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Capillary electrochromatography coupled with dispersive liquid-liquid microextraction for the analysis of benzimidazole residues in water samples

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ABSTRACT

A novel method for the analysis of benzimidazole residues in water samples by capillary electrochromatography-UV detection (290 nm), using laboratory-made packed columns is presented. Capillaries (25 cm packed length × 75 μm inner diameter, 34 cm total length, 25.5 cm effective capillary length) were packed with C18 particles (5 μm, non-encapped) following a high pressure packing procedure and using a compact steel unit designed for packing capillary columns. Acetone was employed as solvent to carry the particles through the capillary and pack it under a pressure of 42 MPa. Outlet and inlet frits were made by sintering the particles of the stationary phase by heating the packed material with a nichrome ribbon connected to a 7 V AC power supply. With the aim of achieving a good analytical performance, the variables that affected the separation were studied, using a mobile phase composition of 60:40 (v/v) acetonitrile/water containing ammonium acetate (1 mM, pH 6.5), a separation voltage of 25 kV and a temperature of 25 °C. In addition, a combined hydrodynamic-electrokinetic injection mode was considered and samples were injected for 75 s under a voltage of 12.5 kV and a pressure of 11.5 bar. Finally, the determination of benzimidazoles in water samples was accomplished by capillary electrochromatography using dispersive liquid-liquid microextraction as sample treatment. Variables affecting the extraction efficiency were optimized, using chloroform and ethanol as extraction and disperser solvents, respectively.

This method was applied to different water samples, obtaining satisfactory results in terms of linearity ($R^2 \geq 0.990$), repeatability (RSD ≤ 1.2%), reproducibility (RSD ≤ 2.2%) and trueness (R ≥ 87.7%). Detection and quantification limits were lower than 2.8 μg L^{-1} and 9.3 μg L^{-1}, respectively.

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1. Introduction

Benzimidazoles (BZs) are veterinary drugs widely used for prevention and treatment of parasitic infections in agriculture and aquaculture [1,2]. Also, some BZs possess fungicidal properties, so they have been used in the control of spoilage of crops during storage and transport and stored fruit and vegetables [3]. As a consequence, BZ residues can be released into the environment through their presence in manure or their disposal into wastewater systems [4]. Once they reach the environment, these pollutants are transported and distributed into water, sediment, soil, and biota. They are subjected to processes (e.g., biodegradation, and chemical and photochemical degradation) that contribute to their elimination or they react with other compounds in the environment [5]. Furthermore, several studies have reported their presence in wastewaters and natural waters [6–8], which is of public concern because only a few studies have been reported about BZs removal from wastewater, aquatic and soil ecosystems surrounding pastures [9]. Therefore, sensitive, efficient, miniaturized and green analytical methods are required for the determination of BZs in environmental samples.

In the last years, several methods have been developed for the analysis of BZ residues, using mainly high performance liquid chromatography (HPLC) [1], coupled to fluorescence (FL) [10,11], ultraviolet (UV) [12–15] and mass spectrometry (MS) detectors [16–18]. The use of gas chromatography (GC) has been limited due to the requirement of a derivatization step, which is a drawback [19,20]. Also, capillary electrophoresis (CE) with UV and MS detection has been evaluated for the separation and determination of BZs [21–24]. It is well-known that CE involves low solvent consumption and offers high separation efficiency, being an alternative to liquid chromatography (LC) in the analysis of residues in

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different fields [25–28]. Among CE modes, capillary electrochromatography (CEC) can be considered as a powerful separation technique because it combines the high efficiency of CE and the selectivity of LC. In CEC, separation occurs due to interactions between the stationary phase and the analytes where the mobile phase flows through the stationary phase because of an electric field rather than an applied pressure [29,30]. CEC columns can be open-tubular (OT), continuous bed, also known as monolithic columns, or packed columns. In general, packed columns using C18 particles are the most employed [31], because they offer the highest specific area among all the electrochromatographic columns and therefore, higher sample capacity can be obtained. As a consequence, higher sensitivity and separation reproducibility can be achieved. Besides, CEC packed columns offer the inherent selectivity and reproducibility of commercially available packing materials [32]. The latest achievements related to stationary phases, columns, as well as method optimization have been recently summarized [33]. CEC is an environmentally friendly separation technique as other CE modes, involving a solvent consumption even lower than UHPLC, which reduces the generated waste in comparison with classical LC methods. Besides, lower amount of stationary phase is required for making a CEC column, so operational costs are reduced and more expensive packing materials can be tested. However, the application of CEC methods to residue determination can be limited by the same drawbacks as CE. A lack of concentration sensitivity can be attributed to them, especially when UV detection is used due to the low sample volume injected. Nevertheless signal sensitivity can be enhanced by injecting the sample in a solvent with lower elution strength than the mobile phase for both, hydrodynamic [34] or electrokinetic [35,36] injection. Although CEC has demonstrated its applicability for residue determination in food [37] and water samples [38–41], it has not been evaluated for BZ determination.

Regarding sample treatment, liquid extraction has been a common approach used in BZ analysis [1,42]. In the last decade, dispersive liquid-liquid microextraction (DLLME) has been proposed as a more efficient extraction alternative to traditional liquid-liquid extraction (LLE) methods [43]. It involves a ternary component solvent system which usually consists of an aqueous sample, a higher-density extraction solvent (a water immiscible organic solvent such as chlorobenzene, chloroform or CS_2) and a dispersive solvent that has to be miscible in both, extractant and aqueous sample such as methanol, acetonitrile, or acetone [44]. It is an environmental-friendly method because only a few microliters of the extraction solvent and a low volume of dispersive agent are required. Furthermore, DLLME is a simple and cheap technique that requires short extraction times (a few minutes, including centrifugation stages). Besides, it provides high recoveries and high enrichment factors. Due to these advantages, DLLME has been widely applied in the last years, mainly to water samples [45,46] and specifically for BZs, the applications include only a few number of these compounds [12,47,48].

In this work, a novel CEC method has been developed for BZ residues analysis in water samples using C18 laboratory-made columns produced following a previously proposed protocol [49]. Moreover, all the variables affecting separation have been studied in detail and the application of an on-line preconcentration technique similar to those used in CZE has been considered in order to improve the sensitivity [50,51]. Additionally, a new DLLME procedure has been developed for achieving a simple and effective extraction of seven BZs from water samples.

2. Experimental

2.1. Materials and reagents

All reagents used in this study were of analytical grade, unless otherwise indicated, and the solvents were of HPLC grade. Ultrapure water (Milli-Q plus system, Millipore, Bedford, MA, USA) was used throughout the work. Ammonium hydroxide (30%), sulphuric acid (98%), and sodium hydroxide were obtained from Panreac-Química (Madrid, Spain). Methanol (MeOH), ammonium bicarbonate, ethanol (EtOH), isopropanol (IPA), isobutanol (IBA), tetrahydrofuran (THF), chloroform, dichloromethane and acetone were purchased from VWR International (West Chester, PA, USA) whereas ammonium acetate, sodium tetraborate decahydrate and MeCN were supplied by Sigma-Aldrich (St. Louis, MO, USA). Tris (hydroxymethyl)aminomethane (TRIS) and hydrochloric acid (37%) were acquired from Merck (Darmstadt, Germany).

Analytical standards of albendazole (ABZ; methyl 5-(propylthio)-2-benzimidazolecarbamate), carbendazim (CBZ; methyl 2-benzimidazolecarbamate), benomyl (BEN; methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate), febantel (FBT; *N*-{2-[2,3-bis-(methoxycarbonyl)-guanido] − 5-(phenylthio)-phenyl}-2-methoxyacetamide), febendazole (FBZ; methyl 5-(phenylthio)-2-benzimidazolecarbamate), mebendazole (MBZ; 5-benzoyl-2-benzimidazolecarbamic acid methyl ester), oxibendazole (OXI; methyl (5-propoxy-1*H*-benzimidazol-2-yl)carbamate) and parbendazole (PBZ; methyl (5-butyl-1*H*-benzoimidazol-2-yl)carbamate) were supplied by Sigma-Aldrich (St. Louis, MO, USA). Individual stock standard solutions of 1000 mg L^{-1} (FBT), 500 mg L^{-1} (ABZ, BEN, PBZ) and 250 mg L^{-1} (FBZ, OXI, CBZ, MBZ) were prepared by dissolving accurately weighted amounts of each compound in MeOH. They were stored in dark at −20 °C, being stable for at least 6 months. Intermediate stock standard solutions containing 100 mg L^{-1} of each BZ were obtained by mixing individual stock standard solutions and subsequent dilution with MeOH. They were stored in dark at 4 °C. Working standard solutions containing all the BZs were freshly prepared by the proper dilution of the intermediate stock standard solutions with MeOH at the required concentration.

The packed columns used consisted of uncoated fused silica capillaries of 75 μm internal diameter (i.d.), which were purchased from Polymicro Technologies (Phoenix, AZ, USA) and LiChrospher RP-C18 non-encapped particles (5 μm particle size, 100 Å pore size) (Agilent Technologies, Waldbronn, Germany), which were used from a LC column.

Acrodisc 13-mm syringe filters with 0.2-μm nylon membrane (Pall Corp., MI, USA) were used for sample extracts filtration prior to their injection in the electrophoretic system.

2.2. Instrumentation

A SP-400 Nanobaume™ column packing unit (Western Fluids Engineering, Wildomar, CA, USA) coupled to a PU-2080 high pressure pump (Jasco, Easton, MD, USA) was employed for capillary packing. Capillary packing process was assisted by a MC-8 magnetic stirrer (Bunsen, Madrid, Spain). Packed capillary was heated with a metallic strip (80%Ni-20%Cr, 28 cm × 2 mm × 0.2 mm, electric resistance 1.3 Ω) connected to a 7 V AC power supply for frit fabrication.

CEC experiments were carried out with an Agilent 7100 CE System (Agilent Technologies, Waldbronn, Germany) equipped with a diode-array detector. Data were acquired using the supplied software with the CE system (HP ChemStation, Version B.02.01).

A pH meter (Crison model pH 2000, Barcelona, Spain), a centrifuge (Universal 320 model from Hettich, Leipzig, Germany), an evaporator with nitrogen (System EVA-EC from VLM GmbH,

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