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

G.N. Piccirilli, G.M. Escandar*

Instituto de Química Rosario (CONICET-UNR), Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Suipacha 531 (2000) Rosario, Argentina

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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.

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

* Corresponding author.
E-mail addresses: escandar@iquir-conicet.gov.ar, gmescandar@hotmail.com (G.M. Escandar).

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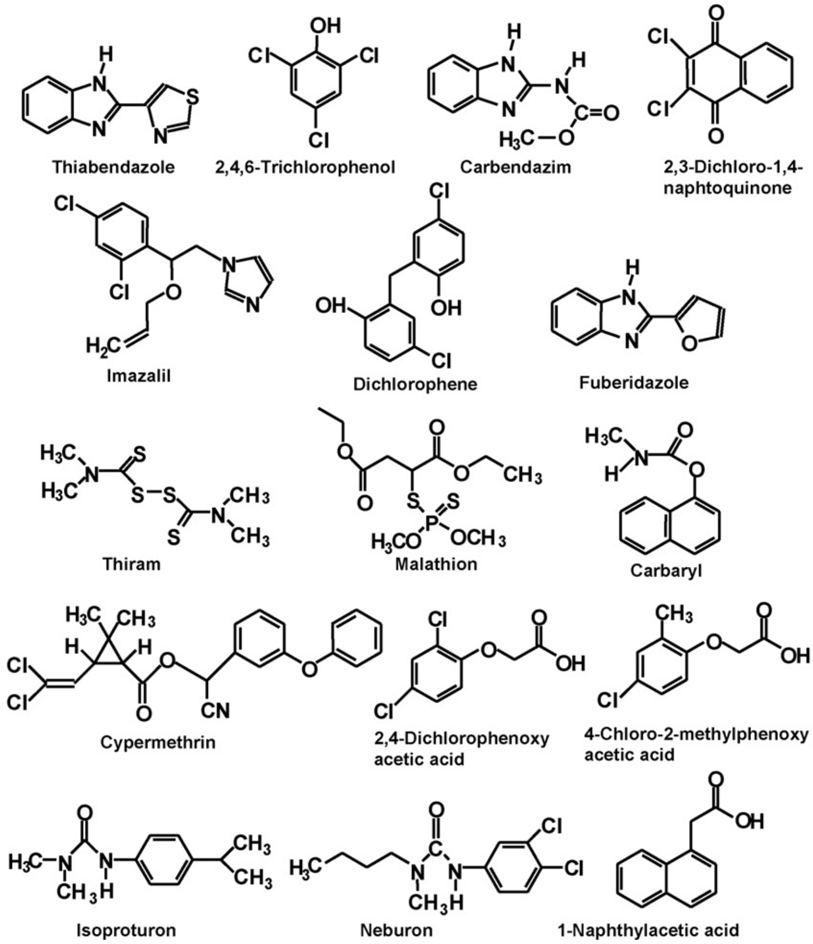

Fig. 1. Structures of thiabendazole and potential interferences.

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 $\mu g\,mL^{-1}$) was prepared in methanol. This solution is stable at 4 °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