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Hollow fiber membrane-protected molecularly imprinted microspheres for micro solid-phase extraction and clean-up of thiabendazole in citrus samples

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ABSTRACT

In the present work, molecularly imprinted polymer (MIP) microspheres were packed in polypropylene hollow fiber (HF) segments for the micro solid-phase extraction and clean-up of thiabendazole (TBZ) in citrus samples. Experimental parameters affecting TBZ extraction were carefully optimized. Hollow fiber membrane was able to protect MIP beads from solid matrix allowing the extraction and clean-up without the inclusion of further filtration and/or centrifugation steps. Under optimum experimental conditions, recoveries for TBZ at 0.83 mg kg^{-1} concentration level ranged from 5.1 to 6.1%, depending upon the sample analyzed (orange or lemon peel samples), with relative standard deviations (RSDs) lower than 4%. The limits of detection were 0.004 mg kg^{-1} in orange and 0.009 mg kg^{-1} in lemon, low enough for the determination of TBZ according to European Union legislation.

1. Introduction

Analytical instrumentation has experienced a huge development in recent years, however sample preparation is still nowadays a key step in the whole analytical process. It is well known that matrix components can interfere in detection and quantification of target analytes by chromatographic techniques, even when MS detection is used, and therefore an adequate sample treatment should be performed before final determination [1].

The main objective of sample preparation is the isolation of target analytes from matrix compounds in a suitable form for detection and separation. During last years, other objectives such as to minimize sample size, reduce the use of glassware and organic solvents and improve the selectivity in extraction have also been established [2]. Consequently, new micro-extraction techniques have been developed including solid-phase microextraction (SPME), stir-bar sorptive extraction (SBSE) and, more recently, matrix solid-phase dispersion (MSPD), micro solid-phase extraction (MSPE) or liquid- phase microextraction (LPME) [3].

Solid-phase microextraction (SPME), introduced by Arthur and Pawliszyn in early 1990s [4], is based on the partition of target analytes between an extracting phase coated to a solid support (i.e. silica fiber) and the sample matrix. Subsequent desorption of concentrated extracts is then performed into an analytical instrument. Since its introduction, SPME has been further developed and is widely used in analytical laboratories, however it is not exempt of some drawbacks such as the lack of selectivity and the fragility of the used fibers. Besides, fiber immersion in complex matrices is not recommended since the coated extracting phase may be damaged. Accordingly, several approaches have been reported in order to improve the selectivity and performance of SPME. At this regard, hollow fiber (HF) membrane-protected SPME was proposed as an alternative allowing the direct immersion of fibers in complex liquid matrices [5]. In this seminal work, a porous cellulose hollow membrane was used to protect the SPME fiber. Later, a polypropylene hollow fiber was evaluated as protective material and was successfully applied in the HF membrane-protected SPME of triazine herbicides from complex matrices such as bovine milk and sewage sludge [6].

More recently, in order to provide selectivity to SPME, molecularly imprinted fibers have been developed. Molecularly imprinted polymers (MIPs) are synthetic materials that are able to rebind specifically a target analyte. The recognition occurs in cavities obtained during polymerization of functional and cross-linking monomers around the template molecule. After polymerization, the template molecule is extracted leaving binding sites complementary in shape, size and functionalities to the template molecule used. Koster et al. described for the first time the preparation of

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a silica fiber coated with a MIP for the SPME of clenbuterol from urine samples [7]. Later, MIP fibers (monoliths) were proposed as an alternative to coated silica fibers and successfully applied to the SPME of triazines in environmental and food samples [8], and parabens from soil sample extracts [9]. Hollow fiber membrane-protected approach was also performed using MIP fibers for the extraction of triazines from sludge water, water-melon, milk and urine samples [10] and thiabendazole (TBZ) from orange juice [11]. However, in spite of the mentioned advantages of this approach, it is important to point out that this procedure is not only tedious and time consuming but also a bit tricky since the fragility of the obtained fibers makes necessary a caution handling in order to prevent their breakage. Alternatively, a rather simple approach, so-called molecularly imprinted micro solid phase extraction (MI-MSPE), has been proposed. It comprises MIP particles packed into the lumen of a hollow fiber membrane [12,13] or enclosed within a flat-sheet membrane envelope [14–16]. Such approach provides selectivity to the extraction, allows the direct immersion of the device in complex liquid samples and prevents the risk of breaking since fragile fibers are not used.

Accordingly, in the present work, TBZ-imprinted microspheres were prepared by precipitation polymerization and then packed into the lumen of a polypropylene hollow fiber. After proper optimization, such device was employed for the MI-MSPE and clean-up of TBZ in citrus samples. TBZ is a post-harvest systemic fungicide very commonly used to prevent vegetables and fruits, particularly citrus fruits, from deterioration during storing and transportation. Typically, TBZ and other fungicides are solvent-extracted from plant samples using ethyl acetate, acetonitrile or mixtures of acetone with other organic solvents [17–19] and then determined by liquid chromatography coupled with UV detection [19], fluorescence (F) detection [20] or, more recently, mass spectrometry (MS) [21] or tandem MS [22]. However, even when using the selective detection provided by MS, direct injections of crude extracts are not recommended since matrix components can inhibit or enhance the analyte ionisation, hampering accurate quantification [22]. Thus, clean-up of the extracts needs to be carried out to remove the matrix components. Authorities have established the maximum residue levels (MRLs) for TBZ in fruits in the range from 0.05 to 15 mg kg^{-1}, depending upon the type of crop. In the case of citrus fruits, the permitted levels have been established in 5 mg kg^{-1} for TBZ [23].

2. Experimental

2.1. Reagents

Thiabendazole (TBZ), carbendazim (CBZ) and imazalil (IMZ) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and stock standard solutions (1 g L^{-1}) were prepared in acetonitrile and stored at −22 °C. The corresponding chemical structures are shown in Fig. 1A. HPLC-grade solvents were purchased from Scharlab (Barcelona, Spain). Water was obtained from a Milli-Q purification system (Molsheim, France). Sodium dihydrogen phosphate, disodium hydrogen phosphate, acetic acid (HOAc), and ammonia (25%) were purchased from Panreac (Barcelona, Spain). Methacrylic acid (MAA), divinylbenzene-80 (DVB-80) and 2,2′-azobis-isobutyronitrile (AIBN) were purchased from Sigma-Aldrich (Madrid, Spain). MAA and DVB-80 were freed from stabilizers by distillation under reduced pressure and by passing through a short column packed with neutral alumina (Sigma Aldrich), respectively. AIBN was recrystallized from methanol (MeOH). The Q3/2 polypropylene hollow fibers (600 μm internal diameter, 200 μm wall thickness and 0.2 μm pore size) were purchased from Membrana (Wuppertal, Germany).

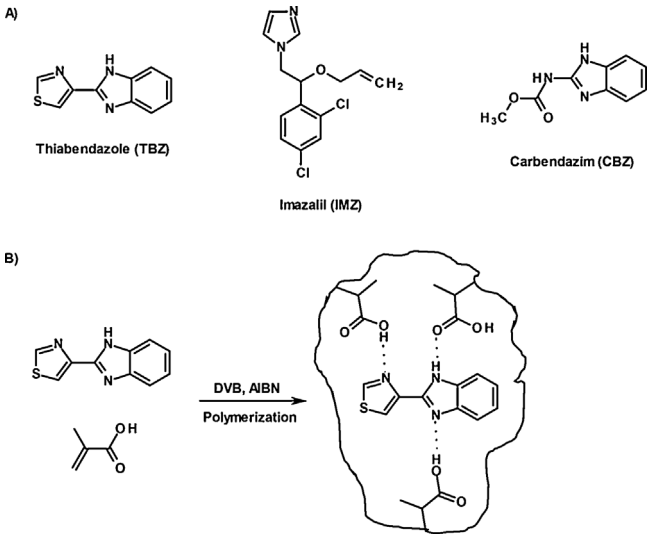

Fig. 1. Chemical structures of TBZ, CBZ and IMZ (A), and schematic representation of a possible TBZ-imprinted site (B).

2.2. Polymers preparation

Polymers were prepared by precipitation polymerization according to the procedure described by Turiel et al. [24]. Briefly, TBZ (0.17 mmol), MAA (0.68 mmol), DVB-80 (3.39 mmol), and AIBN (0.25 mmol) were dissolved in 12.5 mL of a 25:75 (v/v) toluene:acetonitrile (TOL:ACN) mixture in a 20 mL glass tube. The tube was sealed by means of a screw-cap and introduced into a temperature controllable incubator equipped with a low-profile roller (Barloworld Scientific, Staffordshire, UK); the latter allowed for the slow rotation (24 rpm) of the tube about its long axis over the course of the polymerization. The temperature was ramped from room temperature to 60 °C over 2 h and then maintained at 60 °C for a further 24 h. The polymer particles were separated from the polymerization mixture by vacuum filtration trough a nylon membrane filter, and then washed with acetonitrile (ACN). The template was removed by Soxhlet extraction using 200 mL of 1:1 (v/v) MeOH:HOAc mixture for 8 h. Finally, the obtained polymers were washed with MeOH and ACN and were dried at room temperature for 48 h before storage. A non-imprinted polymer (NIP) was prepared in the same manner than MIP but without the addition of template.

2.3. Characterisation techniques: nitrogen sorption porosimetry and scanning electron microscopy measurements

Nitrogen sorption porosimetry measurements were performed on an ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer (Micromeritics Instrument Corporation, Norcross, GA). Prior to measurement, 100–150 mg of the samples were heated at 80 °C under high vacuum (1025 Pa) for at least 3 h. The specific surface areas (S) were calculated using the BET method, and specific pore volumes (Vp) and the average pore diameter (dp) using the BJH theory.

Scanning electron micrographs of prepared materials were imaged at Centro de Microscopía Electrónica "Luis Bru" (Universidad Complutense de Madrid) using a JEOL JM-6400 (Peabody, MA).

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