Flow injection analysis with on-line nylon powder extraction for room-temperature phosphorescence determination of thiabendazole

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ABSTRACT

A fast and very selective flow-through phosphorescence optosensor was designed and characterized for the determination of the fungicide thiabendazole in water samples. For the first time, thiabendazole was determined using a flow-through optosensor based on the phosphorescence signals obtained when it is retained in a solid support. While thiabendazole does not phosphoresce in packing materials commonly used to fill the flow-cell, significant emission signals are observed when it is retained on nylon powder in the presence of iodide and sulfite. The experimental set-up was based on a flow-injection manifold coupled to an on-line phosphorescence detector containing nylon powder packed in a conventional flow-cell. Potassium iodide and sodium sulfite were added to sample aliquots to improve the thiabendazole phosphorescence and injected in the flow manifold using water as carrier. After the phosphorescence emission was registered, the analyte was eluted from the packed nylon with a 65% (v/v) methanol–water mixture. Optimal instrumentation, experimental and flow conditions were evaluated. Using a sample volume of 2000 μL, the analytical signal showed a very good linearity in the range 12.9–110 ng mL^{-1}, with a detection limit of 4.5 ng mL^{-1}, and a sample throughput of about 14 samples per hour. The effects of the presence of concomitant species in the thiabendazole phosphorescence signal were studied, and a comparison with the fluorescence nylon-powder optosensor was carried out and discussed. Finally, the applicability of the proposed optosensor was tested in water samples, and satisfactory recoveries ranging between 97% and 105% were obtained.

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1. Introduction

Optical sensors denote a group of chemical sensors in which electromagnetic radiation is used to generate the analytical signal in a transducing element [1]. Spectroscopic measurements such as absorbance, reflectance, fluorescence, phosphorescence and chemiluminescence have been commonly used in the different types of optical sensors. Although molecular absorption spectroscopy is the most frequently used detection technique due to its high adaptability to a wide variety of analytical problems [2], luminescence-based optical sensors have experienced a significant growth in the last decades because of their advantages of high sensitivity and selectivity [3]. However, while this development has been very pronounced in fluorescence-based optical sensors, it has been less significant concerning sensors based on phosphorescence signals. An explanation could be given considering that phosphorescence is a less usual phenomenon. This fact, which in principle could be seen as a negative quality, provides a superior selectivity to

sensors based on room-temperature phosphorescence (RTP) detection. The research group of Segura-Carretero et al. was the first in developing a sensor based on the direct measurement of a native RTP signal [4]. This optosensor was developed for the determination of the pesticide N-1-naphthylphthlamic acid (naptalam) and its metabolite. The same research group developed a flow-through solid-surface phosphorescence optosensor for the characterization of polycyclic aromatic hydrocarbons and the selective determination of benzo[a]pyrene [5]. In those experiments, commercial resins usually employed as solid supports for packing the flow-cell were tested. Nowadays, more sophisticated molecularly imprinted materials are being employed as attractive packing for the development of RTP sensors [3].

Recently, our research group investigated the 6,6-nylon powder as a new support to be employed as an optosensor packing [6]. In this latter work, the outstanding properties of this material as a fluorescence optosensor for the determination of thiabendazole (TBZ, Fig. 1) were demonstrated. Following a similar approach, the present paper describes the development of an optosensor based on the discovered nylon powder capacity to promote RTP from this fungicide. To the extent of our literature search, this is the first report on a flow-through phosphorescence optosensor method for the determination of TBZ. This compound is of worldwide use as

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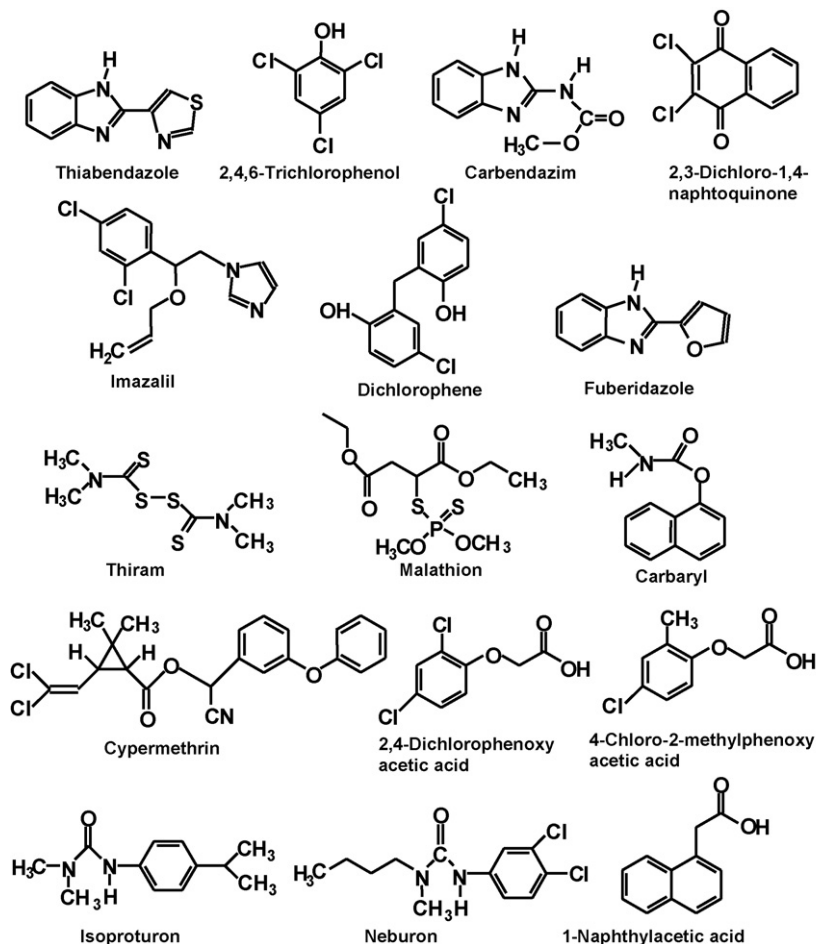(G.M. Escandar).

Fig. 1. Structures of thiabendazole and potential interferences.

fungicide, and in our country it is one of the pesticides applied to fruits before packing and transportation. Unavoidably, the excess remaining in the packing plants reaches rivers and may represent a source of water contamination [7].

The herein proposed method is very simple and consists on the on-line retention of the analyte onto nylon particles, followed by the RTP detection of the immobilized analyte. The interest in analysing this type of signal emerged as a necessity of improving the selectivity of the optosensor, preserving its other important properties such as sensitivity, rapidity, automation and lower consumption of reagents. TBZ optosensors based on the fluorescence emission of the analyte have shown a moderate selectivity due to interferences produced by other fluorescent pesticides which could be present in the samples and could be concomitantly retained by the support [6,8–10].

In the present paper, the different variables which have an influence on the phosphorescence intensity of TBZ retained in the nylon support are analysed, and the application of the developed method in natural waters is evaluated.

2. Experimental

2.1. Chemicals

All reagents were of high-purity grade and used as received. Thiabendazole, carbendazim, imazalil and 2,4-dichlorophenoxy acetic acid sodium salt monohydrate were obtained from Riedel-de Haën. Dichlorophene, 2,4,6-trichlorophenol, 2,3-dichloro-1,4-naphthoquinone, fuberidazole, thiram, malathion, carbaryl,

cypermethrin, 4-chloro-2-methylphenoxy acetic acid, isoproturon and neburon were purchased from Fluka. Potassium iodide, sodium sulfite and methanol were obtained from Merck. Thallium(I) nitrate and sodium phosphate were purchased from Aldrich and naphthylacetic acid was obtained from Sigma. Nitrates of iron(III), aluminium(III), copper(II), cobalt(II) and nickel(II), and sodium sulfate, sodium nitrate and sodium chloride were provided by Sigma–Aldrich. Nylon powder was obtained by scratching 6,6-nylon probes and sieving the resulting powder through a stainless steel strainer of 150 μm grain size. A stock solution of thiabendazole (c.a. 300 μg mL^{-1}) was prepared in methanol. This solution is stable at 4 $^\circ$C for at least 4 months. From this solution, stock aqueous solutions were prepared by taking appropriate aliquots, evaporating the methanol by use of dry nitrogen and diluting with water to the desired concentrations.

2.2. Apparatus

A Varian Cary-Eclipse luminescence spectrometer (Varian, Mulgrave, Australia) equipped with a xenon flash lamp was used to measure the RTP intensity. Instrumental variables were optimised in order to increase the signal/noise ratio and thus to obtain the maximum sensitivity for TBZ detection. The excitation and emission slit widths were of 5 and 20 nm, respectively, and the delay and gate times were of 500 and 2000 μs, respectively. In all cases, the phosphorescence signals were obtained using excitation and emission wavelengths of 300 and 485 nm, respectively.

A Gilson Minipuls-3 peristaltic pump (Villiers-Le-Ber, France), two six-port injection valves with exchangeable fixed volume

loops, and a 25 μL inner volume quartz flow-through cell (Hellma 176.052-QS, Müllheim, Germany) packed with nylon powder were employed to set-up the FIA manifold as described in ref. [6]. PVC tubings of 0.76 mm i.d. were used for all connections. The entire light-path of the cell was filled with a suspension of nylon powder in a 65% (v/v) methanol–water mixture using a hypodermic syringe. The level of nylon support was sufficient to cover the detection area. The cell was blocked at the outlet with some glass wool to prevent displacements of the nylon particles by the carrier, while the inlet of the flow-through cell was kept free.

2.3. Procedure

Volumes of 1000 or 2000 μL of sample solution containing TBZ alone or in the presence of auxiliary reagents were inserted into the carrier stream (water) and pumped through the flow system at a flow rate of 1.0 mL min^{-1}. When TBZ arrives to the cell filled with nylon powder, it is retained on it and the corresponding room-temperature phosphorescence signal is recorded. When the signal reaches the maximum, TBZ is desorbed from the flow-through cell with 500 μL of a 65% (v/v) methanol–water mixture which is injected in the FIA system by means of a second injection valve, and the signal returns to the baseline. Each run was performed at least in triplicate, and the optosensor response was taken as the difference between the maximum emission and the background signal.

The proposed method was applied for the quantification of TBZ in real water samples. Mineral, tap, underground and river water were prepared by spiking them with standard solution of TBZ, obtaining concentration levels between 10 and 96 ng mL^{-1}. With the exception of river water samples, which were filtered through filter paper, the remaining water samples underwent no previous treatment.

3. Results and discussion

3.1. Room-temperature phosphorescence properties on nylon powder

While the native fluorescence of TBZ has been known for more than two decades, few papers related to TBZ phosphorescence have been reported, and most of then refer to measurements in solution [11–17]. Although it was demonstrated that both filter paper and nylon disks are able to induce RTP emission of TBZ retained on their surfaces [12,13,17], RTP signals have not been detected when this analyte was retained in the supports which are usually employed in the implementation of flow-through optosensors for neutral molecules, such as C18 silica gel and non-ionic resins. Apparently, the immobilization in these materials is not efficient enough to prevent the non-radiative deactivation of the excited triplet state of TBZ. In contrast to filter paper, nylon shows good mechanical and chemical resistance and, as was previously established, can be used as optosensor disposed in a flow-cell [6].

Fig. 2 shows the phosphorescence spectra of TBZ retained in powdered nylon under different experimental conditions. While in the absence of auxiliary reagents a broad and weak phosphorescence signal with a maximum around 505 nm is detected, a wide RTP band centred at about 485 nm occurs in the presence of a heavy atom and sodium sulfite as oxygen scavenger. These spectra are similar to those obtained over the nylon membrane [17].

It is important to point out that, in contrast to the fact that fluorescence signals were obtained from several agrochemicals adsorbed in the nylon particle surfaces [6], nylon-adsorbed phosphorescence emission was only detected from TBZ among the investigated agrochemicals. As was suggested in the introduction,
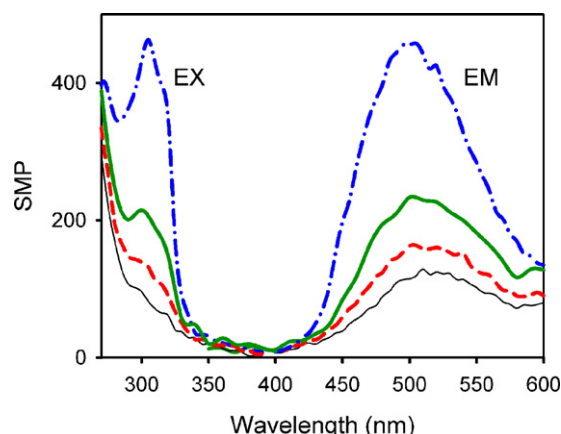
Fig. 2. Solid matrix phosphorescence (SMP) excitation (ex) and emission (em) spectra of TBZ alone immobilized onto nylon powder (red dashed line), in the presence of KI (green solid line), and in the presence of KI and Na$_2$SO$_3$ (blue dash-dotted line). C_{TBZ} = 400 ng mL^{-1}; C_{KI} = 0.6 M; $C_{Na_2SO_3}$ = 0.4 M. The thin black lines correspond to the background signals.

this fact provided selectivity to this type of optosensor, which was confirmed in the interference study (see below).

3.2. Selection of the FIA experimental conditions

After performing exploratory experiments, it was established that RTP emission of TBZ retained in nylon powder reaches a maximum at pH 4 and remains almost constant at higher pH values. The same conclusion has been obtained from the experiments performed in a nylon membrane [17]. Therefore, pure water was selected as a carrier, and TBZ aqueous solutions were injected in the FIA system, allowing us to work without the necessity of using buffer solutions. The retained TBZ was then removed from nylon by using an efficient regenerative agent. On the basis of a previous experience [6], different methanol–water mixtures were tested. It was corroborated that a 65% (v/v) methanol–water mixture provides both the highest RTP signal and a shorter time for a complete recovery of the baseline.

The effect of the flow rate on the RTP intensity of TBZ was studied using rates from 0.5 to 2 mL min^{-1}. It was confirmed that an increase of flow-rate beyond 1 mL min^{-1} decreases the optosensor response, due to a reduction in the retention capability of the solid support. Therefore, an optimum value of 1.0 mL min^{-1} was chosen for the experimental work.

Two sample loops (1000 and 2000 μL) were used. As was expected, a higher sample volume produced an increase in the sensitivity and a decrease on the sampling frequency (see below).

3.3. Selection of the instrumental parameters

The optimization of the instrumental parameters was carried out using excitation and emission wavelengths of 300 and 485 nm, respectively, following a univariate method, as described in ref. [4]. This method consists observing the changes of the phosphorescence intensity/noise ratio when each parameter is modified, and selecting the value which maximizes the signal/noise ratio. It was observed that an increase in the emission slit width produces a better response from TBZ, but an increase in the excitation slit width does also significantly affect the blank signal. Therefore, values of 5 and 20 nm were selected for excitation and emission slits, respectively. The delay time (time elapsed between the flash of the lamp and the start of data acquisition), the gate time (time where the phosphorescence intensity is integrated and measured) and the applied photomultiplier (PMT) voltage were also optimized in order
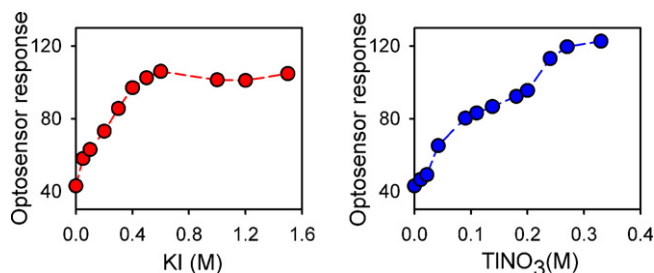
Fig. 3. Influence of the presence of TlNO$_3$ and KI on the RTP signal of TBZ retained on nylon powder. C_{TBZ} = 400 ng mL^{-1}; λ_{exc} = 300 nm.

to increase the signal/noise ratio. Optimal values of 500 and 2000 μs were selected for delay and gate times, respectively, while the PMT voltage was set at 900 V.

3.4. Effect of heavy atoms and oxygen scavenger

The effect of two heavy atom salts (TlNO$_3$ and KI) and sodium sulfite as deoxygenator agent was evaluated on the RTP signal of TBZ. It is important to point out that these salts were not added to the carrier, and were only included in each sample solution with the purpose of avoiding their use in large amounts. Therefore, the obtained results correspond to this working protocol. It is also important to mention that, although lead (II) acetate was checked as heavy-atom salt, its use was avoided because of the high background signal measured in its presence, which was ascribed to interactions between this salt and impurities of the nylon.

As can be observed in Fig. 3, the signal intensity increases with increasing concentrations of either KI or Tl(I) until 0.6 and 0.3 M solutions are introduced, respectively, in the system, and then remains almost constant for larger amounts. However, since the maximum intensity reached with both heavy atoms is similar, and the formation of the Tl(I)-sulfite complex with sulfite ions used for deoxygenation (see below) produces a detrimental effect on the measured RTP at high reagent concentrations [18], iodide at a concentration of 0.6 M was selected for subsequent experiments.

It was confirmed that sulfite ion can be used as an appropriate oxygen scavenger to minimize the quenching effects in a flow-through phosphorescence optosensor [4]. Fig. 4 shows the development of RTP emission from the retained TBZ as a function of the sodium sulfite concentration. As can be appreciated, the emission signal increases until the sulfite concentration is about
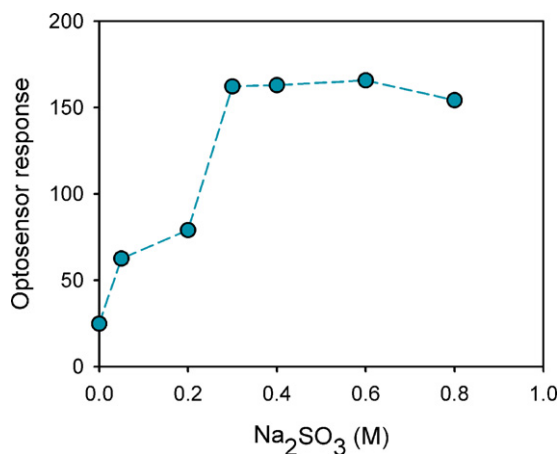

Fig. 4. Influence of the presence of Na$_2$SO$_3$ on the RTP signal of TBZ retained on nylon powder. C_{TBZ} = 300 ng mL^{-1}; λ_{exc} = 300 nm.
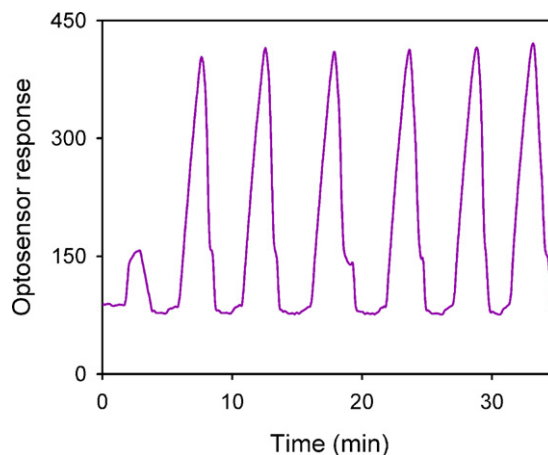

Fig. 5. Flow-injection response for successive 1000 μL injections of a solution containing 240 ng mL^{-1} TBZ, 0.6 M KI and 0.4 M Na$_2$SO$_3$, and using methanol 65% (v/v) as elution solution. λ_{exc} = 300 nm; λ_{em} = 485 nm.

0.3 M and then remains approximately constant. Therefore, a 0.4 M sodium sulfite solution was used in the experimental work.

Although deoxygenation produces a positive result in the measured signal even in the absence of a heavy atom, the signals are significantly improved in the presence of both sodium sulfite and a heavy atom solutions (see Fig. 2). It is important to point out that the high ionic strength of the injected samples, mainly determined by the presence of both potassium iodide and sodium sulfite, does not modify the TBZ adsorption phenomena.

3.5. Stability of the optosensor

The stability of the studied sensor was evaluated using two different sample volumes: 1000 and 2000 μL. Each experiment was carried out as follows: either 1000 or 2000 μL of sample containing a fixed TBZ concentration were consecutively injected in the system (about 14 uninterrupted injections). The carrier was then allowed to flow without sample during about 1.30 h, and a new set of injections was started afterwards.

Fig. 5 displays the phosphorescence response obtained in the optimal working conditions. It can be assessed that the response of the nylon powder optosensor remains almost constant during 8 h when 1000 μL of sample is used, and 6 h if 2000 μL of sample are employed, allowing in both cases to accomplish a large number of determinations. Phosphorescence signals begin to slowly decrease when the measurements are made after the indicated times. As was previously suggested [6], it is possible that the adsorptive properties of nylon are deteriorated with the repeated use/regeneration cycles.

Table 1
Optimum instrumental, chemical and flow parameters.

	Values
$\lambda_{exc}/\lambda_{em}$ (nm)	300/485
Slits (excitation/emission) (nm)	5/20
Photomultiplier voltage (V)	900
Delay time (μs)	500
Gate time (μs)	2000
C_{KI} (M)	0.6
$C_{Na_2SO_3}$ (M)	0.4
pH	∼7
Flow-rate (mL min^{-1})	1.0
Injection volumes (μL)	1000 and 2000

Table 2
Analytical parameters[a].

Sample volume (μL)	1000	2000
Linear range (ng mL^{-1})	63.2–600	12.9–110
Slope[b]	455 (5)	1481 (18)
Intercept[b]	10 (1)	−2 (1)
Correlation coefficients	0.9989	0.9985
(γ^{-1})[c] (ng mL^{-1})	0.009	0.002
LOD[d] (ng mL^{-1})	21.9	4.5
LOQ[e] (ng mL^{-1})	63.2	12.9
RSD (%)[f]	2.1 [240]	3.2 [60]
Sampling rate (samples h^{-1})	16	14

[a] $C_{KI} = 0.6$ M and $C_{Na_2SO_3} = 0.4$ M. The number of data for each calibration curve corresponds to seven different concentration levels, with three replicates for each level.

[b] The corresponding standard deviations are given in parentheses.

[c] The inverse of analytical sensitivity (γ) represents the minimum concentration difference which can be measured [25].

[d] Limit of detection calculated as ref. [20].

[e] Limit of quantitation calculated as $(10/3.3) \times$ LOD.

[f] Relative standard deviation for the concentrations (ng mL^{-1}) given in square brackets.

3.6. Optosensor performance

Table 1 summarizes the optimal instrumentation, experimental and flow variables used on the phosphorimetric determination of TBZ, and these conditions were maintained to evaluate the figures of merit of the proposed method.

Calibration graphs were obtained for two different injection volumes, and the obtained results are shown in Table 2. The data were fitted by standard least-squares treatment and the linear relationship between the TBZ concentration and the phosphorescence intensity was corroborated applying the F test recommended by IUPAC [19]. The detection limits were estimated according to reference [20]. The attained values, at part-per-billion levels, would allow the analysis of trace TBZ residues. Obviously, a higher sample volume leads to a better sensitivity. The evaluated sampling frequencies are very satisfactory, and are comparable to those indicated using other TBZ optonsensors [6,8–10].

3.7. Effect of concomitant species

In order to assess the effect of potential interferences in the measured TBZ signal, different agrochemicals frequently used in our country and which could be present in water samples were evaluated (Fig. 1). These foreign species can interfere in different modes. They can increase the resulting signal if they emit near the TBZ signal, or produce a less intense signal by either inner filter effect or competition for the active sites on the nylon surface. The study also included common anions and cations which could affect the phosphorescence emission through either complex formation with the analyte or interaction with the auxiliary reagents usually employed in phosphorescence systems. As will be demonstrated below, this latter situation would constitute a benefit, considering the masking effect of certain auxiliary reagents over the foreign ion.

A systematic study was undertaken injecting 1000 μL of sample in the FIA system, using potassium iodide as a heavy-atom salt, sodium sulfite as oxygen scavenger and 65% (v/v) methanol–water mixture for elution. Specifically, known amounts of each tested species were added to a solution containing 240 ng mL^{-1} of TBZ. In those systems where the solubility of the foreign species evaluated is high, the added amount was such that the relationship (ng mL^{-1} foreign species/ng mL^{-1} TBZ) ranged up to a value of 100. In the remaining systems, the highest interference concentrations assayed were selected according to their water solubilities. When interference effects occurred, the concentration of the

Table 3
Interference study.

Foreign species	Water solubility (ng mL^{-1})[a]	Tolerated foreign species/TBZ ratio[b]
Fungicides		
2,4,6-Trichlorophenol	800000	100
Carbendazim	2000	[c]
2,3-Dichloro-1,4-naphthoquinone	8000	[c]
Imazalil	440	[c]
Dichlorophene	30000	25
Fuberidazole	71000	2
Thiram	30000	1
Insecticides		
Malathion	145000	100
Carbaryl	40000	25
Cypermethrin	10	[c]
Herbicides		
2,4-Dichlorophenoxy acetic acid	900000	100
4-Chloro-2-methylphenoxy acetic acid	825000	100
Isoproturon	65000	100
Neburon	5000	[c]
Plant growth regulator		
1-Naphthylacetic acid	420000	100
Inorganic ions[d]		
Sulfate		100
Chloride		100
Phosphate		100
Nitrate		100
Al^{3+}		100
Co^{2+}		100
Cu^{2+}		100
Fe^{3+}		50
Ni^{2+}		4

[a] Refs. [26–32].

[b] $C_{TBZ} = 240$ ng mL^{-1}; unless otherwise indicated, the maximum tested tolerance level for organic and inorganic compounds was 100.

[c] These species were probed at concentrations around their water solubilities and no interference was detected.

[d] Other ions are indirectly evaluated in the recovery studies carried out in real water samples (see Table 5).

foreign species was progressively reduced until the effect was non-significant. Tolerance was defined as the relative amount of foreign species that produced an error not exceeding ±6.3% in the determination of TBZ. This value represents three times the relative standard deviation (RSD) of the method. While none of the assayed agrochemicals produced an enhancement on the TBZ phosphorescence signal, a decrease in this emission was detected in a few of the investigated systems. As can be noticed in Table 3, the greatest interferences were produced by fuberidazole and by thiram. The interference from the former can be attributed to an inner filter effect, since fuberidazole possesses an absorption band at near 300 nm [21], near the excitation region of TBZ. On the hand, the interference from thiram, which absorbs below 300 nm and does not possess luminescence properties, was ascribed to a possible competition for the active sites in the nylon structure. The partial retention of thiram in nylon was confirmed by comparing the absorbance spectra of a thiram solution before and after passing through a syringe filled with nylon powder.

Regarding the evaluated inorganic ions, Ni^{2+} produced a decrease in the measured phosphorescence at concentrations higher than 960 ng mL^{-1}, possibly due to a complex formation with TBZ [22]. In contrast to the result obtained with the TBZ fluorescence optosensor [6], Cu(II) ion did not interfere at the evaluated levels. In the present system, where iodide is used as heavy atom, masking reactions between this auxiliary reagent and Cu(II)

Table 4
Analytical features of TBZ nylon-powder fluorescence and phosphorescence optosensors.

	Fluorescence optosensor[a]	Phosphorescence optosensor
Sample volume (μL)	1500	2000
Eluting solution	75% (v/v) methanol–water	65% (v/v) methanol–water
Linear range (ng mL^{-1})[b]	8–120	12.9–110
LOD (ng mL^{-1})[c]	2.8	4.5
RSD[c]	0.9 (for 64 ng mL^{-1})	3.2 (for 60 ng mL^{-1})
Sampling rate (samples h^{-1})	14	14
Interference[d]	Among 19 evaluated species: Fuberidazole [0.5] Carbaryl [1] 1-Naphthylacetic acid [1] Cu (II) ion [2] carbendazim [4]	Among 24 evaluated species: Thiram [1] Fuberidazole [2] Ni(II) ion [4]

[a] Ref. [6].
[b] The lowest value corresponds to the quantitation limit.
[c] See Table 2.
[d] The ratios of tolerated intereference to TBZ are given in square brackets.

ion led to a cuprous iodide complex which decreased the free concentration of this cation avoiding its interference in the TBZ determination.

3.8. Phosphorescence optosensor vs. fluorescence optonsensor

With the purpose of comparing the analytical performance of the herein developed optosensor with the previously evaluated one, which was based on the fluorescence signal of TBZ [6], the main characteristics of both sensors are exposed in Table 4. As can be concluded from this table, while both sensors show similarly good performances related to their sensitivity and sampling frequency, the new phosphorescence optosensor shows much more selectivity. This latter fact is not surprising, since the less common phosphorescence signals provide a better selectivity to methods based on this type of detection. Due to the extensive worldwide use of agrochemicals, it is usual to find mixtures of them in environmental samples and, thus, selectivity plays and important role in the determination of these compounds. The new optosensor represents an alternative for cases where interfering components would not permit the use of absorption or fluorescence methods. The conclusion is that the phosphorescence optosensor is very adequate for the determination of thiabendazole in samples where other pesticide residues and/or different metal ions could be present.

3.9. Determination of thiabendazole in natural waters

The developed method was evaluated by applying it to the quantification of thiabendazole in different water samples in order to demonstrate its usefulness. The estimated concentrations of TBZ in natural waters are at parts-per-billion levels [23,24]. Therefore, in principle, the proposed method could be used to monitor the fungicide. Although the samples were obtained from diverse sources and several of them are near regions of intensive agriculture, where thiabendazole is used as fungicide, these water samples were found to be free from analyte residues. Therefore, spiked samples were prepared by adding known amounts of the fungicide. While 2000 μL of sample were injected for the determination of the first evaluated level (10 ng mL^{-1}), 1000 μL of sample were used in the remain-

Table 5
Recovery study of TBZ for spiked water samples[a].

Sample	Taken (ng mL^{-1})	Found[b] (ng mL^{-1})	Recovery (%)
Mineral water[c]	10.0	10 (2)	100
	30.0	31 (3)	103
	96.0	97.2 (0.7)	101
Tap water[d]	10.0	10 (3)	100
	30.0	29.8 (0.5)	99
	96.0	93 (3)	97
Tap water[e]	10.0	11 (2)	110
	30.0	31 (1)	103
	96.0	95.8 (0.8)	100
Underground water[f]	10.0	10 (1)	100
	30.0	31 (2)	103
	96.0	99 (3)	103
River water[g]	10.0	10 (2)	100
	30.0	31 (3)	103
	96.0	101 (2)	105
River water[h]	10.0	10 (2)	100
	30.0	31 (1)	103
	96.0	99 (2)	103

[a] The volumes of sample used were: 2000 μL for 10.0 ng mL^{-1}, and 1000 μL for the remaining evaluated concentrations.
[b] Mean of three determinations. Standard deviation is given between parentheses.
[c] From Villavicencio hills (Mendoza, Argentina). This water contains NaHCO$_3$ (350 μg mL^{-1}), Ca(HCO$_3$)$_2$ and Mg(HCO$_3$)$_2$ (259 μg mL^{-1}), Na$_2$SO$_4$, CaSO$_4$ and MgSO$_4$ (234 μg mL^{-1}), NaCl, CaCl$_2$ and MgCl$_2$ (47 μg mL^{-1}), CaF$_2$ (1.4 μg mL^{-1}) and oligoelements (1.5 μg mL^{-1}).
[d] From Rosario City (Santa Fe, Argentina).
[e] From Paraná City (Entre Ríos, Argentina).
[f] From Funes City surroundings (Santa Fe, Argentina).
[g] From the Paraná River (Santa Fe, Argentina).
[h] From the Carcarañá River (Santa Fe, Argentina).

ing tested concentrations. As can be appreciated in Table 5, the proposed method provides good recoveries (average of three measurements) of the studied fungicide.

4. Conclusions

Based on the obtained results, it can be concluded that nylon powder is an excellent support for the implementation a phosphorescence optosensor for the determination of thiabendazole in tap, underground, mineral and river water samples. The proposed solid support represents a satisfactory contribution to the area of flow-through phosphorescence optosensor analysis. In comparing this TBZ phosphorescence optosensor with that based on the corresponding fluorescence signal, one may conclude that the former shows a superior selectivity. The results also suggest that the addition of iodide as heavy-atom and sodium sulfite as oxygen scavenger in the samples leads to a very sensitive method. The developed optosensor represents a reliable and straightforward approach for the determination of TBZ in environmental water samples where other pesticide residues could be present.

Acknowledgements

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