using 3200 μL sample volume) provides good mean recoveries of both pesticides. A standard deviation ($n = 3$) lower than 3% was obtained in most cases. Although few data have been proposed as a guidance level for environmental waters, the values stated by different countries are usually in the ng mL^{-1} level (*18*). Taking into account that these pesticides are usually employed at concentration levels of about 0.5% w/w (5000 mg/L), parts-per-billion levels of these pesticides in natural waters can be expected. Therefore, the proposed method could be used to monitor these pesticides at these levels.

Table 2. Selectivity Study

	tolerated interferent/analyte (w/w) ratio[b]	
foreign species	thiabendazole	benomyl
Cl^-, CO_3^{2-}, PO_4^{3-}, Na^+, SO_4^{2-}, AcO^-, NH_4^+, Ca^{2+}, K^+, NO_3^-	100 000[a]	4000[a]
I^-, F^-	10 000	1000
Al^{3+}	1000	80
Fe^{3+}	1000	40
morestan	2000[a]	40
carbendazim	1000	80[a]
simazine	500	80[a]
imazalil	500	40[a]
warfarin	500	8
dichlone	100	20
o-phenylphenol	100	1
α-naphthol	10	2
fuberidazole	0.2	40[a]

[a] Maximum ratio tested. [b] Tolerance level defined as the maximum concentration of foreign species, which caused a relative error of ±5% in the analytical signal.

Table 3. Analytical Applications

	thiabendazole		benomyl	
	added (ng mL^{-1})	recovery ± RSD (%)[a]	added (ng mL^{-1})	recovery ± RSD (%)[a]
river water	1	100.9 ± 0.4	25	101 ± 1
	2	101.1 ± 0.2	50	102 ± 2
	3	100.4 ± 0.8	100	98 ± 1
dam water A	1	99.4 ± 0.8	25	100 ± 2
	2	98.8 ± 0.3	50	100 ± 3
	5	100 ± 1	150	98 ± 2
dam water B	1	99 ± 1	50	98 ± 1
	2	102 ± 1	100	101 ± 2
	10	101 ± 2	200	103 ± 3
formulation A	10	99 ± 2	200	104 ± 2
	20	100 ± 1	400	101 ± 1
	30	102 ± 1	600	99 ± 1
formulation B	5	101 ± 2	300	100 ± 1
	10	101.6 ± 0.8	800	98 ± 1
	15	100 ± 1	1000	99.0 ± 0.6

[a] $n = 3$.

Pesticide formulation A, which was analyzed by the proposed procedure, provided results [% thiabendazole (w/v) = 22.2 ± 0.3% ($n = 3$)] that were in concordance to those claimed by the manufacturer (22.5%). However, the result obtained for

pesticide formulation B [% benomyl (w/w) = 30.1 ± 0.3% ($n = 3$)] did not show agreement with the value claimed by the manufacturer [50% benomyl (w/w)]. This substantial difference could be caused by the moisture present in the product, which probably involved a partial degradation of benomyl into its major degradation product, carbendazim. In fact, benomyl is very unstable in aqueous media at pH > 1 (*7*). To check the accuracy of the proposed method, a recovery study was carried out by adding known amounts of benomyl to the previously analyzed solutions of the pesticide formulation A and also adding known amounts of thiabendazole to the previously analyzed solutions of the pesticide formulation B. Results obtained are summarized in **Table 3**. It can be concluded that the accuracy of this continuous flow fluorescence based method was demonstrated, representing a reliable and straightforward alternative to conventional separation techniques for quality control of pesticide formulations and real-time monitoring of pesticide residues of thiabendazole and benomyl in environmental water samples at ng mL^{-1} concentration levels.

CONCLUSIONS

In this paper, an automated methodology for the simultaneous determination of two widely used fungicides (benomyl and thiabendazole) has been developed, which makes possible the determination of benomyl in its intact form (without degradation to carbendazim). Enhancement in sensitivity was achieved with the preconcentration step performed in the solid support placed in the flow cell, together with the use of a dual fluorescence detection mode, making possible two pair of maxima excitation/emission wavelengths that could be simultaneously recorded. The proposed method is fast, accurate, sensitive, and cost-effective.

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Received for review November 11, 2003. Revised manuscript received February 23, 2004. Accepted February 24, 2004. We acknowledge financial support from the Ministerio de Ciencia y Tecnología (Project No. BQU 2002-02872), partially supported by FEDER funds. J.F.G.R. is also grateful to MECD for an FPU program scholarship.

JF0353279